Energy, Environment, and Sustainability

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Prospects of Alternative Transportation Fuels

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Preface

Energy demand has been rising remarkably due to increasing population and urbanization. Global economy and society are significantly dependent on the energy availability because it touches every facet of human life and its activities. Transportation and power generation are major examples of energy. Without the transportation by millions of personalized and mass transport vehicles and availability of 24 × 7 power, human civilization would not have reached contemporary living standards.

The first international conference on 'Sustainable Energy and Environmental Challenges' (SEEC-2017) was organized under the auspices of 'International Society for Energy and Environmental Sustainability' (ISEES) by the 'Center of Innovative and Applied Bioprocessing' (CIAB), Mohali, from 26 to 28 February 2017. ISEES was founded at IIT Kanpur in January 2014 with the aim of spreading knowledge in the fields of energy, environment, sustainability and combustion. The society's goal is to contribute to the development of clean, affordable and secure energy resources and a sustainable environment for the society and to spread knowledge in the above-mentioned areas and spread awareness about the environmental challenges, which the world is facing today. ISEES is involved in various activities such as conducting workshops, seminars, conferences in the domains of its interest. The society also recognizes the outstanding works done by the young scientists and engineers for their contributions in these fields by conferring them awards under various categories.

This conference provided a platform for discussions between eminent scientists and engineers from various countries including India, USA, South Korea, Norway, Malaysia and Australia. In this conference, eminent speakers from all over the world presented their views related to different aspects of energy, combustion, emissions and alternative energy resources for sustainable development and cleaner environment. The conference started with four mini-symposiums on very topical themes, which included (i) New Fuels and Advanced Engine Combustion, (ii) Sustainable Energy, (iii) Experimental and Numerical Combustion and (iv) Environmental Remediation and Railroad Transport. The conference had 14 technical sessions on topics related to energy and environmental sustainability and a panel discussion on ‘Challenges, Opportunities and Directions of Technical Education & Research in the Area of Energy, Environment and Sustainability’ to wrap up the three-day technical extravaganza. The conference included 2 plenary talks, 12 keynote talks, 42 invited talks from prominent scientists, 49 contributed talks and 120 posters. A total of 234 participants and speakers attended this three-day conference, which hosted Dr. V. K. Saraswat, Member NITI Aayog, India, as a chief guest for the award ceremony of ISEES. This conference laid out the road map for technology development, opportunities and challenges in this technology domain. The technical sessions in the conference included Advances in IC Engines and Fuels; Conversion of Biomass to Biofuels; Combustion Processes; Renewable Energy: Prospects and Technologies; Waste to Wealth—Chemicals and Fuels; Energy Conversion Systems; Numerical Simulation of Combustion Processes; Alternate Fuels for IC Engines; Sprays and Heterogeneous Combustion of Coal/Biomass; Biomass Conversion to Fuels and Chemicals—Thermochemical Processes; Utilization of Biofuels and Environmental Protection and Health. All these topics are very relevant for the country and the world in the present context. The society is grateful to Prof. Ashok Pandey for organizing and hosting this conference, which led to the germination of this series of monographs, which included 16 books related to different aspects of energy, environment and sustainability. This is the first time that such a voluminous and high-quality outcome has been achieved by any society in India from one conference.

The editors would like to express their sincere gratitude to the authors for submitting their work in a timely manner and revising it appropriately at short notice. We would like express to our special thanks to Prof. V. Ganeshan, Prof. P. A. Laxminarayana, Prof. D. V. Patil, Dr. Joonsik Hwang and Mr. Tanmay Kar, who reviewed various chapters of this monograph and provided their valuable suggestions to improve the manuscripts. We acknowledge the support received from various funding agencies and organizations for the successful conduct of the first ISEES conference SEEC-2017, where these monographs germinated. These include Department of Science and Technology, Government of India (special thanks to Dr. Sanjay Bajpai); TSI, India (special thanks to Dr. Deepak Sharma); Tesscorn, India (special thanks to Sh. Satyanarayana); AVL India; Horiba, India; Springer (special thanks to Swati Mehershi); CIAB (special thanks to Dr. Sangwan).

At this stage of technology development, transportation and power generation systems are dependent on conventional fuels such as mineral diesel, gasoline, which resulted in rapid depletion of petroleum reserves. Application of different alternative fuels such as biofuels, renewable fuels, alcohols and other synthetic fuels needs to be explored for sustainable development of automotive sector. This monograph is intended for practitioners working in the energy sector, and we hope that the book would be of great interest to the professionals and postgraduate students involved in fuels, IC engines and environmental research. The main objective of this monograph is to present the status of energy sector, potential alternative fuels and the technologies for promoting the production and utilization of these alternative fuels.

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Editors and Contributors

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Dr. Rashmi Avinash Agarwal is a Young Scientist Fellow at Indian Institute of Technology Kanpur, Kanpur 208016, India. She completed her doctoral degree in Inorganic Chemistry from July 2008 to May 2014 at Indian Institute of Technology Kanpur under the supervision of Prof. P.K. Bhardwaj. The Ph.D. thesis title was 'Coordination Polymers of Transition Metal Ions with Benzimidazole Based Ligands: Single-Crystal to Single-Crystal (SC-SC) Transformations, Gas Storage and Magnetic Studies'. Prior to her doctoral degree, she completed her M.Sc. in Organic Chemistry from Rajasthan University, Jaipur, in 2002 and B.Sc. in Chemistry from Kanoria College, Rajasthan University, Jaipur, in 2000. She has expertise in supramolecular chemistry, coordination chemistry, coordination polymers, organic synthesis, inorganic synthesis, hydrothermal synthesis of coordination polymers, crystallization, crystal structure determination, topology, hydrogen bonding, structural analysis, fluorescence, Single-Crystal to Single-Crystal (SC-SC) Transformations, FTIR, thermo-gravimetric, NMR, mass and PXRD analysis, column chromatography, synthesis of nano-particles utilizing porous materials, TEM analysis. She has published over 20 research papers in leading international journals.

Prof. Avinash Kumar Agarwal joined IIT Kanpur in 2001 and is currently a Poonam and Prabhu Goyal Endowed Chair Professor. He was at ERC, University of Wisconsin, Madison, USA, as Postdoctoral Fellow (1999–2001). His areas of interest are IC engines, combustion, alternative fuels, hydrogen, conventional fuels, lubricating oil tribology, optical diagnostics, laser ignition, HCCI, emission and particulate control and large bore engines. He has published more than 160 peer-reviewed international journal and conference papers. He is Associate Editor of ASME Journal of Energy Resources Technology and International Journal of Vehicle Systems Modelling and Testing. He has edited 'Handbook of Combustion' (5 volumes; 3168 pages), published by Wiley VCH, Germany. He was a Fellow of SAE (2012), Fellow of ASME (2013) and a Fellow of INAE (2015). He is the recipient of several prestigious awards such as NASI-Reliance Industries Platinum Jubilee Award-2012; INAE Silver Jubilee Young Engineer Award-2012; Dr. C.V. Raman Young Teachers Award-2011; SAE International's Ralph R. Teetor Educational Award-2008; INSA Young Scientist Award-2007; UICT Young Scientist Award-2007; INAE Young Engineer Award-2005. He is the recipient of Prestigious Shanti Swarup Bhatnagar Award-2016 in Engineering Sciences. He is the first combustion/IC Engine researcher to get this honour.

Dr. Atul Dhar is Assistant Professor at IIT Mandi since 2013. He received his M.Tech. and Ph.D. degrees from Department of Mechanical Engineering, IIT Kanpur, in 2006 and 2013, respectively. He graduated from HBTI, Kanpur, in 2004. He was awarded the Erasmus Mundus fellowship of European Union for pursuing postdoctoral research at Ecole Centrale de Nantes, France, in 2013. He is the recipient of Young Scientist Award from ISEES in 2015. His areas of interest include reciprocating IC engines, emission control, alternative fuels and lubricating oil tribology. He has co-authored more than 30 international peer-reviewed journal papers.

Mr. Mritunjay Kumar Shukla graduated from Institute of Engineering and Technology, C.S.J.M. University, Kanpur, in 2003. He worked in Joined Engine Research Laboratory of IIT Kanpur from 2003 to 2006 as a Project Associate on various projects related to biogas, biodiesel, emulsified fuels, EGR and automotive coatings. In December 2006, he joined IIP, Dehradun, as Scientist B. Since then he has been working on aspects of next-generation biofuels like bio-butanol, diethyl ethers, straight vegetable oils. He is the member of Internal Combustion Engines Subcommittee, TED 2:1, and Automotive Braking Systems, Vehicle Testing and Performance Evaluation Sectional Committee, TED 4 of Bureau of Indian Standards. He also represents IIP as alternative members in Standing Committee on Emission Legislations of MoRTH. His areas of research interest include combustion emission and spray characteristics of alcohol fuels, automotive exhaust treatment devices, emulsified fuels.

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Part I
General

Chapter 1
Introduction of Alternative Fuels

**Akhilendra P. Singh, Avinash Kumar Agarwal,
Rashmi Avinash Agarwal, Atul Dhar and Mritunjay Kumar Shukla**

Abstract Energy is a basic requirement for economic development. Growing energy consumption has resulted in world becoming increasingly dependent on fossil fuels such as coal, oil and gas; therefore, it becomes necessary to develop a sustainable path of energy. Gaseous fuels and biofuels seem to have the potential to contribute significantly to India's energy security. This monograph shows the current status of different alternative fuels and describes some advanced techniques to improve the quality of alternative fuels. Utilization of these alternative fuels in existing vehicles is another important aspect, which has been covered in this monograph.

Keywords Hydrogen · Biodiesel · Emission · Alcohols · Biomass

Fossil fuels supply more than 80% energy for global consumption and more than 95% energy for transport sector globally. While global fossil fuel reserves are diminishing, worldwide energy demand is constantly increasing due to the evolution of energy intensive lifestyles. To improve the security of the energy supply and to reduce the emissions of greenhouse gases (GHG), it becomes very important to explore alternative fuels for transport sector. US Department of Energy (DoE) has defined the important requirements of transportation fuel as they should be compatible with economic, environmental and societal aspects (Tzimas et al. 2004). Before selecting any alternative fuel, it is important to evaluate its economic and environmental impacts, societal needs, personal beliefs and changes to the quality of life. One chapter of this monograph presents the status of current energy scenario

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and shows the potential options as alternative fuels for automotive applications. Based on this introductory chapter, this monograph is divided into five parts.

Gaseous fuels seem a potential solution for energy supply to automotive sector in near future. These gaseous fuels contain more hydrogen and less carbon; therefore, the emission of greenhouse gases and fine particulates is lower from these fuels. Compressed natural gas (CNG)/liquefied petroleum gas (LPG)/liquefied natural gas (LNG) does not contain poly-aromatic hydrocarbons (PAHs), airborne toxins and sulphur dioxide (SO_2), and CNG/LPG/LNG vehicles have quieter engine operation, less vibrations and odour than conventional diesel engines. However, higher vehicle cost, shorter driving range, heavier fuel tank, expensive distribution and storage network and potential performance and operational problems compared to liquid fuels are some of the drawbacks of using CNG/LPG/LNG vehicles. The second part of this monograph contains few chapters based on production and utilization aspects of these gaseous fuels. One chapter based on hydrogen production from biological routes highlights in prospects and limitations of biohydrogen production including recent developments on this domain and describes the economic feasibility of biohydrogen production. This chapter also emphasizes the importance of integration of conventional hydrogen production technologies with production of value-added bio-based products in a biorefinery approach. Two chapters on hydrogen utilization in internal combustion (IC) engines explain the difficulties involved with use of hydrogen in real engines. These chapters also describe different techniques, which can be used for safe and efficient use of hydrogen in production grade engines. Last chapter of this part is based on utilization of CNG and hydrogen blends in engines, which is a potential solution to issues associated with hydrogen.

As biofuels have emerged as a potential alternative fuel to penetrate the transport sector, utilization of biofuels does not require significant changes in the infrastructure as well as in existing vehicles. There are variety of biofuels utilized in vehicles in which biodiesel and alcohols are the important ones. The production of these biofuels currently relies on proven technologies, characterized however by high costs. The third part of this monograph has three chapters on biofuels, which include status, production and utilization aspects. First chapter of this part gives the overview about different alcohols and presents the feasibility of alcohols' utilization as a replacement of mineral diesel. One chapter in this part shows the potential of methanol and di-methyl ether (DME) as alternative fuel in engine applications. This chapter also describes the chemistry and the sustainability of different pathways for their production from different feedstock such as coal, petcoke, natural gas, biomass and carbon dioxide. Last chapter of this part presents the methodology for utilization of solar energy in biodiesel production, which will certainly eliminate the carbon dioxide (CO_2) formation involved with current biodiesel preparation techniques.

Apart from exploring new alternative fuels, it is also very important to improve the conventional technologies to enhance the properties of alternative as well as conventional petroleum fuels. Fourth part of this monograph is based on such advanced technologies so that alternative fuels can be produced economically. One chapter of this section is based on the various aspects of waste utilization in production of clean energy, which is essential for sustainable development of society and needs immediate attention. Conversion of lignocellulosic biomass feedstock into bioenergy is another interesting chapter in this part. This chapter shows that variations in composition of biomass at optimized process flow affect the quality and quantity of potential product yields. Pyrolysis oil as an attractive option for the conversion of lignocellulosic biomass into liquid alternative fuels is also included in this part of the monograph.

Utilization of these alternative fuels is the most important aspect related to sustainability of these alternative fuels. Last part of this monograph discusses the different techniques for utilization of these alternative fuels in IC engines efficiently. One chapter of this part explains the advancement and opportunities in W/D nano-emulsion fuel preparation using different surfactants and additives, which provides improved engine performance and emission characteristics. Use of peroxy-fuels in IC engines is another important aspect covered in this section. In the last two chapters, use of alternative fuels in advanced combustion technologies such as low-temperature combustion (LTC), reactivity controlled compression ignition (RCCI) and in advanced engine technologies has been explained.

This research monograph presents both fundamental science and applied innovations on several key and emerging technologies involving fossil and alternate fuel utilization in power and transport sectors. Specific topics covered in the manuscript include:

- Introduction to Alternative Fuels
- Evolving Energy Scenario and Role and Scope for Alternative Fuels in Transport Sector
- Hydrogen Production Through Biological Route
- Hydrogen for Internal Combustion Engines
- Advances in Hydrogen-Fuelled Compression Ignition Engine
- Compressed Natural Gas and Hythane for On-Road Passenger and Commercial Vehicles
- Alcohols for Fuelling Internal Combustion Engines
- Different Feedstocks and Processes for Production of Methanol and DME as Alternate Transport Fuels
- Solar Assisted Biodiesel Production
- Fuel from Waste: A Review on Scientific Solution for Waste Management and Environment Conservation
- Thermochemical Conversions of Biomass to Bioenergy: A Review
- Pyrolysis Oil Upgrading to Fuels by Catalytic Cracking: A Refinery Perspective
- Water-in-Diesel Nano-Emulsion Fuels for Diesel Engine: Combustion Properties and Emission Characteristics
- Peroxy-Fuels: Burning Behaviour and Potential Applications in Combustion Engines

- Utilization of Alternative Fuels in Advanced Combustion Technologies
- Fuel Injection Equipment (FIE) Design for the New-Generation Alternative-Fuel Powered Diesel Engines

The topics are organized into five different sections: (i) General, (ii) Gaseous Alternative Fuels: Production and Utilization, (iii) Biofuels, (iv) Advanced Techniques for production of Alternative Fuels and (v) Utilization of Alternative Fuels.

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Chapter 2
Evolving Energy Scenario: Role and Scope for Alternative Fuels in Transport Sector

Akhilendra P. Singh, Atul Dhar and Avinash Kumar Agarwal

Abstract Due to rapidly increasing energy consumption rate, access to clean, affordable and sustainable energy has become one of the important factors for economic development of any country. Depletion of petroleum reserves and associated issues related to their utilization in internal combustion (IC) engines motivated researchers to explore such alternative energy resources. In this quest, researchers have developed various solar-based and water-based energy generation methodologies; however, these techniques are not mature enough to fulfil the current energy requirements of transport sector. Therefore, appropriate alternatives to liquid fossil fuels (mineral diesel and gasoline) have been explored, in which gaseous fuels (compressed natural gas (CNG), liquefied petroleum gas (LPG), dimethyl ether (DME), Hydrogen, HCNG, etc.), biofuels [alcohols, biodiesel, straight vegetable oil (SVO)], synthetic fuels, etc., are the important ones. Utilization of microbes to produce biofuels has also gained significant attention of researchers. This chapter provides a snapshot of the current energy landscape, available options and discusses the path forward, which can be used for the development of sustainable and secure energy options for our nation.

Keywords Alternative fuels · Biofuels · Hydrogen · DME

2.1 Introduction

Energy is a basic requirement for the economic development of any country. The geographical distribution of petroleum resources is changing as reserves are being discovered and accessed using improved exploration technologies; however, this

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distribution of oil supply generally does not coincide with where the demand is located. This results in high fuel costs, which mainly depend on crude oil price. Growing energy consumption has resulted in India becoming increasingly dependent on fossil fuels such as coal, oil and gas. Fossil fuels supply more than 80% energy for global consumption and ~95% energy for the transport sector (Fig. 2.1). Figure 2.1 shows that ~95% of transport energy comes from petroleum, while the rest of transport energy is supplied by natural gas, biofuels and electricity. The light-duty vehicles (LDVs), including light-duty trucks, light commercial vehicles and mini-buses, account for about 52% fuel requirements, while trucks, including medium and heavy-duty, account for 17% fuel requirement. Remaining share of road transport energy is consumed by buses (4%) and two/three-wheelers (3%) (World Economic Forum 2011).

In 2009, the global population was 7 billion, which is estimated to grow to 9 billion by 2050 and ~10 billion by 2100 (Lee 2011). Rapidly growing population is another major factor affecting the energy sector because increasing population

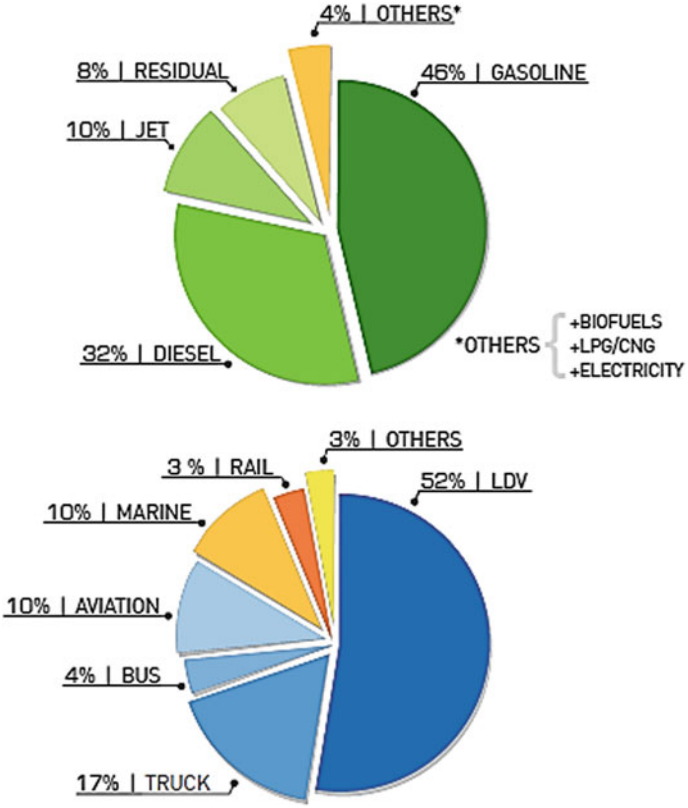

Fig. 2.1 Current global transport energy sources and consumption trends (2011) (World Economic Forum et al. 2011)

requires more energy, which puts extra burden on the global economic development. The International Energy Agency (IEA) has projected that global energy demand will increase from ~12 billion tonne oil equivalents (TOE) in 2009 to ~17 or 18 billion TOE by 2035 under the 'current policies' or 'new policies' scenarios, respectively (International Energy Agency 2017). This data shows that the world is already in an alarming situation, and these figures need to be brought down by a great extent to improve the survival of human species. Figure 2.2 shows the importance of fossil fuel in transport and energy generation sector. The growth in use of fossil fuels is increasingly driven by the transport sector, where fossil fuels make up ~95% of transport energy. Electricity generation is also significantly controlled by fossil fuels because 48% electricity is generated by coal, 19% by natural gas, 21% by nuclear power, 10% by renewables and 1% by oil.

While global fossil fuel reserves are diminishing, worldwide energy demand is constantly increasing due to evolution of energy intensive life-styles. Experts estimate that the global demand for energy could rise by >50% between 2009 and 2030 and the oil production will reach a peak around 2020–30. Burning fossil fuels generates CO_2, a greenhouse gas (GHG), leading to global warming. It is therefore necessary to find cleaner fuels, which do not originate from fossil resources. Vehicular pollution cannot be avoided because the pollutants are emitted at the ground level, close to human breathing level. Severity of vehicular pollution is reflected in increased human mortality and morbidity. Vehicular pollution affects human health adversely due to presence of carbon monoxide (CO), unburned hydrocarbons (HC), oxides of nitrogen (NOx), suspended particulate matter (SPM) and aldehydes, amongst others in the engine exhaust. Apart from these harmful pollutants, CO_2 leads to various long-term global problems including greenhouse effect/global warming. Almost all countries are working on the methods for CO_2 emission reduction from engine tailpipe to combat this menace. Different

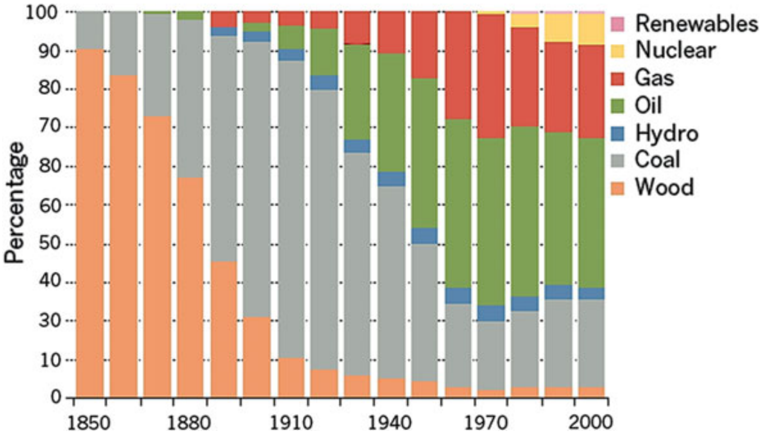

Fig. 2.2 History of relative mix of main energy resource used in the USA (Energy Information Administration. Annual Energy Review 2010)

Table 2.1 Alternative fuels landscape

SN	Fuel	Description	Remarks
1	CNG	Compressed natural gas contains methane, which is an environment-friendly fuel, which lowers CO and HC emissions	Used for three-wheelers, passenger cars, LCVs and HCVs
2	LPG	Liquefied petroleum gas contains propane and butane, which lowers CO and HC emissions	Used for three-wheelers and passenger cars
3	HCNG	Blend of hydrogen and natural gas, used as a trial fuel and not commercially introduced yet	Proposed for HCVs
4	LNG	Liquefied natural gas improves carrying capacity of vehicle and is not yet commercially introduced yet	Proposed for HCVs
5	Biogas	Biogas contains methane, an environment-friendly fuel, lowers CO and HC emissions	Proposed for LCV and HCVs
6	Alcohols	Alcohols are blended with gasoline at a 5% blend, which is proposed to be increased to 10%	Used for some passenger cars and SUVs
7	Biodiesel	Esterified vegetable oils, which can be blended with diesel	Used for SUVs and HCVs
8	Synthetic fuels	Artificial fuels derived from natural fuels using Fischer–Tropsch process	Proposed for passenger cars
9	Hydrogen	Freedom fuel, which is currently under trial	Proposed for Passenger cars and HCVs

air pollutants from vehicles have adverse effects at all levels—localized (e.g. smoke affects visibility, ambient air quality), regional (such as smog, acidification) and global (i.e. global warming).

To resolve these issues, researchers and oil companies have been directed towards promoting the use of alternative fuels, which are affordable, sustainable and environment-friendly and can fulfil the requirements of transport sector. Table 2.1 shows the landscape for potential alternative fuels.

2.2 Available Alternative Fuels

In order to meet increasingly stringent emission norms, researchers are exploring use of alternative fuels, which can be adopted in current generation engines with minimal hardware modifications. It is expected that the emissions from such alternate fuels should be lower than the emissions from conventional fuels. In this quest, several alternative fuels have been researched and developed. Researchers are primarily looking at low carbon fuels in order to reduce greenhouse gas emissions. Several alternative fuels such as biodiesel, CNG, ethanol, hydrogen, vegetable oils, LPG, hydrogen-CNG (HCNG) blends have been investigated for their engine performance in order to assess their technical feasibility.

2.2.1 Gaseous Alternative Fuels

2.2.1.1 Natural Gas

Natural gas is a mixture of ethane, propane, butane, carbon dioxide, nitrogen, etc., with 80–98% methane, which is the main constituent, depending upon source of production (Korakianitis et al. 2011; Ramadhas 2011; Lee et al. 2007). Fossil natural gas is found either together with other fossil fuels (such as crude oil in oil fields, or coal in coal beds) or on its own. CNG has been used in public transport buses, heavy-duty commercial vehicles and light-duty personal vehicles. In SI engines, it offers several advantages such as possibility of increasing engine efficiency (with associated reduction in CO_2 emissions) by increasing engine's compression ratio due to higher octane rating of natural gas compared to gasoline, reduction in quantity and toxicity of HC emissions, reduction in CO emissions, etc. It can be also utilized in retrofitted CI engines, which include modifications such as installing an ignition source, reduction of compression ratio and retrofitting a fuel storage and delivery system, which results in reduction in local pollution. Utilization of natural gas in SI engines results in 10–15% reduction in power output compared to gasoline-fuelled engines, which may be compensated by direct injection of fuel with expected availability of special injectors in near future (Korakianitis et al. 2011). Currently, for vehicular use, natural gas is stored in cylinders at 200 bar pressures, however, range of natural gas-fuelled vehicles still remains significantly lower than gasoline and diesel-fuelled vehicles due to its lower energy storage density (Korakianitis et al. 2011; Ramadhas 2011).

Share of natural gas amongst global transport fuels is predicted to remain in the range of 3–3.7% up to 2035 according to EIA world energy outlook (2011). Though natural gas is a non-renewable source, its main constituent methane can be produced from biomass as well, which is a renewable resource (Porpatham et al. 2008). Waste biomass can be utilized as transport fuel by producing natural gas, biomass-to-liquid (BTL) and ether from it. The process of collecting, purifying and using methane obtained from biomass decomposition is relatively simpler compared to Fischer–Tropsch process used in gas-to-liquid (GTL) and BTL processes (Korakianitis et al. 2011). However, at current stage of technological development, well-to-wheel energy consumption (3.5 MJ/km) of methane (D'Agosto and Ribeiro 2009) obtained from biomass is higher than fossil natural gas, gasoline and diesel (2 MJ/km) (Dimopoulos et al. 2008). Future developments in natural gas-fuelled engine technology and gas purification technology may ensure more efficient utilization of renewable methane.

2.2.1.2 Liquefied Petroleum Gas

Liquefied petroleum gas (LPG), another gaseous, fossil origin, alternative fuel, is mainly a mixture of butane and propane. It is derived from lighter hydrocarbon fractions produced during refining of crude petroleum as well as from the heavier components of natural gas, which are removed before the gas is distributed (MacLean and Lave 2003). Before further processing and transportation of crude oil or natural gas, heavier gases, which constitute LPG, are separated. LPG is also produced during atmospheric distillation, reforming and cracking of crude oil. Separation of propane and butane like gases from crude oil is necessary for its stabilization before its distribution through pipeline or tanker (Ramadhas 2011). Its engine utilization is similar to natural gas with additional advantage of higher storage energy density since it can be easily liquefied and stored as a liquid fuel at moderate pressure of 10–12 bars. However, cold-starting and cold-start emission characteristics of LPG are inferior to natural gas (Ramadhas 2011; MacLean and Lave 2003), which need to be tackled technologically.

2.2.1.3 Hydrogen

In the quest for operating the engine with improved efficiency and lower emissions, hydrogen has emerged as a prominent alternate fuel candidate. For running the engine using hydrogen, several modifications are required to be done in the existing engines. Hydrogen is an energy carrier and not an energy source because free hydrogen is not available in nature and some form of primary energy is required to be spent for hydrogen production (MacLean and Lave 2003; Verhelst and Wallner 2009). Its usefulness as an energy carrier is limited by its low energy content on a volume basis, limiting its on-board storage (MacLean and Lave 2003). Primary advantage of hydrogen over other fuels is its clean exhaust. Its oxidation does not produce carbon dioxide and other carbonaceous harmful species. Hydrogen is used as transport fuel via two routes: hydrogen fuel-cell (H_2 FC) vehicles and hydrogen IC engine (H_2 ICE) vehicles. Addition of hybrid electric vehicle (HEV) technology improves the fuel economy of both the powertrains. Currently, efficiency and cost of H_2 FC powertrain are higher than H_2 ICE powertrain (Verhelst and Wallner 2009). Generally, hydrogen can be produced by electrolysis or thermal decomposition of water, steam reforming of natural gas and other hydrocarbons, pyrolysis of hydrocarbons, plasma refining process, etc. (Ramadhas 2011; Lee et al. 2007). Steam reforming of natural gas converts it into synthesis gas, from which CO_2 and CO are removed (Ramadhas 2011). Method of hydrogen production, which requires production of an interim energy carrier like electricity prior to production of hydrogen has significant efficiency disadvantages (MacLean and Lave 2003). Abbott proposed possibility of using solar hydrogen produced by solar thermal collectors through H_2 ICE route as a viable and promising solution for future transport solution for large-scale application (Abbott 2009).

2.2.1.4 HCNG

CNG, being produced from fossil as well as natural resources, is a good alternative to liquid fossil fuels. It is relatively abundant and easily available compared to hydrogen. However, it has lower flame speed, shorter flammability range and other limitations, which make it a sub-optimum fuel for IC engines. Hydrogen, which can be produced from renewable resources as well, is a possible solution to some of these issues. However, hydrogen has its own limitations in terms of low storage energy density. It occupies very large volume as a gas, and storing it in liquid form is extremely energy intensive. There is a sharp contrast in vital properties of both these fuels; therefore, many researchers proposed blending hydrogen and CNG for IC engine applications. HCNG mixtures result in relatively lower emissions since they have higher H/C ratio. Therefore, they have the potential to replace conventional liquid fossil fuels in an environment-friendly manner. Nagalingam et al. (1983) studied the performance of an AVL research engine using CNG, hydrogen and hydrogen/CNG blends as early as in 1983. Engine Research Lab (ERL) at IIT Kanpur has conducted significant research on HCNG including development of HCNG engines and development of laser ignited HCNG engine, which are cited in this chapter to help understand the characteristics of HCNG as an alternate IC engine fuel (Hora et al. 2016; Hora and Agarwal 2015).

2.2.2 *Biofuels*

Biofuels have attracted growing attention of policy makers, industry and researchers. Biofuels are combustible materials, which can be derived directly or indirectly from biomass, produced from plants, animals and micro-organisms from the renewable organic wastes. Biofuels may be solid, liquid or gaseous and originate from all kinds of biomass and derived products used for energetic purposes. Biofuel production process and typical classification of fuels are shown in Fig. 2.3.

2.2.2.1 Primary Alcohols

Methanol, ethanol and butanol and their blends with gasoline are used as alternative transport fuels in SI engines (Agarwal 2007; Nigam and Singh 2011; Balki et al. 2012). Methanol is the shortest carbon chain primary alcohol and burns cleanly due to its simple chemical structure and high oxygen content ($\sim$50%). Ethanol is similar to methanol, however, it is relatively cleaner, less toxic and less corrosive compared to methanol (Agarwal 2007). Compared to other primary alcohols, butanol is far less corrosive and can be distributed through existing pipeline networks and filling stations (Nigam and Singh 2011). Use of lower gasoline-alcohol blends in SI engines results in reduction of CO, HC and NOx emissions while producing almost similar engine torque output (Agarwal 2007; Balki et al. 2012).

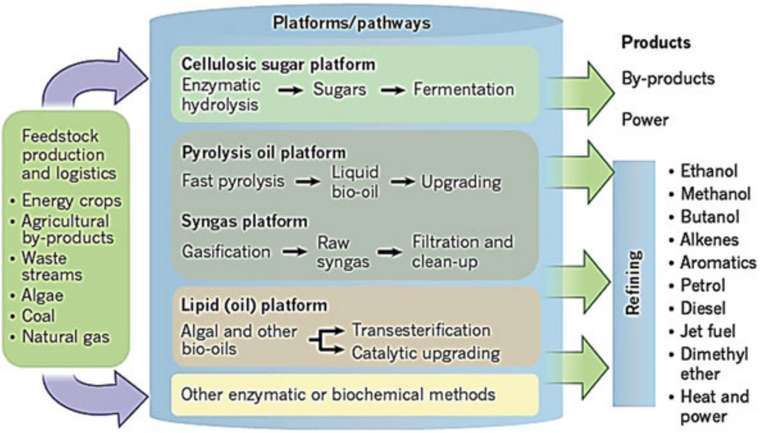

Fig. 2.3 Methods of producing alternative fuels from various biomass feedstocks to products (US Department of Energy 2011)

However, aldehyde emissions increase with alcohol-fuelled operation of IC engines (Agarwal 2007). For using higher blends of alcohols in SI engines, some engine modifications are essential to cater to their higher octane number, lower volatility, lower calorific value and different chemical reactivity vis-à-vis that of gasoline (Agarwal 2007; Kremer et al. 1996). Alcohol blends can also be used in CI engines as supplementary fuels (Ramadhas 2011; Agarwal 2007). For use of higher concentration ethanol blends (>20% v/v), fuel additives are required for stabilizing the mixture and attaining desired cetane number (Ramadhas 2011). Higher percentage of ethanol in diesel requires a double injection or fumigation system, which is helpful in emission and noise reduction but increases control complexity (Ramadhas 2011). Alcohols can also be used in blended form with straight vegetable oils, biodiesel and mineral diesel (Yilmaz and Sanchez 2012; Kumar et al. 2003). Alcohol–biodiesel–diesel blends result in reduction in NOx and particulate emissions in CI engines (Kumar et al. 2003; Shi et al. 2006; Zhu et al. 2010). Transesterification process for biodiesel production utilizes methanol/ethanol and vegetable oils as process inputs. This route of utilizing alcohols as a diesel engine fuel is definitely a superior route because aldehyde emissions and corrosion of engine parts by alcohols are drastically reduced this way (Nigam and Singh 2011).

2.2.2.2 Straight Vegetable Oils and Derivatives

Plant-derived oils, waste cooking oils or any other waste/residue triglycerides can be converted into diesel-like fuels through several routes. Vegetable oil-based fuels are biodegradable, non-toxic, and they have potential to significantly reduce environmental pollution. Vegetable oils have 90% heat content of mineral diesel, and they have a favourable output/input ratio of about 2–4: 1 for unirrigated crop production. In India, the current prices of vegetable oils are almost equivalent to that of petroleum-derived fuel prices. From amongst large number of vegetable oils available in the country, if any specific oil needs to be adopted as a continuing energy crop, then it is essential that this oilseed variety should have higher productivity and oil content. However, these vegetable oils have several issues such as low volatility and ability to polymerize (due to unsaturation). This leads to undesirable issues such as carbon deposits in the engine combustion chamber, injector coking and piston ring sticking (Agarwal 2007; Galle et al. 2012). To eliminate these issues, straight vegetable oils are converted into biodiesel, which has very similar properties as that of mineral diesel, and is currently one of the most accepted routes (Gerhard 2010). Biodiesel as an alternative transport fuel for CI engines is discussed in greater detail in the next section of this chapter. Another fuel with properties and composition similar to mineral diesel can also be produced by hydro-de-oxygenation of triglycerides. It is termed as hydrotreated vegetable oil (HVO) or renewable diesel (Gerhard 2010; International Energy Agency 2011; Huber and Corma 2007) or green diesel. In hydro-de-oxygenation process, a feedstock containing double bonds and oxygen moieties can be converted into hydrocarbons by removal of oxygen and saturation of double bonds (Gerhard 2010). Cold flow properties of renewable diesel are superior to mineral diesel, but currently, technology for its commercial production is in development stage (Gerhard 2010; International Energy Agency 2011).

2.2.2.3 Biodiesel

Vegetable oils in their raw form cannot be used in CI engines due to their inferior fuel properties; therefore, they have to be chemically modified to produce biodiesel, which has improved physical and chemical properties for use as a fuel. Biodiesel is a chemically modified alternative fuel for diesel engines, derived from vegetable oil fatty acids and animal fats. This is done using transesterification process, in which the reaction of triglycerides present in the vegetable oils is done with primary alcohols in presence of a catalyst, which produces primary esters (biodiesel) and glycerol (Agarwal 2007).

Base-catalyzed transesterification is the most common process used for production of biodiesel because it involves low reaction temperatures and pressures, low-cost material of construction and high process yield for good-quality feedstock (of low free fatty acid (FFA) and moisture content). The resulting biodiesel is quite similar to conventional diesel in its main characteristics. The process of transesterification brings about drastic changes in density and viscosity of vegetable oils. The biodiesel produced by this process is completely miscible with mineral diesel in any proportion to create a stable blend. Viscosity of biodiesel comes very close to that of mineral diesel; hence, problems related to fuel handling system are reduced. Transesterification process lowers the flash point of biodiesel and increases the cetane number, which is helpful in reducing the ignition delay. Therefore, lower concentrations of biodiesel can act as cetane improver for biodiesel blends. The heating value of biodiesel is close to mineral diesel. These properties make biodiesel suitable for CI engines without any major hardware modifications.

2.2.3 Unconventional Fossil Oils

Fossil fuel resources, whose extraction and conversion into liquid fuels is comparatively difficult and expensive, are referred as unconventional oils. Extra-heavy oil, natural bitumen (oil sands, tar sands) and oil shale are three important sources of unconventional oils (Mohr and Evans 2010). Extra-heavy oils are much more difficult to recover in comparison to conventional petroleum. Constituents of heavy oil have significantly higher viscosity than conventional petroleum, and primary recovery of heavy oils usually requires thermal stimulation of the reservoir. Natural bitumen also known as 'tar sand' and 'oil sand' is impregnated with dense, viscous organic material called bitumen (Lee et al. 2007; World Energy Council 2010). Oil shales are fine-grained sedimentary rocks, from which significant amount of shale oil and combustible gas can be extracted by destructive distillation (Mohr and Evans 2010; World Energy Council 2010). The presence of large amount of organic matter, known as 'kerogen', is the major source of oil and gas in oil shales. According to EIA, largest fractions of future unconventional liquid fuel production include 239 MTOE/year of Canadian oil sands, 69.7 MTOE/year of Venezuelan extra-heavy oils and 194.2 MTOE/year of biofuels (109.6 and 84.7 MTOE/year of the USA and Brazilian biofuels, respectively) (U.S. Energy Information Administration 2011). Unconventional fossil oils are predicted to account for roughly 7% of global liquid fuel supply by 2035 (U.S. Energy Information Administration 2011).

2.2.4 Other Alternative Fuels

2.2.4.1 Fischer–Tropsch Liquids

Fischer–Tropsch (F–T) process is a process that produces variety of hydrocarbon fuels. The primary product is a diesel-like fuel from syngas (H_2/CO), which can be produced by auto-thermal reforming of natural gas, biomass or coal (MacLean and Lave 2003; Nigam and Singh 2011; Gill et al. 2011). Depending on the starting material, process could be known as coal-to-liquid (CTL), gas-to-liquid (GTL) and biomass-to-liquid (BTL) conversion process. The F–T liquid fuel has no sulphur, almost no aromatics and high cetane number. These properties make this an attractive alternative fuel for CI engines (MacLean and Lave 2003). The feedstock for BTL is renewable and can be produced with biomass residues from food crops with minimal interference to the food economy and much less strain on land, air and water resources compared to alcohols or oilseed-based fuels. However, the conversion technologies such as hydrolysis and gasification are still under development (Gill et al. 2011).

2.2.4.2 Dimethyl Ether

Dimethyl ether (DME: CH_3-O-CH_3) exists in the form of a colourless gas at room temperature with slight odour. It is necessary to keep it in closed containers for normal use and distribution (Ramadhas 2011). Vapour pressure of DME lies in between propane and butane (Ramadhas 2011). DME is considered clean-burning alternative fuel for CI engines and is helpful in reducing local air pollution. It may be easily auto-ignited due to its high cetane number and results in practically soot-free combustion due to easy vaporization and absence of carbon-to-carbon bonds (Park and Lee 2013; Semelsberger et al. 2006). Like hydrogen and F–T liquids, it is also not found in nature. For DME production, organic feedstocks such as biomass, coal or natural gas are converted into synthesis gas, which is a mixture of carbon monoxide, hydrogen and some other gases. Syngas is converted into methanol and finally into DME by dehydrogenation of methanol (Ramadhas 2011; Park and Lee 2013). Power output of DME-fuelled engines is lower than diesel-fuelled engines due to significant differences in properties of diesel and DME such as higher compressibility and lower heating value of DME than mineral diesel. Lower fuel lubricity and viscosity of DME cause durability issues in fuel injection system, which needs to be resolved in order to adopt to this wonderful fuel at a large scale (Park and Lee 2013).

2.3 Conclusions

Above discussions clearly show that the twin crises arising out of fuel starvation and environmental degradation can be resolved by adopting sustainable and environment-friendly alternative fuels. For the developing countries like India, biofuels can provide a feasible solution to tackle these crises. These biofuels may be alcohols, vegetable oils, biomass, biogas, etc. Some of these biofuels can be used directly in the IC engines, while others require to be formulated to bring the relevant properties close to conventional fuels. There are number of serious reasons for using biofuels as alternative fuels, e.g. expected growth of prices of fossil liquid fuels in the near future, gradual depletion of crude oil resources in the next 80–100 years, etc. Devastated land excluded from food production may be used for biofuel production globally. Compared to conventional fuels, the harmful emissions in exhaust gas using biofuels are significantly lower. In India, most of the agricultural and transport energy requirements are fulfilled by mineral diesel as of now; therefore, it is essential that alternatives to mineral diesel should be developed on a priority basis. Apart from renewable energy technologies, a number of steps should be taken for promoting conservation of fossil fuels. These include improving energy efficiency of refineries, increasing fuel efficiency in the transport sector, greater utilization of CNG as a fuel in transport sector, upgradation of lubricants and promotion of fuel-efficient equipment and practices in industrial sector.

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Part II
Gaseous Alternative Fuels: Production and Utilization

Chapter 3
Hydrogen Production Through Biological Route

Sanjukta Subudhi

Abstract Socioeconomic development of a nation primarily depends on energy as a vital input, and thus, the energy strategy of a nation targets at energy security as well as at energy efficiency for its economic development. Owing to the rising population, limited crude oil reserves due to fast depletion of conventional fossil fuel sources along with rising greenhouse gas (GHG) emissions, there has been a global concern for energy security and environmental protection. In view of these concerns, energy production especially from sustainable sources has become the most imperative concern for national as well as for international policies. In this perspective, hydrogen has gained substantial global attention as clean, sustainable, and versatile energy carrier. Existing hydrogen production technologies mainly rely on photochemical, thermochemical processes which are high energy intensive and make use of conventional fossil fuel sources as feedstock either directly or indirectly. On the contrary, hydrogen production processes through biological route are less energy intensive, can be generated from renewable sources from organic wastes, and thus are sustainable. Biologically, hydrogen can be produced by few of the unique microbes/algae though four distinct approaches: (a) biophotolysis of water using algae/cyanobacteria, (b) photodecomposition (photofermentation) of organic compounds using photosynthetic bacteria, (c) dark fermentative hydrogen production using anaerobic (or facultative anaerobic) bacteria, and (d) hybrid biological hydrogen production through integration of dark fermentation process with photofermentation process. This chapter highlights in prospects and limitations of biohydrogen production process including recent developments on this domain. In addition, this chapter also sheds light on economic feasibility of biohydrogen production processes and addresses the need for integration of these technologies with production of value-added bio-based products in a biorefinery approach.

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Biophotolysis · Hydrogen-producing microflora

3.1 Introduction

The faster depletion of fossil fuel sources along with the rising levels of CO_2 emission not only poses global warming threat but also raises the serious concern for energy security. Since 1973, annual CO_2 emission has shown an increasing trend and has reached to 399 ppm of average CO_2 concentration in the atmosphere by 2015. This value is significantly higher (40%) compared to the pre-industrial level with average increase of CO_2 concentration by 2% during last decade (IEA 2016). Approximately 70% of all anthropogenic GHG emissions are from the energy sector, with the largest contribution from CO_2 produced by fossil fuel combustion (Yusuf et al. 2016). Energy-related global CO_2 emissions were estimated to be 30.4 Gt in 2010 (Cozzi 2011).

This has raised the global concern for immediate reduction of CO_2 emission to curb the negative climate effects. With a view to address these concerns, International Energy Agency advocated the document highlighting for no more than 2 °C warming above pre-industrial levels by 2050. This ambitious target emphasizes the urgent need for generation of low-carbon energy in a sustainable manner from alternate sources that are renewable and do not rely on conventional fossil fuel sources. Among the sustainable energy sources, hydrogen is widely recognized as the most promising fuel as it is a clean form of energy, can be easily transported, and not chemically bonded to carbon and when burns generate clean water (Uyar et al. 2007). Hydrogen is a non-toxic, lightest, colorless, and odorless gas (Demirbaş 2005). Hydrogen has the highest energy content per unit weight of any known fuel and is the only fuel that is not chemically bonded to carbon, and thus, its combustion does not contribute to the greenhouse effect, ozone depletion. It has 2.75 times higher energy content (122 kJ/g) than hydrocarbon fuels. Hydrogen has got substantial global attention since last few decades as an energy source owing to its high calorific value, high conversion efficiency, and recyclability including its non-polluting nature (Subudhi et al. 2016; Hallenbeck and Ghosh 2009).

Global hydrogen consumption peaked to 85 million tonnes (equivalent to 253 million tonnes of oil equivalent) in 2016, which is further rising steadily at around 10% per year. Presently, almost half of the hydrogen produced globally is utilized in ‘Haber process’ to produce ammonia (to use directly or indirectly in fertilizer industry), and other half is used for ‘hydrocracking,’ for conversion of heavy petroleum to lighter fractions to make it usable as fuels. With the advent of fuel cell and hydrogen internal combustion engines, use of hydrogen in transport sector got substantial global attention. This is mainly attributed to the ease of hydrogen use in internal combustion engines for conversion to power. Thus, hydrogen holds importance as promising clean fuel for transport sector (Sobrino et al. 2010).

Hydrogen is not available freely in nature and needs to be synthesized to use as primary energy source for conversion to usable forms of energy. Current hydrogen production processes heavily rely on fossil fuel sources. Hydrogen production from fossil-based sources leads to substantial emission of CO_2. Each tonne of hydrogen produced from fossil-based sources leads to generation of 11 tonnes of CO_2 emission. Due to climate change associated with GHG emissions, hydrogen production from non-fossil sources in sustainable manner got substantial global attention.

In order to produce hydrogen sustainably, it is prerequisite to substitute the fossil-based feedstock with renewable feedstocks, i.e., sunlight, water and biomass, and organic wastes. Concern for finding alternate energy forms triggered the global focus toward development of non-polluting and sustainable energy sources that can replace fossil fuels.

3.2 Hydrogen Production Processes

Hydrogen serves as primary energy source and needs to be synthesized for utilization in different energy forms. Currently, 96% of global hydrogen is produced from fossil-based sources either directly or indirectly; 48% from natural gas, 30% from liquid hydrocarbons, and 18% from coal (Ball and Wietschel 2009). Only 4% is produced from water electrolysis.

Hydrogen productions from fossil-based sources are carried out through the employment of thermochemical and photoelectrical processes, by the reactions of natural gas or light oil fractions with steam at high temperatures, coal gasification, and the electrolysis of water, which are highly energy intensive (Fig. 3.1). Photoelectrical hydrogen production process involves harvesting of sunlight coupled with electrolysis of water. The concern for hydrogen production processes is that these processes are highly energy intensive. Thermochemical processes make use of fossil-based sources as feedstock that eventually leads to substantial emission of CO_2. Thus, these processes are not sustainable.

Compared to these processes, hydrogen production through biological processes (known as biohydrogen) got significant advantages in view of the fact that these processes are less energy intensive and have reduced the initial investment cost. In addition, these processes are environmentally friendly and can make use of renewable feedstocks, i.e., biomass, organic waste, organic-rich industrial effluent. Hydrogen produced through biological routes can be channeled into fuel cells or internal combustion engines (White et al. 2006). These avenues indicate for biohydrogen as longer-term fuel option for the transport sector. The challenge of these processes is the purification of hydrogen from other gaseous by-products such as CO_2, which is simultaneously produced during fermentation.

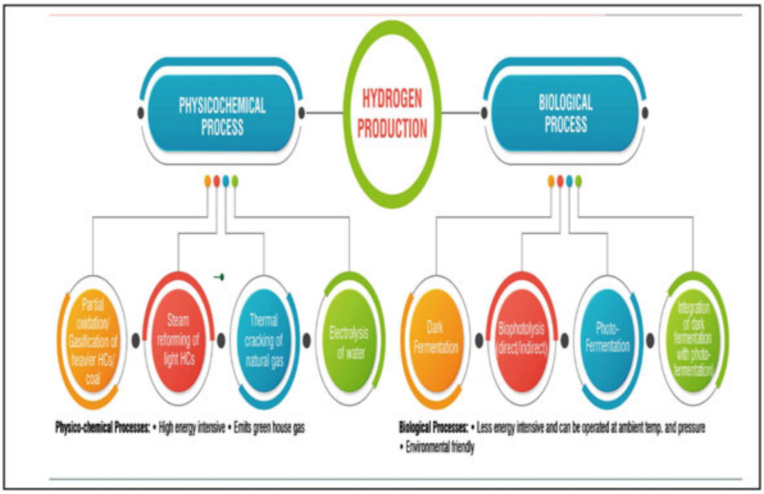

Fig. 3.1 Schematic presentation of hydrogen production through different chemical and biological processes

Biologically, H_2 can be produced anaerobically via (i) biophotolysis of water by microalgae and cyanobacteria (photosynthetic process), (ii) photodecomposition of organic compounds by photosynthetic bacteria (photofermentation process), (iii) dark fermentation of organic compounds (carbohydrates), and (iv) through integration of dark fermentation process with photofermentation process (hybrid process) (Subudhi et al. 2013).

3.3 Hydrogen-Producing Microorganisms and Their Biocatalysts

Few unique microorganisms encompass the biocatalysts, hydrogenase and nitrogenase enzymes, that play key role in catalyzing hydrogen production through different metabolic pathways carried out by these microbes. Based on the metabolic pathways involved, biological hydrogen production processes are distinguished into light-driven processes like photolysis or photofermentation and light-independent processes like dark fermentation, based on their light requirement.

Biological hydrogen production processes are carried out by different microbes (Fig. 3.2). *Escherichia coli*, *Citrobacter*, *Bacillus*, *Enterobacter,* and *Clostridium*, the facultative and obligate anaerobes (Subudhi et al. 2013; Nandi and Sengupta 1998; Junghare et al. 2012), encompass the biocatalysts playing catalytic role in fermentative conversion of organic substrates to molecular hydrogen, and this process do not require light and thus designated as dark fermentation process. Microalgae and cyanobacteria such as *Chlamydomonas*, *Anabaena, Nostoc, Plectonema, Oscillatoria, and Synechocystis* encompass the metabolic pathway to produce molecular hydrogen through light-driven photosynthetic process. Purple non-sulfur bacteria (PNS), *Rhodobacter, Rhodopseudomonas*, *are* composed of biocatalysts that aid in hydrogen production through photofermentation processes (Kruse et al. 2005; Tamagnini et al. 2002; Chen et al. 2006).

Production of soluble metabolites such as short-chain organic acids during hydrogen production through dark fermentation process can serve as feedstock for hydrogen production by PNS during photofermentation process, and thus dark fermentation process can be integrated with photofermentation process. Integration of the dark fermentation process with photofermentation process is carried out though the employment of dark fermentative bacteria in the first stage and then by purple non-sulfur bacteria (PNS) in the second stage which feed on the spent effluent from first process. All these processes have some advantages and limitations which are highlighted in Fig. 3.2.

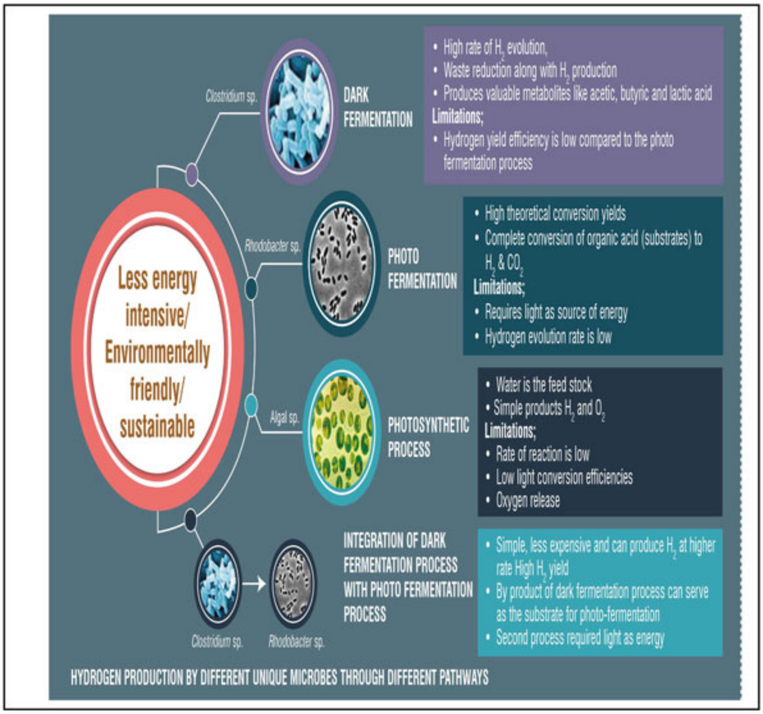

Fig. 3.2 Schematic presentation of hydrogen production by unique set of microbes through different biological routes and advantages and limitations of biohydrogen production processes

Hydrogen production rate is comparatively high through dark fermentation process, and this process can make use of organic waste as feedstock for clean hydrogen production. However, the limitations of this process are low hydrogen yield efficiency. Maximum 4 mol of hydrogen can be produced through this process from one mole of glucose (Junghare et al. 2012), whereas hydrogen yield efficiency of photofermentation process is high (8 mols of H_2/mole of glucose). But this process requires light as source of energy, and rate of hydrogen production is low in this process.

Compared to these processes, photosynthetic process has advantages with respect to feedstock as it can produce hydrogen from clean water. But the major challenge of this process is production of oxygen along with hydrogen, that inhibits the highly sensitive hydrogenase enzyme, which is the biocatalyst for hydrogen production in this process. Integration of dark fermentation process with photofermentation process can lead to overall hydrogen yield efficiency (12 mol of H_2/mole of glucose) enhancement through the use of spent effluent from dark fermentation process as feedstock for photofermentation process (Chen et al. 2006). The limitation of this process is the low hydrogen production rate along with light requirement of photofermentation process.

3.4 Biocatalysts for Molecular Hydrogen Production Mechanism

Hydrogenase and nitrogenase enzymes are both capable of catalyzing H_2 production. The role of hydrogenase enzyme in *Enteric* bacteria was first reported by Stephenson and Strikland (Stephenson and Strickland 1931). Since then, hydrogenase enzymes are reported from diverse group of organisms, ranging from aerobes to anaerobes, from autotrophs to heterotrophs, from prokaryotes to eukaryotic photosynthetic organisms, fermentative organisms, and sulfate reducers (Uyar et al. 2007).

All the reported enzymes serving as biocatalysts for H_2 generation encompass complex metallo-clusters as active sites and are synthesized in complex processes involving auxiliary enzyme and protein maturation steps. Based on the metal center, the H_2-producing enzymes are categorized as nitrogenases, Fe-only hydrogenase, and Ni-Fe hydrogenase (Hallenbeck and Benemann 2002). However, nature's production of molecular hydrogen rarely leads to storage, as it is rapidly consumed and present only in small quantity. It has been estimated that around 200 million tonnes of H_2 are cycled within the ecosystems per year. However, the atmosphere harbors only 7.8×10^{-5} vol.% H_2 (Belaich et al. 1990).

Hydrogenase enzymes catalyze the reversible oxidation of molecular hydrogen and can function in either direction, i.e., in the presence of electron acceptor they consume H_2, whereas under strict anaerobic condition, they produce H_2. Certain microbes like cyanobacteria are reported to contain bidirectional hydrogenase, which can catalyze either H_2 uptake or H_2 utilization, based on the environmental conditions and thus are able to switch between aerobic and anaerobic metabolism. Extensive research studies have been explored by researchers to elucidate the regulation mechanism of these enzymes including their crystal structure and their action mechanisms. Based on the physiological functions, these enzymes are classified under different subgroups (Vignais et al. 2001; Evans and Pickett 2003).

H_2 production performance of dark anaerobes through dark fermentation process mainly depends on the catalytic efficiency of hydrogenase. These enzymes are highly oxygen sensitive. During fermentation, NADH accumulates and hydrogenase is the way by which bacteria maintain their redox balance when electron acceptors as oxygen are not present. H_2-producing enzymes catalyze the basic chemical reaction;

$$2H + 2e^- \leftrightarrow H_2$$

There are several different hydrogenases; hydrogen-producing hydrogenase III found in *E. coli* and Clostridia are inactivated by oxygen.

Two different enzyme systems, pyruvate formate lyase system, pyruvate: ferredoxin oxidoreductase, are reported to play role in hydrogen production through dark fermentation process and are encompassed in different anaerobes, strict (Clostridia) and facultative anaerobes (Enteric bacteria).

(I) ***The pyruvate formate lyase system (Enteric bacteria)***

$$\text{Pyruvate} + \text{CoA} \rightarrow \text{Acetyl} - \text{CoA} + \text{formate}$$

In this metabolic pathway, pyruvate is converted to formate and then formate is decomposed to hydrogen and carbon dioxide by *E. Coli*. However, H_2 yield efficiency through formate is low; 2 mol of H_2/mole of glucose (Nandi and Sengupta 1998).

(II) ***The pyruvate: ferredoxin oxidoreductase (Strict anaerobes)***

$$\text{Pyruvate} + \text{Coa} + 2\,\text{Fd(ox)} \rightarrow \text{acetyl Coa} + CO_2 + 2\,\text{Fd(red)}$$

In this system, hydrogen production provides bacteria the ability to re-oxidize ferredoxin and hydrogen-carrying coenzymes. An increase in H_2 concentration in the liquid may inhibit these reactions.

Nitrogenase enzymes play critical role for nitrogen fixation and are mainly distributed in prokaryotes including blue-green algae. In this process, the enzyme catalyzes the reduction of dinitrogen to ammonia, through utilization of electrons (that are derived from low potential reductants, either ferredoxin or flavodoxin) and ATP. The reaction is irreversible and occurs as:

$$N_2 + 8H^+ + 8e^- + 16ATP \rightarrow 2NH_3 + H_2 + 16ADP + 16Pi$$

Hydrogen production by nitrogenase occurs as a side reaction at a rate of one-third to one-fourth that of nitrogen fixation, even in a 100% nitrogen gas atmosphere. Nitrogen has an intrinsic property to reduce solvent protons along with N_2 and to produce H_2. In the absence of N_2, the total electron flux tends to direct toward the protons to generate H_2 continuously. However, this process has limitations which is energy intensive and consumes large amount of energy in the form of ATP molecules.

Nitrogenases are extremely oxygen-labile. Cyanobacteria have developed mechanism for localization of nitrogenase in the heterocyst, thereby protecting nitrogenase enzymes from oxygen gas. The presence and physiological significance of hydrogenase in nitrogen-fixing bacteria remain controversial (Vignais et al. 2001; Vignais and Colbeau 2004; Adams et al. 1986; Adams 1990; Gaffron 1939).

3.5 Biophotolysis of Water by Microalgae and Cyanobacteria

Few of the green algae and cyanobacterial sp. got the potential to produce molecular hydrogen by water-splitting photosynthetic process rather than fixing carbon, a normal function of oxygenic photosynthesis. Photosynthesis involves two processes: light energy conversion to biochemical energy by a photochemical reaction and CO_2 reduction to organic compounds such as sugar, phosphates, through the use of this biochemical energy by Calvin-cycle enzymes. The physiological significance of H_2 metabolism in algae dates back to 1939 when Gaffron's group reported about the ability of a green alga, *Scenedesmus obliquus,* to metabolize molecular H_2 (Prince and Kheshgi 2005).

Research studies focused on this regard reveal for ability of many microalgae and cyanobacteria viz *Chlamydomonas, Anabaena, Nostoc, Plectonema, Oscillatoria, Synechocystis, Rhodobacter, Rhodopseudomonas, and Chlorobium* to produce molecular hydrogen. Bidirectional hydrogenases in these organisms use electrons from photosynthetic electron transport chain to reduce protons and yield H_2. This approach of hydrogen production is quite promising as the source of electron is water, a clean renewable, carbon-free substrate. Theoretically, the maximal energetic efficiency for direct biophotolysis is about 40% (Kruse et al. 2005; Tamagnini et al. 2002; Chen et al. 2006; Redwood and Macaskie 2006).

It has been observed that under certain conditions, a few group of microbes instead of reducing CO_2 consume biochemical energy to produce molecular H_2. Hydrogenase and nitrogenase enzymes are both capable of catalyzing H_2 production.

3.6 Hydrogen Production Through Dark Fermentation Route

Hydrogen production through dark fermentation process is a complex process carried out by fermentative anaerobes. This process involves the utilization of multi-enzyme system playing important role in hydrolyzing the complex organic polymers to monomers and then eventually ferment the monomers to the mixture of low molecular weight organic acids and alcohol. Subsequently, acetogenic bacteria convert fermentative products to H_2. Since these reactions do not require light energy, fermentative bacteria constantly produce H_2 from organic compounds and have a high evolution rate of H_2. In biological hydrogen production process, theoretical bioconversion of one mole of glucose yields 12 mols of hydrogen gas.

However, with respect to the reaction stoichiometry of the dark fermentation process, bioconversion of one mole of glucose can yield a maximum of 4 mol of hydrogen with acetic acid as the end product [Reactions (3.1) and (3.2)]. Alternatively, only 2 mol of H_2/mol of glucose is formed when butyrate is the end product [Reactions (3.3) and (3.4)].

$$C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CO_2 + 2C_2H_4O_2\ \Delta G\,°C(35\,°C) = -184.2\,kJ \quad (3.1)$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CO_2 + 2C_2H_4O_2\ \Delta G\,°C(60°C) = -20.1\,kJ \quad (3.2)$$

$$C_6H_{12}O_6 \rightarrow 2H_2 + 2CO_2 + C_4H_8O_2\ \Delta G\,°C(35\,°C) = -244.2\,kJ \quad (3.3)$$

$$C_6H_{12}O_6 \rightarrow 2H_2 + 2CO_2 + C_4H_8O_2\ \Delta G\,°C(60\,°C) = -84.2\,kJ \quad (3.4)$$

These reactions imply for the fact that highest theoretical yield of hydrogen is associated with acetic acid as the fermentation end product. This indicates that hydrogen yields of dark fermentative microbes can be enhanced through redirection of metabolic fluxes preferably for the reactions (3.1) and (3.2) with a goal to get acetic acid as fermentation end products (Miranda et al. 2016). The stoichiometric analysis of bioproduction of hydrogen by *Clostridium butyricum* from glucose determined a theoretical maximum hydrogen yield of 3.26 mol H_2/mole of glucose consumed when acetyl-CoA is used through acetate pathway under anaerobic conditions (Chen et al. 2006). At optimum condition, *C. butyricum* TM-9A produced hydrogen 3.1 mol of H_2/mol of glucose (Junghare et al. 2012), close to maximum theoretical hydrogen yield from glucose (4 mol of H_2/mole of glucose).

3.6.1 Anaerobes Encompassing Metabolic Pathway for Dark Fermentative Biohydrogen Production

Diverse group of facultative and obligate anaerobes, *E. coli*, *Citrobacter*, *Bacillus*, *Enterobacter,* and *Clostridium*, are reported to undergo fermentative conversion of organic substrates to molecular hydrogen by a series of biochemical reactions (Subudhi et al. 2013; Nandi and Sengupta 1998; Junghare et al. 2012; Miranda et al. 2017; Kotay and Das 2007; Nath and Das 2004; Nath et al. 2006; Ueno et al. 2001). Mixed cultures also found to play a crucial role in hydrogen production. Extensive investigations have been done to identify the microbial communities present in mixed cultures used for H_2 production (Ueno et al. 2001; Fang et al. 2002; Kawagoshi et al. 2005; Kim et al. 2006; Kumar and Das 2000). Fang et al. (2002) identified the microbial species in a granular sludge used for H_2 production from sucrose (Ueno et al. 2001). Their study pointed out that 69.1% of the microorganisms were *Clostridium* species and 13.5% were *Bacillus*/*Staphylococcus* species. Successful biological H_2 production depends on pretreatment of parent culture as it enables the selection of the requisite microflora. Apart from use of mixed microflora for hydrogen production through dark fermentation process, several studies were also explored on use of pure anaerobes such as *Enterobacter* (Subudhi et al. 2013; Junghare et al. 2012; Miranda et al. 2017; Kotay and Das 2007; Oh et al. 2003), *Citrobacter* (Wang et al. 2003), and *Clostridium* (Najafpour et al. 2004), for hydrogen production through fermentation of monosaccharides (glucose and xylose), cellulose and starch, biomass sugars from aquatic macrophyte, and algae/cyanobacteria.

3.7 Hydrogen Production Through Photofermentation Route

During photofermentation processes, short-chain organic compounds, acetic acid, butyric acid, lactic acid, malic acid, are converted into hydrogen and CO_2 in the presence of sunlight by unique group of purple non-sulfur bacteria (PNS) (Subudhi et al. 2016). Purple non-sulfur bacteria (PNS) have long been explored for their ability for photohydrogen production, catalyzed by their nitrogenase systems. Purple non-sulfur bacteria can utilize versatile substrates such as short-chain volatile fatty acids (VFA) as well as carbohydrates (Subudhi et al. 2016; Basak and Das 2007; Nogi et al. 1985) as electron donors in hydrogen-producing light-driven process that are catalyzed by nitrogenase under nitrogen deficient conditions.

The photosynthetic device of PNS bacteria is simple and comprises of only one photosystem (PS), which is fixed in the intracellular membrane and is not powerful enough to split water (Chen et al. 2008). Under anaerobic conditions, PNS bacteria can make use of the above-mentioned substrates or hydrogen disulfide as electron donor. The electrons that are liberated from the organic carbon or H_2S are pumped through a large number of electron carriers. During electron transport, protons are pumped through the membrane creating a proton gradient that eventually generates ATP in the presence of ATP synthase. The extra energy in the form of ATP used to transport the electrons further to the electron acceptor ferredoxin (Fd). In the absence of molecular nitrogen, the electrons that are placed on ferredoxin are used by nitrogenase to reduce protons to hydrogen. This process takes place under anaerobic conditions.

Maximum theoretical hydrogen yield efficiency of PNS bacteria through photofermentation process is 8 mol of H_2 per mole of glucose. Substrate conversion efficiency is a critical parameter and serves as a measure of how much of the substrate is being utilized for hydrogen production rather than growth or alternative biosynthesis. It was determined as the ratio of moles of hydrogen that have actually been produced per moles of hydrogen expected through stoichiometric conversion of the substrate according to the following hypothetical reaction (Uyar et al. 2007).

$$C_xH_yO_z + (2x - z)H_2O \rightarrow (y/2 + 2x-2)H_2 + xCO_2$$

Substrates' conversion efficiency of malate, lactate, acetate, propionate, and butyrate is (Uyar et al. 2007):

Malate	$C_4H_6O_5 + 3H_2O \rightarrow 6H_2 + 4CO_2$
Lactate	$C_3H_6O_3 + 3H_2O \rightarrow 6H_2 + 3CO_2$
Acetate	$C_2H_4O_2 + 2H_2O \rightarrow 4H_2 + 2CO_2$
Propionate	$C_3H_6O_2 + 4H_2O \rightarrow 7H_2 + 3CO_2$
Butyrate	$C_4H_8O_2 + 6H_2O \rightarrow 10H_2 + 4CO_2$

3.7.1 Anaerobes Encompassing Metabolic Pathway for Photofermentative Biohydrogen Production

Many research explorations have been explored on photofermentative H_2 production by using different substrates: short-chain organic acids, waste water, organic acid spent effluent from dark fermentation process, crop residues (Chen et al. 2006; Kim et al. 2001; Lee et al. 2002; Yetis et al. 2000; Kapdan et al. 2009; Argun et al. 2008; Liu and Shen 2004). Few of the unique PNS bacteria have the ability to utilize directly the carbohydrate sugars such as glucose and sucrose (Subudhi et al. 2016; Kars and Gunduz 2010). Substrate specificity of different PNS bacterial species varies, and carbon sources are critically important as these sources serve as electron donor.

Compared to other PNS bacterial strains, *Rhodobacter sphaeroides* have wide substrate utilization potential. Few strains of *R. sphaeroides* are reported to utilize directly the sugars like glucose and sucrose. These studies demonstrate that few strains of *R. sphaeroides* encompass carbohydrate catabolic pathway as well (Subudhi et al. 2016; Koku et al. 2002).

3.8 Combined Biological Hydrogen Production Through Integration of Dark Fermentation with Photofermentation Process

Dark fermentative microbes partly degrade the substrate during hydrogen production process and convert to hydrogen and soluble metabolites (volatile fatty acids and other metabolites such as ethanol). Hence, the hydrogen yield efficiency though dark H_2 fermentation is low, though H_2 production rate is high during this process. The metabolic products, volatile fatty acids, generated during dark fermentation process can serve as good substrate for purple non-sulfur bacteria that can be further mineralized by these bacteria via photofermentation to produce more H_2 (Oh et al. 2004; Takabatake et al. 2004). This can lead to complete conversion of the substrate employed during dark fermentation process along with overall enhancement in hydrogen yield efficiency. Maximum theoretical hydrogen yield efficiency can be achieved up to 12 mol H_2/mole glucose through integration of dark fermentation with photofermentation process, as mentioned below (Subudhi et al. 2016; Miyake et al. 1984):

(i) **Dark Fermentation in stage-I,**

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2$$

(ii) **Photofermentation in stage-II,**

$$2CH_3COOH + 4H_2O \rightarrow 8H_2 + 4CO_2$$

Miyake et al. (1984) first reported the improved hydrogen yield efficiency of 7 mol H_2/mol glucose through implication of both dark—and photofermentative microbes, by immobilized cells of *C. butyricum and R. spheroids*. Yokoi et al. reported the production of 6.6 mol H_2/mol glucose in fed-batch culture by mixed culture of *C. butyricum* and *Rhodobacter* sp. M-19. In 2001, they further reported that two-step repeated batch cultures by an above-mixed culture produced a high yield of 7.0 mol H_2/mol glucose from the starch remaining in sweet potato starch residue (Yokoi et al. 2001). Kim et al. (2001) reported the hydrogen production from food-processing wastewater and sewage sludge through combined dark fermentation with photofermentation. *Rhodopseudomonas palustris* could utilize the volatile fatty acid of dark fermentation process to produce hydrogen through photofermentation route (Lee et al. 2002).

3.9 Advantage and Limitations of Biohydrogen Processes

Though hydrogen productions through biological routes have several advantages, there are many limitations associated with these biological processes. Advantage of photosynthetic process is that this process can make use of clean water as substrate. Major constraint of this process is simultaneous release of oxygen along with hydrogen, which inhibits highly oxygen-sensitive hydrogenase enzyme. Other challenges of this process are requirement of light and high cost of anaerobic photobioreactors. These constraints pose challenge in scaling up this process. Compared to this process, dark fermentation process has several advantages such as rate of hydrogen production is comparatively high, use of different organic waste as feedstock enabling this process to accomplish waste degradation along with clean energy generation. However, the limitation of this process is low substrate to hydrogen conversion efficiency as the substrates are partially degraded leading to formation of metabolites along with hydrogen. This poses a challenge in scaling up of this process in commercial scale. The advantages of photofermentation process are that the hydrogen yield efficiency is very high and this process can make use of organic acid-rich spent effluent from dark fermentation process as feedstock. This aids in treatment of spent effluent and simultaneous hydrogen production. Hydrogen generated through this process is pure (>96%). However, major constraint of this process is that this requires light as source of energy and rate of hydrogen production is very low. Scaling up of this process is also not economically feasible due to high cost of anaerobic photobioreactors (requiring larger surface area). Combined dark and photofermentation process has considerable significances than all the above three processes, as it leads to enhancement of overall hydrogen yield efficiency through complete utilization of substrate employed in first stage for dark fermentation process. This eventually helps in treatment of spent effluent from dark fermentation process. Hence, it is imperative to address these challenges in order to make biological hydrogen production commercially feasible.

3.10 Conclusion and Future Prospects

Biological hydrogen production is the most promising area of biotechnology with respect to the problems associated with environment. In view of the energy security and environmental concerns, hydrogen production through biological route offers a promising approach for clean energy generation. However, the concern for food security along with energy security raised the concern for the feedstocks. Considering the concerns of food security along with energy security, global energy explorations are shifted toward use of non-food-competitive (next generation) feedstocks such as lignocellulosic biomass, organic waste (that do not compete for food), for production of advanced biofuel (gaseous, liquid biofuel) from next-generation feedstocks.

In the recent past, couple of research explorations reported on biohydrogen production from next-generation feedstock. However, these processes are not yet scaled up in large scale. One major challenge is the cost. To make these processes economically viable, it is imperative to co-produce bio-based products/ biocommodities along with the biohydrogen from non-edible biomass resources in an integrated biorefinery approach. This can help in overcoming the challenges to make the integrated process cost competitive.

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Chapter 4
Hydrogen for Internal Combustion Engines

Anuj Pal and Avinash Kumar Agarwal

Abstract With the scarcity of fossil fuels as well as stringent emission norms, there is a huge shift in the automotive research to develop engines capable of utilizing alternative fuels with superior fuel efficiency and lower emissions. Several alternative fuels have been tried out to cater to ever-increasing needs of better efficiencies and reduced emission. One of the most promising fuel researchers are currently evaluating is hydrogen because of its better combustive properties compared to conventional fuels, as well as the absence of carbon in its molecular structure. While there are various advantages of using this fuel for our needs, there are few challenges also, which form a roadblock for making hydrogen a commercially viable fuel. This chapter discusses the efforts made by several researchers over decades to make hydrogen a suitable fuel for future internal combustion engines.

Keywords Alternate fuels · IC engines · Hydrogen · Emissions

4.1 Introduction

The main intent of this chapter is to demonstrate the advantages of using hydrogen in the internal combustion (IC) engine as well as how researchers have proceeded with the research of using hydrogen in the engine combustion chamber. This chapter initially describes the need of an alternate fuel, potential of hydrogen as a prominent fuel for future, and later it focused on different fuel injection strategies used for introduction of hydrogen into the combustion chamber by various researchers. Also, toward the end, a brief introduction of advanced ignition technique has been covered to show the advantages of using superior ignition system in hydrogen-fueled engines to get overall improved results.

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World has become hugely dependent on energy for their day-to-day activities, and it is almost impossible to think of modern civilization without energy. With an increased global population over the years, demand for energy has increased significantly. Figure 4.1 shows global primary energy demand and its projections in foreseeable future.

As evident from Fig. 4.1, global primary energy demand is increasing rapidly and this trend will continue in future as well. Currently, for meeting most of the energy demand, conventional fossil fuels are the primary resources used. Rapidly increased demand for energy is a burden on the existing fuel reserves, and we are at a juncture, where if we do not take corrective actions, the fossil fuel reserves will deplete in near future. Because of increasing demand for conventional fossil fuels, fuels prices are also rising and fluctuating. Immediate solution to counter this scenario is to find sustainable alternate fuels, especially for transport sector.

In addition to the above issues, biggest concern of the world at present is the environmental degradation and climate changes, primarily caused by vehicular emissions. Various hazardous pollutants are emitted by vehicles, which cause serious environmental issues such as global warming, reduction in atmospheric visibility, acid rains, photochemical smog. Emissions cause serious health hazards like cancer, damage to the central nervous system, lung diseases, asthma, and different allergies (The Harmful Effects of Vehicle Exhaust 2014). For controlling the environmental damage, countries throughout the world have been adopting stringent emission norms which are further evolving with time.

Now, with increased energy requirements and shrinking fuel reserves, the only option for the researchers is to find sustainable solutions to counter depletion of

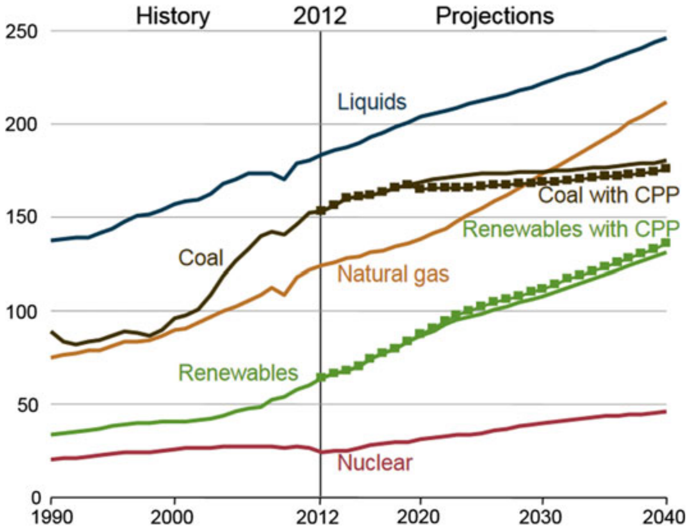

Fig. 4.1 World energy consumption for various primary energy sources (quadrillion Btu) (International Energy Outlook 2016)

fossil fuel reserves. With the enforcement of stringent emission norms globally, researchers have an additional challenge to come up with a cleaner new energy solution. In transport sector, scientists are experimenting with several alternate fuels to power the vehicles. In this journey, researchers have come up with several alternate fuel options such as use of alcohols/blends, liquefied petroleum gas, vegetable oils, biofuels, natural gas, hydrogen. Among all these alternate fuel options, except hydrogen, every fuel option contains carbon, which produces carbon dioxide (CO_2) emissions after the combustion. Since hydrogen is free of carbon, it can emerge to be the cleanest alternate fuel for future transport needs, if other challenges could be taken care of. Table 4.1 shows several important fuel properties of hydrogen compared to other conventional fossil fuels.

Table 4.1 Important properties of hydrogen compared to other fossil fuels (Wallner 2011)

Parameter	Symbol	Unit	Diesel	Gasoline	Methane	H_2
Density	ρ	kg/m^3	830[a]	730–780[a]	0.72[a]	0.089[a] 71[b, c]
Stoichiometric air demand	L_{St}	kg$_{air}$/kg$_{fuel}$	14.5	14.7	17.2	34.3
Lower heating value	H_u	MJ/kg$_{Kst}$	42.5	43.5	50	120
Boiling temperature[c]	$T_{Boiling}$	°C	180–360	25–215	−162	−253
Ignition limits[d]		vol.% λ	0.6–5.5 0.5–1.3	1.0–7.6 0.4–1.4	5.3–15 0.7–2.1	4–76 0.2–10
Minimum ignition energy[c, d, e]	$E_{Ignition}$	mJ	0.24	0.24	0.29	0.02
Self-ignition temperature	$T_{Ignition}$	°C	approx. 250	approx. 350	595	585
Diffusion coefficient	D	cm^2/s	–	–	0.16[a, d] 1.9×10^{-2}[g]	0.61[a, d] 8.5×10^{-2}[g]
Quenching distance[c, d, f]		mm		2	2.03	0.64
Laminar flame speed[d, e]	V_{lam}	cm/s	40–80	40–80	40	200
Carbon content	C	mass %	86	86	75	0

[a]At 1.013 bar, 0 °C, [b]at −253 °C, [c]at 1.013 bar, [d]in air [e]$\lambda = 1$, [f]at 20 °C, [g]at 100 bar, 1000 K

4.2 Hydrogen as an Alternative Fuel

Compared to other conventional fossil fuels such as gasoline, diesel, compressed natural gas (CNG), biodiesel, hydrogen offers numerous advantages as an alternate transport fuel. These are

- Combustion of hydrogen does not produce any greenhouse gas because it is a carbon-free alternate fuel. Only traces of NOx emissions are released from combustion of hydrogen–air mixture. Therefore, its usage drastically reduces harmful emissions from the engine into the environment.
- One major advantage of hydrogen is its availability. It can be easily produced by using primary renewable energy such as wind, solar via water electrolysis, from coal and biomass via gasification, from natural gas via steam reforming of methane, and various other ways (Hydrogen Production).
- On mass basis, energy content of hydrogen is very high compared to other conventional fuels, which means greater energy output per unit mass can be realized upon combustion. However, upon comparing the energy content on volume basis, energy content of hydrogen is significantly lower compared to other conventional fuels. This makes hydrogen storage an extremely important bottleneck in its usage in IC engines. On volume basis, energy content of hydrogen (in liquid state) is 8491 MJ/m^3, and for gasoline, it is 31,150 MJ/m^3 (Gupta 2008).
- Hydrogen requires very low ignition energy and has wider flammability range. Therefore, ignition of leaner fuel–air mixtures is possible without possibility of misfire. This decreases the specific fuel consumption at lower engine loads as well as NOx emissions.
- Auto-ignition temperature of hydrogen is higher than other conventional fuels. Therefore, dedicated engines can be designed to operate smoothly using hydrogen with higher compression ratio without knocking.
- Diffusivity of hydrogen in air is very high compared to other gaseous fuels such as methane (Fayaz et al. 2012); however, its density is very low. Therefore, in the event of an accidental leakage, it moves upward and mixes quickly with ambient air and forms a very dilute mixture, hence chances of accidental fire due to leakage are very slim. Another advantage of higher diffusivity is in formation of homogeneous fuel–air mixture. Due to higher diffusivity, hydrogen quickly mixes with air to form homogeneous fuel–air mixture, which helps in achieving superior combustion thus lowering the emissions further.
- Inside the engine combustion chamber, flame front propagation in hydrogen–air mixture is very rapid compared to other fuels (Gupta 2008; Fayaz et al. 2012; Sorensen 2012; Das 1990). This improves the combustion at higher engine speeds without misfire in any engine cycle. Also, because of higher flame speed, unburned charge gets ignited quickly, which reduces the chances of auto-ignition of the unburnt fuel.
- Hydrogen is colorless, odorless, and non-toxic gas, therefore, does not cause any environment nuisance, when released in atmosphere accidently.

There are few disadvantages and limitations of hydrogen as an alternate transport fuel also. They are

- Flame quenching distance is very small for hydrogen (Gupta 2008; Fayaz et al. 2012; Sorensen 2012). Therefore, flames might propagate backward through the inlet valve gap into the intake manifold, causing backfire.
- With low ignition energy, there are significantly higher chances of preignition and backfire. This limits the amount of hydrogen induction into the combustion chamber.
- Hydrogen has very low density (Gupta 2008; Fayaz et al. 2012; Sorensen 2012). Hence, for obtaining similar power output from an engine, larger volume of hydrogen is required to be inducted into the cylinder, compared to other conventional fuels.
- For longer range of vehicle, large hydrogen storage is required, which poses immense challenge for its utilization as an alternate fuel, especially in light-duty vehicles, which have severe space constraints.

4.3 Use of Hydrogen in IC Engines

Owing to the potential of becoming one of the most efficient and cleanest fuel for future, hydrogen research is progressing at a fast pace. Various studies have been done on using hydrogen as fuel in IC engines. Various groups have attempted using hydrogen in carbureted systems, port fuel injection systems as well as direct injection systems in IC engines. Researchers are also developing hydrogen fuel cells for powering vehicles. The biggest challenge for vehicular use is due to low density of hydrogen, which creates difficulty in storage.

Several studies have been carried out for developing different fuel injection systems for hydrogen. Initially, researchers tried utilizing hydrogen in carbureted systems. While this system was much less complicated and produced some promising results as shown by Das and Mathur (1993), it suffered from several drawbacks such as high probability of backfire, preignition, and several others, which may lead to catastrophic accidents, if flames could not be prevented from propagating backward. This aspect forced researchers to look for an alternate approach, which led to development of port fuel injection systems for hydrogen (Mohammadi et al. 2007). With this new approach, chances of accident reduced significantly but the new challenge was to develop an efficient high volume flow rate injector for injecting sufficient quantity (volume) of low-density hydrogen inside intake port. This approach reduced the volumetric efficiency of hydrogen engine, leading to severe power derating of the engine. With the advantage of potential increase in engine efficiency, reduced emissions as well as complete elimination of major drawbacks with hydrogen utilization in IC engines, researchers tried developing hydrogen direct injection system (Varde and Frame 1984). By using hydrogen direct injection techniques, power density of naturally aspirated hydrogen engine was at par with gasoline-fueled engine operating under similar conditions. To increase the power density of hydrogen-fueled engines, researchers have been focusing on boosting the engines. Pal and Agarwal (2015) performed an experimental study to evaluate the use of hydrogen in the combustion chamber by replacing conventional electric spark ignition system with a newly developed laser spark ignition system.

Following subsections provide details of the studies performed by various researchers to evaluate the engine performance, combustion, and emissions using all these techniques mentioned earlier in this section.

4.4 Hydrogen Induction Using Carbureted System

Because of zero carbon content, various researchers have tried evaluating the advantages and disadvantages of hydrogen in IC engines. For inducting hydrogen into the combustion chamber, the simplest way with no or very less hardware modification in the existing system is to use a carbureted fuel induction system. Various experiments were performed using this technique for hydrogen induction and to evaluate the advantages of hydrogen over the conventional fuels in terms of engine performance, combustion, and emissions. One of the main problems in operating the hydrogen-fueled engine using carbureted system is the occurrence of backfire of richer fuel–air mixtures. In addition, for richer hydrogen–air mixtures, NO_x emissions are also seen to be very high. One way of controlling both NO_x emissions and backfire is to use water injection technique. Billing (1978) used water injection to control NO_x emissions, in addition to prevent backfire in a hydrogen-fueled engine. A heavy-duty bus engine running on gasoline was modified to a hydrogen-fueled engine. Hydrogen was stored in the metal hydrides form. Piston with compression ratio of 12:1 was installed in the engine to improve its performance. Gasoline carburetor was replaced by gaseous carburetor for hydrogen induction into the combustion chamber. Experiments were performed to study the effect of water injection and spark timing on the engine performance and emissions. At 2000 rpm engine speed, NO_x emissions decreased, thermal efficiency remained almost same, and brake mean effective pressure slightly increased upon increasing water/hydrogen ratio in this study. At 3000 rpm, increasing water/hydrogen ratio decreased the thermal efficiency, brake means effective pressure, and NO_x emissions from the engine. Increasing the spark advance increased the NO_x emissions as well as the BMEP. Thermal efficiency initially increased upon advancing the spark timing, but after a certain point, it started decreasing.

Nagalingam et al. (1983) performed experiments in a research engine using hydrogen, natural gas, and hydrogen–natural gas (HCNG) blends as fuel and carried out comparison between these fuels. Results showed reduction in power output and thermal efficiency by 23 and 12%, respectively, on using hydrogen in place of natural gas at 1200 rpm. Lean limit of air–fuel ratio for engine operation was significantly extended for hydrogen compared to natural gas. For hydrogen, optimum spark timing significantly retarded. NO emission was found to be higher for the hydrogen engine. Water injection for controlling NO_x emissions in the hydrogen engine was very effective at higher engine speeds compared to lower engine speeds. For HCNG blends, performance of the engine was found to be somewhere in-between hydrogen and natural gas engine performances, depending upon the percentage of hydrogen in the blend.

One reliable way to control NO_x emissions from an engine is to use exhaust gas recirculation (EGR). For controlling NO_x emissions from hydrogen-fueled engine, Das and Mathur (1993) used different EGR rates in engine during experiments. They performed experiments on a four-cylinder engine using carburetion system for hydrogen induction. Engine performance was evaluated. Increasing EGR reduced the exhaust gas temperature, which reduced NO_x emissions from the engine. At 15% EGR, significant reduction in NO_x emissions was obtained and BSFC also improved. Increasing EGR rate further reduced the BSFC. Advancing the spark timing increased the peak temperature in the combustion chamber, which increased NO_x emissions from the engine.

Ding et al. (1986) studied combustion of hydrogen-fueled engine and compared its advantages vis-a-vis gasoline. For performing the experiments, compression ratio was increased from 6.2 to 7.8 in order to reduce the amount of residual gas in the engine. It was found that for hydrogen-fueled engine, thermal efficiency was higher compared to gasoline-fueled engine. Also, with higher compression ratio, thermal efficiency of hydrogen-fueled engine was higher than observed at lower compression ratio. Gasoline-fueled engine's exhaust gas temperature was higher than that from hydrogen. Also, at lower compression ratio, exhaust gas temperature was relatively higher compared to the one with higher compression ratio. Hydrogen operation in carbureted engine restricts the maximum strength of fuel–air mixture inside the combustion chamber due to engine backfire. Thus, in order to avoid the backfire, better fuel induction techniques have to be adopted so as to increase engine's power output and efficiency. Next, researchers adopted port fuel injection technique to induct hydrogen in the combustion chamber in order to reduce the possibility of backfire and improving the engine performance

4.5 Hydrogen Induction Using Port Fuel Injection System

In order to avoid engine backfire, one alternate way of hydrogen induction is its injection into the engine manifold or inlet port. Hydrogen is injected into the port after the intake valve is opened so that initially, some air is inducted inside the combustion chamber first. Because of delayed hydrogen injection in intake manifold, initial intake air scavenges the hot exhaust gases and cools down the hot spots inside the combustion chamber, which reduces the thermal intensity of prevailing hot spots, if any. This reduces the chances of engine backfire, when hydrogen is injected into the manifold and inducted into the engine cylinder during the intake stroke.

Lee et al. (1995) investigated manifold injection of hydrogen. In order to avoid flashback, precise injection timing was used and hot spots could be prevented in the engine combustion chamber. Compared to gasoline engine, higher efficiency was reported for hydrogen. For hydrogen-fueled engine, peak thermal efficiency was ~36.7%, whereas for gasoline, it was ~35.8%. Peak cylinder pressure in case of hydrogen-fueled engine was 50.8 bar compared to 39.8 bar in case of gasoline engine. NO_x emissions for hydrogen were found to be higher than gasoline due to relatively higher pressure rise rate in the combustion chamber. At $\lambda = 1$ and spark timing of 15° bTDC, flashback was noticed, which could be because of the presence of hot spots inside the combustion chamber due to deposits originating from pyrolysis of lubricating oil. Coefficient of variation (COV) of IMEP in hydrogen engine was very low, which indicated stable engine combustion compared to gasoline.

Haffel (2003) reduced NO_x emissions from hydrogen-fueled engine by using EGR. They reported that at lower air–fuel ratios, NO_x emissions were lower, which increased up to 7000 ppm as the air–fuel ratio increased. NO_x emissions again drastically reduced as the air–fuel ratio became close to stoichiometric. For normal combustion without EGR, maximum engine efficiency was obtained at $\Phi = 0.45$ with lower NO_x emissions. For lower NO_x emissions, using EGR delivered maximum brake torque (MBT) of 87 Nm, which was higher than the lean burn strategy, in which case, MBT was 68 Nm.

Lee et al. (2001) investigated the effect of crevice volume on engine backfire limit. They found that backfire limit (BFL) equivalence ratio for 6 mm deep crevice (471.2 mm^3) was nearly 8.5% lower at 50 and 8% higher at 90% than those in case of no crevice volume. BFL equivalence ratio increased by 5.7% on increasing the crevice volume by ~4.7%. Sirens and Verhelst (2003) varied inlet port geometries numerically to study its effect on efficiency and power output of the hydrogen-fueled engine. They used four different inlet geometries for hydrogen induction, namely T-junction, Y-junction, 45° junction, and 45° junction inverse (Fig. 4.2).

Maximum power output was obtained with Y-junction configuration. It gave highest power output at start of injection (SoI) of 80 °CA and lowest power output at SoI of 40 °CA. Maximum efficiency was obtained with 45° junction configuration.

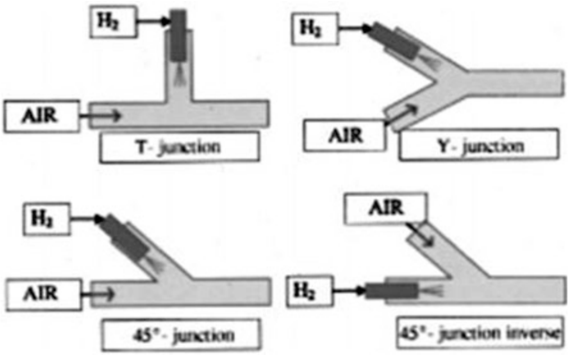

Fig. 4.2 Different inlet port geometries for hydrogen induction (Sirens and Verhelst 2003)

Using timed manifold injection (TMI), Mathur and Das (1991) performed experiments to evaluate hydrogen-fueled engine performance. Tests were carried out by varying the compression ratio and engine speed, while load was varied from no to full load. It was found that IMEP increased upon increasing the compression ratio and also upon increasing the equivalence ratio at a particular compression ratio. Lowest equivalence ratio at which hydrogen was able to burn was 0.218. Indicated thermal efficiency (ITE) was 56.2% with TMI, which was higher by 4.2% compared to hydrogen carburetor. Beyond an equivalence ratio of 0.6, ITE was found to reduce. At high engine speeds, exhaust gas temperature increased to a maximum of 520 °C with TMI.

Ganesh et al. (2008) used electronically controlled manifold injection system for performing hydrogen experiments. They compared characteristics of hydrogen-fueled engine with baseline gasoline-fueled engine. Spark timing was set at MBT. Maximum brake power for gasoline was 9.8 kW, whereas for hydrogen, it was 7.7 kW. BTE of gasoline was 25% and for hydrogen, it was 27%. BSFC was also lower for hydrogen engine (0.11 kg/kWh) compared to gasoline (0.32 kg/kWh). HC emissions from gasoline engine were in range of 2200–4200 ppm, whereas for hydrogen engine, HC emissions were less than 200 ppm. Up to 4.5 kW, NO_x emissions were negligible. As the brake power output increased to 7 kW, NO_x emissions increased to a maximum of 8250 ppm. For gasoline engine operation, maximum NO_x emissions were observed to be 2000 ppm at an equivalence ratio of 1.03. Hydrogen engine operated smoothly in an equivalence ratio range of 0.3–1.0, whereas gasoline engine's equivalence ratio range was found to be 0.83–1.34.

Blarigan and Keller (1998) performed experiments in an engine fueled with hydrogen, HCNG blends (30% hydrogen and 70% natural gas), and baseline natural gas. A compression ratio of 14:1 was used in this investigation. They found that minimum equivalence ratio required for running the engine using hydrogen was 0.2. For HCNG blends, it was 0.48 and for natural gas, it was 0.62. Thermal efficiency of the engine operated by HCNG blend was observed to be 6% lower than that of hydrogen. Maher and Al-Baghdadi (2004) investigated the effect of compression ratio, engine speed, and equivalence ratio on engine performance, and emission characteristics fueled with hydrogen. Highest power output was observed for compression ratio of 11. Indicated thermal efficiency was highest for a compression ratio between 10 and 11. BSFC was observed to be lowest at compression ratio of 11, and it increased with increasing equivalence ratio from 0.6 to 1.2. Exhaust gas temperature was maximum at an equivalence ratio between 0.9 and 1.0. For equivalence ratio less than 0.8, NO_x emissions increased with increasing compression ratio, whereas for equivalence ratio higher than 0.8, NO_x emissions decreased with increasing compression ratio.

Subramanian et al. (2007) used charge dilution technique to control the NO emissions from a hydrogen-fueled engine. For charge dilution, N_2, CO_2, and their combinations were used. For 0.76 kg/h fuel flow rate, addition of N_2 (6.4 kg/h) reduced NO emissions from 8400 to 1000 ppm. It also reduced indicted thermal efficiency by 0.33%. For fuel flow rate of 0.77, 8 kg/h CO_2 was added to reduce NO emission. This led to the reduction in thermal efficiency by 1.97%. Using

12.2% EGR with fuel flow rate of 0.78 kg/h, NO emission reduced to 1000 ppm with 1.8% reduction in thermal efficiency.

In hydrogen-fueled engine, for evaluating the advantages of port fuel injection system over carbureted system in terms of cyclic variation and backfire, Varde and Frame (1984) performed experiments in a single cylinder SI engine at 1800 and 2100 rpm. For PFI system, lean burn limit improved. Also, thermal efficiency in lean region was found to be higher for PFI system. Maximum NO_x emissions were observed with mixture strength slightly leaner than stoichiometric. Flame speed was also higher for PFI system. At 20° BTDC, backfire occurred between $\Phi = 0.9$ and 1.15 for carburetor, whereas for PFI system, backfire occurred between $\Phi = 1.1$ to near stoichiometric mixture.

4.6 Hydrogen Induction Using Direct Injection System

The best technology to counter all these issues of using hydrogen in IC engine, as reported in the previous section, is to go for direct injection of hydrogen in the combustion chamber after closure of the intake valve. Because of this arrangement, chances of backfire are eliminated completely. Moreover, chances of preignition also reduce significantly. One main advantage of this method is increased volumetric efficiency. Because of lower hydrogen density, injecting hydrogen outside the combustion chamber displaces large amount of air going in with the fuel, which in this case does not happen. Because of this, the power loss encountered in previous two methods would not be observed. Researchers reported improved engine performance using this method of hydrogen induction. Hence, in order to produce a desired engine power output, fuel can be injected at high pressure in leaner mixture form, leading to lower NO_x emissions as well. Several researchers have demonstrated this benefit of using direct injection system in hydrogen-fueled engine.

Yi et al. (1996) performed experiments in a hydrogen engine using in-cylinder injection strategy to investigate its performance and emission characteristics. Comparative study was done with baseline data of port injection of hydrogen. A single cylinder engine was maintained at constant speed of 1500 rpm, and experiments were performed for $\Phi = 1$. For direct injection system, volumetric efficiency of the engine was found to be 77.8%, whereas volumetric efficiency was merely 59.7% for port injection system. Peak cylinder pressure inside the combustion chamber was 5.55 MPa in case of direct injection of hydrogen and 5.08 MPa for port injection of hydrogen. However, efficiency for direct injection system was relatively lower (32%) compared to port fuel injection system (36.7%).

Optimum injection timings and ignition timings for direct injection of hydrogen in the engine were studied by Zhenzhong et al. (2002). Hydrogen was injected into a four-cylinder SI engine using a high-speed solenoid valve at 10 MPa. It was observed that for fixed engine speed, fuel injection quantity, and a fixed injection timing of 6° BTDC, combustion of engine was greatly affected by varying the ignition timings. At an ignition timing of 6° bTDC, combustion was found to be smooth, while at an ignition timing of 3° bTDC, cylinder pressure increased rapidly in the initial stage of combustion. Mohammadi et al. (2007) performed experiments by varying fuel injection timings and ignition timings in a direct injection hydrogen-fueled engine and evaluated its performance and NO_x emissions. By injecting hydrogen in the combustion chamber during intake stroke (300° bTDC), maximum BMEP of 6.5 bar was obtained. For this case, maximum BTE was 35% at $\Phi = 0.5$. At $\Phi = 0.7$, NO_x emissions were roughly 8000 ppm. When hydrogen was injected in early stages of compression stroke (140° BTDC), maximum BMEP of 9.7 bar was observed with brake thermal efficiency of 38.9%.

4.7 Boosting a Hydrogen Engine

Hydrogen direct injection technology is more complex compared to other two fuel induction technologies discussed earlier. This is mainly due to unavailability of direct injection fuel injectors for injecting low-density hydrogen, which is commercially challenging. Therefore, a more commercially viable option is to boost the engine with either carbureted or port fuel injected system using a turbocharger or a supercharger.

Lohse-Busch et al. (2007) performed experimental analysis using 2.3L supercharged hydrogen engine and demonstrated engine efficiency as high as 37%. Also, at constant torque conditions, engine efficiency increased by 1–2%, when air/fuel ratio increases from 2 to 3. This leaner mixture also reduces NO_x emissions to single digit ppm levels. NO_x emissions increase exponentially when the air–fuel ratio reaches $\sim$2.25. Rogalinski and Szwaja (2012) also performed experiments on supercharged hydrogen engine to evaluate engine performance and reported improved engine performance compared to naturally aspirated hydrogen engine without potential knock symptoms.

Verhelst et al. (2008) performed experiments to investigate the potential to increase the power output of PFI hydrogen engine while limiting NO_x emissions and maximizing the efficiency. Technologies like variable valve timing (VVT), EGR as well as supercharging the engine were considered to obtain desired results. With VVT, they influenced the equivalence ratio limit for backfire/preignition. They also reduced NO_x emissions by varying EGR rate in the engine combustion chamber. With the use of supercharger, significantly increased power output was observed. However, in order to avoid preignition and backfire during boosted engine operation, equivalence ratio was restricted to $\lambda \sim 1.3$, or $\Phi \sim 0.77$. By using EGR, it was possible to operate the supercharged engine near stoichiometric limits, which increased the engine power output compared to gasoline levels.

Verhelst et al. (2010) performed another experimental study on supercharged PFI hydrogen engine with EGR to increase the power output to gasoline engine levels, while maximizing BTE and minimizing emissions. For this, two different strategies were tested: first was using stoichiometric mixtures with and without

EGR, while using three-way catalyst to reduce NOx emissions, and another was using lean mixtures to limit NOx emissions without using aftertreatment devices. It was finally concluded that supercharged lean burn operation is the best option to obtain similar or even higher power output than gasoline engine, with the advantage of higher efficiencies, absence of EGR, and exhaust aftertreatment devices.

Wallner and Lohse-Busch (2007) performed experimental study on a supercharger PFI hydrogen engine at various loads, air–fuel ratios, and engine speeds to evaluate engine performance, efficiency, and emissions. This extensive study was done to obtain optimum operating regime of the engine. Compared to gasoline engine, 30% lower power output was observed for hydrogen-fueled engine without using any additional measure. With the use of supercharger, peak BTE increased to 37%, slightly higher than comparable gasoline engine. Also, by using leaner mixture, NO_x emissions were reduced to as low as 1 ppm.

Jilakara et al. (2015) developed a 2.5L four-cylinder, turbocharged-intercooled hydrogen engine with MPFI system for injecting hydrogen in the intake manifold. Engine was operated between equivalence ratio of 0.5–0.6 to achieve lower NO_x emissions and to avoid backfire. Best engine performance data was compared with naturally aspirated CNG, and similar engine performance was observed above 2000 engine rpm. At lower engine speed, because of turbocharger limitations, enough torque was not produced by the engine. This was because the turbocharger could not sustain energy required to produce desired boosting at lower rpm because of lower exhaust gas temperature. Combustion stability was also good for hydrogen engine at all IMEP with COV of around 1–2%. Rate of combustion and combustion duration of hydrogen at lean equivalence ratios seems to be almost matching with the hydrocarbon fuels at stoichiometric conditions.

Lohse-Busch et al. (2006) also studied the effect of equivalence ratio on the behavior of PFI V8 supercharged hydrogen engine. They observed lower fuel economy at leaner operation as engine was operated at lower efficiency with supercharger. Engine performance was hampered when the engine was operated with leaner mixtures. However, emissions were extremely low at leaner charge zones. NO_x emissions increased above equivalence ratio of ~ 0.45. This shows a trade-off between engine performance and emissions.

Using hydrogen in commercial IC engine at large-scale is the ultimate step toward reducing carbonaceous emissions as well as improving engine performance. Another path researchers are following which is improving the combustion using advanced engine technologies such as gasoline direct injection (GDI), homogeneous charger compression ignition (HCCI).

4.8 Ways to Improve Hydrogen Engine

As described in the previous section, for each induction method, there are few drawbacks, which need to be addressed to improve the performance of a hydrogen-fueled engine. Few prominent concerns include the presence of hot spots inside the engine combustion chamber, inability to create multi-point ignition, and precise ignition timing. Because of preignition, it is rather difficult to inject hydrogen into the combustion chamber in case of carbureted or port fuel injected system. Since these systems are easy to adopt for commercial vehicles, tackling this problem helps a great deal in reducing the dependency on direct injection system for hydrogen. By creating multi-point ignition, it is possible to create superior combustion with reduced combustion duration. Thus, it will be possible to use higher compression ratio in the engine without worrying about knocking.

To counter these drawbacks, a new ignition system is developed which is known as 'Laser Ignition System.' Here, in place of normal electric spark plug, a laser source is used to create the plasma, which initiates the combustion. Since this system does not have any electrodes, the issue related to hot spots is completely eliminated. With different optical arrangement, it is possible to create multiple ignition points in the combustion chamber along with precise ignition of air–fuel mixture. Following section describes this particular technique in detail.

4.9 Laser Ignition of Hydrogen Engine

Laser ignition has emerged as a promising alternate ignition technology for improving the engine performance using gaseous fuels having possibility of backfire due to hot spots. In laser ignition, a pulsating laser beam is converged at a focal point using a converging lens, which creates intense plasma at the focal point of the converging lens. Plasma is formed when the energy density at the focal point increases beyond a threshold value. For laser ignition of IC engines, short laser pulses of few nanoseconds are used, which are generated by using Q-switched lasers.

Laser ignition of combustible mixture is possible by four different mechanisms (Phuoc 2008) namely:

(i) Thermal Ignition: In this process, thermal energy of the laser beam is used to increase the kinetic energy of the molecules present in the focal region. As a result, molecular bonds are broken and intense chemical reactions take place leading to initiation of combustion.

(ii) Photochemical Ignition: Here, laser beam dissociates the target molecules into respective radicals. If the rate of production of these radicals is greater than their recombination rate, they react with other molecules present in the mixture and form different set of radicals. This leads to a chain reaction, ultimately leading to ignition of combustible mixture.

(iii) Resonant Ignition: Electrons in bound state are excited by absorption of incident laser beam. After certain excitation, ionization takes place and free electrons are produced, leading to cascade breakdown of gaseous mixtures.

(iv) Non-Resonant Ignition: Laser beam is tightly focused to achieve energy density greater than the breakdown intensity of gaseous mixture. This leads

> to ionization of gaseous molecules. Electrons produced then ionize other molecules, leading to formation of spark. The spark produced this way leads to formation of flame kernel and finally combustion of the mixture. Generally, Q-switch lasers are used to produce short duration pulses, which attain necessary threshold intensities at the focal spot.

For engine applications, non-resonant ignition is preferred because this neither depends on resonant frequency of combustible mixture nor on the wavelength of the incident laser beam.

Compared to conventional electrical spark ignition, laser ignition offers several advantages (Srivastava et al. 2009). They are:

- Precise ignition timing using laser ignition system.
- Because of very high energy density and temperature in the laser plasma, leaner mixtures can be easily burned.
- Plasma position can be varied inside the combustion chamber, leading to faster combustion, which is beneficial at higher engine speeds.
- Energy density at plasma location can be changed, which can extend the combustibility of leaner mixtures further.
- With laser ignition system, it is possible to create multi-point ignition, which helps in producing superior and faster combustion inside the combustion chamber.
- Because of the absence of electrodes, problem of electrode erosion is eliminated, leading to longer lifetime of laser ignition system compared to conventional electric spark ignition system.

In case of use of hydrogen in IC engines as alternate fuels, one of the major problems is engine backfire because of presence of hot spots inside the combustion chamber such as hot spark plug electrode, hot carbon deposits, valve edges. In laser ignition system, spark plug is absent; therefore, it reduces the backfire due to hot spark plug electrode. Use of spark plug in a turbocharged/supercharged engine leads to faster electrode erosion because of higher energy required for ignition. In laser ignition, as the pressure in the combustion chamber increases, laser energy required for ignition decreases. This is exactly opposite to that of conventional electrical spark ignition system and is a major advantage of using laser ignition system.

4.10 Summary

Hydrogen has come out to be a promising alternate fuel for future vehicles. It is free from carbon, which makes it the cleanest fuel presently available. Apart from several advantages, use of hydrogen also has few challenges, which is posing difficulty for its use in commercial vehicle. Following points are the summary of key conclusions drawn from the chapter presented above.

- Hydrogen has several properties which make it an excellent fuel for vehicle operation like low ignition energy, high auto-ignition temperature, carbon-free. Apart from its advantageous properties, there are few parameters which are creating difficulty in using hydrogen for vehicle operation like low density, smaller flame quenching distance, and difficulty in hydrogen storage.
- Hydrogen can be used in engine using all three induction techniques. Carbureted injection poses challenges in terms of low volumetric efficiency, preignition, engine backfire, and pumping losses. Port fuel injection somewhat improves engine volumetric efficiency, removes pumping losses but still poses problem of preignition and engine backfire. Also, because of lower volumetric efficiency, power out from engine is lower. These issues can be eliminated by using either a boosting mechanism or injecting hydrogen directly inside the combustion chamber.

In order to further enhance the performance of hydrogen-fueled engine, laser ignition system can be used. It not only reduces the issue of preignition but also can be used to enhance the engine operating range since it has the flexibility to change laser pulse energy. Also, multi-point ignition is possible, reducing overall combustion duration.

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Chapter 5
Advances in Hydrogen-Fuelled Compression Ignition Engine

Priybrat Sharma and Atul Dhar

Abstract The rapacious growth of transport sector in last few decades has made it one of the major contributor of air pollution. This has pushed the governments of different countries around the globe to impose stringent pollution norms on vehicular emissions. Therefore, these days design of automobile engines is greatly influenced by criteria of reducing the emissions. Amongst all automotive engines, compression ignition engines are especially prominent in long-hauling scenarios due to their higher thermodynamic efficiency and better low-end torque. However, they are notorious for the black smoke which they emit. Alternative fuels and combustion technologies are explored extensively to reduce the emissions and improve the combustion efficiency further in such engines. Amongst different alternative fuels explored by researchers, hydrogen is attractive due to its extremely clean combustion properties. This work critically evaluates the amenities and shortcomings of the hydrogen as a fuel in compression ignition engines. Application of hydrogen in advanced compression ignition technologies such as HCCI and PCCI is also explored.

Keywords Compression ignition · Dual fuel · Hydrogen fuel · Low-Temperature combustion · HCCI · Regulated emissions · Unregulated emissions
Particulate matter · Particle number · Engine performance

5.1 Introduction

This chapter aims to give an overview of the research conducted on hydrogen as a fuel in the compression ignition (CI) engine. It also introduces the terminology while critically evaluating advantages and disadvantages of various modes of hydrogen utilisation in CI engines. The main focus stays on hydrogen energy supplementation in dual-fuel CI mode. Also, complete substitution of diesel with

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hydrogen is encompassed in this chapter by reviewing the literature on hydrogen homogeneous charge compression ignition (HCCI).

Use of gaseous fuels in internal combustion engines (ICEs) is considered since as early as 1806 (Eckermann 2001). De Rivaz engine is reported to use hydrogen/oxygen fuel mixture. In 1901, Rudolf Diesel patented the dual-fuel engine concept. The concept is to premix air and fuel and then compress it till the temperature just below of auto-ignition. This is followed by injection of other high reactivity fuel to ignite the mixture. The auto-ignition temperature of the second fuel is lower than that of the premixed air–fuel mixture. In this concept, the premixed fuel is called main fuel, and the injected fuel is called pilot fuel because it pilots the ignition of the main fuel. Soon afterwards, patents were filed for high compression ratio CI engines, which could operate on both gaseous and oil fuels. However, it was not until 1927; attempts were made to burn gas alone in diesel cycle. Cooper-Bessemer in its attempts realised that very high compression ratios were required to achieve ignition in CI engines operating on diesel cycle. In years 1929 and 1930, attempts were made to use hydrogen as a fuel in diesel engines by Cave and Helmore–Sokes, respectively. They were able to save diesel fuel by 20% of volume (Sahoo et al. 2009).

In recent years, due to stiffer emission control norms and fluctuating oil prices, the gaseous-fuelled engines have again gained the interest of the masses. Gaseous fuels are known to carry a distinct advantage of creating a homogenous mixture with air compared to liquid fuels, but they also have a disadvantage due to lower energy density. Their application in commercial transport and power generation has seen a rise in this decade due to the increased availability and reduced prices of liquefied natural gas (LNG) and compressed natural gas (CNG) (Boyer 1949). The increase in availability of these gases is due to the discovery of new gas wells and improvement in gas extraction technology.

Hydrogen gas is one such highly sought gaseous fuel because of its cleanest burning nature, making it ideal for emission reduction. Raw material of hydrogen fuel is water, which exists in huge quantity thus makes it a promising fuel. Hydrogen gas is known to be a high-quality energy carrier, and steam reforming or fossil fuels or electrolysis of water can produce it. It has a high auto-ignition temperature making it suitable for CI engine but also limits its use as a single fuel. Low energy density and the absence of efficient production route are hampering its wide-scale adoption. Hydrogen is reported to improve combustion characteristic of CI engines when used in dual-fuel mode. It also reduces CO and HC emissions but results in higher NO_x emissions (Bose and Maji 2009). This chapter discusses the utilisation of hydrogen in dual-fuel engines and HCCI modes in high compression ratio engines.

5.2 Hydrogen–Diesel Dual-Fuel Compression Ignition Engine

Diesel–hydrogen dual-fuel technology for CI engine operations can be achieved through following three methods (Karim 1983).

- **Fumigation Method**: In this mode, hydrogen is carburetted into the combustion chamber along with air during the intake stroke.
- **Timed port injection**: In this method, injection of gaseous fuel is attempted just before the closing of intake port during the suction stroke. This method allows stratification of charge in the cylinder, making it easier to ignite. In both these methods, the gaseous fuel mixture gets ignited by the injection of liquid pilot fuel close to TDC. These methods are troubled with knock phenomena due to premature self-ignition in the case of most gases.
- **Direct Injection**: Direct injection is attempted using a high-pressure gaseous injector. In this method, the gaseous fuel is injected almost simultaneously with pilot fuel when the piston is close to TDC. This method is better than the previous two options; however, it requires costlier gaseous fuel injectors.

Amongst the above three methods, fumigation and timed port injection are most widely researched methods due to their ease of implementation in a conventional diesel engine (Verhelst 2014; Cipriani et al. 2014; Bhaskar et al. 2013; White et al. 2006). Das (1990) has studied the effects of these hydrogen induction techniques. They reported backfiring as a setback in using carburation as it results in the presence of hydrogen in the intake manifold. While direct injection has durability and reliability issues in the long run due to prolonged exposure to high in-cylinder temperatures, manifold injection, if accurately timed with suction stroke, can overcome both these problems. Hence, timed manifold injection with minimal engine hardware can offer better air–fuel mixing characteristics, reduce the possibility of backfire and also keep the injector far from high temperatures. This section reviews the effects of basic engine-running conditions, load, speed and compression ratio on the hydrogen–diesel dual-fuel CI engine. The effect of each of these engine-running conditions is presented as engine performance, combustion and emissions characteristics.

5.2.1 *Effect of Engine Load*

Engine load is a measure relative to the maximum torque achievable at any fixed speed of the ICE. Diesel engine relies on qualitative governing of the fuel; therefore at a fixed speed, the torque output from the engine depends on the amount of energy supplied by the fuel to the engine. Therefore, engine load is one of the most important parameters to study because the energy required is to be provided by two fuels. This section reports the effect of load on the performance, combustion and emission in a hydrogen–diesel dual-fuel engine.

5.2.1.1 Engine Performance

Karagöz et al. (2015) did a detailed study on the effects of engine load on the performance of H_2-enriched diesel engine at operating compression ratio (CR) of 19

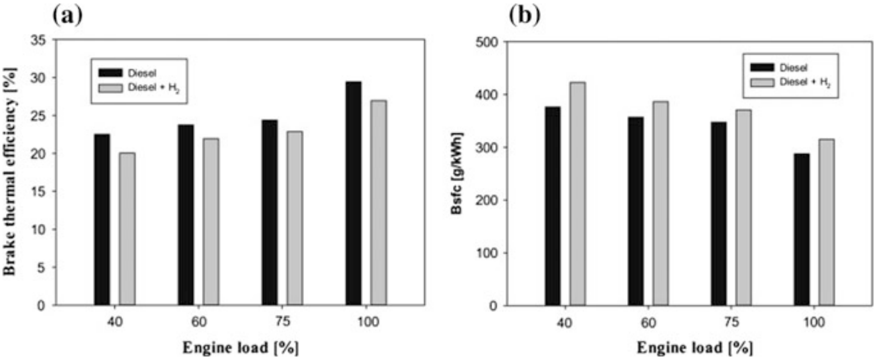


Fig. 5.1 Effect of 30% hydrogen energy substitution on **a** BTE and **b** BSFC (Karagöz et al. 2015)

and engine speed of 1100 rpm. Engine load levels 40, 60, 75 and 100% are tested with 0 and 30% hydrogen energy content. Diesel injection is fixed at 22°CA before Top Dead Centre (bTDC) and hydrogen was injected at TDC during the intake stroke. Figure 5.1 compares brake thermal efficiency (BTE) and brake-specific fuel consumption (BSFC) with and without hydrogen substitution. BSFC is calculated by converting hydrogen energy into diesel equivalent and then adding to total diesel consumption. Their experiments show a reduction in BTE and increase in BSFC with 30% hydrogen substitution of diesel at all tested loads. Reduction of 7.6, 6.3 and 8.4% in BTE while increase of 12.3, 8.3, 6.7 and 9.4 in BSFC is observed at loads with 30% hydrogen energy substitution (HES), respectively. Christodoulou and Megaritis (2013) also reported deterioration in engine performance at low engine speed due to a decrease in hydrogen combustion efficiency. The reduction of engine performance corresponds to a dilution of charge due to the molar heat capacity of hydrogen being higher than atmospheric nitrogen (Pan et al. 2014). The thermal loss also increases with hydrogen addition as it causes the heat flow to rise (Varde and Frame 1983).

Yadav et al. (2015) studied the effect of EGR on performance and combustion characteristics of a CI engine fuelled on hydrogen. They used a single cylinder engine of 4.4 kW capacity with a compression ratio of 17.5, and hydrogen gas was injected into the manifold, close to the port. The flow rate of hydrogen was maintained at 120 g/h during the experiment. In their study, they concluded that till partial loads of 70% substitution of hydrogen improves the brake thermal efficiency. Beyond 70% load, replacement with hydrogen adversely affects the performance of the engine. Homogeneous mixing of hydrogen reduced the BSFC by 11.6% at 70% load. Bose and Maji (2009) also studied the effect of engine load in hydrogen–diesel dual-fuel engine at CR of 17.5. The hydrogen supplied was kept constant at 0.15 kg/h at all loads. They observed an increase in BTE by 3.9% with hydrogen compared to regular diesel at 80% engine load. The increase in BTE is lesser for dual-fuel engines at lower loads in their experiments.

In summary, the key observations from the studies are that molar heat capacity of hydrogen is higher than nitrogen, so it dilutes the charge quality and reduces the combustion efficiency (Varde and Frame 1983). In other words, hydrogen combustion efficiency is lower at lower loads due to lower operating temperatures and increased heat loss from the engine. In volumetric efficiency, a drop is observed compared to regular diesel, but it is not significant enough to be considered as detrimental to the ICE performance (Bose and Maji 2009; Christodoulou and Megaritis 2013; Varde and Frame 1983).

5.2.1.2 Combustion

Karagöz et al. (2015) studied the effect of hydrogen substitution on peak in-cylinder pressure and heat release. Figure 5.2 shows that at all engine loads, the peak pressure increases due to hydrogen's high flame speed. Results also show an increase in the rate of pressure rise (RPR) and heat release rate (HRR). Increase in peak pressure and HRR is more at higher engine loads compared to lower engine loads. This trend is observed due to the extended premixed combustion period. The

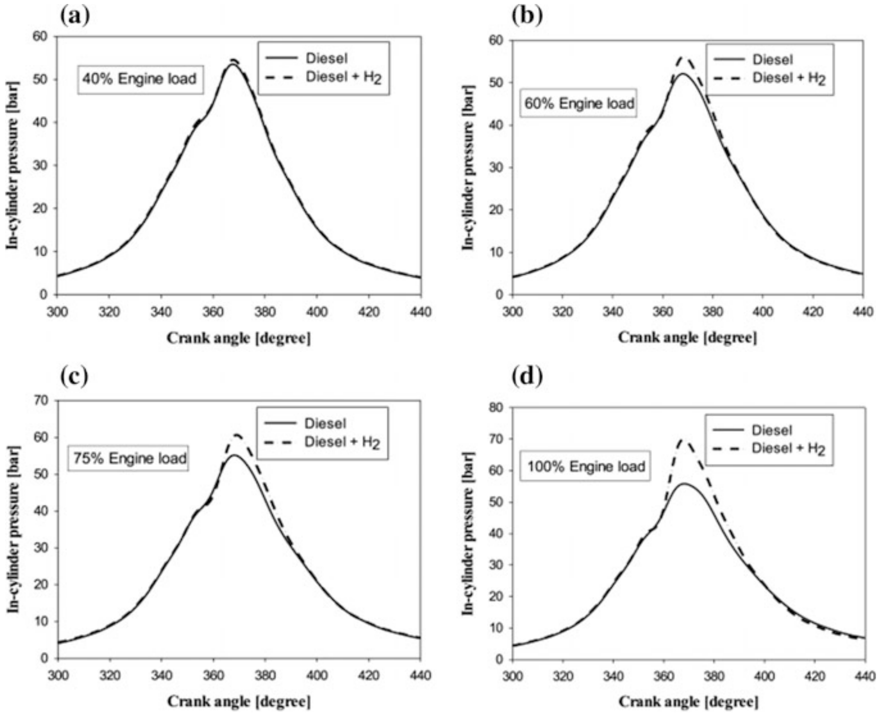


Fig. 5.2 Effect of 30% hydrogen energy substitution on the cylinder pressure at different loads (Karagöz et al. 2015)

premixed type explosive combustion period due to the presence of hydrogen dominates at all loads in their experiments. The lean flammability limits of hydrogen extend with an increase in the charge temperature, resulting in increase of premixed combustion phase even at low hydrogen substitution levels. Varde and Frame (1983) concluded in their study that flame temperature of 1000 K is required to sustain this type of hydrogen combustion.

In another study, White et al. (2006) concluded that at full engine load, the hydrogen's diluting effect is outweighed by high peak in-cylinder temperature. Saravanan et al. (2007) also observed that hydrogen substitution increases the peak pressure, but this can get reduced with proper injection timing and injection duration of hydrogen.

In most studies, we found that hydrogen addition increases the peak pressure and causes the early start of combustion at high loads due to its high flame velocity and superior burn characteristics.

5.2.1.3 Emissions

Deb et al. (2015) varied the engine load through 0, 20, 40, 60, 80 and 100%. At each load, the hydrogen injection duration was varied, as 6500, 7500 and 8500 μs. They concluded that at 20% engine load, 7500 μs hydrogen injection strategy is most optimal. Under these conditions, the trade-off shows moderate increases of soot with low NO_x emissions. Lower NO_x is due to lower in-cylinder temperature but it also reduces the H/C ratio and thus results in higher soot emissions. Better mixing of hydrogen with air accounts for the high flame velocity of hydrogen, enhancing the rate of combustion.

CO emission was significantly reduced up to 68.4% with 30% HES at full load in the investigation of Karagöz et al. (2016). CO_2 also show a drop ranging from 23.1 to 36.1% with hydrogen addition. Although, THC emissions increased but only by limited amount due to decreased volumetric efficiency with hydrogen addition. Due to increased homogeneity of charge, smoke emissions showed considerable decrease ranging from 40.5 to 72.6%. The reduction of smoke was only 50% at full load as compared to 72.6% at 75% engine load. NO_x also decreases in case of all partial loads, but a sharp increase of 51.3% appears at full load. Figure 5.3 compares the NO_x emissions for diesel and diesel–H_2. Liew et al. (2012) experimented with HES on a Cummins ISM370 engine. They observed that at medium and high engine loads relatively greater substitution of H_2 increases the NO_x emissions. However, significant NO_x reduction is observed with under increased H_2 substitutions (above 4% vol) at 10–15% loads. They observed an increase of 25% as hydrogen substitution was increased from 2 to 6% (by volume) at 70% load. While at a load of 10%, NO_x decreased by 88.5% under similar conditions.

As the majority of NO_x production happens through thermal route, trends of NO_x emissions increasing or decreasing are reported, which is mainly due to the variation of in-cylinder mixture temperature at different engine load conditions (Liew et al. 2010). At high loads, the in-cylinder gas temperature is greater, and the

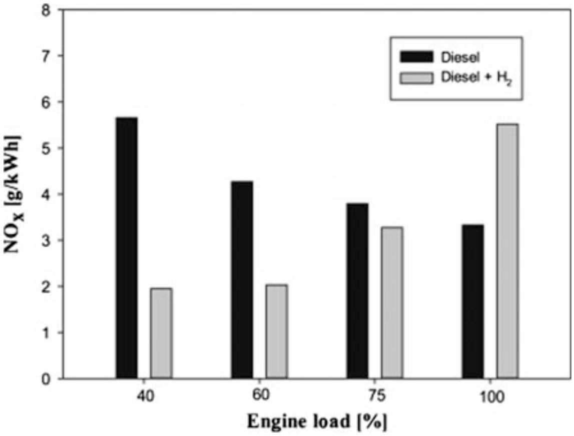


Fig. 5.3 Effect of 30% hydrogen enrichment on NO$_x$ emissions at 40, 60, 75 and 100% engine loads (1.638 bar, 2.457 bar, 3.072 bar and 4.069 bar BMEP) (Karagöz et al. 2016)

engine operates warmers as more fuel burns. Also, the premixed combustion phase duration increases as reported in the previous section. Localised high-temperature zones are formed in-cylinder due to this increase. While at lower loads, HES increases cause inhibition of premixed combustion and elongation of diffusion combustion, resulting in lower localised heat release. This inhibition and leaner charge mixture due to hydrogen addition at low load lead to cooler engine operation, causing a reduction in NO$_x$ emissions (Liew et al. 2012).

Zhou et al. (2015) have investigated the effect of hydrogen enrichment on diesel particulates regarding morphology, structure and oxidation reactivity. These physicochemical properties of the diesel particulates have been studied in naturally aspirated direct injection four-cylinder diesel engine with CR 19. During the experiments, particulate samples were collected at 1200, 1800, 2400 rpm engine speed operating at engine loads of 30 and 70% at 30% HES. They reported that oxidation reactivity of particulate under hydrogen substitution is dependent on engine load. The degree of oxidation reactivity at low and high engine loads with hydrogen addition decreases and increases, respectively. Diesel and hydrogen combustion efficiency decreases at low loads, and the longer diffusion combustion phase allows the particles to oxidise, resulting in the reduction of oxidation reactivity and finer particles in emission resulting in the reduction of particle diameter and radius of gyration. While, at high engine load and speed, shorted diffusion phase results in larger sized primary particles in emissions.

An et al. (2014) investigated the impact of hydrogen enrichment on biodiesel with respect to engine performance, combustion and emissions using a KIVA4 (CHEMKIN II coupled) numerical model. At 2400 rpm and full load conditions, reduction in the CO emissions is 23.5, 35.1, 66.5 and 98.8% with 0.5, 1.0, 2.0 and 3.0% vol. of H_2 induction. Reduction in CO emission is due to a reduction of carbon-based fuel induction. However, it results in higher NO$_x$ formation in cases of high hydrogen supplementation and load. At a low load of 10%, NO$_x$ shows decreasing trend.

5.2.2 *Effect of Engine Compression Ratio*

High auto-ignition temperature of hydrogen (~858 K) makes it ideal for compression ignition. CR of 32 is required for cold start while CR of 26 is needed to sustain the combustion in case of pure hydrogen operation (Lee et al. 2013). Still, the effect of compression ratio relatively less researched for diesel–hydrogen dual-fuel engines, and limited literature is available in context of CR.

5.2.2.1 Engine Performance

Chintala and Subramanian (2015) varied the compression ratio of a single cylinder 7.4 kW engine running at 1500 rpm and increased the amount of hydrogen energy substituted. They reported improvement in thermal efficiency of the engine and decrease in energy consumption (Fig. 5.4b) with increasing HES and attributed it to the reduction in combustion irreversibility and greater charge homogeneity. A similar study by Masood et al. (2007) (Fig. 5.4a) showed that energy efficiency of the engine improves with HES enhancement and this improvement is more at higher CR values.

Homan et al. (1979) experimented using an ASTM-CFR engine first with pure hydrogen and then diesel as fuel. They used glow plugs heated to 1200 K to achieve hydrogen combustion and found that at CR 18 with an equivalence ratio of 0.38, pure diesel gave a BTE of 26% which improved with hydrogen as fuel to 35%. At higher CR of 29 with hydrogen as fuel, the BTE was found to be 40%.

These trends are suggestive that higher BTE and lowered BSFC are achievable with hydrogen substitution if the engine operates at greater compression ratios. However, increasing the compression ratio is strongly restricted by knocking tendency and material limits (Heywood 1988).

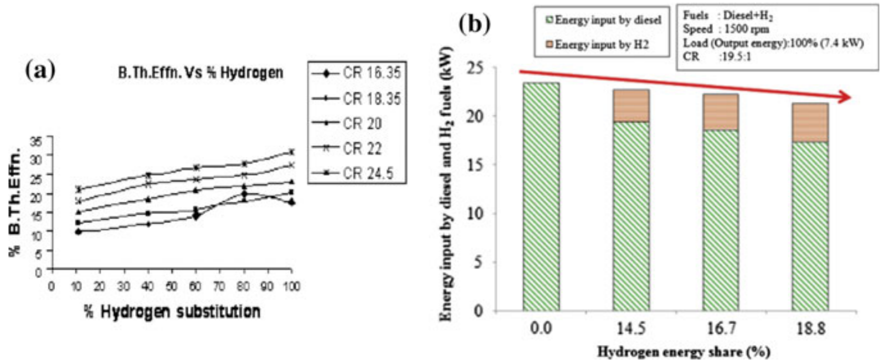


Fig. 5.4 Effect of HES % on **a** energy efficiency at different compression ratios (Saravanan et al. 2007) and **b** energy requirement at CR 19.5 (Chintala and Subramanian 2015)

5.2.2.2 Combustion

Masood et al. found that the peak in-cylinder pressure continues to increase as the HES is enhanced at compression ratios ranging from 16.35 to 24.5 (Varde and Frame 1983). They also found that at low loads combustion duration increases due to reduced ignition centres leading to drop in combustion rate. The peak rate of heat release also increases as the compression ratio increases. Similar trends were reported by Chintala and Subramanian (2015) in the form of heat release rate and cyclic pressure variations (Fig. 5.5a, b). At CR 19.5, auto-ignition of the hydrogen–air mixture is observed before the start of premixed diesel combustion in Fig. 5.5a with HES of 19% but not such observation is made at CR 16.5. At lower CR 16.5, initially, hydrogen addition increases the ignition delay period, reduces the heat release rate and extends the combustion duration, and hydrogen continues to combust in diffused combustion phase. This trend subdues and reveres as the HES increases. The reasons for such a trend are already described in Sect. 2.1.2.

Marin et al. (2011) also reported ignition of the hydrogen–air mixture before diesel combustion for their experiments using CR 20.1 engine with 8.78% HES running at 3000 rpm. CR 19.5 and above allows the air to reach motoring temperature higher than that of hydrogen auto-ignition. At a lower level of HES, no auto-ignition is there, the addition of hydrogen results in the delayed start of combustion (SOC). As the HES increases, SOC starts to advance due to pre-ignition reactions (hydrogen has high reactivity) and low ignition energy requirements at CR 16.5 and 19.5 (Wong and Karim 1999). Figure 5.5c shows the ringing intensity at different CR values as HES is increased and knocking levels at higher CR increases faster as HES is increased. Such high ringing corresponds to knocking and restricts the permissible HES at higher CR.

5.2.2.3 Emissions

Hydrogen is found to be effective in decreasing HC and CO emissions due to its better combustion properties but leads to increase in NO_x emissions (Liew et al. 2010; Zhou et al. 2015). Masood et al. (2007) found a reduction of 93.63% at CR 24.5 and 82.57% at CR 18.35 in HC when HES was varied from 10 to 90% for an engine operating at full load and 1400 rpm. PM emissions also tend to decrease with HES increase. In similar conditions, CO emissions reduced by 95 and 66.67%, while NO_x emissions increased by 38 and 27%, respectively. 0% CO and HC emissions were observed by Chintala and Subramanian (2015) at CR 15.4, 16.5 and 19.5 for HES levels of 14.5, 53.7 and 62.6%. They also reported higher NO_x emissions at higher compression ratios due to increased production of NO_x by thermal route.

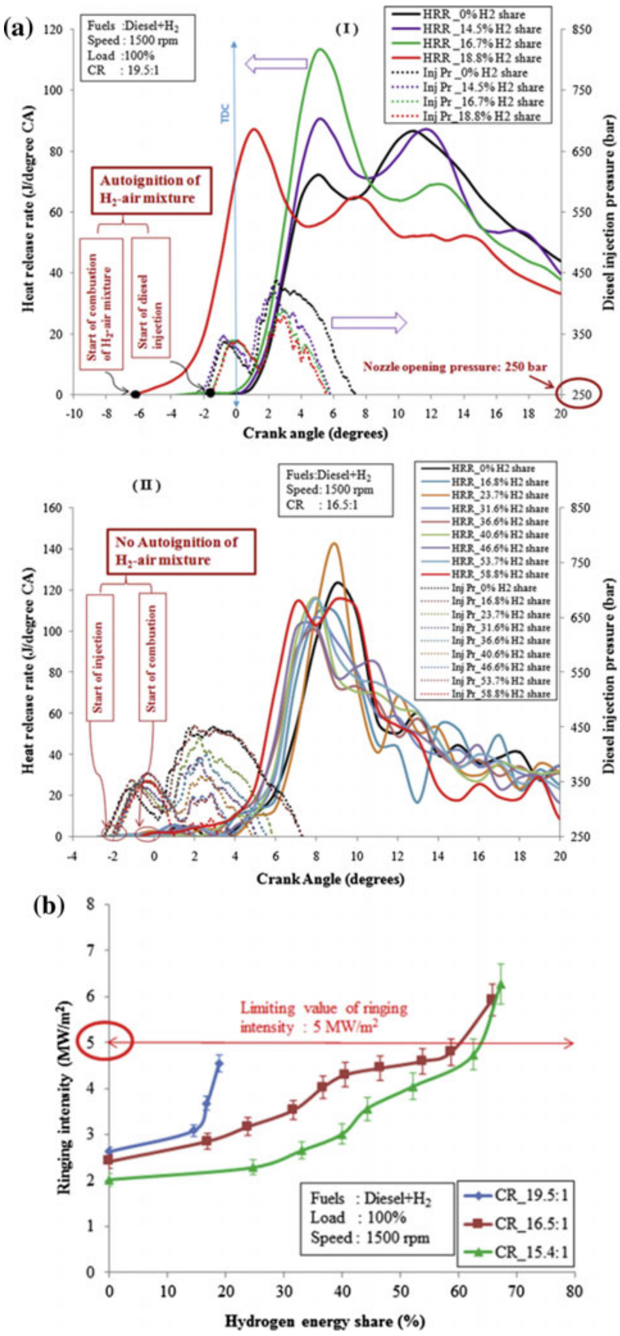


Fig. 5.5 **a** Heat release rate at CR 19.5, 16.5 and **b** Ringing intensity for different CR tested at various levels of HES (Chintala and Subramanian 2015)

5.2.3 Effect of Engine Speed

The engine speed is known to affect the combustion process as the variation of speed results in a change in injection timing, peak pressure and temperature. It also reduces the time available for gas exchange, causing a slight decrease in volumetric and scavenging efficiency. In the case of dual-fuel engines, increase in speed is reported to cause the pressure rise rate (PRR) and coefficient of variation (COV) of PRR to decrease at most output loads in general (Selim 2004). This section briefly summarises the effects of speed on performance, combustion and emissions in case of hydrogen dual-fuel engine.

5.2.3.1 Engine Performance

Köse and Ciniviz (2013) performed experiments using a four-cylinder engine with CR 17. In their experiment, HES was varied as 0, 11, 22 and 33% approx. (0, 2.5, 5 and 7.5 by volume). Engine speed was varied from 1000 to 2500 rpm in steps of 250. They observed a power rise of 6.8, 12.4 and 17.5% at 2250 rpm with hydrogen levels of H2.5, H5 and H7.5 (H2.5 = hydrogen 2.5% by volume, similar for H5 and H7.5). The author attributed this to faster burn rate and better mixing of hydrogen. At 1000 rpm for H7.5, the power output improvement was less due to lowered volumetric efficiency caused by 33% HES enhancement (Fig. 5.6a). Figure 5.6b shows the improvement in BTE obtained when compared to base diesel case. Here, 11% HES gives the best improvement of 40.4% compared to 33% with conventional diesel injection in BTE at max torque speed (1250 rpm). In BTE, also 33% HES lacks in improvement compared to 11 and 22% HES due to lowered volumetric efficiency.

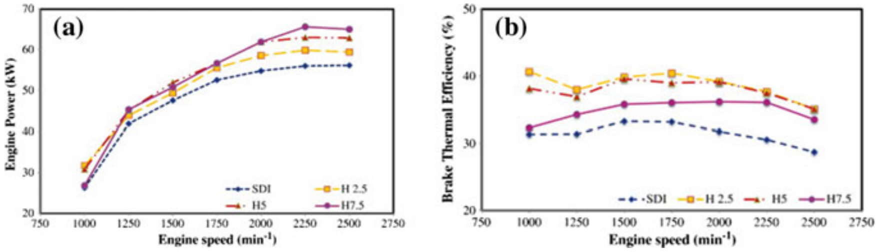


Fig. 5.6 Variation of **a** engine power and **b** BTE with respect to increase in speed for 0, 11, 22 and 33% HES enhancement (Köse and Ciniviz 2013)

5.2.3.2 Combustion

Zhou et al. (2016) in an experimental study ran an ISUZU 4HF1 engine (CR 19) through Japanese 13 mode test cycle with the HES levels of 10, 20 and 30%. They focused on combustion performance in their study by analysing cylinder pressure, cyclic variation of indicated mean effective pressure (COV of IMEP) and cyclic variation of maximum pressure rise rate (COV of Max dP/dφ) as key metrics.

Figure 5.7 shows the pressure and heat release at mode 2 (1280 rpm, load 20% and BMEP 0.15 MPa), mode 3 (1280 rpm, load 40% and BMEP 0.30 MPa), mode 7 (2560 rpm, load 40% and BMEP 0.30 MPa) and mode 10 (1920 rpm, load 80% and BMEP 0.65 MPa) under 0, 10, 20 and 30% HES enhancements. At low speed and engine load under mode 2, the HES enhancement reduces the peak cylinder pressure and HRR and increases the ignition delay marginally. This reduction in peak in-cylinder pressure and HRR occurs mainly in the premixed combustion phase and it is due to lower in-cylinder gas temperature at low loads. Mode 3 has higher load and shows reduced ignition delay, confirming that the increased ignition delay at lower loads is indeed the effect of lower gas temperatures. At high speed and engine load in mode 7 and 10, two peaks occur in heat release rate, first for ignition of premixed diesel, followed by premixed hydrogen ignition. The favourable in-cylinder gas temperature at high speed and load led to this synergetic

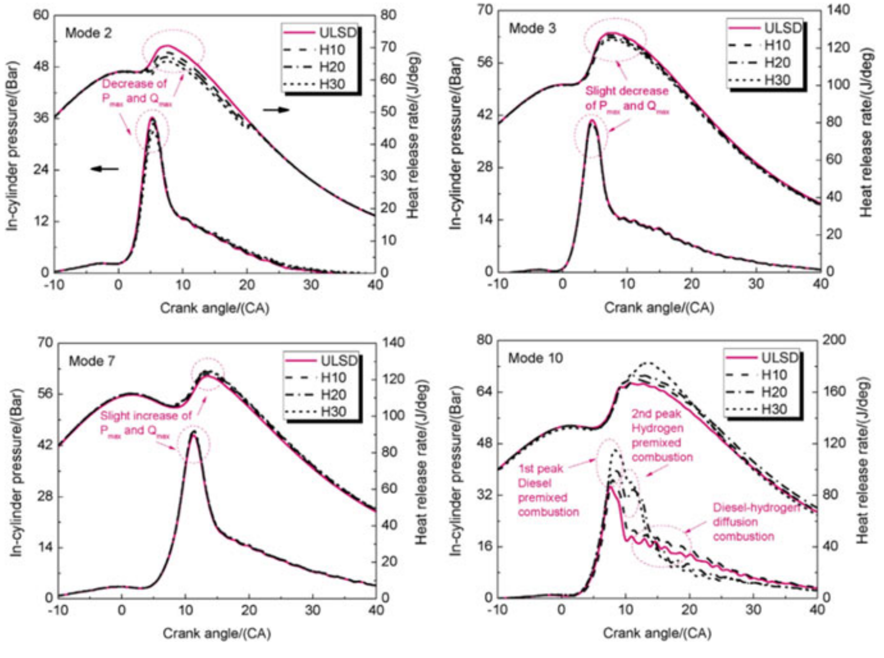


Fig. 5.7 In-cylinder pressure and heat release rate histories for mode 2, 3, 10, 7 (clockwise) of 13 mode Japanese test cycle at HES 0, 10, 20 and 30% (Zhou et al. 2016)

combustion. It has been also observed that pre-ignition of hydrogen before injection of diesel occurs at mode 11 and 12 of the test cycle and was named as abnormal combustion. Similar abnormal combustion trends are also reported by Soberanis and Fernandez (2010).

Cyclic variation is an import study in the case of gas–diesel dual-fuel engines and is used extensively to define the real-world performance of such engines (Karim 1983). Figure 5.8 shows the COV of IMEP and COV of Max $\mathrm{d}P/\mathrm{d}\varphi$. COV of IMEP decreases as the engine load is increased at lower speeds (1280 and 1920 rpm). At a speed of 1920 rpm, observed COV is lesser compared to 1280 rpm (Fig. 5.8a). The trend changes at higher RPM of 2560 as the COV increases at a higher load of 80% due to abnormal pre-ignition of hydrogen observed in Fig. 5.7. Increased speed causes more turbulent mixing of hydrogen resulting in reduced variation in COV of IMEP. The higher temperature is also beneficial in obtaining maximum work out of hydrogen. Further strengthening the results of improved BTE (at higher speed) observed by Köse and Ciniviz (2013). Hydrogen addition reduces the engine noise at low and medium loads as it reduces the COV of Max $\mathrm{d}P/\mathrm{d}\varphi$, which can be observed in Fig. 5.8b. The reduction in COV of Max $\mathrm{d}P/\mathrm{d}\varphi$ is more at lower engine speeds compared to higher speed. This decrease is a result of lower effective in-cylinder hydrogen–air equivalence ratio at low and medium loads. Gatts et al. found that hydrogen substitution reduces diesel plume size, which results in ignition of hydrogen, triggered by hot oxygen–diesel combustion products rather than directly participating in the combustion process (Gatts et al. 2012). Further, the hydrogen–air flame is unstable in nature when the mixture is lean, and they quickly change its nature from laminar to turbulent (Chen and Bilger 2004). Leaving some unburnt hydrogen to escape through exhaust and causes an overall reduction in combustion efficiency. Miyamoto et al. studied the cyclic variation on HES enhancement for single cylinder (CR 16), fixed speed (1500 rpm) at full load condition and observed similar trends (Miyamoto et al. 2011).

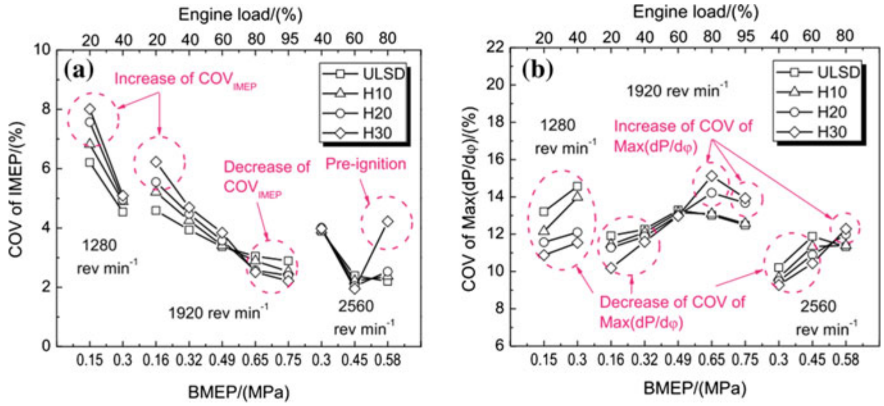


Fig. 5.8 Cyclic variation of **a** IMEP and **b** Max $\mathrm{d}P/\mathrm{d}\varphi$ at different engine loads and speeds (Zhou et al. 2016)

5.2.3.3 Emissions

Emissions are the by-products of improper combustion and hydrogen at high loads, and higher speeds tend to improve the combustion efficiency.

Figure 5.9a shows CO emissions at different engine speeds with H2.5, H5 and H7.5 (HES 0, 11, 22 and 33%) for CR 17 when engine running at full load. At engine speeds of 1000 and 1250 rpm, CO levels increase for 22 and 33% HES due to the displacement of air by hydrogen, resulting in rich in-cylinder mixture formation. The observed trends of CO emissions correspond to the effect of speed on BSFC of the engine, as initially at low speeds rich air–fuel mixture is formed but as the RPM increases the mixture shifts towards lean (Heywood 1988). HES of 11% is found to produce the best reduction in CO emissions and combustion efficiency at all speeds and considered most optimal. On the other hand, it results in maximum NO_x level as the complete combustion of air–fuel mixture results in higher in-cylinder temperature. Figure 5.9b shows the NO_x increase as the speed of the engine increases. With increased speed, the residence time of combusted gases increases because the effective scavenging decreases, causing an increase in NO_x levels (Gomes Antunes et al. 2008).

Zhou et al. reported a reduction in fine and ultra-fine particles as engine speed increased. They also found that HES enhancement, in general, reduces both particle number at all load conditions. They concluded that hydrogen addition reduces soot nucleation rate and surface growth rate by interfering with hydrogen abstraction and C_2H_2 addition process. It is due to the reduced C_2H_4 oxidation process (Zhou et al. 2016). C_2H_4 is premixed ignition phase pyrolysis intermediate of diesel fuel combustion, and its formation is strongly related to the pyrolysis, oxidation rate and air–fuel equivalence ratio. Hydrogen reduces the effective C–H bond ratio, which results in reduced soot precursor species (Westbrook et al. 2006; Westbrook 2000). Hydrogen has prohibition effect on diesel pyrolysis which reduces the overall C_2H_4. While as the speed of the engine is increased, the diffusion combustion phase reduces and deteriorates the oxidation of ethylene. This deteriorated oxidation causes high ethylene emissions. So, even if the speed and load increases, hydrogen is effective in bringing down the total particle count (Zhou et al. 2014).

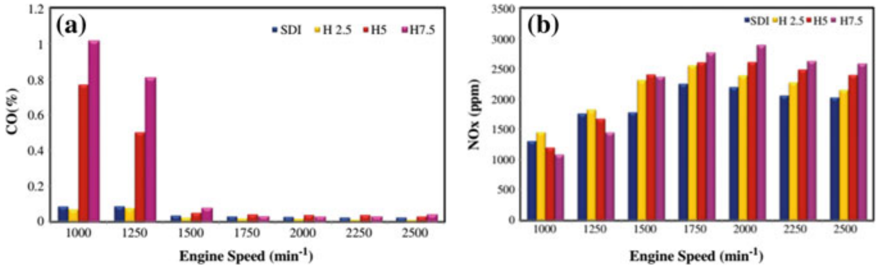


Fig. 5.9 Effect of HES at different engine speed on **a** CO and **b** NO_x (Köse and Ciniviz 2013)

5.2.4 Availability Analysis

The simple reaction of hydrogen combustion in the presence of oxygen to produce water has an overlooked aspect. In this reaction, the complex molecule forms by the combination of simpler hydrogen and oxygen molecules unlike the destruction of complex molecules in diesel to form simpler molecules. It is a well-established fact that due to the second law of thermodynamics that efficiency of thermal systems can be improved by increasing available work and reducing irreversibility (Heywood 1988). Many researchers have carried out detailed availability analysis of hydrogen combustion (Rakopoulos et al. 2008; Taghavifar et al. 2014; Debnath et al. 2012; Kahraman et al. 2007; Khaliq et al. 2012; Jafarmadar 2014; Morsy et al. 2015).

Rakopoulos et al. (2008) created a single zone, zero-dimensional closed cycle model to perform availability balance on combustion of natural gas hydrogen in an internal combustion engine. Increase in hydrogen content from 0 to 10% results in increased injected fuel availability and produced work, but the irreversibility remains unaffected. However, at 40%, HES irreversibility decreases. Jafarmadar (2014) reported similar findings with a simulation model created in AVL fire for dual-fuel engine operating on hydrogen and diesel. The model calculated irreversibility values for gas fuel–air ratios of 0.3–0.8 in steps of 0.1 at 2600 rpm. The irreversibility and cumulative work exergy decreased by 10 and 21.1%, while burned fuel exergy increased by 98.2% (Fig. 5.10). The decrease in irreversibility can be accounted to the burn characteristics of hydrogen as explained earlier.

In another study, Chintala and Subramanian (2014) used experimental data to calculate availability and investigate the effect of HES enhancement at different loads on work, heat transfer and exhaust gas availability. The work availability increases from 29.1% at base diesel case to 31.7% for 18% HES at 100% engine

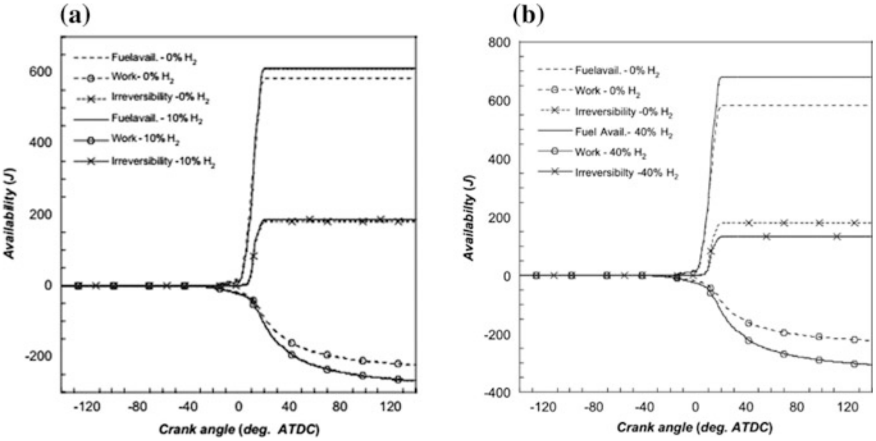


Fig. 5.10 Availability balance for natural gas with **a** 10% and **b** 40% hydrogen in the closed cycle (Rakopoulos et al. 2008)

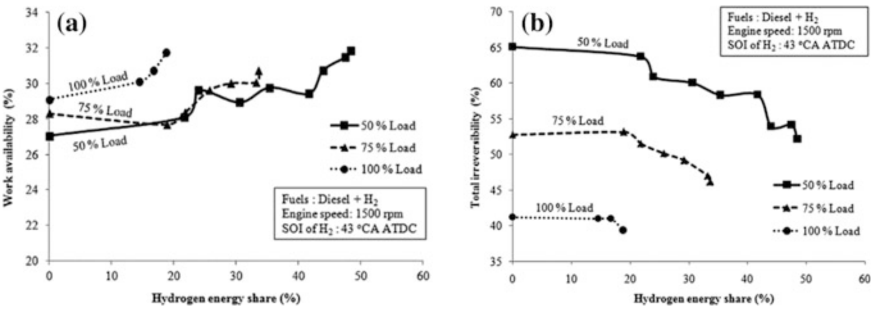


Fig. 5.11 HES % effect on **a** work availability and **b** total irreversibility at different engine loads (Chintala and Subramanian 2014)

load; a similar trend occurs at other load levels (Fig. 5.11a). The increase in availability accounts for, due to a decrease in total irreversibility compared to diesel-only operation. HES increase also results in reduced exhaust gas availability while increasing heat transfer availability.

Total irreversibility of an engine is the summation of irreversibility due to mixing, combustion, unburned fuel and friction. As hydrogen substitution increases, the total irreversibility decreases (Fig. 5.11b). Also, the liquid fuel injected is reduced and replaced with high diffusivity hydrogen. Reducing the mixing irreversibility as gaseous fuel can mix very rapidly compared to liquid fuel (Rakopoulos et al. 2008). The combustion irreversibility is reported to reduce due to high temperature as HES increases (Nieminen and Dincer 2010). The irreversibility due to unburned fuel reduces because as pointed in previous sections of this chapter, hydrogen addition drastically reduced HC and CO emissions. No certain data is present in literature for the irreversibility due to friction.

The certain value of permissible HES substitution possible in dual-fuel engines is not evident clearly from the literature. Table 5.1 summarises some of the published literature on the hydrogen–diesel dual-fuel in CI engine. It emerges that timed manifold injection (TMI) is the most preferred method for hydrogen injection. It offers a relatively safe and easy route to convert a conventional engine to dual-fuel mode, and hence, preferred by most researchers. The maximum hydrogen energy share substitution reported in the table is 30% at CR 19 by Karagoz et al. with speed of 1100. Some authors reported knocking at 20% HES at CR 17.1 while some at CR 19.5 with the engine running at 1500 rpm.

The review of combustion performance under different loads, compression ratio and speed suggests that maximum hydrogen energy share depends on in-cylinder gas temperature rather than other parameters. The following section about HCCI verifies that conclusion further.

Table 5.1 Literature on maximum hydrogen energy substitution possible in hydrogen–diesel dual-fuel engines

Compression ratio	Engine speed (rpm)	Load	HES	Induction strategy	Reference
16.5	1500	100%	10%	TMI	Saravanan and Nagarajan (2010)
16.7	1500	100%	15%	TMI	Nguyen et al. (2013)
16.7	1500	High and low	10% volume share at high 16% volume share at low	TMI	Miyamoto et al. (2013)
17.1	1800	80%	20%	TMI	Marcelino De Morais et al. (2013)
17.4	2400	80, 100%	15 and 20%	Fumigation	Varde and Frame (1983)
17.5	1500	100%	17.6%	TMI	Bose et al. (2013)
17.5	1500	80%	25%	Fumigation	Dhole et al. (2014)
18	2400	60%	20%	TMI	Wu and Wu (2012)
18.2	1500	100%	12.8%	TMI	Christodoulou and Megaritis (2013)
19	1100	40, 60, 75, 100%	30%	TMI	Karagöz et al. (2015)
19.5	1500	100%	20%	TMI	Chintala and Subramanian (2015)

5.3 Hydrogen HCCI Engine

Literature shows seldom exploration of pure hydrogen application in homogeneous charge compression ignition (HCCI) as fuel. Hydrogen requires a compression ratio of 32 for cold start and greater than 25 to maintain the engine operation. It suggests an advantage of obtaining very high thermal efficiency but also presents the material limitation in obtaining such high compression ratios. HCCI combustion of any fuel is controlled by three factors, which are in-cylinder pressure, temperature and equivalence ratio. These factors act as activators for chemical kinetics processes, which cause start of combustion (Sharma and Dhar 2016). Our inability to control the HCCI combustion process directly is due to the lack of spark plug or injection. Failure to control the combustion is problematic in real-life conditions where variation of the engine load or equivalence ratio is required, but the use of hydrogen allows us to operate on wider equivalence ratios due to its wide flammability limits (Najt and Foster 1983). In the next few sections, the impact of intake temperature, equivalence ratio, engine load and compression ratio on combustion and engine performance is discussed, followed by the emissions from a hydrogen HCCI engines.

5.3.1 *Effect of Intake Temperature and Equivalence Ratio*

Ibrahim et al. converted a single cylinder (CR 16) CI engine to operate in hydrogen HCCI mode (Ibrahim and Ramesh 2014). They used an intake air heater to achieve HCCI combustion as higher intake charge temperature allows HCCI combustion at lower CR. Further, they studied the effect of intake air temperature, equivalence ratio and charge dilution using CO_2 on the engine performance, combustion characteristics and emissions.

Figure 5.12a shows that as the intake charge temperature (ICT) is increased, the equivalence ratio needs to be shifted towards the leaner side to prevent knocking. This is because higher temperatures lead to accelerated reaction rates, causing advanced combustion. At a low temperature of 353 and 363 K, with a rich mixture of 0.33 and 0.30 equivalence ratios, higher BTE can be obtained at BMEP of 2.5 and 2. This improved BTE at lower equivalence ratios and temperature is due to better combustion phasing. Gomes Antunes et al. (2008) also reported similar effects of equivalence ratio in their study and reported a drop in IMEP with increasing ICT, suggesting a drop in volumetric efficiency as the cause. Ibrahim et al. also used CO_2 to dilute charge and obtained better combustion phasing and found that CO_2 additions do help in improving BTE and this is more beneficial at higher BEMP as the in-cylinder gas temperature increases as the BEMP increases. They reported that BTE went up from 24.1 to 26.7% with charge dilution at hydrogen flow rate of 0.19 kg/h.

Combustion performance of hydrogen HCCI shows a high dependency on ICT and equivalence ratio and often studied using zero-dimensional chemical kinetics models (Sharma and Dhar 2016). Sharma et al. studied the effect of equivalence ratio of combustion performance at ICT values of 383, 393 and 403 K using zero-dimensional modelling. They found that increasing equivalence ratio at any

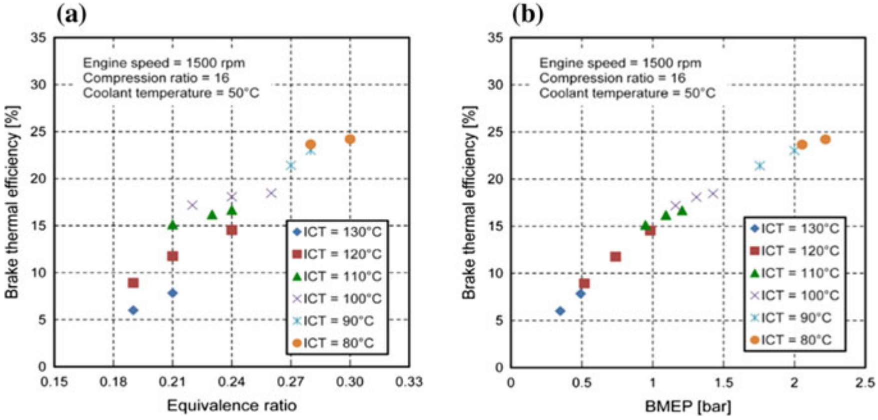


Fig. 5.12 Effect of ICT on **a** BTE at different equivalence ratio and **b** BTE different BMEP (Ibrahim and Ramesh 2014)

given ICT values results in advanced SOC and high heat release. Delay in SOC is required to obtain optimum performance from the H_2–HCCI engine as found by Ibrahim and Ramesh (2013) in another study. However, delayed SOC results lower heat release rates and low BTE, so optimisation study to find the best ICT and equivalence ratio is necessary. Antunes et al. in their study of H_2–HCCI engine concurred with the other studies and found that between highest and lowest loads the cycle-to-cycle, work variation ranged between 7 and 23% (Gomes Antunes et al. 2008). They found that this variation is within an acceptable range when compared with regular diesel operation. They also concluded that ignition angle shares a linear relation with ICT at any given equivalence ratio, suggesting that control of ICT could be a viable solution to control the start of combustion. ICT and charge dilution are the most effective methods found to control SOC by Ibrahim et al. in their experiments (Figs. 5.13 and 5.14).

Fig. 5.13 Effect of ICT on ignition angle (Gomes Antunes et al. 2008)

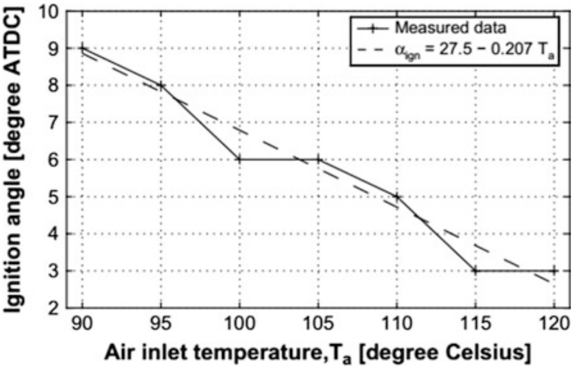
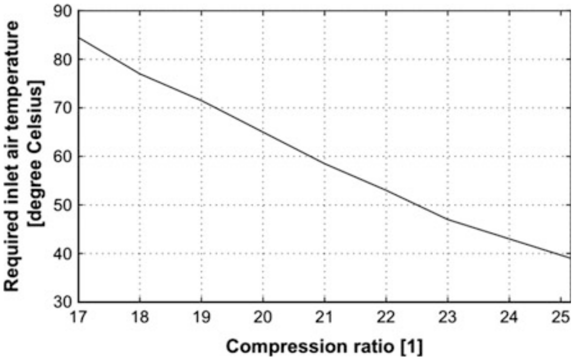


Fig. 5.14 Requirement of ICT with respect to compression ratio (Gomes Antunes et al. 2008)



5.3.1.1 Emissions

In H_2–HCCI engine, due to clean combustion nature of hydrogen, carbon emissions are negligible and hence not reported but NO_x emissions remain a prime consideration. NO_x emissions are reported to increase with lean mixtures due to better combustion leading to higher in-cylinder temperatures. However still, their values are reported to be below that of conventional diesel combustion. Gomes Antunes et al. (2008) reported NO_x levels as 0.01 g/kWh in HCCI mode while conventional diesel produces 6.30 g/kWh. They also found hydrogen emissions due to slipping phenomena occurring during valve overlap period. Ibrahim and Ramesh (2014) found NO_x levels below 25 PPM throughout the experiments and pointed out that LTC in HCCI is responsible for this improvement. They found that with BMEP the NO_x levels increased at both low and high ICT value.

5.3.2 Effect of Compression Ratio

No study has been published studies which directly address the effect of compression ratio on H_2–HCCI, but Gomes Antunes et al. (2008) reported a predictive graph by curve fitting, based on their experiments using 2000 rpm operating with hydrogen at 9 g/min. They found that as the compression ratio increases, the ICT requirement gets reduced, concurring with the findings in a case of hydrogen–diesel combustion.

5.4 Summary

Hydrogen shows excellent combustion properties and enhances the diesel combustion efficiency in dual-fuel mode. However, it requires advance technologies to control the H_2–HCCI combustion, but if achieved, it not only offers excellent combustion efficiency but also reduces the emissions to negligible amounts. Some of the key conclusions drawn from the literature about hydrogen application in CI engines are:

- The possible level of hydrogen supplementation is dependent majorly on the engine load and compression ratio. At high and moderate engine loads, hydrogen supplementation leads to improvement in thermal efficiency. While at low engine loads, hydrogen supplementation reduces the brake thermal efficiency.
- The amount of HES at high loads and the high compression ratio gets restricted by knocking tendency caused due to pre-ignition type abnormal combustion of hydrogen.

- Hydrogen causes the start of combustion to retard at low engine loads and/or low compression ratios while as the in-cylinder temperature increases due to high load or compression ratio, the start of combustion advances. After a critical level of hydrogen supplementation, the knocking starts in the engine.
- Knocking occurs mainly due to a high in-cylinder gas temperature at either high loads or compression ratio.
- Engine speed majorly affects the cycle-to-cycle variability of the combustion process in case of hydrogen–diesel dual-fuel engines by reducing the time available for gas exchanges.
- Hydrogen has excellent carbon-based emission reduction ability. It helps in reducing hydrocarbon, carbon monoxides, carbon dioxides and particulate matter emissions from a diesel engine.
- High NO_x emissions occur due to improved combustion efficiency for any amount of hydrogen energy substitutions.
- Hydrogen reduces the irreversibility of the combustion process in diesel engines. Under suitable engine operating conditions, the reduction in irreversibility results in improved combustion efficiency and BTE.
- Low-temperature combustion (LTC) is a viable solution to reduce high NO_x emissions caused by hydrogen as a fuel in CI engines. H_2–HCCI allows LTC but still needs advanced technology and controlled mode switching from hydrogen–diesel dual-fuel mode to H_2–HCCI.

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Chapter 6
Compressed Natural Gas and Hythane for On-road Passenger and Commercial Vehicles

Tadveer Singh Hora and Avinash Kumar Agarwal

Abstract This chapter discusses implementation of hydrogen-enriched compressed natural gas (HCNG, also called hythane) in automotive engines. Existing passenger vehicles (PV) and commercial vehicles (CVs) are mainly dependent on fossil fuels such as gasoline and diesel. Due to depleting fossil fuel reserves, stringent emission legislations and on-road fuel economy requirements, IC engines are required to use cleaner alternate fuels. Several prominent alternative fuels have emerged such as alcohols, biodiesel and LPG but none of them are widely accepted for large-scale commercial applications. However, most countries have implemented blending of gasoline with alcohol (up to 5–15% v/v) for commercial applications. Compressed natural gas (CNG) has also been widely successful as a commercial automotive fuel. Over last couple of decades, number of CNG vehicles on the roads has increased drastically worldwide. CNG as an automotive fuel is commercially implemented for PVs and heavy-duty CVs. Most important quality of CNG is its lower emissions and it is accepted as a clean transport fuel. However, CNG suffers from severe shortcomings, especially related to its chemical and physical properties such as lower diffusivity, lean-burn limits, high ignition energy requirement, lower flame speed and large flame quenching distance compared to hydrogen. To improvise the properties of CNG as well as for implementing hydrogen for automotive applications, drawbacks of CNG are countered with hydrogen blending. This mixture is known as hydrogen-enriched compressed natural gas (HCNG/H_2CNG or hythane). HCNG also improves feasibility of implementing hydrogen in automotive industry, which otherwise has serious safety concerns because of low ignition energy and wide flammability range of hydrogen. In this scenario, HCNG is fast emerging as a feasible alternative fuel to meet stringent emissions and fuel economy norms with minimal increase in cost and hardware of existing conventional gasoline/diesel engine.

Keywords Hydrogen · Hythane · Emission · Combustion · HCNG projects

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6.1 Gaseous Alternative Fuels

Since the invention of IC engines, fossil fuels such as gasoline and diesel have been used commonly for producing mechanical power, which is derived from the chemical energy stored in these fuels. With growing concerns of climate change and fossil fuel depletion, researchers are investigating various fuels as alternative to conventional gasoline and diesel. Initially, alcohol blends were implemented in the automotive engines but this led to marginal reduction in tailpipe emissions. Figure 6.1 shows reduction in greenhouse gas (GHG) emissions from alternate fuels compared to baseline gasoline.

In this scenario, gaseous fuels such as liquefied petroleum gas (LPG), comprising of propane, propylene, butane and butylene, were investigated as transport fuel. LPG is a by-product of crude oil refining and natural gas extraction. LPG emits 10–15% (Environmental protection agency 2007) lower CO_2 compared to gasoline; however, LPG is still not commercially successful. Major factor is variable composition of LPG, which causes variable engine performance as well as cold-starting issues. LPG also causes safety concerns due to its higher density then ambient air, which makes LPG difficult to disperse in the atmosphere, leading to fire accidents in the event of leakage. However, LPG has higher energy density than gasoline and diesel. Though LPG has emerged as popular cooking gas, its implementation in automotive engines is rather restricted. To achieve the target of lowering the overall CO_2 emission globally, LPG is not the best alternative to fossil fuels. LPG liquefies under moderate pressures at room temperature and is considered dangerous. It can turn explosive or can cause fire if there are traces of LPG in the atmosphere. It can also cause suffocation because its tendency to displace air in enclosed spaces, which decreases the oxygen quantity in the air.

Researchers tested methane, commonly known as natural gas, in automotive engines and found them to be the best alternative to fossil fuels. Natural gas is commonly used either in compressed form or in liquefied form, known as compressed natural gas (CNG) and liquefied natural gas (LNG), respectively. CNG proved to be immediate replacement for gasoline and diesel, and CNG engine generated equivalent power and lower emissions. CNG combustion emits 25% (Environmental protection agency 2007) lower greenhouse gases (GHGs) compared to gasoline. Combustion of CNG produces less soot and particulate matter (PM) making environment less polluting. Also, CNG is cheaper than fossil fuels as well as LPG. Unlike LPG, CNG has lower density compared to air and disperses easily, which makes it less flammable. Benefits of CNG were considered around the world and the number of natural gas-fuelled vehicle (NGV) increased rapidly (Fig. 6.2).

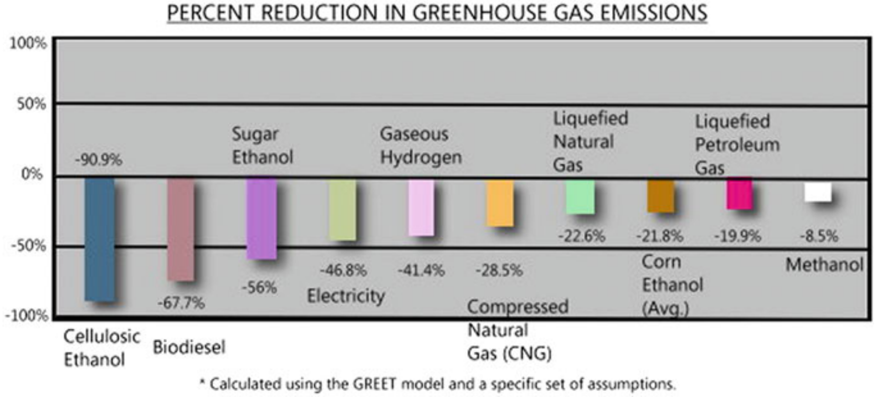


Fig. 6.1 Reduction of GHG emissions from different alternative fuels (Environmental protection agency 2007)

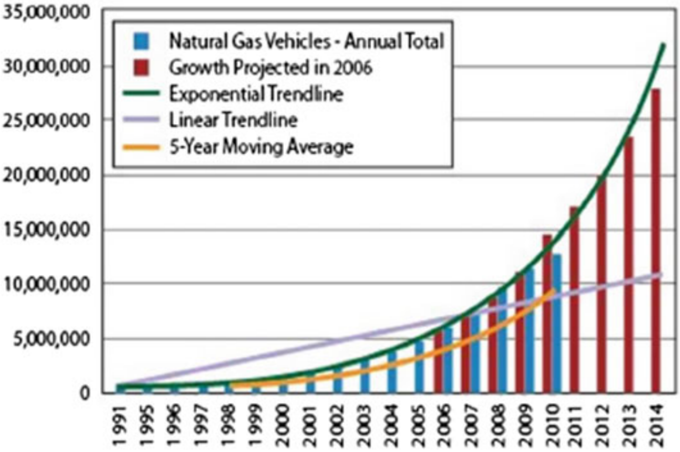


Fig. 6.2 Growth in on-road natural gas-fuelled vehicles worldwide (http://www.investmentu.com/article/detail/2266)

Moreover, CNG can be easily mixed with other gases such as biogas, bio-methane and hydrogen, leading to further reduction in emissions. Conventional diesel and gasoline engines can be easily modified for implementation of CNG. The number of natural gas vehicles has increased globally and CNG dispensing stations have also increased proportionally across the globe.

6.1.1 CNG and Hydrogen

Various chemical and physical properties of CNG make it possible to be utilized as automotive fuel. Following subsection describes the important properties of CNG and hydrogen in contrast to gasoline. Subsection describes technical challenges of CNG as an automotive fuel and a potential solution of introduction of hydrogen-enriched compressed natural gas (HCNG) in the engines. Benefits associated with HCNG compared to CNG are also enlisted.

6.1.1.1 Physico-Chemical Properties of CNG and Hydrogen

Natural gas compressed to high pressures is known as compressed natural gas (CNG) while natural gas stored in cryogenic cylinders in liquid form is known as liquefied natural gas (LNG). Major constituent of CNG is methane, which has one carbon atom attached to four hydrogen atoms.

Other minor constituents include ethane, propane, butane, nitrogen, carbon dioxide and traces of other gases. LNG consists of relatively higher percentage of methane than CNG. Typical composition of CNG available commercially in India is shown in Table 6.1. Since CH_4 is the largest constituent, properties of CNG are in close approximation to that of methane. CNG and Hydrogen, being in gaseous state, do not cause problems of vapour lock and cold starting in the engines. Both gases have higher auto-ignition temperature and cannot be burnt in compression ignition (CI) mode. They require external source of ignition for combustion such as an electrical spark. CNG and hydrogen can be used in spark ignition engines and their properties suggest these gases are better fuels than conventional gasoline.

Octane numbers of natural gas and hydrogen are higher than gasoline; hence, they exhibit superior anti-knock characteristics, which allow combustion at higher compression ratios. Higher octane number makes engine run smoother with low noise levels. Main properties of CNG and Hydrogen in comparison to gasoline are shown in Table 6.2.

Table 6.1 Typical composition of natural gas (% v/v)

Methane	CH_4	94.42
Ethane	C_2H_6	2.29
Propane	C_3H_8	0.03
Butane	C_4H_{10}	0.25
Carbon dioxide	CO_2	0.57
Oxygen	O_2	0–0.2
Nitrogen	N_2	0.44
Other gases		2
Rare gases	Ar, He, Ne, Xe	Traces

(Central U.P. Gas limited)

Table 6.2 Comparative properties of CNG, hydrogen and gasoline (Serrano et al. 2010; Agarwal et al. 2009)

Properties	CNG	Hydrogen	Gasoline
Formulae	CH_4	H_2	$C_{7.1}\ H_{12.56}$
Molar mass	16	2	98
Octane number	120	130	70–97
Auto-ignition temperature (°C)	540	585	230–500
Flammability limit (vol.% air)	5.0–15	4.0–75	1.0–7.6
Quenching distance (mm)	2.03	0.64	2.84
Minimum ignition energy (mJ)	0.29	0.02	0.24
Mass stoichiometric A/F ratio	17.16	34.33	14.7
Lower heating value (MJ/kg)	47.3	120	40–45
Diffusion coefficient (cm^2/sec)	2.0	6.1	0.5
Laminar burning velocity in air (m/s)	0.4	2.9–3.5	0.5
Molar carbon to hydrogen ratio	0.25	0	0.44
Density (kg/m^3)	0.717	0.0899	726

Hydrogen has low ignition energy and high flammability range; therefore, chances of undesirable combustion, pre-ignition and backfire in hydrogen engines are dominant. Pre-ignition is mainly caused by hot spots, heated exhaust valves or hot carbon deposits in the combustion chamber. However, higher diffusivity of hydrogen allows it to disperse rapidly in the air and diffuse out of flammability range in case of leakage. Higher diffusivity of hydrogen allows uniform air and fuel mixture formation, leading to more complete combustion, which gives superior fuel economy.

Quenching distance is defined as the closest gap between engine cylinder walls and flames before the flames are extinguished. Smaller quenching gap is a desired feature for a good fuel. Quenching distance for CNG and gasoline is higher than hydrogen. Smaller quenching distance allows the flame to travel and reach even in smaller spaces, therefore, producing lesser unburnt hydrocarbon (UHC) emissions and particulates. Lower quenching gap, however, can also increase the chances of backfire in intake manifold, since the flames can travel through the nearly closed intake valves into the intake manifold, where the fuel–air mixture is available. Thus for hydrogen-fuelled engines, low quenching gap is desirable but it also is a major drawback. Flame speed of combustion affects efficiency and cyclic variability in the engine. Higher flame speed allows the combustion to approach ideal cycles, i.e. combustion takes place closer to TDC and lesser cyclic variations in power are observed. High flame speed engines are operated with retarded ignition timings, i.e. ignition closer to the TDC. Hydrogen has very high flame speed (2.9–3.5 m/s), while CNG has low flame speed (0.4 m/s). Higher flame speed of hydrogen also causes concerns related to knocking in the engine.

Lower heating value (LHV) of CNG and gasoline is close to each other but hydrogen has almost three times higher LHV than CNG; therefore, significantly lesser quantity of hydrogen is required to produce unit power; thus, it improves the BSFC. Hydrogen combustion leads to high flame temperature and combustion temperature, resulting in higher thermal NO_x emissions but leads to more complete combustion, therefore, lower HC and CO emissions. Combustion equations for methane and hydrogen are shown below. Lower C/H ratio of CNG and hydrogen makes them better fuel than liquid petroleum fuels for GHG emissions. Application of CNG and hydrogen results in lesser HC, CO and CO_2 emissions. Increased NO_x emissions observed in case of hydrogen can be reduced by use of HCNG.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
$$2H_2 + O_2 \rightarrow 2H_2O$$

6.1.2 Implementation of HCNG

Pure hydrogen theoretically has qualities of an ideal engine fuel such as higher diffusivity, infinite hydrogen/carbon ratio (Carbon-free fuel), lower quenching gap, wide flammability range, high burning velocity and high calorific value. However, operating an IC engine on 100% hydrogen is practically challenging and inherently unsafe. Benefits of excellent combustive properties of hydrogen can be used to improve combustion of CNG by adding certain fraction of hydrogen into it. Mixture of 5% hydrogen with CNG on energy basis or 20% on volume basis is known as Hythane®, which is a commercially available fuel and is regarded as optimum mixture.

The idea of blending hydrogen and CNG was first realized in 1989, when a company called Hydrogen Components, Inc. (HCI) prepared blends of different proportions of hydrogen and natural gas. They reported that 20% (v/v) blend produces significantly lesser emissions. This particular blend was named as Hythane®. Many countries have actively shifted their research to explore HCNG as potential engine fuel. Most of them tried different percentages of hydrogen to detect optimum mixture with lowest emissions and higher power output.

Hydrogen and CNG are two different prospective alternate transport fuels with significantly different properties, while properties of HCNG blend lies in between these two fuels. Comparative properties of Hydrogen, HCNG 5% (v/v) blend and CNG are shown in Table 6.3. Table 6.3 shows that various important combustive properties of HCNG fall in-between hydrogen and CNG, thus offering advantage from both fuels and disadvantages of none.

Flammability limit of HCNG is much wider compared to CNG. This improves lean-burn limit of CNG, therefore, reduces the NO_x emissions. Lower ignition energy of hydrogen increases in HCNG, thus making HCNG safer than hydrogen. Burning velocity of HCNG also increases with addition of hydrogen, providing higher efficiency than CNG engines. Higher quenching gap of CNG is reduced in HCNG, which results in lower HC emissions compared to CNG. Equivalence ratio

Table 6.3 Properties of HCNG, CNG and hydrogen (Nanthagopal et al. 2011)

Properties	H_2	HCNG	CNG
Flammability limit in air (% v/v)	4–75	5–35	5–15
Stoichiometric composition in air (% v/v)	29.53	22.8	9.48
Minimum ignition energy in air (mJ)	0.02	0.21	0.29
Auto-ignition temperature (K)	858	825	813
Flame temperature in air (K)	2318	2210	2148
Burning velocity at NTP (cm/sec)	325	110	45
Quenching gap in air at NTP (cm)	0.064	0.152	0.203
Thermal energy radiated (%)	17–25	20–26	23–33
Diffusivity in air, (cm^2/sec)	0.63	0.31	0.2
Normalized flame emissivity	1.00	1.50	1.70
Equivalence ratio	0.1–7.1	0.5–5.4	0.7–4

Table 6.4 Properties of HCNG blends (Flekiewicz et al. 2012)

Properties	CNG	HCNG10	HCNG20	HCNG30
H_2 (% v/v)	0	10	20	30
H_2 (% w/w)	0	1.21	2.69	4.52
H_2 (% energy)	0	3.09	6.68	10.94
LHV (MJ/kg)	46.28	47.17	48.26	49.61
Density (kg/m^3)	0.717	0.653	0.590	0.526

(inverse of excess air-to-fuel ratio) is increased for HCNG, which increases the lean-burn limit at different excess air ratios. Lower density of hydrogen requires more storage volume for given fuel mass. Hythane has higher density than hydrogen, therefore, requires relatively lower volume storage tank. Properties of HCNG differ with varying proportion of hydrogen in the mixture. As the hydrogen percentage increases, combustive properties approach that of hydrogen. LHV and density of different HCNG blends (on volume basis) are listed in Table 6.4.

6.1.3 Advantages of Gaseous Fuels Over Petroleum Fuels

Major benefits of HCNG/CNG are:

1. They can be effectively used in existing petrol–diesel engine with minor hardware modifications.
2. HCNG is safer to handle compared to hydrogen.
3. HCNG engines produce lower emissions and are capable of comply with the Euro-6 emission legislations.
4. HCNG emits lesser greenhouse gases, NO_x, CO, particulates and soot.

5. HCNG has lower lean-burn limit and delivers better fuel economy.
6. HCNG has higher flame speed and combustion temperature, which ensures greater degree of complete combustion of fuel.
7. C/H ratio decreases as the hydrogen fraction increases in HCNG mixture.
8. HCNG demonstrates lower coefficient of variation (COV) or cyclic variability of engine power output and maintains stable engine operation with higher efficiency.
9. CNG is cheaper than fossil fuels and lower government taxes are imposed on it.
10. Existing CNG networks can be utilized for HCNG dispensing with minor hardware modifications.

6.2 Single Cylinder HCNG Engine Development

To study the effect of hydrogen addition to CNG, extensive experiments were performed at Engine Research Laboratory, IIT Kanpur, India. The study was performed in a modified diesel engine which was converted to a manifold injection HCNG-fuelled engine by appropriate hardware changes. Intake manifold was modified to accommodate HCNG rail and injector. Cylinder head of diesel engine was modified to accommodate a spark plug instead of the diesel injector. The pistons were machined to reduce the compression ratio from 17 to 10/11/12. Test cell housed this customised single cylinder engine, which was coupled to an AC dynamometer. The experiments were performed at constant engine speed (1500 rpm) at varying engine load and HCNG fractions at fixed injection timing at the start of intake stroke and ignition timing of 20° CA before top dead centre (BTDC). HCNG injection quantity was governed by a customized electronic solenoid injector control circuit, which controlled the solenoid CNG injector (Bosch; 280150842). The injector was supplied gas (HCNG/CNG) at a constant injection pressure (4 bar) at all operating conditions. Figure 6.3 shows the schematic of the experimental setup with its subassemblies and instrumentation.

A Coriolis mass flow meter (Emerson; CMF010M) was installed to measure fuel (gas) consumption at each engine operating point. Suction line was connected to a laminar flow element (LFE) (Cussons; P7205/150) for smoothening the intake air flow pulsations. Engine crankshaft was coupled to a precision angle encoder (Encoder India; ENC 58/6-720ABZ), which generates a square signal at every 0.5° CA rotation of the shaft. A piezoelectric pressure sensor (Kistler; 6631CQ09-01) was mounted flush on the cylinder head for measuring the in-cylinder pressure. A high-speed combustion data acquisition system (Hi-technique; Me-DAQ) acquires in-cylinder pressure signal at each crank angle position. A capacitive discharge ignition (CDI) system was used to initiate the combustion of the fuel–air mixture. An exhaust gas emission analyser (Horiba; Mexa-584L) was used to measure gaseous species in the exhaust. A Lambda sensor

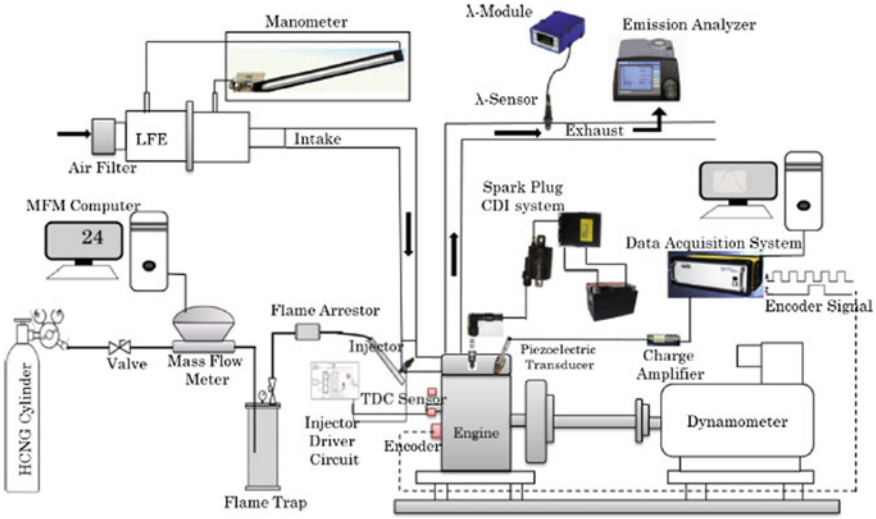


Fig. 6.3 Experimental setup for HCNG evaluation (Hora and Agrawal 2015)

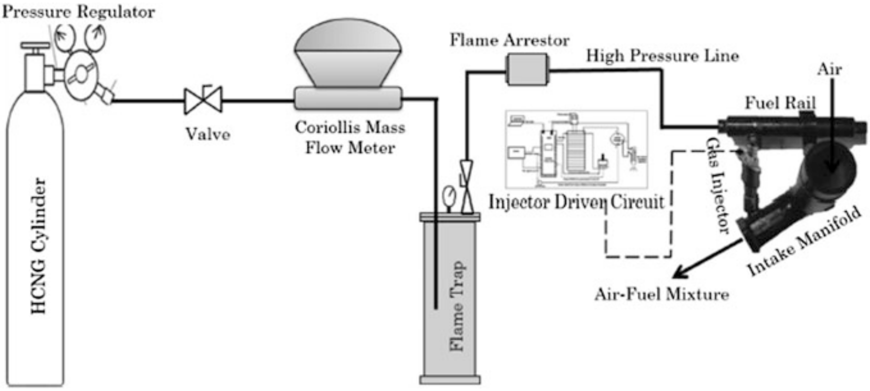


Fig. 6.4 Fuel system layout (Hora and Agrawal 2015)

(Bosch; LSU 4.9) and a K-type thermocouple were also mounted in the exhaust pipe in order to measure the air-to-fuel ratio (AFR) and the exhaust gas temperature.

Figure 6.4 shows the schematic of fuel system layout and gaseous injection system, which delivers HCNG to the engine cylinder during the intake stroke. HCNG mixture of desired mixture strength was pre-bottled before each experiment. Mixtures were prepared using Dalton's law of partial pressures. Experiments were performed at different engine loads (2.98, 4.10, 5.30 to 6.18 bar BMEP) to analyse the effect of varying content [0, 10, 20 and 30% (v/v)] of hydrogen in the HCNG mixture at constant engine speed of 1500 rpm. Engine in-cylinder combustion, performance and emission characteristics were experimentally evaluated and the results are shown in the following subsections. Nanoparticles emitted by CNG/HCNG cannot be ignored due to their potentially carcinogenic nature. Hence, particulate number, particle surface area and particle mass distributions w.r.t. particle size were also analysed.

6.2.1 Effect of Hydrogen Fraction

6.2.1.1 Performance Characteristics of HCNG Engine

Figure 6.5 shows various critical engine performance variables such as brake thermal efficiency (BTE), brake-specific fuel consumption (BSFC), brake-specific energy consumption (BSEC), relative excess air–fuel ratio (λ) and exhaust gas temperature (EGT) at different loads (BMEP) for 0, 10, 20 and 30% HCNG mixtures. BTE shows the overall conversion efficiency of fuel's chemical energy into mechanical energy, which is available at the engine shaft. HCNG enhanced the BTE of CNG at all loads. Increase in hydrogen fraction increased BTE due to

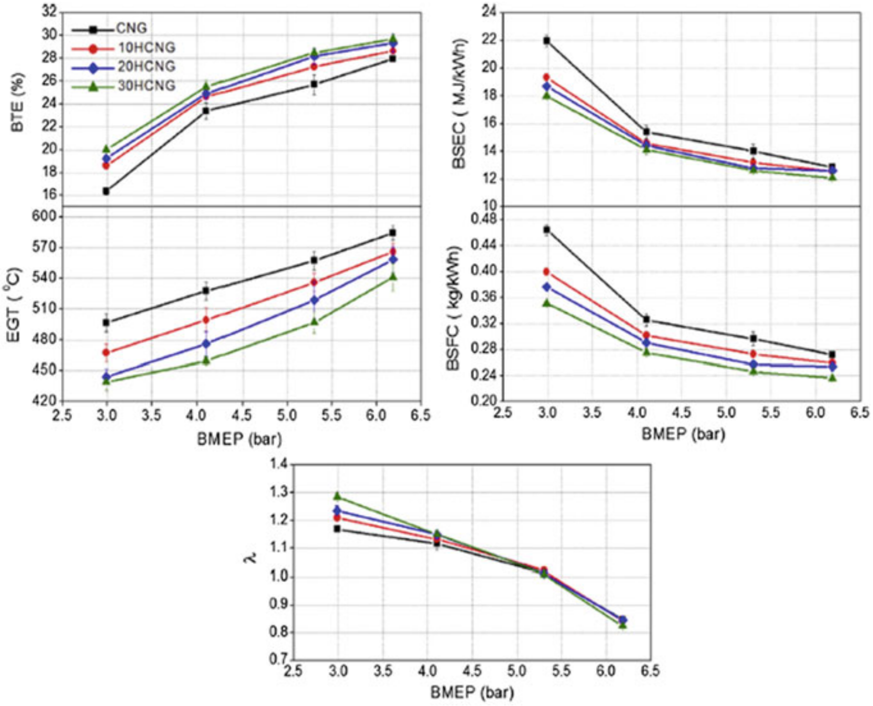


Fig. 6.5 Performance characteristics of HCNG mixtures (Hora and Agrawal 2015)

relatively higher combustion efficiency and superior combustion stability. At lower BMEP, same power output could be produced by slightly leaner HCNG–air mixture compared to CNG–air mixture, while at higher BMEP, relatively richer fuel–air mixture was required. This showed that hydrogen addition to CNG increased lean limit of CNG operation.

EGT increased for all fuels with increasing BMEP. Relatively lower EGT was observed for HCNG mixtures in spite of higher combustion temperatures due to hydrogen. Addition of hydrogen to CNG increased the burning speed (rate of heat release) of HCNG, resulting in shorter combustion duration. Due to this, large fraction of chemical energy was released earlier in the expansion stroke as heat and relatively lesser after-burning took place.

Reduction in BSFC with increasing BMEP shows that less fuel quantity was consumed to generate unit power at higher engine loads and vice versa. This is because BTE was higher at higher engine loads. HCNG showed lower BSFC compared to CNG at a given BMEP. This was due to increasing calorific value (Lower heating value: LHV) of HCNG because of hydrogen addition, which was responsible for lower BSFC. BSEC showed reducing trend with increasing BMEP and increasing hydrogen fraction in HCNG at a given BMEP. This reflected that lesser fuel input energy was required to produce unit power output for HCNG vis-a-vis CNG due to improved BTE.

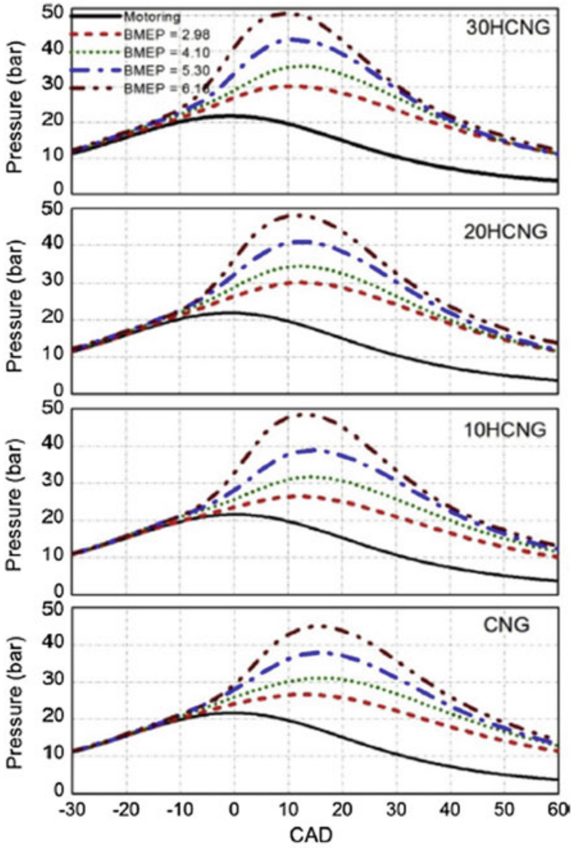
6.2.1.2 Combustion Characteristics of HCNG Engine

Figure 6.6 shows the in-cylinder pressure variations observed at different BMEP for baseline CNG and various HCNG mixtures. Peak cylinder pressure increased with increasing load due to higher fuel quantity requirement. For a given fuel, crank angle position corresponding to peak cylinder pressure shifted towards TDC side due to reduced combustion duration with increasing BMEP. This improved the fuel utilization; therefore, BTE also increased. At a given BMEP, peak cylinder pressure shifted towards TDC with increasing hydrogen fraction in HCNG due to higher flame speed. HCNG delivered higher peak cylinder pressure at the same BMEP. The tendency of knocking would enhance, if the hydrogen fraction in the HCNG mixture increased since the rate of burning would also proportionally increase. However, optimum hydrogen content in the fuel–air mixture would result in higher BTE compared to CNG.

Figure 6.7 shows variations in rate of pressure rise (RoPR) and heat release rate (HRR) of HCNG mixtures at different BMEP. RoPR and HRR increased with increasing engine load for a given fuel. This was primarily due to relatively earlier start of combustion (SoC) observed at higher BMEP and high fuel quantity at higher BMEP. Additionally, at a constant BMEP, RoPR was relatively higher for HCNG mixtures.

Maximum RoPR was obtained for 30HCNG due to its highest hydrogen fraction amongst all test fuels. Hydrogen has relatively higher flame speed, which increases the HRR and RoPR. Crank position for maximum RoPR and HRR shifted towards

Fig. 6.6 In-cylinder pressure-crank angle diagrams of HCNG mixtures (Hora and Agarwal 2015)



TDC, similar to peak cylinder pressure. HRR was higher for HCNG mixtures due to higher flame speeds because of hydrogen addition.

Figure 6.8 shows variations in cumulative/total heat release (CHR), mass burn fraction (MBF) and combustion duration with BMEP for different HCNG mixtures. CHR increased with increasing engine load due to higher fuel consumption. At a given BMEP, CHR was higher for HCNG mixtures due to their higher HRR. High HRR and CHR were the reasons for improved fuel economy of HCNG.

Combustion in SI engines has three distinct combustion stages namely flame development, flame propagation and after-burning. Flame development phase is considered to be over at crank angle position for 10% MBF. Combustion duration is considered as the crank position duration between 10 and 90% MBF. Period after 90% MBF till the end of combustion is considered as after-burning phase, which is considered as the least significant. Figure 6.8 shows the variations in 10, 50, 90% MBF and combustion duration for all test fuels. Flame development phase shortened with increasing hydrogen fraction in the test fuels due to significantly lower ignition energy requirement of hydrogen, which also led to rapid formation of

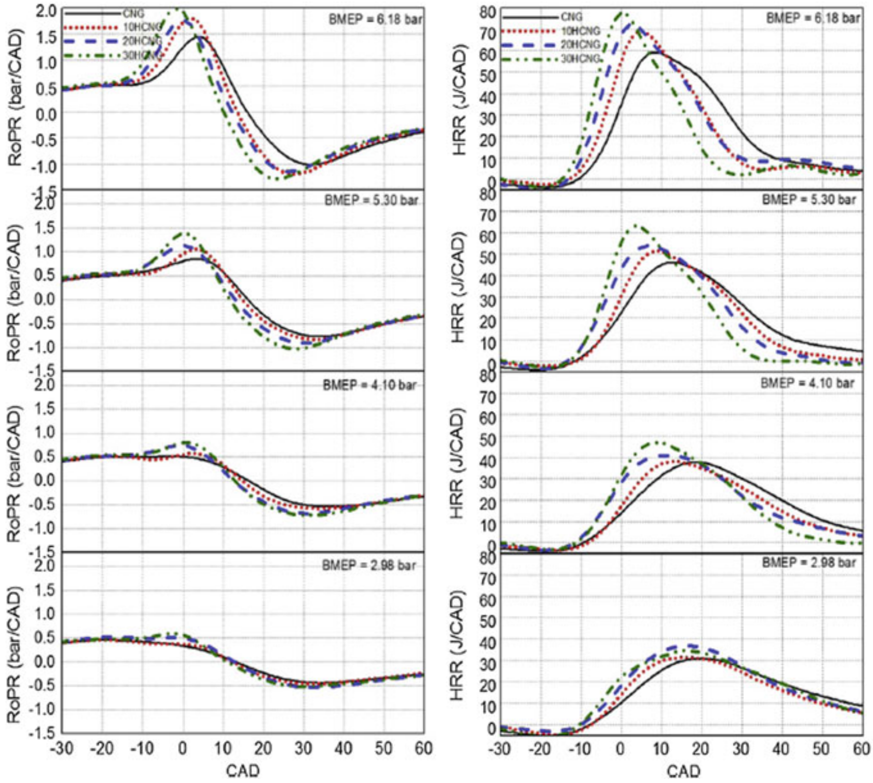


Fig. 6.7 Rate of pressure rise and heat release rates of HCNG mixtures (Hora and Agrawal 2015)

OH radicals during combustion. Similarly, crank angle position for 50% MBF also retarded towards TDC for HCNG mixtures, primarily due to higher flame speed due to hydrogen. As the fuel burns, oxygen available for combustion reduces, thus slowing down the propagation of flames leading to after-burning. Crank angle for 90% MBF was relatively earlier for HCNG compared to CNG. Combustion duration for 10HCNG, 20HCNG and 30HCNG was shorter than CNG.

6.2.1.3 Emission Characteristics of HCNG Engine

Figure 6.9 shows raw exhaust emissions and brake-specific mass emissions of regulated gaseous pollutant species from a HCNG engine at different BMEP. Thermal NO_x formation depends on peak combustion temperature and oxygen content, which was relatively higher in case of HCNG mixtures. NO_x emissions were higher due to relatively higher in-cylinder temperatures because of hydrogen addition to the CNG, which favoured NO_x formation. Flame front temperature increased with increasing hydrogen fraction in HCNG mixtures. At lower

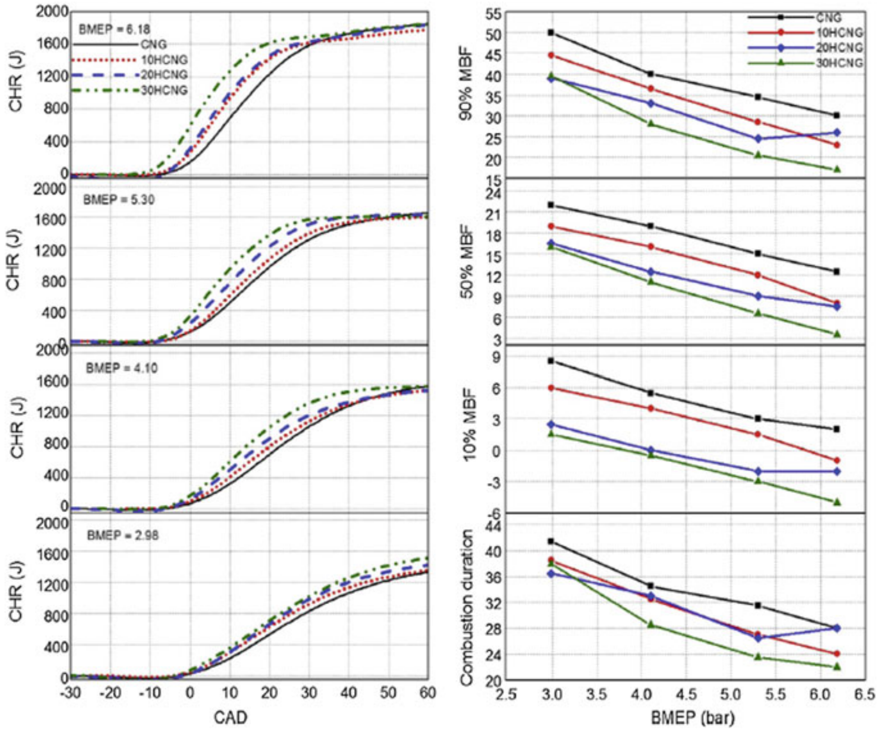


Fig. 6.8 Cumulative heat release and mass burn fractions of HCNG mixtures (Hora and Agrawal 2015)

BMEP of 2.98 bar, negligible difference in NO_x formation was observed amongst all test fuels. This was due to leaner fuel–air mixtures and relatively lower peak cylinder temperatures, which were outside the NO_x formation window. This, however, changed at higher loads, and higher NO_x emissions were observed. Both the raw emissions and brake-specific NO_x emissions increased with increasing BMEP and increasing hydrogen fraction in HCNG mixtures.

Formation of CO_2 in the engine exhaust is an indicator of degree of completion of combustion of hydrocarbon fuel. Higher CO_2 and lower CO emissions indicate superior combustion quality and effective fuel utilization. CO_2 emissions were relatively lower for HCNG mixtures due to reduction in C/H ratio with increasing hydrogen content in the HCNG mixtures. This was in addition to higher BTE observed for HCNG mixtures. HC emissions were formed because of inefficient combustion of hydrocarbon fuel, wherein exhaust contained some unburnt fuel fractions, which remains trapped in the crevice volume at the time of combustion, essentially unaffected by combustion.

Both raw and mass HC emissions reduced with increasing BMEP because at higher BMEP, higher peak cylinder temperatures favoured the oxidation and

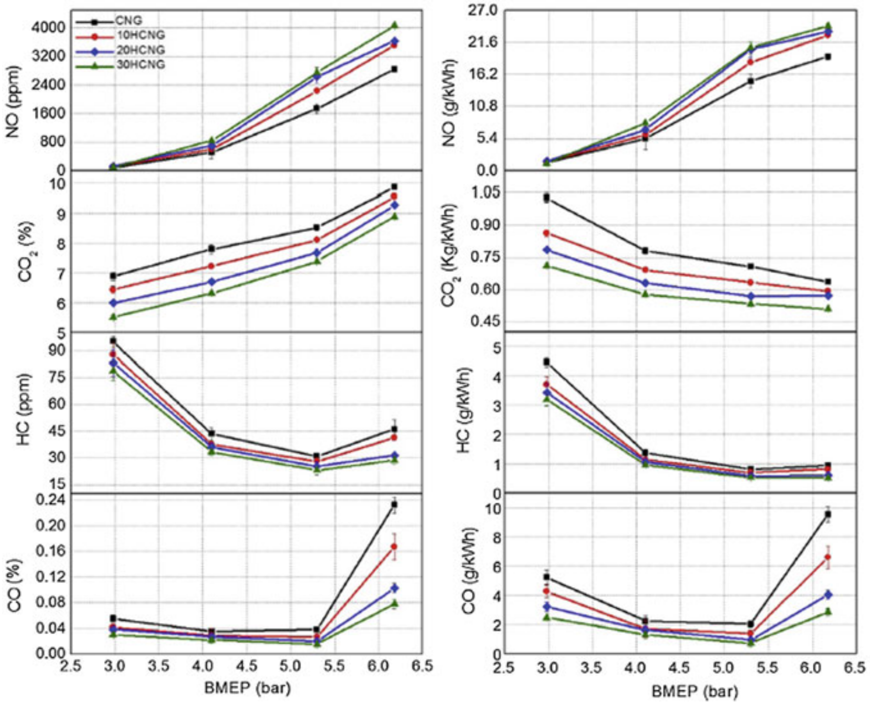


Fig. 6.9 Exhaust tailpipe emission from HCNG mixtures (Hora and Agrawal 2015)

combustion of unburnt fuel/hydrocarbons. For HCNG mixtures, HC emissions were relatively lower because of improved combustion efficiency and relatively lower quenching gap. CO is formed due to incomplete combustion and it reduced with increasing BMEP because higher peak cylinder temperature at higher BMEP favours oxidation of CO into CO_2. HCNG mixtures showed lower CO emission than baseline CNG due to higher peak cylinder temperatures and lower C/H ratio of HCNG mixtures.

6.2.2 Nanoparticle Emissions from HCNG Engine

6.2.2.1 Particle Size-Number Distribution of HCNG Engine

Figure 6.10 shows particle size-number distribution from HCNG engine at various loads. It can be observed that number of nanoparticles (nucleation mode particles Dp > 50 nm) were high from all test fuels, while accumulation mode particles (0.1–0.3 μm) were relatively lower in number. 30HCNG showed emission of higher number of particulate amongst the test fuels. Abrupt change of particle

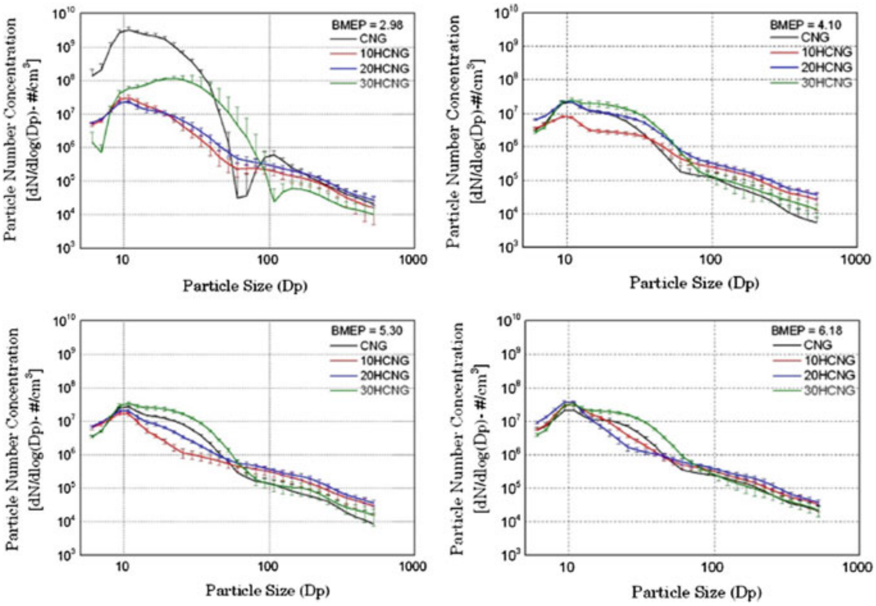


Fig. 6.10 Particle number versus size distribution from HCNG mixtures (Hora and Agrawal 2016)

numbers for CNG at BMEP = 2.98 bar was due to poor engine stability, because of poor lean-burn capability of CNG. When hydrogen was mixed with CNG, the flame speed and combustion speed increased, resulting in lower particulate emissions of all sizes. Same behaviour of particle emissions was observed for all HCNG mixtures as well. CNG- and HCNG-fuelled engines emit negligible particulate emissions, which originate from the fuel. The main source of particulate emissions is unburnt lubricating oil, which is consumed during combustion.

Lubricating oil enters the combustion chamber through the piston and liner interactions. Pyrolysis of this lubricating oil leads to formation of unburnt hydrocarbons and particulates. Lubricating oil contains high molecular weight hydrocarbon compounds, which remain unburnt, resulting in formation of nanoparticles. The engine was operated at constant speed (1500 rpm) at all loads; therefore, contribution of lubricating oil in the particulate formation essentially remains similar at all loads.

6.2.2.2 Particle Size-Mass Distribution of HCNG Engine

Figure 6.11 shows the particle size-mass distribution for the test fuels at different BMEPs. It was observed that majority of particulate mass was composed of accumulation mode particles, while contribution of nanoparticles was significantly

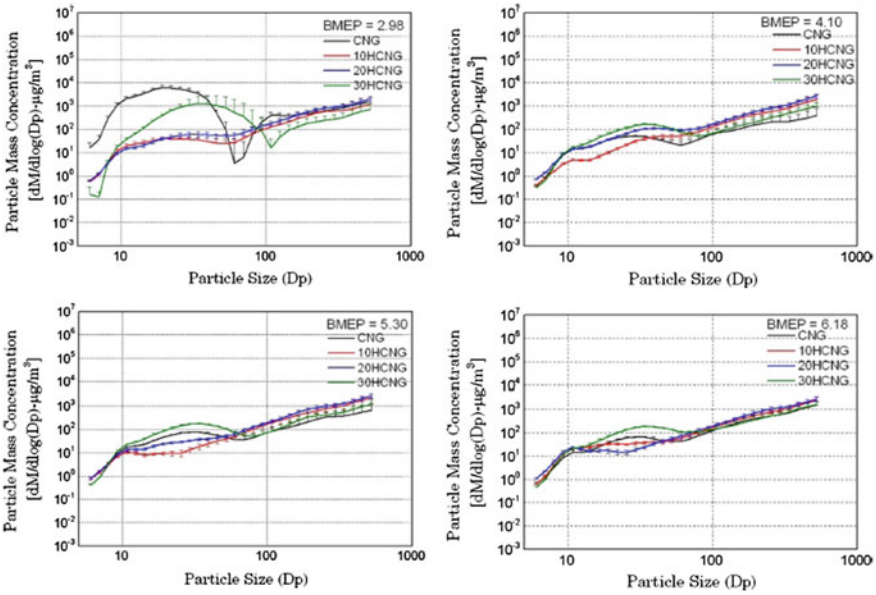


Fig. 6.11 Particle size versus mass distribution (Hora and Agrawal 2016)

lower. Particle size-mass distribution showed that CNG/HCNG mixtures were prone to generate very high number of nanoparticles, which have very low contribution to the particulate mass emissions. Nanoparticles can easily enter human body during inhalation and can cause significant risk because of their toxicity, while larger particles have tendency to settle down due to their weight. Nanoparticles pose greater risk due to their higher atmosphere retention time. Euro-6 emission regulations restrict the particle numbers emitted by the engine; therefore, it is important to emphasize on reducing the emission of number of particles from CNG/HCNG-fuelled engines.

6.2.2.3 Particle Size-Surface Area Distribution of HCNG Engine

Particle size-surface area distribution was studied for CNG and HCNG mixtures (Fig. 6.12). Particle surface area is calculated by assuming particles as spherical. Particle surface area provides the quantification of active sites available for adsorption of high boiling point organic compounds present in the exhaust gas. Particulate surface area distribution was slightly higher for 30HCNG compared to other test fuels. Both nanoparticles and accumulation mode particles contribute significantly to higher surface area, while larger particles have relatively smaller contribution to surface area per unit mass of particles.

Practically, particles emitted are mostly in fractals or branched shapes, which provide far greater surface area than assumed spherical shapes.

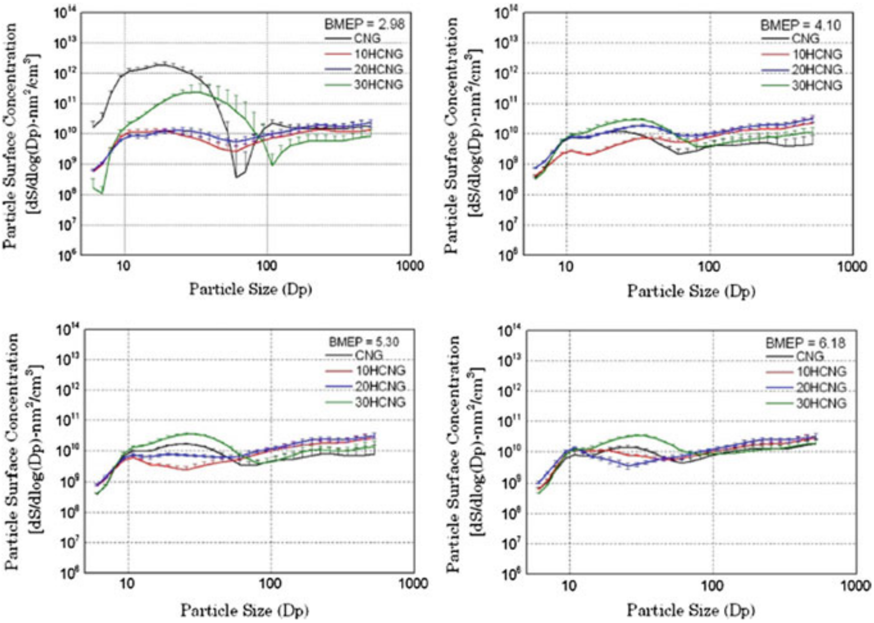


Fig. 6.12 Particle size versus surface area distribution from HCNG mixtures (Hora and Agrawal 2016)

6.3 HCNG Vehicle Development

Growing concerns of environmental and health issues originating from fossil fuels have led to implementation of gaseous fuels such as CNG/HCNG across Asia, Europe and America. Though the conversion requirements of conventional gasoline/diesel engines to CNG/HCNG are minimal, however, engine needs hardware changes, especially in the fuel injection system. Technologies available for gaseous fuels include direct injection combustion, dual-fuel combustion or bi-fuel combustion. Both these techniques are depicted in Fig. 6.12. Next subsection discusses additional components required to manufacture a CNG/HCNG engine. In a direct injection technology, CNG/HCNG is injected directly into the combustion chamber, and while in bi-fuel/dual-fuel engine, CNG is injected in the intake manifold. Direct injection technology is not widely implemented though for gaseous fuels due to the challenges arising because of high injection pressure (Fig. 6.13).

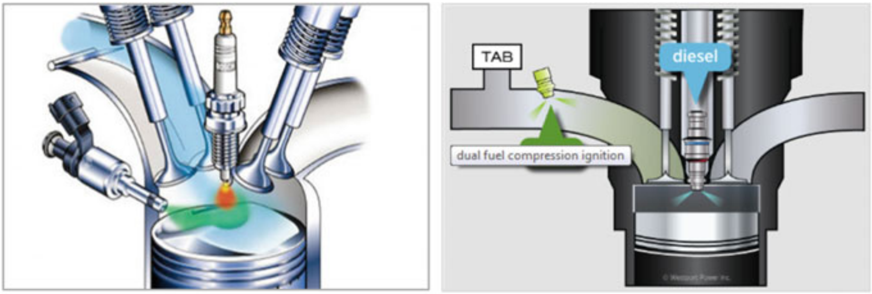


Fig. 6.13 Direct injection and dual-fuel techniques (http://www.full-race.com/articles/inside-the-ecoboost-f-150.html; http://www.westport.com/is/core-technologies/combustion/dual-fuel)

6.3.1 Technology Requirements

Major modifications in the gas engines compared to conventional engines include changes in fuel injection systems. Depending on the fuel injection technology used, requirements of fuel injection components vary. Commonly, CNG/HCNG engines require components such as gas injectors, fuel lines, pressure regulator, fuel tank, CNG sensors, shut-off valves, CNG rail in order to induct high-pressure fuel gas to the engine combustion chamber. The technology of direct injection of CNG is commonly known as high-pressure direct injection (HPDI) technology. Figure 6.14 shows the direct injection CNG injectors and port fuel CNG injector from one of the OEMs. CNG injectors can also be utilized for HCNG injection. Direct injection CNG engines are capable of generating equivalent power and performance as that of equivalent petrol/diesel engines with superior fuel economy. However, direct injection CNG engines are rare. Most CNG/HCNG engines commercially available are manifold injected engines. These engines are capable of meeting stringent

Fig. 6.14 Direct injection and port fuel injection CNG injectors (http://www.delphi.com/manufacturers/auto/powertrain/alternative-fuel-systems/multec-cng-injector)

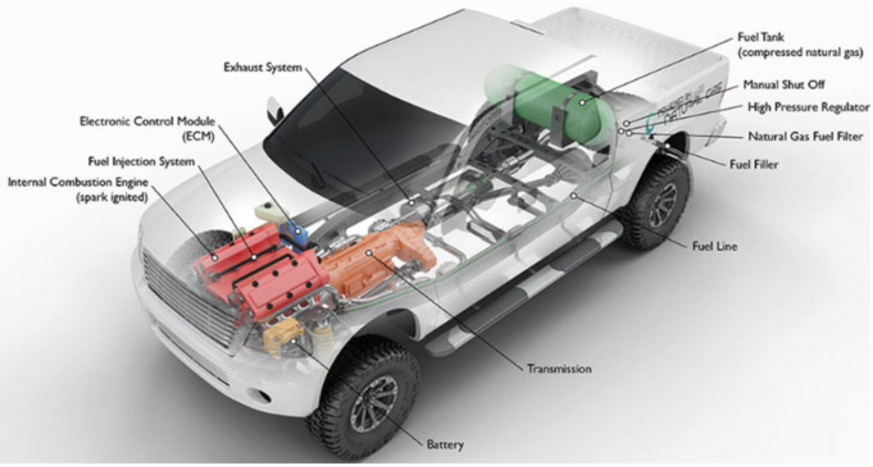


Fig. 6.15 CNG/HCNG configuration of a pickup (LCV) (Central U.P. Gas limited)

emission norms such as EU-6/BS-6. CNG/HCNG engines produce nearly zero particulate emissions; hence, the effort of engine calibration is significantly lower than that of diesel engines. Port injection technology is commonly used in bi-fuel and dual-fuel engines.

A bi-fuel engine can operate in two modes, either on 100% fossil fuel or on 100% CNG/HCNG; while a dual-fuel engine can operate on either 100% diesel or a mixture of diesel and CNG/HCNG. In a dual-fuel engine, diesel is directly injected into the combustion chamber, while a definite amount of CNG/HCNG is injected into intake manifold, which is drawn in along with the intake air. Bi-fuel engine requires a spark plug to initiate the combustion, and while in a dual-fuel engine, diesel pilot initiates the combustion of CNG/HCNG. Dual-fuel engines have improved fuel economy and reduced emissions. Bi-fuel technology is suitable for light-duty engines typically used in passenger vehicles, while HPDI/dual mode is suitable for heavy-duty engines typically used in commercial applications. Bi-fuel engines operate with petrol and CNG since they require a spark-plug, while dual-fuel engines do not require a spark plug.

Figure 6.15 shows a typical layout of a CNG pickup vehicle and Fig. 6.16 shows a similar typical layout of a heavy-duty vehicle.

For an optimized engine, combustion bowl and piston should be designed as per CNG fuelling, injection and combustion characteristics. Heavy-duty HCV engines require fuel system capable of withstanding high pressure, typical to CNG (200–225 bars). Number of CNG storage cylinders for this type of application is more in order to provide it a long range. One of the major concerns is to accommodate large number of CNG cylinders in the limited space available on-board. Hence, most commonly, these cylinders are packaged behind the cabin vertically or beneath the chassis horizontally.

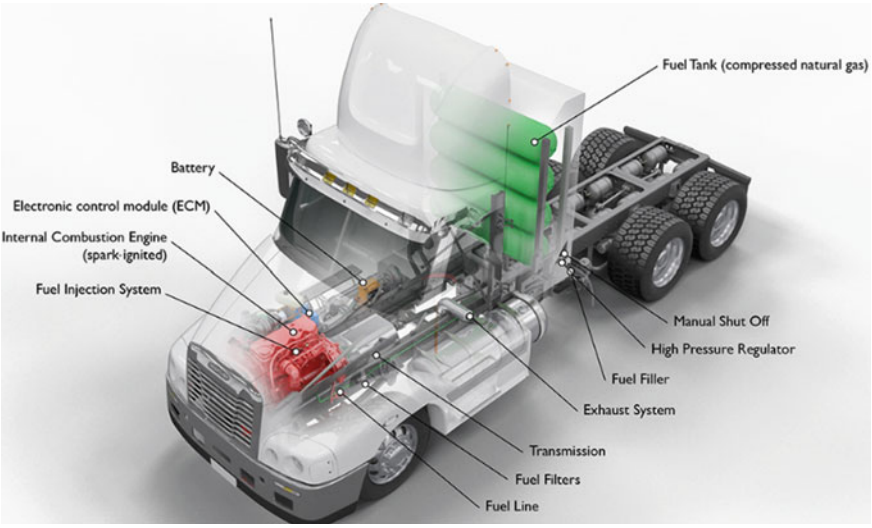


Fig. 6.16 CNG/HCNG configuration of a heavy-duty truck (HCV) (https://www.afdc.energy.gov/vehicles/natural_gas.html)

Some of the major components required for a CNG vehicle development are described below. These components have to be specifically designed for CNG/HCNG application.

1. **Fuel tank, Pressure gauge and High-pressure lines**: CNG is lighter than air and to accommodate high volume of gas, CNG is compressed and stored in high-pressure cylinders. The typical pressure of a CNG cylinder is 200–225 bars. These cylinders are designed to withstand jerks during vehicle operations as well as mishandling. Hydraulic testing of cylinder is performed to verify the cylinder quality. A pressure gauge is installed on each cylinder to show the gas pressure. High-pressure lines which can withstand 200–225 bar pressure (with some factor of safety) are fitted for CNG transport from storage cylinder to the engine cylinder.
2. **High pressure shut-off valve**: To address the safety concerns, an electronic shut-off valve is installed in the CNG passage lines. A CNG sensor is installed in the vicinity of cylinder bank, which can detect CNG leakages and can give command to the shut-off valve to close. This communication can be initiated through the engine ECU, which can take inputs from gas sensors and command the electronic shut-off valve. Shut-off valve is usually a solenoid valve, which remains in normally shut-off state and delivers the gas only when the ignition is ‘on’ from the driver’s cabin. The location of shut-off valve should be close to the gas storage cylinders in order to minimize the plumbing requirement. Figure 6.17 shows a typical electronic shut-off valve.

Fig. 6.17 Typical electronic shut-off valve

3. **High-pressure fuel filters**: In order to prevent the foreign particles from entering the combustion chamber, a pre-filter is installed in the cylinders and a main filter is installed in the CNG/HCNG passage to the injectors. Function of the filters is to prevent fuel contamination by arresting any debris from reaching the high-pressure regulator and the injectors, thus avoiding possible serious damages. Pre-filter is located between the cylinders and the fill connection. The filters showed are designed such that pressure drop/restriction is rather minimal. The maximum pressure drop in fuel system from the outlet of the high-pressure regulator to the engine inlet must not be more than 25 psi. These filters have a life cycle in terms of vehicle kilometres and have to be replaced after regular intervals.
4. **High-pressure regulators**: The function of a pressure regulator is to expand high-pressure CNG from the cylinders to a nominal working pressure (approx. 4–10 bar), depending on application. This regulator reduces vehicle fuel tank pressure to required engine pressure levels. Cummins recommends regulator settings to be at 6–8 bars. During reduction of gas pressure, these regulators can be frozen to very low temperature as the gas expands to lower pressures. To ensure proper functioning of these regulators and to prevent ice-lock in the gas pressure, these regulators require warm coolant from the engine to prevent freezing of regulators. Figure 6.18 shows a typical CNG regulator.
5. **Low fuel pressure lamp**: To provide comfort to the drivers and to ensure vehicle is running safe and within emission limits, legislation provides inclusion of on-board diagnostics (OBD). To comply with OBD, vehicle manufacturer has to provide various messages to the vehicle dashboard. One of the requirements is the vehicle fuel level, thus vehicle manufacturers have to provide fuel level indicator on the vehicle dashboard. Functioning of the low fuel pressure lamp is controlled by the inputs from the fuel pressure sensor. In case of low fuel pressure, drop in vehicle power and performance can be observed.

Fig. 6.18 Electronically controlled CNG pressure regulator (http://www.landiusa.com/)

6. **CNG common rail**: For a multi-cylinder engine, a common rail is required to deliver gas into each cylinder manifold, at a constant pressure. The timing of injection depends on engine calibration and opening of injector. Injection timing is controlled by the engine ECU. An optimized injection timing is decided based on requirement of better fuel economy, performance and emissions.
7. **Electronic control unit and wiring harness**: Most advanced engines electronically regulate fuel quantity as per driver's demand and load condition. Engine's electronic control unit (ECU) precisely controls the fuel requirement. An engine-mounted electric shut-off valve is provided in the fuel system to cut-off the fuel supply in case of emergency such as over-speed and stopped engine (no speed detected). This valve is controlled by the engine ECU. Engine complying with EU-4 and beyond norms are electronically controlled. The actuators and throttle are controlled based on sensor inputs and ECU control strategy. A dual-fuel CNG engine requires two ECUs. One ECU is used for mono-mode, i.e. only diesel operation, while the other ECU is used for CNG and diesel dual-mode operation. During dual-mode functioning, CNG ECU is master and engine is governed based on the calibration of dual-mode, while in case of mono-mode, diesel ECU is master and base diesel calibration governs the engine speed and load demand.

Figure 6.19 shows the layout of various components of a CNG/HCNG fuel system in a typical vehicular setting.

With the evolution of CNG as established engine fuel and advancement in technology, instead of injecting CNG in the intake manifold, it is mixed with the intake air before the turbocharger to ensure complete mixing. This method of CNG induction provides higher power output from the engine. A typical fuel injection layout for a bi-fuel turbocharged engine is shown in Fig. 6.20.

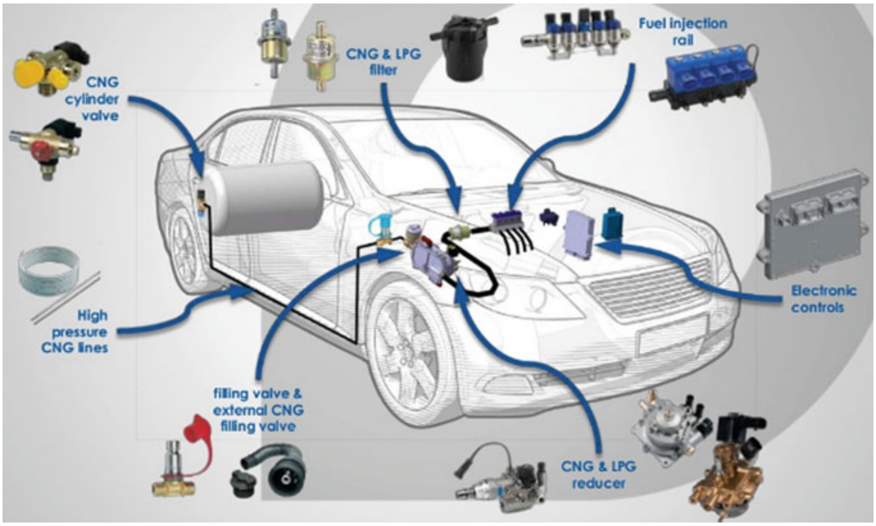


Fig. 6.19 CNG/HCNG fuel system components and layout in a vehicle (www.westport.com)

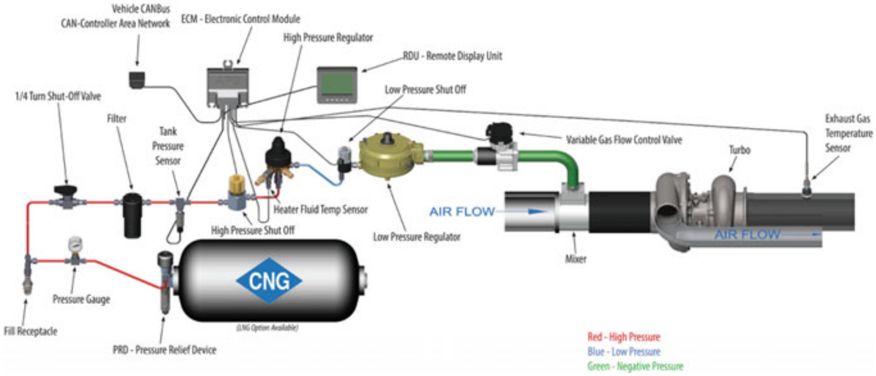


Fig. 6.20 Typical CNG induction system layout for a turbocharged bi-fuel engine (http://www.americanpowergroupinc.com/apg-technology.html)

6.3.2 Global Experience of HCNG Vehicles

Benefits of HCNG have been realized by industries, scientists and researchers but most of studies of HCNG engines were limited to laboratories and restricted in practical implementation on road. HCNG vehicles are not commercially available in market in most countries. Major restrictions of HCNG are due to lack of infrastructure for distribution. Most countries have scarcity in CNG fuelling stations and are required to increase the proximity between CNG refilling stations just like gasoline/diesel fuelling stations. Countries such as Italy, Korea and China, where sufficient CNG stations are commercially viable, are shifting gradually from CNG to HCNG, while other countries have this technology developed only as pilot projects. Another major concern related to commercial availability of HCNG vehicles is the safety concerns that come with hydrogen and its cost. OEMs are not interested in manufacturing HCNG vehicles due to lack of infrastructure, investments and government policies.

Section below shows some of the successful HCNG vehicle projects implemented across the world:

City of Malmo, Sweden introduced few hythane buses in its transport fleet. Malmo has abundant CNG filling stations and CNG buses are widely used for local transport. Since 2003, 8% hythane blend was introduced in few buses and CNG filling stations were upgraded to deliver pure hydrogen and hythane blends along with CNG. These hythane buses covered 1,60,000 km and proved superior in performance and emission compared to conventional gasoline/diesel vehicles. Also, HCNG bus resulted in better fuel economy. Other parts of Europe such as Germany, Italy, France are also promoting use of HCNG, CNG and LNG as transport fuel to displace diesel/petrol. Germany in collaboration with Solbus, a Polish bus manufacturer, demonstrated LNG bus for public commute. France started a project called ALT-HY-TUDE with support from French agency ADEME and GDF SUEZ. ALT-HY-TUDE means alternate hydrogen in urban transport in Dunkerque. The project was aimed to initiate application of hydrogen in vehicles, performance measurement and technical and economic analysis. The engine was operated with 6 and 20% HCNG mixture (ALT-HY-TUDE project 2009) (Fig. 6.21).

Italy which has more than 80 years of experience in using CNG has 6,00,000 CNG vehicles on the roads. CNG infrastructure is fairly matured and normalized in Italy and slowly Italy is shifting towards using HCNG. Italy has tested HCNG buses on the roads and observed significant reduction in emissions. These buses were operated for different hydrogen fractions ranging from 5 to 25% over urban and suburban duty-cycles (Fig. 6.22).

In Asia, India, Korea and China are investigating HCNG as transport fuel. In India, CNG network is limited and not widespread; therefore, HCNG is limited to laboratory experiments only. India has more than 200,000 CNG vehicles. IOCL and SIAM collaborated to demonstrate HCNG vehicles and fifty HCNG vehicles are to be manufactured and implemented for a pilot study before introducing HCNG in the mainstream. IOCL investigated 18% HCNG and claimed maximum reduction in emissions amongst other HCNG mixtures. MNRE and Eden energy are collaborating to introduce HCNG vehicles in India by 2020. Automotive OEMs such as TATA Motors, Ashok Leyland, Eicher Motors, Mahindra & Mahindra have already developed HCNG engines for demonstration projects. Indian government is taking major steps to increase the number and density of CNG station across the country.

Fig. 6.21 HCNG projects in Germany and France (http://busnews.blogspot.in/2012)

Fig. 6.22 HCNG project in Italy (http://www.eltis.org/discover/case-studies/testing-hydromethane-buses-emilia-romagna-italy)

Korean researchers have demonstrated pilot project of HCNG buses. Moreover, Korean researchers have developed a HCNG engine compliant with Euro-6 emission norms. They appreciated the levels of reduction in nitrogen oxides and greenhouse gases from these vehicles. China is also promoting switching to LNG and CNG vehicles. Figure 6.23 shows the emissions from a HCNG bus compared to Euro-6 legislative requirements. HCNG meets the emission requirements with sufficient margins.

In USA, Hythane® a subsidiary of Eden energy has initiated many projects to convert the buses, pickups and trucks to HCNG. HCNG demonstration projects started as early as in 1900–93 with hythane pickup trucks. Denver project operated 5% (w/w) hydrogen blended with methane. In 2002–04, a HCNG bus pilot project was started in California (Fig. 6.24).

In 2007, Eden energy received tender to convert shuttle fleet of San Francisco International Airport to HCNG. Twenty-seven buses were converted to hythane. A Ford 6.8L V10 engine was calibrated for hythane and certified by California Air Resource Board (CARB). This engine resulted in reduction of 10% CO_2, 40%

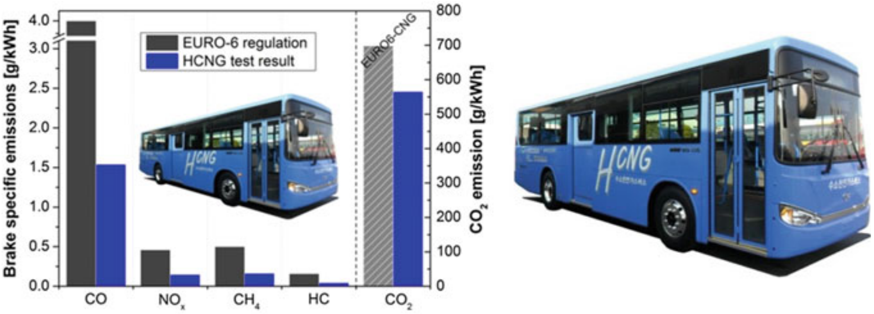


Fig. 6.23 Euro-6 HCNG bus project in Korea (http://www.businesskorea.co.kr/english/news/sciencetech/1420)

Fig. 6.24 HCNG bus project in USA (http://edeninnovations.com/)

NMHC, 49% methane and 70% particulate matter compared to similar natural gas engine (ASX Quarterly report 2009). Volvo has also developed a vehicle, which can be operated on five fuels, including hythane and CNG.

6.4 Conclusions

Based on the research studies and field trials of HCNG engines, the following conclusions can be drawn:

1. HCNG reduces GHG emissions and has good potential to slow down climate change.
2. HCNG is superior alternative to fossil fuels delivering superior power and reduced emission.
3. Hydrogen addition in CNG improves engine performance and reduces emissions; however, nanoparticles need to be controlled.

4. Hydrogen addition in CNG improves lean-burn limit of CNG and results in superior fuel economy.
5. HCNG engines are capable to successfully meeting Euro-6 emission legislations, which will be implemented in India by 2020.
6. Existing CNG networks can be improvised to dispense HCNG into vehicles.
7. Usage of HCNG vehicle is to be encouraged by the government.

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Part III
Biofuels

Chapter 7
Alcohols for Fueling Internal Combustion Engines

Dev Prakash Satsangi, Nachiketa Tiwari
and Avinash Kumar Agarwal

Abstract The balance between production and consumption of energy is an important factor, which drives future direction of energy resource development. This largely depends on the decision made by producers, consumers, and governments. The deciding factors for aforesaid choices are their cost, quality, reliability, convenience, and social impact. Globally, the most commonly used automotive technology includes Otto- and diesel-cycle engines. Consequently, their fuels are gasoline and diesel. "Alternative fuels" are those existing fuels, which are neither gasoline nor diesel. Commonly available alternative fuels are alcohols, vegetable oils, and their derivatives such as biodiesel, gaseous fuels (natural gas, hydrogen, and liquefied petroleum gas), ethers, etc. Alcohols are oxygenates of primary hydrocarbons with hydroxyl groups. Presence of oxygen in them contributes to smoothness of combustion process in the IC engines. This results in cleaner burning characteristics compared to fossil fuels. Also, alcohols can help in lowering emission of hazardous gases and can reduce dependency on non-renewable energy sources.

Keywords Alcohols · Alternative fuels · Methanol · Ethanol · Propanol
Butanol · Internal combustion engines

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7.1 Current Energy Scenario

Over last few decades, global energy demand has been increasing primarily because of developing countries. This rise in energy demand is influenced by economy expansion, industrialization, population growth, and urbanization. For fulfilling the current energy demand, the world is heavily relying upon fossil fuels, which have negative impacts on the society as well as on the environment. Considering this, researchers around the world are looking for alternate energy sources. According to one of the reports, in 2015, the increment in global renewable energy resources (mainly wind, solar photovoltaic, hydropower, etc.) contributed to the world's electricity sector extensively. An increase of 9.3% was recorded in renewable power generation capacity globally, which reached 154 gigawatts (GW) more compared to the previous year (IRENA 2017). In the year 2015, for the first time, increment sum of wind power (66 GW) and solar photovoltaic (47 GW) was more than that of hydropower (Fig. 7.1).

To expand and upgrade the electricity infrastructure of the world, renewable power technologies are the most preferred route. Figure 7.2 illustrates that since 2012, growth of renewable energy sources has overcome the growth in non-renewable energy resources. Renewable power generation capacity accounted for 61% of the overall new power generation capacity worldwide in the year 2015 (IRENA 2017).

By the year 2035, global population is projected to increase by 1.5 billion and reach 8.8 billion. In terms of economic growth, China and India together are responsible for almost half of the annual increase in global gross domestic product (GDP), while Organization for Economic Co-operation and Development (OECD) countries account for just about a quarter. Thus, the demand for global liquid fuel is projected to reach 112 Mb/d by 2035 (Fig. 7.3). This increase in demand will primarily come from emerging economies (BP 2016). On the supply side,

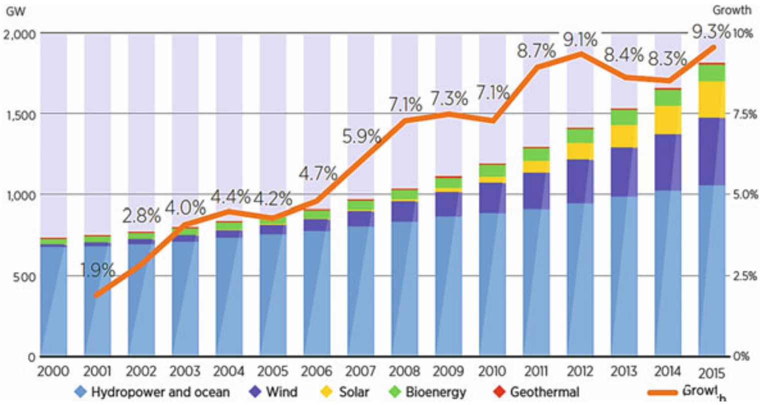
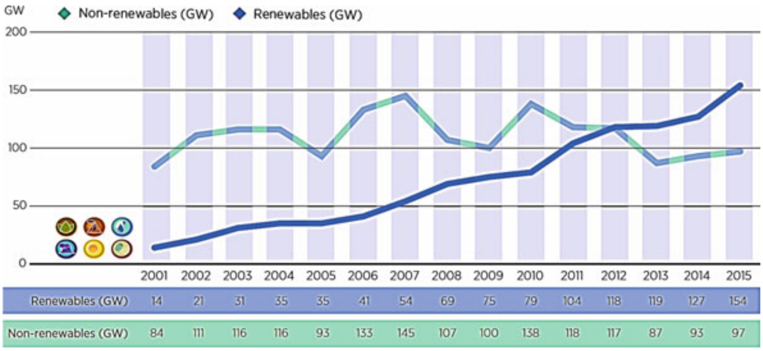


Fig. 7.1 Renewable energy source power capacity and increment rate (IRENA 2017)



	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015
Renewables (GW)	14	21	31	35	35	41	54	69	75	79	104	118	119	127	154
Non-renewables (GW)	84	111	116	116	93	133	145	107	100	138	118	117	87	93	97

Fig. 7.2 Non-renewable and renewable energy resources (IRENA 2017)

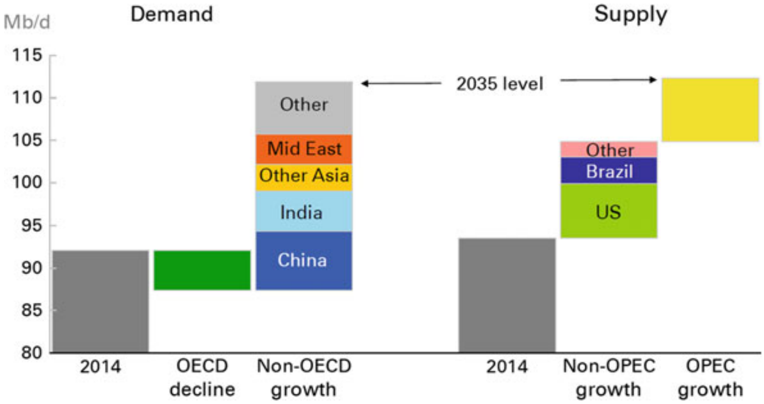


Fig. 7.3 Global oil demand and supply trends (BP 2016)

Organization of the Petroleum Exporting Countries (OPEC) will expectedly provide for supply increase of 8 Mb/d, while non-OPEC will provide for 12 Mb/d of liquid fuels.

The growth in global consumption of liquid fuels is primarily due to transport and industrial sectors of the economy. The transport sector alone accounts for approximately two-thirds of the increase in demand for liquid fuels (Fig. 7.4). The other source of such growth in demand for liquid fuels is industries. Use of liquid fuels is rapidly increasing in industries such as petrochemicals. Much of petroleum used by industries is not burnt as fuel. Rather it is used for production of organic chemicals.

India, which is home to approximately 18% of the humanity, uses only 6% of the world's primary energy (BP 2016). However, its energy consumption is increasing rapidly and has doubled between 2000 and 2013. This rapid acceleration in demand is expected to continue in foreseeable future as well. Figure 7.5 provides details of demand and how this rapidly increasing demand was met over the period 2000–2013.

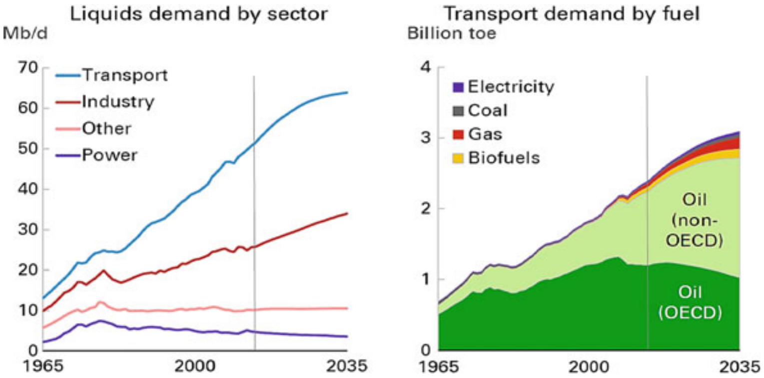


Fig. 7.4 Sector-wise fuel demand trends (BP 2016)

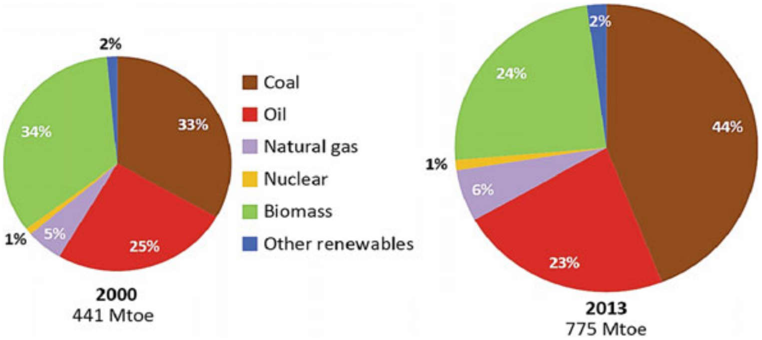


Fig. 7.5 Fuel-wise energy demand in India (BP 2016)

Much of this demand is coming from transport sector. However, a very large amount of oil is also used to produce electricity by burning diesel. There are millions of diesel generator (DG) sets, which service the power shortage in industries and commercial units in the event of power failures. DG sets have a cumulative installed capacity of approximately 90,000 MW in India. Further as per Power Regulatory of India report, it is growing at a rate of 5–8 GW each year. Hence, there is a strong need to evaluate alternative fuels, which are relatively greener, cleaner, and cost-effective compared to mineral diesel.

India's need for alternative fuels has become even more important as it heavily depends on imports to meet its crude oil requirements. Crude oil production in India is 900,000 barrels per day (b/d). This amount is barely 26% of India's daily need of 3800,000 b/d (BP 2016). Thus, detailed investigation of viability of alcohol–diesel blends as a substitute for genset engine application is very important. For such blends, the alcohol portion can be produced on farms, thereby reducing India's carbon footprint in this sector of the economy.

7.2 Alternative Fuels for Internal Combustion Engines

The term alternative fuel has been coined to describe any fuel that can be suggested for use in the place of gasoline and diesel in IC engines. Each alternative fuel possesses some characteristics that make them environmentally advantageous compared to commercially available petroleum-based fuels. Also, alternative fuels are less prone to damage the environment in case of accidental spilled and can reduce hazardous emissions compared to gasoline/diesel. Earlier, the work on alternative fuels was focused on the basis of their technical feasibility, production capability, and cost of production. However, with the latest technological developments in the field of IC engines, the focus has been shifted to the production cost of alternative fuels (Bechtold 1997).

There are two types of IC engines: Otto- and diesel-cycle-based. These Otto- and diesel-cycle engines use gasoline and diesel as their primary fuels, respectively. These fuels are distilled directly from crude petroleum in refineries. Alternative to these fuels are mostly not derived from mineral sources. There are many alternative fuels that can be used directly in gasoline or diesel engines without making significant changes to the engine hardware. The major advantages related to the use of alternative fuels in IC engines include cleaner burning, lesser emissions, and reduced dependency on petroleum fuels (Ramadhas 2016). There are several parameters, which should be considered before selecting such alternative fuels (Agarwal 1999). These are the following:

- Energy density on mass as well as volume basis.
- Storage life and ease of handling and distribution.
- Easy of transportation from production plants to end users.
- Engine performance.
- Amount of regulated and unregulated emissions.
- Engine life.
- Cost of operation.
- Engine modifications required to facilitate use of these fuels.

There are several alternative fuels being evaluated globally. Principle ones among these are as follows:

(a) **Alcohols**

One of the potential alternative options to the fossil fuels is alcohol. It has been used as an industrial reactant, solvent, and fuel since long time. The primary alcohols (methanol, ethanol, propanol, and butanol) are preferred to be used as an IC engine fuels. This is because these alcohols possess characteristics, which permit them to be used as fuel in current generation IC engines. Alcohols can be synthesized chemically or biologically. Among these primary alcohols, methanol and ethanol are the most promising ones. Being in liquid state, alcohols are easy to store and transport. The chemical formula of alcohol can be represented as $C_nH_{2n+1}OH$.

(b) Vegetable oils

The use of vegetable oils as an alternative fuel was first introduced in the agricultural sector for tractors and other equipments. In an international conference, agricultural engineers of ASAE (American Society of Agricultural Engineers) proposed that vegetable oils could be a viable alternative fuel source, especially for diesel engines (Lipinsky et al. 1982). Vegetable oils can be produced from popular crops like rapeseed, peanuts, sunflowers, and soybeans. Vegetable oils have high viscosity and high pourpoints compared to mineral diesel. The higher viscosity of vegetable oils influences in-cylinder spray behavior and fuel impingement on interior surfaces. Thus, various investigations show that the use of vegetable oils in diesel engines leads to problems related to fuel injection system, piston rings, and oil stability. These characteristics of vegetable oils make them impractical to be used as transport fuels in most engines. Thus to get desirable characteristics of vegetable oils, esters were formed by reacting the vegetable oils with methanol or ethanol, which shows better fuel characteristics and gives the generic name of "biodiesel" (Bechtold 1997). The most favorable vegetable oils for transesterification are rapeseed oil, soybean oil, and sunflower oil. Table 7.1 shows different properties of biodiesel (rapeseed and soybean methyl esters).

Biodiesel and diesel blend (B20) is a combination of 20% v/v biodiesel and 80% v/v diesel and widely utilized as fuel in typical transit buses. It was noted that biodiesel blend reduced smoke, particulates, and gaseous emissions. Worldwide research accepted that biodiesel is a good alternative to diesel but restricts its usage due to their higher cost of production (Bechtold 1997).

(c) Gaseous fuels

Gaseous fuels are the class of fuels which are commonly obtained either naturally or through processing of solid or liquid fuels. Compressed natural gas (CNG) and liquefied petroleum gas (LPG) are two important types of naturally obtained gaseous fuels. These are obtained from natural gas or methane and possess high calorific values. Compared to liquid fuels such as gasoline and diesel, gaseous fuels

Table 7.1 Properties of biodiesels, gasoline, and diesel (Sarathy et al. 2014; Reece and Peterson 1995; Zhang and Van Gerpen 1996)

Fuel	Structure	Molecular weight	Oxygen content (%w/w)	LHV (MJ/L)	Stoichiometric air/fuel ratio	Boiling point (°C)	Specific gravity at 20 °C
Gasoline	Average C_8H_{15}	111.19	0	30–33	14.58	27–225	0.72–0.78
Diesel	Average $C_{14}H_{30}$	198.4	0	35.66	14.95	125–400	0.81–0.89
Soybean methyl ester	C_{18} to C_{19}	~300	11	~32	–	–	0.87
Rapeseed methyl ester	C_{18} to C_{19}	~300	7	~37	–	~350	0.88

have higher energy content on a mass basis. Gaseous fuels are preferred over liquid fuels due to their capability to reduce greenhouse gases emissions as well as exhaust pollutants. To determine the thermal output of the equipment, both calorific value and specific gravity of gaseous fuel are required. An important rule to express gaseous fuels is Wobbe number or Wobbe index which is defined as (Sarkar 1974):

$$\text{Wobbe number} = \frac{\text{calorific value}}{\sqrt{\text{specific gravity}}}$$

Different kinds of gaseous fuels are as follows:

Natural gas

Natural gas is one of the excellent fossil fuels available in ample quantity in various parts of the world. It is commonly used for space heating, electricity generation, and industrial processes. It is a mixture of various gases (methane, ethane, propane, butane, pentane, hydrogen sulfide, etc.), but major constituent is methane, which comprises of one carbon and four hydrogen atoms. Natural gas with high and less amount of hydrogen sulfide is referred as sour gas and sweet gas, respectively (Sarkar 1974). The composition of natural gas is responsible for its heating value and physical properties, which affects the engine combustion process. Calorific value of natural gas is in the range of 8400–9100 kcal/Nm^3. CNG is stored at high pressure, whereas liquefied natural gas (LNG) is cooled to −160 °C, due to which it becomes liquid at atmospheric pressure. CNG and LNG both are common fuels for light passenger vehicles.

Liquefied petroleum gas

Liquefied petroleum gas is also referred as LP gas or LPG. It is a colorless, volatile hydrocarbon gas, which is largely obtained from refinery gas or natural gas through pressurizing, cooling, and liquefaction. The constituents of LPG while obtained from refinery gas are propane, butane, propylene, butylene with traces of pentane, pentylene, and sulfide. However, LPG obtained from natural gas mainly contains olefins (Rojey and Jaffret 1997). LPG has major usage in industries, combustion engines, and as domestic fuel. It is a flammable gas and explodes when become high in concentration in the air. LPG remains at gaseous state at standard pressure and temperature. For storage of LPG in the cylinders, it is liquefied by applying moderate pressure or reducing temperature sufficiently. LPG is produced in association with production of natural gas or with refining of crude oil.

Propane and butane are the most common constituents of LPG for vehicle application. In the USA, propane gas has been used as a fuel in vehicles for the last 60 years (Bechtold 1997). Today also, most vehicles used in the USA are propane-based and these are converted from gasoline engines. LPG has the following advantages over other fuels (Rojey and Jaffret 1997).

(a) Less pollution, i.e., free of smoke, dust, and carbon residues.
(b) Higher calorific value leads to higher heat of generation.
(c) Easy to transport through roads (tankers) or waterways (vessels).

Although LPG is a convenient fuel, it is dangerous also. Once the released amount of LPG reaches its explosion limit in the air, a little spark can cause explosion. Thus, LPG processing plants mix an odorous chemical (mercaptan or thio-ether derivatives) with LPG to detect its leakage.

Hydrogen

Hydrogen possesses many characteristics, which make it an ultimate alternative to fossil fuels. Hydrogen is an energy carrier that can be used in IC engines with production of water vapor as a major emission and some oxides of nitrogen at high temperature. When hydrogen is used in fuel cells, it gets oxidized and emitted only as water vapor. It is a colorless, odorless, and non-toxic fuel. Hydrogen can be produced through steam reforming of natural gas, gasification, solar hydrogen, or electrolysis of water (Bechtold 1997). There is a lot of research is going on all around the world to address the issue of its storage and better and efficient production techniques. There are some advantages and disadvantages associated with the use of hydrogen as a transport fuel (Chamousis 2009).

Advantages

(1) Can be produced from many primary energy sources.
(2) Possesses very high energy yield on mass basis (122 kJ/g).
(3) Most abundant element on the earth.
(4) High diffusivity.
(5) Most promising alternative fuel.
(6) Wide flammability range.
(7) Water vapor is produced as major oxidation product.

Disadvantages

(1) Possesses low volumetric energy density thus requires large storage.
(2) Low ignition energy than gasoline.
(3) High cost of production.

Hydrogen can be used for various applications such as fuel for transport vehicles, liquid propellants for rockets, boats, airplanes, portable fuel cells. The major obstacle in use of hydrogen is its difficulty to be stored. Most commonly hydrogen is stored either in very high-pressure cylinders or in cryogenic tanks.

(d) Ethers

Ethers are the organic compounds that contain an ether group (an oxygen atom connected to two alkyl groups). Alternative fuel ‘dimethyl ether’ (DME) is the simplest ether with chemical formula ‘CH_3OCH_3’. The physical properties of DME are similar to those of LPG. It is a volatile organic compound, but a non-carcinogenic, non-teratogenic, non-mutagenic, and non-toxic with sweet-ether-like odor. The production of DME consists of two steps. In the process steps, syngas is first converted to methanol, followed by methanol dehydration to DME. The feedstock for producing DME involves natural gas, coal, and biomass.

The transportation of DME is similar to that of LPG, and for transportation through ocean, DME can use conventional LPG tankers.

DME is gaining attention, especially for diesel engines. As compared to conventional diesel engines, DME engine emits significantly lower emissions of NO_x, hydrocarbons, and carbon monoxide. Also, DME combustion does not produce soot. Significant modifications to the diesel engine are not needed for the operation on DME as a fuel. However, the fuel storage tank of DME must be twice the size of a conventional diesel tank due to lower energy density of DME compared to diesel (Semelsberger et al. 2006). The major problem arises due to physical properties of DME, which are significantly different from diesel. The viscosity of DME is 20 times lesser compared to diesel. This leads to higher leakage in fuel pumps and injectors. Improper lubrication due to DME results in premature wear and eventual failure of fuel pumps and injectors (Semelsberger et al. 2006). To resolve this issue, additives are used to increase the lubricity of DME.

(e) **Fuel cells**

Fuel cell is a device, which basically works on energy conversion phenomena and generates electricity and heat by combining a gaseous fuel (hydrogen) and an oxidant gas (oxygen from the air) electrochemically. Water is formed during the process. Fuel cell does not need any recharging unlike a battery and works perfectly as long as fuel is supplied to it. Fuel cell is a thermochemical system, which gives exceptional chemical to electrical energy conversion efficiency. It is virtually a pollution-free system with quieter operation since it does not have any moving parts. Figure 7.6 shows a typical fuel cell. It consists of an electrolyte sandwiched between two electrodes. Hydrogen as a fuel is input through the anode and air from the atmosphere through the cathode. Hydrogen, in the presence of a catalyst, splits into protons (hydrogen ions) and electrons, which follow different routes and move toward cathode. The proton passes through the electrolyte, and the electrons create

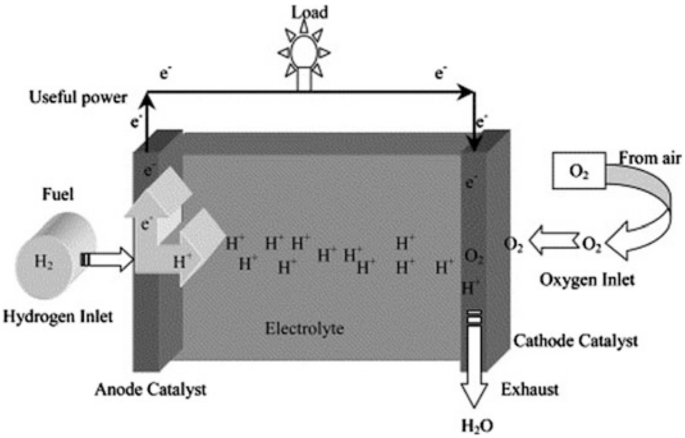


Fig. 7.6 Configuration of a typical fuel cell (Stambouli and Traversa 2002)

a separate current that can be used in some applications before reaching the cathode, to be reunited with the proton and oxygen to form pure water molecule and heat (Stambouli and Traversa 2002).

Fuel cells are classified based on the nature of electrolyte used. Table 7.2 shows different kinds of fuel-cell technologies available today.

Fuel cell is a good energy source compared to fossil fuels due to following reasons (Stambouli and Traversa 2002).

(1) Reliable in nature.
(2) Low operating cost.
(3) Constant power production.
(4) Virtually no emissions.
(5) Choice of fuel.
(6) High efficiency.
(7) Quite operation.

Fuel cells use oxygen and hydrogen to produce electricity. Due to the problem of storage and distribution with hydrogen, other fuels such as hydrocarbon fuels or alcohols are employed.

Table 7.2 Types of fuel cells (Stambouli and Traversa 2002)

Type	Electrolyte	Operating temperature (°C)	Fuel
Alkaline (AFC)	Potassium hydroxide (KOH)	50–200	Pure hydrogen or hydrazine
Direct methanol (DMFC)	Polymer	60–200	Liquid methanol
Phosphoric acid (PAFC)	Phosphoric acid	160–210	Hydrogen from hydrocarbons and alcohol
Sulfuric acid (SAFC)	Sulfuric acid	80–90	Alcohol or impure hydrogen
Proton-exchange membrane (PEMFC)	Polymer, proton-exchange membrane	50–80	Less pure hydrogen from hydrocarbons or methanol
Molten carbonate (MCFC)	Molten salt such as nitrate, sulfate, carbonates	630–650	Hydrogen, carbon monoxide, natural gas, propane, marine diesel
Solid oxide (SOFC)	Stabilized zirconia and doped perovskite	600–1000	Natural gas or propane
Solid polymer (SPFC)	Solid sulfonated polystyrene	90	Hydrogen

7.3 Alcohols as a Fuel for IC Engines

Among all alternative fuels discussed in the earlier section, alcohols are preferred alternatives for IC engines. Important advantages and disadvantages of using alcohols as alternative fuels are given below (Rajput 2008):

Advantages of using alcohols as a fuel

- Alcohols have higher octane rating. Thus, they work very well in gasoline engines.
- Alcohols can be produced from several natural resources that can be cultivated.
- Alcohols generate overall lower emissions compared to other alternate fuels.
- Alcohols have lesser sulfur content.
- Alcohol combustion produces higher number of moles of exhaust gas. This generates higher pressure and consequently more power during the expansion stroke.
- Alcohols are generally less toxic compared to gasoline and diesel.

Disadvantages of using alcohols as a fuel

- In general, alcohols exhibit inferior ignition characteristics in diesel engines on account of their lower cetane rating relative to diesel.
- Their usage may lead to serious problems such as vapor lock in the fuel delivery system. This has serious consequence, particularly for aerospace applications.
- They have low vapor pressure; thus, their lower evaporation makes it difficult to start the engine during cold conditions.
- They are needed in larger volume and mass to produce the same amount of energy relative to gasoline/diesel because of their lower calorific value.
- Alcohols emit more aldehydes compared to gasoline/diesel.
- Due to higher moisture content in the engine exhaust, alcohols exhibit higher corrosive effects on copper, brass, aluminum, rubber, and plastic components compared to gasoline/diesel.
- Alcohols have almost invisible flames; hence, they need to be used carefully.
- Headache and dizziness can occur, if alcohol vapors are inhaled.

Theoretically, complete combustion of alcohols produces just carbon dioxide and water. However in reality, their oxidation in engines remains incomplete. Thus, many by-products such as carbon monoxide, aldehydes, carboxylates, and ketones are also produced. These by-products are toxic in nature and need special attention for control (Minteer 2006). Use of alcohols in unmodified gasoline engines is rather effortless compared to diesel engines. This is due to limitations possessed by alcohols such as (a) low cetane number of alcohols compared to diesel, which leads to improper combustion, when used in appreciable quantity and (b) miscibility challenges while mixing alcohols with diesel. Alcohols have somewhat different chemical and physical properties compared to petroleum fuels. Thus, using them may require modifications to the engine design. Alcohols can be used as a fuel in four different ways (Can et al. 2004; Agarwal 2007):

(a) **Mixing of alcohols and diesel prior to injection into the diesel engine.**

The separation of alcohols with diesel results in improper vaporization, atomization, and combustion characteristics. This method involves mixing of alcohols with diesel using some external means before introducing it into the engine cylinder. In most cases, a mechanical stirrer is fitted into the fuel tank to make fuel mixture stable.

(b) **Alcohol fumigation**

Alcohol fumigation is the injection of alcohol into the intake air upstream of the manifold either by spraying, carbureting, or injecting. As alcohol is premixed with the air in the intake manifold, it improves air utilization. Fumigation process requires minor modifications to the engine by the addition of low-pressure fuel injector, separate fuel tank, fuel lines, and controls (Imran et al. 2013). This results in better engine efficiency using fumigation method.

(c) **Alcohol–diesel blending using emulsion or additives**

Some additives are required to prevent phase separation between alcohol and diesel blends and maintaining properties such as cetane number, lubricity in a permissible limit for self-ignition of fuel in the engine cylinder. It does not allow a large percentage of alcohol for blending and to be used in engine operation.

(d) **Dual fuel injection**

In dual fuel injection method, separate fuel injection systems for diesel and alcohols are incorporated in the engine. In this system, diesel droplets ignite first, followed by alcohol vapors. This results in higher rate of heat release, due to which thermal efficiency of engine increases.

The description of primary alcohols (methanol, ethanol, propanol, and butanol) along with some case studies is discussed in the following subsections.

Methanol

Methanol (methyl alcohol or wood alcohol) is the simplest of all alcohols and has been proposed as a future biofuel. Its chemical formula is CH_3OH. Methanol can be produced from wood, coal, natural gas, crude oil, biomass, or organic waste. It is colorless, toxic, and corrosive to the rubbers in fuel delivery lines and gaskets. Methanol has a melting point of −98 °C and a boiling point of 65 °C. It does not contain any sulfur or complex organic compounds. Methanol can be naturally produced through anaerobic metabolism. It can also be produced by catalytic reaction of synthesis gas. This is produced from natural gas or from organic materials such as biomass (Minteer 2006). Large quantities of methanol may be produced by reforming the natural gas. In this process, hydrogen and carbon monoxide are passed over a suitable catalyst at an appropriate pressure and temperature (Warring 1993). Methanol is similar in behavior to petroleum-based fuels and can be stored and transported using protocols similar to those needed for shipment of petroleum products. Methanol possesses excellent anti-knock characteristics. Hence, it is very suitable for SI engines. It can also be used in CI engines. It emits lesser amount of polluting gases compared to gasoline and diesel. However, care must be taken while using methanol, since it produces invisible flames, which might cause explosion in the tank. Since many years, methanol has been used in racing cars as a fuel but nowadays, possibility has been explored to use it for commercial vehicles too. It is also environmentally hazardous in case of accidental spill since it is completely miscible with water.

Sayin et al. (2009) investigated performance and emission characteristics of methanol blends using a direct injection diesel engine. It was reported that brake-specific fuel consumption (BSFC) increased due to lower calorific value of methanol relative to diesel. However, brake thermal efficiency (BTE) decreased due to higher rate of increase in fuel consumption compared to rate of reduction in lower calorific value. Emissions levels of brake-specific carbon monoxide (BSCO) and smoke opacity decreased due to superior combustion in the presence of oxygen. However, brake-specific hydrocarbon (BSHC) emissions decreased due to reduced ignition delay, while advancing injection timing.

Ciniviz (2011) investigated performance and emission parameters in a four-cylinder turbocharged direct injection diesel engine fueled on methanol blends. In this study, BSFC increased due to lower calorific value of methanol and BTE decreased due to higher rate of increase in fuel consumption compared to rate of reduction in lower calorific value. CO emissions decreased due to improvement in combustion process in the presence of oxygen and also due to turbocharging. Oxides of nitrogen (NO_x) increased due to combined effect of in-cylinder temperature, oxygen concentration, and residence time of the gases. HC emissions decreased due to improved combustion process at relatively higher combustion temperatures in the presence of oxygen.

In another study, Mishra et al. (2013) investigated performance and emission characteristics of methanol blends using a direct injection diesel engine. They reported that BTE decreased due to the presence of oxygenated fuel, lesser calorific value, and lesser cetane number. The latent heat factor increased the ignition delay and made combustion erratic. HC emissions increased due to polar nature of methanol molecules relative to nonpolar nature of lubricating oil. NO_x emissions increased due to higher in-cylinder pressures and temperatures. Smoke opacity decreased due to improved atomization, thereby improving combustion.

Datta et al. (2014) investigated performance and emission characteristics using numerical simulations in a direct injection diesel engine. They reported that BSFC and BSEC increased due to lower energy content of methanol. Also, BTE increased marginally due to superior combustion of blended fuels in the fuel-rich zone. This led to enhanced combustion efficiency and reduction in in-cylinder heat loss due to reduced flame temperature. Smoke opacity, NO_x, CO_2, and PM emissions reduced for diesohols. This was attributed to oxidation of soot nuclei in fuel-rich zones, which in turn improved the combustion.

Ethanol

Ethanol or ethyl alcohol has the chemical formula C_2H_5OH. It is a colorless liquid with a melting point of −144 °C and a boiling point of 78 °C. It can be produced from corn, sugar, barley, grass, fruits, sugar beet, sugarcane, or even cellulose. Ethanol can be produced from a wide variety of plants and thus has potential capability to be used as alternative fuel. Although production of ethanol is costly even then, it has often been called as the "fuel of the future" because of the following reasons (Minteer 2006):

- It can be produced from agriculture-based renewable resources.
- It is significantly less toxic and corrosive compared to other alcohols.
- Its incomplete oxidation produces lesser amount of toxic by-products compared to other alcohols.

Further, a switchover to ethanol would require very large tracts of agricultural land to be used only for alcohol production. This switchover has significant implication in terms of global food security, soil degradation, and water scarcity. Compared to methanol, ethanol is less corrosive and non-toxic but produces toxic exhaust gases.

Ethanol is frequently used as an additive to fuels in many countries. Average addition of ethanol in fuel is roughly 5.4% worldwide (by volume), but some countries are using even 25% or even 100% in automotive engines. Worldwide the largest producers of ethanol are the USA and Brazil (http://biofuel.org.uk/bioalcohols.html). E85 is a fuel blend made up of 85% ethanol and 15% gasoline by volume. This blend is widely used in countries like Sweden and the USA since many years ago, and gaining attention around the world where corn is a major crop, mainly Midwest. To run the E85 blend, engines need some hardware modifications.

Gnanamoorthi and Devaradjane (2013) investigated combustion, engine performance, and emission characteristics of a direct injection diesel engine fueled on ethanol blends. They reported increase in heat release rate (HRR) due to lower cetane number of fuels, thereby enhancing ignition delay. BTE increased due to low overall energy input to the engine to produce constant power output. Exhaust gas temperature (EGT) decreased due to evaporations of ethanol and subsequent cooling. NO_x emissions decreased due to cooling behavior of ethanol, which tends to lower down overall in-cylinder temperature. No significant difference in CO and HC emissions is seen till ethanol content approaches 30%. However, CO and HC emissions increase significantly for blends with ethanol content exceeding 30%.

Putrasari et al. (2013) investigated performance and emission characteristics of ethanol blends in a two-cylinder, direct injection stationary diesel engine. They reported an increase in BSFC due to increase in fuel consumption for producing equivalent power compared to diesel. BTE increased and decreased at lower and higher engine loads, respectively, due to interplay of fuel consumption rate and calorific value. CO, HC emissions, and smoke opacity decreased due to the presence of oxygen, which increases oxygen/fuel ratio, hence improving combustion of fuel.

Labeckas et al. (2014) investigated combustion, performance, and emission characteristics of ethanol blends in a four-cylinder direct injection diesel engine. They reported an increase in peak in-cylinder pressure due to longer ignition delay compared to diesel. BSFC increased due to lower calorific value of ethanol. NO_x emissions decreased due to lowering of in-cylinder temperature. HC emissions decreased due to complete combustion of fuel in the presence of higher oxygen quantity.

In another study, Singh and Agarwal (2016) investigated combustion, performance, and emission characteristics of ethanol blends in a homogeneous charge compression ignition (HCCI) engine. They reported increased peak cylinder pressure and rate of pressure rise due to lower cetane number of diesohols compared to diesel. At lower loads, EGT was almost equal for both fuels due to lower reactivity of leaner charge. At higher loads, EGT decreased due to evaporation of moisture traces present in diesohol, which had a cooling effect. Indicated thermal efficiency decreased due to dominating effect of moisture traces present in diesohol, which affect the reaction rates. Indicated specific fuel consumption was minimum at medium loads due to relatively higher increase in power output compared to increase in fuel consumption. At higher loads, indicated specific carbon monoxide was almost equal for both fuels; however, diesohol showed relatively higher indicated specific carbon monoxides (ISCO) at lower engine loads. It was due to reduced reactivity of alcohol in case of diesohol that the power output was lower which resulted in higher ISCO. Moisture traces in diesohol absorbed some combustion-generated heat, which resulted in relatively lower peak in-cylinder temperature, and decreased oxidation of CO into CO_2. NO_x formation decreased due to lower peak in-cylinder temperature in HCCI engine. Smoke opacity decreased due to relatively higher volatility of these diesohol compared to diesel.

Propanol

The chemical formula of propanol is C_3H_7OH. Production of propanol is difficult and much more expensive compared to other alcohols. Although there is a little energy gain compared to methanol and ethanol, current technology for large-scale production of propanol is not feasible. In automotive sector, 2-propanol is used due to its drying property, which helps in preventing freezing of gasoline (http://biofuel.org.uk/bioalcohols.html). Although propanol has higher calorific value and cetane number compared to methanol and ethanol, researchers have shown less interest in it. This is because of its more exotic production methods, which are costlier and complex.

Atmanli (2016) investigated performance and emission characteristics of propanol blend in a four-cylinder, IDI diesel engine generator. He reported an increase in BSFC due to lesser heat content and higher latent heat of vaporization compared to diesel. BTE decreased compared to diesel due to an inverse relationship between BTE and BSFC. HC emissions of propanol blend increased due to higher density and viscosity of diesel, which created fuel-rich regions inside the cylinder. CO emission also increased for propanol blend compared to diesel due to lack of oxygen or rich air/fuel ratios. NO_x emissions decreased due to lower in-cylinder temperature compared to diesel.

Butanol

The chemical formula of butanol is C_4H_9OH. The properties of butanol are quite closer to gasoline compared to methanol/ethanol. It has four carbon atoms in its molecular structure and thus has four possible butanol structures. It is a colorless and refractive liquid. It has a melting point of −89 °C and a boiling point of 118 °C. It is often used as a solvent. It is also a good choice as an alternative fuel. Earlier, butanol was produced by fermentation of agricultural products. The process was named as "ABE method" since it yielded acetone, butanol, and ethanol. Currently, butanol is usually produced from petroleum feedstocks (Minteer 2006). Butanol is less toxic and less volatile compared to methanol.

Rakopoulos et al. (2010) investigated performance and emission characteristics of a high-speed direct injection diesel engine using n-butanol blends. They reported an increase in BSFC and BTE due to lower calorific value of n-butanol blends compared to diesel. Also, EGT reduced for n-butanol blends compared to diesel. This was attributed to high latent heat of vaporization of n-butanol. Emissions of smoke, CO, and NO_x reduced, while those for HC increased for n-butanol blends compared to diesel.

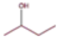
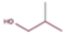
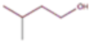
Yao et al. (2010) studied performance and emission characteristics of a turbocharged intercooled heavy-duty direct injection diesel engine using n-butanol blends. They reported an increase in BSFC for n-butanol blends and attributed this to lower calorific value of n-butanol blends compared to diesel. Reduction in soot and CO emission levels were also reported for n-butanol blends. Such a reduction was attributed to relatively longer injection duration compared to diesel.

Doğan (2011) investigated engine performance and emission characteristics using a small high-speed diesel engine run on n-butanol blends. He reported an increase in BTE and BSFC for these blends compared to diesel. He attributed this to lesser calorific value of n-butanol and presence of inherent oxygen in fuel. EGT was also reportedly lower for n-butanol blends than diesel due to blend's lower calorific value, presence of inherent oxygen content in it, and its higher latent heat of vaporization. Similar to previous work, he also reported a reduction in the smoke opacity, CO, and NO_x but an increase in HC emissions for n-butanol blends.

Siwale et al. (2013) investigated combustion and emission characteristics of n-butanol blends using a turbocharged compression ignition engine. They reported minor changes in peak in-cylinder pressure for n-butanol blends vis-à-vis diesel. They also observed an increase in heat release rate for n-butanol blends relative to diesel and attributed it to longer ignition delay. They also reported an increase in NO_x, CO, and HC emissions but lower soot emissions for n-butanol blends.

The requirement for any fuel to be used in gasoline and diesel engines is guided by ASTM D4814 and ASTM D975, respectively. Some important chemical and physical properties of popular fuels such as alcohols, diesel, and gasoline are presented in Table 7.3 (Sarathy et al. 2014). It is seen from this table that increasing molecular weight of alcohols corresponds to reduction in their oxygen content.

Table 7.3 Properties of alcohols, gasoline, and diesel (Sarathy et al. 2014)

Fuel	Structure	Molecular weight	Oxygen content (%w/w)	LHV (MJ/l)	Stoichiometric air/fuel ratio	Boiling point (°C)	Specific gravity at 20 °C	Solubility in water (25 °C) % wt
Methanol		32.04	50	15.8	6.46	64.7	0.792	Miscible
Ethanol		46.06	35	21.4	8.98	78	0.794	Miscible
n-Propanol		60.09	27	24.7	10.33	97	0.804	Miscible
Iso-Propanol		60.09	27	24.1	10.33	83	0.789	Miscible
n-Butanol		74.11	22	26.9	11.17	118	0.81	7.4
2-Butanol		74.11	22	26.7	11.17	99	0.808	18.1
Iso-Butanol		74.11	22	26.6	11.17	108	0.802	8.1
tert-Butanol		74.11	22	25.7	11.17	83	0.789	Miscible
n-Pentanol		88.14	18	28.5	11.74	138	0.816	2.2
3-Methyl-l-Butanol		88.14	18	27.8	11.74	130	0.8	2.7
n-Hexanol		102.16	16	29.3	12.15	157	0.814	0.6
n-Heptanol		116.19	14	30.1	12.47	175	0.822	0.2
n-Octanol		130.21	12	31.1	12.71	195	0.826	0.05
Gasoline	Average C_8H_{15}	111.19	0	30–33	14.58	27–225	0.72-0.78	Negligible
Diesel	Average $C_{14}H_{30}$	198.4	0	35.66	14.95	125–400	0.81-0.89	Negligible

Thus, the calorific value of alcohols increases with increasing molecular weight. It is also noted that alcohols have lower calorific value compared to gasoline and diesel. Alcohols containing four or more carbons have calorific values closer to gasoline, and these fuels improve fuel economy (Gautam and Martin 2000).

The hydroxyl group present in alcohols is responsible for their liquid state at room temperature, thus making them easier to transport. However, lighter alcohols (methanol and ethanol) possess relatively lower boiling points, which depress front-end distillation, when these alcohols are mixed with gasoline or diesel. Changing the distillation curves impacts fuel spray formation, fuel droplet vaporization, and mixture stratification in the engine combustion chamber. These factors play an important role in the design of modern low temperature combustion (LTC) engines (Saxena and Bedoya 2013; Yao et al. 2009).

Lower heating value (LHV) is lesser in case of alcohols compared to gasoline and diesel. Specifically, LHV for alcohols increases with increasing molecular weight. LHV for methanol, ethanol, iso-propanol, and iso-butanol are 15.8, 21.4, 24.1, and 26.6 MJ/l, respectively. In contrast, LHV for diesel is 35.66 MJ/l. Alcohols have higher latent heat of vaporization compared to gasoline and diesel. A higher latent heat of vaporization for alcohols can lead to problem in cold-starting of the engine. Higher latent heat of vaporization of alcohols can also affect thermal stratification in the cylinder, which is important for high in-cylinder pressure rise (Saxena and Bedoya 2013; Yao et al. 2009).

Alcohols are polar compounds as their molecule has a hydroxyl group. Lower alcohols such as methanol, ethanol, and propanol have relatively shorter hydrocarbon chains and thus exhibit higher polarity. Their strong polarity makes them highly soluble in water. Their polarity also makes them less suitable for fuel blending, if the content of petroleum-based fuel is significant. Their affinity with water also makes them more prone to moisture contamination. For these reasons, developing large-scale distribution network for such fuels is challenging. In contrast, higher alcohols have lower polarity compared to lower alcohols. This is why higher alcohols are easier to blend with nonpolar hydrocarbon fuels and they also exhibit lower affinity toward water (Gautam and Martin 2000).

7.4 Future of Alcohols as Fuel

Meeting the demand of various fuels to fulfill growing energy needs is a challenging task because of population growth and industrialization. Today, energy is a basic necessity of mankind and modern civilization. To meet current energy demand, we are largely depending upon non-renewable energy resources such as coal and petroleum products. According to one of the reports, natural gas and oil may last for another 50 years. Once these oil and gas reserves shrink, the demand of coal will drastically increase which will get exhausted in another 500 years, leaving us with much bigger environmental problems to deal with. So to look for alternative energy source is a necessity now, which should be renewable in nature. Toward this goal, alcohols can play a vital role in replacing fossil fuels, especially in IC engines for transport sector.

The most clean alternative renewable energy resources are solar and wind. The technologies to manage and use these energy sources are at initial stages and will take more time due various constraints. Hence, a major hope as an alternate fuel is ‘alcohols’, because they can be synthesized by both chemical and biological means.

Since last few decades, a lot of research is going on usage of alcohols in vehicles. Model-T engines were one of the earliest IC engines. These were designed to run on either alcohol or gas. With some technical modifications to the existing engines, one can use alcohols as fuel for the production of power. Production of ethanol around the world is reported to be nearly 85 billion liters, to which US and Brazil contribute about 87%. In Brazil, over two billion cars have been modified to run on ethanol blends (http://ezinearticles.com/?Alcohol—An-Alternative-Fuel-For-the-Future&id=1815138; https://www.linkedin.com/pulse/20140628112411-68252428-alcohol-ethanol-future-fuel-of-the-world). These cars have flexi-fuel engines, which can use ethanol–petrol blend at any ratio. US Government have directed the use of 10% or 85% ethanol as fuels in different states. Other countries, which have taken serious initiatives in this direction, are Germany, France, Sweden, Spain, China, Canada, India, Australia, Thailand, etc. It will not be too far for other countries to switch to alcohols for their transport sector, which will not only reduce their dependence on imported natural oil and oil but it will reduce air pollution locally and globally as well.

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Chapter 8
Different Feedstocks and Processes for Production of Methanol and DME as Alternate Transport Fuels

Piyali Das and Anubhuti Bhatnagar

Abstract Methanol and DME are emerging as greener substitute of gasoline and diesel, respectively, due to soot-free combustion and low NOx emissions with high EGR of these fuels. Focused research efforts are thus needed not only for developing technologies but also on defining complete value chain to establish sustainable production routes. Majority of the present methanol and DME production processes utilize coal and natural gas as the feedstock, whereas other feedstocks are not found techno-economically viable for commercial plants. Thus, there is a significant research gap and scope of innovation to make these fuels particularly from alternate resources like biomass, bio-oil, and carbon dioxide. This chapter delineates pervasiveness and potential of methanol and DME in the world as fuel, the chemistry, and the sustainability of different pathways for their production from each of the possible feedstock like coal, petcoke, natural gas, biomass, and carbon dioxide.

Keywords DME · Methanol · Alternate fuels · Transport fuels

8.1 Introduction

According to the International Energy Outlook 2016, energy consumption in the transportation sector is likely to increase at an annual average rate of 1.4%, from 110 EJ (exa joules) in 2012 to 163.5 EJ in 2040 (business-as-usual scenario). While in 2012, OECD held more than 50% share in the total transportation energy consumption, and by 2040, the non-OECD nations are expected to account for 61% of global transportation energy consumption. It is envisioned that fossil fuels are most

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likely to remain the dominant source of energy, although their share of total energy consumed is likely to decline in 2040 compared to the 2012 level (World Energy Council 2011; U.S. Energy Information Administration 2016).

However, globally, transport sector-related CO_2 emissions are found to be 14.5% of the total CO_2 emissions (International Transport Forum 2010) and with likely escalation in fuel consumption in transport sector, these emissions would invariably increase. Indeed, since the oil crisis of 1970s, there has been volatility in the nature of crude availability and cost, and the unexpected decline in crude prices in 2014 should be considered as an opportunity to reduce fossil fuel subsidies, introduce carbon pricing, and bring alternate fuels at a level playing field with the conventional fuel sector (World Energy Outlook 2015).

Since the reach of present technology in vehicles—internal combustion or direct ignition engines, implies that liquid fuels are going to continue to be indispensable for vehicular transport due to their energy density, more technologies for renewable-based liquid fuels need to unfold (U.S. Energy Information Administration 2016; Dinjus and Dahmen 2010).

An idea that is gaining a foothold in the conversation on alternate cleaner fuels is that of a methanol economy which suggests a future wherein methanol will replace liquid fuels for transportation (Olah 2005). The carbon emissions from methanol used in combustion engine are found to be 15–20% lesser than those from gasoline (Methanol Institute 2011) leading to lower emissions of NOx and volatile organic compounds which are responsible for ground-level ozone or "smog." Dimethyl ether on the other hand is obtained from methanol through dehydration and used as a gaseous fuel to substitute diesel. The absence of a C–C bond in DME ensures a substantial reduction in soot, whereas oxygen content leads to low particulate matter (PM) emission, thus reducing overall pollutants and toxicity (Chen et al. 2012).

These advanced transport fuels can be derived from greenhouse gases like carbon dioxide through hydrogenation (Huang and Tan 2014), natural gas reforming (Lunsford 2000), and thermochemical conversion (e.g., gasification, pyrolysis, or liquefaction) of coal, petcoke, biomass, etc. (Lv et al. 2009; Shui et al. 2010; Dahmen et al. 2012a; Khosravi and Khadse 2013; Murthy et al. 2014).

8.2 DME and Methanol as Fuels

Methanol is liquid at room temperature, while DME is a gas. A comparison of properties of diesel, gasoline, methanol, and DME is given in Table 8.1.

It is evident from Table 8.1 that despite a lower heating value, the high octane rating ($\sim$100) of methanol makes it a suitable additive/substitute for gasoline in internal combustion (IC) engines because of higher compression ratio achievable which results in a better energy use and lower emissions from the exhaust. It has also been found useful in diesel engines as an additive called M10 (Lee et al. 2010). On the other hand, fuel characteristics of DME are comparable to diesel. Although

Table 8.1 Comparison of methanol, gasoline, DME, and diesel (Methanol Institute; Shell 2014a; b; BioEnergy 2007)

	Methanol	Gasoline	DME	Diesel fuel
Formula	CH_3OH	C_{9-12}	CH_3OCH_3	C_{10-26}
Oxygen content	50%	0	35%	0
Boiling point (°C)	64.7	38–204	−24.9	180–360
Vapor pressure at 20 °C (MPa)	0.013	–	0.51	–
Liquid density at 20 °C (kg/m^3)	792	719	668	840–890
Heating value (MJ/kg)	22.88	47.99	28.78	42.47
Octane number	112	84–93	–	–
Cetane number	–	–	55–60	40–55
Auto-ignition temperature (°C)	257	480	235	200–300

it is a gas at ambient temperature and pressure, it can be easily being liquefied, stored, and transported due to its low vapor pressure (0.6 MPa at 25 °C). Its cetane rating makes it a suitable alternate for diesel.

Life-cycle analysis (LCA) conducted by Sweden Petroleum Institute suggests that emission of hydrocarbons, particulates, and CO_2 over the life cycle of DME is 21, 3.3, and 6700 mg/MJ fuel consumption, respectively, whereas for diesel in light-duty vehicles, it is 54, 26, and 7500 mg/MJ, respectively, although NOx emissions from DME (325 mg/MJ) marginally exceed the value for diesel (281 mg/MJ) in LDVs (Song et al. 2009).

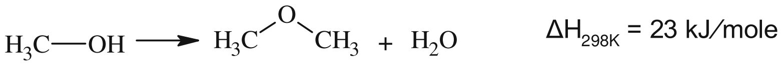
8.3 Current Scale of Production and Utilization of Methanol and DME

Worldwide, over 90 methanol plants have a combined production capacity of about 110 MT at present, rising from 75 MT in 2011. This is due an increase in global methanol demand for emerging energy applications accounting for 40% of methanol consumption. China's share in global methanol demand has risen from 12% in 2000 to 54% in 2015 (Alvarado 2016). The world's largest supplier, Methanex, reported that the worldwide demand of methanol is likely to increase at a cumulative aggregate growth rate (CAGR) of 7% over the next four years (Methanex 2016). This is due to rising demand of light olefin production for direct blending with gasoline along with the traditional demand for methanol derivatives, such as formaldehyde and acetic acid.

The global DME production was reported as 3740.46 kT in 2014. By 2024, conventional DME share is projected to rise at 8% CAGR, while for bio-based DME, it is 11% (Methanol Institute 2016; Research and Markets 2015). Table 8.3 shows the current operational commercial plants for DME production. Oberon Fuels in the USA has the maximum production capacity at present, but China, Korea, and Europe are increasing their capacity for DME production at a quick pace. Bio DME project, concluded in 2013, in Sweden entailed development of a black liquor gasification route for synthesis of DME. Based on the success of these projects, China is likely to attain a Bio DME production capacity of 20 MT by 2020, while South Korea and EU are aggressively targeting a multifold increase in their respective DME production capacities (Salomonsson 2013).

Among the future precursors identified for methanol and DME synthesis are pyrolytic bio-oil, carbon dioxide, and petcoke along with increased use of conventional sources like coal and natural gas.

DME has been commercially synthesized by methanol dehydration as shown in Eq. 8.1.



$$H_3C{-}OH \longrightarrow H_3C{-}O{-}CH_3 + H_2O \qquad \Delta H_{298K} = 23\ \mathrm{kJ/mole} \tag{8.1}$$

In these processes, the first step is to convert the feedstock into syngas either alone or in combination with each other. Subsequently, in the second step, syngas is converted to methanol/DME. Figure 8.1 indicates the possible pathways of methanol/DME synthesis from different feedstocks. The selection of a particular route to synthesize methanol or DME, however, depends upon the feedstock and the composition of syngas produced in terms of relative ratio of CO, H_2, and CO_2.

Technology developers like Lurgi, E-Gas, Siemens, Shell, and GE have developed commercial gasification technologies for producing syngas. Some of the major commercial gasification-based plants presently operational worldwide for making methanol and FT fuels are given in Table 8.2.

Tables 8.2 and 8.3 show the major units worldwide involved in production of methanol and DME. From Table 8.2, it is evident that majority of the methanol plants are operating with coal or natural gas as the single feedstock. There is a

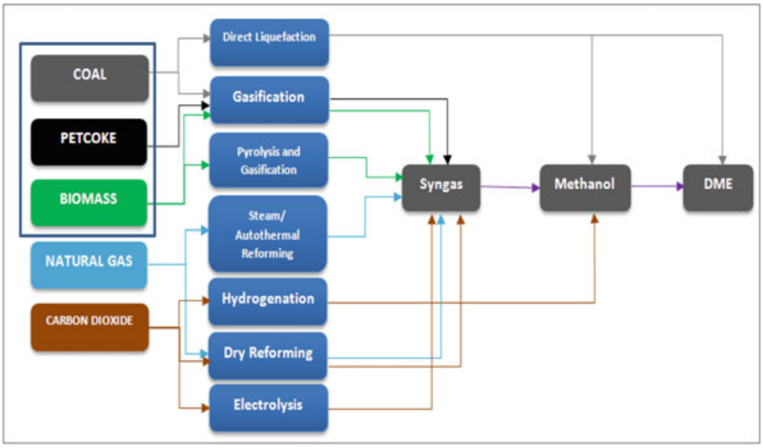


Fig. 8.1 Possible routes to produce methanol and dimethyl ether (DME)

Table 8.2 Commercial methanol plants in operation (National Energy Technology Laboratory 2014)

S. No.	Gasification plant/owner	Location	Gasification technology provider	MW_{th} SG output	Feed/product
1	Sasol Synfuels West	South Africa	Lurgi FBDB	7048	Sub-bituminous coal/FT liquids
2	Sasol Synfuels East	South Africa	Lurgi FBDB	7 048	Sub-bituminous coal/FT liquids
3	Datang Duolun MTP Plant	China	Shell	3 373	Lignite/methanol
4	Shenhua Ningxia Coal to Polypropylene II	China	SEDIN	2500	Coal/methanol-PP
5	Shenhua Ningxia Coal to Polypropylene I	China	Siemens	1912	Coal/methanol-PP
6	Shenhua Baotou Coal-to-Olefins Plant	China	GE	1750	Coal/methanol-olefins
7	Rongxin Inner Mongolia Methanol Plant	China	ECUST	1400	Coal/methanol
8	Sanwei Neimenggu Methanol Plant	China	GE	1167	Coal/methanol
9	Yunnan Methanol & DME Plant	China	BGL	1120	Coal/methanol
10	Bintulu GTL Plant	Malaysia	Shell	1032	Natural gas/FT liquids
11	Leuna Methanol Plant	Germany	Shell	984	Vis-breaker residue/methanol

Table 8.3 Commercial operational plants for DME production

S. No.	DME producer	Location	Production capacity (metric ton/annum)	Reference
1	Akzo Nobel Industrial Chemicals	Rotterdam, The Netherlands	45,000	AkzoNobel Industrial Chemicals (2017)
2	China Energy	Linyi, Nansha and Zhangjiagang cities, China	900,000	China Energy (2017)
3	Aestar (Zhongshan) Co. Ltd.	Guangzhou, China	10,000	Aestar (Zhongshan) Co. Ltd. (2009)
4	Toyo Engineering Corporation	Niigata, Japan (Plants located in China)	460,000	(Toyo Engineering Corporation)
5	Fuel DME Production Co. Ltd.: (Mitsubishi Gas Chemical, ITOCHU, JAPEX, Taiyo Oil, Total Di-Methyl Japan, Toyota Tsusho, JGC, Mitsubishi Heavy Industries and Mitsubishi Chemical)	Niigata, Japan	80,000	Japan DME Association (2017)
6	Grillo-Werke AG	Duisburg, Germany	1,000,000	Grillo Werke (2012)
7	Korea Gas Corporation	Incheon, Korea	300,000	Unitel Technologies (2011)
8	Oberon Fuels	San Diego, USA	DME: 3,650,000 Bio DME: 3,650,000 Partial Bio DME: 3,650,000	Oberon Fuels (2016)

significant research gap particularly for decentralized small- to medium-scale plants for producing methanol from alternate feedstocks such as biomass or cofeedstock.

Table 8.3 indicates that the global DME production is currently concentrated in Asia. Among other notable DME producers are Xinao Group Co. Ltd., China; Arrtu Mega Energie, Indonesia; Zagros Petrochem, Iran; Royal Dutch Shell PLC, the Netherlands; and the Chemours Group, USA. However, major new capacity additions are planned or under construction in Trinidad and Tobago, North America, Indonesia, India, and Uzbekistan (Research and Markets 2015).

Technological routes of production of methanol and DME from each of the possible feedstock coal, petcoke, carbon dioxide, and biomass are discussed in detail in the following subsections. Section 8.4 deals with conversion of feedstock to syngas, while Sect. 8.5 deals with downstream conversion of syngas to methanol and DME.

8.4 Use of Different Feedstocks for Production of Syngas

8.4.1 Coal

Direct coal liquefaction (DCL) and indirect coal liquefaction (ICL) are the two prominent processes for coal-to-methanol conversion. DCL primarily involves thermal breaking of the polymeric coal structure at elevated temperatures with subsequent hydrogenation of the fragments to generate lighter molecules. The product can be used directly in static fuel application, whereas it needs to be catalytically upgraded for application as a transport fuel. Indirect coal liquefaction, on the other hand, converts coal to syngas followed by conversion of syngas to various target compounds such as FT liquids, methanol, DME.

High-rank coals are poor candidates for liquefaction because of limited reactivity, but since their share in total coal produced worldwide is low, it is not considered for gasification. Coal properties that generally affect the gasification process are its elemental composition, surface characteristics, reactivity, and mineral content (Hoover 1983; van Heek and Muhlen 1987). High ash coal is reported to be misfit for DCL. However, with the improvement introduced in the gasification technology, there has been an interest in utilization of this coal (Jha 2016; Business Standard 2016).

8.4.1.1 Direct Coal Liquefaction (DCL)

In DCL, coal, dissolved in a solvent at around 400 °C and 27.5 MPa, is catalytically cracked in the presence of H_2. This process has a thermal efficiency of around 60–70% (Boroujeni 2008). The exact mechanism of conversion is unknown, but temperature is a vital criterion for the free radical reaction mechanism to proceed

(Shui et al. 2010). High pressure is required in DCL process to ensure solvents and products remain in liquid phase, and this prevents coal buildup in the reactor and coking of the catalyst. With further improvements in this process, the pressure required could be lowered to 20 MPa. The foundation of DCL is through Bergius process as shown in Eq. 8.2.

$$nC + (n+1)H_2 \rightarrow C_nH_{2n+2} \tag{8.2}$$

Presently, direct characterization of coal is carried out using nondestructive techniques like IR, NMR, TEM, XRD, XPS, and XAS. This is useful to establish the relation between products, conditions required for liquefaction, and the original chemical structure of the coal. In a study by Boroujeni (2008), the approximate analytical formula for the coal is designated as $CH_{0.81}O_{0.08}S_{0.02}N_{0.01}$. The stoichiometric amount of oxygen required in this conversion process is calculated as per Eq. 8.3 (Boroujeni 2008).

$$\begin{aligned}
&CH_{0.81} + 0.395H_2 \rightarrow CH_{1.6}\\
&0.02S + 0.02H_2 \rightarrow 0.02H_2S\\
&0.04O_2 + 0.08H_2 \rightarrow 0.08H_2O\\
&0.005N_2 + 0.015H_2 \rightarrow 0.01NH_3\\
&1\,\text{kmol}(14.9\,\text{kg})\text{Coal} + 0.51\,\text{kmol}(1.0\,\text{kg})H_2 \rightarrow 1\,\text{kmol}(13.2\,\text{kg})\text{synthetic crude}
\end{aligned} \tag{8.3}$$

The role of solvent in DCL is multifold. Besides facilitating the heat and mass transfer during the chemical reaction, it also allows hydrogen shuttling from gas phase to coal. These solvents are classified as specific, non-specific, reactive, and degrading solvents. Pyridine and NMP (N-methyl-2-pyrrolidone) are examples of specific solvents and can dissolve 20–40% coal at 200 °C. Alcohol, benzene, ether, and acetone are examples of non-specific solvents which are used to dissolve only trace amount of coal at 100 °C. Solvent such as phenol reacts with coal during liquefaction, and thus, it is called reactive solvent (Shui et al. 2010; Kamiya et al. 1986). Degrading solvents like phenanthridine, anthracene oil in contrary are able to extract more than 90% coal at 400 °C. The DCL solvents have also been categorized into donor and non-donor solvents. Tetralin, tetrahydrofluoranthene, dihydroanthracene, etc., are widely used donor solvents, while decalin, pyrene, anthracene, fluoranthene, etc., are commonly known non-donor solvents. It is reported that non-donor solvents such as anthracene or creosote oil in presence of Mo catalyst result in higher liquefaction efficiency compared to donor solvents such as tetralin. Further, some studies successfully demonstrated the use of water as a cosolvent during DCL due to enhanced dispersion of the catalyst (Shui et al. 2010; Kamiya et al. 1986; Ali et al. 2015). Catalysts have been used to escalate the rates of cracking, hydrogenation, denitrification, desulfurization, and deoxygenation leading to better quality products (Li et al. 2008).

Cracking of DCL-derived products using hydrogen under high pressure and temperature breaks down coal into shorter fractions of alkanes which resemble crude oil (Höök et al. 2013). DCL processes are classified into single-stage and two-stage liquefaction (Vasireddy et al. 2011). In a single-stage DCL process, the solvent facilitates coal extraction and hydrogen cracking in a single reactor. Processes like Shenhua, Kohleoel, NEDOL, Exxon Donor Solvent (EDS), and H-Coal are developed to operate at high temperature of up to 470 °C and high pressure up to 30 MPa yielding 50–60% products (Boroujeni 2008; Comolli et al. 1999; Onozaki et al. 2000; Hirano 2000; Epperly and Taunton 1979). On the other hand, in a two-stage DCL process two reactors are used in series. Initially, coal is dissolved in a solvent for first stage of thermal liquefaction in the presence of catalysts like iron (Cugini et al. 1994) and red mud (Garg and Givens 1985) which operates in the range of 400–440 °C and 15–20 MPa. The residence time is generally around 15 min but may vary for different processes. In the second stage, hydrogen is introduced for catalytic hydrogenation in the presence of catalyst like Ni–Mo/Al_2O_3 to synthesize liquid products at a temperature of 425°–470 °C and pressure up to 20 MPa pressure. The residence time is generally around 100 min but may vary for different processes (Shui et al. 2010; Shinn 1984).

Processes like Lummus ITSL, Pyrosol, Liquid Solvent Extraction (LSE), brown coal liquefaction (BCL), Kerr-Mc-Gee ITSL, Chevron coal liquefaction process (CCLP), consol synthetic fuel (CSF), Mitsubishi Solvolysis, Amoco CC-TSL, and supercritical gas extraction (SGE) are commercial processes developed for two-stage DCL. The oil yield from a two-stage liquefaction process is 60–65% which is more than that from single-stage liquefaction, and the hydrogen consumed in the process is lesser. Mechanically, multistage processes hold an advantage over single-stage processes because of in situ hydrothermal pretreatment and the enhanced hydrogen transfer (Shui et al. 2010; Boroujeni 2008). Table 8.4 lists some of the significant DCL plants operational worldwide for making transport fuel.

It is shown in Table 8.4 that Shenhua Clean Coal Technology Development Company, Ltd. (SCCT) has set up one of the largest plants for direct coal liquefaction (DCL) in the world. The first phase of the facility opened in July 2009 and employed US-developed technology from Headwaters Inc. and Hydrocarbon Technologies Inc. (HTI) in conjunction with technologies from West Virginia University and the US Department of Energy (US DoE). It has conversion efficiency of 93.5% at a temperature of 440–450 °C and pressure of 1.70 MPa (Hydrocarbon-Technology 2016).

Table 8.4 DCL plants operational worldwide (Shui et al. 2010; Tennant 2014)

Country	Plant developer	Production capacity	Products
China	Shenhua Corporation of China	1,080,000 t/a	Diesel oil, LPG, and naphtha
China	Jincheng MTG Plant	300,000 t/a	Methanol
South Africa	Sasol (Pty) Ltd.	3,960,000 (Nm^3/d) syngas	FT liquids
China	Shanxi Lu’an Co. Ltd.	160,000 t/a	FT liquids

8.4.1.2 Indirect Coal Liquefaction

Indirect coal liquefaction (ICL) proceeds through gasification producing syngas as an intermediate. The resulting syngas is subsequently modified to obtain hydrogen and carbon monoxide in a desired ratio through water gas shift (WGS) reaction. This is followed by gas cleanup including desulfurization and removal of impurities. Finally, the syngas is converted to desired fuels/products over catalyst (Höök et al. 2013). In Table 8.5, ICL plants operational globally are listed where Sasol is among the major companies in the field of ICL processes (Boroujeni 2008). Sasol uses both low-temperature Fischer–Tropsch (LTFT) and high-temperature Fischer–Tropsch (HTFT) reactors to convert coal into FT liquids (van der Laan and Beenackers 1999). While LTFT utilized cobalt- or iron-based catalysts at 220–250 °C and 2–3 MPa to produce paraffins and other distillates (C12-19), HTFT reactors use iron-based catalyst at 330–350 °C and 2–3 MPa to produce smaller olefinic compounds (C5-10) which can be used for petrochemicals. Another process developed by ExxonMobil called the MTG or methanol-to-gasoline process produces high-quality gasoline (research octane number: 92.0–92.5, aromatic content: 26.5%, sulfur: 0 ppm) using methanol as an intermediate. This process can utilize syngas from either coal or natural gas (ExxonMobil 2014). The effluents generated in this process are of high quality and do not require significant treatment. This process was first established in early 1970s using ZSM-5 zeolite catalyst. This methanol is then dehydrated to convert to hydrogen and hydrocarbons, with up to 11 carbons. Catalyst and process design are key to high yield and gasoline selectivity. The reactions proceed as shown in Eq. 8.4:

$$\begin{aligned} &2\mathrm{CH_3OH} \rightarrow \mathrm{CH_3OCH_3} + \mathrm{H_2O} \\ &\mathrm{CH_3OH, CH_3OCH_3} \rightarrow \text{Light Olefins} + \mathrm{H_2O} \\ &\text{Light Olefins} \rightarrow \text{C5 + Olefins} \\ &\text{C5 + Olefins} \rightarrow \text{Paraffins, Naphthalenes, Aromatics} \rightarrow \text{Gasoline} \end{aligned} \tag{8.4}$$

Table 8.5 ICL plants operational worldwide (Shui et al. 2010; Boroujeni 2008; Jager 2003; National Energy Technology Laboratory 2003, 2014)

Country	Process/technology/company	Scale/ capacity	Products
South Africa	Sasol, low-temperature Fischer–Tropsch (LTFT)	17,000 bbl./day	LTFT produces paraffin, wax, gasoline, light olefins
South Africa	Sasol, high-temperature Fischer–Tropsch (HTFT)	20,000 bbl./day	HTFT produces lighter products, gasoline, and oxygenated chemicals (*n* = 5–10)
Kingsport, Tennessee, US	LPMEOH (Liquid-phase methanol) process by Air Products and Chemicals Inc. and Eastman Chemical Company	300 TPD	Methanol

One of the many gasifier technologies applicable for this process belongs to Chevron/Texaco. The gasification is carried out using oxygen from the inherent oxygen content of coal along with external air/oxygen from air separation unit. The coal is fed as water-based slurry at pressures of 7.5 MPa. The hydrogen in the slurry enhances the hydrogen in syngas. After the cleaning and removal of contaminants from raw syngas, the gas is cooled. The ratio of H_2 and CO is then adjusted through WGS using Co-Mo catalysts which are also tolerant to sulfur. Additional steam can be introduced in the shift reactor to ensure coking does not take place (Larson and Tingjin 2003).

There are significant differences in the quality of products produced through these two processes (Boroujeni 2008; Williams and Larson 2003). DCL produces a semi-refined crude oil which needs catalytic upgradation prior to its application. The upgraded DCL product is highly aromatic with a lower cetane number (~30) compared to crude-derived diesel (40–55). In comparison, LTFT process yields paraffinic distillates with less than 4% aromatic content and high cetane number (~70). An advantage of DCL process is that it is slightly more efficient (65–70%) than ICL process (55–60%) as it is carried out at about 400 °C and 15–30 MPa allowing for an easier process handling compared to ICL processes which otherwise involves gasification, syngas purification, and liquid fuel production. In ICL process, the gasifier operates at 1400–1600 °C and 4–6 MPa pressure and the synthesis reactors operate at 200–350 °C and 2–3 MPa pressure, making it more energy-intensive. However, overall process efficiency of ICL could be improved through effective heat recovery from gasifier.

8.4.2 Petcoke

Petcoke is a nonvolatile heavy residue obtained from the final catalytic cracking process in a petroleum refining unit. It is classified on the basis of physical structure such as sponge, needle, honeycomb, and shot coke, whose production is dependent on the reaction conditions in the coker unit. Needle coke is the highest quality coke with very low percentage of sulfur. Delayed and fluid are two major types of coking units that involve thermal cracking of the crude oil into products such as naphtha and distillate at atmospheric pressure and 480 °C leaving behind coke as a heavy residue (US Energy Information Administration 2013). Petcoke is one of the richest sources of carbon (~90% carbon) and emits 5–10% more CO_2 per unit of energy produced on combustion compared to coal. However, petcoke is very stable and thus can be easily transported (Murthy et al. 2014).

The global petcoke production capacity is close to 127 MT pa with USA holding a major share in the total petcoke production. The petcoke market is likely to increase at a rate of 3% per annum. It is at present being used by five major industries—refineries, power, cement, steel, and aluminum (Roskill Information Services 2015).

Although petcoke is being conventionally used as fuel in furnaces, increased restriction on SOx emissions from refineries arising due to high sulfur (5–7 wt%) and mineral content such as vanadium ($\sim$500 ppm) in petcoke (Furimsky 1999) is becoming a limiting factor for such applications. This along with shift of crude oil from "sweet crude" to heavier crudes, and the escalating use of delayed coking process, in order to maximize the production of usable refinery products, is likely to ensure a flood of petcoke in the refineries (Schabron et al. 2002; Bridjanian and Samimi 2011). Hence, the efficient conversion of this huge amount of refinery by-product to high-value products is becoming an unavoidable destiny for economic operations of the refineries.

Specifically, gasification is being looked at as an economically viable route for petcoke utilization for power, chemicals, and fuel synthesis through syngas (Schabron et al. 2002; Nemanova et al. 2014; Zhan et al. 2011). The moderate heating value (30.25–34.91 MJ/kg) and low ash content (0.1–0.3 wt%) make it a usable feed for gasification (Murthy et al. 2014). Gray and Tomlinson (2000) claim that hydrogen can be generated from syngas obtained to establish a hydrogen-based economy (Gray and Tomlinson 2000).

Equation 8.5 lists out the generalized reactions take place in the gasifier:

$$\begin{array}{ll}
C_nH_m + 1/2nO_2 \rightarrow 1/2mH_2 + nCO & \\
\text{Partial Oxidation: } C + 1/2O_2 \rightarrow CO & \Delta H_{298K} = -123\,\text{kJ/mol} \\
\text{Steam Treatment: } C + H_2O \rightleftharpoons CO + H_2 & \Delta H_{298K} = 130.96\,\text{kJ/mol} \\
\text{Water Gas Shift: } CO + H_2O \rightleftharpoons H_2 + CO_2 & \Delta H_{298K} = -41\,\text{kJ/mol} \\
\text{Reverse Boudard Reaction: } CO_2 + C \rightleftharpoons 2CO & \Delta H_{298K} = 170.07\,\text{kJ/mol}
\end{array} \tag{8.5}$$

The water gas shift (WGS) reaction allows adjustment of H_2-to-CO ratio. This is followed by reverse Boudouard reaction for comproportionation of carbon dioxide, carbon, and carbon monoxide.

The most prevalent coal gasifiers for commercial use are fixed-bed, fluidized-bed, and entrained flow gasifiers. The fixed-bed technology requires large sized highly reactive coal, and fluidized-bed gasifier requires low ash, reactive coal. Both the systems operate between 550 and 1000 °C. In contrary, petcoke being a low reactive feedstock finds entrained flow gasifiers, operating at higher temperature (>900 °C) than fixed bed and fluidized bed, to be the most appropriate reactor. However, the high-temperature operation necessitates continuous removal of slag and ash from the process.

In view of this, gasification of petcoke is riddled with technological challenges such as reactor design and efficient conversion of feed with high sulfur and mineral contents. There is a severe need to address this challenge with more exhaustive modeling studies involving Computational Fluid Dynamics (CFD).

Petcoke gasification has been explored in various laboratories and pilot-scale studies to evaluate the product and reaction characteristics to obtain maximum benefits from this feed and can be divided in particle characteristics, reaction temperature and pressure, and catalyst loading. These have been briefly discussed in this section.

Petcoke is pelletized and gasified in an early study by Revankar et al. (1987) in the presence and absence of K_2CO_3/Ni with bentonite as a binder (Revankar et al. 1987). The effect of particle size, porosity, and thickness of the reacting pellet is studied. Rate of reaction is found to increase for higher particle size and decrease with increasing thickness. Nguyen and Watkinson (1990) showed that gasification of delayed coke and fluid coke did not take place below 850 °C at atmospheric pressure (Nguyen and Watkinson 1990). However, during a catalytic steam gasification, the operating temperature could be lowered to 750 °C (Wu et al. 2011). Potassium-based catalysts have been studied for improving catalytic gasification because these catalysts effectively promote water-carbon reaction, WGS, methane–steam reforming and provide high selectivity toward CO_2 production leading to high hydrogen production. The proportion of hydrogen in final gas could be as high as 55.5–60.4% (Wu et al. 2011). Combination of $Ca(OH)_2$ and iron species as a catalyst for petcoke gasification have been explored by Wang et al. (2007), to lower the temperature of the reaction to 950 °C from 1050 °C that was required for non-catalytic gasification (Wang et al. 2007).

To eliminate the limitations posed due to petcoke composition, cogasification of petcoke with biomass and coal has been proposed (Nemanova et al. 2014; Fermoso et al. 2010). Nemanova et al. (2014) found that during petcoke/biomass blend gasification using TGA, increasing share of biomass in the blend leads to reduction in activation energy for the process (Nemanova et al. 2014). It fell from 121.5 kJ/mol for pure petcoke to 96.3 kJ/mol in a 1:1 blend. Fermoso et al. explored both coal and petcoke blends and coal–petcoke–biomass blends in fixed-bed gasifier (Fermoso et al. 2010). In this study it is found that for a 1:1 blend of coal and petcoke, an addition of 10wt% biomass improves the syngas quality, but a higher proportion is detrimental for the reaction. Other studies have also reported similar conclusions (Shen et al. 2012; Rodriguez et al. 2007; Schoedel et al. 2015).

On a commercial scale, Air Liquide, GE Energy, Royal Dutch Shell, RWE, Siemens are the major global players in petcoke gasification. In Asia, India is investing in petcoke gasification projects. Reliance Industries, India, completed construction of petcoke-based gasification facility of 20,000 tons per day (TPD) (Mukherjee 2012; National Energy Technology Laboratory). Table 8.6 presents a comparison of coal, petcoke, and biomass as feedstock for gasifiers. It shows that coal that coal has a high C/H ratio (~ 1), whereas petcoke and biomass have low C/H ratios. Moderate amount of volatile matter present in coal and high volatile matter in biomass imply that gasification temperature for these could be medium (900–1000 °C) to low (800–900 °C) unlike for petcoke which requires very high gasification temperature (1400–1500 °C). The ease of availability and utilization makes petcoke an attractive option for alternate fuel synthesis, but the high sulfur content in comparison with coal and biomass requires an in situ sulfur removal or external gas cleanup system to remove sulfur containing compounds from the syngas. While biomass has the highest amount of moisture, the highest amount of ash is present in coal. On the downside, the high moisture and lower carbon content of biomass lead to generation of syngas with lower heating values

Table 8.6 Characteristics of coal, petcoke, biomass (Murthy et al. 2014; Lee et al. 2010; Mondal et al. 2011; Bocci et al. 2014)

S. No.	Parameter	Coal	Petcoke	Biomass (Nut Shell)
Proximate analysis (wt%)				
	Moisture	5.80	6.23	11–14
	Volatile matter	23.8	12.88	74–78
	Fixed carbon	30.4	86.78	20–25
	Ash	40	0.34	1–2
Ultimate analysis (wt%)				
	C	83.32	89.45	48–51
	H	5.95	2.8	6
	N	1.98	0.05	0.2–0.5
	O	7.14	0.01	41–44
	S	1.59	7.48	0.01–0.03
Syngas composition from oxy-gasification (mol%)				
	CO	60.72	47.72	30–37
	H2	28.5	30.33	30–34
	CH4	–	0.01	2–4
	CO2	2.56	17.88	25–29
	N2	8.43	1.27	–
	Others	–	2.6	–
	Heating value (MJ/kg)	11.36	10–16	7–8

and the high ash content of coal creates an issue in the utilization of coal in the gasifier. Biomass for gasifier has been discussed in Sect. 8.4.4 in further detail. In an attempt to promote use of petcoke for fuel applications, US Department of Energy recently made the “first ever offer for a conditional commitment” of loan guarantees under the aegis Advanced Fossil Energy project to Lake Charles Methanol, LLC, for a petcoke-to-methanol facility (Research and Markets 2017). This facility is designed to emit 36% less greenhouse gases than typical methanol facilities (on a life-cycle basis) and will capture 77% of its carbon emissions, with an estimated annual sequestration of 4.2 million metric tons of carbon (Markham 2016).

8.4.3 Natural Gas

Natural gas is a mixture of several small chain gaseous hydrocarbons such as methane, butane, propane with methane having the largest proportion (~70–90%). Small amount of carbon dioxide, nitrogen, and hydrogen sulfide is also found in natural gas. The present global natural gas production is reported to be 3552 bcm, whereas consumption is approximately 3543 bcm (British Petroleum 2017). There is major rise in the production of natural gas in Australia (19 bcm) and Iran (13 bcm) offsetting the marginal decline by 21 bcm in production in North America. At the end of 2016, 186.6 bcm of natural gas reserves were identified in the world. Presently, its major consumption is in the residential and commercial sectors for heating in fertilizer industry and power sector (International Energy Agency 2015).

Semin (2008) highlighted the need for addressing the challenge of rising CO_2/GHG emissions from transport sector by using natural gas a transport fuel (Semin 2008). Compressed natural gas (CNG) or liquefied natural gas (LNG) could "de-carbonize" the transport sector by substituting gasoline/diesel. CNG also has high octane rating and reduced particulate matter, NOx, SOx, and hydrocarbon emission, making it an excellent fuel for light-duty vehicles. In countries like Argentina, Pakistan, India, and Brazil, national policies are favorable towards use of CNG for light-duty vehicles because of reduction achieved in air pollution due to these fuels. However, in majority of Asia-Pacific region, there is a need to use natural gas (both CNG and LNG) for heavy-duty commercial vehicles as well (ExxonMobil 2013). Natural gas could reduce petroleum dependence by converting it into liquid fuels which would be easier to transport and safer to use. Among the fuels from natural gas, methanol has been produced for the longest time at industrial scale although so far it has been majorly consumed as a chemical source rather than fuel.

The first step in synthesis of methanol is conversion of natural gas to syngas in the temperature range of 800–1000 °C. This is primarily carried out through two processes, partial oxidation and methane reforming. Methane reforming in turn is classified into steam reforming and dry reforming. Most recently, Bi-reforming concept is established for a synergistic interaction of both steam reforming and dry reforming.

The chemistry of natural gas conversion through different routes is described below.

8.4.3.1 Partial Oxidation

$$\begin{aligned} &CH_4 + 1/2O_2 \rightleftharpoons CO + 2H_2 && \Delta H_{298K} = -35.98\,\text{kJ/mol} \\ &CO + 1/2O_2 \rightleftharpoons CO_2 && \Delta H_{298K} = -282.83\,\text{kJ/mol} \\ &H_2 + 1/2O_2 \rightleftharpoons H_2O && \Delta H_{298K} = -241.42\,\text{kJ/mol} \end{aligned} \tag{8.6}$$

Partial oxidation, as shown in Eq. 8.6, is a reaction of methane with less than stoichiometric amount of oxygen to produce a mixture of hydrogen and CO in the ratio of 2:1. This is suitable for synthesis of methanol in the presence or absence of a catalyst (Choudhary and Choudhary 2008). The gas mixture ultimately formed also contains CO_2 and water vapor due to parallel oxidation of H_2, CO, and methane.

8.4.3.2 Steam Reforming

In this method, natural gas reacts with steam in the presence of a catalyst to produce hydrogen, carbon monoxide, or other useful products (Goeppert et al. 2014).

$$\begin{array}{ll} CH_4 + H_2O \overset{\text{Ni Catalyst}}{\rightleftharpoons} CO + 3H_2 & \Delta H_{298K} = 205.43\,\text{kJ/mol} \\ CO + H_2O \rightleftharpoons H_2 + CO_2 & \Delta H_{298K} = -41\,\text{kJ/mol} \end{array} \tag{8.7}$$

Since the ratio of hydrogen to CO (3:1) is very high (Eq. 8.7), this process is generally employed for commercial production of hydrogen which is subsequently used in ammonia production. The CO present in the reaction further reacts with steam to form H_2 by WGS reaction. While the first step is highly endothermic, the second step is slightly exothermic.

8.4.3.3 Dry Reforming with CO_2

Dry reforming is so named because of the absence of steam for production of syngas from methane using CO_2. Nickel-based catalysts are conventionally used for conversion of methane and carbon dioxide to syngas with H_2/CO ratio of 1, as shown in Eq. 8.8. CO_2 and methane were found to react at a temperature of 750 °C in the presence of modified nickel catalyst and a pressure range of 2–5 MPa to form syngas. This gas is fed to a second reactor containing Cu-based bifunctional catalysts to form DME. The advantage of this process is that both the steps are performed at the same pressure eliminating the need for compression of syngas (Olah 2005). The product gas also contained CH_4 and H_2O along with carbon deposits, due to the reactions listed below. This process is also being used commercially in Calcor process to form high-purity carbon monoxide (Wang and Gong 2011).

$$\begin{array}{ll} CO_2 + CH_4 \rightleftharpoons 2CO + 2H_2 & \Delta H_{298K} = 247.27\,\text{kJ/mol} \\ \text{Methanation: } CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O & \Delta H_{298K} = -252.71\,\text{kJ/mol} \\ \text{Boudouard: } 2CO \rightleftharpoons CO_2 + C(s) & \Delta H_{298K} = -170.70\,\text{kJ/mol} \\ \text{Methane Decomposition: } CH_4 \rightleftharpoons C(s) + 2H_2 & \Delta H_{298K} = 75.73\,\text{kJ/mol} \end{array} \tag{8.8}$$

Natural gas sources inherently contain carbon dioxide which need not be eliminated through gas purification before dry reforming. Superiority of dry reforming process lies in its effective utilization of a greenhouse gas like CO_2 as one molecule of CO_2 is consumed for each molecule of methane. If this CO_2 can be economically obtained from CO_2-rich streams such as flue gas from thermal power plants and the heat required for the process is supplied from renewable sources, this process can be made completely sustainable and environmentally benign.

However, one of the shortcomings of this process is the coking of catalysts resulting from the Boudouard reaction and thermal decomposition of methane. The

H_2/CO ratio obtained from dry reforming is around 1 which is insufficient for methanol formation but adequate for DME synthesis. Hence, it is a widely used process for producing DME from natural gas.

8.4.3.4 Bi-Reforming^{TM}

To overcome respective shortcomings of steam and dry reforming, the concept of Bi-reforming^{TM} is resorted to. This gives a H_2/CO ratio of 2 in the presence of Ni/MgO between 800–1000 °C (Eq. 8.9). This process has an advantage of reduced coking due to presence of steam, which enhances WGS rather than Boudouard reaction. This process also eliminates the need for removing small chain hydrocarbons such as those found in wet shale gas (Olah and Prakash 2012; Olah et al. 2009).

$$3C_nH_{2n+2} + (3n - 1)H_2O + CO_2 \rightarrow (3n - 1)CO + (6n + 2)H_2 \tag{8.9}$$

In a pioneering study by Olah et al. (2013), MgO-supported NiO catalyst with a NiO content of 5–35% was used for the feed gas containing $CH_4/CO_2/H_2O$ (Eq. 8.10) in the molar ratio of 3/1.2/2.4 at 800–950 °C and 0.5–3 MPa (Olah et al. 2013). This was different from the conventional approach wherein steam and dry reformings are performed at atmospheric pressure.

$$\begin{array}{lll}
\text{Steam Reforming: } 2CH_4 + 2H_2O \longrightarrow 2CO + 6H_2 & & \Delta H_{298K} = 411.70\ \text{kJ/mol} \\
\text{Dry Reforming: } CH_4 + CO_2 \longrightarrow 2CO + 2H_2 & & \Delta H_{298K} = 247.27\ \text{kJ/mol} \\
\text{Bi-reforming: } 3CH_4 + 2H_2O + CO_2 \longrightarrow 4CO + 8H_2 & & \Delta H_{298K} = 658.98\ \text{kJ/mol} \\
\hline
\end{array}$$

$$\begin{array}{c} \text{Metgas} \\ \downarrow \\ CH_3OH \end{array} \tag{8.10}$$

The production of methanol is generally conducted at pressures between 3 and 10 MPa. This eliminates the need for compression of the syngas.

8.4.3.5 Oxidative Bi-Reforming

Olah (2013) suggested an improvement in the Bi-reforming^{TM} process introduced by their research group earlier (Olah 2013). This combined the complete combustion of methane to provide CO_2, steam, and reaction heat generated with the Bi-reforming^{TM} process. This process gives H_2 and CO in the ratio of 2:1 which is ideal for methanol synthesis (Eq. 8.11).

Table 8.7 GTL plants operational worldwide (The Oil and Gas Year 2015)

S. No.	Name of facility	Operator	Location	Production capacity (bpd)	Product
1	Oryx GTL	Qatar Petroleum and Sasol	Qatar	34,000 bpd	Diesel and naptha
2	Pearl GTL	Qatar Petroleum and Shell	Qatar	140,000	Cleaner-burning diesel and aviation fuel, oils for advanced lubricants, naphtha to make plastics, and paraffin for detergents
3	Mossel Bay	PetriSA	South Africa	45,000	Unleaded petrol, kerosene (paraffin), diesel, propane, liquid oxygen and nitrogen, distillates, eco-fuels, process oils, and alcohols
4	Escravos	Chevron, Nigerian National Petroleum Corp.	Nigeria	33,000	Diesel, naphtha products, LPG

$$\begin{gathered}\text{Methane Combustion: } CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \Delta H_{298K} = -802.9\,\text{kJ/mol} \\ \text{After admixing, bi-reforming is carried out} \\ 3CH_4 + 2H_2O \rightarrow 4CO + 8H_2 \quad \Delta H_{298K} = 658.98\,\text{kJ/mol}\end{gathered} \tag{8.11}$$

Natural gas-based methanol plants have three main steps—natural gas conversion to syngas, reaction of syngas to form methanol, and purification of methanol for tail-end applications. Auto-thermal reforming (ATR) plants using low steam-to-carbon ratio are preferred industrially for commercial scale plants. Haldor Topsøe, Denmark, is one of the pioneers in this sector and has developed reactor for combined partial oxidation and catalytic steam reforming to produce syngas which can be converted to more than 10,000 MTPD of methanol. The first such plant was established in 2002 in Europe. Other similar units are discussed in Table 8.7. ATR gives syngas with H_2/CO of 1.7–1.8, and the proportion of hydrogen in the reactor is to be increased for methanol synthesis by removing CO_2 or introducing a loop for reuse of hydrogen from purge gas (Aasberg-Petersen et al. 2007).

In order to increase the sustainability and renewable quotient of methanol and DME production from natural gas, methane through biological treatment of MSW and other waste streams, as well as hydrogen production through renewable energy sources, needs to be explored.

8.4.4 Biomass

Given the drivers like energy security, massive base of existing vehicles and the alarming rise of toxic vehicular emissions, the production of clean synthetic fuels in decentralized manner from biomass at a scale to fit the economic collection radius of biomass resources makes considerable sense (Olah 2013; International Energy Agency 2011; Bansal and Bandivadekar 2013; Ahmad and Choi 2010; Bruins and Sanders 2012). Since plant biomass is the only sustainable source for obtaining organic carbon, fuels derived from it can be naturally called sustainable liquid fuels. Lignocellulose biomass is accepted as the cheapest form of biomass. It comprises of polymers such as cellulose and hemicellulose along with lignin. This polymeric source is converted to liquid fuels by breaking down the complex structure into simpler oligomers or long-chain compounds of high calorific value and removal of oxygen as either CO_2 or H_2O. This process involves removal of existing functionality from a thermally unstable molecule. It is thus completely opposite to the conversion of crude petroleum to fuels which involves adding functionality to a thermally stable molecule (Huber et al. 2006). To convert biomass into methanol/DME via syngas, direct biomass gasification and pyrolysis oil gasification are the two most prominent technologies available at present. Biomass gasification yields over 80% of producer gas or raw syngas with impurity (Zinoviev et al. 2010; Rajvanshi 1986; Couto et al. 2013). Major reaction equation in biomass gasification is shown in Eq. 8.12.

Reaction occurring in a biomass gasification process

$$\begin{array}{lll}
\text{Process} & \text{Reactions} & \\
\text{Lignocellulosic feedstock} & \text{Drying} & \\
 & \text{Feedstock} \rightarrow (\text{Char/Carbon}) & \\
\text{Pyrolysis} & + \text{Liquid}(\text{Tar} + \text{Heavy Hydrocarbons} + H_2O) & \\
 & + \text{Gases}(CO_2, H_2O, CO, C_2H_2\ \text{etc.}) & \\
 & C + 1/2O_2 \rightarrow CO & \Delta H_{298K} = -111\ \text{kJ/mol} \\
\text{Combustion/Oxidation} & CO + 1/2O_2 \rightarrow CO_2 & \Delta H_{298K} = -283\ \text{kJ/mol} \\
(\text{Temp } 700 - 100\ ^{\circ}\text{C}) & H_2 + 1/2O_2 \rightarrow H_2O & \Delta H_{298K} = -242\ \text{kJ/mol} \\
\text{Boudouard/Reduction} & C + CO_2 \rightarrow 2CO & \Delta H_{298K} = 172\ \text{kJ/mol} \\
\text{Water Gas/Reduction} & C + H_2O \rightarrow CO + H_2 & \Delta H_{298K} = 131\ \text{kJ/mol} \\
\text{Methanation/Reduction} & C + 2H_2 \rightarrow CH_4 & \Delta H_{298K} = -75\ \text{kJ/mol} \\
\text{Water Gas Shift} & CO + H_2O \rightarrow CO_2 + H_2 & \Delta H_{298K} = -41\ \text{kJ/mol} \\
\text{Steam Reforming} & CH_4 + H_2O \rightarrow CO + 3H_2 & \Delta H_{298K} = 206\ \text{kJ/mol}
\end{array} \tag{8.12}$$

Equation 8.12 shows that H_2 and CO are formed mostly in the reduction zone in the biomass gasifier. In a recent study by Couto et al. (2013), a global perspective about the producer gas or raw syngas final composition and its strong dependence on the biomass type, oxidizing agent (air or oxygen), type of gasifiers, and pressure and temperature of the process is given based on a literature benchmarking (IRENA and IEA-ETSAP 2013). This study reveals urgent need of development of experimentally validated mathematical models for numerical simulation that could be a useful tool to determine the final composition of syngas.

Among thermochemical options, biomass gasification is most advanced in terms of technology maturity and has been adapted for various biomass feedstocks in multiple countries at different scales for thermal and power applications. However, the production of biomass-based synthetic fuels through the gasification route is still in a nascent stage, as the syngas composition requirements for making these fuels are more stringent than those met by conventional gasification for power and thermal applications. The level of gas purification and conditioning needed to ensure efficient catalyst performance for synthetic fuel production from biomass-based syngas is the main barrier for this process to be techno-economically viable for commercial application. Also, downscaling of gasification technology to make it commercially viable at scales more in sync with biomass availability is a challenge. Thus, though the FT synthesis (FTS) as such is the most commercially advanced technology for a large scale (>5 million liters daily output) with coal and/or natural gas as the resource, further research, development, and demonstration (RD&D) is required for adaptation and application to the bio-based feedstocks at that scale. The composition of the syngas from biomass gasification processes is generally not suited for direct use in the downstream synthesis of methanol and DME.

Oxygen gasification instead of air gasification is preferred for getting cleaner syngas appropriate for making such synthetic fuel. Downstream shift reactors, membrane separators or pressure swing adsorption, etc., are the commonly employed techniques for H_2/CO ratio adjustment. Further syngas cleaning is important to remove elements such as excess oxygen, sulfur, alkalis, halides which are major catalyst poisons and likely to reduce the process efficiency (Dagle et al. 2007). In addition, downscaling of gasification technology is a major challenge at a scale in sync with biomass availability.

Oxygen-rich gasification of corncob as a biomass feed for producing syngas in a two-stage fixed-bed gasifier is reported at a 100-ton scale (100 t/y DME) to study the direct synthesis of DME from bio-syngas by the Chinese Academy of Sciences (Lv et al. 2009). In this process, gasification at 1100 °C produced syngas with H_2/CO ratio of 0.98–1.17 suitable for DME synthesis. In order to enrich the gas, CO_2 is removed by polypropylene carbonate under a pressure of 1.2–1.4 MPa; O_2 and sulfur are removed by passing through activated carbon and deoxygenation catalysts under 4–4.5 MPa pressure. DME is synthesized by hybrid catalytic conversion of syngas at 180–200 °C at same pressure. 80% CO conversion is observed, and 99% pure DME is obtained after rectification. This direct conversion increases CO conversion, ensures longevity of catalyst life, and improves overall process efficiency. However, limitations of this process are reported in terms of tar formation, high production cost, and catalyst reliability (Prins et al. 2005).

In a recent review, it is shown that biomass gasification leads to a loss of 23% of the feedstock energy content (Spath and Dayton 2003). Subsequent downstream conversion of the obtained syngas to FTS alkanes, methanol, ethanol, etc., is expected to have an overall process thermal efficiency (PTE) in the range of 0.2–0.4

(Dahmen et al. 2012b). No further advancement in syngas conversion is anticipated for improvement in the PTE because these processes have been thoroughly evaluated for quite a long period. Thus, gasification route is not viable techno-economically in comparison with the route for fuel production from petroleum at present. However, for correct evaluation of the true benefit for renewable biomass-based methanol and DME synthesis, an integrated approach inclusive of chemistry, catalysts used in conversion processes in conjunction with life cycle, and economic analysis hold critical importance. These economic and environmental assessments are presently based on numerous assumptions, and hence, it is recommended to be viewed as first-order indicators only (Huber et al. 2006).

To address the concerns associated with centralized large-scale biomass gasification processes, decentralised fast pyrolysis is increasingly being considered beneficial as it converts biomass to high-density intermediate liquid which is easier to transport, store, and handle as compared to biomass. Smaller units could be set up for biomass pyrolysis operating at moderate 400–600 °C under atmospheric pressure to produce “bio-crude” or bio-oil (Goeppert et al. 2014). In the case of biomass pyrolysis, technology development and commercial applications have been largely concentrated in a few regions like Canada, USA, and some European counties. There are many technologies for bio-oil production operating in the range of 100–400 TPD. However, these plants are mostly operated using wood- and forestry-based bio-oil as an intermediate for power and chemicals. The feasibility of bio-oil upgradation to green fuel via syngas has been proven technically, at laboratory and pilot scale, but large-scale demonstration of biomass-based synthetic fuels has not yet been realized.

Karlsruhe Institute of Technology (KIT), Germany, has developed the unique Bioliq process for production of syngas through biomass pyrolysis and subsequent bio-oil gasification. The syngas is then converted to DME. Fast pyrolysis of lignocellulosic biomass (e.g., wood and straw) is performed to produce energy-dense slurry containing pyrolysis condensates and char (bio-syncrude). The slurry contained 20% coke (char) and 50–60% bio-oil (water and ash free basis). The bio-syncrude, thus generated, contains 85% of the original energy content of the biomass and is gasified in a pressurized entrained flow (PEF) gasifier with technical oxygen, at nearly 1200 °C. The gasifier operates at 8 MPa pressure and has a thermal fuel capacity of 5 MW. A drawback of Bioliq process is generation of raw syngas with a low H_2/CO ratio (0.5–0.7), while H_2/CO ratio of 2 is optimum for methanol synthesis with Cu-based catalysts or FT synthesis with Co catalysts. After removal of particles, ammonia, HCN, $CO_{2,}$ and other impurities, the syngas obtained is catalytically converted at 250 °C and 5 MPa pressure in the presence of Cu/ZnO/Al_2O_3 as a catalyst for methanol synthesis and γ-Al_2O_3 for dehydration of methanol to produce DME (SUPRABIO Newsletter 2013). The highlight of the Bioliq process is the use of lignocellulosic biomass and single-step production of DME taking advantage of low H_2/CO ratio with bimetallic catalysts. Air Liquide, in association with KIT, completed the second stage of the Bioliq process for second-generation biofuels at Karlsruhe. All the stages, namely fast pyrolysis, entrained flow gasification, hot gas cleanup, and synthesis, were integrated.

An important aspect of the gasifier is being the refractory material accounting for the high ash content and gas purification unit which is designed to operate at the same conditions as the gasifier. But a challenge for the high-pressure slurry reactor is the loss of heat to the tune of 100–200 kW/m^2 through the layers of silicon carbide and slag material. A factor that plays major role in assessing the cost of such heat loss is the surface-to-volume ratio. It has been found that for large-scale gasifiers operational at a capacity of several hundred MW$_{th,}$ these heat losses become negligible, whereas in small-scale units, the high surface-to-volume ratio increases heat loss. This shows pressure entrained flow (PEF) gasifiers are not viable for such scale.

These bio-oil gasification processes are typically conducted at a higher pressure to reduce the number of syngas compression steps needed to reach the operating pressure of the methanol/DME production unit (5–10 MPa). It also reduces the size of gasifier for the same gas output. However, one of the major drawbacks of such high-pressure gasifiers is the need of high-pressure and high-temperature gas cleanup systems, which is not as advanced or common as lower-pressure temperature processes. The complexity and safety aspect of such high-pressure reactor is also a barrier for decentralized operation of such gasifiers in rural or remote areas for medium- and small-scale units.

Similarly, under the project titled “Sustainable Products from Economic Processing of Biomass in Highly Integrated Bio-Refineries” or SUPRABIO, ETC from Sweden and BTG from the Netherlands developed a two-stage unit for conversion of biomass to DME through bio-oil gasification in entrained flow reactor and conversion of syngas directly to DME. The highlight of this process is the ability to ensure steady continuous flow of the acidic, pyrolysis oil into a pressurized environment at 1000 °C and 0.3 MPa pressure (Wang et al. 2010).

In Sweden, a 1.5 kT/year bio-methanol synthesis facility had been established under a temporary consortium called Bio DME to prove feasibility of synthesizing DME from black liquor gasification. Similarly, Bio-MCN in the Netherlands aimed at synthesizing methanol from crude glycerin obtained after bio-diesel production to bio-methanol in a plant of 200 kT/year capacity. Enerkem, Canada, also started a plant of 4 kT/year capacity via gasification. Many plants have been proposed globally or have been under construction in the last five years. The most common feed is forest residue and woody biomass, and the scale varies from 2 to 500 kT/year (Dagle et al. 2007). It is reported that for the biomass to DME technology to be economical, the production capacity of plants should be around 3000–10,000 t/a. Due to limited capacity of feedstock collection, transportation, and utilization, dispersed mode of setting up of plants is highly recommended as a more sustainable option (Goetsch et al. 2008).

Goetsch et al. (2008) showed that glycerol which was obtained from bio-diesel production could be utilized to generate syngas after reaction with superheated steam and oxygen (Markewitz et al. 2012). This syngas is converted to methanol in a catalytic process using a copper-based catalyst. The temperature in the gasifier was 800–1000 °C with a pressure of 1.4–4 MPa. This resulted in a hot syngas which needed to be cooled to room temperature and then pressurized to 5–10 MPa before feeding into methanol synthesis reactor where the temperature was increased to 150–300 °C.

As mentioned above, research on bio-oil char slurry is limited largely due to the studies of oxygen-blown pressurized entrained flow gasification at 1200–1600 °C. However, there are few research groups which have recently started working on steam gasification of bio-oil. Successful laboratory-scale experiments with steam gasification of bio-oil and bio-oil–char mixture in atmospheric fluidized-bed gasifier in the presence of nickel-based naphtha steam reforming catalyst and silica sand at bed material have reported high H_2/CO ratio suitable for synthetic fuel production.

In view of the limitations and challenges of the high-pressure entrained bed slurry reactor and the positive aspects in the atmospheric steam gasification of bio-oil–char mixture, the future research needs to be focused on innovation in bio-oil gasification at slightly above atmospheric pressure in oxygen and steam conditions for decentralized and sustainable production of methanol and DME.

The seasonality of biomass production demands cogasification of biomass and coal/petcoke mix. An integration of solar thermal or wind power with the gasification plant could also provide further carbon reductions in the life cycle of methanol or DME synthesis process.

8.4.5 Carbon Dioxide

The first prerequisite for methanol or DME synthesis from carbon dioxide is the capture of carbon dioxide from the readily available concentrated sources of CO_2 such as flue gases from power plants and industries like steel, cement, aluminum. Several techniques have been developed for CO_2 removal and capture from gas streams over the past few years. Exhaustive review of such processes has been conducted which can be referred for detail understanding of the concept (Goeppert et al. 2014; Choi et al. 2009; Boot-Handford et al. 2014; D'Alessandro et al. 2010; MacDowell et al. 2010; Wang et al. 2011; Shulenberger et al. 2007).

Production of methanol from CO_2 has reached demonstration scale. Carbon Recycling International (CRI) has opened its first plant in Iceland that is operating on cheaply available geothermal energy. The hot water and steam sources are utilized for conversion of CO_2 to methanol, with the hydrogen being produced from electrolysis of water using geothermal energy. The initial capacity of the plant was 10 tpd of methanol (EN Archives 2008). The methanol produced was trademarked as Vulcanol, and at present, this is blended with gasoline. Other planned ventures for CO_2 recycling are in Japan by Mitsui Chemicals and Canada by Blue Fuel Energy (BFE). Mitsui Chemicals is planning a construction of 100 tons per annum (TPA) methanol plant using CO_2 from industrial flue gas and hydrogen from photochemical splitting of water using solar energy. BFE plans to use hydroelectricity and CO_2 from natural gas processing (Blue Fuel Energy 2014; Razali et al. 2012). In China, Australia, and EU, significant interest is generated in CO_2-based methanol synthesis. China, as mentioned in Sect. 8.1, is also moving toward becoming one of the leading consumers of methanol.

The single-step hydrogenation of CO_2 to methanol (Eq. 8.13) is a preferable process (Grabow and Mavrikakis 2011).

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \quad \Delta H_{0\,298K} = 49\,\mathrm{kJ/mol} \tag{8.13}$$

Recently, Grabow and Mavrikakis (2011) suggested a reaction mechanism based on DFT calculation for synthesis of methanol as given in Eq. 8.14 (Kondratenko et al. 2013).

$$\begin{aligned}
&H_2 + {}^*2 \rightleftharpoons 2H^*\\
&CO_2(g) + {}^* \rightleftharpoons CO_2^*\\
&CO_2^* + H^* \rightleftharpoons HCOO^* + {}^*\\
&HCOOH^* + H^* \rightleftharpoons HCOOH^* + {}^*\\
&H_2COOH^* + {}^* \rightleftharpoons H_2CO^* + OH^*\\
&H_2CO^* + H^* \rightleftharpoons H_3CO^* + {}^*\\
&H_3CO^* + H^* \rightleftharpoons CH_3OH^* + {}^*\\
&CH_3OH^* \rightleftharpoons CH_3OH(g)\\
&OH^* + H^* \rightleftharpoons H_2O^* + {}^*\\
&H_2O^* \rightleftharpoons H_2O(g)\\
&{}^* : \text{ free surface site}\\
&X^* : \text{ adsorbed atom or molecule}
\end{aligned} \tag{8.14}$$

This model claims formation of HCOOH from HCOO* which is further hydrogenated to H_2COO^*. This intermediate is thus believed to be the final intermediate for the formation of methanol.

Hydrogen directly converts CO_2 to hydrocarbon and is obtained from steam reforming of natural gas and electrolysis of water commercially. It can also be obtained from physicochemical, photolytic, electrolytic, and biological treatment of oil, coal, and biomass (Steinberg 1997). The recycling of CO_2 to produce methanol and DME could be achieved through dry reforming of methane, as shown in Sect. 8.4.3. In Carnol process, proposed in 1997, CO_2 captured from flue gases, using monoethanolamine (MEA), of a coal-fired plant and hydrogen obtained from steam reforming of natural gas was reacted to form methanol. A reduction of up to 65% in emission was observed from the thermal power plant (Goeppert et al. 2014; Saito 1998).

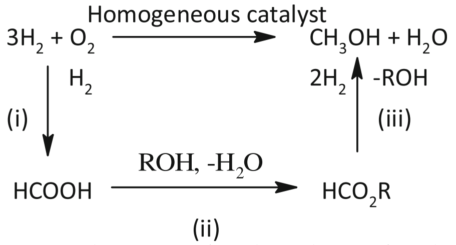
It was a startling revelation that CO_2 hydrogenation and syngas conversion both occur through a similar mechanism with key intermediate being CO_2 (Goehna and Koenig 1994; Ostrovskii 2002). Syngas conversion is proposed to follow two steps: the conversion of CO–CO_2 through the water gas shift reaction and subsequently, hydrogenation of CO_2 to methanol (Fujita et al. 1995; Chorkendorff and

Niemantsverdriet 2005a; Chinchen et al. 1987). Chinchen et al. (1987) suggested that CO behaves like a scavenger in water for oxygen atoms and reacts with it to form CO_2 (Cheng 1994). This is critically important because water inhibits catalytic activity of the metal sites and needs to be eliminated from the reaction. This was also verified when CO-H_2, purified from carbon dioxide and water, was reacted in the presence of commercial methanol catalyst and very little methanol was generated. While the synthesis of methanol from syngas has been known (Köppel et al. 1998), using CO_2 for its synthesis is still a relatively new topic of research.

Heterogeneous catalysts from metals and their oxides, primarily copper and zinc, have been found to be effective for conversion of CO_2 to methanol. These are similar in nature to the ones used for syngas conversion. Majority of the newly developed syngas to methanol catalysts are based on Cu/ZnO. Among the additional metals used for this catalysis are Zr, Ga, Si, B, Cr, Ce, V, Cr, Ti or a combination of those with Cu/ZnO. Cu/ZnO/ZrO_2 has been found to be the most effective catalyst system. While ZnO allows maximum dispersion of Cu on the surface, thus maximizing the activity, ZrO_2 further enhances catalytic activity because it is hydrophilic and does not allow H_2O to hinder with the catalyst reactivity. The accepted reaction mechanism involves a dual-site or bifunctional mechanism. Hydrogen is adsorbed on Cu site, and the CO_2 molecule is adsorbed on ZrO_2 surface as bicarbonate. Atomic hydrogen then spills over to the copper site, and hydrogenation of the bicarbonate species takes place to form methanol (Chorkendorff and Niemantsverdriet 2005a).

An exhaustive review on the catalytic development and their inherent chemistry is presented in the literature (Goeppert et al. 2014; Clarke and Bell 1995; Fujita et al. 2001; Zhang et al. 2006; Qi et al. 2001; Nitta et al. 1993; Arena et al. 2007; Ma et al. 1998; Arena et al. 2013; Tominaga et al. 1993).

Among the hydrogenation catalysts for CO_2 to methanol, homogeneous catalysts have not been explored in much detail. $Ru_3(CO)_{12}$, $Ir_4(CO)_{12}$, $Rh_4(CO)_{12}$, $W(CO)_6$, $Mo(CO)_6$, $Fe_2(CO)_9$, and $Co_2(CO)$ are some of the reported homogeneous catalytic systems (Tominaga et al. 1995; Li et al. 2014). The mechanism for the reaction goes through 3 steps—reduction of CO_2 to formic acid, formation of esters from formic acid, and finally hydrogenation of the ester to methanol (Eq. 8.15). The reaction proceeds at 135 °C and 4 MPa (Pontzen et al. 2011).



(8.15)

A need to improve upon the conventional catalysts arises because at higher CO_2 partial pressure the catalysts tend to get deactivated. However, this effect is due to the water formed in the process, and in the presence of CO, this water can be utilized for WGS reaction as described by Clarke and Bell (1995) and Fujita et al. (2001). Lurgi AG, Germany, is a pioneer in methanol synthesis process and through collaboration with Süd-Chemie, Germany, has developed and tested high-activity Cu/ZnO-based catalyst called C79-05-GL (Simbeck and Chang 2002). This reaction is performed at 260°C, and the selectivity for methanol is found to be higher than conventional catalysts, but the activity over time was found to be almost constant. Other companies commercializing methanol synthesis catalysts include Sinetix, Haldor Topsøe, and Mitsubishi Gas Chemicals. An advantage of CO_2 hydrogenation is that the energy-intensive process of syngas generation from coal, petcoke, and biomass can be avoided (Chaplin 2014).

While the process of CO_2 conversion to methanol has been demonstrated at pilot scale, there are major economic hurdles in scaling-up this process to replace fossil fuel-based methanol processes. Carbon dioxide hydrogenation from industrial and other point sources is a technically viable route although the economics of the process is dependent on cost of CO_2 capture and hydrogen production. While CO_2 does not have the issue of availability unlike other sources such as biomass or natural gas, the price of carbon dioxide may vary locally due to carbon credits/ taxing mechanism. Hydrogen, at present, is produced at a low cost from methane. But to enhance sustainability of the process, alternate sources of hydrogen such as electrolysis of water have to be considered. Chaplin (2013) estimated that 1 kg of hydrogen production from electrolysis requires close to 50 kWh electricity (Mbuyi et al. 2012). Generation of such an amount of power for large-scale CO_2 hydrogenation plants may become economically prohibitive (Ren et al. 2003). One solution here is to generate electricity using renewable sources such as small hydro, biomass, solar, geothermal . Electricity from these sources is becoming competitive to conventional thermal power and may soon become commercially viable.

To completely understand the cost of methanol production from any source, a life-cycle analysis is required which also accounts for emissions during production, distribution, and consumption. In order to analyze methanol and DME as viable transport fuel alternatives, a well-to-wheel analysis is required. In the case of methanol synthesized from CO_2 and hydrogen, the CO_2 emissions were found to be 1.74 g CO_2e/MJ which is much lower than conventional routes of methanol (Goeppert et al. 2014). It is likely, in the future, to make fuel more economical from sources such as CO_2 or biomass with possibility of recycling carbon dioxide directly from air and addressing the issue of rising greenhouse gases.

8.5 Methanol and DME Synthesis from Syngas

Conversion of syngas to methanol has been known for centuries with some of the earliest cases been recorded from the twentieth century. In fact, methanol synthesis was done using CO and H_2 being generated by fermentation (Chinchen et al. 1987).

Methanol is synthesized from syngas (CO: $2H_2$), also called met gas (Eq. 8.16). In the process, WGS reaction, which is endothermic, is required to produce more CO to push methanol production. The reactions are reversible, and the specific conditions need to be maintained according to Le Chatelier's principle. Water produced in the reaction needs to be removed to prevent deactivation of the catalyst. Catalysts such as $Cu/ZnO/Al_2O_3$ and $Cu/ZnO/Cr_2O_3$ are used for conversion of syngas in a gas-phase process at high pressures and temperatures (Larson and Tingjin 2003).

$$\begin{gathered} CO + 2H_2 \rightleftharpoons CH_3OH \quad \Delta H_{298K} = -90.7\,\text{kJ/mol} \\ \text{Water gas shift reaction: } CO + H_2O \rightleftharpoons H_2 + CO_2 \quad \Delta H_{298K} = 41.00\,\text{kJ/mol} \end{gathered} \tag{8.16}$$

In a fixed-bed reactor, syngas reacts on the catalyst surface in gas phase. Here, in order to control the temperature during the reaction, excess syngas generated is recycled to remove the heat. H_2-rich syngas is a preferred medium for heat removal owing to higher heat capacity of H_2 over CO. Hence, the single-pass conversion efficiency for CO is maintained at a relatively low level. The recycling and compression of syngas are energy-intensive processes (Larson and Tingjin 2003). Liquid-phase processes have also been developed to address the inherent challenges of the gas-phase process during methanol production (Boroujeni 2008). New liquid-phase processes have evolved where a higher one-pass CO conversion is achieved, single-pass conversion efficiency for CO can be higher, and H_2-rich syngas need not be used (Larson and Tingjin 2003).

DME is synthesized by dehydration of methanol using zeolite or alumina-type heterogeneous acid catalyst (Larson and Tingjin 2003). Since this is an exothermic process, low temperature and pressure are favorable. Typically, it is conducted as a gas-phase reaction at temperature range of 220–250 °C in 1–2 MPa pressure (Eq. 8.17). In a direct DME synthesis method, methanol synthesis is followed by water gas shift reaction to produce more hydrogen which further drives methanol synthesis. The copper catalyst for methanol production, however, gets deactivated because of water. Gold-based catalyst has also been suggested for methanol synthesis (Mbuyi KG et al. (2012)).

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \quad \Delta H_{298K} = -23.4\,\text{kJ/mol} \tag{8.17}$$

By using a combination of the catalysts for both syngas conversion to methanol and subsequent dehydration, syngas can be directly converted to DME. Furthermore, CO-rich syngas obtained from coal gasification undergoes both methanol synthesis and WGS in the presence of the same catalyst. This provides a cascading effect because the water released during dehydration increases H_2 production, which in turn increases methanol production. The entire single-step DME synthesis is represented in (Eq. 8.18).

$$3CO + 3H_2 \rightleftharpoons CH_3OCH_3 + CO_2 \quad \Delta H_{298K} = -246\,\text{kJ/mol} \tag{8.18}$$

In this case, H_2/CO ratio of 1 is maintained which is lower than the ratio required for methanol synthesis.

A complete life-cycle analysis of methanol and DME derived from biomass or CO_2, when used as fuel substitutes for engines, revealed the positive environmental impact of these fuels on a well-to-wheel (WTW) as well as tank-to-wheel (TTW) basis. The impact was assessed on GHG emissions as well as emissions of other pollutants including NOx, CO, particulate matter. Renewable methanol was found to offer a carbon reduction in the range of 65–95%. Trucks operated using DME in Japan and Sweden were found to satisfy the most stringent environmental regulations of the EU, the USA, and Japan.

WTW emissions for methanol derived from black liquor are found to be 3.3 g CO_{2eq} per MJ compared to 4.57 g CO_{2eq} per MJ and 30.6 g CO_{2eq} per MJ for methanol derived from CO_2 and H_2 (from renewable sources) and crude glycerin, respectively. Up to 98% reduction in CO_2 emissions is reported for methanol derived from these sources (Goeppert et al. 2014).

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Chapter 9
Solar Assisted Biodiesel Production

Amit Pal, Amrik Singh and R. S. Mishra

Abstract Due to the scarcity of fossil energy sources and high combustion generated pollution, new alternative greener energy sources became the necessity of the time. Biodiesel is a potential alternative for depleting energy sources since it is produced mainly from vegetable oils and animal fats, which are a renewable resource and are biodegradable and non-toxic. The production process of biodiesel involves heating and mixing triglyceride with methanol (or ethanol) in the presence of various catalysts. Currently, biodiesel is produced via transesterification reactions catalyzed by chemical catalysts, which produces higher fatty acid alkyl esters in shorter reaction time. The amount of electricity required for heating and mixing in this process need to be replaced with renewable resources. An effective means for minimizing the amount of power required to drive chemical reactions to completion is proposed through the use of various solar systems. In this study, CSP is used to incorporate solar energy for biodiesel production. Experiments are conducted with various solar techniques and with different process parameters to propose the optimized solution. Through the utilization of solar energy, the generation of carbon dioxide waste during biodiesel production has been eliminated. Biodiesel produced is comparable to the petro-diesel in properties and production process economical.

Keywords Solar energy · Biodiesel · Combustion · Renewable

9.1 Introduction

As the population is increasing, the demand for energy is also growing at a faster rate. Our exhaustible resources such as fossil fuels are conscientiously exploited to meet up the energy requirements. Fossil fuels also contain different types of harmful hydrocarbons such as toluene, sulfur, and aromatics rings. In recent times, due to combustion of petrol and diesel, an alarming increase in pollution levels has been

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observed. And also their stocks are diminishing. As a result, pollution levels, as well as depletion of these resources, are increasing at a shocking rate. Renewable fuel like biodiesel is easy to produce at domestic level as they are manufactured from algae, animal fats, or from various vegetable oils like Jatropha, Karanja, Sesame, Cotton seed. Due to its high-lubrication and clean-burning properties, it can be used as a substitute fuel. Also, it is suitable for blending in diesel to use it in existing, unmodified diesel engines; this indicates that a small quantity of biodiesel is required to blend with diesel. According to the Energy Statistics Report (2015) (released by Ministry of Statistics and Program Implementation), the estimated consumption of coal, lignite, crude oil, natural gas, and petroleum products has increased by a significant margin since 2005–2006. (Energy Statistics Report 2015) Table 9.1 shows the growth of installed capacity of power plants in India.

It shows that the present status of conventional energy sources, and it is not adequately meeting the global demand for the energy. So there is a need to develop unconventional and renewable sources of energy such as solar energy, wind energy, bioenergy, biofuels, tidal power.

9.1.1 Renewable Energy Sources

Present energy scenario and depletion of conventional energy sources have led to the development of renewable energies such as solar energy, wind energy, biofuels and bioenergy, and geothermal energy. The renewable energy could be a sustainable and reliable option when more than one technology is incorporated such as hybrid solar–biomass technology, cogeneration power plant, combined solar thermal polygeneration system.

9.1.2 Various Feedstocks for Biodiesel Production

At present, more than 300 biodiesel feedstocks have been identified. Biodiesel can be produced from both edible and non-edible oilseeds. Edible oils such as soybean, rapeseed, sunflower, palm, peanut, corn, cotton seed, camelina, pumpkin, canola can be used as feedstocks for biodiesel production and in case of non-edible oil crops jatropha curcas, pongamia pinnata, sea mango, palanga, karanja, tallow, Nile tilapia, poultry, etc., are mainly used. Recently, non-conventional feedstock (algae, fungi, microalgae, etc.) for biodiesel is becoming an area of interest. These also include edible oils, non-edible oils, wild oils, waste cooking oils, animal fats, and non-conventional feedstocks (Shahid et al. 2011).

Table 9.1 Growth of installed capacity in India (Energy Statistics Report 2015)

	Thermal (MW)				Renewable (MW)					
Installed capacity as on	Coal	Gas	Diesel	Subtotal thermal	Nuclear (MW)	Hydel	Other renewable	Subtotal renewable	Total (MW)	% Growth (on yearly basis)
31 Dec 1947	756	–	98	854	–	508	–	508	1362	–
31 Dec 1950	1004	–	149	1153	–	560	–	560	1713	8.59
31 Mar 1956	1597	–	228	1825	–	1061	–	1061	2886	13.04
31 Mar 1961	2436	–	300	2736	–	1917	–	1917	4653	12.25
31 Mar 1966	4417	137	352	4903	–	4124	–	4124	9027	18.80
31 Mar 1974	8652	165	241	9058	640	6966	–	6966	16,664	10.58
31 Mar 1979	14,875	168	164	15,207	640	10,833	–	10,833	26,680	12.02
31 Mar 1985	26,311	542	177	27,030	1095	14,460	–	14,460	42,585	9.94
31 Mar 1990	41,236	2343	165	43,764	1565	18,307	–	18,307	63,636	9.89
31 Mar 1997	54,154	6562	294	61,010	2225	21,658	902	22,560	85,795	4.94
31 Mar 2002	62,131	11,163	1135	74,429	2720	26,269	1628	27,897	105,046	4.49
31 Mar 2007	71,121	13,692	1202	86,015	3900	34,654	7760	42,414	132,329	5.19
31 Mar 2012	112,022	18,381	1200	131,603	4780	38,990	24,503	63,493	199,877	9.00
31 Mar 2015	169,118	23,062	1200	188,898	5780	41,267	35,777	77,044	271,722	11.98
31 Mar 2016	185,172	24,508	993	210,675	5780	42,783	42,727	85,510	301,965	11.13
31 May 2016	186,243	24,509	919	211,670	5780	42,783	42,849	85,632	303,083	9.88

9.2 New Trends in Biodiesel Production

To increase the yield of biodiesel, some new technologies are developed such as microwave irradiation techniques in which microwave irradiation in reactants causes the necessary heating and mixing of reactants. Supercritical transesterification process is effective even without any catalyst, but at a very high temperature and pressure conditions, ultrasonic baths and ultrasonic horn reactors techniques utilize the generation of very large number of cavitation bubbles and their collapse and use of solar energy in the chemical heating process of esterification (Pal and Kachhwaha 2013). The use of these technologies reduces reaction time and enhances the quality of biodiesel as a product. New trends in biodiesel production process are shown in Fig. 9.1.

9.2.1 Use of Solar Energy in Biodiesel Production

Transesterification is the most commonly used process for biodiesel production. Leung et al. (2010) presented a review of biodiesel production using transesterification process with the utilization of a catalyst (Leung et al. 2010). In the present work, solar energy is used for chemical heating in transesterification process. This concept of the assistance of solar irradiation in biodiesel production is new, but it is

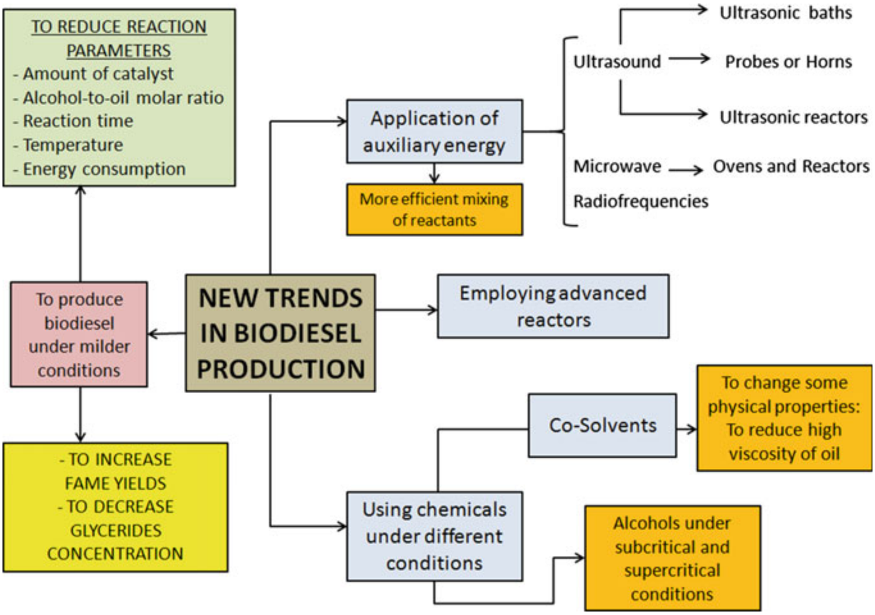


Fig. 9.1 New trends in production process of biodiesel (Pal and Kachhwaha 2013)

similar to microwave irradiation technique of biodiesel production. The main difference between these two techniques is of reaction time. In microwave method, no catalyst is used and the reaction time is only 2–6 min. While in solar assisted biodiesel production, reaction time is around one hour and the catalyst is also used in this process. Moreover, the microwave-assisted biodiesel production is a costly procedure as compared to solar assisted biodiesel production.

In conventional transesterification process, a triglyceride with methanol (or ethanol) is heated under strongly basic condition. This heat is given using an electrical heater. Our objective is to skip the use of the electric heater in transesterification process. Agee et al. (2014) used a parabolic solar reflector made of satellite dishes to concentrate solar irradiation on its focal point. Feedstock oil with alcohol and catalyst was placed on the focus of the reflector and then transesterification process takes place approximately in 1 h. Generally, oil with low FFA content (which requires single-stage transesterification) should be used to produce biodiesel with the assistance of solar energy. In this work, soybean oil was used. For successful processing of transesterification, solar irradiation should be greater than 400–450 W/m^2. In this experiment, the synthesis process of biodiesel took place without generating any chemical and electrical waste. All thermal energy was supplied through solar energy without any electricity use, so no electrical waste was there. Figure 9.2 shows the schematic of solar energy utilization for steam and electricity generation during biodiesel production.

Hou and Zheng (2009) proposed a new concept of utilizing solar energy application for biodiesel production. For example, thermoelectric or PV cells can directly convert the energy of solar irradiation into electricity. Also, the solar collectors can directly convert solar radiation into steam (Hou and Zheng 2009).

In this work, a new parameter ‘renewability index’ was also introduced. It is the ratio of energy of renewable to the total energy. In this experiment, the proposal started with the reported process of biodiesel production using fossil fuels utility; then an alkali-catalyzed transesterification process was developed with the use of solar energy utility on an 8000 t per annum scale. The results indicated that renewability index of the biodiesel production process with the solar utility is 99.9% which is 10.5% higher than the renewability index in the conventional method. Also, the 4676 t of CO_2 gas release was eliminated in a year. About 1275 t of coal consumption was saved per year (Hou and Zheng 2009).

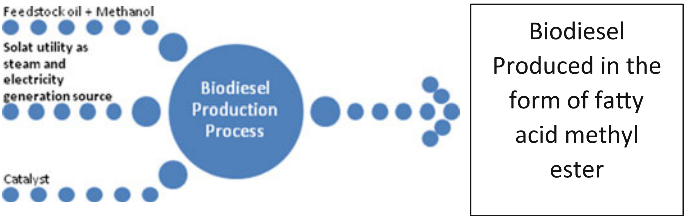


Fig. 9.2 Schematic of solar energy utilization in steam and electricity generation during biodiesel production

Rasmussen and Minteer (2014) presented a review regarding the development of photo bioelectrochemical cells over the past few decades. In this work, they used photosynthetic catalysts (e.g., Thylakoid membrane) for biodiesel production and also for solar energy conversion. Several types of photo bioelectro-catalyst were discussed such as whole cells, organelles, and enzymes (Rasmussen and Minteer 2014). The analytical review of solar energy potential in biofuel production was presented by Agrawal and Singh (2010); they concluded the alternative should be found for sustainable future.

9.2.2 Basic Theory Related to Solar Assisted Biodiesel Production

There are various phenomena which are used in the solar assisted production of biodiesel. The conventional process of biodiesel and basic terminology of solar energy utilization are discussed separately.

9.2.2.1 Selection of Catalyst for Transesterification Process

For transesterification process, the catalyst should be selected appropriately. Three types of catalyst are generally used—alkali, acid, and enzymes. Alkali and acid catalyst are subdivided into the homogeneous and heterogeneous catalyst. Positives and negatives of different type catalyst are discussed in Table 9.2.

9.2.2.2 Optimization Approach of Reaction Parameters in Transesterification

Taguchi method is used for the optimization of reaction parameters in transesterification. The main purpose of using this method is to maximize the yield of biodiesel produced.

9.2.2.3 Introduction of Taguchi Method

The Taguchi method recognizes that not all factors that cause variability can be controlled. The uncontrollable factors are called noise factors. This approach also tries to identify controllable factors that minimize the effect of the noise factors. If biodiesel synthesis is handled with this Taguchi approach, the conversion yield will be more and efficiency of biodiesel production process will also be more.

Table 9.2 Different types of catalysts used in transesterification (Leung et al. 2010)

Type	Example	Advantages	Disadvantages
Alkali homogeneous	NaOH, KOH	High catalytic activity, low cost, favorable kinetics, modest operation conditions	Low FFA requirement, anhydrous conditions, saponification, emulsion formation, more wastewater from purification, disposable
Alkali heterogeneous	CaO, $CaTiO_3$, $CaZrO_3$, CaO–CeO_2, $CaMnO_3$, $Ca_2Fe_2O_5$, KOH/Al_2O_3, KOH/NaY, Al_2O_3/KI, ETS-10 zeolite, alumina/silica supported K_2CO_3	Noncorrosive, environmentally benign, recyclable, fewer disposal problems, easily separation, higher selectivity, longer catalyst lifetimes	Low FFA requirement, anhydrous conditions, more wastewater from purification, high molar ratio of alcohol-to-oil requirement, high reaction temperature and pressure, diffusion limitations, high cost
Acid homogeneous	Concentrated sulfuric acid	Catalyze esterification and transesterification simultaneously, avoid soap formation	Equipment corrosion, more waste from neutralization, difficult to recycle, higher reaction temperature, long reaction times, weak catalytic activity
Acid heterogeneous	Carbon-based solid acid catalyst, carbohydrate-derived catalyst, Vanadyl phosphate, niobic acid, sulfated zirconia, Amberlyst-15, Nafion-NR50	Catalyze esterification and transesterification simultaneously, recyclable, eco-friendly	Low acid site concentrations, low microporosity, diffusion limitations, high cost
Enzymes	Candida Antarctica fraction B lipase, Rhizomucor mieher lipase	Avoid soap formation, nonpolluting, easier purification	Expensive, denaturation

9.2.2.4 Design of Experiment for Transesterification Process Using Taguchi Method

To optimize the process parameters in transesterification, ‘Minitab 17’ software is used. Software uses an orthogonal array based on the number of factors and type of design. The number of runs in orthogonal array is also decided according to the type of design. Some standard orthogonal arrays are shown in Table 9.3.

The signal-to-noise ratios (S/N) for different number of runs help in the optimization for process. S/N ratios are generally the log functions of desired output, and we use these ratios as the objective functions for optimizing process. S/N ratios also help in data analysis and the estimation of the optimum results. The

Table 9.3 Standard orthogonal arrays (Mishra et al. 2015)

Orthogonal array	Number of rows	Max number of factors	Maximum number of columns at these levels			
			2	3	4	5
L4	4	3	3	–	–	–
L8	8	7	7	–	–	–
L9	9	4	–	4	–	–
L12	12	11	11	–	–	–
L16	16	15	15	–	–	–
L16’	16	5	–	–	5	–
L18	18	8	1	7	–	–
L25	25	6	–	–	–	6
L27	27	13	–	13	–	–
L32	32	31	31	–	–	–
L32’	32	10	1	–	9	–
L36	36	23	11	12	–	–
L36’	36	16	3	13	–	–
L50	50	12	1	–	–	11
L54	54	26	1	25	–	–
L64	64	63	63	–	–	–
L64’	64	21	–	–	21	–
L81	81	40	–	40	–	–

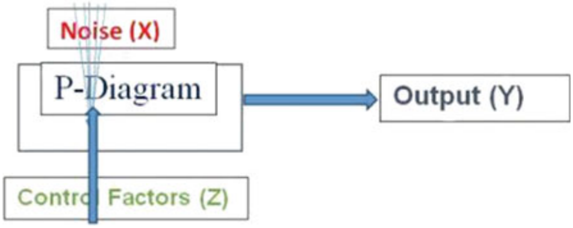


Fig. 9.3 *P* diagram in Taguchi optimization approach using static problem (Ouannene et al. 2009)

optimization problems are treated by two methods in Taguchi approach. One is static problem and other is dynamic problem optimization. In the static problem, process parameters directly decide the desired value of output. After this the best levels of the control factor are determined by this optimization technique so that the output remains as the target function. *P* diagram (process diagram or product diagram) is used to accurately explain the Taguchi approach based on the static problem.

In Fig. 9.3, *P* diagram shows that the output is not affected due to the presence of noise. Thus, the variation in the output values is minimized which is the primary objective of the Taguchi experiments. In transesterification process, the process parameters are alcohol to oil molar ratio, catalyst concentration, reaction time, and temperature. An orthogonal array is decided on the basis of the number of these parameters and types of level of design (e.g., 2-level design, 3-level design, 4-level design, 5-level design, and mixed-level design).

Table 9.4 shows the different iterations of four process parameters at 5-level design. On the basis of above-mentioned table, the following orthogonal array is developed by the Taguchi method is shown in Table 9.5. The columns of an orthogonal array represent factors to be studied, and the rows represent individual

Table 9.4 Design of experiments with four parameters at five levels

Parameters	Levels				
	1	2	3	4	5
Molar ratio	4.5:1	5:1	5.5:1	6:1	6.5:1
Time (min)	50	60	70	80	90
Temp (°C)	50	55	60	65	70
Catalyst conc.	0.5	0.75	1.0	1.25	1.50

Table 9.5 Orthogonal array used to design of experiments with four parameters at five levels

S. No.	Molar ratio	Time	Temp	Catalyst concentration
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	1	4	4	4
5	1	5	5	5
6	2	1	2	3
7	2	2	3	4
8	2	3	4	5
9	2	4	5	1
10	2	5	1	2
11	3	1	3	5
12	3	2	4	1
13	3	3	5	2
14	3	4	1	3
15	3	5	2	4
16	4	1	4	2
17	4	2	5	3
18	4	3	1	4
19	4	4	2	5
21	5	1	5	4
22	5	2	1	5
23	5	3	2	1
24	5	4	3	2
25	5	5	4	3

experiments; If we use 5-level, 4-parameter design without Taguchi method, require $5^4 = 625$ experiments. But Taguchi method reduces the number of experiments to only 25.

9.2.2.5 Determination of Optimal Experimental Condition by the Design of Experiment

The yield of biodiesel produced under twenty-five sets of experimental conditions is estimated by performing operations under the same experimental conditions. This study is associated with four parameters with each at five levels for which L25 orthogonal array which is used as design matrix. After conducting all the twenty-five experiments and measuring the percentage yields. According to the analysis for the case of larger-the-better, the mean squared deviations (MSD) of each experiment were evaluated using the following equation (Mishra et al. 2015). Where n is the number of repetitions of each experiment and y_i is the yield of biodiesel.

$$\mathrm{MSD} = \frac{1}{n}\sum\nolimits_{i=1}^{n}\left(\frac{1}{y_i}\right)^2 \tag{9.1}$$

Signal-to-Noise (S/N) Ratio

In Taguchi, optimization signal-to-noise ratio is an important parameter which is used to estimate the extent of deviation of quality function from the expected value. Taguchi approach uses three types of S/N ratios on the basis of the objective of the problem.

i. Nominal-the-best
ii. Smaller-the-better
iii. Larger-the-better.

In nominal-to-best S/N ratio, normalization problems are solved. Smaller-the-better S/N ratio is used for minimization problem, and larger-the-better is used for maximization of the problem. In the transesterification process, we need to maximize conversion yield of biodiesel, so the larger-the-better ratio is used.

The mathematical equations for these three types of S/N ratios are as follow:

$$\begin{aligned}
\mathrm{SNR}_i &= 10\log\left(\frac{\bar{y}_i^2}{s_i^2}\right)(\text{Nominal the best})\\
\mathrm{SNR}_i &= -10\log\left(\sum\nolimits_{j=1}^{n}\frac{y_j^2}{n}\right)(\text{smaller the better})\\
\mathrm{SNR}_i &= -10\log\frac{1}{n}\left(\sum\nolimits_{j=1}^{n}\frac{1}{y_i^2}\right)(\text{larger the better})
\end{aligned} \tag{9.2}$$

$$\bar{y}_i = \frac{1}{n}\left(\sum\nolimits_{j=1}^{n} y_{i,j}\right)(\text{mean value of response})$$
$$s_i^2 = \frac{1}{n-1}\left(\sum\nolimits_{j=1}^{n} y_{i,j} - \bar{y}_i\right)(\text{variance})$$

where

i	Experiment number
j	Trial number
n	Number of trials.

So the optimum level of design factor will be the level with maximum signal-to-noise ratio.

9.2.2.6 ANOVA Table

Signal can simply determine the optimal value of different process parameters to noise ratio analysis. But this S/N ratio analysis cannot distinguish the reason for various fluctuation of each factor level. Improper experimental conditions or experimental errors might be the cause of this. Therefore, the experimental error cannot be estimated by S/N ratio analysis. Additionally, S/N ratios cannot systematically calculate the differences among the mean values and specify the magnitudes of the factor effects using the same standard.

The analysis of variance (ANOVA) is conducted for identification of the optimum set of process parameters. Response data is used for ANOVA analysis. The most significant process parameter can be identified by calculating the percentage contribution of each parameter on the conversion yield of biodiesel. The percentage of contribution can be calculated using the following equations.

$$\%\,\text{contribution} = \frac{SS_i}{SS_T} \times 100$$

Here SS_i is the sum of the square for ith parameter and SS_T is the total sum of the square of all parameters.

$$\begin{aligned} SS_i &= \sum\nolimits_{j=1}^{3} \left[(SNR_L)_{ij} - SNR_T\right]^2 \\ SS_T &= \sum\nolimits_{i=1}^{4} SS_i \end{aligned} \tag{9.3}$$

9.2.2.7 Maximum Yield Prediction

The theoretical maximum yield of biodiesel can be predicted by using the following equation. The process parameters are taken in optimum condition.

$$Y_o = 10^{\left(\frac{\mathrm{SNR}_o}{5}\right)} \tag{9.4}$$

where

SNR_o	S/N ratio under optimum conditions
Y_o	Theoretical optimum yield.

9.2.3 Harnessing Solar Energy in Biodiesel Production

There are various types of solar collectors available for utilizing the thermal energy of solar irradiation. Selection of solar collector is made on the basis of heat flux and temperature needed. A small reflective parabolic mirror served as the only heat source in the chemical heating during transesterification process. Different types of the solar collector are shown in Fig. 9.4.

9.2.3.1 Mathematical Analysis of Concentrating Solar Paraboloid Reflector

Stine et al. (1985) discussed various design parameters for paraboloid collector. The knowledge of the actual amount of heat required and flux temperature range is necessary to design point focusing solar reflector of paraboloidal shape. The following formula is used for calculating the focal length of paraboloid (Kalbande et al. 2008).

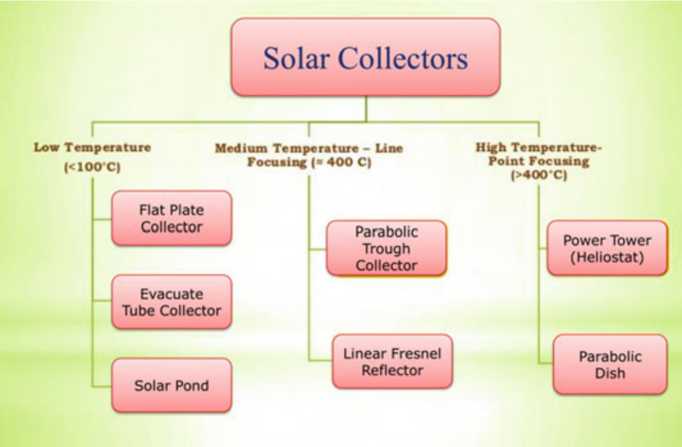


Fig. 9.4 Solar energy in biodiesel production

$$f = \frac{h^2}{4 * R} \tag{9.5}$$

Heat energy falling on the absorber plate at the focal point in reaction time can be determined as (Kalbande et al. 2008).

$$Q_u = H \cdot \rho(\tau \cdot \alpha)_e \alpha \cdot \gamma \tag{9.6a}$$

where

H	Mean insolation per unit area
ρ	Specular reflectance of the reflector
$(\tau\alpha)_e$	Effective transmittance absorptance ratio
α	Absorptance
γ	Intercept factor

The equation for three-dimensional revolution of the paraboloid is determined as:

$$X^2 + Y^2 = 4fZ$$

The rim angle ϕ_{rim} of the solar paraboloidal reflector can be calculated as (Kalbande et al. 2008):

$$\tan\, \varphi_{\text{rim}} = \frac{1}{\left(\frac{d}{8h}\right) - \left(\frac{2h}{d}\right)}.$$

The surface area of the solar paraboloid reflector can be calculated for following formula.

$$AS = \frac{8\pi f^2}{3}\left[\left(\left(\frac{d}{4f}\right)^2 + 1\right)^{3/2} - 1\right].$$

where '*d*' is the aperture diameter, '*f*' is the focal length, and h is the depth of paraboloid. The arc length '*S*' can be given by (Kalbande et al. 2008).

$$S = \frac{d}{2}\sqrt{\left(\frac{(4h)}{d}\right)^2 + 1} + 2f\, \ln\left(\left(\frac{4h}{d}\right) + \sqrt{\left(\frac{4h}{d}\right)^2 + 1}\right).$$

The circumference length of circular aperture for the paraboloid reflector equals to 2πR, and we can determine the concentration ratio for the reflector as follows:

$$CR = \frac{A_a}{A_r} \tag{9.6b}$$

where A_a is the projected area of the reflector, on a plane normal to its axis and A_r is the receiver area. The receiver size is determined after fabrication of paraboloidal solar reflector. When the paraboloid is flattened, it occupies a smaller circumference equal to $2\pi X$ in the paraboloid after fabrication, where X is the aperture radius of the paraboloid. For a symmetric paraboloid, R can be calculated in terms of X as follows:

$$R = X + \frac{X^3}{24f^2}\,\mathrm{cm}.$$

For general conditions, the non-symmetric 'R' would be

$$R = \frac{1}{4f}X(X + 4f)^{1/2} + 4f^2 \log \frac{X + (X^2 + 4f^2)^{1/2}}{2f}.$$

The efficiency of using paraboloid solar reflector for chemical heating in transesterification process can be given as the ratio of heat utilized in transesterification to the total heat received due to solar irradiation.

Efficiency

$$\eta = \frac{m \cdot C \cdot \Delta T}{A_s \cdot \int_o^t I \cdot dt} \tag{9.7}$$

Here, m is the mass of the oil and chemicals used in transesterification and C is the specific heat, ΔT is the temperature change in the oil and chemicals mixture during transesterification. Denominator shows the total heat supplied by solar irradiation during reaction time 't.' A_s is the surface area of paraboloid and I is the intensity of solar irradiation in watt/m^2 (Ouannene et al. 2009).

9.2.3.2 Heat Transfer Mechanism in Solar Assisted Transesterification

Heat energy of solar irradiation is transferred to the mixture of oil and chemicals by four mechanisms. First, by direct solar rays, i.e., sunlight directly strikes the vessel containing oil and alcohol mixture. The second mechanism of heat transfer in transesterification process is by convection in which the hot air surrounding the oil–alcohol mixture inside the vessel. The third mechanism is by conduction in which heat is transferred from the platform on which the container rests. The fourth mechanism of heat transfer to oil–alcohol mixture is reflected by the solar rays from the surface of paraboloid solar reflector (Ouannene et al. 2009).

9.2.4 Conventional Method of Biodiesel Production from Cotton seed Oil

In this work, cotton seed oil is used as the feedstock oil, and methanol and potassium hydroxide (KOH) are used as alcohol and catalyst in the transesterification process. Taguchi approach for optimization of process parameters is also used to make the production process efficient and effective. Free fatty acid content is calculated taking an average value of the FFA content in cotton seed oil is around 0.74 wt%. This value of FFA content is less than 2.5 wt%, so we use alkali base catalyzed transesterification for production of biodiesel from cotton seed oil. Titration process and change of color are shown in Fig. 9.5 (Table 9.6).

9.3 Design of Experiments for Biodiesel Production from cotton seed Oil (CSO) Using Taguchi Method

With four process parameter: molar ratio, reaction time (minutes), reaction temperature (°C), and catalyst concentration (wt%). We use 3-level design in this experiment. Table 9.7 shows the factors and their level.

On the basis of this 3-level 4-factor design, adapt L9 orthogonal array by creating Taguchi design in Minitab 17 software. Table 9.8 shows the possible nine

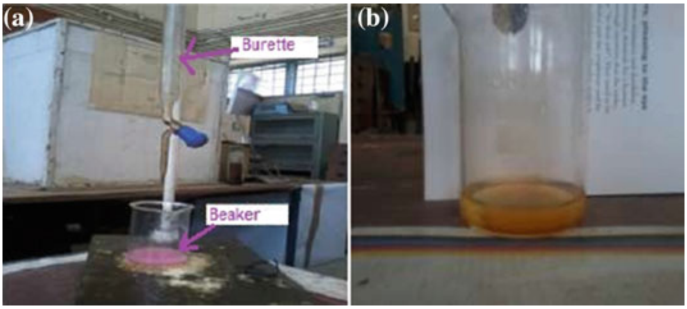


Fig. 9.5 **a** Titration process taking place in beaker; **b** mixture of cotton seed oil and methanol

Table 9.6 Data of FFA content for three samples of cotton seed oil

S. No.	ml used in titration	%FFA
1	1.1	0.79
2	1.0	0.72
3	1.0	0.72

Table 9.7 Process parameters and their levels

Level	Factors			
	Molar ratio	Time (min)	Temperature (°C)	Catalyst conc. (wt%)
1	4:1	30	50	0.50
2	5:1	40	60	0.75
3	6:1	50	70	1.00

Table 9.8 L9 orthogonal array

S. No.	Levels of design for different factors				
	Molar ratio	Time	Temperature	Catalyst concentration	Yield (%)
1	1	1	1	1	90.33
2	1	2	2	2	92.36
3	1	3	3	3	94.60
4	2	1	2	3	94.26
5	2	2	3	1	93.36
6	2	3	1	2	93.21
7	3	1	3	2	96.20
8	3	2	1	3	95.64
9	3	3	2	1	94.12

iterations of experiment as described by L9 orthogonal array along with the corresponding conversion yields of biodiesel found after performing nine experiments.

Taguchi software shows, Tables 9.9 and 9.10, the response table for the signal-to-noise ratio and mean using 'larger-is-better' condition.

From the response table of the signal-to-noise ratios and means, it is understood that conversion yield of biodiesel mostly affected by molar ratio and then by catalyst concentration, reaction temperature, time, respectively. Main effect plots for signal-to-noise ratio and mean data are found using Taguchi approach as shown in Figs. 9.6, 9.7 and 9.8.

Table 9.9 Response table for signal-to-noise ratios (larger-is-better)

Level	Molar ratio	Time	Temperature	Catalyst concentration
1	39.31	39.42	39.37	39.33
2	39.43	39.44	39.42	39.45
3	39.58	39.46	39.53	39.54
Delta	0.27	0.04	0.16	0.21
Rank	1	4	3	2

Table 9.10 Response table for means

Level	Molar ratio	Time	Temperature	Catalyst conc.
1	92.43	93.60	93.06	92.60
2	93.61	93.79	93.58	93.92
3	95.32	93.98	94.72	94.83
Delta	2.89	0.38	1.66	2.23
Rank	1	4	3	2

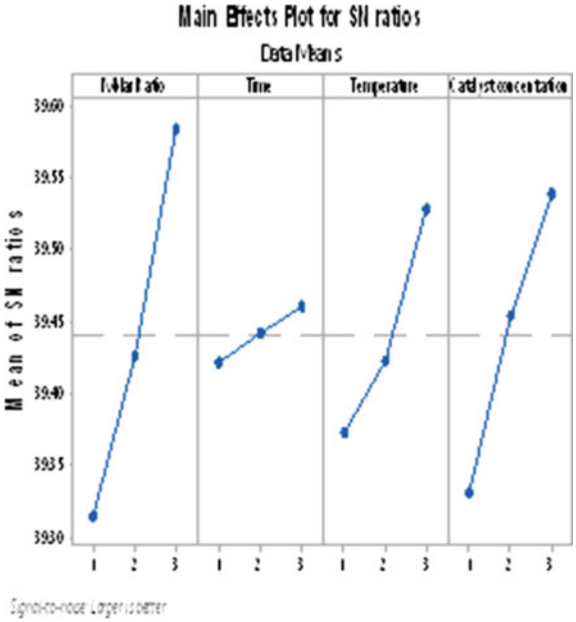


Fig. 9.6 Main effects plot of signal-to-noise ratios with respect to factors

9.3.1 Effect of Molar Ratio on Conversion Yield of Biodiesel

The most important factor, which affects the yield of biodiesel, is molar ratio. The main effect plot generated after application of Taguchi shows that conversion yield increases with increase in oil to alcohol molar ratio from 4:1 to 6:1.

9.3.2 Effect of Reaction Time on Conversion Yield

The conversion yield increases when reaction time increases from 30 to 50 min that shown in Fig. 9.9.

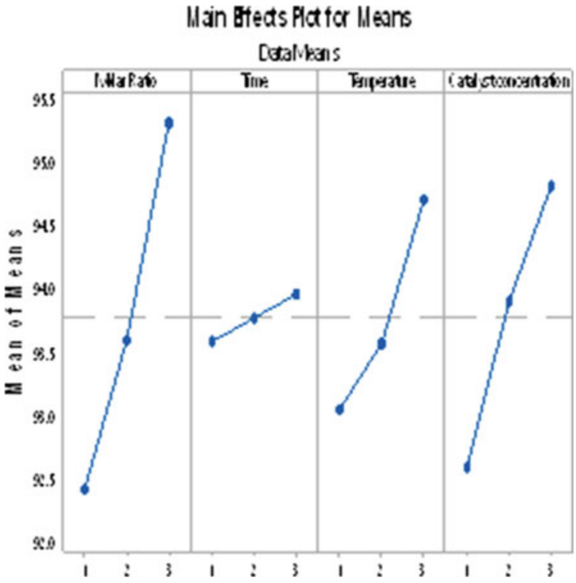


Fig. 9.7 Main effect plot for means

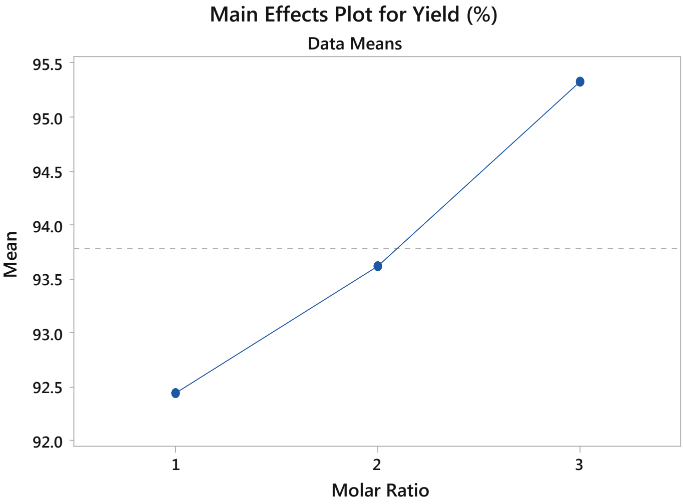


Fig. 9.8 Main effect plot for yield versus molar ratio

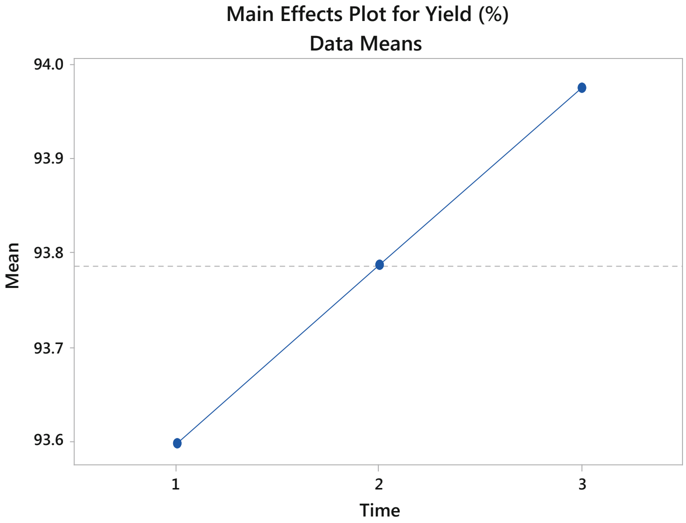


Fig. 9.9 Main effect plot for yield versus time

9.3.3 Effect of Reaction Temperature on Yield

In this experiment, we kept reaction temperature in the range of 50–70 °C. The main effect plot for yield with respect to temperature shows that the conversion yield increases when the reaction temperature is increased from 50 to 70 °C illustrated in Fig. 9.10.

9.3.4 Effect of Catalyst Concentration on Yield

In this experiment, we use KOH as a catalyst in the transesterification reaction. The tests are performed on different wt% of catalyst concentration such as 0.5, 0.75, and 1.0 wt% shown in Fig. 9.11. The conversion yield increases as we increase the catalyst concentration from 0.5 to 1.0 wt%. The reason for less yield in case of 0.5% KOH is that it is not enough to enhance the chemical reaction. It is observed that transesterification reaction does not take place due to an insufficient amount of catalyst concentration. The maximum yield occurs at the level 3.

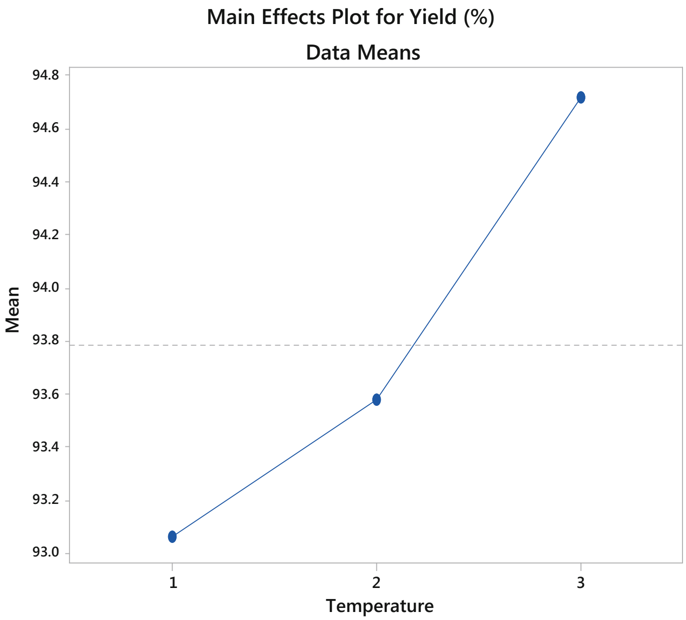


Fig. 9.10 Main effect plot of yield versus temperature

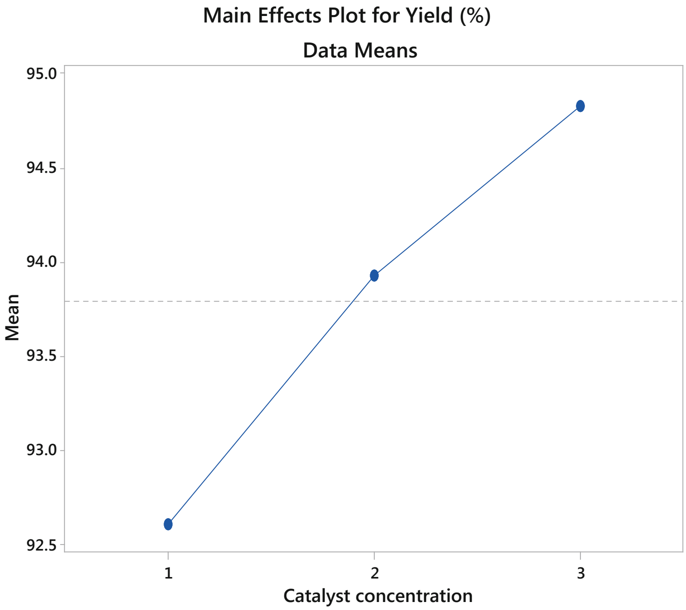


Fig. 9.11 Main effect plot for yield versus catalyst concentration

9.3.5 ANOVA Table

Different parameters affect the conversion yield of biodiesel to a different extent. The relative magnitude of the parameter effects is listed in Table 9.11. A better feel for the relative effect of the various factors is obtained by the decomposition of variance, which is commonly known as analysis of variance (ANOVA). The ANOVA table made by Taguchi software is shown in Table 9.11.

In the present study, the degree of freedom for the error is zero. Hence, an approximate estimate of the error sum of squares is obtained by pooling the sum of squares corresponding to the factors. The larger the contribution of a particular parameter to the total sum of squares, the larger will be the ability of that factor to influence S/N ratio. Moreover, the lower *P* value, the more significant, will be the factor effect in comparison with the error mean square. For the molar ratio, *P* value is very small; hence, it has more contribution in the yielding of biodiesel.

9.3.6 Optimum Conditions

The optimum conditions for all factors in this experiment are at level 3. Hence, the conversion yield will be maximum when oil to alcohol molar ratio is 6:1, the reaction time is 50 min, reaction temperature 70 °C, and catalyst concentration is 1.0 wt%. At this condition, the experiment was performed and the conversion yield was found as 96.58% which is quite higher than the yields obtained at other conditions.

9.3.7 Physiochemical Properties of Diesel and cotton seed Oil Methyl Ester

Table 9.12 depicts that the properties of CSOME (biodiesel) is comparable to the properties of diesel. Hence, it can be used in vehicle with and without making its blends.

Table 9.11 Analysis of variance

Source	Degree of freedom	Sum of squares	Mean of squares	*F* value	*P* value
Molar ratio	2	12.6686	6.3343	3.14	0.116
Reaction time	2	0.2166	0.1083	0.03	0.974
Reaction temp	2	4.3256	2.1628	0.64	0.562
Catalyst conc.	2	7.5434	3.7717	1.31	0.336
Error	0				
Total	8	24.7542			

Table 9.12 Properties of CSOME

Name of properties	Diesel	CSOME
High calorific value (MJ/kg)	42.232	39.5
Density (kg/m^3)	0.831	0.9148
Kinematic viscosity@ 40 °C(mm^2/s)	3.21	18.2
Cloud point, °C	−12	1.7
Pour point, °C	−17	−15
Flash point, °C	–	234
Cetane number	–	41.8

9.4 Experimental Setup

In this experiment, a small paraboloid solar reflector was used which concentrate heat at the platform placed on its focal point. The specifications of the solar reflector are shown in Table 9.13.

The high concentration ratio of parabolic dish collector helps in rapidly increasing the temperature of the oil, alcohol, and catalyst mixture. The condition for the feasibility of this method is that the intensity of solar irradiation should be greater than 400 W/m^2. The objective of this type of setup is to produce biodiesel without the use of any fossil fuels for electricity. The vessel containing oil, methanol, and catalyst mixture should be placed on the platform provided at the focal point of the reflector. The parabolic solar collector is installed in such a way that it concentrates reflected solar rays to the base of the vessel used for transesterification process. The figure of the solar reflector is shown in Fig. 9.12.

The need of magnetic stirrer is omitted in solar assisted transesterification, and the black-painted or thermally conductive vessel is preferred in this experiment.

9.4.1 Design of Experiments in Solar Assisted Biodiesel Production Using Taguchi Optimization Technique

As we have used Taguchi optimization technique in the conventional method of biodiesel production, similarly, we will use a mixed-level 5-factor design for experiments. In this experiment, we are using 4-levels for average intensity of solar radiation while only 2-levels used for other factors are shown in Table 9.14. The

Table 9.13 Specifications of the parabolic dish collector

Diameter of outer ring	1.4 m
Focal length of dish	0.2 m
Dish rim angle	120.5°
Aperture area of dish	1.539 m^2
Concentration ratio of dish	33

Fig. 9.12 Concentrating solar reflector employed in the experiment

Table 9.14 Factors and levels for design of experiments

Level	Factors				
	Intensity of solar radiation (W/m^2)	Molar ratio	Time (min)	Temperature (°C)	Catalyst Conc. (wt%)
1	562	4.5:1	50	60	0.75
2	678	6:1	60	70	1.0
3	750	–	–	–	–
4	813	–	–	–	–

catalyst utilized in this experiment is alkali base catalyst KOH, so transesterification completes in one step and alcohol used is methanol (CH_3OH).

On the basis of this mixed-level 5-factor design, we adapt L8 orthogonal array by creating Taguchi design in Minitab 17 software. Table 9.15 shows the possible iterations of experiment as described by L8 orthogonal array along with the corresponding conversion yields of biodiesel found after performing eight tests.

Based on the design of experiments, according to the above L8 orthogonal array, the mean effective plots for means and signal-to-noise ratios are found as shown in Figs. 9.13 and 9.14.

Table 9.15 L8 orthogonal array

S. No.	Levels of design for different factors					
	Intensity of solar radiation	Molar ratio	Time	Temperature	Catalyst concentration	Yield (%)
1	1	1	1	1	1	89.28
2	1	2	2	2	2	93.46
3	2	1	1	2	2	93.24
4	2	2	2	1	1	93.48
5	3	1	2	1	2	95.20
6	3	2	1	2	1	95.68
7	4	1	2	2	1	96.48
8	4	2	1	1	2	97.28

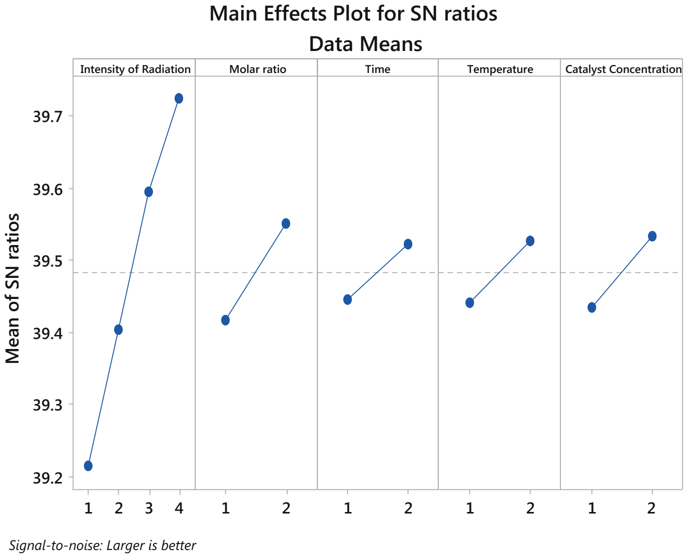


Fig. 9.13 Main effect plot for SN ratio

The main effect plots for the signal-to-noise ratios and means of yield depict that optimum condition for solar assisted transesterification process is A4B2C2D2E2. It means that yield will be maximum if average intensity of solar radiation is 813 W/m^2, oil to alcohol molar ratio equals to 6:1; their action time is 60 min, the temperature is 70 °C, and catalyst concentration equals to 1.0 wt%. On experimenting with these conditions, the conversion yield of biodiesel is found as 97.46%.

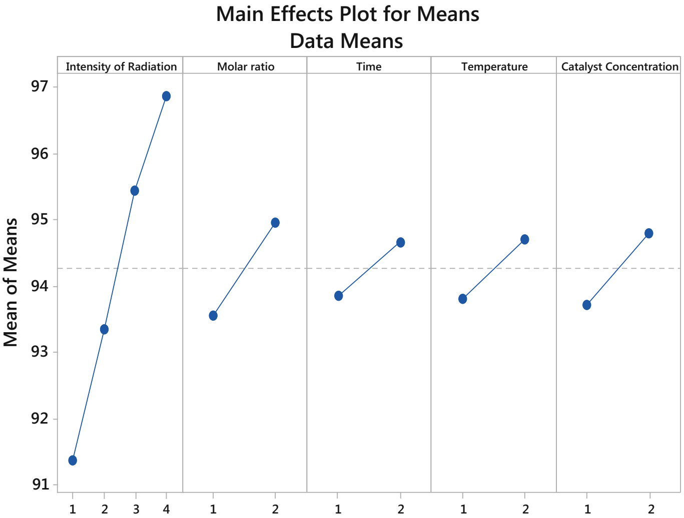


Fig. 9.14 Main effect plot for means

9.4.2 ANOVA Table

The table for analysis of variance (ANOVA) in the case of solar irradiation assisted biodiesel production is shown in Table 9.16.

In the present study, the degree of freedom for the error is zero. Hence, an approximate estimate of the error sum of squares is obtained by combining the sum of squares corresponding to the factors. The larger the contribution of a particular parameter to the total sum of squares, the larger will be the ability that factor to influence S/N ratio. Additionally, for the lower *P* value of a factor, the factor effect will be larger in comparison to the error mean square. For the intensity of solar radiation, *P* value is smallest. Hence, it has the most contribution in the yielding of biodiesel among the five factors.

Table 9.16 ANOVA table made by Taguchi software

Source	Degree of freedom	Sum of squares	Mean of squares	*F* value	*P* value
Intensity of radiation	3	34.838	11.613	5.05	0.076
Molar ratio	1	4.061	4.061	0.61	0.465
Reaction time	1	1.232	1.232	0.17	0.692
Reaction temp	1	1.638	1.638	0.23	0.647
Catalyst conc.	1	2.268	2.268	0.33	0.589
Error	0				
Total	7	44.038			

9.4.3 Experiment Procedure

In this experiment, we require maintaining the flux temperature around 70 °C for one hour. At first, we performed our research at a small level. The cotton seed oil quantity used was just 50 g, and we used other process parameters such as oil-to-methanol molar ratio, reaction time, reaction temperature, and catalyst (KOH) concentration according to the iterations shown by L8 orthogonal array. Steps in this process of solar assisted transesterification are with the help of diagram in following paragraphs and shown in Figs. 9.15 and 9.16.

i. Take 100 g of cotton seed oil and heat up the oil using solar energy to remove the water content present in it.
ii. Then cool the heated oil up to 60 °C in ambient air.
iii. Then prepare a mixture of methanol and KOH in a separate beaker, and after mixing, pour this solution into cotton seed oil.
iv. Transesterification reaction starts after this; we have to maintain flux temperature around 70 °C for one hour to accomplish the transesterification reaction correctly.
v. After completion of transesterification, two layers appear in the beaker. The lower layer is of glycerol which is higher in density and appears as dark brown color. The upper layer is of cotton seed oil methyl ester (CSOME) which is our required product.
vi. Separate CSOME from glycerol using a buret and then purify the crude biodiesel using the water washing process. In this process, warm water (30% of oil quantity at 60 °C) is poured into the crude CSOME and the contaminants of remaining alkali catalyst are neutralized due to water washing process.
vii. The final product is gained by heating the CSOME after water washing to remove remaining water content. Thus, quality of biodiesel production is maintained.

9.4.4 Biodiesel Preparation at Medium Scale Using Solar Energy

To perform solar assisted transesterification at the medium scale, we used Scheffler reflector in place of small solar paraboloid reflector as it can rapidly heat up the oil–methanol–KOH mixture to flux temperature, and then, we maintain flux temperature approximately for 40–50 min. The specifications of Scheffler reflector are shown in Table 9.17.

The advantage of using Scheffler reflector over small parabolic collector is that the reaction time is reduced without affecting the yield too much. In our experiment,

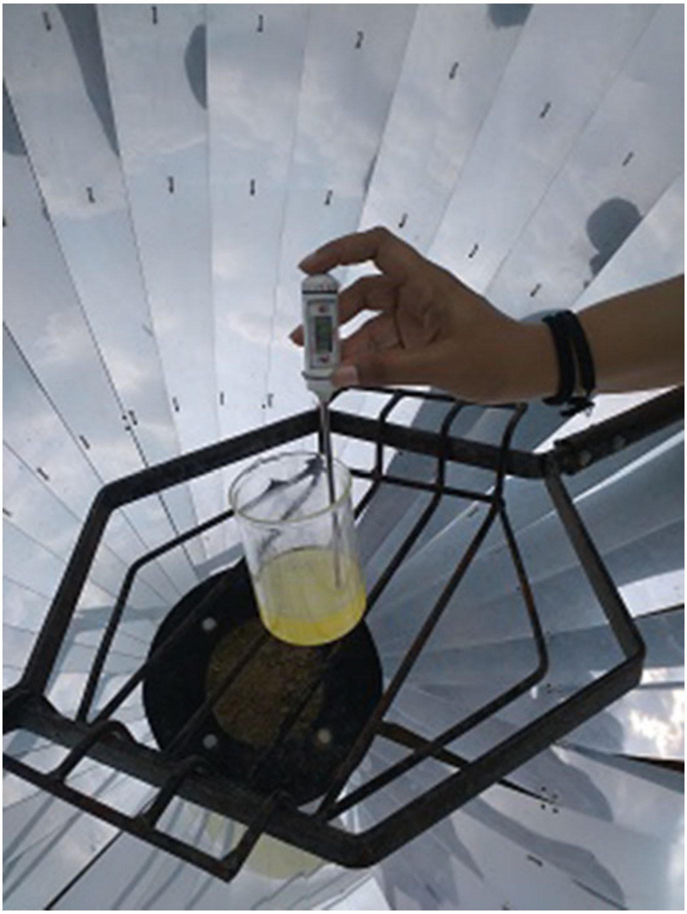


Fig. 9.15 Cotton seed oil used

we use 500 g of cotton seed oil to produce CSOME (biodiesel). The rest parameters are used same as the optimum parameters in case of small-scale production except the reaction time, i.e., oil-to-methanol molar ratio 6:1, reaction temperature 70 °C, and catalyst (KOH) concentration equals to 1.0 wt%. But the reaction time is reduced to around 40 min or less depending upon the intensity of radiation. Figure 9.17 shows the experimental setup of Scheffler reflector. Figure 9.18 shows the crude biodiesel produced after transesterification at medium scale.

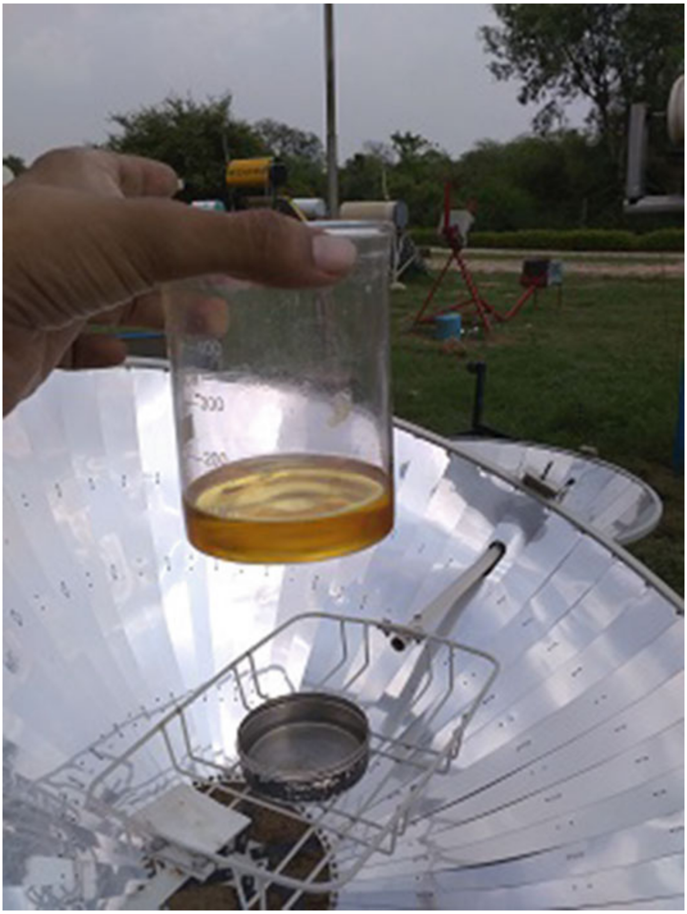


Fig. 9.16 Heating of oil before transesterification

Table 9.17 Specifications of the Scheffler reflector

Major axis	2.2 m
Minor axis	1.6 m
Focal length of reflector	2.45 m
Aperture area of reflector	2.7 m^2
Concentration ratio of reflector	135

Fig. 9.17 Transesterification process using Scheffler reflector

9.4.5 Conversion Yield Calculation in Medium Scale

Cotton seed oil used = 500 g
Methanol quantity = 500/6 = 83.33 g
Catalyst (KOH) amount = 1.0 wt% = 5 g

Amount of cotton seed oil methyl ester (CSOME) produced after transesterification and separation from glycerol = 468 g. Hence, the percentage yield of CSOME (biodiesel) produced = 468 * 100/500 = 93.60%.

Fig. 9.18 Crude biodiesel produced after transesterification at medium scale

9.5 Results Based on the Experiments Done Using Conventional Method of Biodiesel Production

We performed nine experiments using convention method of biodiesel production from cotton seed oil. The conversion yield found from these experiments show that yield was greater for oil-to-the molar ratio 6:1 than in the case of the molar ratio of 4:1 or 5:1. Figures 9.19 and 9.20 show the variation of yield with respect to reaction time at different catalyst concentrations.

Fig. 9.19 Yield versus time curve for molar ratio 6:1 and different catalyst percentage

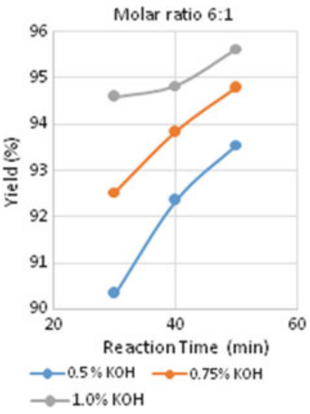
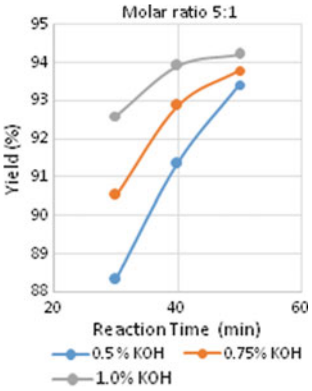
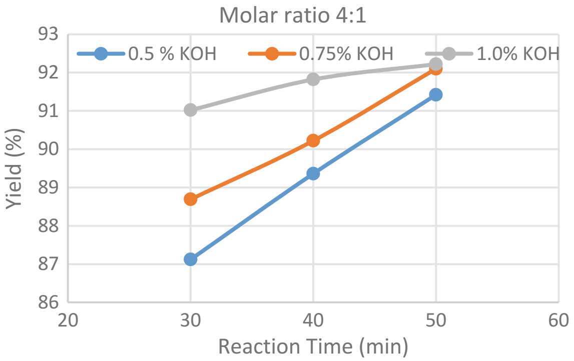


Fig. 9.20 Yield versus time curve for molar ratio 5:1



Figures 9.19, 9.20 and 9.21 show that yield of biodiesel is higher for molar ratio 6:1 and 1.0% KOH concentration. Yield also shows an increasing trend when reaction time is increased from 30 to 50 min.

Fig. 9.21 Yield versus time graph for molar ratio 4:1



9.5.1 Effect of Various Factors on Yield in Case of Solar Assisted Biodiesel Production

In solar assisted biodiesel production, we used five factors in Taguchi optimization, such as average intensity of solar irradiation, oil–to-alcohol molar ratio, reaction time, reaction temperature, and catalyst concentration. So we can see the dependence of yield on these factors as shown in Fig. 9.20.

9.5.2 Effect of Average Intensity of Solar Irradiation

Figures 9.22 and 9.23 show the variation of yield with respect to solar intensity for different concentration of KOH at oil-to-alcohol molar ratio of 6:1 and 4.5:1, respectively. Reaction time and the temperature are kept constant in determining this correlation. Yield increases with increase in solar radiation intensity. Hence, it can be said that yield of biodiesel will be more in the case of solar assisted biodiesel

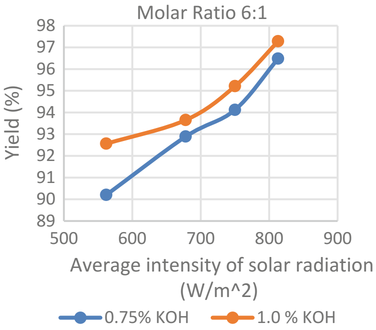


Fig. 9.22 Yield versus average intensity of solar irradiation at molar ratio 6:1

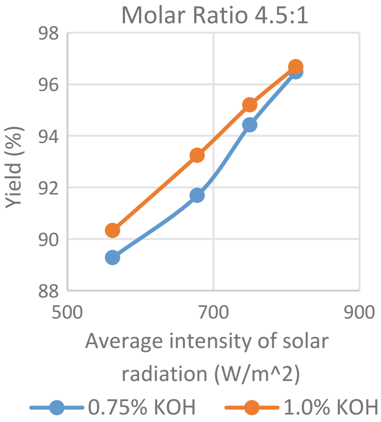


Fig. 9.23 Yield versus average intensity of solar irradiation at molar ratio 4.5:1

production if the experiment is performed when the higher intensity of solar radiation is available. The temperature in the inner beaker needs to be kept around 70 ° C by adding cold water in outer beaker.

9.5.3 *Effects of Reaction Time*

In our experiment of solar assisted biodiesel production, we take readings at reaction times of 50 and 60 min. The better yield is found at 60 min. In this case, the reaction temperature is kept constant at 70 °C, and average intensity of solar radiation is assumed 700 W/m^2. Though yield shows an increasing trend when reaction time is increased from 50 to 60 min, there is a possibility that yield may reduce at certain temperature after 60 min reaction time. So we need to take more reading using higher size orthogonal array using Taguchi approach for optimization of transesterification shown in Fig. 9.24.

9.5.4 *Effect of Reaction Temperature*

The reaction temperature is a significant factor which affects the yield of biodiesel produced. In our experiment, we maintain the mixture at the flux temperature of 60 and 70 °C, respectively. Results show in Fig. 9.25 that better yield is found in the case of 70 °C reaction temperature than in the case of 60 °C.

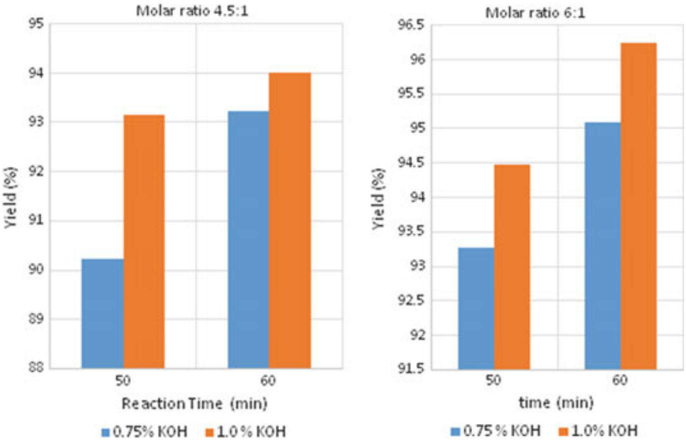


Fig. 9.24 Bar chart of yield versus time at different catalyst conc. **a** For molar ratio 4.5:1, **b** for molar ratio 6:1

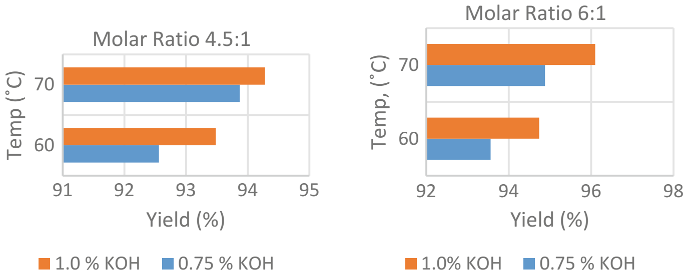


Fig. 9.25 Effect of temperature on yield on different catalyst conc. **a** At molar ratio 4.5:1, **b** at molar ratio 6:1

9.6 Comparison of Yields in Different Methods of Biodiesel Production

Table 9.18 shows the conversion yield of biodiesel at various scales and also for various methods of biodiesel production.

The yield of conventional, microwave assisted, and solar assisted method of biodiesel production in the case when optimum conditions are used in all these processes shown in Tables 9.18, 9.19 and Fig. 9.23. Figure 9.26 demonstrates the comparison of yield at a different scale. The biodiesel conversion through solar assisted method is comparable to the conventional mechanical stirring method. Both at small-scale production and medium-scale production yield are slightly better (Fig. 9.27 and Table 9.20).

Table 9.18 Comparison of yield for various methods at small and medium scale

Method of biodiesel production	Yield at small scale (50 g oil)	Yield at medium scale (500 g oil)
Conventional	96.58	93.2
Solar assisted	97.46	93.60

Table 9.19 Maximum yield of CSOME in various methods of biodiesel production

Technique of biodiesel production	Maximum yield of CSOME at optimum condition (%)
Conventional	96.58
Microwave irradiation assisted	98.12
Solar irradiation assisted	97.46

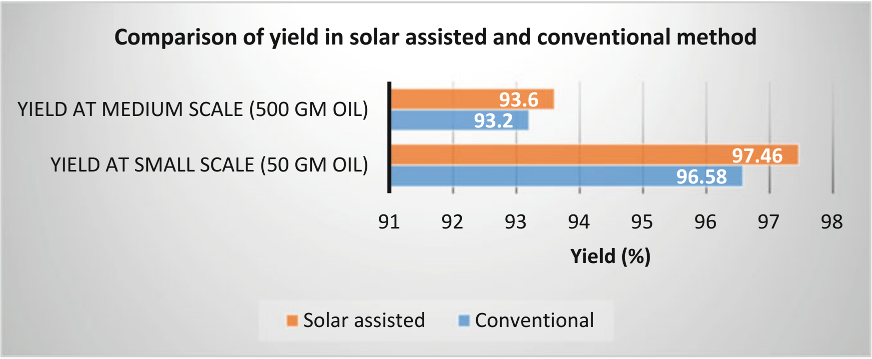


Fig. 9.26 Comparison of yield at different scale

Fig. 9.27 Maximum yield of CSOME in different method of biodiesel production

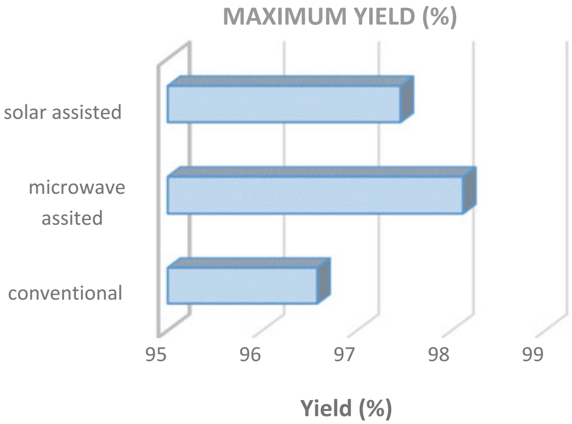


Table 9.20 Properties of biodiesel prepared from conventional and solar assisted method

Properties	Conventional	Solar assisted
Density (kg/m^3)	852	846
Kinematic viscosity (mm^2/s) at 40 °C	6.1	5.9
Higher calorific value (MJ/kg)	41.68	42.05

9.7 Conclusion

In present work, biodiesel is produced using solar energy. It can be concluded that using solar energy for heating in transesterification could be a better option as conventional method of biodiesel production requires heat from electrical sources. Conventional method of biodiesel production is also not so cost-effective that it can be commercialized easily. In solar parabolic reflector setup, the necessary flux temperature is maintained by utilizing the thermal energy of solar irradiations. The main advantage of solar assisted biodiesel production is that the need of magnetic stirrer is skipped. There is no need to stir mixture during transesterification. Also, the conversion yield of biodiesel produced is better than the in the case of the conventional method. So efficiency and quality of biodiesel production become greater. The sunshine should be better at installation location as more than 400 W/m^2 intensity of solar radiation is required for transesterification. In India, Rajasthan, Gujarat, Haryana are the place where the availability of sunshine remains sufficient throughout the year.

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Part IV
Advanced Techniques of Alternative Fuels

Chapter 10
Fuel from Waste: A Review on Scientific Solution for Waste Management and Environment Conservation

Arvind Kumar Bhatt, Ravi Kant Bhatia, Sumita Thakur, Nidhi Rana, Vaishali Sharma and Ranju Kumari Rathour

Abstract Millions of tons of solid wastes are produced as a result of various household, agricultural, and industrial activities around the globe every year, which if not managed and disposed properly can create serious health and environmental issues. At the same time, huge amounts of coal, oil, and natural gas are burnt daily to generate electricity and power to run domestic, workplace, and industrial appliances. The excessive and un-managed use of fossil fuels has not only put pressure on already limited resources, but has also resulted as major contributor of environment pollution. The scientific community has been continuously searching for the renewable and alternate sources of fuel on one hand and an amicable solution to manage the waste on the other hand. These two biggest challenges before the world presently, if diagnosed and managed scientifically, can provide solution to each other by providing clean renewable energy from solid and liquid waste materials. Waste-to-energy technologies physically convert waste matter into more useful forms like bioethanol, biobutanol, biogas, biohythane, CNG, and syngas through various processes such as combustion, pyrolysis, gasification, or biological treatments. The processes like anaerobic digestion and fermentation and combinations of various technologies can be used to tackle the rising demand of energy. Utilizing these wastes would not only provide supply of fuels on sustainable basis but would also be helpful in conserving our environment. The selection of appropriate raw material and efficient technology for biofuel production is of immense importance in order to produce high-quality product with reduced environmental impact. Various aspects of waste utilization through clean renewable source of energy for sustainable development of society are of paramount significance in today's context and need immediate attention.

Keywords Waste management · Biofuel · Energy · Sustainable development
Environment conservation

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10.1 Introduction

The unprecedented population growth, changing lifestyle, rapid urbanization, and industrialization have resulted in various environmental challenges including solid waste management and energy crisis. The solid waste management is becoming the foremost issue in view of the public health and environmental concern especially in most of the developing countries (Buenrostro et al. 2001). A careful management of the waste can limit the damage by finding a viable solution to the waste management problems in a constructive manner. The discarded items can be the useful resources awaiting reclamation by reuse or recycling and converting these into valuable products (Lundström 2007). The latest solution for the waste management has emerged its meaningful utilization for fuel production. The world is already running out of natural fuels because of increasing energy demand which has led to a rise in crude oil prices. In addition, due to high emission of greenhouse gases, conversion of solid waste to fuel has emerged as one of the most suitable way out.

Among various bioenergy sources, solid waste biomass is considered as an attractive energy feedstock due to its abundance and availability (Duku et al. 2011). Among other categories of wastes, biomass from forest, crop residues, and industries has great potential for energy generation. The plant biomass mostly comprises of lignocellulose, i.e., cellulose, hemicellulose, and lignin in the ratio of 3:2:1, respectively (Bhatt 1990; Bhatt et al. 1992, 1994) (Fig. 10.1). Although it is possible to convert all these components into the renewable fuels using different physico-chemical and biological methods, biological conversion using microbial enzymes provides an economical and eco-friendly option (Edward et al. 2008; Bhatt 1990; Sharma 1991; Khan et al. 1986). There is an urgent requirement to make sincere efforts through science and technology to come out with new ways to transform the waste biomass to various products including fuels in order to tackle the issues of waste management. The innovative way of waste management will not only help in the design of new ways for energy generation from the waste, but this also helps to protect the environment from further deterioration and sustainable development.

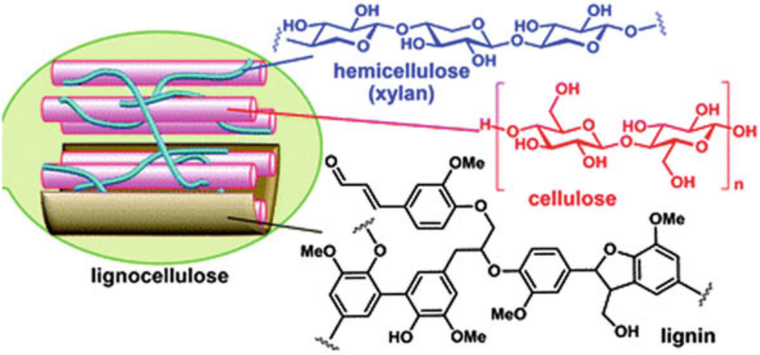


Fig. 10.1 Composition of lignocellulosic biomass (Bhatt 1990)

A variety of wastes are produced as a result of different human interventions which can be broadly classified as biomass and residues, municipal solid waste, and industrial wastes.

Biomass/residues: The lignocellulosic biomass is one of the most economical sources of biomass. Around 220 billion tonnes of lignocellulosic waste which remains unexploited worldwide annually can be utilized for production of energy, chemicals, polymers, and materials (French and Czernik 2010; Ghosh 2016). Lignocellulose is like a packed matrix, which is composed of various polysaccharides, phenolic polymers, and proteins. Among these, cellulose, a glucan polysaccharide, has proved as a main reservoir for the biofuel production (Bridgwater 2003; Cedric et al. 2008). Residues from agricultural practices, forests, and energy crops are the important alternate for food crops which can be used for production of second-generation biofuels. Lignocellulosic biomass can supply about 12.2% of total energy consumption worldwide (Elliston et al. 2015). The conversion of lignocellulosic biomass is very much feasible, but there are several challenges which are required to be addressed in order to move a step further. Bioprocessing of lignocellulosic biomass to the useful products includes several sequential steps: pretreatment, enzymatic hydrolysis, and then finally fermentation (Bhatt et al. 1992, 1994; Sharma et al. 1993, 1996; Hamelinck et al. 2005; Lynd et al. 2005).

Municipal Solid Waste (*MSW*): The waste generated from household activities, shops, hotels, offices, schools, and other institutions is commonly known as municipal waste (MSW). Due to various household and other commercial and institutional activities, approximately 1,27,486 tons of municipal solid waste per day is being generated globally (Sharholy et al. 2007). Energy conversion of MSW can be possible by direct combustion or natural anaerobic digestion in the engineered landfill (Barlaz 1998). Approximately 50% methane and 50% carbon dioxide can be collected from the stored material for use in the gas into internal combustion engines or gas turbines to generate heat after it is scrubbed and cleaned. Aerobic digestion of sewage can produce biogas which is good source of energy. A high-rate anaerobic digester can also be used for the organic fraction of MSW in order to obtain biogas for cooking purpose or electricity generation (Srivastava et al. 2005).

Industrial Waste: The industrial waste constitute the waste produced during various manufacturing processes and generally considered useless. US-EPA has categorized wastes as chemical waste, toxic waste, industrial solid waste, and municipal solid waste. Industrial wastes are a major cause of environmental pollution and health hazard since these are dumped and discharged into the open lands, water sources without treatment which is against the Hazardous Waste (Management & Handling) Rules, 1989. Food industry also produces a large number of residues and by-products such as meat, sugar, juice prod, and processed food to confectioneries. All such wastes can be utilized as source of biomass for energy production through anaerobic digestion (Lundstrom 2007). Few commercial examples of waste-to-energy conversions have been shown in Table 10.1. Pulp and paper industry is one of the highly polluting industries because of the large amount

Table 10.1 Classification of solid waste based upon the source and their types

Urban waste	Industrial waste	Other waste	
		Biomass waste	Biomedical waste
Municipal solid waste • Paper, glass, metals • Synthetic polymers (cables, wires, toys, and plastic goods) • Inert (stones, sand, and pebbles) • Hides and leather discards • Pharmaceutical wastes (tablets, ointments, lotion, etc.), • Rags and Sanitary wares • Kitchen wastes (fruit and vegetable peels, raw and processed food ingredients, etc.) • Sewage—bulk excretory matters (feces and urine) • Body wastes (sweat, oil, nails, dead tissue, saliva, tears, and hairs) • Bath wastes, laundry wastes	**Solid** • Pulp and Paper wastes • Bagasse (sugarcane, bamboo, etc.) • Brine mud • Metallurgical slags • Gypsum • Fly ash • Oil sludge • Synthetic fibers (scrapings of nylon, polyesters, etc.) **Liquid** • Waste oil and oil emulsions • Tarry waste/Heavy metals • Slurries and spent washes • Whey from dairy plants • Alcohol distillery wastes • Molasses • Miscellaneous dissolved organics (synthetics and biologicals)	**Crop debris** (stalks, straws, cobs, husks, oil cakes, shells, pods, etc.) **Livestock** • Wastes (cattle, pig, poultry, and sheep waste) • Abattoir wastes (flesh, bones, organs, blood, etc.) • Bulk forest wastes (wood, stubbles, and humus) • Alternative forest wastes (leaf litters, dead seeds, and spores) • Microbial biomass (algae and bacteria from cultured systems)	• Human anatomical wastes • Animal waste from veterinaries • Laboratory reagents • Discarded medicines and cytotoxic drugs • Body fluids (blood, urine, semen, and saliva) • Surgical wares • Incineration ash • Microbial cultures (pathogens, etc.)

of energy and water consumption in various operative steps (Marshall and Farahbakhsh 2013). Black liquor, which is also a paper and pulp industry product, can be judiciously utilized for production of biogas using anaerobic UASB technology (Misra and Pandey 2005; Chatterjee et al. 2002, 2004; Chatterjee 2012).

Waste Management: Waste disposal and its management are of paramount concern for prevention and minimizing its hazardous effects on mankind and the environment (Ackerman 2000; Couth and Trois 2011). 3-R, i.e., ***R***educe, ***R***euse, and ***R***ecycle are the necessity for present time to minimize the waste and its ill effects. These also help to save the natural resources, energy, and landfill sites (Elliott and Mahmood 2005). Reuse and proper disposal as per the environment conservation and regulation rules can help to reduce the waste burden on the environment and can contribute for a healthier future (Gupta et al. 1998; Vergara and Tchobanoglous 2012).

Reduce: Reduction of waste will need less effort to recycle or reuse the same. Reducing process starts with the prior analysis that what is being used, for what, and how much? (Misra and Pandey 2005). If the purpose and amount is known in advance, it becomes easier to evaluate the reduction value of an item or process which will automatically reduce the waste. Items which have multiple uses are quiet essential to begin reduction. Purchasing actually encourages production which leads to wastage of resources (Chang and Davila 2008). Therefore, this must be always taken into consideration that what is to be consume and also whether it is really needed or not and if needed till what level, so as to minimize wastage.

Reuse: Reusing things is one of the best practices nowadays, e.g., using cellulosic waste for the production of ethanol and then finally the left over slurry or waste can further used for the production of biomethane. Likewise there are immense possibilities of reusing the intermediary or end waste products during industrial processes for value-added products. It also reduces the extra expenditure to be incurred for disposing them off. So reusability must be enhanced as much as possible (Turan et al. 2009).

Recycle: Recycling is transforming the older version to the newer one, e.g., gas generated from biomethanation plant can be used for boilers and similarly the waste from kitchen can again be used for biomethanation. Any item which is a waste can be changed into something useful by bringing some alterations to minimize the waste accumulation (Goel 2008). Collection and sorting of materials is not difficult, but the transportation of sorted material and further transformation are to be tackled with care. Which type of waste material can be converted to new one and whether recycling plants and the industries are willing to unite together to process the waste material through agreements and incentive credits in economical manner are also important (Sharholy et al. 2008). Therefore, the selection of recyclable materials for the desired product, e.g., fuel is of paramount significance.

10.2 Composition of Solid Waste

Data on generation and composition of waste are the key factor for success of waste management. Factors such as culture, economic development, climate, and energy source affect the waste composition. According to data available comparatively low-income countries have the highest contribution in organic waste generation. On other hand, high-income countries contribute majorly in paper, plastics, and other inorganic materials which are the highest proportion of MSW (Kumar et al. 2016). Waste generation rate affects socioeconomic development and economic prosperity of the country or the region to a greater extent. Urbanization, standard of living, and climate have influenced the waste composition because of accumulative industrialization and flying incomes. Therefore, waste quantities and composition are undoubtedly linked to the vitality of economic action and resource consumptions in the waste-generating societies (Amin and Sinha 2000).

Solid waste is mostly classified as organic and inorganic. Composition of waste is largely influenced by factors such as economic development rate, cultural practices, geographical location, energy resources, and also the climatic conditions.

With improvement in the developmental index (wealth and resources wise), consumption rate of inorganic materials (such as plastics, paper, and aluminum) get enhanced and the relative portion of organic matter decreases (Bolaane and Ali 2004). Paper, plastic, glass, and metal fractions increase in the waste stream of middle- and high-income countries, and low- and middle-income countries have a high percentage of organic matter. There is an integrated approach for organic waste which is particularly important in high-income countries (Elliott and Mahmood 2005; Chang and Davila 2008).

10.3 Products from Waste

Utilization of waste and its conversion into value-added product are need of the hour in current scenario. Waste means any organic material apart from primary material for which the process was initiated and plants were originally grown (e.g., corn from maize, wheat straw, paddy straws, any of agricultural, forest or domestic residues or lignin from paper pulping). The products which can be produced from the wastes are of following:

10.3.1 Primary Products

Primary products of waste refer to the production of organic matter directly by photosynthesis or direct utilization of waste for burning as wood, fodder for animals (Demirbas and Balat 2007).

10.3.2 Secondary Products

Secondary products of waste involve biochemical, chemical, and electrochemical conversion of biowaste into value-added products such as biomaterial and chemical, biofuels, biogases.

10.3.2.1 Biomaterials and Chemicals from Waste

Wastes can not only provide fuel and energy, but can also be a source for the production of countless useful biomaterials and biochemicals, e.g., paints, detergents, industrial adhesives, bioplastics, and composite materials (Xu et al. 2008). Conventional biomaterials have been used to build houses and to make clothes since the earliest times. Half of the fibers used in the textile industry come from natural materials such as ramie, cotton, wool, and flax.

Biomass in the form of pulpwood (lignocelluloses) is used to make paper, packaging materials, drugs, antibiotics, biopolymer in paper, pharmaceutical, and plastic industries (Ahmed et al. 2012). There are numerous ways to obtain chemicals from biomass. Natural chemicals, such as polysaccharides, sucrose, triglycerides, and natural rubber, can only be separated from biomass by physical methods. Biochemicals such as cellulose and starch-derivative chemicals, glucose, glycerol, citric acid, and lactic acid can be obtained by chemical modifications and fermentation of natural chemicals. The basic building blocks of petroleum-based chemicals can be produced indirectly from the synthetic gas of biomass gasification, such as sorbitol, amines, and succinic acid (Brown 2003; Cedric et al. 2008).

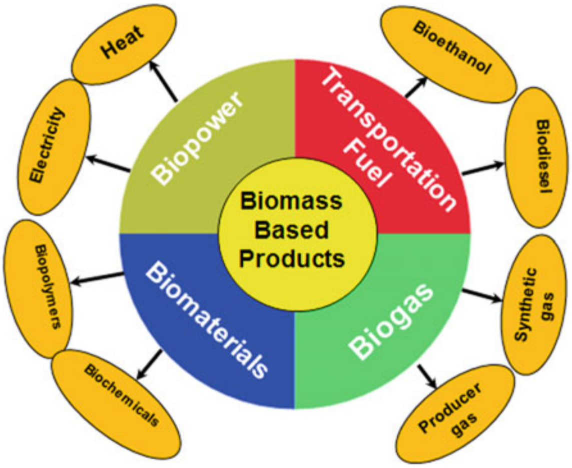
10.3.2.2 Fuel from Waste the Most Valuable Product

Heat and electricity as energy/power have been generated from waste. Most of the waste-to-energy processes generate electricity directly through combustion. Bioenergy (firewood) can be produced directly by burning of biomass, which is the easiest and simplest way to convert waste into valuable product. Heat thus produced can be used for cooking food and to warm homes during winters (Lewis 2007; Conley and Tao 2006). Lignocellulosic biomass can also be transformed into liquid or gaseous fuels and can also be used as transportation fuels. Alkanes, alcohols, and esters are main components of these fuels that can be easily vaporized and burnt in a heat engine. Traditional transportation fuels are gasoline, diesel, or jet fuel. Being non-renewable fossils, fuels can extinct after the available sources are exhausting, and hence biofuels are best alternative to replace these fuels (Nigam and Singh 2010). These alternatives involve conversion of plant biomass to bioethanol and methanol and production of biodiesel from waste and vegetable oils (formerly from oilseed crops) Fig. 10.2. Because of lower detonation requirements, ethanol and methanol are appropriate for spark-ignition engines; this in one hand reduces the engine damage and on another improves the fuel economy. Because of the delayed ignition and characteristics comparable to conservative diesel fuel, biodiesel has been suggested an appropriate option for compression–ignition engines (Peterson and Andrew 2008).

10.4 Types of Fuels

Biofuels can be obtained directly or indirectly from plants, plant products, or their residues a well as from the various organic wastes produced by human beings. Renewable biofuels generally involve the fixation of carbon, similarly, as occur in green plants through photosynthesis. This biomass can be converted to convenient energy-containing substances in three different ways: thermal conversion, chemical conversion, and biochemical conversion. These all different types of biofuels can be classified on the basis of different features which are as follows:

Fig. 10.2 Products from waste



10.4.1 Based Upon the State of Matter

Most of the materials used for burning and on burning produce heat and light are fuels. Based on their physical state, fuels can be classified as solid, liquid, and gas as shown in Fig. 10.2.

10.4.1.1 Solid Fuels

Different solid materials, e.g., wood, charcoal, peat, wheat, rye, coal, hexamine fuel tablets, wood pellets, corn, and other grains can be prickled to release heat, energy, and light by the course of combustion and are recognized as solid fuels (Behandlung et al. 2014). These fuels have been used all through human history to generate fire and are still being used (Hill et al. 2006).

(a) **Wood**: Most common form of fuel in many areas is wood in the form of chips sheets, firewood, charcoal, pellets, and sawdust. It is used for heating and cooking and in condensation engines and turbines to generate electricity. Wood can be used within blast furnace, stove, or fireplace, or outdoors in oven, campfire, or bonfire. Burning of wood produces numerous by-products, both useful (heat and steam), and unwanted, irritating or hazardous (Jared 2005).

(b) **Peat**: Peat is accumulation of moderately decayed undergrowth flora or organic matter that is exceptional to ordinary areas known as peat lands, bogs, mires, moors, or muskegs (Hans and Clarke 2002). Soils comprising of peat are identified as histosols. *Sphagnum* moss (peat moss) is the major constituent of peat, though various other plants can also contribute (Sandrine et al. 2013). In some parts of world, peat is picked and used as an alternative resource of fuel. About 4 trillion cubic meters (5.2 trillion cubic yards) of peat is produced worldwide, covering 2% of total global land, containing around 8 billion Tera joules of energy. Formation of peat is the foremost step in the formation of fossil fuels such as coal (especially low-grade coal, i.e., lignite) (Keddy 2010).

(c) **Coal**: Coal is a black, hard, sedimentary rock, combustible, solid fossil fuel formed from peat. It is primarily made up of 65–95% carbon and also comprises of hydrogen, sulfur, oxygen, and nitrogen (Funk and Wagnalls 1989). Coal is an important component of activated carbon, carbon fiber, and silicon metal used in equipments used for water filtration, air purification, kidney dialysis, mountain bikes, tennis rackets, lubricants, water repellents, resins, cosmetics, hair shampoos, and toothpastes (Richard and Edward 2016). The mining of coal, and its consumption for production of energy and its by-products have serious certain environmental as well as health concerns besides their effect on climate change.

10.4.1.2 Liquid Fuel

Most of the liquid fuels used in present scenario are hydrocarbons which are liquid at room temperature. Hydrogen fuel (for automotive), ethanol, and biodiesel liquid at room temperature have also been classified as liquid fuel. Most of liquid fuels play a significant role in transportation and economy (Edward et al. 2008).

(a) **Petroleum**: Petroleum is a simplest natural fuel. This gelatinous mineral oil, dark greenish brown, igneous fuel, is found deep in earth's crust. It is made up of various hydrocarbons (such as paraffins, cycloparaffins or naphthenes, olefins, and aromatics) and small amount of organic compounds (oxygen, nitrogen, and sulfur). It is slightly denser and harder to some extent than diesel (Livetech 2017). Petrol is more commonly used fuel in cars and motorized equipment (chainsaws and lawnmowers) and has more "explosive" properties than diesel.

(b) **Diesel**: Diesel is the most commonly used fuel for transportation vehicles, with commercial trucks, buses, and modern trains. Artificially, it can be produced from a number of different sources (petroleum, natural gas, biogas, and animal fat). Petroleum diesel, the most common type of diesel fuel, is manufactured from crude oil (Apple et al. 2010).

(c) **Kerosene**: Kerosene is also known as paraffin, domestic heating oil. It is used in entertainment/performance industry, also used by fire-breathers and dancers due to its low flame temperature, especially when burnt in free air (Nicholas et al. 2012; Apple et al. 2010).

(d) **Liquid petroleum gases**: LPG usually called as butane or propane is used as fuel for cooking and domestic heating usages. It is used as a substitute to electric heating in residential areas and workplaces.

(e) **Compressed natural gas**: CNG commonly the methane gas can be stored at a high pressure and used as a replacement for LPG, diesel, and petrol. It is known as supercritical fluid and is safer alternative to other fuels being lighter than air.

(f) **Alcohols**: Alcohols have distinction, the first organic chemicals as produced by humans. Beside ethanol, all other alcohols can be charred as a fuel. Ethanol and methanol as most common alcohols that are extensively used (Weber et al. 2010).

10.4.1.3 Gaseous Fuels

These comprise of fuels existing as gas at room temperature and made by treatment of coal. Fuel gases can be produced from hydrocarbons (methane or propane), carbon monoxide, hydrogen, or their mixture. These gases are main foundation of heat energy or light energy (Table 10.2). Fuel gases are although different from liquid and solid fuels; however, some fuel gases are liquefied for storage or transport (Trainer 2007). Fuel gas is undetected and may pose threat of a gas explosion. To avoid this, some odorizers are added to most the fuel gases. It is used to illuminant fuel, during metallurgical operations, as source of hydrogen gas, laboratory gas, for central heating, incinerators (in steel and glass manufacture), muffle furnaces, retorts (used for coke and coal gas manufacture), etc. (Zevenhoven 2001).

(a) **Natural gas and petroleum gases**: Natural gas is obtained from mines dug in the oil-bearing regions and is generally associated with petroleum deposits. It is primarily composed of methane. Natural gas is sometimes pooled with hydrogen to form a mixture known as HCNG.

(b) **Biogas**: The rising prices and non-reusability of fossil fuels have forced the mankind to think about an alternative process. Biogas produced by anaerobic conversion of wastewater, agricultural waste, and sludge to gas has emerged as a one of the technological alternatives (El-Mashad and Zhang 2010). It is metabolically produced by methanogens and acidogenic bacteria in the absence

Table 10.2 Different fuels and their calorific value (Weber et al. 2010)

	Fuel	Calorific value (Kcal/kg)	Applications
Solid fuels	Wood	2500	Household purpose
	Peat	3500	Industries
	Lignite coal	3000	Thermal plants
	Bituminous coal	7500	Thermal plants
	Anthracite	8500	Thermal plants
Liquid fuels	Gasoline	11,200	Aviation fuel
	Kerosene	11,100	Household
	Diesel	11,000	Vehicular fuel
	Petrol	10,500	Vehicular fuel
Gas fuels	Coal gas	7630	Industries
	Coke oven gas	5100	Industries
	Producer gas	1200	Industries
	Blast furnace gas	970	Industries

of oxygen, at a pH range of 6.5–7.5 and at temperature psychrophilic (10–25 °C), mesophilic (35–45 °C), and thermophilic (45–65 °C) within 10–30 days depending on the type of waste material used. The anaerobic digestion occurs preferably in mesophilic range. Biomass can be transformed into a gaseous from by a process called gasification (pyrolysis). Biogas, i.e., carbon monoxide and hydrogen, can be directly used in vehicles as a replacement of gasoline with a filtering and cooling treatment (Qiaoa et al. 2011).

10.4.2 Types of Fuels on the Basis of Reusability

On the basis of reusability, fuels can be categorized as non-renewable and renewable. The detail of these types of fuels is as given below.

10.4.2.1 Non-renewable Fuels

Non-renewable or restricted resources cannot be renewed or replenish itself in short period of times. They are present in limited quantity due to the fact that it takes for them to be replenished by carbon-based, organically derived fuel (Eisenberg and Nocera 2007). Organic material is converted into fuel (oil/gas) by heat and pressure treatment. Non-renewable resources like earth minerals and metal ores, fossil fuels (coal, petroleum, and natural gas), and ground water are virtually needed to be conserved (Kamat 2007).

(a) **Fossil fuels**: Fossil fuels are the resultant products of transformation of organic matter (plant and animal part) which remained trapped in the earth's crust layers of sediments for decades. The organic matter (usually plants) has rotten and compressed for long time and forms fossil fuel sums. The materials thus produced are highly flammable and can be used as ideal energy sources. Usually recovered through drilling or mining, these fossil fuels are known to produce large amount of energy (Paul et al. 2009). Fossils are formed by anaerobic decomposition of dead and decayed organisms which contain large amount of carbon (Hodgson 2008). Petroleum, coal, kerosene, propane, and natural gas are frequently used by-products of fossils. Fossil fuels produced from volatile materials having low carbon include methane, liquids like petroleum as non-volatile materials composed of pure carbon like anthracite coal (Novaczek 2000). Fossil fuels are major source of energy. All fossil fuels are non-renewable, but not all non-renewable energy sources are fossil fuels. Various advantages and disadvantages of non-renewable fossil fuels are listed in Table 10.3.

The world energy consumption is increasing day by day; as per past records, it is doubling in every fourteen years. However, the reservoirs of fossil fuels are estimated to be extinct in next few decades. Therefore, there is urgent necessity to look

Table 10.3 Advantages and disadvantages of non-renewable fuels (Bilkadi 1992; Ball et al. 1965; Rashad 2007)

Non-renewable fuels	
Advantages	Disadvantages
• Provide large amount of energy and are low cost	• The withdrawal of non-renewable sources of energy and their by-products cause harmful effect to the environment
• Generate large amount electricity to fulfill the need of global needs	• Burning of fuels releases nitrous oxides and sulfur dioxide gases to environment which are responsible for photochemical pollution and acid rain
• Transportation is relatively easy through pipelines	• The burning of fossil fuels increases the levels of carbon dioxide, responsible for global warming
• Natural gas is a clean green energy fuel, extremely efficient, and widely used for heating, cooking, and various other day-to-day activities	• Burning of coal generates large amounts of ash which pollutes the environment
• Coal and petroleum are used in the fire steam engines which facilitated the industrial revolution	• Odors of natural gases (hostile) cause irritation, and their transportation is also problematic
• Coal was used in furnaces to melt metal ore • Semi-solid hydrocarbons burned in ancient times are presently used for water proofing and embalming	• Use of crude oil which contains toxic chemicals causes environmental pollution and is hazardous to mankind

for sustainable alternatives of biofuels which are renewable and efficient besides being environment-friendly.

10.4.2.2 Renewable Biofuels

Renewable fuels are more efficient than conventional fuels because they produce less carbon and very less amounts of greenhouse gases and are sustainable (Xu et al. 2008). The geopolitical complications related to the use of these fuels are also of greater interest, particularly to industrialized countries who desire independence from Middle-Eastern oil. Advantages and disadvantages of renewable fuels have been summarized in Table 10.4.

(a) **Hydrogen fuels**: Hydrogen gas (H_2) which is used as a source of energy or an energy carrier is referred as hydrogen fuel. These fuels, considered as a green power sources for the twenty-first century, can make the “hydrogen economy” a reality (Cheng et al. 2007). Hydrogen fuel can be produced biologically as well as through chemical routs (Veziro and Barbir 1992). Hydrogen gas can also be produced from agricultural and forest waste biomass by two processes, i.e., gasification (conversion of biomass into flammable gas) and pyrolysis (similar

Table 10.4 Advantages and disadvantages of renewable fuels

Renewable fuels	
Advantage	Disadvantages
• With the increasing demand of biofuels, these are expected to become cheaper in future as well	• Production is expensive
• Generally, require less preservation and maintenance than conventional fuels. Capital investment of biofuel production is fairly low and can match the present demand	• For biofuels produced from crops, crops need fertilizers, have harmful effects on environment and water sources as they contain nitrogen and phosphorus
• Most of the sources (manure, corn, switch grass, soybeans, waste) are renewable and can be used again and again, thus making these biofuels more efficient	• Large amount of water is required to irrigate the biofuel crops and thus impose stress on local as well as on regional water resources, if not managed wisely
• Being produced from cheapest feedstock hence are cost-effective	
• Since these are made up of renewable resources, cause less pollution and release lower levels of CO_2 on burning	
• Form a self-sustaining system as their production generates carbon dioxide as a by-product	

to gasification suitable for fuel-cell applications). Algae are another important resource for biological production of hydrogen fuel. During late 1990s, it was revealed that if algae are devoid of sulfur, they will lead to production of hydrogen under standard photosynthesis thus providing rich source of energy (George 2007).

(b) **Biofuels**: Biofuel produced by contemporary biological processes has emerged as an attractive, economically viable plant-based solution to meet the energy demands which can be effectively used in the current scenario. Biofuels are produced by transformation of biomass into suitable energy-containing substances by thermal, chemical, and biochemical conversion, resulting in solid, liquid, or gas form of fuel (Cedric et al. 2008). Biofuels can be produced by the process of photosynthesis from plants, agricultural and forest residue, commercial, domestic and industrial wastes and also involved in carbon fixation (Ghosh 2016). Most commonly used biofuel is bioethanol or biodiesel which are mixed with gasoline and used as an alternative fuel for transport vehicles.

10.4.3 On the Basis of Their Generation

On the basis of generations, biofuels can be categorized as first, second, third, and fourth generations. The detail of these types of fuels is as given below (Fig. 10.3, Table 10.5).

Fig. 10.3 Classification of fuels

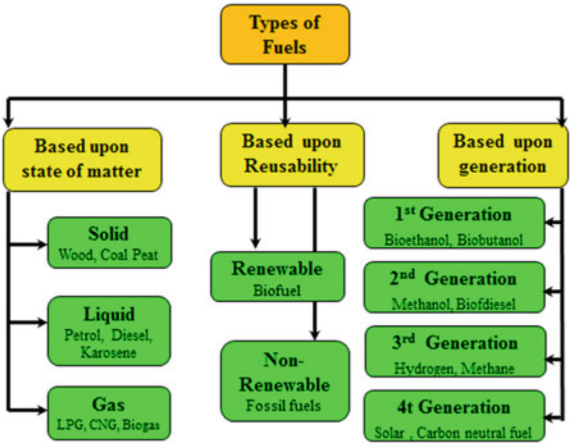


Table 10.5 Different types of renewable/biofuels

Sr. No	Fuels	Substrates
First-generation biofuels		
1	Bioethanol	Starch from wheat, corn, sugarcane, molasses, and potatoes
2	Biopropanol	
3	Biobutanol	
4	Biodiesel	Oils and fats (animal fats, vegetable oils, nut oils, oleaginous microbes, and algae)
5	Biogas	Methane from waste crop material
Second-generation biofuels (*lignocellulosic material*)		
1	Methanol	Non-edible plant material/wastes
2	Dimethyl-furan	Made from fructose present in fruits and vegetables
3	Biodiesel	Waste from pulp and paper manufacturing
Third-generation biofuels (*biowaste and algae based*)		
1	Hydrogen	Traditional crops, oilseeds, water-deficit crops
2	Acetone	
3	Methane	
Fourth-generation fuels (*solar-to-fuel*)		
1	Solar fuels	Solar energy, CO_2 crops
2	Carbon capture and storage	

10.4.3.1 First-Generation Biofuels

These biofuels are made up of sources like sugars, vegetable oil, starch, and animal fats, e.g., bioethanol, biodiesel, biogas. These fuels have limitations such as lower production/yield, and they are unable to produce in adequate supply frightening food supplies and biodiversity by diverting use of food crops for biofuels. Many first-generation biofuels are cheaper than existing fossil fuels (Evans 2008; Mohr and Raman 2013).

10.4.3.2 Second-Generation Biofuels

These fuels, also recognized as advanced biofuels, can be produced from numerous types of biomass and material of plant as well as animal origin, e.g., biomethanol and biodiesel. Second-generation biofuels can help in resolving the problems associated with first-generation fuels and can provide affordable, sustainable, and environmental-friendly supply of fuel (Peterson and Andrew 2008; Schenk et al. 2008; Carriquiry et al. 2011).

10.4.3.3 Third-Generation Biofuels

These biofuels include hydrogen, acetone, and methane considered as viable alternative energy sources and derived from microalgae are devoid of the major shortcomings, encountered with first- and second-generation biofuels (Nigam and Singh 2010; Tseng et al. 2016).

10.4.3.4 Fourth-Generation Biofuels

Biofuels which can be obtained using non-arable land and do not require the destruction of biomass, e.g., electro fuels have been kept in this category. These are either created by using petroleum like hydroprocessing, advanced biochemistry, or innovative processes like solar-to-fuel methods.

10.5 Biofuel Production

A number of biofuels can be produced from a variety of biomass which helps to balance the demand and supply of transportation fuels while simultaneously maintaining the economic sustainability. Currently, two major technologies for the conversion of biomass into biofuels are available: (A) biochemical conversion technology and (B) thermochemical process. The choice of the conversion technology is largely dependent on the type of feedstock used as raw material, the desired end product of the process, environmental considerations, and economic sustainability and security (Araujo et al. 2017).

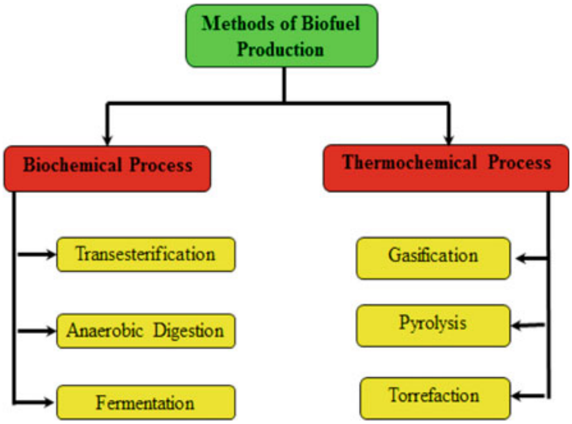
10.5.1 Biochemical Pathway

Three different types of biofuels (bioalcohols, biodiesel, and biogas) are mainly produced from lignocellulosic and oil waste via biochemical processes. This involves three main processes (Fig. 10.4).

10.5.1.1 Transesterification

Biodiesel, a biodegradable, non-toxic, and alternative transportation fuel, having similar properties to conventional diesel fuel can be produced by transesterification of animal fats, vegetable, and cooking oils (Boza et al. 2009). Waste oils and fats represent the most potent source for its production but have yet to be commercialized on an industrial scale in most of the countries. Prior pretreatment to remove the impurities like free fatty acids (FFA) before it can be utilized as a feedstock, it is essential for the success of technology (Aransiola et al. 2014). However, certain advantages are also associated with the use of waste oil and animal fats for biodiesel production, e.g., (a) no extra land input required, (b) free supply of waste oil is available through various food industries, and (c) being biodegradable and does not threaten the food chain. Biodiesel production process involves the reaction of triglycerides (glycerin backbone to which three fatty acids are attached) with an alcohol (methanol or ethanol) in the presence of a suitable catalyst which may be an enzyme, alkali, or acid to form fatty acid methyl esters (biodiesel) and glycerol (Zabeti et al. 2009). After the transesterification, these two layers of biodiesel get separated from each other. Being heavier than biodiesel, glycerol gets settle down to the bottom which can be sold to various food, cosmetics, and oleo-chemical industries (Gnansounou et al. 2016) (Fig. 10.4).

Fig. 10.4 Biofuel production



10.5.1.2 Anaerobic Digestion

Biogas, a mixture of different gases (mainly biomethane and carbon dioxide) is produced by anaerobic digestion of different agricultural residues, sewage, animal, food processing, and other biodegradable wastes to increase the efficiency and sustainability of waste-to-energy concept. It is a well-established and flexible technology of fuel production. Biogas produced from anaerobic digestion process can be used on both domestic (for cooking purpose) and industrial scale (as renewable transportation fuel: LNG and CNG). Meanwhile, it can also be used for generation of electricity in a gas engine (Chynowetha et al. 2001). In this process, the organic matter present in the biomass is converted into a mixture of methane, carbon dioxide, and small amount of other gases like hydrogen sulfide and siloxanes by anaerobic microorganisms in the absence of oxygen. Biogas has high energy content and is considered to be a clean form of renewable energy as it releases no net carbon dioxide into the atmosphere, i.e., it is carbon neutral (Mata-Alvarez et al. 2000). The inorganic matter left in the anaerobic digester after biogas production can be used as fertilizer for agriculture. Increased biogas production has also been reported using lignocellulosic residues like corn and rice straw, when subjected to enzymatic and chemical pretreatments (Gunaseelan 1997).

10.5.1.3 Fermentation

A metabolic process of chemical breakdown of sugars to acid, gases, or alcohols by microbial action is known as fermentation. Bioethanol is the most common first-generation conventional fuel prepared by fermenting sugar extracted from starch-laden edible crops. However, the current scenario of dwindling fossil reserves, depletion of world's energy supply, and increase in the food prices have necessity of the large-scale production of conventional biofuels in the energy sector (Khan and Dwivedi 2013). Therefore, an inevitable attempt is required to find the alternate and cost-effective reason for production of biofuels. In this context, the use of various sugar-rich lignocellulosic feedstocks is gaining global attention as a promising approach for sustainable development and world energy security (Saha et al. 2014). The biochemical route of bioethanol production comprises of enzymatic hydrolysis and fermentation of pretreated of lignocellulosic biomass. During the past two decades, a significant amount of research has been done on the use of alternative fermentation and product recovery techniques for biofuel production. Although lignocellulosic plant material represents a valuable and renewable source of fermentable sugars for ethanol production, the crystallinity of cellulose, presence of lignin, porosity, and particle size hinder the enzymatic hydrolysis of cellulose and hemicelluloses present in the biomass (Chiaramonti et al. 2012). Various pretreatment methods have been investigated over the years by different researchers to improve the digestibility of the lignocellulosic feedstock for maximizing the yield of monomeric sugars from the biomass macrostructure and making it easily accessible for the enzymatic hydrolysis step (Klinke et al. 2004). Various pretreatment methods have been proposed, developed, and utilized including physical pretreatment (dry or wet milling of biomass), physicochemical pretreatment, viz. steam explosion, liquid hot water pretreatment, ammonia fiber explosion, and chemical pretreatment including alkaline pretreatment and dilute acid hydrolysis and a combination of different pretreatment technologies (Khan et al. 1986; Bhatt 1990; Bhatt et al. 1991, 1992; Sharma et al. 1993, 1996). The choice of pretreatment technique for a particular raw material depends on several factors, such as patterns of sugar release and enzymes employed. Thus, the composition of substrate, type and dosage of pretreatment, and efficiency of the enzymes used for the hydrolysis have a great influence on digestibility of biomass; although the individual impact of these factors on the enzymatic hydrolysis is still not clear (Alvira et al. 2010).

The main purpose of hydrolysis is the effective utilization of the lignocellulosic biomass. This is achieved by disruption of cell wall physical barriers and splitting of the polymeric and crystalline lignocellulosic material to produce readily fermentable monomeric reducing sugars (pentoses and hexoses) that are subsequently fermented to produce ethanol (Bhatt et al. 1992; Dale et al. 1996; Fujita et al. 2004; Berlin et al. 2005). Cellulases and xylanases are used for the hydrolysis of cellulosic and hemicellulosic portion of the biomass, respectively. Utilization of hemicellulases and other accessory enzymes needed for complete degradation of lignocellulose components has become an important issue. Recent studies have revealed the importance of new balanced enzymatic complexes containing optimal combinations to effectively modify the complex structure of lignocellulosic materials.

The fermentable sugars (both hexoses and pentoses) obtained after the pretreatment and hydrolysis of lignocellulosic biomass are subjected to fermentation by microorganisms under controlled pH and temperature conditions to enable their conversion to ethanol (Agbogbo and Coward-Kelly 2008). A number of yeasts have the ability to ferment pentose sugars into ethanol; *Scheffersomyces stipitis, Pichia segobiensis, Candida shehatae, Pachysolen tannophilus,* and *Kluyveromyces marxianus* can directly ferment xylose into ethanol (Bhatt et al. 1992; Den et al. 2007), while *Saccharomyces cerevisiae* is mainly used for bioethanol production from hexose sugars. Two different strategies for the production of ethanol, i.e., separate hydrolysis and fermentation (SHF) and simultaneous saccharification and fermentation (SSF), have been successfully utilized (Elliston et al. 2015). In SHF, enzymatic hydrolysis (saccharification) of polysaccharides and the microbial fermentation are performed sequentially in separate units while in SSF, enzymatic hydrolysis and microbial fermentation are carried out in one step and sugars released are immediately consumed by the fermentative microorganism for ethanol production technology (Walter et al. 2011). Recently, consolidated bioprocessing (CBP) technology has been developed where cellulase and xylanase production, pentose and hexose sugar hydrolysis, and fermentation can be performed in a common reactor using one or more microorganisms.

10.5.2 *Thermochemical Process Technology*

Thermochemical biomass conversion technology involves the production of biofuels under conditions of extreme temperature and pressure in comparison to biochemical route. The technology consists of following different steps.

10.5.2.1 Gasification

Gasification is more cost-intensive process and involves the partial oxidation of organic material (having <20% moisture content) at high temperature (>700 °C) into syngas, the highly combustible mixture of carbon monoxide (CO), hydrogen (H_2), and carbon dioxide (CO_2) (Molinoa et al. 2016). Syngas can be burnt directly or in a fuel cell or can be used for the production of synthetic fuels like Fischer–Tropsch liquids (FTL), dimethyl ether (DME), and various alcohols such as methanol, ethanol, and butanol. In addition, it can also be used for the generation of electricity via gas engines and turbines.

Production of liquid fuel is not well established commercially (Patra and Sheth 2015). Mixed alcohol fuels are produced catalytically by passing clean syngas over a catalyst while ethanol and butanol are produced by microbial action through fermentation of the syngas. FTL is a mixture of low molecular weight hydrocarbons which is produced by reacting carbon monoxide and hydrogen in the presence of catalyst (iron/cobalt/ruthenium) at a temperature range of 150–300 °C (Puig-Arnavat et al. 2010). DME also known as methoxymethane is a colorless, inert, and non-toxic gas which is obtained by the dehydration of methanol present in the syngas and can ultimately be converted into liquid fuels with application of slight pressure (Wang et al. 2015).

10.5.2.2 Pyrolysis

Pyrolysis involves the thermochemical decomposition of lignocellulosic biomass under high temperatures (350–550 °C) and pressures in the absence of oxygen resulting in gaseous or liquid products (bio-oil) and ash (Bridgwatera 2012). In this method, the biomass is heated at high temperature for short duration of time generally less than 2 s (Demirbas and Balat 2007). A range of biomass including wood waste, agricultural residues, animal waste, and manures can be used as feedstock for bio-oil production which after removal of certain impurities can ultimately be used as fuel in engines, boilers, and turbines (Chen et al. 2013). The fast pyrolysis process results in higher yields and efficiency.

10.5.2.3 Torrefaction

Torrefaction is carried out at temperature range of 200–320 °C in the absence of air under atmospheric pressure which decomposes the complex lignocellulosic biomass mainly into biocoal which in turn can be used efficiently in coal-fired power plants. Alternatively, the torrefied biomass can be utilized as a sustainable feedstock for production of liquid fuels to be used in transportation sector (Onuegbu et al. 2012; Smith and Ross 2016).

10.6 Cost Economics of Biofuel

The global efforts to find new sustainable and economically viable options to diminishing fossil reserves have increased the worldwide production and consumption of biofuels. Furthermore, efforts have also been made to mitigate problems related to greenhouse gas emissions due to the combustion of fossil fuels which have direct bearing on global warming and climate change. Therefore, to meet the increased energy requirements and combat serious environment concerns, many countries have made blending of biofuels with the fossil-based fuels to be used in the transportation sector mandatory (de Gorter and Just 2010). This has also resulted in rise in the food prices as most of the commercial first-generation biofuel technologies use food-based crops for fuel production. Therefore, more emphasis has been given to the production of biofuels from sustainable and reliable non-food resources. It has been reviewed that biofuel production has a considerable impact on food prices globally and may be considered as a critical factor governing the economic viability. It is believed that the economic consideration of biofuel production technology is necessary for the commercial production of fuels (Hill et al. 2006).

Biofuel production cost has been estimated to be 3 times in comparison to the petroleum fuels. The cost of biofuel production is influenced by multiple factors such as the type of feedstock, land requirement, labor cost, government subsidies, transportation and distribution costs, and by-product credits. Operational cost varies depending on the plant process, production scale, and site of production. Among these, cost and availability of the biomass feedstock used for biofuel production is the major parameter representing about 80–90% of the product cost (Haas et al. 2006). Further, discerning attention has to be paid on land and water requirements because they are equally important factors to consider as they need extra capital investment, for instance, large quantity of water is required especially for the cultivation of feedstock alone.

Therefore, use of waste as a raw material for biofuel production will promote technologic development because it has a low water footprint as well as will open new doors to access energy services (Keeney and Hertel 2009). But the use of lignocellulosic biomass needs an extra pretreatment step in order to efficiently utilize the potential of this feedstock, i.e., physical, chemical, and biological treatment. However, these methods pose an additional cost on fuel production. Further, in some cases, detoxification step is also required to remove the toxic compounds formed during the pretreatment step which otherwise inhibits the microbial fermentation process resulting in decreased yield and productivity of biofuel (Lambert et al. 2016). Thus, the main challenge lies in finding robust microorganisms which can utilize all the fermentable sugars present in the biomass to produce biofuel even under adverse conditions. This can be achieved by technological interventions including genetic engineering of the fermentative microorganism but it although beneficial itself is an extra investment and will add to the overall cost (Ragauskas 2006).

Biofuel production is also accompanied by the formation of some by-products which are generally regarded as beneficial for overall process (Behandlung et al. 2014). The quality and nature of such coproduct depends on the type of biofuel produced, e.g., glycerol (by-product from biodiesel manufacture) which is used in food, cosmetics, beverage and pharmaceutical industries, and oil cakes used for animal feeds (coproduct of oilseed crushing). These coproducts of biofuel production process can contribute modestly in maintaining the economic viability standards with subsequent reduction in the cost of biofuel production (Moschini et al. 2012).

Since the cost of biofuel production is the key factor for development and use of advanced biofuel technologies, the overall operation must be financially stable and efficient enough to produce a cost-competitive and economically viable product in the market. The major challenges of commercial production of biofuel, specifically cost of raw material, logistics, technological problems, transportation cost and lower product yield besides cost intensive downstream processing need to be addressed properly. Therefore, serious techno-economic analysis is required to find an economically viable technology of biofuel production (Jorgensen et al. 2007; de Gorter and Just 2010).

10.7 Bottlenecks of Biofuel Production

Technology, bioethical, and socioeconomic factors of biofuel production are important assets to be considered under the present scenario of renewable energy use. Some of the major bottlenecks that are being faced by the biofuel refineries to commercialize large-scale production of microbial fuels (Fig. 10.5) have been discussed below:

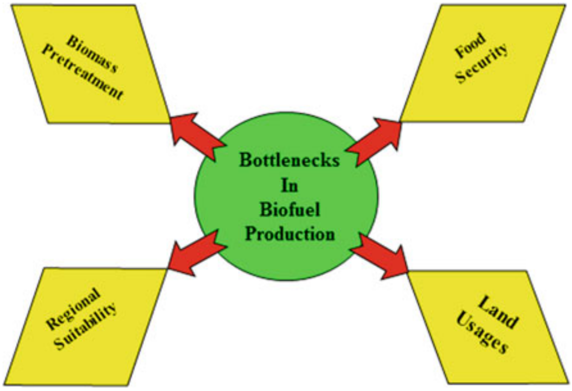


Fig. 10.5 Major bottlenecks in biofuel production

10.7.1 *Land-Use Practices*

One of the major challenges associated with the production of biofuels is the land-use changes which are mainly specified by (a) loss of habitat since more and more land would be used for the cultivation of biofuel feedstocks which may destroy habitat for various species of plants and animals, causing a negative effect on biodiversity, (b) less availability of land for food production, and c) increased carbon credits and greenhouse gas production mainly because of deforestation, thereby reducing the overall health of an ecosystem (Kamp and Forn 2016). In this context, the non-food-based waste feedstock for biofuel production offers remarkable advantage which will minimize pressure on land.

10.7.2 *Food Security*

The biofuel production resulted in increase in food and feed prices and the shortage of food supply has started serious “food vs fuel” debate. The increased demand of biofuels has diverted the cultivation of crops mainly for fuel production instead of food which leads to the inflation in food prices resulting in food insecurity especially in the developing countries (Koizumi 2015). Most of the well-established and commercial biofuel technologies use the major food crops as raw material, e.g., the USA has the world’s largest corn-based bioethanol industry while sugarcane is mainly used in Brazil for bioethanol production which is a matter of serious concern. Studies have shown that when corn was diverted for fuel use, there was an increase in the price of corn-based products like tortilla in Mexico as there are many more such examples which need to be addressed on priority. Substantial attempts and research should be focused on the development of biofuels from non-food resources to reduce the food gap (Urffyon 2007).

10.7.3 Regional Suitability

Most of the first-generation biofuel feedstock is grown on regional basis. For instance, some crops may be cultivated well in one region while they may not perform better in the other. Some 1G biofuel feedstock like corn and soybean require fertile land for their cultivation which may be achieved by the use of certain nitrogenous- and phosphorous-containing fertilizers (Asif and Muneer 2007). But the extensive use of fertilizers in biofuel production is also questionable because of various serious health and environment issues arising due to the dissemination of these into the environment and water bodies. Also, some of the feedstock requires large quantity of water which again puts an extra pressure on water reserves especially in the dry areas (FAO 2011).

10.7.4 Biomass Pretreatment

Pretreatment of lignocellulosic biomass accounts for approximately 33% of the total production cost because of the fact that pretreatment is accompanied with the formation of certain undesired by-products that are inhibitory for biofuel production and decrease the overall yield and productivity of the process (Yang and Wyman 2008). Screening and use of highly resistant microorganisms may provide an effective and more sustainable approach for fuel production which may be achieved by metabolic engineering or other methods of strain improvement. But again the use of genetically modified organisms is debatable and remains controversial because of their serious ill effects on public health, biodiversity, environment, and food supply chain (Banerjee et al. 2010).

10.8 Future Prospectus of Biofuel Production

The dramatic expansion in the global biofuel production suggests a long-term future of biofuels. It is evident from the fact that demand for the alternate form of renewable energy will continue to rise mainly due to massive population growth, climate change, and environment concerns, besides exhausting fossil reserves (Dutta et al. 2014). Growing market potential of biofuels especially in transportation sector has made biofuels an interesting candidate for a sustainable future in terms of energy security and sustainability (Demirbas 2009). Factors like reduced fossil oil dependence and foreign imports, dwindling fossil reserves, economic and environment growth, reduced GHG emissions, and economic development are needed to be taken into consideration to assess the future prospects of biofuel production. It also stimulates the rural development by reducing poverty through employment generation which further strengthens the future expansion of biofuel industry (Viikari et al. 2012). The growth of biofuels is also dependent on certain government policies and subsidies and also on the extent of mandatory biofuel blending in conventional transportation fuels.

The use of the lignocellulosic biomass, and oil and animal waste as the main feedstock for the commercial production of biofuels can be tested to meet the energy needs to a greater extent. The crops used as raw material can also be grown on wastelands which are not suitable for farming thus requiring no extra land inputs (Walter et al. 2011). Use of biotechnological and computational tools can be applied to combat the problem associated with the use of these wastes for fuel production. Integration of different processes like rigorous screening for potent microbes and continuous efforts for their improvement including development of more stable recombinant microorganisms through genetic engineering certainly help us. Utilizing the waste as feedstock for fuel production, encouraging domestic farming which is less labor and cost intensive, and employment opportunities for rural stakeholders can provide a sustainable solution as alternative to fossil reserves without disturbing the environment (Hill et al. 2006). Additionally, continuous R&D efforts for production of fuels from wastes undoubtedly offer tremendous prospects for the management of waste disposal problem as well as meeting the global energy crisis and other environmental issues.

10.9 Conclusion

It can be concluded that biofuels can provide technological solution for longer reduced dependences on conventional fuel and lose the potential to progressively replace fossil fuels as global transportation fuel besides minimizing greenhouse gas emissions. However, an inevitable endeavor is required for the development of robust and low-cost technologies of fuel production which could be achieved by utilizing waste from different sectors including agriculture, household, and industries. Huge amount of leftover plant biomass and used oil and fats generally regarded as “waste” offers a promising option for their conversion into value-added products mainly biofuels. This will also help in providing social security to the youths by proving employment especially in the developing countries besides a positive control on agricultural prices.

Proper processing and reuse of waste materials could be a valuable practice from both environmental and economic view point which on one hand will reduce their effect on environment, human health, or local community, while on the other will help combat the environmental issues by addressing the problem of waste accumulation in the environment. Further, agricultural by-products and waste materials will reduce pressure on available crops as food resources, but will provide additional profit to the farmers in rural areas. Thus to conclude, biofuel production from waste biomass can not only provide a techno-economic, renewable, and alternative solution to fossil fuels but will also help to manage the waste, safeguard on environment, and help to keep our citizens healthy for longer.

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Chapter 11
Thermochemical Conversion of Biomass to Bioenergy: A Review

Krishnendu Kundu, Ayoma Chatterjee, Tamashree Bhattacharyya, Madhuka Roy and Ajit Kaur

Abstract Increasing global energy demand is being substantially contributed by the bioenergy sector. For the rural communities, bioenergy provides opportunities for social and economic development by improving the waste and other resource management. The contribution of bioenergy proves to be significant in terms of maintaining social, economic as well as environmental health, ensuring energy security. Biomass, when converted to bioenergy, may undergo different suitable processes. Thermochemical conversions are no exception. The process technologies include combustion, torrefaction, pyrolysis, and gasification. All these processes having the common backbone of thermal decomposition are optimized by different factors and yield specific products of different states such as solid, liquid, and gases. The characteristics of generic types of reactors used to carry out such processes are described with their special features, advantages, and disadvantages. Though researches have called for three types of possible biomass for conversion such as lipid, sugar/starch, and lignocellulose in the present chapter, conversion of lignocellulosic biomass feedstock is focused. It has been discussed how the variations in composition of biomass at optimized process flow differ the quality and quantity of potential product yields.

Keywords Thermochemical conversions · Biomass · Bioenergy
Combustion · Torrefaction · Pyrolysis · Gasification · Bio-char
Bio-oil · Syngas

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11.1 Introduction

Long history of civilization had put forward the use of various biomass sources for generating energy and fuel. There is very low utilization of biomass fuels due to exploration of nature's relatively inexpensive, conventional fossil energy which is easy to handle and convenient to transport and contains high energy content. However, due to the strong energy crisis, need for sustainability, sharp escalating price, environmental issues global interest have been again shifted to renewable alternative sources of fuels. Renewable alternative energy provides many options and different routes for sustainability and freedom in energy sector. Here, bioenergy along with biofuel certainly can solve various societal needs of clean energy and challenges associated with them (Lee et al. 2012).

11.1.1 Biomass

Biomass in a broad sense refers to various materials originated biologically and which can be used for energy content or the chemical counterparts. The word "recent" is of logical significance, as it separates it from fossil fuels from prehistoric origin. Thus, biomass includes all type of biology from agricultural, forestry, algal sectors as well as wastes from manufacturing units including food and beverage effluents, manures, sludge, organic fractions or by-products from industry as well as households as given in Table 11.1. Biomass can also be defined as the solar energy which has been captured and stored from photosynthesis of growing plants. The carbon from the atmosphere is utilized at the time of photosynthesis and is again returned to the atmosphere for decomposition or combustion, thus creating a circle system. This system is also referred as "carbon neutral" system as a balance is maintained leaving zero impact on amount of atmospheric carbon.

According to the report of IEA 2008, biomass played a significant role in global energy consumption, as 285 EJ for the year 2005. Potential biomass supply has also been modeled at regional and national levels under a variety of assumptions, including economic drivers. Thus, Bailey et al. (2011) recommended that the entire

Table 11.1 Biomass sources and types

Types	Sources		
	Forests	Agriculture	Wastes
Woody	– Whole-tree chips – Bole chips – Mill chips	– Short-rotation woody crops	– Industrial – Construction – Municipal
Non-woody	Nil	– Sugar/starch – Lipids – Crop residues – Perennial crops	– Oils, fats, and grease – Livestock waste

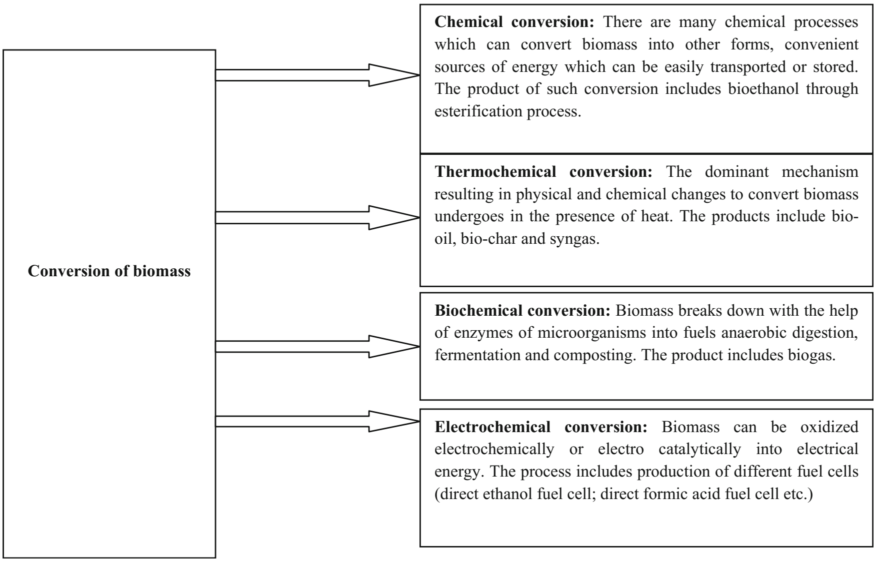
value and supply chain of advanced biofuel need to be carefully planned as well as managed for limited negative impact on human livelihoods.

11.1.2 Bioenergy

The energy derived from biomass fuel along with metabolic by-product yields is termed as bioenergy. Bioenergy has immense potential to meet the renewable energy demands for the future (Ward et al. 2013). India has now shifted much of its concern for the growth of bioenergy to fulfill the demands of improved living standards, economic, and industrial expansions, population growth, etc. Although India is considered as a leading bioenergy sector, still the basic needs for energy for millions of citizens are at high risk. The native resources of energy in India are not enough to meet the demand and that is why the country is still dependent on energy imports, creating a serious imbalance in energy supply demand. Research and development in the field of bioenergy may lead to a permanent solution to the problem and as hoped for.

11.1.3 Conversion Routes of Biomass to Bioenergy

Biomass conversion to bioenergy can be classified into different pathways according to the decomposition reactions and factors relating it. The major types of conversion pathways are shown in Fig. 11.1 with their important features.



Chemical conversion: There are many chemical processes which can convert biomass into other forms, convenient sources of energy which can be easily transported or stored. The product of such conversion includes bioethanol through esterification process.

Thermochemical conversion: The dominant mechanism resulting in physical and chemical changes to convert biomass undergoes in the presence of heat. The products include bio-oil, bio-char and syngas.

Biochemical conversion: Biomass breaks down with the help of enzymes of microorganisms into fuels anaerobic digestion, fermentation and composting. The product includes biogas.

Electrochemical conversion: Biomass can be oxidized electrochemically or electro catalytically into electrical energy. The process includes production of different fuel cells (direct ethanol fuel cell; direct formic acid fuel cell etc.)

Fig. 11.1 Conversion routes of biomass

11.1.4 Thermochemical Conversion

Thermochemical conversions are processes that are carried out in the dominant presence of heat and at times also with a catalyst and higher pressure gradient, much faster than biochemical processes (in the range of a few seconds, minutes, or hours) to produce high-valued hydrocarbons. The process is less feedstock specific or even mixed feedstock can also convert for single pathway. The process involves multiple stages converting a solid biomass into oil or gases. The conversion pathway can be subdivided into four important alternative processes which have been found efficient for conversion of biomass to bioenergy such as combustion, torrefaction, pyrolysis, and gasification. These pathways are further elaborated in the rest part with factors responsible for the entire process flow, the reactors and machineries involved and the products yield at each process.

11.2 Combustion

Combustion or burning or incineration is an exothermic, thermochemical, or redox chemical conversion process taking place in between an oxidant (mostly atmospheric, like oxygen) and reductant (fuel) producing mainly a mixture of gaseous compounds (smoke), flame, and heat. It is often referred to be much complicated sequence of elementary radical reactions It is a common practice to combust biomass and other materials as a commercial basis in order to provide heat and power. Also, new technologies are rising for a wide range of waste incineration to reduce its volume and hazardous characteristics as well as generation of heat and electricity. The reductant or organic fuel when reacts with the atmospheric oxidants, heat is evolved, when the weak double bonds of oxygen break to form carbon dioxide (CO_2) or water as it releases more amount of free energy, though initially heat may be needed to start the reaction. Researchers found that for per mole combustion reaction of oxygen molecule, approximately 418 kJ of heat energy gets evolved. Some industries have been found to incinerate or combust biomass waste by following process shown in Fig. 11.2.

11.2.1 Combustion of Biomass

Around 11% of the world's primary energy is being supplied by combustion of biomass. Combustion is useful in several ways:

- For daily heat consumption
- For community level heating applications
- Industrially for heat as well as electricity production in form of combined heat and power (CHP)
- For pulp and paper industry
- Processing of sugarcane.

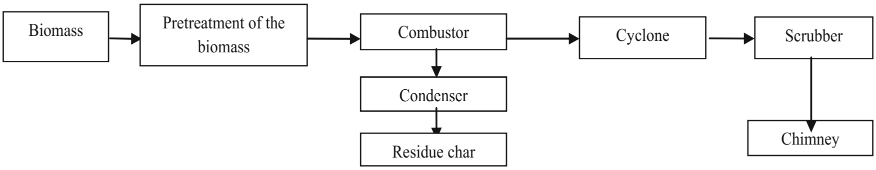


Fig. 11.2 Flow diagram of combustion of biomass

Different variety of biomass is used for each of above application depending on their local availabilities. Preferably, lignocellulosic fiber (straw, wood, nut shells, stalks, etc.) is used as source of biomass. According to Ralph P. Overend 2003 (National Renewable Energy Laboratory, Golden, Colorado, USA), during combustion of biomass released CO_2 is photosynthesized by plants which maintain equilibrium in the atmosphere. However, combusting the fossil fuels increases the CO_2 storage in atmosphere leading to environmental crisis such as global warming. The additional elements present in the harvested or wild biomass sources like nitrogen, potassium, phosphorus, sulfur, chlorine; essential for biological systems for respiration and growth; creates additional challenges for the internal structure of burner and transfer surfaces for heat in form of fouling, deposition, slagging, and corrosion. Depending upon the process quality and emission control system, the biomass as fuel can either be cleaner like natural gas or maybe polluting as coal.

11.2.2 Phases of Combustion

There are mainly three phases by which solid biomass residues (agricultural or forest wastes, etc.) undergoes the reaction of combustion.

11.2.2.1 Preheating Phase

In preheating, biomass is heated first to its flash point and then to the fire point. In this process, flammable gases can also evolve.

11.2.2.2 Gaseous or Distillation Phase

Flammable gas evolved from preheating mixes with oxygen and gets ignited. The energy is produced in form of luminance and heat, with visible flames.

11.2.2.3 Solid or Charcoal Phase

In the end, the gases are no longer capable of causing further ignition of the biomass fuel, and the un-burnt residues form char or charcoal.

Table 11.2 Important features of the common combustors (The Asian biomass handbook 2008)

Methods	Apparatus	Features
Fixed bed combustion	– Dumping grate – Water cooling grate – Inclined or horizontal grate	– Level or sloping grate – Surface combustion of the biomass – For use in batch furnaces of small type to yield ash from biomass
Moving bed combustion	– Step grate – Louver grate – Reverse and forward moving grate	– Grate is divided into two zones as combustion and post-combustion zones – Grate is found moving slowly – Ash deposition can overload the grate thus may be avoided – Applicable to various fuels ranging from chip to block type
Fluidized bed combustion	– Bubbling and circulation fluidized bed	– Sand used as bed material which helps in thermal storage and heat transmission – In a furnace, sand and fuel are kept at boiling state and a high pressure – Suitable for high-moisture fuel
Rotary hearth furnace combustion	– Kiln furnace	– High-moisture fuel combustion preferred – Restricted to fluidity and the size of fuel
Burner combustion	– Burner	– Finly powdered masses are burned mostly

11.2.3 Types of Combustion

Combustion can be categorized according to some literature, but these types are still in debates (The Asian biomass handbook 2008). Different types of combustors are used for this process (Table 11.2).

11.2.3.1 Complete Combustion

Reactants burn in oxygen to produce limited products mainly oxides. Though the process involves simple oxidation, it is moreover temperature dependent.

11.2.3.2 Incomplete Combustion

Incomplete combustion of biomass can happen due to insufficient presence of oxygen or an abrupt heat sink in the system. This type of oxidation causes formation of hazardous gaseous particles in atmosphere.

11.2.3.3 Smoldering

Smoldering is a slow form of combustion which is flameless or incomplete. During interaction of oxygen and condensed-phase fuel surface, heat is generated and smoldering is sustained. It occurs as a heat-generated decomposition at a temperature lower than the volatile fuel component's ignition temperature. Some solid matters have the capability to sustain this type of reactions, for example, wood cellulose, coal, tobacco, cotton, humus, synthetic foam, etc.

11.2.3.4 Rapid Combustion

This type of combustion can also be termed as "explosion" accompanied by large amount of heat and light energy release. The general phenomenon of "fire" is the common term used for rapid combustion.

11.2.3.5 Spontaneous Combustion

This type of self-heating process takes place due to heat generation caused by internal exothermic reactions and after that the thermal runaway, rapid temperature rise and finally ignition.

11.2.3.6 Turbulence

Externally fed combustion process used mainly at industrial applications for better mixing of the fuel with oxidizer. The working procedure of gas turbines and gasoline engines is based on this principle.

11.2.3.7 Microgravity

This process is influenced by gravitational state and buoyancy of the reductant. Studies related to microgravity help in understanding the various aspects relevant to the spacecraft environment as well as to the terrestrial conditions.

11.3 Torrefaction

Torrefaction is a thermochemical process which involves drying and incomplete pyrolysis where biomass is subjected to thermal heating in absence of air, typically in temperature range of 200–300 °C at atmospheric pressure, reason why also termed as isothermal pyrolysis (Tumuluru et al. 2011). The term "torrefaction" is derived from roasting process of coffee beans performed at low temperature in oxygenic condition. The similarity lies in the mechanical effect which is same for torrefaction on biomass as for the coffee beans. Torrefaction is also called as mild pyrolysis as it is conducted under similar conditions as pyrolysis which occurs at temperature ranging from 350 to 650 °C. Although, torrefaction differs from pyrolysis process where:

- Purpose of torrefaction is to retain the maximum solid mass yield along with enabling its energy content to be conserved and incomplete removal of volatile matters (Matali et al. 2016).
- Torrefaction reduces the hydrogen and oxygen contents in bio-solids as a result which releases less smoke and water vapor during its combustion (Pimchuai et al. 2010).

11.3.1 Components of Biomass

The process of torrefaction improves the biochemical, physical, and chemical properties of biomass. The thermal treatment temperature and time greatly influence the chemical and physical characteristics of biomass. The variation in formation and functioning of cells, combination of cells to form a tissue and then to a tissue system results in the complex structure of plant body. The plant cell wall is usually flexible, tough and gives support to the structure, which provides protection from stress of thermal and mechanical level. The major components of primary cell wall are—hemicellulose, cellulose, and pectin. The outer part of primary cell wall mainly consists of cutin and wax which together makes the plant cuticle layer. Secondary cell wall mainly consists a wide range of polymers that make up the physical and chemical properties of cell wall. The polymer includes—cellulose, xylan—which is a type of hemicellulose, a complex phenolic polymer named lignin and structural proteins.

11.3.2 Reactions Involved

11.3.2.1 Cells and Tissues

At a temperature range of 100–150 °C, the wall of cell shrinks and the volume of pore size decreases; this leads to changes in structure of cells and tissues.

11.3.2.2 Hemicellulose

Hemicellulose degradation starts at 150 °C, varying with its chemical nature and bond with internal lignin. Major decomposition reactions occur at temperature range of 200–300 °C. This results in a range of non-condensable and condensable products.

11.3.2.3 Cellulose

Cellulose degrades at a temperature between 240 and 350 °C giving levoglucosan and anhydrous cellulose. The crystalline structure resists the thermal depolymerization of cellulose as compared to hemicellulose. The amorphous part of cellulose contains water of hydration which holds free water. Thus, the structure of cellulose is ruptured by vaporization of water when exposed to thermal stress. During depolymerization reaction, polymer restructuring occurs in cellulose but lower than that of hemicellulose. Also, the acids and water released during depolymerization of hemicellulose are responsible for thermal degradation of cellulose.

11.3.2.4 Lignin

Lignin is highly branched, amorphous in nature and is cross-linked polyphenolic resins. It is present in spaces between other components in the cell wall. Lignin is aromatic and hydrophobic character, which degrades at a temperature range between 280 and 500 °C and produces phenols by cleaving the ether bonds and breaking the carbon–carbon bonds. However, since lignin is more difficult to dehydrate, its most of the part gets converted to char.

11.3.2.5 Organic Extractable

Organic extractable includes waxes, proteins, alkaloids, pectins, mucilages, gums, terpenes, phenolics, resins, simple sugars, glycosides, starches, essential oils, and saponins. The amount of these extractables present differs from biomass to biomass. Thus, location and quantity of biomass extractables decide the devolatilization behavior.

11.3.3 Process of Torrefaction

The parameters influencing the process of torrefaction are

- Residence time
- Absence of oxygen
- Heating rate
- Feedstock moisture
- Flexible feedstock
- Ambient pressure
- Gas flow rate
- Reaction temperature
- Feedstock particle size

Biomass feedstock is initially dried so that 15–10% of moisture is retained. The mechanism of the reaction, its kinetics, time for the process at a specific heating rate is mainly influenced by the particle size of the feedstock. To obtain the energy dense hydrophobic biomass fuel, the duration of the process is adjusted. The process duration can vary from some minutes to many hours. For example, Felfri et al. (2005) studied that wood briquettes when torrefied for 0.5, 1, and 1.5 h at 250 °C, the higher heating values increased from 20.0 to 21.2, 22.1 and 22.7 kJ kg^{-1}, respectively. The particle heating rate in torrefaction process must be less than 50 °C/min.

Based on Table 11.3, at 50–150 °C, i.e., the nonreactive drying range, the biomass loses moisture and shrinks as a result of which the porosity in biomasses decreases. Although, at this temperature range, cells may have the ability to retain its structure if rewetted and most of the chemical constituents remain intact. At higher range, i.e., 120–150 °C, the biomass becomes suitable for densification by softening of lignin, which acts as a good binder. At 150–200 °C reactive drying range temperature, the bond between carbon and hydrogen breaks and thus lipophilic extractives and compounds are emitted by the degradation due to heat. Then the permanent type of structural deformation occurs. Bergman and Kiel (2005) concluded that the hemicellulose depolymerization produces short-condensed polymers with secondary structures. The higher temperature leads to destructive drying range, i.e., 200–300 °C which represents the range of torrefaction process. As this temperature, maximum inter- and intra-molecular hydrogen bonds and the C–O, C–C bonds are disrupted resulting in formation of hydrophilic extractives, alcohols, ether, carboxylic acids, aldehydes, and gases like carbon monoxide (CO), CO_2. Due to this, the structure of cell is also completely destroyed by destruction of fibrous nature of biomass and it then becomes brittle. Also, during torrefaction, mass loss predominantly results due to the process reactions occurring at the temperature range as mentioned in the table above. Hemicellulosic xylan, however, decomposes at around 250–280 °C. The decomposition of lignin occurs very slowly, but it gradually increases when at about 200 °C. The behavior to thermal decomposition of individual biomass greatly depends on whole integrated structure. According to Bergman (2005), further increase in temperature >300 °C causes extensive carbonization and devolatilization of polymers. Degree of torrefaction can be indicated by the color change in the raw material. It indicates that the biomass turns brown to black at 150–300 °C mainly due to the changes in chemical compositional. By this, even the impurities, namely ash, bark, or other foreign material can also be indicated.

Table 11.3 Parameters affecting torrefaction

Temperature (°C)	Time (minutes)	Reactions	Yield (%)
50–150	30–120	Drying of nonreactive type (moisture is removed and structure changes)	~90–95
150–200	30–120	Reactive drying (removal of moisture and damage of structure due to collapse of cell wall)	~90
200–300	<90	Drying of destructive type a. Depolymerization and devolatilization of cellulose b. Depolymerization and softening of lignin c. Devolatilization and carbonization of hemicellulose	~70

11.3.4 Reactors of Torrefaction

Table 11.4 compares the performances of some common torrefaction reactors available in market, describing their key advantages and disadvantages.

Chemical, physical, and storage-related properties of biomass change due to the release of volatiles. Condensable and non-condensable product emission from biomass depends upon temperature of torrefaction, its rate of heating, time for heating, moisture content of biomass, and composition of biomass. If the moisture content is high, the surfactants like fatty acid, oleic acid, resin acid which are present in the biomass, hydrolyze the monoterpenes, and transport them through matrix of wood. If moisture is low, vapor pressure and the temperature cause emission of different compounds (terpenes). When thermal treatment is applied, there is loss of moisture and other volatiles from the raw biomass which have a low heat value.

Table 11.4 Comparison of different types of reactors (Batidzirai et al. 2013)

Reactor type	Advantages	Disadvantages
Moving type compact bed reactor	– High heat transfer – Relatively simple and low-cost reactor – No moving parts in the reactor – Can process biomass with lower density – High capacity of the reactor is able to support large biomass input	– The dust particles present can cause high pressure drops resulting in automatic reactor shut down – Limited biomass type and size due to pressure drop – Non-uniform temperature distribution – Temperature controlling is difficult – Channel formation between biomass may occur causing unequal torrefaction
Torbed reactor	– Low residence time (<100 s) – The fast heat transfer leads to high throughput capacity – Low maintenance since there is no moving parts	– High utility fuel demand – Higher temperature may lead to increased loss of volatiles – More loss of volatiles leads to higher yield of tar
Belt dryer	– Better temperature control – Can work for a wide range of biomass particle size – Relatively low investment cost – Easy control over residence time through the speed of the belt	– Unequal torrefaction is caused due to clogging of holes of the belt with tar and dust, resulting into inhomogeneous torrefied product – Limited temperature control – High maintenance cost since the system has too many mechanical parts
Rotary drum	– Various methods to control torrefaction process. Both direct and indirect heating can be employed – Uniform heat transfer – It can take different types of biomass and waste size and types	– Lower heat transfer – Poor temperature control – There is more friction between biomass and wall of the drum which accumulates dust – Expensive with large footprint

(continued)

Table 11.4 (continued)

Reactor type	Advantages	Disadvantages
Screw conveyer	– Relatively economical reactor – Better biomass flow – Can take wide range of biomass sizes	– Biomass on the outer wall of reactor is comparatively more heated-causing hot spots and unequal torrefaction – Poor heat exchange capacity
Multiple hearth furnace	– Good heat transfer – Good temperature control – Compatible with wide range of biomass	– Large footprint – The process is less sustainable as the heat is provided by gas consumption, which leads to the production of moisture in flue gas. This results to lower combustion of the flue gas
Fluidized Bed	– Efficient heat transfer	– Selective particle size – Slow temperature response – Excessive biomass attrition and loss of fines – Separation of bed solids and biomass
Microwave	– The heat transfer is based on radiation rather than conduction and convection – Better temperature control – High heat transfer and fast torrefaction – Size of biomass has low effect on the heat transfer	– Electric energy required for the process – Non-uniform heating, for uniformity, it requires integration with other conventional heaters

11.3.4.1 Condensable Products

Among the condensable products of torrefaction, mainly the water is released during moisture evaporation and dehydration within organic molecules. As the temperature increases, the yield of volatiles also increases resulting in the transfer of energy to the volatiles in the form of combustibles (methanol, acetic acid). Other condensable products include acetic acid originated from acetoxy and methoxy groups which are present in xylose sugar units of hemicellulose as side chains. Also according to Ronsse et al. (2013), small amount of furfural, lactic acid, hydroxyl acetone, formic acid, and some phenol are present in volatile emissions.

11.3.4.2 Non-condensable Products

The non-condensable products include CO, CO_2 and small amount of other gases as given in above schematic. CO becomes the source of calorific value in these non-condensable products. The formation of CO_2 occurs due to acid group's decarboxylation in the biomass. CO forms by CO_2 reaction with steam and porous char. Some amount of hydrogen and methane (CH_4) is also present in non-condensable products.

11.3.5 *Process Efficiency of Torrefaction*

The process of torrefaction increases mainly the energy density, and thus, the fuel properties of the product are improved. The process is considered as technically feasible method, and the products can be used in residential as well as commercial combustion and also in gasification.

11.3.5.1 Moisture Content

A biomass typically contains 10–50% of moisture which gets reduced to 1–3% after the torrefaction process on weight basis. Reduced moisture can be advantageous in three ways: better for conversion process, low-cost transportation due to removal of unwanted water, and easy transportation and storage due to no biomass decomposition and absorption of moisture.

11.3.5.2 Bulk and Energy Density

The biomass becomes more porous after the thermal treatment process as the mass is lost in all the forms like gas, liquid, and solid. As a result, the volumetric density gets reduced to a range typically between 180 and 300 kg/m^3.

11.3.5.3 Calorific Value

During the process of thermal treatment, biomass loses maximum amount of hydrogen and oxygen, and least amount of carbon which results to increase in the calorific value of the product. The torrefied biomass gives an average of 18–23 MJ/kg CV, i.e., low heating value [LHV] and 20–24 MJ/kg, i.e., higher heating value [HHV].

Therefore, due to the above benefits, large amount of torrefied biomass is used in commercial scale for production of:

- For household, commercial, and industrial sector, it provides a good quality smoke-free solid fuel
- Co-firing of solid fuel directly with pulverized coal to be used at electric power plants
- Good quality of feedstock for pellets, fuel briquettes, or other dense biomass fuels.

11.4 Pyrolysis

The Greek word "Pyrolysis"; where "pyro" means fire and "lysis" means separating exactly justifies the primary methods of destruction and removal to remove the contaminants from desired product. The organic contaminants are first broken down into lower molecular weight compounds during destruction; and during the removal, these are separated from the "contaminants" (residual material). Pyrolysis, like other thermochemical conversions, is an alternative where by using heat, the biomass is converted into other chemical forms within a closed-loop system. This process has been separated from the other methods principally by the oxygen concentration and the conversion temperature, which control the extent to which chemical reactions are involved. Higher value products can be obtained by different chemical decompositions of biomass, especially carbon-rich (hydrocarbons) through this technology. It is also one of the most efficient pathways in liquid condensation from dried heated organic matter. Pyrolysis is often considered as the initial step of combustion and gasification. The rate of pyrolysis increases with temperature and the production potential of the process also vary accordingly.

11.4.1 Pyrolytic Products

The products obtained by pyrolysis are:

- Bio-char: Solid residues of carbon and ash
- Bio-oil: Quenched or condensed liquid
- Syngas: Mainly consisting of hydrogen, CO_2, CO, CH_4 along with other carbon species in traces.

Lanzetta and Blasi (1998) showed that at the first step in pyrolysis (250–300 °C), the volatile release is ten times faster than that of the other steps. The relative proportion of the end products may also vary with the composition and the structure of biomass. Based on the temperature advancement, the procedure alters resulting different products with typical compositions (Table 11.5).

The products obtained during the reaction are collected separately and also treated to purify. Like electrostatic precipitators are used in most of the cases for capturing pyrolysis aerosols, but their operations are observed to be tricky and also expensive (Scott et al. 1985). According to Demirbas (2000a, b), products from pyrolysis not only depend on the temperature or the reactor bed at which they had been subjected but also on the water present inside the biomass that can influence the liquid phase product and contributes in extracting some water-soluble products from the gas and tar phases and leads to huge decrease in gaseous and solid products (Arni 2010).

Table 11.5 Features of different products obtained in pyrolysis (Jahirul et al. 2012)

Temperature range	Process reaction	Characteristics of the products
Below 350 °C	Due to depolymerization, some free radicals are formed and water is eliminated	CO and CO_2, carbonyl and carboxyl compound and char residues are formed
350–450 °C	Substitution results in glycosidic bond breakage	Tar fraction is formed by the mixture of oligosaccharides, levoglucosan, and anhydrides
Above 450 °C	Dehydration to form units of sugar	Carbonyl compounds are formed
Above 500 °C	Mixture of all type of reactions	Different types of products are formed
Condensation	Products which are unsaturated gets condensed	Char residue which is very reactive containing trapped free radicals

11.4.1.1 Bio-Char

Char can be described as the intermediate in form of a solid residue which is obtained from the thermal degradations of lignin and hemicelluloses when efficiently separated; as it can act as a catalyst for cracking of vapors and can form some harmful hydrocarbons which can lower the efficiency of the process. According to the investigation of Rocha et al. (2002), the temperature regions were classified into three zones, where the production of bio-char was found to vary dramatically, and it was noted that when there is increase in the temperature, bio-char production rate decreased (Jahirul et al. 2012). The physical characters of char are greatly affected by the pyrolytic characters like—type of biomass, type of reactor, drying, chemical activation, particle size of feedstock, rate of heating, pressure flow of the inert gas, residence time. The char consists of mainly carbon, hydrogen, various inorganic species of both crystalline and amorphous aromatic structures, where elements like hydrogen, oxygen, nitrogen, phosphorus, and sulfur can be incorporated as heteroatoms (Bourke et al. 2007). Bio-char is used in many industries, depending upon the composition, chemical and physical properties, to produce carbon nanotubes, briquettes, hydrogen-rich gas or to be used as simple solid fuels.

11.4.1.2 Bio-Oil

The liquid produced by the condensation of the vapors is called pyrolysis oil. This is found to be much advantageous rather than that of other liquid fuels due to CO_2 balance, possibilities to be used in small-scale power generation, ability to store and transport, and high-energy density (Chiaramonti et al. 2007; Balat et al. 2009). The oil obtained is dark colored with distinctive acrid smoky smell, high density, and viscosity and less volatility and immense miscibility with polar solvents. Lignin content of the biomass affects the high molecular weight of the oil. This oil can be upgraded to the transportation fuel, but it needs further development. New technologies are found to be evolving which not only includes its up-gradation to liquid fuels but also in fields like chemical, heat, and power generations such as for production of resins, fertilizer, flavor, adhesive, acetic acid, industry feedstock.

11.4.1.3 Syngas

High temperature favors tar decomposition and thermal cracking which evolves volatile species capable of undergoing many secondary reactions like dehydrogenation, decarbonylation, decarboxylation, deoxygenation which decrease the yield of char and oil to form syngas. Biomass with very less moisture content is mostly influenced to yield more of syngas. Chemically, syngas is composed of hydrogen and CO. Traces of CO_2, nitrogen, CH_4, tar, ash, etc., are also found to occur depending upon the feedstock type and pyrolysis conditions. These components undergo endothermic reactions affecting the temperature of the reactor as well. Syngas can be used in internal and industrial combustion engines as renewable alternative fuel for and combustion processes. However, they are mostly avoided for economic as well as environmental concerns.

11.4.2 Process Flow of Pyrolysis

Pyrolysis of biomass as schematically represented in Fig. 11.3 is quite complex and includes both successive and simultaneous reactions of organic matters inside nonreactive (inert) atmosphere. The thermal decomposition is carried out at various temperature ranges, starting from 350 to 550 °C finally reaching up to 800–1000 °C. The long chains of carbon, hydrogen, and oxygen are obtained in the form of condensable vapors, gases, and solid residues as stated earlier.

Once the biomass is dried and reduced to the desired size, they are put into the reactor, which undergoes pyrolysis for the optimum residence time, at a particular temperature. The condenser acts as a special quenching unit where the vapors produced are passed and later collected. The remaining gas fraction is flared, whereas the solid char is collected in char cyclone.

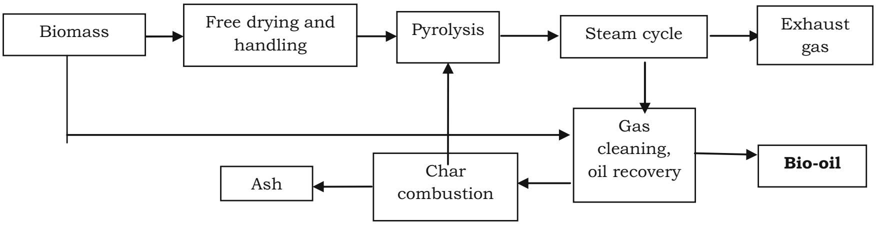


Fig. 11.3 Flow diagram of fast pyrolysis

11.4.3 Suitable Biomass for Pyrolysis and Their Advancement for Maximum Production

According to US Department of Energy, 2011 different factors are taken into account for the production efficiency to produce biofuel and bioenergy. Such factors determine the utility of that particular biomass in terms of sustainability. Similarly, for pyrolysis, the selection of biomass depends on following factors:

- Arable land requirement
- Sustainable feedstock production
- Regional strength
- Feedstock logistics
- Grains or non-grains
- Feedstock properties and compositions
- Pretreatment cost
- Availability of efficient conversion or transformation technology
- Feedstock cost
- Capital investment and operating cost involved
- Environmental benefits
- Desirable products and their values
- Food crops or waste residues

11.4.3.1 Composition of Biomass

The most efficient biomass for pyrolysis is found to be composed of lignocelluloses, i.e., cellulose, hemicellulose, and lignin, whose decomposition at varied temperature gives suitable results on the basis of thermochemical reactions undergone by them, each of which is different in their decomposition behavior. During the process of pyrolysis, all the three components are decomposed at different times. Hemicellulose is first to be pyrolyzed, followed by cellulose, and lignin is decomposed at last. Interestingly, the lignin, as well as hemicellulose, can affect the cellulosic decomposition characteristics but still cannot affect the main overall pyrolysis process (Wang 2008). Yang et al. (2007) observed that cellulose is the main source of bio-oil from the biomass, while the lignin provides the solid residue or bio-char.

11.4.3.2 External Factors of Pyrolysis

During the entire process flow, some of the vital parameters which are specially taken care of are as follows:

- Pressure value inside the reactor
- Screw rotation of the feeder
- Flare operation
- Condenser operation
- Feeding rate

Several experiments are taking place all over the world to optimize the factors for particular biomass varieties to have better process and production efficiencies and immense yield to check the energy crisis faced by all. The international research community has gathered information which carried out researches and put forward the topic to the world to spark interest in the field of Applied Science over a long period of time and now has summed up their attempts into pertinent matters which are very significant for the advancement of pyrolysis. The primary requirement of pyrolysis is to impart high heat flux to increase the rate of heating at desired level. The high temperature splits the bonds of cellulose, hemicellulose, and lignin (Ringer et al. 2006) to produce various oxygenated fragments with diverse ranges of molecular weight. The compounds or fragments with lower molecular weights remain as permanent gases, whereas compounds having higher molecular weights condense to collectively result to “bio-oil” and the others yield as “bio-char” (solid).

11.4.3.3 Requirement of Heat Transfer Mechanisms for Uniform Heating

The thermal degeneration of the lignocelluloses of biomass feedstock requires a lot of heat to cleave the macro-polymeric bonds of the biomass to smaller fragments. When the temperature reaches about 400 °C, the oxygen in these fragments become unstable and various chemical changes take place till they are quenched thermally. The heat flux to the biomass should be maintained with a corresponding high heating rate where the heat transfer from one particle to other takes minimum time. Hence, a short residence time is needed during the reaction which also terminates immediate cooling of vapors and brings “cracking severity” (Ringer et al. 2006). If the vapors are not condensed properly, then the compounds can get fragmented to smaller particles and/or it can also polymerize to large particles. According to Reed et al. (1980), 600–1000 W/cm^2 is the optimum rate of the heat transfer. Many researchers have cited various data for the most appropriate measurement of “heat of pyrolysis” for sublimation of biomass residues to bio-oil vapors. Thus, the exact value is still a debate as because the value does not solely depend on the energy supplied to the reaction vessel but also it is dependent on the quality and quantity of the by-products produced at the time of reaction such as gas and or char.

11.4.4 Classification of Pyrolysis

Pyrolysis can be classified into three types depending on the following factors (Table 11.6).

Table 11.6 Classification and salient features of pyrolysis (Balat et al. 2009)

Types	Temperature (K)	Rate of heating (K/s)	Residence time (s)	Particle size (mm)	Yield (%)		
Slow	550–950	0.1–1	450–550	5–50	30	35	35
Fast	850–1250	10–200	0.5–10	<1	50	20	30
Flash	1050	>1000	<0.5	<0.2	75	12	13

11.4.4.1 Slow Pyrolysis

The process of slow pyrolysis, also known as carbonization, is mainly the process of heating the substrate (biomass/coal) in an anoxic (oxygen-free) or oxygen-limited environment. Slow pyrolysis is basically a traditional application for charcoal production with the main intention to produce smokeless fuel. The process of slow pyrolysis is characterized by long solid and gas residence time along with low temperature and heating rate. Slow pyrolysis process is mainly used for enhanced char production (Jahirul et al. 2012). The process also produces tar and some gaseous components. The main gaseous constituents include CO, NO_x, CO_2, H_2, CH_4, hydrocarbons, and dust. The quantity of products produced from the process greatly depends on the composition of feedstock and process set-up (Jonsson 2016).

The slow pyrolysis process flows as schematically represented in Fig. 11.4 is carried out in a two-chambered apparatus. The inner chamber is filled with solid feedstock. Electronic controllers are set to heat the material with a uniform rise in temperature (~10 °C/min) can be made up to maximum (~500 °C in case of slow pyrolysis) which is to be maintained for defined period (Chhiti et al. 2013). A continuous stream of nitrogen gas flushes the gases and vapors generated during the reaction time through the second chamber. These gases and vapors form the tar portion of the product. This heavy tar portion is condensed and distilled; the distillate is further decanted to obtain settled tar and aqueous phase. The solid residence time ranges from few hours to several days. The solid portion obtained after the completion of the reaction is the char portion of the product.

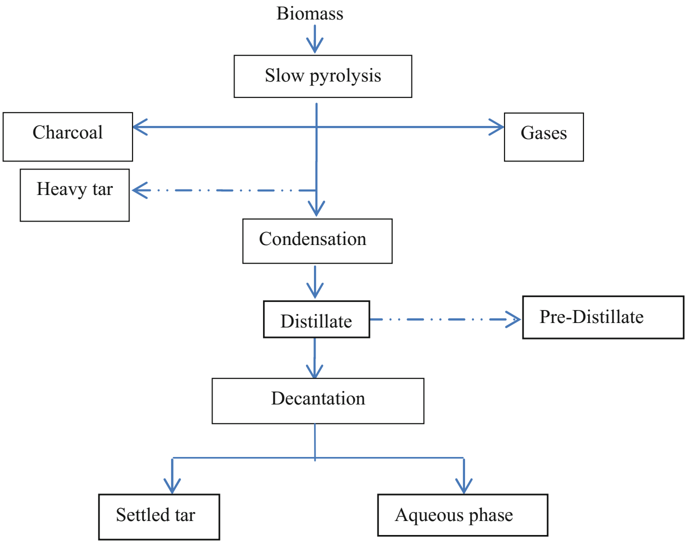


Fig. 11.4 Process flow diagram of slow pyrolysis (Fagernäs et al. 2012)

Benefits of Slow Pyrolysis

- This process can be operated on a wide range of feedstock, also with the biomasses which are hard to handle and are of low quality.
- The feedstock used can be used in larger particle size.
- Slow pyrolysis reactor can handle feedstock having ~50% moisture content.
- The primary product (charcoal/bio-char), can be used for domestic as well as industrial (chemical/pharmaceutical/metallurgical) purpose (Karaosmanoglu et al. 1999).
- Other than energy production, the products can also be used for other purposes in areas like agriculture, fertilizer production, pesticide production (Jonsson 2016).

Limitations of Slow Pyrolysis

- The key product of this process, i.e., char has very less industrial value.
- Since bio-oil is more valuable commodity, this might prove fast pyrolysis to be more competitive.

11.4.4.2 Fast Pyrolysis

Fast pyrolysis is a process that implies very high heat influx on the feedstock in the absence of air (mainly oxygen) so that it gets vaporized and later condensed into dark brown mobile liquid (main product as bio-oil) which may have a heating value alike to the conventional fuels (Ward et al. 2013). Fast pyrolysis differs from traditional charcoal or bio-char yielding slow pyrolysis process in terms of higher heating rates as well as production potential of liquid products. Pyrolysis reactors are having certain criteria for feedstock, and accordingly, feedstock is preprocessed before feeding into the reaction chamber (control panel). Preprocessing may include particle size reduction, grinding, moisture content analysis, and maintaining it to the range of 10%, drying, weighing, etc. Drying is an essential step as it includes removal of water which can be a serious interference in the stability, pH value, calorific value, or corrosiveness of the product yield. As soon as the lignocellulosic feedstock that enters the reaction chamber from the feeder, as shown in the schematic; Fig. 11.5; the intense temperature results in macromolecular depolymerization, and formation of all the three types of products which are collected separately as char, oil, and vapor. Bio-oil is collected after condensation of the vaporized fragments and the rest uncondensed remnants leave the system with the carrier gas, whereas the solid residues are expelled frequently from the system so that it can cause less interference in oil yield.

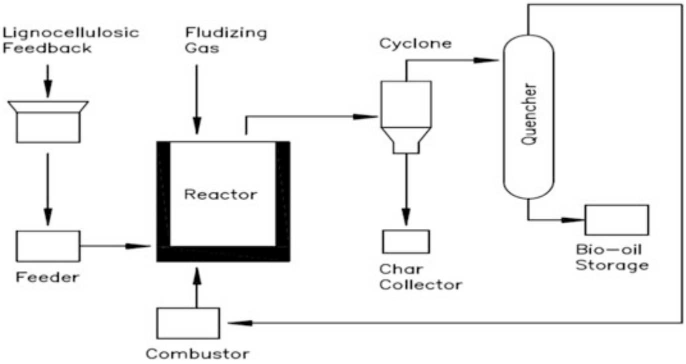


Fig. 11.5 Schematic of fast pyrolysis

Fast Pyrolysis Reactors

In recent studies researches have categorized the reactor beds used for fast pyrolysis process on the basis of the maximum utilization of the machines in an inexpensive way to have the maximum production. Some of the most common reactor beds used worldwide is described in Table 11.7.

11.4.4.3 Flash Pyrolysis

The process is often claimed as an up-gradation of fast pyrolysis with a promising amount of bio-oil yield. It is characterized by reactive flash volatilization method (RFV); converting non-volatile solids and liquids to volatile compounds by thermal decomposition in an anoxic condition, at high heating rates between 400 and 1000 °C and a very short vapor residence time. However, Mohammad I. Jahirul et al. in their work had cited some limitations such as

• Presence of solids in the oil • Inferior thermal stability	• Corrosiveness of the oil • Chemical instability of the oil

11.4.5 Future Challenges of the Process

Commercial production and utilization of bio-oil are still in natal stage. Biomass selection, it is drying, commercial level catalyst development, process optimization, reactor design, separation of oil and gas needs to be studied in terms of laboratory-scale production and up-scaling to industrial model. However, cost of production should be commercially and socially acceptable. Use of bio-oil in different paradigm should be documented and standardized.

Table 11.7 Features, advantages, and disadvantages of different fast pyrolysis reactors

Reactor type	Features	Advantages	Disadvantages
Fixed bed	– Stainless steel, concrete, or firebricks with fuel feed unit, an ash removal unit, etc. – Feedstock enters through simple vertical shaft and the expelled vapors after heating is collected with carrier gas – Cleaning system includes scrubber, cyclones, filters, etc. – Bio-oil yield 35–50%	– Simple design – Independent of biomass particle size – Reliable with gas cooling and self-cleaning system	– Operated with long residence time, high carbon conservation, low ash carry over and low gas velocity – Difficulty in removing the char
Bubbling fluidized bed	– Sand is used frequently as a solid phase to heat the biomass in anoxic condition, and the carrier gas stream conveys the oil vapors out of the reactor – High heat transfer rates and uniform bed temperatures from number of flexible heating sources – The vapor residence time can be manipulated and controlled by the carrier gas flow rate – Bio-oil yield 70–75%	– The simple construction encourages easy operations – Better control in temperature, transfer, and storage of heat	– Particle size not more than 3 mm – Discharging char which accumulates at the upper level of the bed
Circulating fluidized bed	– Much similarity with bubbling fluidized bed – Shorter residence times (0.5–1.0) s – Use of more amount of sand – Flow rate of sand is 10–20 times higher than biomass feeding rate – Bio-oil yield 70–75%	– User-friendly technology – Good control in temperature – Particles of larger size can also be used	– Movement of char and particles causes abrasion of char and forceful interactions between them which can also cause incomplete pyrolysis – High energy cost
Ablative	– Vortex reactor to exploit the phenomena of ablation – Biomass is pressed against the heated	– The particle size can be up to 20 mm – Reactor configuration avoids the basic need of carrier gas which	– Expensive reactor – Less economic – Reaction rate is lower

(continued)

Table 11.7 (continued)

Reactor type	Features	Advantages	Disadvantages
	walls of the control panel, by the high centrifugal force created by the vortex – The materials are found melting to generate both oil (pyrolysis vapors) and residual char – A "solid recycle loop" redirects large incompletely pyrolyzed particles back to the feeder – Bio-oil yield 70%	can dilute the concentration of bio-oil – No excess pressure gradient needed – Temperature to be maintained at 500–700 °C	
Rotating disk reactor	– The reactor enforces the biomass to slide on to the hot disk during rotation under high pressure – Heat transfer results into particle softening, vaporization and collection to separate condensation tank – Bio-oil yield 60%	– No carrier gas needed – Heated sand and biomass are moved by centrifugal force	– Complex process – Small particle size needed
Rotating cone reactor	– Intensive mixing between biomass and hot sand to provide efficient heat and mass transfer – At the time of spinning, it causes centrifugal force to move the solids upward to the lip of the cone – After the reaction, the char and hot sand are recycled to a combustor – Bio-oil yield 65%	– No need of additional heat and inert gas – Undiluted vapor can be obtained	– Complex process – Particle size should be small – Not applicable for large-scale
Vacuum	– Lower heat transfer rates – Induction heater and burner with molten salts are used as heat carrier	– The absence of carrier gas is the primary factor in lowering the aerosol formation	– Slow process – Solid residence time is very high – Heat and mass transfer rates are not adequate

(continued)

Table 11.7 (continued)

Reactor type	Features	Advantages	Disadvantages
	– Biomass is carried by a moving belt into high-temperature (500 °C) vacuum chamber where a mechanized agitator stirs the biomass on the belt with chemically inert quartz as packing material – As prevention for condensing the products in the tube before the cold trap, the tube is warmed with a heating tape at the end of the furnace – Bio-oil yield 35–50%		– Produces liquid effluents as volatile matter which cannot be collected in the scrubbers
PyRos	– It assembles both fast pyrolysis cyclonic reactor and high-temperature gas cleaning system in one unit for production of particle free bio-oil – The temperature should be maintained at the range of 450–550 °C, with a typical gas residence time 0.5–1 s – Hot gas filtration is mainly done by the principle of the rotational particle separator (RPS) – Biomass and the carrier gas are introduced which moves downward by centrifugal force at periphery of the cyclone – Bio-oil yield 70–75%	– Low-cost compact technology – Both small- and medium-scales which make 70–75% oil production in a decentralized way for easy transport of oil	– Reactor is complex compared to other types – Presence of solids in oil (mostly alkali) – High temperature is needed

(continued)

Table 11.7 (continued)

Reactor type	Features	Advantages	Disadvantages
Auger	– Advanced screw assembly – Biomass and hot sand are driven through an anoxic reactor vessel – Space through the tube raises the feedstock to the desired temperature (400–800 °C) – Bio-oil yield 30–50%	– Operating procedure is similar to that of a polymer twin-screw extruder – Influence well mixing and enhance heat and mass transfer efficiency – Residence time can be modified as per convenience	– Heat transfer process is not suitable for large-scale reactors
Plasma	– Cylindrical quartz reactor bed surrounded by two copper electrodes, within which different size of biomass can be inserted by screw-feeder – Inert gas induces production of plasma – Vapors are evacuated from the reactor by vacuum pump – Bio-oil yield 30–40%	– High temperature and energy provide the system of immense potential to generate heavy tarry compound with low productivity of the syngas	– Heavy power consumption – Expensive – Small particle size is needed
Microwave	– Biomass absorbs the microwave radiations effectively at lower initiation time for the reaction. – Microwaves lie between infrared and radio frequencies and cause motion by migration of ionic species or rotation of dipolar species or both to generate heat – Addition of catalyst fastens the reaction rate thus sodium hydroxide, sodium carbonate, aluminum oxide, etc., can be used for higher yield of solids and lower yield of gas – Bio-oil yield 60–70%	– Size of biomass need not be reduced as the uniform microwave heat causes well heat transfer to each particle – Drying of the biomass takes place inside the reactor – Temperature or heat utilizations can be reduced to (150–300 °C)	– High operating cost – High-power requirement

(continued)

Table 11.7 (continued)

Reactor type	Features	Advantages	Disadvantages
Solar	– The reactor bed made up of quartz provides a suitable way of storing solar energy in the form of chemical energy – A parabolic solar concentrator is adhered to the reactor to concentrate the radiation and generate a temperature of nearly 700 °C – Bio-oil yield 40–50%	– Utilization of solar reactor bed overcomes the prolusion problem – Capable of faster start-up and shutdown periods than other reactors	– Weather dependent – Expensive

11.5 Gasification

Gasification is a type of partial oxidation process, a class of thermochemical conversion, carried out in the presence of steam of high pressure and temperature. Volatile matters release as the fuel heated to some extent gets oxidized to produce water, CO_2, CO, hydrogen, CH_4, and other gaseous hydrocarbons along with heat to continue the endothermic gasification process. Water is vaporized, and pyrolysis continues as the fuel is heated. Biomass gasification is a relevant technology which can contribute to develop green energy system which is effective and environment friendly in order to increase the share of renewable energy in all sectors (Chhiti et al. 2013). The syngas generated is found to be directly combustible and can be applied in prime movers such as engines, turbines.

11.5.1 Chemical Reactions of Gasification

The gasification is very complex and includes different chemical reactions such as:

- Decomposition of organics and hydrocarbons such as carbohydrates and cellulose
- Fragmentation of hydrocarbons to other low molecular species
- Recombination of methylene and methyl radicals
- Shift reaction of water gas
- Formation of polycyclic aromatic hydrocarbons
- CO_2 gasification of carbonaceous materials or Boudouard reaction (Sikarwar et al. 2016).

If the biomass is pretreated prior to the reaction, the reaction dynamics have been found varying at equilibrium values.

11.5.2 Routes of Gasification

Research combines all the reactions in five basic steps to understand the process flow of biomass conversion and production of syngas.

11.5.2.1 Dehydration

Drying the biomass at 100 °C, resulting steam which evolves is mixed into the gas flow.

11.5.2.2 Pyrolysis

Pyrolysis is non-oxygenating thermal process which enhances the formation of char (solid residues) and tar (mixed form of liquid and gaseous products). Biomass is found to decompose rapidly at 200–300 °C evolving tar which is more complicated volatiles composed of hydrogen, carbon, and oxygen molecules. The reaction rate is very slow, and the overall reaction is too complicated.

11.5.2.3 Cracking

Decomposition of complex molecules likes tar to lighter gaseous products in the presence of heat. The gaseous products are found to be cleaner and compatible with internal combustion engines. Ensured proper combustion occurs at absolute presence of oxygen and at high temperature.

11.5.2.4 Reduction

This is the process of removing oxygen atoms to form hydrocarbons, water, and heat. The oxygen is drawn toward the bond site on the carbon than to itself, thus no free oxygen can remain in its diatomic form, and the oxygen available will be directed in the same way until number of molecules end up. Combustion and reduction are exactly opposite and equal reactions taking place at the same process flow.

11.5.2.5 Combustion

The heat which is involved in drying, pyrolysis, reduction, etc., comes either directly from combustion or is recovered from heat exchange processes in a gasifier.

11.5.3 Types of Gasifier

The patent literature have mentioned about different types of gasifiers or reactors carrying out gasification of solid and dry biomass. Most of them have been developed and commercialized for generating heat and power from syngas. According to Chhiti et al. (2013), the prime differences between gasifiers are:

• Type of injection • Gasification agents • Type of heating	• Temperature range • Pressure range of operation

Based on the density factor, which is a ratio of the solid matter, a gasifier can burn to the total volume of the biomass. The main two reactor types for such operations are

- Dense phaserReactors
- Lean phase reactors.

Both the types are having special features for individual operations, advantages and disadvantages as given in Table 11.8.

11.5.4 Products of Gasification

11.5.4.1 Syngas

It is basically a mixture of gas released at high temperature followed by a clean-up to remove components like syngas and tar can be used to produce organics like liquid fuel or natural gas. It mainly consists of:

- CO (30–60%)
- Hydrogen (25–30%)
- CO_2 (0–5%)
- Traces of CH_4, water vapor, hydrogen sulfide, ammonia, etc.

Biomass having low ash content is generally used for syngas production, as more ash content result in slagging (Sikarwar et al. 2016). Syngas can be used for following purpose for production of liquid fuels:

Table 11.8 Classification of gasifiers

Types	Features	Advantages	Disadvantages
Dense Phase Reactors			
Updraft	– Simplest and oldest known as countercurrent gasifier – Biomass gets in through the top of the reactor – Steam comes through the bottom of the reactor – Combustion occurs at the bottom of the bed producing water and CO_2	– Effective thermal efficiency – Insignificant pressure drop – Heat production for small-scale applications – Slag formation – Feedstock with high moisture can be used	– Size limit for feedstock – High yield of tar – Poor reaction capability of the syngas cannot be used directly
Downdraft	– Convert biomass or charcoal into fuel – Co-current reactor – Gasification agent and fuel move in the same direction	– Moderate sensitivity to charcoal dust and tar – Flexible adaptation of gas production	– Feedstock drying is required – Syngas exiting at high temperature – Secondary heat recovery system needed
Crossdraft	– Simplest and lightest gasifier – Air enters through a single nozzle at high velocity, induces substantial circulation, and flows across the bed of fuel and char – Production of low tar is noticed – Generates high temperature – Fuel and ash serve as insulation for the walls of the reactor – Air-cooled and water-cooled nozzles and grates are often required	– Very fast response time for loading – Short height – Gas production is flexible	– Severe pressure drop – Very high sensitivity to slag formation
Lean Phase Reactors			
Fluidized bed	– Fine particles of biomass, steam get in the bottom of the reactor – Heat and mass are transported through an inert – Gasification agent blows to lift the bed against gravity – Operating temperature is 700–900 °C and pressure ranges between 0 and 70 bar – It can be classified into three categories	– Temperature distribution is almost uniform – Exhibits high rates of heat transfer – Low tar and unconverted carbon	– Complex design – Limited usage of feedstock having high moisture – Blowers required to inject – Alkali contents form silica

(continued)

Table 11.8 (continued)

Types	Features	Advantages	Disadvantages
	Circulating fluidized bed • Two integrated systems • First unit (riser) is kept fluidized, overall residence time is higher • Second unit differentiates the product gas from bed and sends it back to riser **Bubbling fluidized bed** • Feeding done from side or bottom • The velocity of gasifying agent is controlled • The gas produced, exits from the top • Ash is generally removed using a cyclone **Dual fluidized bed** • Separates gasification and combustion part using two beds • Biomass is fed into the base using steam • The second bed is used as char combustor • The bed mainly acts as a medium for heat transfer to produce nitrogen-free syngas		
Entrained flow	– Sample can be used in powder form – Reaction time is less – Contact surfaces are quite high – Air and feed move together, and reactions occur at more than 1000 °C – It is basically classified into two families: **Top-fed gasifier** • Cylindrical shaped vertical reactors • Refined particles of fuel and gasifying agents are used • Combustion by inverted burner • Product gas is recovered from the side of the lower section and slag remains at the bottom	– Syngas produced is free from tar – Ash is collected at the bottom of the reactor in the form of slag – Conversion is found to be close to 100%	– Slagging, fouling, and corrosion are the most vital issues – Dependent on biomass composition – Generation of acid gas with sulfur and chlorine

(continued)

Table 11.8 (continued)

Types	Features	Advantages	Disadvantages
	Side-fed gasifier • Gasifying agent and feedstock are fed through the nozzles at lower part • Perfect mixing of oxygen and fuel • Product gas is recovered from the top and slag from the bottom		

- Mixed alcohol synthesis (production of a mixture of ethanol, propanol, methanol, butanol, and lesser amounts of heavier alcohols)
- Fischer–Tropsch synthesis (catalytic process used to produce liquid fuel from coal-derived natural gas and syngas)
- Syngas fermentation (biological process which involves anaerobic microorganisms to ferment the syngas to produce alcohol)
- Methanol synthesis (catalytic process of methanol production).

11.5.4.2 Tar

Tar production is an important problem in biomass gasification as it causes blockage in the instruments and makes operation difficult. It is basically a thick dark brown liquid with a low condensation temperature. Light hydrocarbon particles avoid condensation and form tarry aerosols. According to Sikarwar et al. (2016), tar is mainly composed of benzene (38%), toluene (14.5%), single-ring aromatic hydrocarbons (14%), dual-ring aromatic hydrocarbons (8%), heterocyclic compounds (6.5%), phenolic compounds (4.5%), triple-ring aromatic hydrocarbons (3.5%), and quadruple-ring aromatic hydrocarbons (1%). As such, there is no limitation for the amount of tar if the fuel gas is used directly for combustion, provided the gasifier outlet and burner inlet should not allow the gas to cool down below the dew point of tar. Tar minimization and degradation methods to be undertaken for better process efficiencies and better production of syngas.

11.5.5 Benefits of Gasification

Biomass gasification was initially started to utilize organic wastes to produce higher value products to reduce landfill of solid wastes and decrease in CH_4 emission. It also reduces the risk of groundwater contamination. Production of different categories of alcohols or phenolics from non-food sources is one of the prime benefits of the process. Biomass of high moisture content and wastes can be used with ease at the process flow. Some of the important economic benefits of the process are listed below:

- Low-priced or negative-value feedstock can be transformed into higher valued products
- Provides a high range of fuel flexibility
- Reduces the cost of handling wastes
- Provides a source of income from wastes generated at municipal areas
- The by-products can also be consumed like sulfur has utility as fertilizer and slag has usage in construction or as a roofing material
- Reduces dependence on expensive imported natural gas
- Less emission causes reduction in the operation cost of the reactor.

11.6 Conclusion

The utilization of biomass or rather biomass residues as feedstock appears to be an useful solution for producing green energy in future. However, various technical issues remain to be fulfilled,in particular, the recalcitrant nature of the second generation feedstock. The technologies should be analyzed, modeled, and optimized based on a number of factors such as feedstock selection, pretreatment methods, reaction and separation process, water recycling, energy integration, by-products’ production, and its utilization to emphasize on economic efficiency as well. Among variety of technologies, thermochemical processing has gained particular attention for converting biomass into more useful and valuable products. Though combustion is the most traditional form of conversion or processing of biomass, torrefaction, pyrolysis, and gasification are still evolving technologies which are creating new blooms in the field of bio-alternative sources of fuel or energy enhancing net usefulness of biomass maintaining the cycle of constituents in nature as well. Not only these processes enhance sustained power or energy generation but also emphasizes on the specificity of bioenergy forms. Products obtained from these thermochemical conversions can be used in various sectors of the society as bioenergy sources which are less polluting as well as have the capability to meet the rising energy demand in a sustainable way. However, systematic research is needed in various aspects starting from feedstock selection, preprocessing, reaction parameters optimization, reactor design, product separation, value addition, utilization, and finally, a business model to make the technology economically viable and socially acceptable.

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Chapter 12
Pyrolysis Oil Upgrading to Fuels by Catalytic Cracking: A Refinery Perspective

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Abstract Pyrolysis oil produced using lignocellulosic material is an alternate source of energy. Pyrolysis is an attractive option for the conversion of lignocellulosic biomass into liquid, pyrolysis oil, and gaseous hydrocarbons and is considered as an emerging and challenging research area in the current scenario of renewable energy. To ensure the production of “drop-in” liquid hydrocarbons from biomass, there is urgency of integration of pyrolysis process with conventional petroleum refinery’s trillion dollars worldwide infrastructure. This will happen into reality only after going through the necessary actions and precautions at various process development stages, such as biomass pyrolysis, pyrolysis oil upgrading, and effective integration of biomass pyrolysis with refinery. Herein, the opportunities lie in upgrading of pyrolysis oil in petroleum refinery units such as catalytic cracking and steam reforming, is described. The challenges arise ahead of pyrolysis oil upgrading in fluid catalytic cracking (FCC) approach have been reviewed. The extent of pyrolysis oil coprocessing with vacuum gas oil (VGO) in a refinery FCC unit is discussed. The advances in biomass pyrolysis process integration schemes with petroleum refinery have been revealed.

Keywords Alternative fuel · Biomass · Fluid catalytic cracking
Pyrolysis · Pyrolysis oil · Upgrading

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12.1 Introduction

The energy demand has increased due to an increase in worldwide population. The depletion of fossil fuel and concerns of environmental impact due to the usage of fossil energy resources forced the nations to take part in the development of alternative energy resources. Lignocellulosic biomass has been the potential feedstock for partial fulfillment of primary energy demand, and its demand will increase by 41% between 2012 and 2035 (Dudley 2014). Pyrolysis technology is considered to be the most promising one for getting higher (50–75%) yields of pyrolysis oil as an alternative to crude petroleum. The produced pyrolysis oil cannot be used as such because of its lower heating value, 15–20 MJ/kg, and the presence of oxygenated compounds, which are self-reactive during handling at ambient temperatures (Elliot et al. 1984).

The pyrolysis oil is a complex mixture of water, hydroxyaldehydes, hydroxyketones, phenolics, guaiacols, carboxylic acids, catechols, syringols, vanilins, sugars, and levoglucosan (Elliot et al. 1989). The composition and physicochemical properties of pyrolysis oil are different from petroleum or petroleum-derived fractions. This makes the pyrolysis oil immiscible with petroleum or petroleum-derived fractions. Besides, the pyrolysis oil is highly oxygenated ($\sim$40 wt%), acidic (pH $\sim$ 2–3), thermally and chemically unstable; therefore, it cannot be directly utilized for fuel applications. Therefore, it requires additional upgrading to convert it into usable liquid hydrocarbons. A number of upgrading techniques have been proposed in last few decades, such as thermal treatment (Demirbas 2010), high-pressure thermal treatment (Venderbosch et al. 2010), thermal hydrotreating (Samolada et al. 1998), catalytic hydrotreating (Mercader 2010), catalytic emulsion (Zapata et al. 2012), and catalytic cracking (Graca et al. 2009). Among the aforementioned upgrading techniques, FCC seems to be a good option for effective use of refinery infrastructure as well as seeking an integration scope of pyrolysis process with refinery (Jones et al. 2009).

Hence, the chapter is aimed to discuss the key issues need to be addressed before upgrading the pyrolysis oil via refinery infrastructure, such as (i) opportunities available to process the pyrolysis oil in petroleum refinery infrastructure; (ii) challenges arise ahead of processing in catalytic cracking; (iii) upgrading of pyrolysis oil by catalytic cracking; (iv) options available for integration of biomass pyrolysis process with the petroleum refinery. This will enable to know the possibility of processing of pyrolysis oil with petroleum fraction in refinery in an effective way and also to find an application as an alternative fuel to fossil-based hydrocarbons.

12.2 Opportunities for Pyrolysis Oil Upgrading in Refinery

The first option available for pyrolysis oil processing in petroleum refinery infrastructure is FCC process, wherein, the straight chain hydrocarbons and the side chain of cyclic ring hydrocarbons are easily cracked and produce gasoline and olefins. The other option is the steam reforming from where the hydrogen can be produced.

12.2.1 Fluid Catalytic Cracking

The FCC process is extensively used for cracking hydrocarbons having high molecular weight into low molecular weight petrochemical feedstock like C3-C4 olefins, liquefied petroleum gas (LPG), gasoline, and light cycle oil (LCO). Herein, the cracking mechanism follows the carbonium ion theory. The cracking occurs over a catalyst containing hot-fluidized-microspherical particles of acidic SiO_2–Al_2O_3 with a short contact time. The main advantages of catalytic cracking are (i) cost-effectiveness when compared to hydrocracking; (ii) enhanced product quality and selectivity over thermal cracking process; (iii) flexibility in processing of various types of feeds such as atmospheric gas oil (AGO), VGO, thermally cracked gas oil, hydrotreated VGO, hydrocracker bottom, coker gas oil, solvent deasphalted oil, reduced crude oil, and vacuum residue. The FCC process in petroleum refining has evolved over the last 60 years in fulfilling the challenges like cracking heavier and metallic contaminated feeds (with Ni and V), increasing operating flexibility, accommodating environmental legislation, and maximizing reliability.

Routinely, FCC plants have been operated on either gasoline or middle distillates modes; however, the developments in new generation catalysts led to LPG mode operation. The main reactions involved in the catalytic cracking are cracking (primary reaction) and many secondary reactions such as isomerization (double bond and skeletal), dehydrogenation, hydrogen transfer, cyclization, condensation, alkylation, and dealkylation. Besides, the non-condensable gases like methane, ethane, and ethylene are also obtained due to the cleavage of terminal bonds of hydrocarbon feedstock. Thus, ultimate composition of catalytic cracking product is a function of relative rates of different competing reactions (Scherzer 1990).

Globally, there are more than 400 FCC units operating in various capacities with fresh feed, wherein the UOP has been participated in the original nameplate design of FCC units from the scale of minimum 2000 bpsd, barrel per stream day, (Montana Refining, Great Falls, USA) to maximum 135,000 bpsd (Reliance Industries, Jamnagar, India) (Ibsen 2006). Presently, India and China have emerged as the key players for the growth of refinery FCC capacity. In the period 2005–2010, both countries reached the refinery FCC capacity of 43.0 MMTPA, which is

43.0% of the global refinery FCC capacity. In which, India alone is having the refinery FCC capacity of ~18.0 MMTPA to process fresh feed (Ghosh 2002). It helped in becoming net exporters of gasoline and other light hydrocarbons to the regions like Asia Pacific and the Middle East.

The acidic behavior of FCC catalyst is known for deoxygenation reactions, e.g., dehydration, decarboxylation, and decarbonylation, beyond the conventional FCC reactions (Sadeghbeigi 2000), wherein the β-scission is a primary reaction in FCC process, which occurs by breakage of the β C–C bond. The secondary reactions are alkylation, hydrogenation (Sedran 1994), isomerization (Mortensen et al. 2011), and condensation (Sedran 1994). According to the Whitmore (1934), the catalytic cracking of high molecular weight hydrocarbon is a chain reaction, which follows the carbonium ion theory. Adjaye and Bakhshi (1995a) proposed a reaction mechanism for FCC of pyrolysis oil, wherein it was reported that during catalytic cracking of pyrolysis oil over acidic zeolites undesirable products (such as tar and char) are produced. Corma et al. (2007) described the catalytic cracking mechanism in two stages, erstwhile one results in hydrogen production and the latter one leads to hydrogen consumption. Furthermore, a simplified mechanism proposed by Fogassy et al. (2010) for deoxygenation of pyrolysis oil is as follows:

$$\mathrm{C_xH_yO_z \rightarrow aC_{x-b-d-e}H_{y-2c}O_{z-2b-c-d} + bCO_2 + cH_2O + dCO + eC}$$

Chen et al. (1986) reported that the effective hydrogen index (H/C_{eff}) is related to the amount of hydrogen available for energy production. It is defined as $H/C_{eff} = (H–2O–3N–2S)/C$; where H, O, N, S, and C correspond to the number of moles of hydrogen, oxygen, nitrogen, sulfur, and carbon present in the FCC feedstock. For energy production, the H/C_{eff} should be above the inflection point of 1.2, which is applicable to either processing or coprocessing of the pyrolysis oil with VGO or LCO in a FCC unit. Thus, it is very much needed to partially deoxygenate the pyrolysis oil in order to improve the H/C_{eff} of FCC feedstock. Otherwise, it makes the process problematic as the FCC process is originally designed and developed for petroleum fractions. In spite of several studies on coprocessing at laboratory and pilot plant level, the understanding of the blending limits and the presence of type of pyrolysis oil components on the FCC product distribution is still limited. The same holds for the understanding on the ways to optimizing the process parameters, to further obtain the limitations on coprocessing of pyrolysis oil with fraction and specifically the effect of type of pyrolysis oil compounds on FCC product distribution.

12.2.2 Steam Reforming

Worldwide, the steam reforming process has been used for the production of hydrogen (energy carrier), wherein a methane gas reacted with steam to produce hydrogen and carbon monoxide in a catalytic tubular reactor, which operates at around 850 °C. The requirement of hydrogen is large for the (i) ammonia synthesis;

(ii) methanol production; (iii) hydrotreating (including hydrodesulfurization, hydrodenitrogenation, and hydrodemetalization) and hydrocracking of petroleum fractions.

Keeping in view of the possibility to produce the hydrogen from pyrolysis oil, various techniques such as catalytic steam reforming (Czernik et al. 2002; Wang et al. 2007; Kechagiopoulos et al. 2006), aqueous phase reforming (Vispute et al. 2009), electrochemical steam reforming (Ye et al. 2009), chemical looping reforming (Lea-Langton et al. 2012), catalytic steam gasification (Dinjus et al. 2004), and sequential cracking (Iojoiu et al. 2007) have been developed. Among them, the catalytic steam reforming is one of the well-known techniques and it is a part of refinery infrastructure. It is very well understood that the biomass-derived pyrolysis oil contains both water soluble (aqueous) and water insoluble (organic) fractions. The water soluble fraction can be effectively utilized by processing in very well-established steam reforming unit for the production of hydrogen. The added advantage of this technique is that the resulted hydrogen can be utilized for the upgradation of pyrolysis oil and the whole process can be integrated. The typical status of steam reforming of pyrolysis oil and their model compounds are shown in Table 12.1.

The overall stoichiometry of steam reforming of pyrolysis oil is 17.2 g H_2 per 100 g pyrolysis oil (Milne et al. 2002). The thermodynamic calculations of Kechagiopoulos et al. (2006), reported the hydrogen yield is almost 90% for the chosen mixture of compounds (acetic acid, acetone, acetaldehyde, ethylene glycol, formic acid, methanol, formaldehyde, and ethanol). Czernik et al. (2001) mentioned that the NREL group employed a fluidized bed reactor configuration and used Sud-Chemie-supplied C11-NK catalyst for the coprocessing of natural gas, containing 82.4% CH_4, 6.6% C_2H_6, 2.6% CO_2, and 8.4% N_2 (by volume.), with pine sawdust derived aqueous fraction of pyrolysis oil, containing 20 wt% organics and 80 wt% water and consisted of 11.8% carbon, 9.6% hydrogen, and 78.6% oxygen. It was reported that during co-reforming the hydrogen yield was about 80% of the stoichiometric value. It was mentioned that 25% yield of hydrogen was obtained from pyrolysis oil and remaining 75% from natural gas.

12.3 Challenges for Pyrolysis Oil Upgrading in Refinery FCC

The pyrolysis oil is a mixture of over 300 compounds including carboxylic acids, hydroxyl ketones, hydroxyl aldehydes, lignin-derived monomers, and anhydrosugars. The typical physical properties of biomass-derived pyrolysis oils are compared with fuel oil in Table 12.2. In the present scenario with these physical properties, the pyrolysis oil cannot be used in any engine or to upgrading equipment. Therefore, there is a need for stabilization of pyrolysis oil before taking into FCC for upgrading. Currently, the available standards for pyrolysis oil are ASTM

Table 12.1 Status of pyrolysis oil model compounds and aqueous fraction steam reforming

Feedstock	H_2O/C ratio	Temp. (°C)	Space velocity (h^{-1})	Catalyst	Reactor	% C-to-gas conversion	H_2 Yield	Time on stream (h)
Model compounds								
Acetic acid (Wang et al. 1998)	13	700	780 (GHSV)	UCI G-90 C	Fixed	>99	86	8
Syringol/methanol (Wang et al. 1998)	7	700	1990 (GHSV)	UCI G-90 C	Fixed	>99	76	4
Ethylene glycol (Kechagiopoulos et al. 2006)	6	700	1500 (GHSV)	C11-NK	Fixed	>94	93	12
Aqueous fraction of pyrolysis oil								
Poplar (Wang et al. 1998)	5	700	1010 (GHSV)	ICI 46-1/4	Fixed	92	75	6
Beech wood (Kechagiopoulos et al. 2006)	8.2	700	600 (GHSV)	C11-NK	Fixed	–	60	4
Pine (Magrini-Bair et al. 2002)	–	750	–	C11-NK	Fluidized	–	90	3
Rice husk (Lan et al.2010)	18	800	1.8 (LHSV)	Ni/MgO-La_2O_3-Al_2O_3	Fixed	–	68	1
Rice husk (Lan et al.2010)	9.8	800	0.5 (LHSV)	Ni/MgO–La_2O_3–Al_2O_3	Fluidized	–	75	1
Co-reforming of pyrolysis oil with natural gas								
Saw dust (Czernik et al. 2001)	4.6	850	1000 (GHSV)	C11-NK	Fluidized	–	75	–

Table 12.2 Comparison of physical properties of biomass-derived pyrolysis oils with fuel oil (Zacher et al. 2014)

Components	Pyrolysis oil	Fuel oil
C (wt%)	56.0	85.0
H (wt%)	6.0	11.1
O (wt%)	38.0	1.0
Water (wt%)	20–30	0.025
Solid (wt%)	0.01–0.1	0.0
Ash (wt%)	0.01–0.2	0.01
Nitrogen (wt%)	0–0.4	0.0
Sulfur (wt%)	0–0.05	0.2
Stability	Unstable	Stable
Viscosity @40 °C (cSt)	15–35	3.0–7.5
Density @15 °C (g/cc)	1.10–1.30	0.89
Flash point (°C)	40–110	60
Pour point (°C)	−9 to −36	−15
LHV (MJ/kg)	13–18	40.3
pH	2–3	Neutral
Boling range	Decomposes	140–400 °C

D7544, which can be specifically applied for direct use in the furnaces and automobile engines.

From the view of maintaining heat balance of the FCC unit and to limit the fresh catalyst consumption within a reasonable level, the feed to the FCC should meet certain specifications with respect to its boiling point, coking tendency, and metal and sulfur contents. In addition to the above effective hydrogen index, composition of feedstock also plays an important role for coprocessing of pyrolysis oil with VGO in FCC unit. To meet the aforementioned specifications before feeding pyrolysis oil into FCC is a real challenge for the development of process in a view of integration of pyrolysis process with refinery FCC unit.

Moreover, the quality of biomass-derived pyrolysis oil is a function of pH, heating value, viscosity, nitrogen, water, ash, and char content. The properties (physical, chemical, and combustion) of pyrolysis oil changes with time. It is reported that over a period of six months the viscosity of pyrolysis oil increases from 1127 to 2283 cP (Tiplady et al. 1991). A few of the important challenges for meeting the specifications of feed and their significance are given below.

12.3.1 API Gravity

The American Petroleum Institute (API) gravity refers to the specific gravity at 60 °F by the formula: API = ((141.5-Specific Gravity)-131.5). It is a measure of how petroleum is heavier or lighter in comparison with water. The higher API value indicates that the feed is more saturated and less aromatic, which helps in easy cracking and the higher gasoline yield with slightly lower octane. The API gravity of feed to the FCC unit varies from 16 to 48. Therefore, it is very much essential to maintain the API gravity within the range, so that the pyrolysis oil can be easily cracked in FCC for maximization of gasoline yield.

12.3.2 UOP Characterization Factor

UOP or UOP K value is a factor used to measure the paraffinicity of petroleum oils based on its boiling point and specific gravity, which is related by the relation: UOP characterization factor = UOP K = {(Cubic average boiling point)$^{1/3}$/(Specific Gravity)$_{60°F}$}. The K value of 12.5 would designate that a feed is highly paraffinic (saturated), whereas the value of 11.2 would show more aromatic (unsaturated cyclic). Thus, the pyrolysis oil with K value of 12.5 and above is preferable for processing or coprocessing with pyrolysis oil in a FCC unit.

12.3.3 Boiling Range

The boiling range of FCC hydrocarbon feed usually varies from 260 °C (initial boiling point) to 540 °C (final boiling point). However, the biomass-derived pyrolysis oil boiling range starts at room temperature and goes up to even 560 °C as it contains multicomponents lower to higher boiling points. The presence of heavy components in FCC feed would throw in the formation of undesirable coke. Hence, the heavy components (poly-nuclear aromatics, organometallic, and high sulfur compounds) are considered as coke precursors.

12.3.4 Carbon Residue

The terminology of carbon residue provides a measure of the carbon deposition tendencies of FCC feed when heated in a bulb under prescribed conditions. It can be determined by either Conradson or Ramsbottom methods. The petroleum-derived vacuum gas oil containing Conradson carbon residue (CCR), indicative of coke-forming potential, of 0.74 wt% can be processed through FCC unit (Naik et al. 2014b), whereas the residual fluid catalytic cracking (RFCC) process can handle up to CCR of 4.06 wt%. Therefore, it is recommended to carry out the hydrotreatment of pyrolysis oils until predetermined level of conversion (<10 wt% of CCR) is achieved (Ardiyanti et al. 2012). Typically, the CCR ranges from 18 to 23 wt% for woody (oak, eucalyptus, and pine) biomass-derived pyrolysis oil, whereas it varies from 17 to 18 wt% for pyrolysis oil from wheat straw (Oasmaa et al. 1997).

12.3.5 Metal Content

Specifically, in the refinery FCC unit the presence of metals (Ni, V, Cu, and Fe) causes undesirable dehydrogenation reactions resulting in an increase of hydrogen, coke, olefins, and lighter hydrocarbons in the cracked products at the expense of LPG or gasoline. Nickel and copper are more effective in promoting these hydrogen-producing reactions. Thus, an increase in the volume ratio of hydrogen/methane (which is a measure of the extent of metallic poisoning) or the olefinic content of C_3 stream is all indications of contaminations of the catalyst. The ratio of H_2/CH_4 from 0.3 to 0.8 is preferred, whereas the value >1.0 specifies significant degree of poisoning.

Further, the contamination of a feedstock to FCC like unit is measured by a metal factor (Fm), i.e., Fm = Fe + V + 10 (Ni + Cu); where Fe, V, Ni, Cu are the concentration in ppm of iron, vanadium, nickel, and copper. A metal factor of 1.0 is considered as safe and feedstock with metal factor of above 3.0 may result in poisoning the catalyst. The presence of sodium weakens the molecular structure and decreases the hydrothermal stability of catalyst resulting in damage due to sintering at lower temperatures and subsequent loss of surface area. Thus, the control of ash content before pyrolysis oil processing in refinery units is very much required to control the side reactions and poisoning of FCC catalyst. In regard to biomass, the inorganic materials, especially the potassium and calcium, catalyze biomass decomposition and char-forming reactions (Garcia-Perez et al. 2009).

12.3.6 Nitrogen

Nitrogen acts as a temporary catalyst poison which reduces the catalyst activity by neutralizing the acid sites of cracking catalyst available for promoting reactions. The presence of nitrogen compounds in the FCC feeds is undesirable as the organic nitrogen converts into basic nitrogen compounds (like ammonia, pyridine, quinoline) in FCC riser, which act as a poison by neutralizing the active acid sites of the cracking catalysts, which results in rapid loss of activity (Fu et al. 1985). The loss of activity results in changes in product selectivity of FCC. A FCC feed with total nitrogen concentration of <1000 ppm is not detrimental to activity, whereas it is detrimental on above 1500 ppm.

In case of woody biomass-derived pyrolysis oil, the nitrogen content is less than 0.4 wt% (wet basis) (Oasmaa and Peacocke 2010), whereas corn-derived pyrolysis oil is 1% (Elliott et al. 2009), which are highly dependent on type of biomass feedstock. The basic and nonbasic nitrogen species in petroleum also falls in the range of 0.1–0.9% (Abdel-A et al. 2003), whereas the conventional FCC feedstock, gas oil, contains the nitrogen in the range of 0.1–0.8 wt% (Scherzer 1987).

12.3.7 Hydrogen Effective Index

Typically, the number of hydrogen molecules available for the production of energy is related by the index called effective hydrogen index, which can be defined by the equation ($H/C_{eff} = (H–2O–3N–2S)/C$) as proposed (Chen et al.1986), wherein, H, O, N, S, and C are the number of moles of hydrogen, oxygen, nitrogen, sulfur, and carbon present in the FCC feedstock. The effective hydrogen index is less than 1 for highly oxygenated compounds, close to 1.5 for triglyceride-based biomass, whereas for hydrocarbons it varies from 2 (liquid alkanes) to 1 (for benzenes) (Melero et al. 2012); while it is 0, 1/3, and 2/3 for glucose, sorbitol, and glycerol, respectively (Corma et al. 2007). Zhang et al. (2011) reported that on conversion of lignocellulosic biomass-derived feedstocks over ZSM-5, the feedstocks with H/C_{eff} less than 0.15 produce more coke and it is suggested to have a minimum of H/C_{eff} of 1.2 (as an inflection point) to produce optimum aromatics and olefins in refinery setups.

12.3.8 Composition

It is very difficult to describe the overall composition of pyrolysis oil as it depends on many factors like feed structural composition, type of pyrolysis reactor, pyrolysis operating conditions, liquid collection systems that have been used for condensing vapors, and by the storage stability of pyrolysis oil. Earlier, the typical range of pyrolysis oil composition is reported by Diebold (2005). Further, Brown (2009) also reported the composition of pyrolysis oil obtained from auger pyrolyzer, however, which is out of the range for some compounds as mentioned by Diebold (2005). Branca et al. (2003) compared the pyrolysis oil composition (with the identified 40–43% of compounds) of four major commercial pyrolyzers: bubbling fluidized bed (Dynamotive), rotating cone (BTG), circulating fluidized bed (ENSYN), and vacuum pyrolyzer. However, the recent ASTM D7544-12 covers the specification of pyrolysis liquid biofuel (obtained from biomass) as a fuel for industrial burner, whereas the same is not applicable to home heaters, small-scale boilers, and engines applications.

12.3.9 Acid Value

The acidity of pyrolysis oil is derived mainly from the presence of low volatile acids (60–70%) with lowest pKa values as compared to hydroxy acids in sugar (20%) (Oasmaa et al. 2010). These acids do not react with pyrolysis oil components at a moderate temperature of $\leq$ 80 °C. The acidity of pyrolysis oil causes corrosion

Table 12.3 Standard test methods for pyrolysis oil (Oasmaa 2005)

Property	Typical range	Applicable test methods
Higher heating value (MJ/kg)	14–19	DIN51900, ASTM D240
Lower heating value (MJ/kg)	13–18	DIN51900, ASTM D240, ASTM D5291 for H
Water (wt%)	20–30	ASTM E203
pH	2–3	ASTM E70
TAN (mg KOH/g)	70–100	ASTM D664
Kinematic viscosity@40 °C (mm^2/s)	15–40	EN ISO 3104, ASTM D445
Density at 15 °C (kg/dm^3)	1.11–1.30	EN ISO 12185, ASTM D4052
Pour point (°C)	−9 to −36	EN ISO 3016, ASTM D97
Carbon (wt%)	50–60	ASTM D5291
Hydrogen (wt%)	7–8	ASTM D5291
Nitrogen (wt%)	<0.5	ASTM D5291
Sulfur (wt%)	<0.05	EN ISO 20846, ASTM D 5453
Oxygen (wt%)	35–40	As difference
Solids (wt%)	<1	ASTM D7579
MCR, CCR (wt%)	17–23	ASTM D4530, ASTM D189
Ash (wt%)	<0.3	EN ISO 6245
Flash point (°C)	40–110	EN ISO 2719, ASTM D93B
Sustained combustibility	Does not sustain combustion	EN ISO 9038
Na, K, Ca, Mg (wt%)	<0.06	EN ISO 16476
Chlorine (ppm)	<75	Not specified

in pipelines and process equipment of processing units. Hence, the selection of material for transportation and reactions becomes most vital in order to see the feasibility of integration of pyrolysis process with refinery. Table 12.3 shows that pyrolysis oil derived from different types of pyrolyzers, the pH value varies from 2 to 3.

In the case of FCC, the feedstock with high total acid number (TAN) would not affect the stability of FCC catalyst as the large number of acidic compounds decomposes rapidly at FCC riser operating temperature. However, naphthenic acid is highly active at its boiling point, and hence it causes severe corrosion in condensation equipments. Thus, the TAN of crude oil fractions >1.5 is believed to be significantly corrosive in the temperature range of 232–398 °C.

12.3.10 Water

Typical formation of water during the pyrolysis reaction is due to the presence of bound moisture in feed biomass (>10 wt% leads to phase separation aqueous and oily viscous) and alkali metals, especially potassium (which catalyze secondary pyrolysis reaction (Agblevor and Besler 1996). In addition to this, the aging reactions (like etherification and esterification between hydroxyl and carbonyl compounds) also take part for the formation of water as a by-product (Lehto et al. 2013). This cannot be separated from pyrolysis oil by means of centrifugation (Oasmaa et al. 2010). From NREL report (Ringer et al. 2006), it has been observed that even if the bone-dry biomass is subjected to pyrolysis, the resulting pyrolysis oil still contains a minimum of 12–15 wt% water.

The formation of high water content in pyrolysis oil will lead to decrease in the heating value, adiabatic flame temperature, and viscosity. Further, the high water content will lead to phase separation, leading to non-homogeneous mixture (Bardalai et al. 2015). This can be analyzed by Karl Fischer volumetric titration technique as per ASTM Standard E 203 (Oasmaa et al. 2010). The water content should be low (<0.2 vol.%) in order to prevent shocks and vibrations, resulting from flash vaporization of water droplets in FCC operation. Free water in bulky quantities is dangerous as it can upset the pressure balance of the reactor regenerator system in FCC process. The updated list of recommended analysis methods along with properties is summarized in Table 12.3 as reported by Oasmaa (2005). In addition to the above-mentioned typical challenges of pyrolysis oil properties, the role of proper modeling of biomass decomposition is very much needed in order to get high quality of pyrolysis oil (Sadhukhan et al. 2008).

12.4 Upgrading of Pyrolysis Oil in FCC Approach

12.4.1 Upgrading of Pyrolysis Oil Model Compounds

The order of reactivity and reaction pathways of model pyrolysis oil compounds (such as 1- and 2-propanol, 1- and 2-butanol, acetic acid, acetone, acetaldehyde, phenol, and 2-methoxy phenol) over an acid zeolite (H-ZSM-5) catalyst in an isothermal fixed bed reactor at different temperatures ranging from 200 to 450 °C were ascertained by Gayubo et al. (2005). The coke formation order is as follows: aldehyde > acetone (or) acetic acid > alcohols. It indicates that the deoxygenation is favored by decarboxylation and decarbonylation at around 400 °C temperature, and deoxygenation is favored by dehydration at around 250 °C temperatures on catalytic transformations of acetone and acetic acid. Alcohols have higher reactivity over acid zeolite catalysts leads to the formation of light olefins ($\sim$200 °C) then to higher olefins (at 250 °C) followed by the considerable amount of C_{5+} paraffin and the smaller amount of aromatics at temperatures above 400 °C. Acetone was less reactive as compared to alcohols; however, they also produced C_{5+} paraffins and aromatics (more than obtained from alcohols).

The reactivity of acetic acid was very low up to the temperature of 400 °C, whereas due to autocatalytic effect the acetic acid was converted into acetone at a temperature more than 400 °C. Once the acetone is formed from acetic acid, it follows similar path of acetone on catalytic transformations. The phenol has low reactivity to produce hydrocarbons over an acid HZSM-5 zeolite catalyst; they produce small amount of light olefins and thermal coke. Aldehyde also has the lower reactivity over HZSM-5 catalyst and resulted higher amount of thermal coke. Therefore, the recommended presence of aldehydes in pyrolysis oil is 3.6 wt% excluding water (Aguado et al. 2000). The ethers and phenolic compounds have low reactivity, while high conversions can be achieved with the compounds of acids, esters, alcohols, aldehydes, and ketones (Adjaye and Bakhshi 1995a, b; Adjaye et al. 1996). However, the catalyst deactivation by coke formation is particularly important with aldehydes and phenols.

12.4.2 Upgrading of Pyrolysis Oil Model Compounds with VGO

The FCC of mixtures of gas oil and pyrolysis oil representative model compounds (acetic acid, hydroxyacetone, and phenol) in a laboratory scale unit using an E-CaT and a mixture of E-CaT and ZSM-5 additive was carried out by Graca et al. (2009). It has been reported that the coprocessing of oxygenated compounds with vacuum gas oil results in (i) increase of gasoline, gaseous products (CO, CO_2, fuel gas, LPG); (ii) decrease of coke yield except for phenol; (iii) decrease of hydrogen yield (follows the order of hydroxyacetone > acetic acid > phenol) in the product and it is confirmed by increase in $C_{2–4}$ olefins/$C_{2–4}$ paraffins ratio. Further, it was concluded that these oxygenated compounds can be processed in a FCC unit up to 10 wt%. However, the presence of phenol might be critical due to the limitations in benzene content specification in the gasoline (max. 1 vol.%). The typical product distribution pattern on catalytic cracking of pyrolysis oil model representative compounds with vacuum gas oil is shown in Table 12.4. The catalytic cracking of pyrolysis oil model compounds using zeolite catalyst resulted in the decrease of hydrogen yield for two carbon-oxygenate (e.g., acetic acid) and three carbon-oxygenates (e.g., hydroxyacetone), wherein the hydrogen is consumed during the deoxygenation reactions like decarbonylation and decarboxylation. These observations indicate to further focus on catalytic pyrolysis reactions instead of typical pyrolysis reaction to get the product having lower carbon number based oxygenates, which can be easily converted into products in similar to FCC distillates without changing much the existing FCC infrastructure.

To further understand the coprocessing of pyrolysis oil with VGO in FCC unit, the studies have been extended with the model compounds such as C2-C3

Table 12.4 Status of catalytic cracking of pyrolysis oil model compounds with VGO over FCC catalyst

Product yields @ Iso-conversion of 63.0 wt.%					
Feed/products	VGO	VGO+Guaiacol	VGO+Acetic acid	VGO+Acetol	VGO+Phenol
References	Graca et al. (2011)		Graca et al. (2009)		
Fuel gas (wt%)	2.7	3.3	3.7	3.0	2.5
CO (wt%)	–	0.05	0.47	0.07	0.04
CO2 (wt%)	0.25	0.33	0.54	0.35	0.17
LPG (wt%)	12.5	13.8	15.7	14.0	13.2
Gasoline (wt%)	36.0	36.2	33.4	35.9	38.1
LCO (wt%)	19.7	18.8	18.9	20.0	18.6
DO (wt%)	17.3	17.3	17.7	16.8	18.0
Coke (wt%)	11.8	9.5	9.4	9.6	8.6

carbonyls (hydroxyacetone and glycolaldehyde dimer), acetic acid, and 2-methoxy phenol (Naik et al. 2014a, b). For the case of coprocessing of C2-C3 carbonyls and VGO, the blending ratios were varied within the range of 5–20 wt%. From the experimental investigations, it was observed that the presence of acetol increased the FCC conversion from 68 to 78% with blending ratio. It was due to the increase in the yield of LPG from 21 to 47 wt.%. It happens at the cost of gasoline from 39 to 23 wt.% followed by LCO from 18 to 12 wt.% and HCO from 11 to 7 wt.%, respectively. It was observed that the yield of LPG increased linearly on increasing the blending ratio. Further, the presence of acetol reduced the coke formation in comparison to pure VGO catalytic cracking over equilibrium FCC catalyst at a constant C/O ratio (with 5).

While on coprocessing the glycolaldehyde dimer with VGO, the FCC conversion increased from 69 to 75% with an increase in blending ratio from 5 to 10%, whereas beyond that the conversion decreased to 65% for the blending ratio of 20%. The dry gas and LPG yield first increased from 1.8 to 2.4 wt% and 35 to 43 wt %, respectively, with an increase in blending ratio. The further increase of blending ratio to 20% the yields of dry gases and LPG decreased to 1.8 and 27 wt%, respectively. Furthermore, it was observed that the gasoline yield first decreased from 27 to 25 wt% and then increased to 32 wt% with an increase in blending ratio, while the LCO yield first decreased from 17 to 15 wt% and then increased to 20 wt %, whereas the yield of HCO first decreased from 11 to 9 wt% and then increased to 13 wt% with an increase in blending ratio from 5 to 10 wt%. The yield of ethylene and propylene also followed the same trend with an increase of glycolaldehyde blending ratio up to 10 wt% blending, and thereon the yields were decreased with further increase in blending ratio. The increase in coke formation was observed beyond the blending ratio of 10%, which is due to the increase in poly-aromatics formation.

The simulation distillation-based product analysis shows the presence of guaiacol increased the product selectivity of gasoline fraction, whereas the presence of acetic acid clearly increased the yield of light olefins, CO, and CO_2 (Naik et al. 2014b). The FCC conversion was higher on coprocessing of guaiacol followed by acetic acid with VGO as compared to FCC of VGO. An increase in coke and aromatics formation was observed in the order of guaiacol + VGO feed > acetic acid + VGO feed > VGO. The higher yields of light olefins, CO, and CO_2 were observed during FCC of acetic acid and VGO feed over E-Cat. Subsequently, the light olefins were reduced for the case of guaiacol and VGO feed as compared to other feeds.

The cracking pattern of acetic acid and guaiacol with VGO were supported by FTIR analysis, by observing carboxylic acid peaks in the range of 1650–1720 cm^{-1}. The analysis shows that the acetic acid and VGO feed were completely absent in their distillates, which gives a clear indication of complete conversion of acetic acid, while the formation of phenolic peaks was observed in the distillate of guaiacol and VGO feed. Therefore, it is preferable to separate the aromatic oxygenated compounds from pyrolysis oil before coprocessing it with VGO in refinery FCC unit by keeping in mind the limitations of total aromatics and the benzene percentages in gasoline. Moreover, an increase in coke and aromatics content was observed with the insertion of guaiacol while coprocessing with VGO in FCC.

Likewise, the acetol can be co-processed with VGO up to a blending ratio of 5:95 without major changes in the original FCC product slate; beyond that, the LPG range products were increased (Naik et al. 2014b). However, there is a limit for the coprocessing of glycolaldehyde with VGO in refinery FCC unit because of the increase in poly-aromatics formation.

12.4.3 Upgrading of Pyrolysis Oils with VGO

Directly, one cannot upgrade or catalytically crack the pyrolysis oil with VGO in FCC approach due to the challenges mentioned in Sect. 12.3. Therefore, one has to stabilize or partially upgrade the pyrolysis oil before coprocessing it with petroleum fraction in FCC. Among the various stabilization techniques, the hydrodeoxygenation or catalytic pyrolysis route is considered to be the best choices before coprocessing.

A mixture of hydrodeoxygenated (over Ru/C catalyst) pyrolysis oil with VGO in a ratio of 80:20 was processed in a fixed bed reactor under FCC conditions and compared the results with the processing of pure VGO (Fogassy et al. 2010). It was observed that during coprocessing major part of the oxygen is removed in the form of carbon dioxide and water by means of decarboxylation and dehydration reactions. Cracking of this particular 80:20 mixture produces more dry gas and coke yields, lower LPG yield, while gasoline and light cycle oil yields were comparable to those of the products obtained on cracking of VGO. Their results indicate that C-C bond cleavage takes place before decarboxylation and decarbonylation reactions while cracking hydrodeoxygenated pyrolysis oil as it contains unsaturated hydrocarbons, whereas, Osmont et al. (2007) mentioned that C–O bond breaking reactions proceeds faster than carbon-to-carbon (C–C) bond cleavage for saturated hydrocarbons. It was also emphasized that hydrogen-consuming reactions dominate by water formation and hydrogenation reactions besides some hydrogen-elimination reactions which leads to favor higher yields aromatics (continuation of reaction which leads to coke formation) in the products while cracking VGO/HDO oil, wherein the decrease of LPG may be due to the well-known fact that HDO oil containing more aromatics. It is known that aromatics are difficult to crack than aliphatic hydrocarbons over an E-cat. Similarly, Ng et al. (2006) also mentioned that the aromatic-rich feedstock side chains could be detached and fragmented using acid catalysts but the cracking of refractory aromatic rings needs the presence of hydrogen at higher pressure.

Samolada et al. (1998) performed the catalytic cracking experiments on heavy fraction of hydrotreated pyrolysis oil (80% deoxygenated) in a modified microactivity test (MAT) fixed bed reactor system (ASTM D3907-80), with the LCO in a ratio of 15:85 by wt%. It was reported that both saturated naphthenes (from 3.8 to 4.2%) and aromatics (from 50.5 to 53.8%) were increased on using $ReUSY_2$ catalyst. Lappas et al. (2009) extended the work of Samolada et al. (1998) and carried out the experiments with thermally hydrotreated pyrolysis oil fraction with conventional VGO in the Chemical Process and Energy Resources Institute (CPERI) FCC pilot plant. In order to avoid the feeding nozzle plugging difficulty of FCC unit with such feed, the upgraded oil was diluted in LCO in a portion of 15:75 by wt% and the mixture was blended with VGO. Their experimental result showed that the VGO/upgraded pyrolysis oil co-feed produces about 1 wt% more gasoline, about 0.5 wt% more coke, and more LCO as compared to the VGO feed expected. Their PIONA analysis of liquid product also indicated more aromatics and less olefins and paraffins in comparison to pure vacuum gas oil cracking. It was suggested that the option of co-feeding VGO with upgraded oil is technically viable for refinery FCC unit running with quality feedstock.

The high amounts of oxygen can be allowed in upgraded HDO oil (i.e., up to $\approx$28 wt%) during coprocessing in FCC unit without any deterioration of the yield pattern (Mercader 2010). It was also mentioned that the coprocessing of HDO oil (20 wt%) with a long residue, a promising yields of FCC gasoline (44–46 wt%) and LCO (23–25 wt%) were obtained without an increase of coke and dry gas yields, as compared to the base feed only.

The tar fraction of Jatropha curcas cake pyroloysis oil was hydrodeoxygenated over Pd/Al_2O_3 catalyst in an autoclave reactor at 300 °C temperature and 80 bar pressure (Naik et al. 2015). It resulted into the reduction of oxygen content of pyrolysis oil from 32 to 10 wt% and becomes hydrodeoxygenated pyrolysis oil (HDO). The HDO was catalytically cracked with VGO by varying blending ratios from 5 to 20%. On coprocessing of pyrolysis oil with VGO indicated that the yields of gasoline and LCO increased from 29 to 35 wt% and 14.8 to 20.4 wt%, respectively, whereas the yields of dry gas and LPG decreased from 2.1 to 1.4 wt% and 38.8 to 23.7 wt%, respectively, with an increase in blending ratio from 5 to 20%. Their product distribution was compared with the pure VGO and pyrolysis oil with VGO at similar conversion (Table 12.5). The iso-conversion results on coprocessing of HDO with VGO shows a higher yield of LPG, whereas lower

Table 12.5 A selectivity data of for catalytic cracking of VGO, VGO with pyrolysis oil and VGO with HDO at different blending ratios

Feeds	VGO: Pyrolysis Oil				VGO: HDO	VGO	VGO: Pyrolysis Oil
Blending ratio	95:5	90:10	85:10	80:20	95:5	100	83:17
FCC conversion	75.6	74.6	69.3	64.3	66.9	66.8	66.0
Yield (wt%)							
Dry gas	2.1	2.0	1.4	1.4	1.5	1.7	1.4
LPG	38.8	35.7	28.6	23.7	28.7	15.5	25.4
Gasoline	29.0	31.1	35.1	35.0	32.5	44.0	35.0
LCO	14.8	15.4	17.9	20.4	18.9	19.8	19.1
HCO	8.0	8.4	10.6	14.0	13.2	12.4	12.3
Coke	5.4	5.2	4.2	4.1	4.1	5.5	4.1

yields of gasoline and LCO have been observed as compared to pyrolysis oil coprocessing with VGO and coprocessing of pure VGO.

Thegarid et al. (2013) performed the coprocessing studies of catalytic pyrolysis oil obtained from commercial lignocellulosic biomass (i.e., Lignocel HBS 150–500 originated from beech wood) with VGO in a fixed bed quartz reactor with FCC catalyst in a ratio of 10:90. Their results indicated higher yields of coke, dry gas, and gasoline; lower yields of hydrogen, LPG, LCO, and bottoms as compared to pure vacuum gas oil processing. Further, their observations were (i) the presence of more oxygen (27 wt%) in CPO resulted in hydrogen consumption reactions via water formation; (ii) the presence of alkyl phenols already in the CPO and narrow pore size limitation of ZSM-5 catalyst lead to significant amount of alkyl phenols in the gasoline fraction; (iii) the aromatic-rich gasoline fraction leads to less reactive for further cracking and thereby decreases LPG yield; (iv) P-NMR data showed that all oxygenated compounds (except the phenolic fraction) has been converted. It was also mentioned that the overall yield of organic oil is 30% as compared to 24% on coprocessing of HDO oil with VGO.

12.5 Schemes for Integration of Pyrolysis with Refinery FCC

It is clear that the pyrolysis oil cannot be processed directly or co-processed with fossil hydrocarbons in order to convert into fuel range hydrocarbons. The option of coprocessing of biomass-derived fractions with petroleum fraction is relatively inexpensive and also helps in increase of profitability of present low margins of petroleum refineries (Alhajri et al. 2014). A list of petroleum refinery units like FCC, hydrotreating, hydrocracking, and steam reforming units can be utilized for the specific applications by approaching the specific pathways. In this scenario, several options have been pointed out by various research groups for the effective use of a refinery infrastructure for upgrading of biomass-derived pyrolysis oil into liquid hydrocarbons, chemicals, and materials. Moreover, this kind of option is more viable in countries like India, wherein the demand of petroleum-derived fraction is extremely high. It also helps the refineries with a safe and secured domestic feedstock source. With this scenario, it has been tried to put some of the schemes for integration of pyrolysis process with petroleum refinery in and another approaches in the following sections.

12.5.1 Biorefinery and Refinery Integration

Zacher et al. (2014) proposed a way for the conversion of biomass into companionable petroleum-derived hydrocarbons by the pyrolysis and HDO route, as shown in Fig. 12.1. The pathway has been divided into a series of stages, wherein the scope of insertion into the hydrocarbon economy has been considered. The stages of pyrolysis oil upgrading have been classified into the pyrolysis oil purification by physical and chemical modifications, heteroatom removal by mild hydro treating, cracking into small hydrocarbons, and separations into various products by various unit operations. The well-treated pyrolysis oil (after purification and heteroatom removal) can be utilized in the refinery units wherever it is suited.

12.5.2 BIOCOUP Biorefinery

Venderbosch et al. (2010) proposed a different pathway against overall biorefinery concept for the conversion of biomass residues into conventional energy, fuels, and chemicals. This follows hydrothermal liquefaction followed by separation of various fractions like hydrocarbon-rich pyrolysis oil, lignin-rich pyrolysis oil, and derivatives of holocelluloses and process residues, as shown in Fig. 12.2, in which

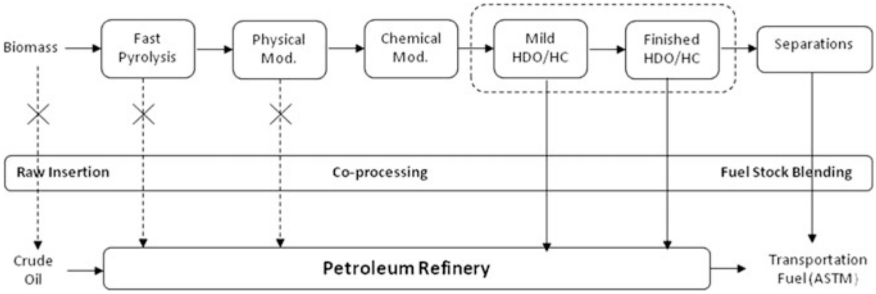

Fig. 12.1 Biorefinery and refinery integration (Zacher et al. 2014)

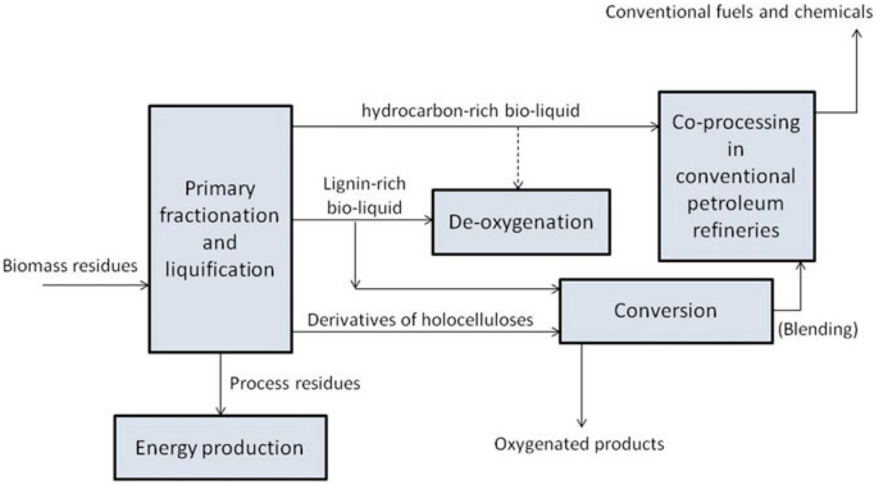

Fig. 12.2 BIOCOUP consortium's overall biorefinery concept (Venderbosch et al. 2010)

they have emphasized to use the hydrocarbon-rich pyrolysis oil with petroleum-derived fraction for coprocessing in refinery processes. They quoted that hydrodeoxygenation is very much suitable for decreasing the oxygen and acidity of pyrolysis oil before coprocessing in refinery processes. Further, it was reported that the 20% of HDO oil can be co-processed with VGO with slight decrease in the yield of gasoline and the presence of more unsaturated compounds and oxygenates (Way et al. 2011).

12.5.3 Biomass Feedstocks Integration with Refinery

Melero et al. (2012) proposed a biomass feedstock integration pathway for the conversion of feedstock's like sugar-rich, starch-rich, and lignocellulosic biomasses into biofuels using standard petroleum refinery processes, as shown in Fig. 12.3. This pathway has been critically described on the basis of feedstock's effective hydrogen index, energy density, and specific chemistry involved in the conversion or upgrading processes. With this approach, the other refinery process (hydro treating) can also be effectively utilized for the processing of biomass-derived feeds. Hydrotreating processes (HDO, HDS, and HDN) are aimed for higher selectivity toward the liquid fraction (diesel) by minimizing the lighter hydrocarbons, gases, and coke as compared to the catalytic cracking units. Herein, this process can be used for the mild hydrotreating of pyrolysis oil or triglycerides. Further, the

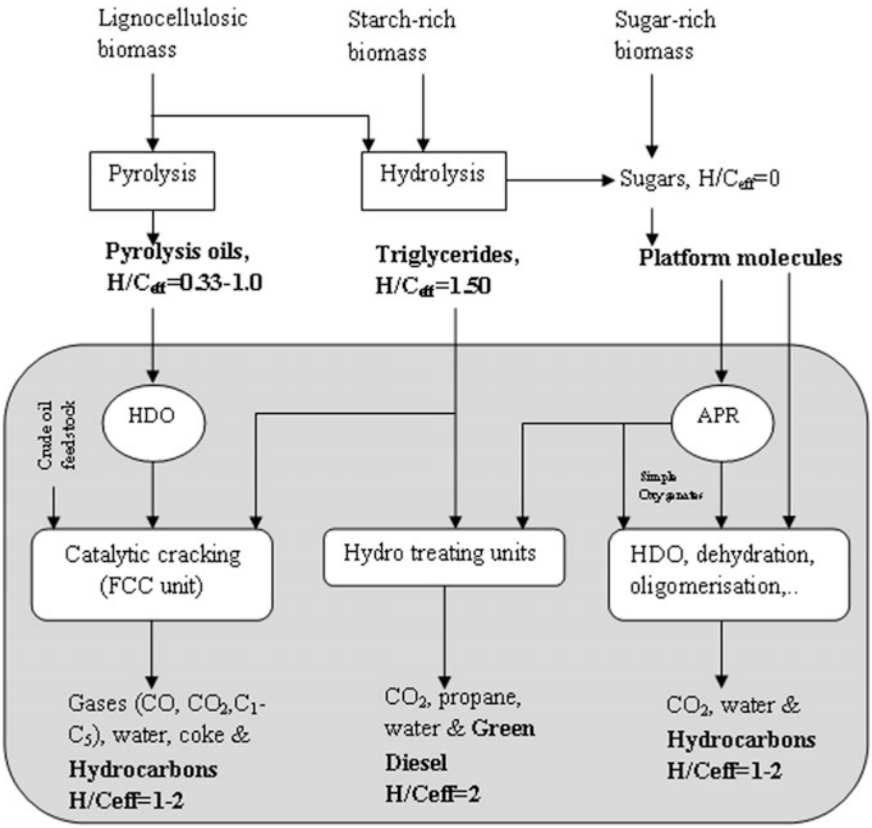

Fig. 12.3 Integration of biomass-derived feedstocks in conventional refinery processes (Melero et al. 2012)

hydrogen required for hydrotreating process can be produced from aqueous phase reforming (APR) process with sugar-rich biomass feedstock, which helps in reducing the cost of overall biorefinery integration with petroleum refinery and to produce more energy-dense products.

12.5.4 A Stand-Alone Refinery Process

Jones et al. (2009) proposed a design case for the conversion of hybrid poplar into gasoline and diesel, and its block diagram is shown in Fig. 12.4 in terms of

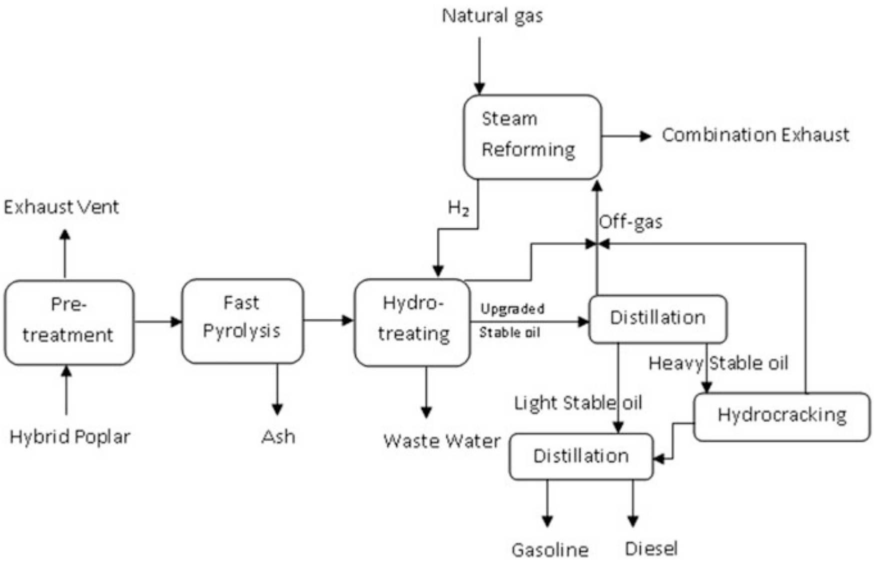

Fig. 12.4 A design case stand-alone refinery for fast pyrolysis-hydrotreating-hydrocracking process to produce hydrocarbons (Jones et al. 2009)

stand-alone refinery for fast pyrolysis-hydrotreating-hydrocracking approach. This approach has tried to use the refinery's hydrocracker unit for the upgrading of pyrolysis oil into drop-in liquid hydrocarbons like gasoline and diesel by avoiding the challenges (like the presence of oxygen and a high intensity of aromatic content in diesel cut of hydrotreated pyrolysis oil, which mismatches the specifications of fossil-derived diesel fuels) on using hydrotreating process. Hence, the hydrotreatment process can be used for getting stable pyrolysis oil and then further crack its heavy stable pyrolysis oil into drop-in diesel fuel in a hydrocracker, which can be a more viable option in terms better economy.

Their process economics analysis suggested that the production of transport fuels range hydrocarbons from biomass via the pyrolysis route is potentially economically attractive. Further, the cost becomes even more economical if the integration of conversion and upgrading processes are brought together under one roof with an existing refinery to take the advantage of infrastructure. The catalytic steam reforming is one of the techniques which can utilize the refinery equipment. It is very well understood that the pyrolysis oil contains both aqueous and organic fractions. The aqueous fraction can be effectively utilized for the production of hydrogen by processing in very well-established steam reforming unit. The added advantage of this technique is that the resulted hydrogen can be utilized for the hydrodeoxygenation of pyrolysis oil and as a result the whole process can be integrated.

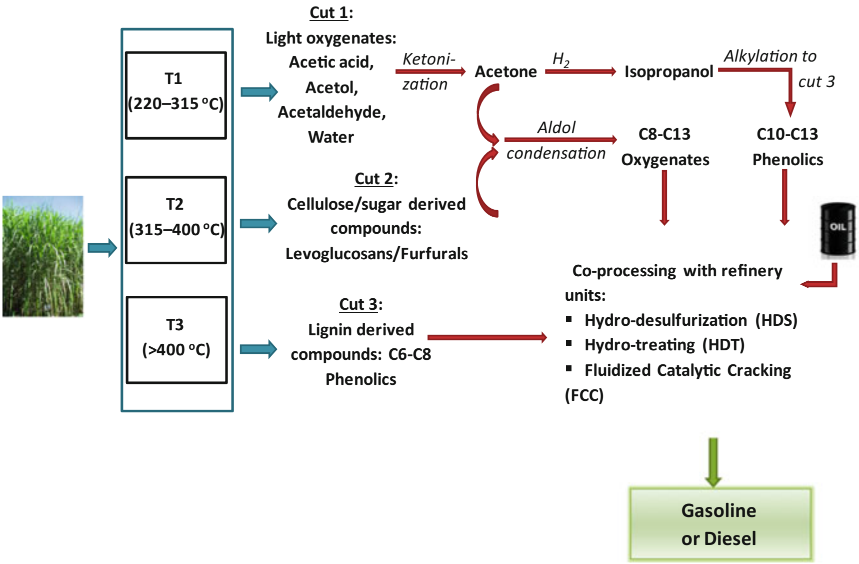

Fig. 12.5 Integration of multistage biomass torrefaction with catalytic upgrading (Anh 2014)

12.5.5 Cascading Catalytic Upgrading

The complex nature and multicomposition of pyrolysis oil leads to difficulties in direct processing in refinery processes. Anh (2014) proposed a different kind of biorefinery integration with thermochemical conversion of biomass route, i.e., torrefaction, as shown in Fig. 12.5. The motive of this scheme is to collect the pyrolysis vapors on torrefaction of biomass by condensation in the form of oil at three different pyrolysis temperature zones.

The first zone temperatures varies in between 220 and 315 °C wherein the pyrolysis oil fraction is enriched with light oxygenates and water. The second zone temperatures would be from 315 to 400 °C in which the oil fraction contains cellulose-derived compounds, whereas the third zone is from 400 °C in which the oil fraction contains lignin-derived compounds. Then it has proposed several chemical synthesis techniques like ketonization, aldol condensation, and alkylation for converting zone-1 and zone-2 fractions into C8-C13 oxygenates and C10-C13 phenolics, as shown in Fig. 12.5. Further, it has been emphasized to use the refinery process units like hydro treating, hydrodesulphurization, and FCC unit for final upgrading into fuel range hydrocarbons.

12.5.6 Kior Process

The KIOR group proposed a scheme for FCC of biomass-derived oxygenates like glycerol and pyrolysis oil with VGO in traditional refinery FCC unit at various levels (Cantu et al. 2012). The first option is to feed the biomass separately into the riser reactor bottom from where the pyrolysis vapors and char particles move toward the cyclone separator, from where the char and FCC catalyst particles are separated and moves into regeneration reactor wherein the char and the deposited coke on FCC catalyst are combusted with air to produce process heat. In alternative to first option, the three other options have been encouraged to co-process the biomass along with VGO either just before VGO feeding or along with VGO or just after VGO feeding.

12.5.7 Pyrolysis Oil Processing in Refinery

Based on the results (Naik et al. 2014a, b) obtained from the coprocessing of pyrolysis oil model compounds, such as acetic acid, 2-methoxy phenol, hydroxyacetone and glycoldehyde dimer, with VGO in FCC unit, it has been observed that the aliphatic oxygenates are easily crackable in FCC process at lower blending ratios, whereas the aromatic hydrocarbons are not easily cracked. Therefore, Naik et al. (2014b) proposed to first separate the aliphatic and aromatic oxygenates from the pyrolysis oil either by solvent extraction or other techniques. Accordingly, an approach for processing of pyrolysis oil in refinery infrastructure is proposed in Fig. 12.6. This kind of approach may help petroleum refineries to integrate it with fast pyrolysis process to increase the yield of liquified petroleum gas and also the valuable and most demanded petrochemical feedstock, i.e., propylene.

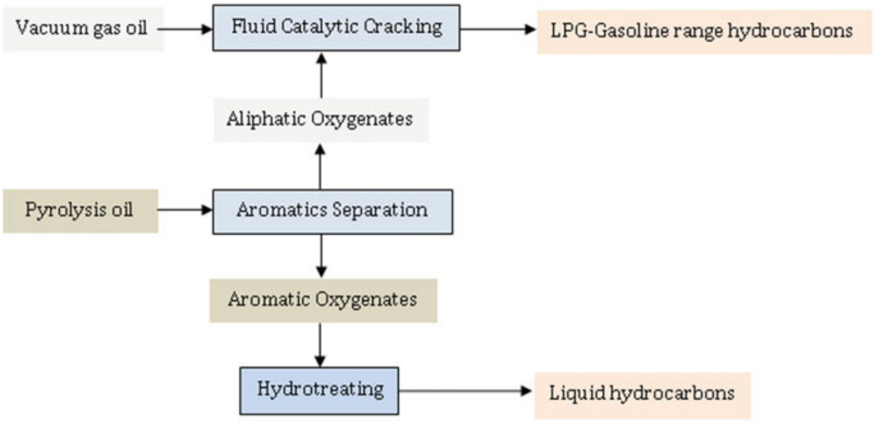

Fig. 12.6 An approach for the processing of pyrolysis oil in refinery units

12.6 Summary

This chapter sets out to be a comprehensive review of pyrolysis oil upgrading through refinery processes. The refinery infrastructure like FCC, steam reforming, hydrotreating, and hydrocracking unit can be utilized for upgrading of biomass-derived pyrolysis oil in effective way. The FCC catalyst is able to crack straight chain hydrocarbons or oxygenates of pyrolysis oil. Therefore, it is better to co-process the aliphatic oxygenates with VGO in FCC process after separating the compounds of lignin-derived monomers, whereas the steam reforming unit is able to crack the aqueous fraction of pyrolysis oil and the produced hydrogen can be utilized for the refinery utilization and make it economical. While the lignin-derived monomers or aromatic fraction of pyrolysis oil can be cracked in hydrocracking unit along with petroleum-derived fractions. The scope of integration of pyrolysis process with refinery units opens up the opportunity in reducing the processing and transportation costs of biomass-derived oxygenates while coprocessing. The concept of coprocessing of pyrolysis oil with petroleum fraction is feasible by means of effective utilization of refinery's infrastructure without major modifications.

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Part V
Utilization of Alternative Fuels

Chapter 13
Water-in-Diesel Nanoemulsion Fuels for Diesel Engine: Combustion Properties and Emission Characteristics

Hemant Kumar, M. K. Shukla and Vimal Kumar

Abstract Diesel engines are used in heavy transportation vehicles and heavy machineries as they produce higher torque at low speeds for a given power meeting the primary requirement for a heavy engine. Moreover, diesel engines provide higher compression ratio and, if gasoline has to be used in bigger engines, they will produce higher knocking due to preignition. Therefore, the use of diesel in heavy vehicles is indispensable; however, exhaust gases emerging from the engine contain pollutants predominantly nitric oxides (NO_x) and particulate matter (PM). Nowadays, there is an extensive focus toward improving emission characteristics and enhanced combustion properties with pure diesel oil in an IC engine. One of the recent ways to achieve the similar characteristics is to develop a water-in-diesel oil (W/D) nanoemulsion that reduces the pollutants and at the same time enhances combustion properties. Therefore, the proposed chapter is aimed to discuss the advancement and opportunities in W/D nanoemulsion fuel preparation using different surfactants and additives that provide improved emission characteristics and engine performance.

Keywords Nanoemulsions · Diesel engines · Engine performance
Emission characteristics

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13.1 Introduction

Energy consumption is increasing day by day, and the demand is expected to increase in the coming years. According to the report of international agency outlook 2016, 48% increase in energy demand is projected from 549 quadrillion Btu in 2012 to 815 quadrillion Btu in 2040, as shown in Fig. 13.1. To overcome the need, dependency on fossil fuels such as gasoline and diesel may cause a threat of energy crisis. On the other hand, environment issues such as emission of greenhouse gases, level of NO_x, and particulate matter in the environment pose a serious threat in using the fuels. To overcome the issues of heavy consumption of fossil fuel and environment concerns, there is a need to blend these fuels with some additives or renewable sources. Diesel engine is advantageous over gasoline engine because of their high thermal efficiency, less consumption efficiency, durability, and less CO_2 emissions (Khalife et al. 2017; Kim and Choi 2010; Şahin et al. 2014).

Compression ignition engines are most trustworthy, robust, and powerful engines and extensively used for heavy-duty vehicles/machines. High compression ratio and energy content of diesel give high turbo boost pressure even at low loads, which makes it suitable for heavy transportation vehicles. Principally, CI engine differs from gasoline engine in the sense that compressed air producing high temperature ignites the diesel in the cylinder in contrast to spark in gasoline engines. High thermal efficiency is achieved in case of diesel engines because of high compression ratio. In the last decade, CI engine technology has been improved a lot. Due to rapid advancement in technology, diesel engines are run by more sophisticated electronic controllers giving enhanced fuel economy and regulated emissions of engine discharge compared to the previously used IC engines. Table 13.1 shows the emission standards of USA for heavy-duty IC engines including more stringent emissions for NO_x and PM after 2007. Currently, the efficiency of diesel engine is ≈45%, and for

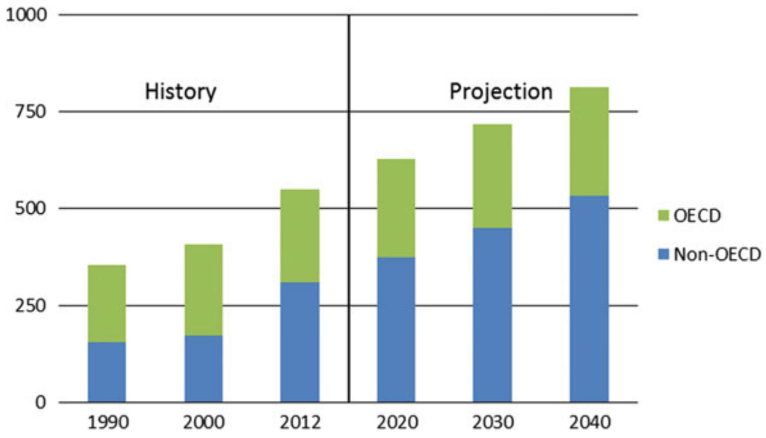

Fig. 13.1 World energy consumption (history and projection) quadrillion Btu. [*Source* U.S. Energy Information Administration (May 2016)]

Table 13.1 Emission standards of USA for heavy-duty IC engines (g/bhp hr)

Year	CO	HC	NO_x	PM
2004	15.5	2.4[a]	0.20	0.1[b] 0.05[c]
2007	15.5	0.14[d]	0.20[d]	0.01
2015	15.5	0.14	0.02[e]	0.01

Note [a]Stands for combined HC + NO_x; moreover, alternative standard in 2014 was NMHC + NO_x = 2.5 g/bhp.hr and NMHC = 0.5 g/bhp.hr; [b]General; [c]Urban Bus; [d]NO_x and NMHC standards were phased-in on a percent-of-sales basis: 50% in 2007–2009 and 100% in 2010. Most manufacturers certified their 2007–2009 engines to a NO_x limit of about 1.2 g/bhp.hr, based on a fleet average calculation. [www.dieselnet.com/standards/us/hd.php accessed on June 29, 2017]

gasoline engine, it is ≈35–40% (Hagos et al. 2017). For diesel engines, there is still a scope to take it up to 55–63% with the advancement in technology. In spite of attaining improved characteristics, obnoxious emissions such as PM (particulate matter), HC (hydrocarbon), NO_x, and CO from the IC engine outshine the improvement and severely affect the human health. Technology to overcome these unbearable emissions is of high cost and cannot be fitted in all types of diesel engines. Moreover, stringent government rules imposed on manufacturers toward reduction of emissions necessitate the development of diesel engines to save the human health. Therefore, there are two ways to improve the current scenario, either by changing the engine design or by altering the diesel fuel. However, it is economical to modify the existing fuels to meet the challenge.

Moreover, a limited source of petroleum fuels available on Earth is going to deplete soon in the coming years threatening to find out new ways of energy that will meet the increased energy demand. Therefore, the most economical way is to find out alternative sources of energy suitable to meet the engine demand. Consequently, in the recent years, work is going on blending the diesel oil with some renewable compounds such as alcohol, biodiesel, and water giving the cost-effective and eco-friendly solutions to the market.

Therefore, this chapter assesses the prospects of alternative and emulsified fuels as the alternatives of non-renewable resources like diesel that can be used in IC engines with improvements in performance and emission characteristics.

13.1.1 Limitations of Pure Diesel Fuels

Diesel fuels are product of middle distillate with a different array of hydrocarbons (carbon number series: C9-C28) in the boiling point range of 163–390 °C at atmospheric pressure (Hagos et al. 2017). Based on operation speeds, three types of diesels engine are categorized: (i) high-speed diesel engine (>1000 rpm) used in trucks, cars, and locomotives; (ii) medium-speed (300–1000 rpm) diesel engine used in marine applications and stationary power plants; and (iii) low-speed (<300 rpm) diesel engine used in agricultural machinery, ships, and fishing boats.

The first diesel engine was patented by Rudolf Diesel in 1898. Since the advent of IC engines, they are widely used for power generation, heavy machineries, and transportation. The basic difference between IC or CI engine and SI engine lies in the fact that combustion in diesel engine is initiated with compressed air having temperature higher than ignition temperature of fuel. During compression stroke, air is introduced in the cylinder at high compression ratio in the combustion chamber, thereby increasing the pressure and temperature of compressed air up to 30–50 bar and 500–600 °C, respectively (Pulkrabek 1997). Fuel is injected toward the end of the compression stroke at high velocity through small orifice or nozzles in the injector tip (Heywood 1988). Small droplets are formed due to atomization, taking heat from compressed air, and vaporizing. Autoignition of the fuel at this stage starts in the combustion chamber. Improvement in the injection system and combustion chamber design leads to the proper mixing of the air and diesel fuel that improves the combustion and emissions (Heywood 1988).

There are four stages in the combustion of diesel after injection into the combustion chamber: atomization, vaporization, mixing, and self-ignition. In the atomization step, very small droplets are formed and the smaller the droplet size, the faster and the efficient will be atomization process.

Vaporization of small droplets occur by taking heat from the compressed air generated by high compression ratio. Minimum compression ratio required in this process is 12:1, and about 90% of injected fuel vaporizes in a very short time of 0.001 s after fuel injection. During vaporization, surrounding temperature is cooled due to evaporative cooling, affecting further evaporation. Near the core of the fuel jet, high concentration of fuel and evaporative cooling brings the phenomena of adiabatic saturation. At this point, evaporation stops and no further evaporation occurs until additional mixing and heating take place.

Mixing of air and fuel should be such that the A/F ratio should lie in the combustible limit (equivalence ratio $0.8 < \Phi < 1.8$). Distribution of equivalence ratio is shown in Fig. 13.2 developed around the injected fuel jet. Zone A represents fuel–air mixture too rich to burn, B rich combustible, C burning at stoichiometric ratio, D lean combustible, and E too lean to burn (Pulkrabek 1997). Air–fuel mixture starts autoignition at 8° before TDC (BTDC) and 6–8° after starting of fuel injection in the chamber. After self-ignition, combustion starts at locations where A/F ratio is within combustible limit (1 to 1.5). Solid carbon soot is generated mostly in zones A and B. (The equivalence ratio, λ, is the actual A/F ratio divided by the theoretical.) Although CI engine is more efficient than SI engine, emissions from diesel engine puts a limit.

13.1.1.1 Particulate Matter Emissions

Particulate matter (PM) is formed at the zones of high fuel-to-air ratios in the cylinder during combustion in the form of smoke of solid carbon soot and

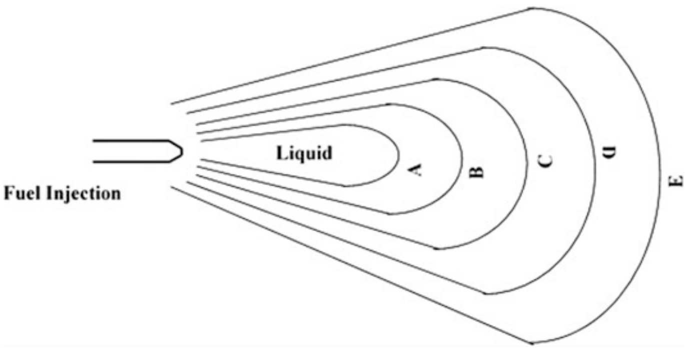

Fig. 13.2 Fuel jet of a CI engine depicting equivalence ratios of air–fuel vapor zones around the inner liquid core. Vapor zones are shown in the figure by notations A–E (Pulkrabek 1997)

condensed hydrocarbons (Pulkrabek 1997; Ferguson and Kirkpatrick 2016). Hagos et al. (2017) reported that aggravation of hydrocarbons is formed by the fuels of lower volatility, late injection of fuel, during high-load and high-speed operations. He further explained that due to low volatility fuel or late injection, some drops of fuel remain unburnt and emit carbon soot. Maximum emission of PM takes place during the condition of wide open throttle (WOT) referring to the condition of maximum intake of air and fuel of IC engine under load. Maximum fuel and air will give maximum power and low fuel economy.

Soot contains the carbon spheres formed due to the incomplete combustion of the carbon in the fuel-rich zone during combustion because of insufficient amount of oxygen:

$$C_xH_y + zO_2 \rightarrow aCO_2 + bCO + cH_2O + dC(s) \tag{13.1}$$

The carbon particles after reaction find sufficient oxygen, and most of them are converted to CO_2:

$$C(s) + O_2 \rightarrow CO_2 \tag{13.2}$$

The overall combustion taking place in the diesel engine is with lean air. Therefore, PM emission will greatly reduce if combustion is according to the stoichiometric ratio instead of lean air.

13.1.1.2 NO_x Emissions

Nitrogen oxide is a mixture of different oxides of the nitrogen including predominantly nitric oxide (NO), minimally nitrogen dioxide (NO_2), and in trace amount nitrous oxide (N_2O) (emission standards like engine exhaust are allowed up to 2000 ppm NO_x). Most of the NO_x is produced by oxidation of nitrogen present in air that is detrimental of human health. Some important reactions responsible for nitric oxide (NO) formation can be summarized as

$$O + N_2 \rightarrow NO + N \tag{13.3}$$

$$N + O_2 \rightarrow NO + O \tag{13.4}$$

$$N + OH \rightarrow NO + H \tag{13.5}$$

NO may further reacts to form NO_2 by various routes

$$NO + H_2O \rightarrow NO_2 + H_2 \tag{13.6}$$

$$NO + O_2 \rightarrow NO_2 + O \tag{13.7}$$

Nitrogen molecule (N_2) is stable at low temperatures, but at very high temperature (2500–3000 K), nitrogen molecule breaks into monatomic reactive state. Moreover, oxygen and water also break down at high temperature and their reactive forms (O and OH) react further with NO to form NO_x at high temperatures. Therefore, more the temperature, more will be the production of NO_x. Furthermore, NO_x in the exhaust decomposes in the presence of sunshine to NO and O. The reactive form of oxygen (O) initiates numbers of reactions; among them, most severe to human health is the combination of reactive oxygen with oxygen molecule to form ozone at Earth's surface. As a result, ozone thus formed is damaging for lungs and biological tissues. Therefore, a technology is needed to overcome the environmental issues such as PM, CO, and NO_x related to IC engines discussed in further sections.

13.1.2 Alternative Fuels Used in Compression Ignition Engine

Major fuel additives blended with diesel are oxygenated fuels, such as alcohol, ether, ester, apart from the water-emulsified fuel which is a main concern of this study. The reason for adding the oxygenated compounds such as alcohol in the diesel fuel lies in the fact that they possess high oxygen content responsible for clean combustion as an effect reduces considerable amount of particulate matters from the engine discharge. Among commonly tested alcoholic groups, methanol (Yilmaz 2012; Yao et al. 2008; Soni and Gupta 2017) and ethanol (Shi et al. 2006; Caro et al. 2001; He et al. 2003; Xing-cai et al. 2004; Kwanchareon et al. 2007) are blended with diesel fuel because of their specific properties such as high latent heat of vaporization and low boiling point. As the carbon atom in the alcohol increases the self-ignition temperature, vaporization latent heat also decreases (Table 13.2). Further, alcohol blending reduces NO_x emissions due to their capability to tolerate

Table 13.2 Properties of alcohol blended with the diesel/biodiesel (Hagos et al. 2017; Khalife et al. 2017; Geng et al. 2017)

Properties	Methanol	Ethanol	n-butanol	Diesel
Formula	CH_3OH	C_2H_5OH	C_3H_7OH	C_nH_{2n} or C_nH_{2n+2}; n = 13–17
Viscosity at 20 °C (cP)	0.5645	1.074	2.802	1.3–2.4 @ 40 °C (1-D; ASTM D975)
Boiling Point (°C)	64.70	78.37	117.40	180–360
Flash point (closed cup) (°C)	11	13	37	67
Oxygen content (wt%)	49.94	34.71	21.75	0
Cetane number	5	5–8	25	40–55
Latent heat of vaporization (kJ/Kg) at 25 °C	1165.41	918	706.3	–
Lower calorific value (kJ/Kg)	20,094	26,952	34,366	–
Higher calorific value (kJ/Kg)	22,884	29,847	37,334	42,677

high exhaust gas recirculation ratios (EGRs) and also lowers the ignition temperature depending on the chemical structure of the blended fuel (Khalife et al. 2017). Hagos et al. (2017) reported that blending of 15% alcohol in diesel is technically acceptable in IC engines with no further improvements. However, lower calorific value of alcohol in comparison with diesel oil results in lower energy of the blended fuels. Moreover, major limitation of using alcohol is their economic feasibility due to higher production cost.

In spite of similar function groups or similar molecular formulas (DME and butanol), alcohol and ethers have different properties due to the presence of −OH group in alcohol that is missing in ethers. Most popular ethers used in blending are DEE and DME due to their high cetane numbers. In CI engines, alcohol and ethers (such as DEE and DME) are advantageous because of their NO_x and PM reduction capabilities. On the other hand, blending of these fuels to the unmodified diesel engines brings corrosion, vapor lock, and high latent heat (Khalife et al. 2017).

Biodiesel is a renewable resource of energy consisting of mono-alkyl ester-based oxygenated fuel derived from the natural renewable resources such as vegetable oils and animal fats derived from transesterification reaction. Moreover, biodiesel can dissolve in diesel completely. Its high cetane value, high oxygen content (10–12 wt %), and absence of sulfur and aromatic contents make it blendable with diesel and hence reduce dependency on diesel fuels (Dwivedi et al. 2011; Khalife et al. 2017). Important findings regarding engine performance and emission characteristics of alternative fuels are summarized in Table 13.3.

13.1.2.1 Engine Performance of Blended Diesel Fuels

Brake thermal efficiency (BTE) is an important parameter to assess the performance of diesel engines using different fuels, which is defined as the ratio of brake power output to the energy introduced through the fuel injection (Sayin and Canakci 2009; Fang et al. 2013; Khalife et al. 2017). BTE increases significantly with the alcohol content in the alcohol–diesel test fuel. Blending of alcohol with diesel gives increased combustion efficiency, which is due to the increased amount of oxygen content that improves combustion and reduces the heat losses. The use of alcohol in the test fuel increases injection delay period that lead to a higher cylinder peak pressure, higher maximum heat release rate, and shorter combustion duration (Saravanan 2015; Geng et al. 2017). As a consequence, heat loss by combustion is reduced on account of requirement of lesser time to transfer the heat to the coolant.

Biodiesel blended with the diesel fuel showed the decreased values of BTE (Nabi et al. 2009; Kumar et al. 2013; Can 2014); however, when alcohol were mixed with the biodiesel–diesel blends, it showed increased values of BTE (Ashok 2011; Imdadul et al. 2016). This increased value in BTE can be explained by low cetane values of ethanol–biodiesel–diesel blends owing to the low values of oxygenates. Low cetane value of alcohol leads to the more precombustion mixing, which further leading to the high percentage of constant volume combustion. The second reason responsible for the increased value of BTE was due to the complete combustion credited to the additional lubricity of biodiesel. A study revealed increase in BTE by using blend of biodiesel and diesel with nanoadditive (aluminum oxide) and achieved enhanced BTE values (Aalam et al. 2015).

Another important parameter to assess the engine performance is brake-specific fuel consumption (BSFC), which is the ratio of rate of fuel flow in the engine per unit brake power output; therefore, lower values of BSFC are required (Lin and Wang 2004b). BSFC is certain to increase in case of using alcohol-blended diesel fuels because of their low heating value and energy content, resulting in injection of more fuel to get the same power output (Xing-cai et al. 2004; Fang et al. 2013). Methanol-blended diesel fuel results in higher values of BSFC compared with ethanol-blended diesel fuels. As the percentage of methanol or ethanol in the diesel fuel is increased, BSFC increases accordingly and the effect is more profound with methanol-blended diesel fuel (Khalife et al. 2017). According to Geng et al. (2017), no significant effect was observed on BSFC in case of alcohol in fuels (Geng et al. 2017). Improved values in the BSFC and cleaner exhaust in CI engine are suggested by preheating the intake air introduced into the combustion chamber. Biodiesel–diesel blends, diesel–biodiesel with additives, and diesel–biodiesel with nanoparticles showed increased values of BSFC in most of the studies (Hossain et al. 2013; Can 2014; Roy et al. 2014; Annamalai et al. 2016).

13.1.2.2 Combustion Characteristics

Combustion characteristics such as heat release rate and compression pressure vary with type of alternative fuels used in the IC engine (Geng et al. 2017). In case of alcohol blend in diesel, a significant decrease in compression pressure was observed when tested with increased percentage of alcohol content in diesel fuel (Li et al. 2013; Cao et al. 2005; Tutak et al. 2015) which may be responsible for high latent

Table 13.3 Performance of alcohol/biodiesel and diesel fuel blends in IC engine

Test fuel	Composition (vol. %)	Type of engine	Purpose of study	Remarks	Ref.
Diesel-ethanol additive	E (10–20), A (2)	1-cylinder, 4-stroke IDI mode	Exhaust emissions with/without additives to the blend	DI: Introduction of additive in the blend reduces increase in HC, 20% decrease in CO compared to neat diesel. No significant reductions in NO_x IDI: Introduction of additive reduces CO, HC and NO_x	Caro et al. (2001)
Diesel-ethanol-additive (cetane improver)-ignition improver (isooctyl nitrate)	E0 [D (100)]; E10 [E (10), D (90)];E30 [E (30), D (70)]; E10AI [E(10), A (2), I (0.1)]; E30AI [E (30), A (2), I (0.1)]	4-cylinder DI mode	Emission characteristics of five fuels: E0 (0% ethanol blend), E10, E30, E10AI, and E30AI at low and high loads	E10 and E30: with an increase in ethanol, smoke, NO_x, CO_2 emissions decrease, whereas CO, acetaldehyde emissions and unburned ethanol emissions increase E10AI and E30AI: CO, acetaldehyde, and unburned emissions are moderately decreased. THC emissions are significantly reduced even less than that of E0 at low loads	He et al. (2003)
Diesel-ethanol-solubilizer-additive (cetane no. improver)	A1 [E (15), So (2), D (83)] A2 [(1) + A (0–0.4)]	4-cylinder, 4-stroke high-speed DI mode	Heat release rate and emissions with/without additive and compared to baseline diesel fuel	A1: BSFC and thermal efficiency improved. NO_x and smoke improved. Ignition delay prolonged and total combustion delay shortened compared to neat diesel	Xing-cai et al. (2004)

(continued)

Table 13.3 (continued)

Test fuel	Composition (vol. %)	Type of engine	Purpose of study	Remarks	Ref.
				A2: NO_x and smoke emission further improved compared to blend alone At low to medium loads, CO emissions increased, whereas with CN addition CO emission decreased. At large loads, combustion characteristics of blend improved by addition of CN improver but limitations at lower loads	
Diesel-biodiesel-ethanol	E (0–100), B (0–100), D (0–100)	4-cylinder DI mode	Fuel properties and emissions of blend and comparison with neat diesel	The blend [E (5), B (5), D (90)] gave heating value near to diesel and also blend [E (5), B (15), D (85)] gave highest cetane index. At high engine loads, CO and HC reduced considerably, whereas NO_x increased compared to neat diesel	Kwanchareon et al. (2007)
Diesel-ethanol-additive (hydrogen peroxide)	B0 [D (100)]; B1 [E (50), D (50)]; B2 [B1 (88), A (12)]	1-cylinder, 4-stroke engine	Performance and emissions of B0, B1, and B2 fuels	B2-emulsified fuel showed an increase in BTE, whereas a decrease in specific fuel consumption, smoke density, PM, NO_x, HC, and CO was observed compared to B0 and B1 fuels	Ashok and Saravanan (2008)

(continued)

Table 13.3 (continued)

Test fuel	Composition (vol. %)	Type of engine	Purpose of study	Remarks	Ref.
Diesel-methanol-air-oxidation catalyst	Premixed air/methanol ignited by diesel	4-cylinder DI mode	Compare engine emissions operating on pure diesel/DMCC with or without oxidation catalytic converter	DMCC method reduced simultaneously soot and NO_x emissions, whereas increased the HC and CO emissions compared with original diesel engine DMCC method with oxidation catalyst reduced the CO, HC, NO_x, and soot emissions simultaneously	Yao et al. (2008)
Diesel-ethanol-surfactant (between 80)-additive (DME)	C1 [E (49.5), D (49.5), S (1)]; C2 [C1 (93), A (7)]	1-cylinder, 4-stroke DI mode	Emission characteristics using C1 and C2 fuels	C2 fuel showed increased BTE and decreased SFC, PM, SD, and NO_x compared to C1 fuel	Ashok (2011)
Biodiesel-pyrolysis oil (DSPO)	B (70–80), P (20–30)	3-cylinder IDI mode	Physical and chemical properties of pyrolysis oil and its blends were measured and compared with those of fossil diesel (FD) and biodiesel (B)	B/P blend at full load conditions showed increased BSFC compared with FD, whereas higher in case of biodiesel. Moreover, BTE is lower than B but similar to FD. CO_2 and NO_x increased for B/P blend	Hossain et al. (2013)
Biodiesel	B (100)	1-cylinder, 4-stroke engine	Performance and exhaust emissions	Less BP and BTE. Increased CO and NO_x, higher $T_{Exhaust}$ and peak pressure.	(Shehata 2013)
JME (Jatropha Methyl Esters)-water-CNT	D0 [JME (100)]; D1[JME (93), W (5), S (2)]; D2 [D1 + CNT (25 ppm)]	1-cylinder, constant speed engine	Performance and emissions using D0, D1, and D2	D2 fuel increased BTE compared with D0 and D1. NO_x and smoke significantly removed for D2 limiting CNT as environment pollutant	Sadhik Basha and Anand (2014)

(continued)

Table 13.3 (continued)

Test fuel	Composition (vol. %)	Type of engine	Purpose of study	Remarks	Ref.
Diesel-biodiesel	B (5–10), D (90–95)	1-cylinder, 4-stroke, DI mode	Performance and emissions of D/B blend at four engine loads	BSFC increased and BTE decreased. Increased NO_x, decreased smoke and HC for all loads. No change in CO at low to moderate loads, and CO decreased slightly at high loads	Can (2014)
Diesel-glycerol-surfactant (tween 80 + span 80)	Glycerol [W (0–40), G (60–100)], S (2)	Air-cooled, 4-stroke, DI mode	Formation of diesel–glycerol emulsion and testing it for engine performance and discharge emissions	With glycerin 10% and 20%, NO_x reductions were 5–15% and 25–50%, respectively. Increased thermal efficiency at high load	Eaton et al. (2014)
Diesel-surfactant (span 80)-additive (NP of Fe, Al and B)	S (0.1 wt%), A (0.5 wt%)	1-cylinder, 4-stroke, DI mode	Performance and emissions using nanofuels formulated by sonicating nanoparticles of aluminum (A1), iron (F1), and boron (B1) in base diesel	Reduced peak cylinder pressures and SFC for A1 compared to diesel. Increased exhaust gas temperatures and BTE for A1, F1, and B1 as compared to diesel at maximum loads. Reduced CO and HC with A1, F1. Minimal rise in NO_x at elevated temperatures	Mehta et al. (2014)

(continued)

Table 13.3 (continued)

Test fuel	Composition (vol. %)	Type of engine	Purpose of study	Remarks	Ref.
Diesel-biodiesel-additive (Wintron XC 30); kerosene-biodiesel	E1 [B (0–100), D (0–100)]; E2 [B (5–98), D (0–93), A(2)]; E3 [B (0–100), K (0–100)]	4-stroke 2-cylinder DI mode	Performance and emissions of diesel engine with three fuel series: E1, E2 and E3	BSFC increases with an increase in biodiesel (B) concentration in E1 and E2. CO emissions reduced with both E1 and E2 at low and medium loads, and HC reduced at all loads. E3 reduced CO at high loads only. NO_x reduced in E3 at all loads, but increase in B increases NO_x in E1 and E2	Roy et al. (2014)
Diesel-biodiesel-ethanol-NP (cerium oxide)-CNT	E (20), B (10), D (70), NP-CNT (25–100 ppm)	DI mode variable compression ratio engine	Performance and emissions	Addition of NP and CNT increases BTE, peak pressure and peak heat release. Increases CO at 50 ppm addition of NP and CNT with no change in NO_x	Selvan et al. (2014)
Peanut methyl ester (PME)-ethanol; PME-methanol; PME-butanol	PME (100); PME (80)-M (20); PME (80)-E(20); PME (80)-Bu (20)	4-cylinder, 4-stroke, naturally aspirated, DI mode	Effect of alcohol addition to PME biodiesel on engine performance and emissions	Alcohol addition to PME improves engine performance values compared to PME, but decreased performance results are attained compared to neat diesel fuel. Reduced CO and increased NO_x compared to PME (100%)	Tosun et al. (2014)

(continued)

Table 13.3 (continued)

Test fuel	Composition (vol. %)	Type of engine	Purpose of study	Remarks	Ref.
Diesel-biodiesel-additive (1, 4-dioxane)	[B (25), D (75)] + A (0.5–1)	1-cylinder, 4-stroke, DI mode	Performance and emissions	HC and CO emissions were reduced for B25-A (0.5) by 25.3 and 22.5%, respectively NO_x and smoke emissions were reduced for B25- A (1) by 15.2 and 24.6%, respectively	Vedharaj et al. (2014)
Diesel-biodiesel-additive (aluminum oxide NP)	[B (25), D (75)] + NP (25–50 ppm)	4-stroke, 1-cylinder, common rail DI mode, (CRDI) system-assisted diesel engine	Performance and emissions	Increased BTE and heat release rate. Decreased CO and increased NO_x	Aalam et al. (2015)
Diesel-biodiesel-additive (CeO_2 on amide-functionalized multiwall CN)	[B (5–20), D (80–95)] + A (30–90 ppm)	Heavy-duty DI mode, 4-cylinder engine	Performance and emissions	B (20) +A (90 ppm) improved emission characteristics such as NO_x, CO, HC, and soot. Improved engine performance such as decreased fuel consumption and increased power and torque	Mirzajanzadeh et al. (2015)
Diesel-biodiesel-ethanol-surfactant (isopropanol)-additive (alumina)	F1 [B (20), D (80)]; F2 [(B (15), E (4), D (80), S (1)) + A (100 mg/l)]	4-stroke, 1-cylinder, DI mode	Performance and emissions	F2 fuel blend gave high cylinder pressure and heat release rate with high BTE compared to neat diesel. CO and UBHC reduced, whereas NO_x increased slightly	Shaafi and Velraj (2015)

(continued)

Table 13.3 (continued)

Test fuel	Composition (vol. %)	Type of engine	Purpose of study	Remarks	Ref.
Biodiese-water-surfactant (span 80-additive (CeO_2 NP))	G1 [B (93), W (5), S (2)]; G2 [G1+ + NP (30 ppm)]	1-cylinder, 4-stroke engine	Performance and emissions	G1 fuel reduced smoke and NO_x emissions and improved BTE, BSEC compared with neat biodiesel, whereas HC and CO marginally increased G2 fuel reduced CO, HC, and NO_x with marginal reduction in smoke	Annamalai et al. (2016)
Diesel-biodiesel-additive (CeO_2 NP)	[B (20), D (80)] + A (10–30 ppm)	1-cylinder CI engine	Performance and emissions	Using (D/B/A) NO_x and smoke reduced compared with biofuel blend (D/B), whereas BTE, cylinder pressure, and heat release rate increased	Dhinesh et al. (2017)
Diesel-additives (A1: Al_2O_3 and A2: TiO_2)	D (100) + A1 (300 ppm); D (100) + A2 (300 ppm)	Water-cooled, reversal flame tube boiler	Performance and emissions	Thermal efficiency increased slightly and CO emission reduced to 200 ppm by A1, whereas 50 ppm by A2. No effect on NO_x emissions observed	Sungur et al. (2016)
Diesel-lemongrass oil (LGO)-surfactant (span 80 + tween 80)-DEE (diethyl ether)-A (CeO_2-NP)	H0 [LGO (25), D (75)]; H1 [LGO (25), D (63), S (2), W (10)]; H2 [LGO (25), D (63), S (2), W (10 including 50 ppm A)]; H3 [LGO (25), D (58), S (2), W (10 including 50 ppm A), DEE (5)]	1-cylinder, 4-stroke, variable compression ratio engine	Performance and emissions	H3 fuel reduced NO_x, smoke, HC, and CO emissions, whereas BTE and BSFC improved compared to H0. BTE and BSFC improved, and cylinder pressure and heat release rate increased by H3 fuel compared to H0 Combustion duration and ignition delay increased for H3, whereas they are decreased for H2	Sathiyamoorthi et al. (2017)

(continued)

Table 13.3 (continued)

Test fuel	Composition (vol. %)	Type of engine	Purpose of study	Remarks	Ref.
Diesel-lemongrass oil (LGO)-ethanol	G0 [LGO (25) D (75)]; G1 [LGO (25) D (75), E(2.5)]; G2 [LGO (25)D (75), E(5)]	1-cylinder, DI mode	Performance and emissions	G1 and G2 fuels increased combustion pressure, heat release rate, BSFC, and BTE than G0. However, higher NO_x and CO_2, lower smoke, and HC emissions observed for G1 and G2	Sathiyamoorthi and Sankaranarayanan (2017)
Biodiesel-water-surfactant (span80 + tween 80)	B (88), W (10), S (2)	4-stroke, 4-cylinder DI mode	Performance and emissions	Significant reduction in NO_x and smoke. Slightly higher BTE than pure biodiesel and lower noise than the pure diesel. Increased HC emission and reduced CO emission compared to diesel but higher than biodiesel	Shrivastava (2016)
Diesel-aegle marmelos oil (AMO)-diethyl ether (DEE)	D (50–100)—AMO (0–40)—DEE (0–10)	1-cylinder, 4-stroke, variable compression ratio engine	Performance and emissions by observing combined effect of CR and number of nozzle holes	For D/AMO/DEE (60/30/10), BTE improved, NO_x reduced for 100% load and 17.5 CR with 5 nozzle hole. Increasing number of holes improved performance by reducing brake-specific energy consumption (BSEC), increasing BTE and reducing emissions of HC, CO, and smoke	Krishnamoorthi and Malayalamurthi (2017)

(continued)

Table 13.3 (continued)

Test fuel	Composition (vol. %)	Type of engine	Purpose of study	Remarks	Ref.
Diesel-methanol-water	H1 [D (70–90), M (10–30)]; H2 [D (59.5–66.5), M (25.5–28.5), W (5–15)]	1-cylinder, 4-stroke, diesel engine	NO_x emissions from a methanol-blended fuel	H1 fuel consisting of D (70) + M (30) produced lower emissions than other blends, whereas NO_x emission was higher. H2 fuel consisting of D (59.5) + M (25.5) + W (15) significantly reduces NO_x emissions	Soni and Gupta (2017)

Note A Additive; *B* Biodiesel; *BP* Brake power; *Bu* Butanol; *CNG* Compressed natural gas; *CNT* Carbon nanotubes; *CR* Compression ratio; *D* Diesel; *DI* Direct injection; *DMCC* Diesel methanol compound combustion; *DME* dimethyl ether; *DSPO* Delinking sludge pyrolytic oil; *E* Ethanol; *EGR* Exhaust gas recirculation; *G* Glycerol; *H* Hydrogen; *I* Ignition improver; *IDI* Indirect injection; *K* Kerosene; *M* Methanol; *NC* Nanocatalyst; *NP* Nanoparticles; *P* Pyrolysis oil, *S* Surfactant; *SD* Smoke density; *SFC* Specific fuel consumption; *So* Solubilizer; *UBHC* Unburnt hydrocarbon; *W* Water heat of vaporization of alcohol as compared to diesel. Alcohol when injected into the intake port are vaporized by taking heat from the intake air causing decreased in-cylinder pressure and temperature during compression stroke.

Cetane number for diesel and ethanol is usually in the range of 40–45 and 5–15, respectively. Lower values of cetane number signify longer ignition delay allowing more fuel to vaporize in the prolonged time before ignition starts. There is an inverse relationship between the cetane and octane numbers, and as the ethanol percent is increased in the test fuel blend, cetane number keeps on decreasing (Hansen et al. 2005). If the cetane number of a fuel is low, long delay in ignition will be observed and that will cause more injection of fuel than desired before combustion starts. If the cetane number of the fuel is higher, combustion will start too early before TDC, resulting in the loss of engine efficiency.

According to Shehata, peak pressures for biodiesel fuels are always higher than diesel due to the presence of high oxygen content in the biodiesel molecules, leading to the increased rate of combustion, peak temperature, and pressure (Shehata 2013). Physical properties of biodiesel fuels such as high viscosity and low volatility correspond to reduced atomization and poor mixing with air. As a result, decreased burning rate of biodiesel fuels is obtained during the ignition delay period. Therefore, as engine speed increases, peak pressure decreases accordingly (Shehata 2013).

13.1.2.3 Emission Characteristics of Blended Fuels

Diesel engines are used in heavy vehicles due to their high combustion efficiency and power performance. NO_x emissions from IC engine include oxides of nitrogen such as nitric oxide and nitrogen dioxide (Hill and Smoot 2000; Hulwan and Joshi 2011; Khalife et al. 2017). However, NO_x and PM emissions pose detrimental effects to the human health. It is important to understand the emission characteristics of different diesel blends before studying emulsified diesel fuels. Alternative fuel such as alcohol blended with diesel reduces harmful emissions without changing the engine performance (Tosun et al. 2014; Geng et al. 2017). Emission characteristics, i.e., NO_x, CO, particulate matter (PM), are discussed as follows:

NO_x emission

It has been observed that using alcohol in diesel blend, there is reduction in NO_x formation in the engine discharge (He et al. 2003; Xing-cai et al. 2004; Yao et al. 2008; Sadhik Basha and Anand 2014; Eaton et al. 2014; Roy et al. 2014; Vedharaj et al. 2014; Mirzajanzadeh et al. 2015; Annamalai et al. 2016; Dhinesh et al. 2017; Sathiyamoorthi and Sankaranarayanan 2017; Shrivastava 2016; Krishnamoorthi and Malayalamurthi 2017), whereas other studies indicate increase in NO_x emissions (Kwanchareon et al. 2007; Ashok 2011; Hossain et al. 2013; Can 2014; Mehta et al. 2014; Roy et al. 2014; Shaafi and Velraj 2015; Sathiyamoorthi and Sankaranarayanan 2017; Soni and Gupta 2017). Basically, NO_x formation in the discharge depends on the specific engine and its operating conditions that explain the contradictory statements by different researchers (Hulwan and Joshi 2011). Hence, there is no consensus for the NO_x emission in the discharge because of complex combustion process in case of oxygenated compounds–diesel blends. It has been found that there is a reduction in NO_x emissions in the discharge on blending alcohol with a mixture of diesel–biodiesel. NO_x emissions are also influenced by the variation of load on the engine. At low loads, NO_x emission reduces significantly in case of alcohol–diesel or alcohol–biodiesel–diesel blends owing to high latent heat of vaporization of ethanol and methanol causing reduced in-cylinder temperature. On the other hand, alcohols contain high oxygen content which may further increase combustion temperature or NO_x (Geng et al. 2017) . As the load is increased, no sufficient cooling due to excessive temperature in the cylinder supported by high oxygen content in the alcohol groups responsible for increased NO_x level in the discharge. A reduction in NO_x emissions, sulfur, and soot formations is observed by using alcohol–diesel blends. However, the alcohol blends have several disadvantages, such as greater ignition delay of air–fuel mixture because of low cetane number and high latent heat of vaporization of the alcohol (Geng et al. 2017). NO_x emissions are reduced in the engine discharge depending upon the oxygen content in the combustion zone and the combustion temperature (Hora and Agarwal 2015).

CO

Carbon monoxide formation is the consequence of incomplete combustion of the fuels. Generation of CO in the exhaust is the result of low-temperature combustion, and ethanol test fuels are responsible for producing low-temperature combustion in the in-cylinder charge. Therefore, CO emission increases in the exhaust of ethanol-blended test fuels as the alcohol concentration is increased in the alcohol–diesel blend (Yao et al. 2008; Shehata 2013; Yilmaz 2012; Annamalai et al. 2016; Geng et al. 2017). Low cetane number and high latent heat of vaporization of the alcohol lead to the ignition delay, causing reduced temperature in the cylinder, and are responsible for increased concentration of CO in exhaust. Further, it was also reported that increase in oxygen content in the alcohol increases the CO content, which was justified by the fact that CO content in the exhaust was maximum for methanol–diesel as compared to ethanol–diesel blend (Table 13.2) and for n-butanol slight change in CO. For the case of ethanol–biodiesel–diesel blend, CO emissions increased drastically at lower load and decreased at higher loads (Hossain et al. 2013; Can 2014) which may be due to the decrease in combustion temperature in the chamber at low loads because of delayed combustion retarding the oxidation process, though enough oxygen was present in the chamber. Injection timing also plays an important role in deciding the CO content in the exhaust for ethanol–biodiesel–diesel blend; however, retardation of injection timing increases CO in the emission (Sharon et al. 2013; Tosun et al. 2014; Vedharaj et al. 2014).

Moreover by adding additives such as carbon nanotubes (Xing-cai et al. 2004; Selvan et al. 2014), hydrogen peroxide, or aluminum (A1), iron (F1), boron (Mehta et al. 2014), Al_2O_3, and titanium oxide (Sungur et al. 2016) in the ethanol–diesel blends reduced CO generation in the exhaust (He et al. 2003; Kwanchareon et al. 2007; Mirzajanzadeh et al. 2015; Sungur et al. 2016; Shrivastava 2016).

Hydrocarbon (HC) emissions

Hydrocarbon emissions or unburnt fuel may be initiated at low-temperature regions, which may take place near the boundary layer, near the wall, and crevice layer (Fang et al. 2013; Rakopoulos et al. 2007). It has been reported that engine speed and load also affect the HC emissions (Labeckas et al. 2014). For alcohol–diesel fuel blend, HC emission increased at low loads because of low in-cylinder temperature caused by high latent heat of evaporation of alcohol effecting fuel/air mixing to be poorer. In contrast, HC emissions increased at low loads in case of n-butanol–diesel blend, which may be due to the low heat of vaporization of n-butanol compared to methanol and ethanol. At high speeds and loads, HC emissions decreased for alcohol–diesel blend and reduction in the HC value was more prominent in case of ethanol–diesel blend compared to methanol–diesel blend (Kwanchareon et al. 2007). It has been reported that hydrocarbon emissions increase in case of ethanol–diesel test fuels owing to the presence of high amount of single hydrogen radicals in the ethanol (Geng et al. 2017). Pure biodiesel is viscous in nature that sprays improperly in the biodiesel–diesel blend giving poor combustion, and as a result, HC emission increases under the full load condition. However, lesser percent of biodiesel in the test fuel at partial engine load conditions gives reduced emissions of HC because of the presence of high amount of oxygen and lower viscosity of biodiesel–diesel fuel (Geng et al. 2017).

For ethanol–biodiesel–diesel blends, different findings have been reported where HC emissions reduced at low ethanol concentration in the blend compared to the increased emissions at high ethanol concentration in the blend. This may be due to the high value of cetane number of biodiesel as compared to diesel which attributes to the easier ignition and complete combustion at low concentrations of ethanol. The effect of A/F ratio in case of ethanol–biodiesel–diesel blends has been reported for significant reduction in the HC values. The increase in the A/F ratio from 1.5 to 5.5 decreased HC emissions by $\approx$30-folds.

Particulate matter (PM) emissions

Particulate matter in exhaust is majorly discharged by diesel engines and consists of soot, liquid, or solid phase components (Khalife et al. 2017). PM is formed at the zones of high fuel-to- air ratios in the cylinder during combustion in the form of smoke of solid carbon soot and condensed hydrocarbons (Pulkrabek 1997; Ferguson and Kirkpatrick 2016). Hagos et al. (2017) reported that aggravation of hydrocarbons is formed by the fuels of lower volatility, late injection of fuel, during high-load and high-speed operations. Further, for low volatility or late injected fuels, few drops of fuel remain unburnt and exhausted with carbon soot. Maximum PM emission takes place during the wide open throttle (WOT) condition, referring to the condition of maximum intake of air and fuel of IC engine under load (Hagos et al. 2017).

Using alcohol, blended test fuels decrease the PM in the atmosphere (Ashok 2011). Compounds such as alcohol consist of oxygen content, which is responsible for PM reduction in the discharge. It has been observed that increased amount of oxygen content in the fuel significantly reduces the PM emissions. Further, other factors such as cetane number, viscosity, type of oxygenated additive, and its chemical structure also affect the PM emissions. PM emission increases at high loads; however, for ethanol, PM emission reduces considerably due to the fact that high in-cylinder temperature is reached in case of ethanol blending compared with diesel alone.

Alcohol–diesel blend behaves differently from biodiesel–diesel blend in terms of PM reduction, which can be explained by the fact that alcohol blending in diesel delays ignition whereas biodiesel–diesel blending advances the ignition.

13.2 Water-in-Diesel Emulsion Fuels

13.2.1 Principles

An emulsion system consists of two or more immiscible phases, one dispersed in another. The inner encapsulated phase is dispersed or internal phase, and the other outer phase is known as continuous phase or external phase. Since immiscible liquids cannot be blended due to high surface tension or interfacial tension, a surface active agent is then required to form the dispersion of one phase to another by reducing the interfacial tension through reduction in Laplace pressure (Kumar and Kumar 2017). Other role of surfactant is in stabilizing the system by avoiding coalescence between dispersed droplets by providing electrical double layer near the interfaces (Baskar and Senthil Kumar 2017; Bidita et al. 2014). Two types of emulsions are possible: two-phase and three-phase emulsions. Two-phase emulsion depends on continuous phase and dispersed phase concentration, surfactant properties, and mixing type (Stalidis et al. 1990; Chen and Tao 2005; Kundu et al. 2013; Hasannuddin et al. 2015). Classification of these emulsions is water-in-oil (w/o) and oil-in-water (o/w) (Chiaramonti et al. 2003). If the dispersed phase is water, emulsion is known as w/o emulsion, whereas the reverse is known as o/w.

Three-phase emulsions are classified based on the dispersed phase and continuous phase as w/o/w and o/w/o. Application of water-in-oil-in-water emulsions lies in cosmetics, food, and pharmaceutical products, whereas oil-in-water-in-oil emulsion has application in engines as fuels (Lin and Wang 2004b). NO_x and CO emissions are appreciably reduced compared to other types of emulsions for three-phase emulsions with the drawback of increased viscosity (Lin 2003). An emulsion may be macro-, micro-, and nanoemulsion depending on the average droplet size of dispersed phase in thermodynamically stable macro-sized droplets, kinetically stable nanosized (20–200 nm) droplets, or thermodynamically stable micro-emulsion in the size range of 5–50 nm (Solans et al. 2005; Kumar and Kumar 2017). HLB system determines the type of surfactant used for a particular emulsion system (4–8: w/o; 8–10: bicontinuous; 10–18: o/w). The important property a surfactant should possess is its burning without polluting the environment (Lif and Holmberg 2006; Nadeem et al. 2006). Some of the studies revealed that the burning of non-ionic surfactants in the combustion chamber is eco-friendly (Vellaiyan and Amirthagadeswaran 2016; Kumar and Kumar 2017).

Formation of emulsions may take place by either of two ways: mechanical devices or chemical potential of the components. Mechanical devices implement high energy methods such as agitators or mixers, high-pressure homogenization, ultra-sonication, and micro-fluidization, whereas low energy method is mainly phase inversion temperature method. Formation of macro-emulsion may take place by blending or mixing of the dispersed and continuous phases in the presence of surface active agents, altering their interfacial tension, and however, nano- or micro-emulsion formation requires high shear to form smaller size droplets; therefore, high energy methods are required (Tadros et al. 2004; Al-Sabagh et al. 2011; Solans et al. 2005).

Diesel engines are favored in transportation and heavy industry sectors due to its high power output, better efficiency, and fuel economy compared to spark ignition engine (Ithnin et al. 2014; Vellaiyan and Amirthagadeswaran 2016), although major constraint lies in its obnoxious emissions consisting specifically of NO_x and particulate matter (Bidita et al. 2014). These days, more stringent government policies against discharge of harmful gases and pollutants need either some changes in the engine design or improvements in the fuel properties. One of best ways toward improving the emission standards is to bring changes in fuel properties used in the system. One of the new research areas in this context is to use w/o emulsion fuels. The most important factors considered using w/o emulsions can be summarized as (i) reduced NO_x and PM emissions caused by reduced temperature in the combustion chamber and (ii) improved combustion efficiency.

13.2.2 Emulsification Mechanism

Emulsification process being non-spontaneous shows tendency to separate the phases; therefore, high energy is required for the preparation of emulsion oil. In this process, expansion of interface takes place by the energy input of $\Delta A\gamma$ magnitude, where ΔA is the incremental interfacial area from A_1 of the bulk of the oil to the A_2 of new large number of droplets produced ($A_2 > A_1$) and γ is the interfacial tension of dispersed and continuous phase system.

As γ has positive value, energy required to expand the surface is large and positive. Since the term $T\Delta S$ (entropy of dispersion) in Eq. (13.8) is also positive and small, ΔG is positive, indicative of non-spontaneous emulsification process. Hence, energy is required to form the droplets (Tadros et al. 2004).

$$\Delta G = \Delta A\gamma - T\Delta S \tag{13.8}$$

The formation of macro-emulsion consisting of large droplets of few micrometers is, therefore, comparatively easy, and as a result, high-speed mixers are sufficient to form the emulsion. Instead, formation of very small droplets of the order of nanoscale requires either high energy requirement or large amount of surfactant or both simultaneously.

13.2.2.1 High Energy Requirement

Formation of nanoemulsions by implementing high energy can be explained by Laplace pressure p, the difference in pressure between inside and outside the droplet (Tadros et al. 2004).

$$p = \gamma \left[\frac{1}{r_1} + \frac{1}{r_2} \right] \tag{13.9}$$

where principle radii of curvature of the drop are r_1 and r_2. Since, for a spherical drop, $r_1 = r_2 = r$, Eq. (13.9) reduces to

$$p = 2\gamma \left[\frac{1}{r} \right] \tag{13.10}$$

Breaking of a droplet into smaller drops needs high shearing that increases the value of p. Deformation of spherical drop into the smaller prolate ellipsoidal drops needs more stress for deformation. This stress is transmitted by the surrounding liquid requiring violent agitation, and hence, more energy is required to form small droplets.

13.2.2.2 Role of Surfactant

In the formation of emulsions, significant role is played by surfactants. Surface active agents lower the interfacial tension and hence reduce the value of p (Eqs. 13.9 and 13.10). Consequently, lower stress is required to deform the drops. Moreover, surfactants avoid coalescence of newly formed drops.

Emulsification process is basically a dynamic process in which two competing process takes place: disruption of the bulk liquid into smaller droplets and recombination of newly formed droplets.

13.2.3 Stability of Emulsion

Stability criteria is an important factor of emulsified fuels considered for proper running in the engines as it influences the fuel injection system (Vellaiyan and Amirthagadeswaran 2016). Destabilizing the emulsion during engine operation may bring failure of engine, and it may damage the engine parts (Ithnin et al. 2014).

According to Chen and Tao (2005), surfactant concentration is important for stability of emulsion and an optimal dose is suitable for a particular system (Chen and Tao 2005). Going away from the optimal dosage or high concentration, emulsion stability decreases due to rapid coalescence, whereas, at low concentration, destabilization occurs due to agglomeration of the oil drops. Other factors such as oil-to-water ratio (stability increases with decrease in o/w ratio), stirring intensity (high), mixing temperature (optimum), and mixing time (high). Nadeem et al. (2006) reported that the factors responsible for emulsion stability depend on water content, surfactant percent, temperature, viscosity, and specific gravity. Watanabe et al. (2010) emphasized on selection of the surfactant, appropriate agitation frequency, and emulsification period. Stability of the emulsion is a measure of resisting the change in properties with time. The more stable is the emulsion, lesser is the change in its properties in terms of creaming, flocculation, coalescence, and Ostwald ripening. Creaming or sedimentation is observed due to the density difference of the two immiscible phases. Dispersed phase either rises to the surface or moves downward. In case of w/o emulsion, dispersed phase accumulates at the bottom and forms a creamy layer. Flocculation takes place when droplets associate together due to the colloidal forces and forms large aggregates while individual drops remain separated by a thin film of continuous phase. Thin film reduces in thickness attributable to the van der Waals forces and forms large flocks promoting coalescence process. Therefore, flocculation could be understood as a precondition to coalescence. Flocculation process may be reversible or irreversible depending on the nature of interactions of the drops to be weak or strong. Coalescence is the process of merging two or more droplets in a single larger unit of reduced surface area compared to the individual droplets. Droplets now are no longer separated by a thin continuous film, and the areas where the films are weak have tendency to fuse together eventually due to the attractive forces or hydrodynamic instabilities (Velev et al. 1997). Ostwald ripening differs from coalescence in the fact that the film surrounding the droplets does not involve rupture of the thin film. Instead, mechanism involves different in solubility of different size of droplets as they possess different Laplace pressure (Eq. 13.10). Larger the difference between the droplet sizes, the greater will be the Ostwald ripening rate. Therefore, mechanism is driven by difference in chemical potential of the differently sized droplets (Kumar and Kumar 2017).

13.3 Performance of Water-in-Diesel Emulsions

Performance of water-in-diesel (W/D) emulsions in terms of engine performance and emissions is explained in the following sections, and the work performed on water-emulsified systems is summarized in Table 13.4 .

Table 13.4 Performance and emission characteristics of water-in-diesel fuels in IC engine with/without additives

Test fuel	Composition (vol. %)	Type of engine	Objectives	Fuel property improvement	Ref.
Diesel-water-surfactant (span 80 + tween 80) + additive (diglyme)	W (10), S (2)	4-stroke, water-cooled, DI mode	Performance and emissions of three-phase emulsion (O/W/O) using additive as combustion improver	Additive in O/W/O emulsion increased NO_x and combustion efficiency. Lowered fuel consumption rate and BSFC. PM and CO decreased, whereas CO_2 increased	Lin and Wang (2004b)
Diesel-water-surfactant (*)	W (5–20), S (2)	1-cylinder diesel engine (1200–3300 rpm)	Performance and gases exhaust temperature	Torque, power and BTE increased (for 20% W, 3.5% increase over diesel) with water percentage, whereas BSFC and gases exhaust temperature decreased with water %	Abu-Zaid (2004)
Diesel-water-surfactant (polyethylenglycole monoleate and sorbitole sesquioleate)	W (10), S (†)	Turbocharger, intercooler, IDI mode	Performance and emissions	Improved brake efficiency and significantly reduced thermal NO, soot, hydrocarbons, and PM	Armas et al. (2005)
Diesel-water-additive (cerium-based additive)	HD emulsion: D (88), W (12), S(†) LD emulsion: D (94), W (6), S(†) HD/LD emulsion + Additive (0.35) to the blend	EURO-3 LD diesel vehicles	Emissions of experimental LD emulsion, HD emulsion, and combustion improver additive	The emulsion fuel reduces the PM emissions with −32% for LD vehicles and −59% for the HD engine NO_x emissions remained unchanged, +26% hydrocarbons (HC), +18% CO, and +25% PM increased for LD vehicles In contrast, CO (−32%), and NO_x (−6%) were reduced by the emulsion for the HD engine and only hydrocarbons were slightly increased (+16%) Additive was insufficient to reduce the emissions in HD engine but improved all emissions in LD engine	Farealetti et al. (2005)

(continued)

Table 13.4 (continued)

Test fuel	Composition (vol. %)	Type of engine	Objectives	Fuel property improvement	Ref.
Diesel-water-surfactant (sorbitan monooleate/gemini)	W (5–15), S (†)	4-cylinder, 4-stroke, DI mode	Performance and emissions	PM, NO_x, CO, and SO_x decreased using W (15) with surfactant but no change in engine's efficiency	Nadeem et al. (2006)
Diesel-water-surfactant (*)	W (15), S (2)	4-cylinder, 4-stroke, DI mode	Performance and emissions of two-phase and three-phase emulsions	In comparison with two-phase (w/o), three-phase emulsion (o/w/o) found decreased NO_x and smoke. Increased CO and CO_2. BSFC and BTE increased	Lin and Chen (2006)
Diesel-water-surfactant (*)-additive (2-EHN)	W (13), S (2), A (0.2) Emulsion	4-stroke, 4-cylinder, DI mode	Performance and emissions	Improved NO_x and HC. Retarded fuel injection, smaller ignition delay. Lower cylinder pressure and temperature	Ghojel et al. (2006)
Diesel-water-surfactant (Triton X-100)	D (65–100), W (0–30), S (0–5)	1-cylinder, 4-stroke, IDI mode	Stability and performance of the emulsion	Emulsion with specification: 10% W, 0.2% S at 15,000 rpm found stable Maximum pressure rise rate increased with increasing the amount of water and reduction in engine speed At water >20%, higher compression ratio (>22) required to run engine smoothly Water addition reduced brake power output to drop slightly and BSFC to increase slightly, reduced power but improved NO_x emissions	Selim and Ghannam (2009)
Diesel-water-surfactant (Tween 20)	W (5–30), S (2)	4-stroke, 4-cylinder, DI mode (1000–3000 rpm)	Performance and emissions	Increased water content (5–30) resulted in high thermal efficiency, improved NO_x, decreased NO, and increased BSFC, although CO_2 emission was higher than that of pure diesel	Alahmer et al. (2010)

(continued)

Table 13.4 (continued)

Test fuel	Composition (vol. %)	Type of engine	Objectives	Fuel property improvement	Ref.
Diesel-water-surfactant (span 80 + tween 80)-additives (alumina NP)	W (15), S (2), A (25 ppm)	1-cylinder, 4-stroke, DI mode (1500 rpm)	Performance and emissions	Low cylinder peak pressure and heat release rate (short ignition delay). BTE improved by 28.9%; NOx emission reduced (at full load is 891 ppm)	Basha and Anand (2011)
Diesel-water-surfactant (*)-additive (nanoorganic additive (glycerin)	W (10 and 15), S (†)	4-cylinder engine with common rail fuel injection system	Performance and emissions	For 10% emulsion fuel: BTE was significantly improved by 14.2% compared to pure diesel, and there was reduction NO_x emissions by 30.6% and considerable reduction in CO emissions	Yang et al. (2013)
Diesel-water	W (20), D (80)	4-cylinder, 4-stroke, turbocharged engine (2000 rpm) at full load	Performance and emissions of oxygen-enriched combustion (OEC)	Lower BSFC, higher cylinder pressure and shorter ignition delay using OEC alone. Opposite trends found using WDE. PM and NO_x reduced simultaneously by applying OEC combined with WDE	Liang et al. (2013)
Diesel-water-surfactant (*)	W (10), S (10)	4-cylinder, DI mode (800–3600 rpm) at 25–100% load	Performance and emissions of emulsion ED [10] (10% w) at different engine loads	In-cylinder pressure and heat release rate gave similar values such as base diesel fuel alone. Reduced engine power output with higher. Lower exhaust gas temperature and NO at all loads and engine speeds. High CO emissions at low load and low engine speeds	Fahd et al. (2013)
Diesel-water-surfactant (Triton X-100)-additive (CeO_2)	W (0.7–1), S (0.25–0.4), A (80 ppm)	Compact air-cooled diesel engine (Model YANMAR L48N)	Performance and emissions with or without fuel additive	Reduced BSFC and exhaust mass flow rate, increased BTE using emulsion with additive compared to neat diesel. There was reduction in CO_2, NH_3, and NO_x emissions with additive	Bidita et al. (2014)

(continued)

Table 13.4 (continued)

Test fuel	Composition (vol. %)	Type of engine	Objectives	Fuel property improvement	Ref.
Diesel-water-surfactant (Span 83 and Tween 80)	W (0–15), S (5) in wt% Surfactants	1-cylinder, 4-stroke DI mode	Thermal efficiency and emissions	Thermal efficiency increased up to 19.9%. Significant reduction in NO. PM emissions decreased at high loads. However, CO and HC significantly increased	Syu et al. (2014)
Diesel-water + air	W (2–10)	4-cylinder, 4-stroke, turbocharged, common rail injection, 1.461 L, CR: 18.25:1	Water injection (WI) into intake air on the performance and exhaust emissions	Smoke index, K and NO_x emissions decreased as WR (water ratio) increased by WI method. Maximum decrease in NO_x emission (12.5%) for 9.4% WR at full load (149 N m) and 2500 rpm. At a particular load and 2000–3000 rpm, there was no change or slight increase in BSFC. BSFC decreased by 4% water at a particular load and 3500 rpm, showed no change in-cylinder pressure, and indicated power	Şahin et al. (2014)
Diesel-water-surfactant (*)	[W (2–10), D (90–98)] + S (2)	6-cylinder, DI mode	Evaluate engine power, torque, and noise emission	Higher water addition showed decreased engine power, torque and no effect on noise. For 2% water addition showed improved engine power, torque, and noise emission	Seifi et al. (2016)
Diesel-water-surfactant (*)	D + 21% air; [D (90), W (10)] + S; D + 27% air.	1-cylinder, 4-stroke engine	Engine discharge and performance by two methods diesel with different percent of O_2 in air and with water	BTE enhanced, improved combustion characteristics, and reduction in HC emissions	Baskar and Senthil Kumar (2017)

Note A Additive; *BSEC* Brake-specific energy consumption, *D* Diesel; *EHN* Ethylhexyl nitrate; *DEE* Diethyl ether; *W* Water; *S* Surfactant; *NP* Nanoparticles, *DI* Direct injection; *IDI* Indirect injection; *NA Data not available; † Surfactant percent not specified

13.3.1 Engine Performance

13.3.1.1 BSFC

In case of water-emulsified fuels, comparison of BSFC with base diesel requires modification in BSFC equation used for base diesel fuel so that equivalent fuel consumption is considered to evaluate for different fuels

$$m^{\cdot}_{f1} = \frac{(100 - W)\rho_d}{(100 - W)\rho_d + W\rho_w} m^{\cdot}_{f0} \tag{13.11}$$

$$BSFC = \frac{m^{\cdot}_{f1}}{W^{\cdot}_b} \tag{13.12}$$

where $m^{\cdot}_{f0}$ is the rate of addition of blended fuel consumption, W is the percentage (vol. %) of water, ρ_d and ρ_w are the densities of diesel and water, respectively, and $W^{\cdot}_b$ is output brake power. BSFC value for W/D emulsion fuel is higher as compared to base diesel fuel because of lower calorific values, as shown in Fig. 13.3 (Fahd et al. 2013). Low heating value or energy content results in injection of more

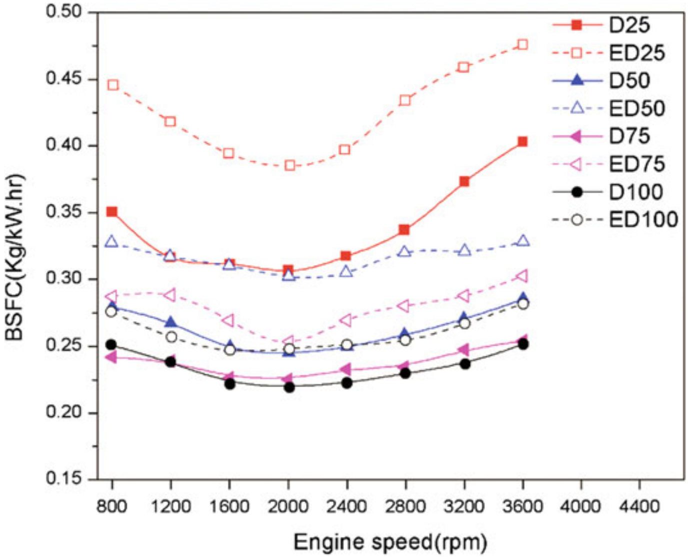

Fig. 13.3 Variation of BSFC values at different engine speeds and loads for 10% water in emulsion (ED) considering diesel (D) as a total fuel. D25 to D100 and ED25 to ED100 indicates 25–100% load conditions for diesel and emulsion (Fahd et al. 2013) (Reprinted from Elsevier Publications, 102, Fahd et al., Experimental investigation of the performance and emission characteristics of direct injection diesel engine by water emulsion diesel under varying engine load condition, 1042–1049)

fuel to get the same power output, consequently increasing values of BSFC (Fig. 13.3). BSFC value may be calculated by two ways: (i) by considering the W/D emulsion fuel as a total fuel and (ii) by calculating the actual amount of diesel burnt. In both ways, as engine speed increases, at fixed load, BSFC value first decreases and then goes through minimum; thereafter, the value starts increasing for higher speeds, as shown in Fig. 13.3 (Selim and Ghannam 2009; Alahmer et al. 2010).

An increase in engine torque decreases the brake-specific fuel consumption. BSFC is the ratio of mass flow rate of fuel to the engine brake power. At smaller range of load conditions, there is a sharp reduction in BSFC values (Fig. 13.4) due to small friction variability increasing mechanical efficiency, hence producing high power output, whereas, at high range of loads, smooth reduction in BSFC can be seen. For W/D emulsion fuel, the similar trends were observed for two-phase (w/o) and three-phase (o/w/o) emulsions with the condition of slightly more BSFC values, which may be due to the larger fuel flow rate, as shown in Fig. 13.4 (Lin and Wang 2004a; Abu-Zaid 2004). Moreover, an increase in percent of water in emulsion increases the BSFC value, as equal amount of diesel is displaced by water (Watanabe et al. 2010; Lin and Wang 2004a). The reason behind this increment lies in the fact that an increase in parameters such as engine speed, torque, and compression ratio increases engine brake power. Addition of water in the diesel causes a reduction in brake power compared with neat diesel because of ignition delay.

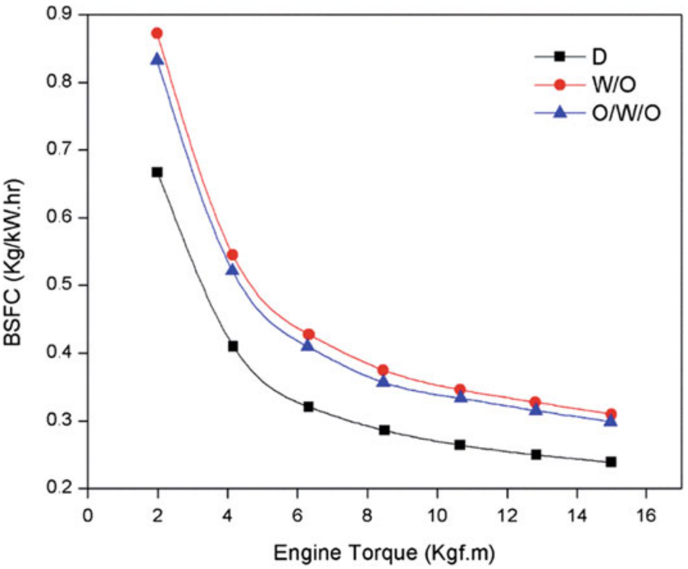

Fig. 13.4 Variation of BSFC with torque at constant engine speed of 1800 for neat diesel, two-phase (w/o), and the three-phase systems (o/w/o) with 20% water and additive (Lin and Wang 2004a) (Reprinted from Fuel, 83, Lin and Wang, Diesel engine performance and emission characteristics using three-phase emulsions as fuel, 537–545)
]

A study depicts that increase in water from 0 to 30% causes a decrease in values of brake power output in comparison with pure diesel because of ignition delay, though merely a slight decrease in the brake power output was observed at lower water percent (≈10%) as compared to high water percent (≈30%) (Selim and Ghannam 2009; Alahmer et al. 2010; Liang et al. 2013). One of the reasons for increasing BSFC at high water percent in W/D emulsion fuel is high latent heat of vaporization of water that absorbs energy content and brings it out to the exhaust gas. Hence, the proportion of exhaust gas to the energy consumed will have adverse effect on BSFC, specifically, for high water content. Although at high compression ratios, BSFC value is low; therefore, it was reported to run diesel engines for emulsified fuels at high compression ratios (Selim and Ghannam 2009).

13.3.1.2 BTE

Brake thermal efficiency (BTE) of emulsified fuels is an important parameter as it measures useful energy conversion efficiency. Thermal efficiency of water-emulsified diesel fuel has shown a great increase in the brake thermal efficiency. Figure 13.5 shows the variation of BTE with different engine speeds at different percentages of water (0–20%) in diesel. As shown in Fig. 13.5, BTE first increases till it reaches maximum value; thereafter, it starts decreasing at all percentages of W/D emulsion fuel. In the beginning of low engine speed, BTE is low

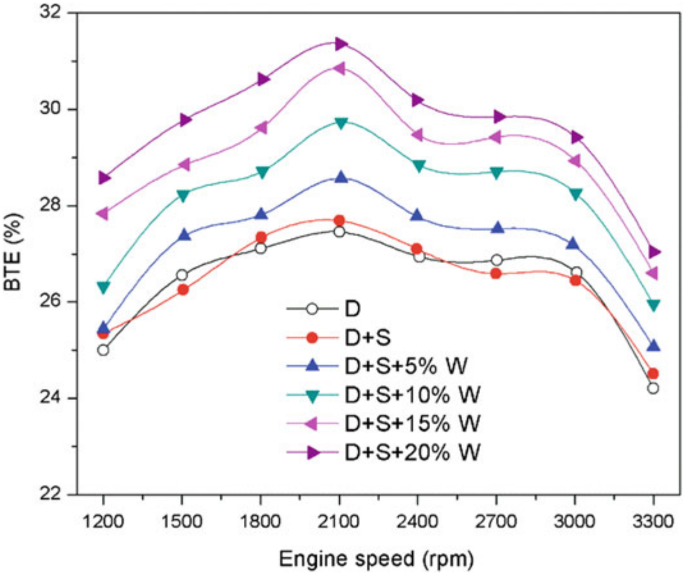

Fig. 13.5 BTE values at different engine speeds for water-in-diesel emulsions (Abu-Zaid 2004) (Reprinted from Energy Conversion and Management, 45(5), Abu-Zaid, Performance of single cylinder, direct injection Diesel engine using water fuel emulsions, 697–705)

due to the availability of sufficient time to transfer the heat to the cylinder walls. As engine speed increases, thermal efficiency increases till it reaches a maximum value. At high speeds, BTE starts decreasing owing to the high frictional losses and inertia to the moving parts (Fahd et al. 2013; Alahmer et al. 2010). Higher values of BTE for water-emulsified fuel are observed in comparison with the base diesel fuel because of ignition delay and micro-explosion phenomenon (Fig. 13.5) (Ithnin et al. 2014).

Addition of nanoparticles (alumina) in the W/D emulsion fuel brings about further increase in BTE of engine at all loads. BTE value of 28.9% for W/D emulsion (15% W) fuel blended with nanoparticles was reported as compared with 26.9 and 25.2% for W/D emulsion and base diesel fuels, respectively (Basha and Anand 2011). Enhanced results with nanoparticles may be attributed to the catalytic combustion, leading to the higher thermal efficiency. Moreover, addition of oxygen-enriched air to the W/D emulsion further increases the BTE value owing to complete combustion (Baskar and Senthil Kumar 2017).

13.3.2 Emissions

13.3.2.1 NO_x

The main objective of adding water to diesel is to reduce NO_x and PM emissions without any modifications in the IC engine design and change in engine performance. A number of studies regarding reduction of NO_x formation in case of W/D emulsion fuels are summarized in Table 13.4. Water addition in the fuel lowers the temperature inside the cylinder by vaporization as high latent heat of vaporization of water causing absorption of heat from the surroundings. Figure 13.6a, b depicts the effect of variation of engine speed and brake power on NO_x formations for pure diesel and emulsified fuels (ED10 and ED15) at different water concentrations (10–15%). An increase in NO_x emissions with engine speed is shown in Fig. 13.6. At engine speed of 3200 rpm and full load conditions, the lower concentration of NO_x (30.6%) emission was observed for ED15 as compared to base diesel fuel, as shown in Fig. 13.6. The phenomena of increase in NO_x concentrations at high speed may be attributed to the conversion of elemental nitrogen to nitric oxide (NO) caused due to condition of high gas temperature, which easily combines with O_2 to produce NO_2 (Nadeem et al. 2006; Lin and Chen 2006). A significant reduction in NO_x formation is observed in case of emulsion fuels compared to base diesel fuel; moreover, an increase in water percent in W/D emulsion fuel reduced the NO_x formations. A decrease in NO_x concentration with high water percent is linked with heat sink phenomena caused due to partial absorption of heat caused by finely dispersed water droplets decreasing combustion temperature, thus avoiding the NO_x formation. Various studies for decrease in NO_x formation with water-emulsified fuels have been performed; among them, Armas et al. (2005) tested for 10% water and Alhamer et al. (2010) tested for 5–30% W. At an increased load conditions,

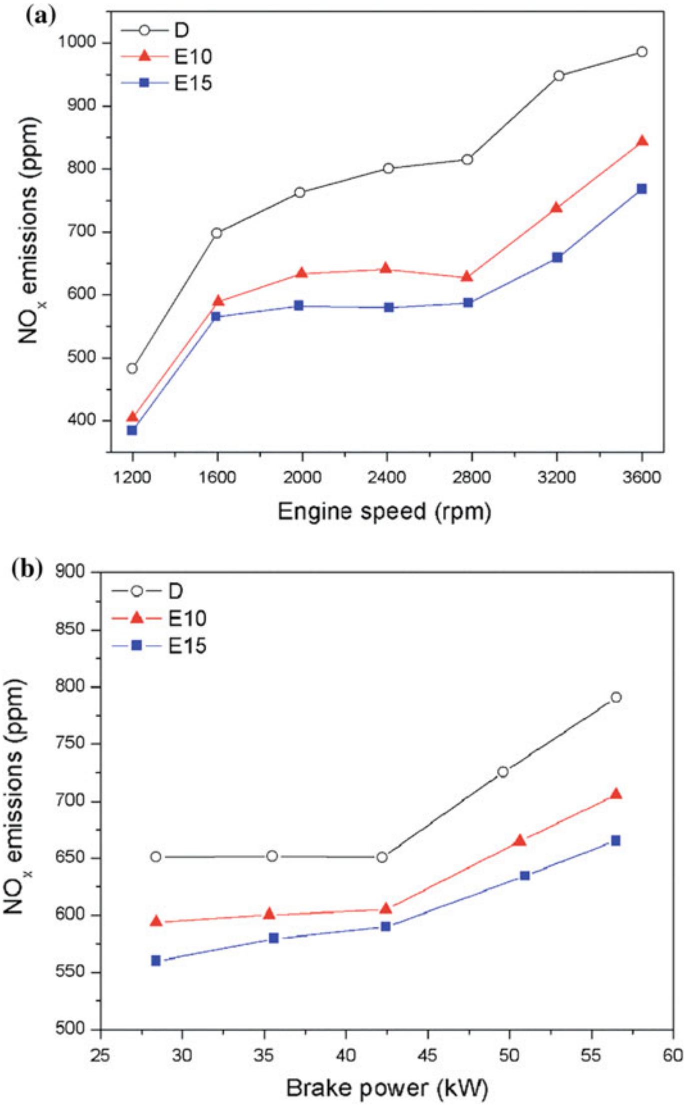

Fig. 13.6 NO$_x$ emissions with variation of (**a**) engine speed and (**b**) brake power (Yang et al. 2013) (Reprinted from Fuel, 104, Yang et al., Emulsion fuel with novel nano-organic additives for diesel engine application, 726–731)

there is an increase in NO$_x$ concentration in case of base diesel. This phenomenon is attributed to the excessive increase in burning temperature at high loads in the combustion chamber, according to Zeldovich NO thermal mechanism (Basha and Anand 2011). Conversely, in case of W/D emulsions, there is a drastic reduction in NO$_x$ emissions as compared to the base diesel at all load conditions. This phenomenon of reduced NO_x concentration is observed due to the addition of finely dispersed water droplets that bring about heat sink effect during combustion in the cylinder. In heat sink effect, water droplets present in the dispersed phase reduce calorific value of emulsion and in turn lower the combustion temperature in the chamber that causes reduction in NO_x formation (Nadeem et al. 2006).

Ghojel et al. (2006) tested W/D emulsion fuel for engine performance and emissions and compared results with base diesel fuel in four-stroke four-cylinder DI diesel engine. The NO_x reduction of 31.12 and 30.74% was reported as compared to base diesel fuel at two different loads of 150 Nm and 200 Nm, respectively, at a constant speed of 1800 rpm. Increasing the engine speed to 2200 rpm, the NO_x formation was reduced from 37.69 to 29.2% (i.e., 674 to 420 ppm) at 150 and 200 Nm loads, respectively. Therefore, at a constant speed, increasing the load showed comparatively low reduction in NO_x. It may be due to the fact that at high loads, NO_x emissions will be high for both W/D emulsion and base diesel fuel, showing less deviation in the values. Therefore, percent reduction in NO_x compared with base diesel oil increased in all conditions.

The W/D emulsion fuels have also been tested with additives, such as nanoparticles and cerium-based combustion improver. The W/D emulsions blended with nanoparticles shortened ignition delay and lower cylinder peak pressure. NO_x concentration was reduced to 891 ppm in case of W/D emulsion blended with nanoparticles (Basha and Anand 2011). In another study, the addition of additives in the water-emulsified fuel was tested for two different fuels: 6% W/D emulsion in a EURO-3 LD diesel vehicles (Test 1) and 12% W/D emulsion blended with cerium-based combustion improver additive in a EURO-3 HD engine (Test 2) (Farealetti et al. 2005). In test 1 (LD diesel vehicles), no significant change in NO_x emission was observed, whereas, in test 2 (HD engine), there was 6% reduction in NO_x emissions. Nadeem et al. (2006) tested W/O emulsion with variable water percent stabilized by surfactant and observed that with 15% water content there was a higher reduction in NO_x compared with base diesel fuel and other combinations of tested fuels (Nadeem et al. 2006) (Table 13.4).

Liang et al. (2013) experimented with oxygen-enriched combustion (OEC) in the engine fueled with W/D emulsion fuel keeping maximum possible oxygen concentration of 24% (vol.), as shown in Fig. 13.7. It can be seen that as the water content increases, NO_x ppm starts reducing in the emissions, whereas increment of oxygen percent increases the NO_x emissions. It was due to the fact that oxygen enrichment increases the adiabatic flame temperature; moreover, it provides enough oxygen to the surrounding fuel. Therefore, the optimum condition found was to keep lower oxygen content and higher water percent for reduction in NO_x emissions. Similar observations, in context of reductions in NO_x emissions with water, have been reported by number of researchers (Fahd et al. 2013; Bidita et al. 2014; Syu et al. 2014).

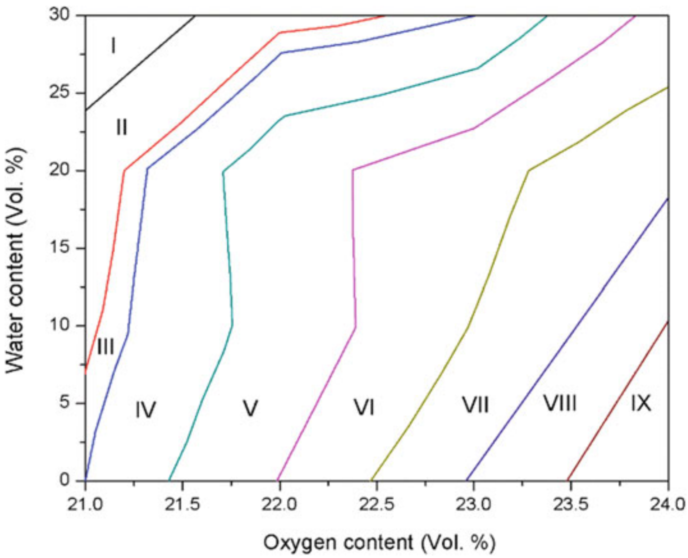

Fig. 13.7 Influence of oxygen % mixed with WDE on NO_x emissions (ppm) (Liang et al. 2013). Levels I to IX shown in the figure are values of NO_x concentration (ppm) at particular water and oxygen content. I—255 ppm, II—441.3 ppm, III—627.5 ppm, IV—668.0 ppm, V—813.8 ppm, VI—1000 ppm, VII—1186 ppm, VIII—1373 ppm, IX—1745 ppm (Reprinted from Energy Conversion and Management, 73, Liang et al., Effect of oxygen-enriched combustion and water–diesel emulsion on the performance and emissions of turbocharged diesel engine, 69–77)

13.3.2.2 PM

Formation of PM in the engine discharge is the indicator of combustion efficiency. For more efficient combustion, there should be reduction in the PM formation. Various experimental studies confirm reduction in PM by the addition of water in the diesel (Lin and Chen 2006; Ghojel et al. 2006; Liang et al. 2013). PMs are mostly combination of soot and ash, where soot comes from the lubricating oil, whereas ash-containing unburnt hydrocarbons originate from the fuel. In a study, higher reduction in PM was reported by using micro-emulsions (89%) as compared to W/D emulsion fuels (81%) (Ochoterena et al. 2010). Micro-emulsions are thermodynamically stable emulsions having dispersed water droplets of the order of 5–50 nm in diesel as continuous phase. A comparative study of micro-emulsion with W/D emulsion and base diesel fuels is shown in Fig. 13.8. A drastic reduction in soot formation was observed using micro-emulsion fuels, followed by W/D emulsion and then base diesel fuels. These phenomena may be attributed to the micro-explosion caused by the difference in volatility of water and diesel followed by secondary atomization (Kadota et al. 2007; Mura et al. 2012). This vigorous disintegration of droplets promotes better mixing of fuel and air, hence better combustion and lesser formation of PM. In another study, it was observed that PM reduction by micro-explosion causes an increase in −OH radical leading to the

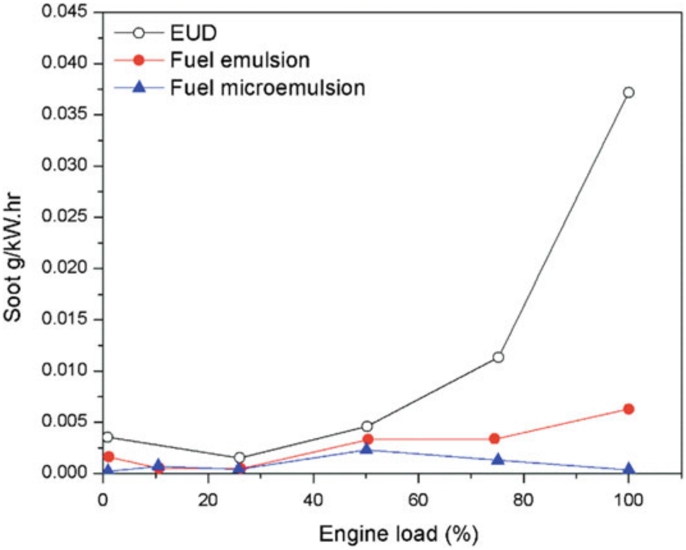

Fig. 13.8 Comparative soot formation by using European ultra-low sulfur diesel (EUD), fuel emulsion, and fuel micro-emulsion (Ochoterena et al. 2010) (Reprinted from Fuel, 89, Ochoterena et al., Optical studies of spray development and combustion of water-in-diesel emulsion and micro-emulsion fuels, 122–132)

oxidation of soot precursors (Ithnin et al. 2014). According to a study, PM reduction trend is twice of the mass of water used in the emulsion.

13.3.2.3 CO

A reduction in CO concentration using W/D emulsion fuel has been reported by many researchers (Lin and Wang 2004a; Nadeem et al. 2006; Yang et al. 2013), whereas some of the researchers have shown increase in CO emissions (Lin and Chen 2006; Bidita et al. 2014). Farfaletti et al. (2005) for LD vehicle with 6% water in WDE reported that CO increases by 18%, whereas for HD engine with 12% water, a 32% decrease in CO emissions was reported. A decrease in CO concentration is due to the conversion of CO to CO_2 by Eq. (13.13):

$$CO + OH \rightleftarrows CO_2 + H \tag{13.13}$$

where oxygenation rate of CO is K_{CO} (cm^3/gmol), which is a temperature-dependent term and given as follows:

$$K_{CO} = 6.76 \times 10^{10} \exp[T/1102] \tag{13.14}$$

Equation (13.14) illustrates that at lower temperature, CO oxygenation is low, but on the other hand, the addition of water increases the −OH and oxygen

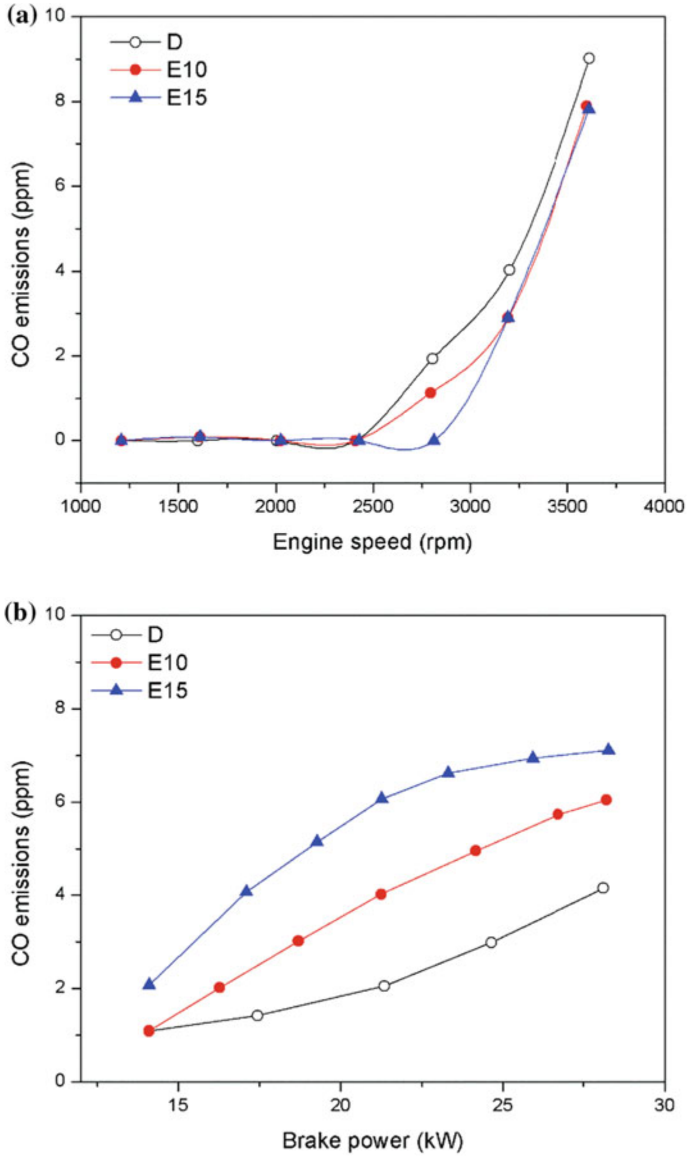

Fig. 13.9 Comparison of CO emissions for WDE with pure diesel. (**a**) Tested at variable engine speed and full load. (**b**) With variable brake power (Yang et al. 2013) (Reprinted from Fuel, 104, Yang et al., Emulsion fuel with novel nano-organic additives for diesel engine application, 726–731)

concentration; hence, net result comes out to be the reduction in CO formation as compared to the pure diesel oil and increased amount of water, as shown in Fig. 13.9. Moreover, the addition of water brings low fuel-to-air ratio; therefore, higher oxygen content is available for complete oxygenation of fuel therefore air-to-fuel ratio >1 brings complete combustion of fuel (Khalife et al. 2017; Yang et al. 2013).

However, equivalence ratio of one indicates stoichiometric ratio and in that case reduction in CO concentration was also observed. This phenomenon of lowering the CO with W/D emulsion fuels may be attributed to the micro-explosions followed by secondary atomization, as they bring about better mixing of fuel with air and in turn reduce unburnt reactant mixture. It has been reported that at higher load (no load to 50% load), less formation of CO takes place (Fig. 13.9b). However, further increment in load brings about high generation of CO (Ghojel et al. 2006; Fahd et al. 2013) (Fig. 13.9a). An increase in CO concentration is ascribed to the low temperature of the combustion bringing down by high latent heat of vaporization of water. Poor oxidation rate is responsible for incomplete oxidation of fuel and hence increased CO emissions.

13.4 Conclusions

In the present chapter, potential of water-emulsified diesel fuels was studied toward their improvements in engine performance and emissions. Alternative fuels have some advantages of adding oxygen to the fuel enhancing combustion, but on the other hand, their specific properties such as high latent heat of vaporization bring cooling effect to the cylinder. Further, addition of water to the diesel fuel is considered more beneficial in terms of remarkable reduction in PM and NO_x. Micro-explosion followed by secondary atomization of W/D emulsion fuel increases the thermal efficiency. The potential of mini-emulsion (nanosized) was also explored toward improving emissions. Some of the findings can be summarized as follows:

1. Alcohol and biodiesel blending with diesel has been explored because of their renewable nature, whereas alcohol has an edge over biodiesel in the sense of easy availability and formation, and low sulfur contents.
2. Oxygenated additives such as alcohol and biodiesel reduce BTE and BSFC of the engine because of their low calorific value.
3. Alcohol induces ignition delay because of high latent heat of vaporization and low cetane number and hence decreases power and torque. Cetane number signifies a longer ignition delay, allowing more fuel to vaporize in the stipulated time before ignition starts. Therefore, alcohol having very low cetane values when blended with biodiesel and diesel fuel showed improvement in BTE. Further, this may also lead to increase in CO emissions.
4. Higher NO_x emissions in case of biodiesel and alcohol are problematic due to their high oxygen content; therefore, antioxidant blending is required for the reduction of NO_x emissions.

5. There is a considerable reduction in emissions of particulate matter and sulfur by blending alcohol and biodiesel with diesel oil. High oxygen content and lower aromatics may be the cause of this behavior. However, properties specifically of biodiesel such as high density and viscosity make them difficult for atomization in air.
6. Water-in-diesel oil emulsions on the other hand have emerged as a new alternative toward reducing the engine emissions and performance remarkably due to its specific properties such as high latent heat of vaporization and micro-explosion.
7. It has been now consistently reported that NO_x and PM are specifically reduced by water-emulsified fuels. NO_x reduction up to 30% and PM reductions up to 60% have been reported by emulsified water up to 15% in emulsions.
8. Thermal efficiency of engine reduces promisingly while using water-emulsified fuels due to increase ignition delay.
9. On the other hand, CO emissions increased using W/D emulsions with possible reason of high latent heat of vaporization of water.
10. One of the limitation using W/D emulsion is its increased BSFC value at high water percent, which can be reduced by operating diesel engines at high compression ratio.
11. Water-in-diesel oil nanoemulsions have shown good potential toward, further reducing the NO_x and PM to a higher level. Not much attention has been made toward engine emissions and performance. Therefore, there is a need for the formation of nanoemulsions and their testing for the potential of engine performance. Further, limitations, such as emulsion stability and ethanol/biodiesel blends stability, need to be studied.
12. Adding additives such as nanoparticles, carbon nanotube, and metal-based additives have shown impact on reductions of emissions and performance of engine. Emissions such as CO and NO_x are improved with performance parameters toward improvement in combustion such as improved BSFC, ignition delay, oxidation rates. A safety issues toward additives such as carbon nanotubes and metallic additives and their proper mechanism of operation need to be studied.

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Chapter 14
Peroxy-fuels: Burning Behavior and Potential Applications in Combustion Engines

Kirti Bhushan Mishra and Klaus-Dieter Wehrstedt

Abstract In present chapter, the potential usage of peroxy-fuels (usually known as organic peroxides) either in technically pure or in a blended form in engine combustion processes are explored. Although as additives (in small quantities <5% to conventional fuels, e.g., diesel, gasoline) peroxy-fuels are well known for many years their commercial applications as a main or primary fuel are not investigated in detail as such except a few. Their thermal instability and energy density demand great care during processing, which restricts their commercial exploitation. However, once the issues with safety are resolved they can be much more advantageously employed than conventional fuels. Some of these advantages are significant amount of fuel saving, reduction in amount of inducted air, or even the complete absence of air, i.e., anaerobic combustion, smaller volume of combustion (chamber), oxygenated fuel quality, and low emissions. An idea to develop the components of an engine operating solely on peroxy-fuels is also introduced. The engine concept is based on single and multiple injectors in a cylinder with special material coating to ensure a temperature-controlled processing.

Keywords Peroxy-fuels · Hydrocarbons · Blends · Engine combustion
Engine performance

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14.1 Introduction

Due to strict regulations imposed by the environmental protection authorities to reduce emissions today combustion engines utilize a wide variety of fuels. These fuels are either derived from conventional ones or produced from the biological means. However, whatever may be the choice of fuel, the engine should not compromise on efficiency, economy, and emissions (Taylor 2005). Considering the same a lot of research nowadays focuses mainly on possibilities of various fuels, blends, processes for efficient combustion and modifications in the existing engine design. Peroxy-fuels (usually known as organic peroxides) are known to chemical and process industries for many decades. The following sections describe their characteristics and applications.

14.2 Peroxy-fuels

There is a wide variety of peroxy-fuels that can be explored for their potential utilization in various combustion applications. In this particular study, the discussion is limited only up to four peroxy-fuels whose chemical structures are shown in Fig. 14.1 and important combustion-related properties are listed in Table 14.1.

Peroxy-fuels contain at least one O–O bond in their chemical structure which is more or less easy to break (Akzo 2008; Chun 2007; Mishra 2010; Mishra and

Table 14.1 Properties of different peroxy-fuels and hydrocarbons

Parameter	Type of fuel						
	INP	TBPEH	TBPB	DTBP	Kerosene	Gasoline	Diesel
Formula	$C_{18}H_{34}O_4$	$C_{12}H_{24}O_3$	$C_{11}H_{14}O_3$	$C_8H_{18}O_2$	–	–	–
Molar mass (g/mol)	314.5	216.32	194.2	146.2	–	–	–
Active oxygen (%)	5.09	7.40	8.24	10.94	–	–	–
Enthalpy of combustion (kJ/kg)	30100	34455	30113	36600	46300	44400	45400
T_{SADT}(K)	293	308	338	358			
Air to fuel ratio (−)	10.7	10.52	9.23	10.86	~15.6	~15	~15
$\dot{m}''_f$ (kg/m^{2}s) ($d = 6$ cm)	4	0.53	0.83	0.18	0.012	0.055	0.035

INP Di-(3, 5, 5-trimethylhexanoyl) peroxide; *TBPEH* tert-Butyl peroxy-2-ethylhexanoate; *TBPB* tert-Butyl peroxybenzoate; *DTBP* Di-tert-butyl peroxide

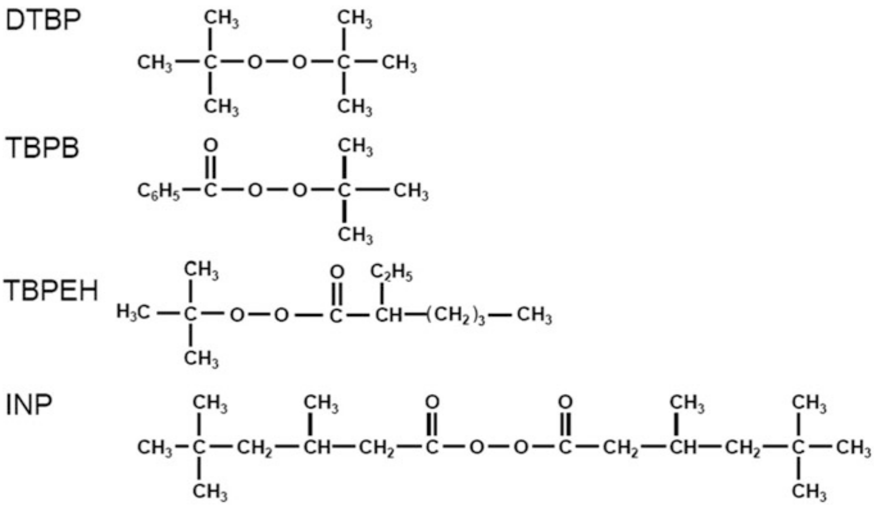


Fig. 14.1 Chemical structure of studied peroxy-fuels

Wehrstedt 2012a) (Fig. 14.1). Upon thermal decomposition they release a complete range of products. The major decomposition products, e.g., of DTBP are acetone and ethane (Chun 2007). The interesting thing in the structure of DTBP is the symmetry and the associated protection of the O–O bond given by the two tert-butyl groups (+ I-effect) which stabilize the molecule and influence significantly the combustion process and make it different from the others. In contrast, such a stabilization effect does not exist in case of INP, e.g., due to the length of the side chains and the influence of the two carbonyl groups (−I-effect) with the consequence that the so-called self-accelerating decomposition temperature (SADT) is lower. Based on their structure, the (thermal) stability of TBPB and TBPEH is between DTBP and INP (Mishra 2010; Mishra and Wehrstedt 2012a).

Blended forms

The selected peroxy-fuels for blending were the same as before (Mishra and Wehrstedt 2013). As a blending agent, a pure hydrocarbon fuel isododecane was used. The proportions of isododecane were varied between 25 and 75 wt%. The reason behind selecting isododecane as a reference fuel was being a possible surrogate for JetA and other aviation fuels. Because of its inertness and higher boiling point, it is also a recommended type A diluent for the safe transportation of peroxy-fuels (Mishra and Wehrstedt 2013a, b). The basis for blending weight % was chosen so as to see the proximity of burning behavior against the dilution % and to verify the options for hazard reductions. Or in other words it was aimed to achieve the best possible combination of fuels with minimum concern for safety.

14.3 Background

In the past, several studies were performed on the addition of peroxy-fuels in conventional hydrocarbons, e.g., diesel, gasoline, and others up to $\sim 15\%$ (Eng et al. 2003; Coughenour et al. 1997; Nandi 1996; Mack et al. 2005; Pritchard 1986; Pritchard and Clothier 1986). The important findings were: (1) reduction of total amount of fuel and air required for a given heat flux, (2) considerable reduction in size of chamber/cylinder; (3) efficient combustion and less pollutants (NO_x and CO_x). Importantly, in (Eng et al. 2003; Mack et al. 2005) a peroxy-fuel (DTBP from 5 to 15%) was added in diesel and burned in homogeneous charge compression ignition (HCCI) engine. It was found that $\geq 15\%$ addition of DTBP helps to reduce the fuel consumption and emission. Another study (Pritchard 1986; Pritchard and Clothier 1986) demonstrated that a spark ignition (SI) engine can be run in the total absence of air when DTBP was used as a fuel. However, the above studies dealt only with one peroxy-fuel, i.e., DTBP and with a fixed range of concentrations for practical applications, e.g., in engines.

To understand the fuel blends better, four different peroxy-fuels (including DTBP) burning behavior under different proportions of dilution with a hydrocarbon, i.e., isododecane were studied. Isododecane was added in all peroxy-fuels in the range of 25–75 wt%. Major characteristics of diffusion flames of these fuel blends were measured by burning them in form of pool fires. Pool fires are diffusion flames where fuel and air mix and combust simultaneously (Chun 2007; Mishra 2010; Mishra and Wehrstedt 2012a, 2013a, b).

Another important aspect of the present work is to study the effects of dilution on thermal instabilities and burning behavior of peroxy-fuels to ensure their safety during transportation (Akzo 2008; Mishra and Wehrstedt 2013b).

Peroxy-fuels due to their thermal instabilities possess energetic properties and therefore demand greater safety precautions. When ignited, they burn at a rapid rate and therefore produce large flames, higher temperature, and thermal radiation (Mishra and Wehrstedt 2009, 2012a, 2013a, b).

It has been shown (Mishra and Wehrstedt 2012a) that the mass burning rates of peroxy-fuels can be best correlated with their self-accelerating decomposition temperatures (SADT, T_{SADT}). These measured T_{SADT} values for investigated peroxy-fuels are given in Table 14.1 (Mishra 2010; Mishra and Wehrstedt 2012a). It can be seen that the lower SADT implies peroxy-fuel to burn faster.

The measurements of mass loss (of liquid fuel) versus time of hydrocarbon fuels and peroxy-fuels revealed that a given amount of peroxy-fuel was consumed in much lesser time than in case of hydrocarbons. The dilution/blending increases the burning times for peroxy-fuels and vice versa for hydrocarbons. The burning times for the above three kinds of fuels can be written in ascending order as follows hydrocarbon > blended fuels > peroxy-fuels. Moreover, the faster burning of peroxy-fuels leads to small residence times (the reaction time to convert a given quantity of fuel into products) (Mishra and Wehrstedt 2011b, 2012b) of fuel elements in the combustion process, smaller air to fuel ratios, and available oxygen atoms help to ensure less pollutants and much cleaner combustion (Eng et al. 2003; Coughenour et al. 1997; Nandi 1996; Mack et al. 2005; Mishra and Wehrstedt 2011b, 2012b).

There are almost no studies available which describe the burning behavior of hydrocarbon fuel blends with peroxy-fuels (>15%). Therefore, the present results are novel to the fuel, combustion, and energy community.

In the engine combustion literature, they are used as additives to conventional fuels, e.g., diesel, gasoline (Eng et al. 2003; Coughenour et al. 1997; Nandi 1996; Mack et al. 2005). Sometimes they are also called as agents for combustion (cetane and octane) improvement (Nandi 1996; Mack et al. 2005). Number of works have been published on engine combustion (Eng et al. 2003; Coughenour et al. 1997; Nandi 1996; Mack et al. 2005; Pritchard 1986; Pritchard and Clothier 1986) highlighting the advantages of peroxy-fuels addition in hydrocarbon fuels. Since they are thermally unstable and may pose a chemical hazard, their content was limited only in the range of 5% (Eng et al. 2003; Nandi 1996; Mack et al. 2005; Pritchard 1986) to 15% (Eng et al. 2003). The presence of active oxygen content in the molecule and energy release due to thermal decomposition help peroxy-fuels to burn faster and produce higher heat release than conventional fuels. The following sections give an overview of advantages obtained when a peroxy-fuel is added in a conventional fuel.

In gasoline: For instance it has been shown that the ignition delay was reduced and emission was significantly cut down when 2% of a peroxy-fuel Di-tert-butyl peroxide (DTBP) was added to gasoline (Eng et al. 2003). A further fact to note is that an addition of 15% of DTBP in gasoline in a homogeneous charged compression ignition engine enhanced the heat release rate and reduced the fuel supply per cycle by 31% (Eng et al. 2003). Furthermore, the addition of DTBP in gasoline leads to advancement in location of peak energy release rate for a fixed fueling rate. The advancement of auto-ignition point enables other parameters like initial temperature, pressure, and the fueling rate to be lowered.

In diesel: In order to reduce aromatic content and improve cetane rating, DTBP and 2-ethylhexyl nitrate were added to diesel (Coughenour et al. 1997). It was found that diesel containing DTBP produces much lower NO_x than nitrate-based additive (Coughenour et al. 1997; Nandi 1996). The methods to synthesize DTBP cheaply with certain mechanisms were also discussed. Also, it is thermally and oxidatively stable for the general fuel system temperatures (Coughenour et al. 1997).

In Bio-fuels: DTBP was added in ethanol and di-ethyl ether in ethanol (DEE) and applied to a homogeneous charge combustion engine. Here also similar results (those obtained with gasoline and diesel) were described where DTBP was added (1–3%) in pure ethanol and di-ethyl ether (DEE) in ethanol mixture (Eng et al. 2003; Coughenour et al. 1997; Nandi 1996; Mack et al. 2005). The major findings were the advancement in ignition timings and burning of more ethanol + DEE than ethanol alone. However, in both cases the heat release rates were not enhanced.

In Liquefied Petroleum Gas (LPG): The effectiveness of DTBP addition in LPG was also investigated (Eng et al. 2003). LPG has a cetane number of 3. It was found that 1% DTBP addition enhanced the cetane number of LPG to 48 and 15% addition increased to cetane numbers ranging between 60 and 75 (Eng et al. 2003).

Anaerobic operation The use of peroxy-fuel as a primary fuel in an internal combustion engine led to the fact that the engine can be run in the total absence of air, i.e., anaerobically (Pritchard 1986; Pritchard and Clothier 1986). Since peroxy-fuels are capable of undergoing thermal explosion they do not require an ignition source. This kind of anaerobic operation is very useful in the regions where lack of oxygen prohibits the engine operation, e.g., chain saws in underground mines (Pritchard 1986; Pritchard and Clothier 1986).

This chapter presents authors' own investigations on burning behavior and some additional features of variety of peroxy-fuels that can be beneficially exploited over hydrocarbon fuels when using as main fuel or as additives. Majority of results presented here are for fuel burning properties along with some of the engine combustion test results which can be considered for primary selection of fuels and further development.

14.4 Experimental Setup

14.4.1 Diffusive Burning Tests

The peroxy-fuels shown in Table 14.1 are burned in form of pool fires, diameters ranging from 1 cm to 1 m (Chun 2007; Mishra 2010; Mishra and Wehrstedt 2012a, 2013a, b). A typical arrangement for a pool fire test is shown in Fig. 14.2. Tests

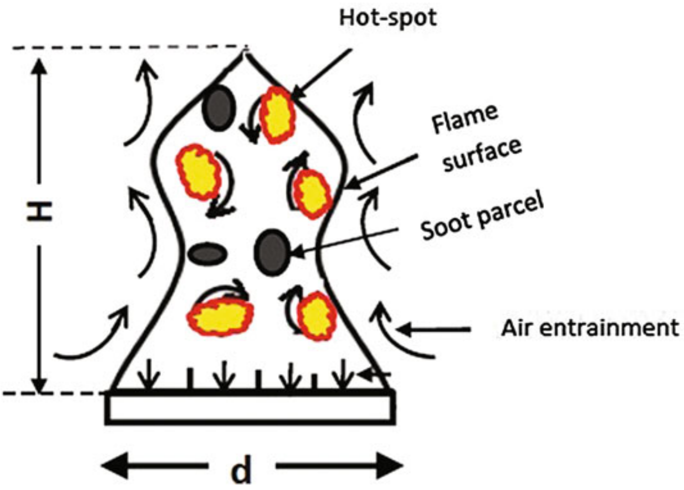


Fig. 14.2 Typical burning experiment of a pool fire

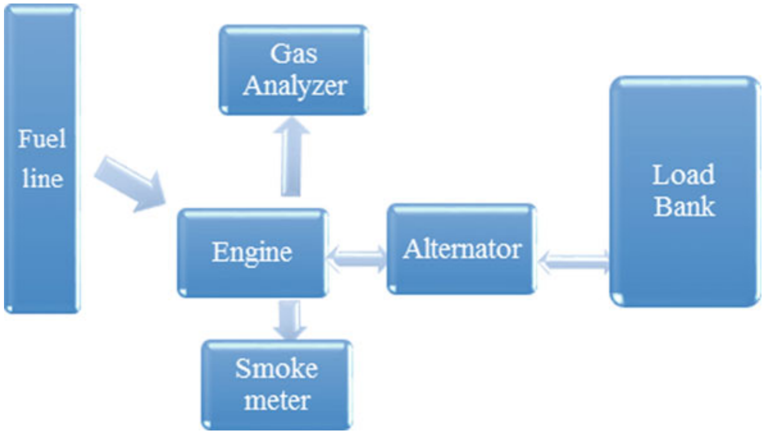


Fig. 14.3 Experimental setup for engine performance testing

with diameter up to 18 cm were performed in house facility, and larger were carried out at BAM Test Site Technical Safety. The fuel height was 5 cm in all tests, and ignition was done with the help of a hand torch. The major parameters that were measured are mass burning rates, flame lengths, flame temperatures, and thermal radiation. A load cell, video cameras, thermal cameras, heat flux sensors, and thermocouples were used to measure the above parameters.

14.4.2 Diesel Engine Setup

A single cylinder, constant speed water cooled compression ignition engine, coupled with a 7.5 kVA AC alternator as shown in schematic diagram of the experimental setup is shown in Fig. 14.3 (Naresh et al. 2017). A resistive load bank along with voltmeter, ammeter, and frequency meter was used for loading the engine. The load bank was a single-phase load circuit consisting of a combination of stable resistive elements for appropriate rating, wired such that the load current is adjustable to any value up to 30% of maximum value with an accuracy of ±0.1 A.

Engine output was measured in terms of electrical power by measuring output current and voltage. Volumetric fuel consumption was recorded for every 5% load variation starting from 0 to 30%. Portable automotive emission analyzer (Horiba MEXA-584L) was used to measure engine exhaust emission levels of CO, HC (volatile hydrocarbons), CO_2, NO along with equivalence ratio. The exhaust sampling arrangement consisted of an extension pipe fitted with an exhaust sample probe connected to the outlet of normal exhaust system of the engine.

14.5 Results and Discussions

14.5.1 *Burning Rate Tests*

Mass burning rates

In Fig. 14.4, the diffusive burning rates of peroxy-fuels and isododecane (kerosene, diesel, gasoline were also used in several studies) are shown. Technically, pool fires are non-premixed buoyant flames where liquid fuel has very low initial momentum. Whereas measurement indicates that quantitatively peroxy-fuels are burning 10–333 times faster (higher momentum) than corresponding hydrocarbon fuel, i.e., isododecane which implies the similar magnitude of higher heat release rates (Mishra and Wehrstedt 2011a, b; 2013a, b). Additionally that means this amount of excess mass of fuel is coming into combustion process within the same time and without the support of any mechanical device, e.g., hydraulic pump. For an incompressible fluid (liquid fuel), the pressure drop Δp and mass flux $\dot{m}''_{\mathrm{f}}$ can be written as in Eq. (14.1). Applying the same leads to an approximation that this excess pressure is coming from fuel (and associated combustion) itself which would have not been possible for a hydrocarbon fuel without the aid of a pump.

$$\Delta p \propto \left(\dot{m}''_{\mathrm{f}}\right)^2 \tag{14.1}$$

In other words, for a fixed heat flux $\dot{q}''$ (Eq. 14.2) 10–333 times less mass of peroxy-fuels will be required as the heat of combustion Δh_{C} is a constant for a given fuel (Mishra 2010; Mishra and Wehrstedt 2011a, b; 2012a).

$$\dot{q}'' = \dot{m}''_{\mathrm{f}} \times \Delta h_{\mathrm{C}} \tag{14.2}$$

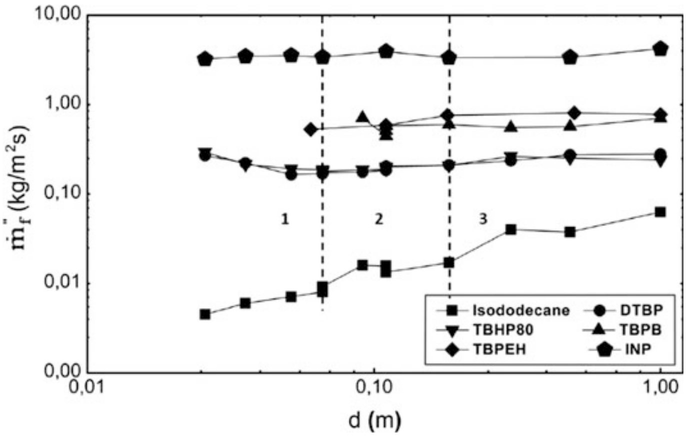


Fig. 14.4 Measured mass burning rate versus source diameter of peroxy-fuels and isododecane

As a result of less volume of combustion, the cylinder volume will be reduced and therefore the compression ratio for a given power can also be brought down.

Peroxy-fuel pool fires show negligible dependence on d (pool diameter) unlike hydrocarbons (Mishra 2010) and are turbulent right from the smallest possible *d* (Mishra 2010; Mishra and Wehrstedt 2012a) (where the flame sustained until the pan ran out of fuel) which can also be seen for DTBP and INP in Fig. 14.4.

The mass burning rates ($\dot{m}_f''$) of five blended peroxy-fuels (diluted with 25% isododecane) are plotted against the d in Fig. 14.5. Dilution helps the peroxy-fuels to burn slower than in their technical pure forms (Mishra and Wehrstedt 2012a). Quantitatively, the burning rates were decreased by factors of 2–10 after 25% isododecane addition. For small pools $d < 5$ cm, DTBP showed the strongest decrease of burning rate of up to a factor of 10, whereas for $d > 5$ cm almost all peroxy-fuels showed the similar decreasing factors of 3–4.

Figure 14.6 shows the comparison in pure and blended forms for DTBP and INP, respectively. It can be seen that 25% addition of isododecane initiates the deviation from the burning under pure form. The burning rates were found to be decreased by 2–10 times for DTBP and INP in the above case. Dilution had the strongest effect on DTBP, lowering the burning rate by up to ten times.

Flame lengths

The visible flame lengths (H) of kerosene (right) and three peroxy-fuels (left) are shown in Fig. 14.7. The measured time-averaged flame length of DTBP was 3 times larger than of kerosene. The reason behind such larger flame was the higher burning rates. In general, both technically pure and blended peroxy-fuels exhibit 5–2 times larger flames than hydrocarbons.

The variation of relative flame lengths with pool diameters for four blended fuels (in 25% isododecane) is shown in Fig. 14.8. Due to significantly higher burning rates, INP exhibited 2–5 times larger flame lengths than the others. INP blended fuel flames produced negligible soot when compared with others. Due to low decomposition temperature, fast vaporization and high momentum in the case of

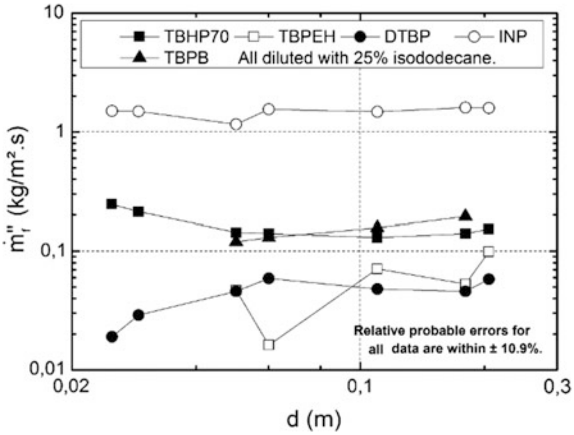


Fig. 14.5 Mass burning rate versus pool diameter of different blended peroxy-fuels

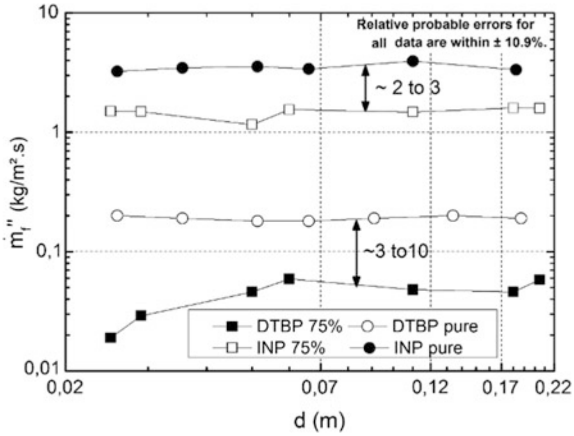


Fig. 14.6 Mass burning rate versus pool diameter of technical pure and blended peroxy-fuel

INP, a great amount of ascending vapor was produced leading to a larger flame. In the case of INP which was the fastest burning peroxy-fuel among all, it was found that the fuel vapors which rise up do not burn completely due to the improper mixing with air. It is the same a in the case of a liquid fuel jet fire where fuel vapors due to their higher density fall down across the source and burn in a form of small droplets.

Flame temperatures

The time-averaged flame (T) of DTBP and kerosene are shown in Fig. 14.9. As can be seen, DTBP flames are showing 150–400 K higher temperatures than kerosene. The higher temperatures are a result of the lower soot contained in the DTBP flame.

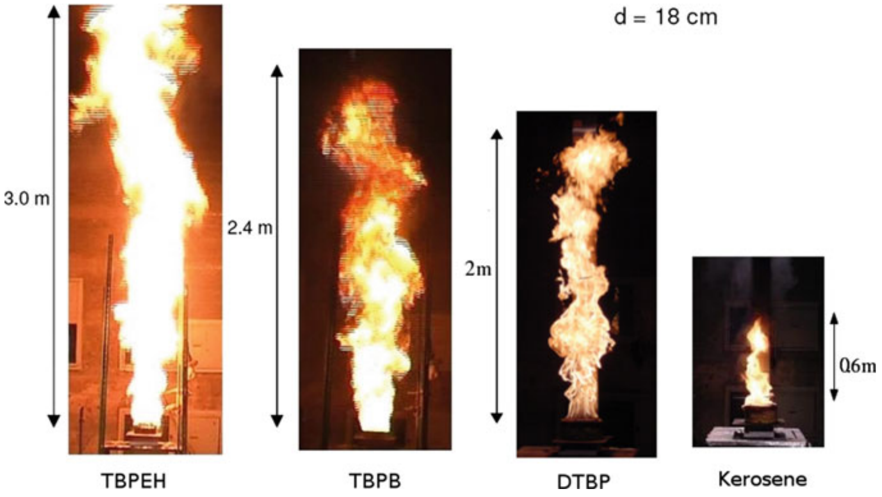


Fig. 14.7 Measured flame lengths of peroxy-fuels and (d = 18 cm)

Fig. 14.8 Measured flame lengths of technically pure and blended peroxy-fuels

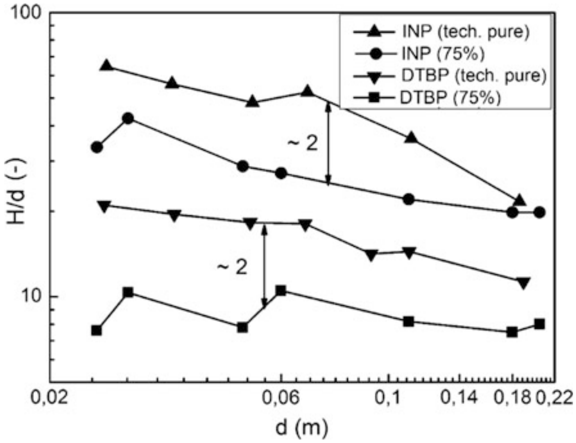
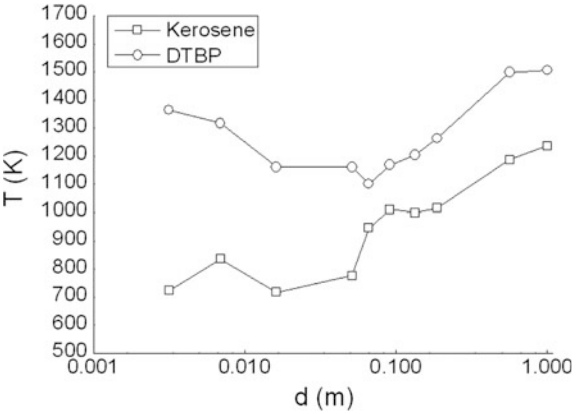


Fig. 14.9 Flame temperatures of DTBP and kerosene (Chun 2007; Mishra and Wehrstedt 2013a)



Furthermore, the flame temperatures measured with thermographic camera can also be seen in Fig. 14.10. The flame emissivity was set as 0.9 depending on the previous studies carried out for optically thick fires (Mishra 2010). There, also a difference of 250 K between kerosene DTBP flame is measured (Mishra 2010; Mishra and Wehrstedt 2012a). The temperatures measured by the thermocouples located at the flame axis (Fig. 14.2) were always 50–150 K smaller than those measured with thermographic camera because of the blockage of the thermocouples by smoke and soot.

Emissions

The emissions especially NO_x and CO_x are measured for $d = 6$ cm pool burning inside a closed chamber. The total burning time was around 3–4 min. The flame exit gases (on top) were collected in a hood and taken further to FTIR analyzer to identify different species. In all tested peroxy-fuels, we found no NO_x production at all. Furthermore, DTBP did not even produce CO which was not the case for other

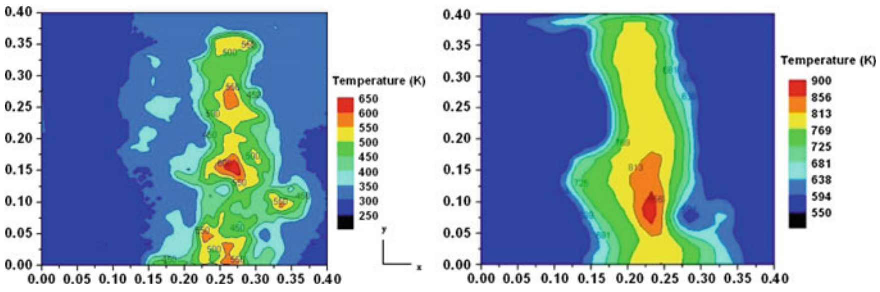


Fig. 14.10 Flame temperatures of kerosene and TBPB

peroxides (Mishra and Wehrstedt 2012a, 2013b). However, these measurements do not represent combustion in real engines therefore should therefore be treated only as symbolic.

14.5.2 Engine Performance Tests

With the aim to study peroxy-fuels application in commercial engines, different tests were performed. The potential of DTBP when used along with biodiesel and ethanol to reduce the CO and HC while maintaining lower NO_x have been examined. DTBP with peroxy linkage is expected to make combustion much cleaner and efficient. It is observed that the fuel blend containing 85% (v/v) biodiesel + 10% (v/v) ethanol + 5%(v/v) DTBP (B85E10P5) reduced the NO, CO, and HC emissions significantly. Figure 14.11 shows the NO emission by the different fuel samples in standard tests.

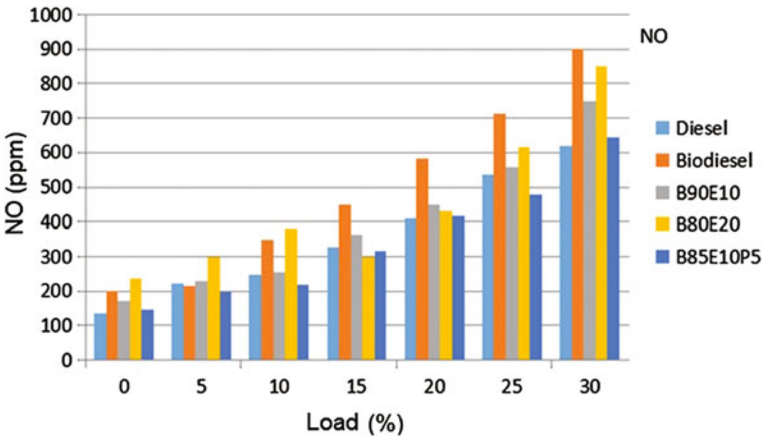


Fig. 14.11 Emission (*X*-axis represents applied load (in %) on engine and *Y* axis NO in ppm) from different fuels (B: Biodiesel, E: Ethanol, P: Peroxide)

On comparing all the parameters for different samples, it is observed that the biodiesel has more brake specific fuel consumption (BSFC) with less brake thermal efficiency and high NO but with significantly less amounts of CO and unburnt HC. The addition of ethanol slightly reduced the NO at cost of slight increase in unburnt HC. The final sample with peroxide showed a significant reduction in NO (Naresh et al. 2017). At 30% load, this whole increase in the NO content was completely reduced to within 4%. In addition to this, CO content was reduced by 75% and HC content by about 34%. These results at low load conditions show a trend of reduction in emissions and give an indication that addition of peroxide can enhance the overall combustion and promote much cleaner burning of fuels. These blends of biodiesel and ethanol with DTBP as additive can be a significant option for alternative fuel to replace petroleum-based fuels. The same trends observed at low load conditions must be examined under medium and full load conditions.

Due to thermal (decomposition) and chemical effects (faster reactions, small residence times, and readily available oxygen atoms), tests carried out in combustion engines (diesel, gasoline, ethanol + DEE and DTBP < 15%) have shown that the emissions especially NO_x production was significantly reduced (Eng et al. 2003; Mack et al. 2005).

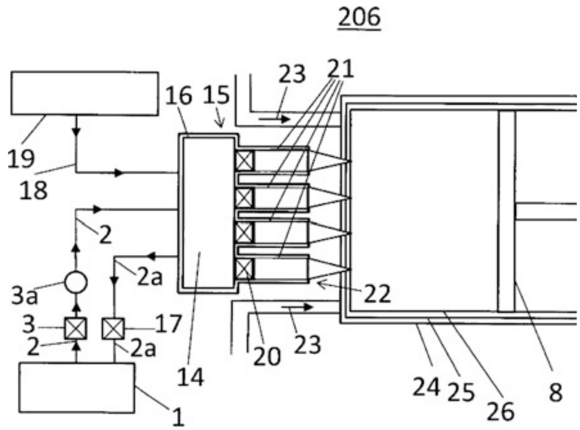
It is also possible that with the addition of DTBP airless combustion is possible as a decrease in equivalence ratio was obtained in the current analysis. This would be useful for vehicles in hilly regions and which move in tunnels.

Possible applications in combustion engines

An engine concept for peroxy-fuels is developed, and components for the same are described in (Mishra and Wehrstedt 2012b). In Fig. 14.12, example of a single cylinder (24) multiple fuel injectors (21) combustion engine is depicted. Due to the temperature-controlled processing of peroxy-fuels, special coatings on the cylinder and supply lines are provided.

Therefore, Fig. 14.12, the tank 1, the fuel supply line 2, the fuel injector 21, 22 and contacting fuel distribution system 15 lined with a chemically inert material. As lining for a superficially applied insulation layer 16 was proposed. This layer

Fig. 14.12 Components of a model engine operating on peroxy-fuels (Mishra and Wehrstedt 2011b)



may be formed entirely by a chemically inert polymer or a different type, fuel rail 15 and its constituent reservoir 14 and fuel injector 21 or multiple injector system 22 at least partly with an insulating layer 16 feature, 18 and 19 are provisions to control the temperature of peroxy-fuel; 2 and 2a are return path and valve for excess or remaining fuel in the common rail; 23 is the air supply via turbo/supercharger; 24, 25 and 26 are the cylinder liners, and 8 is piston.

The major potential advantages of engines running with peroxy-fuels (in both spark and compression ignition mode) as proposed above are reduction in compression ratio for a given power, smaller volume of cylinders, reduction in ignition delay, low emissions, anaerobic operation, and oxygenated fuel qualities. Above all compactness of the entire unit will be enhanced (Mishra and Wehrstedt 2012b).

14.6 Conclusions

This chapter has highlighted the burning behavior of different peroxy-fuels and blends thereof along with their potential application (either as additives or as main fuels) in engine combustion process. Their free burning characteristics, emissions, and potential application in combustion engines were looked at. It was shown here and in some pearlier works that the fuel blends with peroxy-fuels also reduce compression ratios. Experimental evidences have shown that they can be used both as additives and as primary fuels. In either case depending on the proportions, due to oxygenated fuel quality, low air to fuel ratio and fast reactions, peroxy-fuels possess great potential to become a strong option for reducing emissions especially NO_x in combustion engines. Furthermore, an engine concept for peroxy-fuels was developed and demonstrated. The key challenges in the applications of peroxy-fuels as primary fuel in commercial engines are to ensure temperature-controlled processing to avoid any chance of thermal decomposition. Second challenge is related to safe storage and transportation of large quantities of peroxy-fuels which are sometimes subjected to different regulations worldwide.

The ongoing work is focussing on finding right combination of fuels and their commercial exploitability. We encourage partners from industries and research organizations to come forward and co-operate with us to extend the technology further.

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Chapter 15
Utilization of Alternative Fuels in Advanced Combustion Technologies

Akhilendra P. Singh and Avinash Kumar Agarwal

Abstract In the past few decades, rapid technological advancements have resulted in significantly fast depletion of petroleum resources. Extensive utilization of gasoline and mineral diesel in automobiles sector has led to an increase in the worldwide fuel consumption. Today compression ignition (CI) engines are being widely used in light-duty and heavy-duty vehicles, mainly because of their higher efficiency, greater reliability, and superior fuel economy compared to gasoline engines. However, CI engines experience major drawbacks of very high emissions of oxides of nitrogen (NO_x) and particulate matter (PM). Although several after-treatment devices such as lean NO_x trap (LNT), diesel particulate filters (DPFs), diesel oxidation catalysts (DOCs) are being used to meet stringent emission norms, however, high initial cost, operational issues, and system complexity put serious limitations on their usage. Therefore, researchers have been actively working to explore and develop new combustion strategies such as low-temperature combustion (LTC) in order to control harmful exhaust emissions. Utilization of alternative fuels in these advanced combustion concepts has given a new direction to IC engine research through which issues such as rapid petroleum consumption rate and engine exhaust emissions can be resolved simultaneously. This chapter describes various derivatives of LTC technique and methodology for utilization of various alternative fuels.

Keywords Low temperature combustion · Particulate matter · Alternative fuels Biofuels

15.1 Introduction

Today, internal combustion (IC) engines have become an integral part of the modern society. Since the nineteenth century, the invention and enhancement of IC engines have affected human life. Spark ignition (SI) engines and compression

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ignition (CI) engines are being widely used in the automotive industry today for global mobility. Other substitutes such as fuel cell technology, electric vehicles are also emerging as promising alternatives, but the complications in their practical implementation put a limit on their usage in commercial engines.

During the past few decades, evolution and development of sophisticated technologies have enabled conventional energy resources to be extracted at an unexpectedly higher rate. At the same time, the rate of depletion of fossil fuels has increased exponentially. These nonrenewable resources including mineral diesel, gasoline, natural gas are predominantly being consumed in automotive sector. These serve as sources of environmental pollution in the form of exhaust gas emissions from IC engines. Figure 15.1 shows the rate of increase in CO_2 emission in last few decades and future projections. This shows that developing countries are emerging as a major source of CO_2 emission, and they will exceed emission from developed countries in near future.

It should be noted that, although both SI and CI engines have their own advantages and disadvantages, diesel engines are widely used in light-duty as well as heavy-duty vehicles simply because of their higher thermal efficiency compared to conventional SI engines. SI engine exhaust consists of unburnt hydrocarbons (HCs) and carbon monoxide (CO) primarily. However, oxides of nitrogen (NO_x) and particulate (PM) emissions are released in lower quantities. Further, CI engines produce high concentrations of NO_x and PM and significantly lesser concentrations of CO and HC. Inspite of higher NO_x and PM, certain important characteristics of diesel engines, including higher durability, reliability, lower pumping, and throttling losses, along with superior fuel economy give them an edge over the gasoline

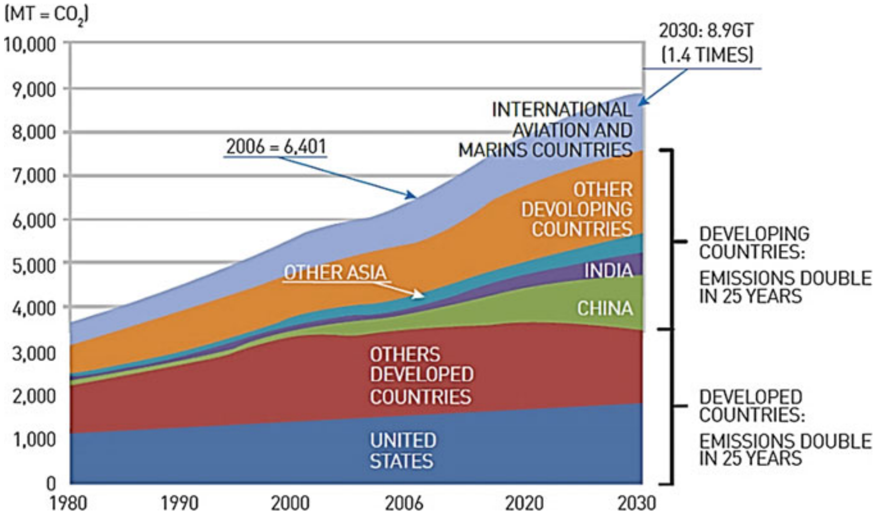


Fig. 15.1 CO_2 emission from different countries [International: IMO Marine Engine Regulations (www.dieselnet.com)]

engines. However, the problem of high PM and NO_x in the diesel exhaust still needs to be tackled with seriousness.

Stringent emission norms have been put into practice globally. Therefore, it has become a top priority for researchers and automotive manufacturers to control PM and NO_x emitted by diesel engines either by using after-treatment devices or by using alternative fuels in addition to using advanced combustion techniques. Various after-treatment devices such as diesel particulate filters (DPFs), NO_x traps, diesel oxidation catalysts (DOCs) are being used in diesel engines to curtail PM and NO_x emissions. However, use of these devices has been rather limited because of high initial investments and high maintenance costs.

Considering stringent emission regulations and scarcity of primary energy resources, development of new, highly efficient, and environment-friendly combustion concepts and systems, capable of utilizing alternative fuels in addition to conventional fuels, has become increasingly important. Several experimental studies have been carried out to develop novel combustion concepts such as low-temperature combustion (LTC), which has demonstrated prospects of meeting stringent environmental challenges faced by automotive engines. In recent years, researchers have focused on LTC technology development, primarily because of its extremely low NO_x and PM emissions and high efficiency potential.

15.2 Advanced Low-Temperature Combustion Techniques

The concept of LTC has caught significant attention among researchers in recent decades. By definition, LTC refers to a combustion methodology, which is capable of lowering the in-cylinder combustion temperatures. The domain of LTC covers all advanced combustion strategies including homogeneous charge compression ignition (HCCI), premixed homogeneous charge compression ignition (PHCCI) combustion, partially premixed charge compression ignition (PPCCI), premixed charge compression ignition (PCCI) which are capable of simultaneously reducing NO_x and PM emissions and resolve the problem of 'PM–NO_x dilemma' of the conventional diesel engines.

Akihama et al. (2001) explored the effects of ultrahigh exhaust gas recirculation (EGR) rates on diesel combustion for simultaneous reduction of NO_x and PM. Observations made are present in Fig. 15.2, which also represents the 'soot–NO_x dilemma' in CI engines. It is clearly evident from the figure that smoke-less combustion can be realized for any equivalence ratio at temperatures below 1500 K. However, at temperatures above 2000 K for excessively richer mixtures, NO_x formation is relatively lower but soot formation increases significantly with the reverse happening at relatively lesser loads ($1 < \varphi < 2$). Therefore, in order to meet stringent emission norms, various LTC methodologies are extensively investigated by researchers worldwide.

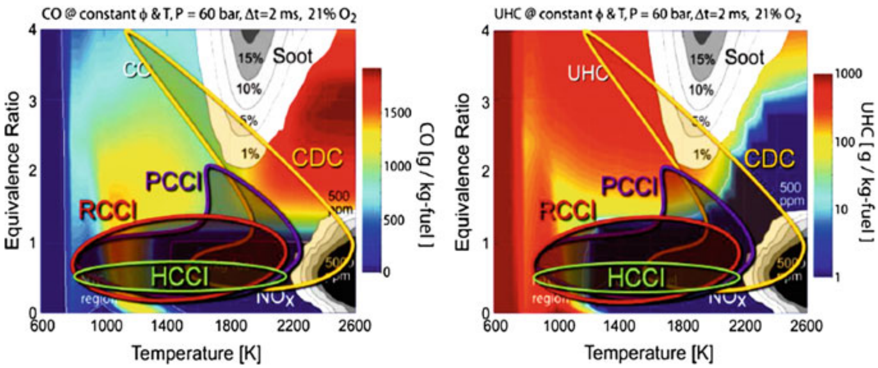


Fig. 15.2 φ-T diagram for soot and NO_x emissions (Wissink 2015)

LTC is one of the early diesel combustion techniques extensively researched during past three decades. The underlying principle of LTC is early fuel injection for preparation of well-mixed fuel–air mixtures (in case of SI engines) or early injection of fuel in the intake stroke (in case of CI engines) to provide enough time for formation of a physically homogeneous air–fuel mixture (Fig. 15.3). This mixture is then compressed up to temperatures much higher than auto-ignition temperatures of the fuel–oxidizer mixture, resulting in reactions that initiate combustion at multiple sites in the combustion chamber. Therefore, LTC ensures complete and smoother low-temperature combustion, leading to reduced NO_x and soot emissions.

The concept of LTC was first coined by Onishi et al. (1979) in 1979 and was termed as Active Thermo-Atmosphere Combustion (ATAC). They were able to

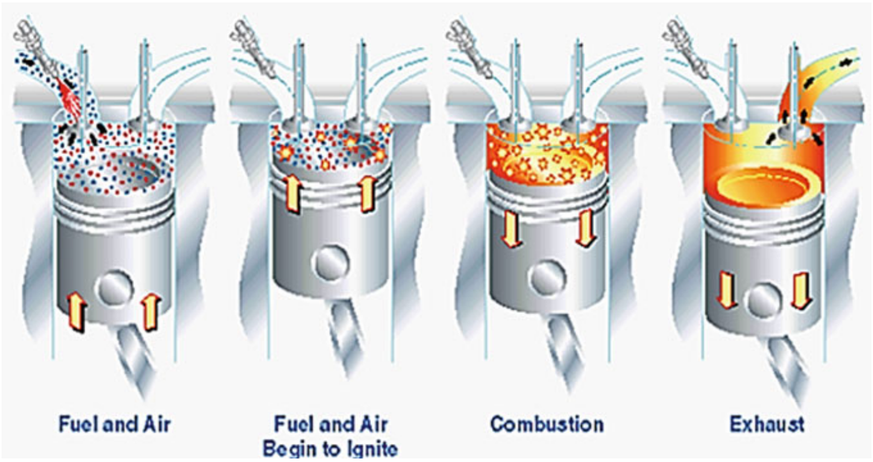


Fig. 15.3 Homogeneous charge compression ignition combustion principle (Ryan and Matheaus 2002)

achieve stable combustion in a gasoline 2-stroke engine at part-load condition. Low engine noise and vibrations along with significant emission reduction due to relatively lean mixture combustion were also reported. Since then, several researchers including Thring (1989), Christensen et al. (1997), and Maurya and Agarwal (2011) have successfully demonstrated this novel combustion concept in SI engines. After realizing the potential of LTC in gasoline engines, there is continued interest in examining this concept in diesel engines. Recently, Singh and Agarwal (2012) reported combustion characteristics of diesel-fueled LTC. Singh et al. (2014) also presented promising results using biodiesel in LTC engines.

Even though the adaptation of LTC resulted in reduced NO_x and PM in diesel engines, HC and CO emissions increased significantly due to reduction in cylinder temperatures and employment of very high EGR rates, necessary for HCCI combustion. This resulted in rather poor overall thermal efficiency since LTC suffers from the problem of control over the combustion phasing, in particular, with mineral diesel due to its relatively lower volatility and lower auto-ignition temperature. Researchers observed that either too advanced or too retarded combustion phasing, both, resulted in lower thermal efficiency of the engine. These drawbacks motivated researchers to develop a new low-temperature combustion strategy known as PCCI combustion. Premixed charge compression ignition (PCCI) combustion is an advancement over the HCCI combustion. In PCCI technique, fuel is injected at an intermediate timing between that of HCCI and conventional CI combustion. Thus, a partially premixed air–fuel mixture is formed since the time available for mixing is not as high as it is in case of HCCI combustion. PCCI combustion seems to be a very promising method that leads to a single-stage combustion and shifts the combustion regime toward the premixed phase. Diffusion combustion peaks are absent in case of PCCI combustion, which results in locally high but overall lower temperatures in the combustion chamber. Moreover, high load PCCI operates at high boost pressures thus providing enough supply of oxidizing agent (air) to the fuel. This helps in reduction of HC and CO emissions, thereby offering an advantage over the HCCI combustion. PCCI combustion therefore not only offers convenience of lower NO_x and PM emissions from the engines but also reduces the prominent problem of combustion phasing along with significant reduction in HC and CO emissions. PCCI combustion has several issues such as limitations for high load application, combustion control, which motivated the researchers to develop another LTC technique namely reactivity controlled compression ignition (RCCI) combustion. RCCI combustion depends on the stratification versus homogenization of fuel–air mixture. In this technique, combustion phasing can be controlled by in-cylinder blending of fuels with different reactivity. In this technique, low reactivity fuels such as gasoline or natural gas are injected into the intake port and high reactivity fuels such as mineral diesel or biodiesel are injected directly into the combustion chamber using high-pressure fuel injection system. It has been suggested that the operating window of RCCI combustion can be extended to include high load conditions, while attaining thermal efficiencies close to the conventional CI combustion. The heat release in case of RCCI occurs in three stages: the cool flames, the PRF burn, and the late burn. The first-stage reaction occurs due to the n-heptane injection, which corresponds to the cool flames. The first stage of high temperature heat release (HTHR) occurs due to the PRF burn, where n-heptane and the entrained iso-octane combust result in a heat release. The final stage of heat release occurs due to the late burn of the lower reactivity fuel, i.e., iso-octane. The changing fuel ratio results in the change of shape and the magnitude of the heat release (Splitter et al. 2012).

15.3 Fuel Properties for LTC

A large number of studies have shown that chemical properties of fuel–air mixtures in the combustion chamber can be optimized using different fuel design concepts such as addition of fuel additives, fuel blending, dual-fueling, and optimized fuel proportion (Lu et al. 2011). Different physical and chemical properties of fuel affect several processes occurring in the combustion chamber. High cetane number (CN) fuels have potential to improve engine cold-start capability, widen the lean-burn limit, lower the cycle-to-cycle variations and improve the mode transition characteristics, but they have negative effect on rich-burn limits. High octane fuels have almost an opposite effect to that of high cetane fuels (Lu et al. 2011). Foster (2003) performed a series of experiment to investigate the effects of CN, volatility, and total aromatic content on highly dilute low-temperature diesel combustion. At 5.5 bar net IMEP, experimental results showed that increasing CN reduces the CO and HC emissions, improves the indicated specific fuel consumption (ISFC), and reduces the combustion noise due to more favorable combustion phasing. Figure 15.4 shows the effect of CN on the combustion characteristics of a test engine (Foster 2003).

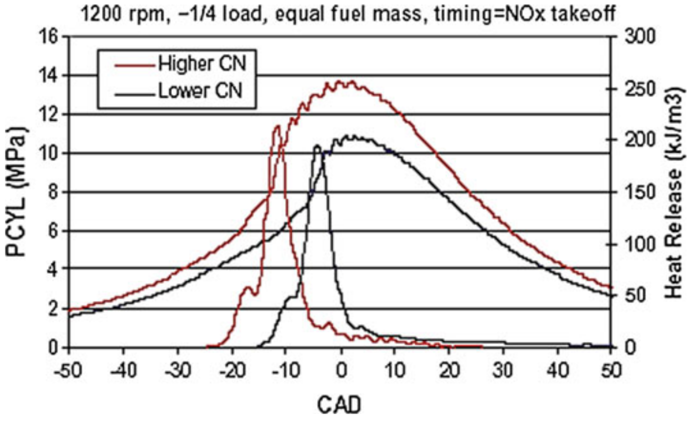


Fig. 15.4 Effect of cetane number (CN) on the engine performance (Foster 2003)

Starck et al. (2010) carried out experiments in quest of impact of fuel properties on HCCI combustion and found lower CN fuels as better HCCI fuels. They brought to light that a lower CN fuel and an optimum combustion speed could improve the HCCI operation range because lower combustion speed results in more time responsible for homogenization, thus resulting in superior HCCI combustion. Tanaka et al. (2003) used pure hydrocarbon fuels and mixtures to investigate the effects of fuel structure and additives on HCCI combustion using a rapid compression machine (RCM). They reported that fuels with saturated compounds led to two-stage combustion and those with unsaturated compounds led to single-stage combustion. Higher octane number results in higher ignition delay and a lower burn rate.

Fuel composition mainly affects the speed of low-temperature reactions that occur in HCCI engines. These in turn are affected depending on when these reactions are initiated and where in the cycle, the main reactions occur. Fuels like gasoline exhibit little or no low-temperature reactions, and combustion initiation temperature is close to 950 K in HCCI engines. Fuels such as mineral diesel exhibit significant low-temperature reactions, and corresponding initiation temperatures are in the range of 750 K in HCCI engines (Ryan and Matheaus 2002). The volatility or distillation characteristics of the fuel dominate fuel evaporation in the combustion chamber. For HCCI engine operation, fuel must be evaporated and at least partially mixed prior to the SOC reactions taking place (Ryan and Matheaus 2002). It has been observed that if liquid fuel survives the start of reactions, these fuel droplets or packets would burn as diffusion flames, which would dramatically elevate the production of soot and NO_x in the engine (Gray and Ryan 1997). Therefore, it is important to improve the fuel distillation characteristics, which directly influence fuel–air mixture homogeneity. This results in absence of localized fuel-rich zones, thereby reducing the maximum combustion temperature, leading to reduction in NO_x and PM formation (Heywood 1988). Volatility and ignition characteristics are the two main properties that will ultimately differentiate HCCI fuels from the gasoline and mineral diesel (Komninos 2009). Figure 15.5 shows the range of auto-ignition and volatility characteristics of different fuels and some common refinery components. Gasoline-like fuels have an advantage over conventional mineral diesel-like fuels because they are more volatile and also because conventional mineral diesel is prone to auto-ignition. Kerosene would therefore be better for HCCI combustion compared to conventional mineral diesel because of its superior volatility and lower CN (Fig. 15.5) (Kalghatgi 2007).

Biodiesel-fueled LTC is a new area of research because it has combined advantages of both biodiesel and HCCI combustion. Main advantage of burning biodiesel in HCCI combustion mode is simultaneous reduction of NO_x and soot, as well as reduction of fossil CO_2 emission. In LTC mode, biodiesel combustion happens at significantly lower in-cylinder temperature; therefore, it reduces NO_x emissions. Use of EGR further reduces the NO_x emissions to ultralow levels. Biodiesel LTC also enhances the fuel efficiency because of combustion of ultra-lean mixtures, which brings the actual thermodynamic combustion closer to the theoretical Otto cycle. Low volatility and high vaporization temperatures are the two important properties of biodiesel, which are major impediments in formation of

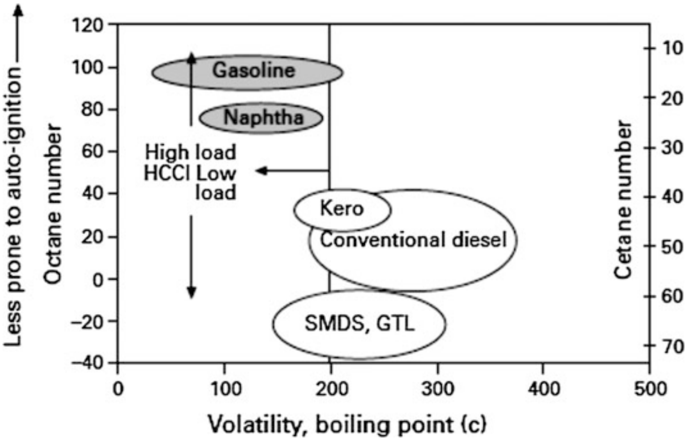


Fig. 15.5 Auto-ignition quality versus volatility of different fuels and refinery streams (Kalghatgi 2007)

homogeneous fuel–air mixture. Biodiesel also has higher flash point, which affects its auto-ignition in the combustion chamber. Relatively lower calorific value of biodiesel is another important factor, which increases its volumetric fuel consumption. Biodiesel has higher viscosity and ash content compared to baseline mineral diesel, which might possibly choke the fuel injector upon long-term usage. It has shorter ignition delay and higher bulk modulus of compressibility, due to which ignition control may become difficult. High bulk modulus shortens the response time of injectors, leading to earlier fuel injection than expected (Heywood 1988).

15.4 Alternative Fuels in LTC Derivatives

LTC techniques such as HCCI, PCCI, and RCCI have emerged as promising alternatives to the conventional SI and CI combustion due to their capability of achieving lower localized in-cylinder temperatures and the absence of fuel-rich zones simultaneously. An engine can be operated in LTC mode using practically any fuel by choosing the right design and operating conditions. However, practical commercial engines cannot be operated in LTC mode because they operate over a wide range of speed and load conditions with acceptable levels of noise, stability, and emissions. A suitable fuel selection enables this breadth of operation. The development of fuels for use in IC engines has been an evolutionary process, in which fuel-related problems are encountered and critical fuel properties are identified; specific limits (or specifications) are defined to mitigate these issues.

Previous studies have proved that chemical kinetics of fuel–air mixtures dominantly control LTC, which is dominated by decomposition of H_2O_2 radicals (Westbrook 2000) and reactions between OH radicals and fuel (Peters et al. 2002) under practical engine operating conditions (Kalghatgi 2007). In LTC, ignition and combustion are controlled by physical and chemical properties of the fuel, in which spatial and time history plays a dominant role in combustion control. Several studies have been undertaken, where different fuels with different chemical compositions have been used in the LTC engines (Aroonsrisopon et al. 2002; Jeuland et al. 2003; Kitano et al. 2003; Koopmans et al. 2004; Montagne and Duret 2001; Oakley et al. 2001; Risberg et al. 2003; Shibata and Urushihara 2006). All these studies showed that different fuels exhibited different combustion phasing in most cases, but the differences were small under some operating conditions. In most cases, combustion phasing did not correlate with the conventional measures of fuel auto-ignition quality such as research and motor octane numbers (RON and MON). During the last few years, a large number of studies on LTC using different alternative fuels have shown the need of specific fuel properties for combustion, which could not be fulfilled using single-component fuels. Therefore, it becomes important to reform the molecular structure of different fuel components to change their overall physical and chemical properties according to the specific LTC requirements (Lu et al. 2011). In the following subsections, utilization of different alternative fuels in various advanced combustion techniques has been discussed. Each LTC derivative requires different fuel properties due to different fuel–air chemical kinetics involved during combustion (Fig. 15.6).

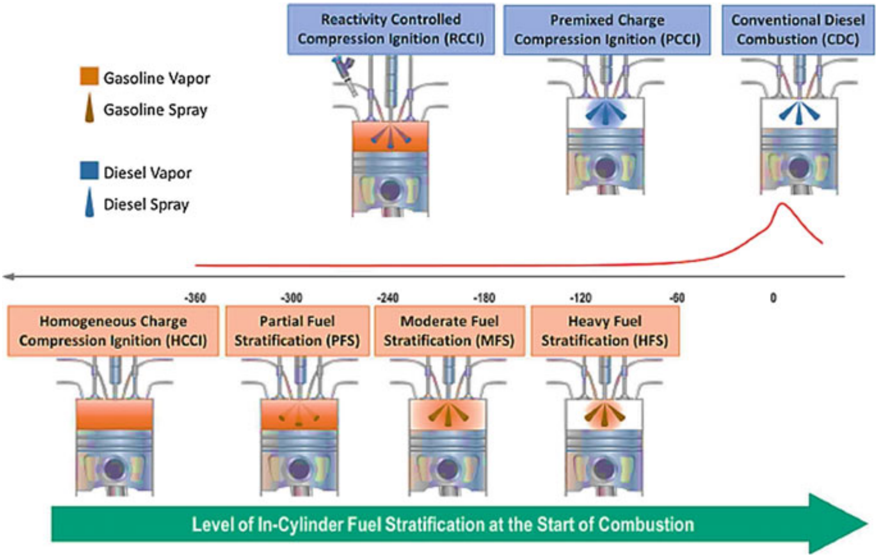


Fig. 15.6 Comparison of diesel, gasoline, and LTC engines (Dempsey et al. 2016)

15.4.1 HCCI Combustion

Extensive utilization of gasoline and mineral diesel in the transport sector has led to an increase in petroleum consumption worldwide. In such a scenario, compatibility with alternative fuels is an important criterion in development of any advanced combustion technology such as HCCI. HCCI combustion concept has high fuel flexibility and can be applied to a wide range of liquid and gaseous fuels having different octane numbers. HCCI fuels include biodiesel (Tsolakis et al. 2008; Arrègle et al. 2009), alcohols (Maurya and Agarwal 2011), natural gas (Fiveland et al. 2001), hydrocarbon fuels (Yao et al. 2009), and reformulated fuels (Kongsereeparp and Checkel 2008; Stenlåås et al. 2004; Hosseini and Checkel 2008).

Although HCCI combustion is a flexi-fuel technology, the fuel properties have a substantial effect on the HCCI combustion. During last few years, HCCI technology has been adopted to nonconventional fuels such as alcohols, natural gas, hydrogen. Yap et al. (2004) achieved natural gas HCCI combustion using exhaust gas reforming. They reported that natural gas HCCI required high compression ratio as well as high intake air temperature due to high auto-ignition temperature of natural gas. Natural gas HCCI was controlled by hydrogen blending, and addition of hydrogen lowered the intake temperature requirement. This resulted in lower NO_x emissions; however, it also increased HC and CO emissions. Bastawissi et al. (2010) investigated CNG-hydrogen blend-fueled HCCI by using multidimensional computational fluid dynamics (KIVA-3VR2) code coupled with detailed chemical kinetics. They utilized hydrogen as an additive to control the auto-ignition timing and combustion phasing of CNG-fueled HCCI combustion. Relatively higher formaldehyde and hydroxyl radical formation was an important finding of this study. Formation of these species due to low-temperature oxidation was further promoted by hydrogen addition.

Noran et al. (2011) compared the HCCI combustion characteristics of CNG with pilot injection of gasoline and overall lean SI combustion of CNG in stratified charge mode. Homogeneous charge from gasoline was created by manifold injection, and the charge was heated by an air heater in order to achieve HCCI combustion. High temperature charge helped in ignition of directly injected stratified CNG at 80° BTDC. They reported that HCCI combustion had higher fuel conversion efficiency compared to SI and lower emissions in a certain range of loads. Ishiyama et al. (2005) explored natural gas direct injection PCCI combustion with the main objective to resolve the issue of combustion control for natural gas. They reported that by reducing the dissemination of fuel–air mixtures, higher combustion efficiency could be obtained under leaner conditions, but at the expense of engine knock. Antunes et al. (2008) discussed hydrogen-fueled HCCI combustion, in which combustion was controlled by controlling the intake air temperature. Due to high energy density of hydrogen, they achieved high brake thermal efficiency and higher in-cylinder temperature with relatively leaner charge. However, high in-cylinder temperature resulted in higher NO_x emissions as well. Goldsborough and Van Blarigan (1999) investigated a free-piston hydrogen-fueled HCCI engine using simulations. They discussed piston dynamics and gas exchange process in a free-piston, two-stroke engine. Biogas has also been explored as a potential fuel for HCCI combustion. Biogas is produced from organic matter using a series of metabolic stages. Biogas contains of methane (CH_4: 50–75%), which is the energy carrier, carbon dioxide (CO_2: 25–50%), and traces of other components. Both of these main constituents of biogas are GHG, and several times these gases are produced as unavoidable byproducts; therefore, proper use of biogas can protect the environment. Relatively higher auto-ignition temperature ($\sim$1100 K) of methane and presence of huge amount of CO_2 result in lower in-cylinder pressure and temperature at TDC. Therefore, higher intake temperatures are required to achieve stable HCCI combustion, which leads to lower intake charge density, resulting in lesser power output from a biogas-fueled engine. Swaminathan et al. (2010) investigated the performance of the biogas-fueled HCCI combustion, in which combustion was controlled by diesel blending. They reported that high charge temperature could be used in biogas HCCI because biogas did not knock even beyond 100 °C intake charge temperature. Biogas HCCI showed relatively lower maximum rate of pressure rise, leading to higher CO and HC emissions (Fig. 15.7).

Haggith et al. (2010) performed HCCI experiments using a simulated biogas that resembled in composition to the producer gas. Various compositions of the producer gas constituents were investigated, and stable combustion was achieved over a wide range of equivalence ratios with moderate fuel–air mixture preheating. Achilles et al. (2011) also carried out HCCI experiments using alternative fuels. Main objective of their study was to expand the load range of HCCI combustion. Sudheesh and Mallikarjuna (2010) used diethyl ether (DEE) as an ignition improver to achieve biogas-fueled HCCI combustion at ambient intake conditions.

They increased biogas content in the blend to increase the engine load; however, quantity of DEE was kept fixed. In the experiment, they achieved 4.5 bar BMEP

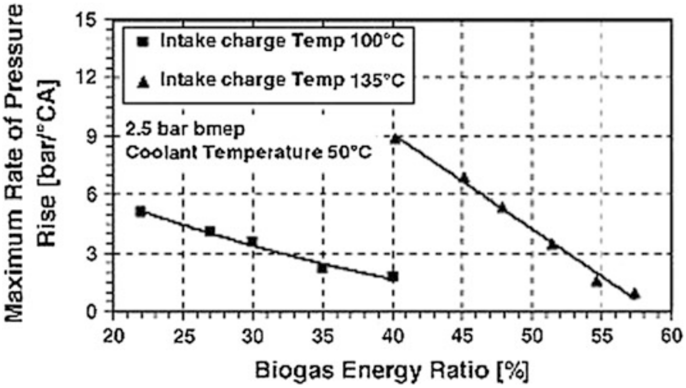


Fig. 15.7 Variations in MRPR from biogas–diesel HCCI operation at 2.5 bar BMEP (Swaminathan et al. 2010)

using approximately 80% biogas in the test fuel blend (Fig. 15.8). They suggested that biogas can be effectively used in HCCI combustion mode compared to conventional combustion modes. Maurya (2006) and Maurya and Agarwal (2009, 2011) investigated the performance of a HCCI engine fueled by alcohol. Experiments were carried out to investigate the performance of HCCI combustion at different fuel–air ratios. They reported reduction in HC emissions and increase in CO emission with increasing fuel–air ratio. Yang et al. (2010) investigated fundamental properties of a C_5 alcohol (iso-pentanol) as a possible alternative fuel for HCCI combustion. They performed HCCI experiment over a wide range of engine speeds, intake air temperatures, intake pressures, and equivalence ratios. They observed different ignition characteristics of iso-pentanol compared to gasoline since iso-pentanol did not show two-stage ignition, which was similar to ethanol. Ng and Thomson (2004) performed model analysis of ethanol-fueled HCCI combustion and focused on effects of ethanol reformed gas on the ignition requirement and NO_x emissions.

Szybist et al. (2007) performed HCCI combustion experiments in a single-cylinder engine using blends of soy biodiesel and ultralow sulfur diesel (ULSD). The results of HCCI combustion were also compared with simulation results, and major differences were found such as its dependence on biodiesel concentration, duration of low-temperature heat release (LTHR), and main combustion event. Brakora and Reitz (2010) performed experiments to compare formation of nitric oxide (NO) and nitrogen dioxide (NO_2) in biodiesel and diesel-fueled HCCI combustion. They showed higher NO_x from biodiesel-fueled HCCI combustion compared to mineral diesel-fueled HCCI combustion. Cinar et al. (2010) experimented with diethyl ether (DEE), which acted as a cetane improver. During HCCI combustion, premixed DEE burned and generated suitable conditions for ignition of accumulated mineral diesel during the ignition delay. Like

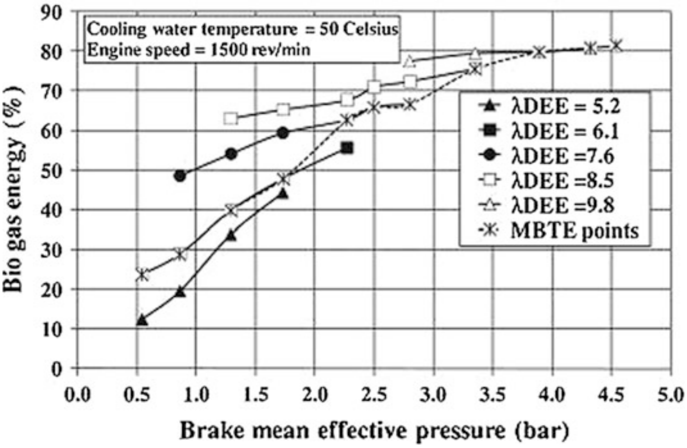


Fig. 15.8 Energy share of biogas and DEE at various loads (Sudheesh and Mallikarjuna 2010)

all other test fuels, DEE-fueled HCCI produced significantly lesser NO_x and relatively higher CO and HC emissions. Ibrahim et al. (2015) investigated biogas–diesel-fueled partially premixed charge compression ignition (PPCCI) combustion, in which biogas was inducted along with intake air and mineral diesel was injected directly into the engine cylinder using a high-pressure CRDI system. In the experiments, they varied the SOI timings of mineral diesel, premixed ratio of biogas in the test fuel, and intake charge temperature. They reported that the thermal efficiency of the biogas–mineral diesel PPCCI mode was better than the biogas–mineral diesel dual-fuel mode. HC and NO_x emissions from mineral diesel–biogas PPCCI mode were also significantly lower compared to dual-fuel mode.

15.4.2 PHCCI Combustion

PHCCI combustion is an intermediate technique of HCCI and PCCI combustion modes. Singh and Agarwal (2015) investigated PHCCI combustion using different fuels namely diesohol (15% v/v ethanol with diesel), diesoline (15% v/v gasoline with diesel), and diesosene (15% v/v kerosene with diesel) vis-a-vis baseline mineral diesel. They developed a dedicated fuel vaporizer for preparing homogeneous fuel–air mixture. They found stable combustion characteristics for diesosene at lower engine loads; however, diesoline and diesohol showed improved emissions compared to baseline diesel HCCI combustion. They concluded that addition of volatile fuel additives such as alcohols and kerosene improved the combustion, performance, exhaust emissions, and particle emission characteristics of PHCCI combustion. In another investigation carried out to investigate the effect of fuel properties on PHCCI combustion, Singh et al. (2017) carried out experiments using a variety of additives blended with mineral diesel, which included low-quality high volatile fuel (kerosene), low cetane high volatile fuels (ethanol and gasoline), and high cetane less volatile fuel (biodiesel). Combustion phasing was significantly affected by the fuel properties and improved start of combustion (SOC); combustion phasing and heat release rate (HRR) at lower engine loads were observed; however, excessive knocking at higher engine loads was observed too.

Singh and Agarwal (2016) performed PHCCI experiments using B20 (20% v/v biodiesel with diesel). The experiments were performed at three different intake charge temperatures (160, 180, and 200 °C) and three different EGR ratios (0, 10, and 20% EGR) at different engine loads. Results showed that biodiesel-fueled PHCCI engine performance characteristics improved with increasing EGR due to optimization of combustion phasing. However, increasing EGR led to slightly higher nanoparticles emissions from B20-fueled PHCCI combustion, which reduced with increasing intake charge temperature (Fig. 15.9).

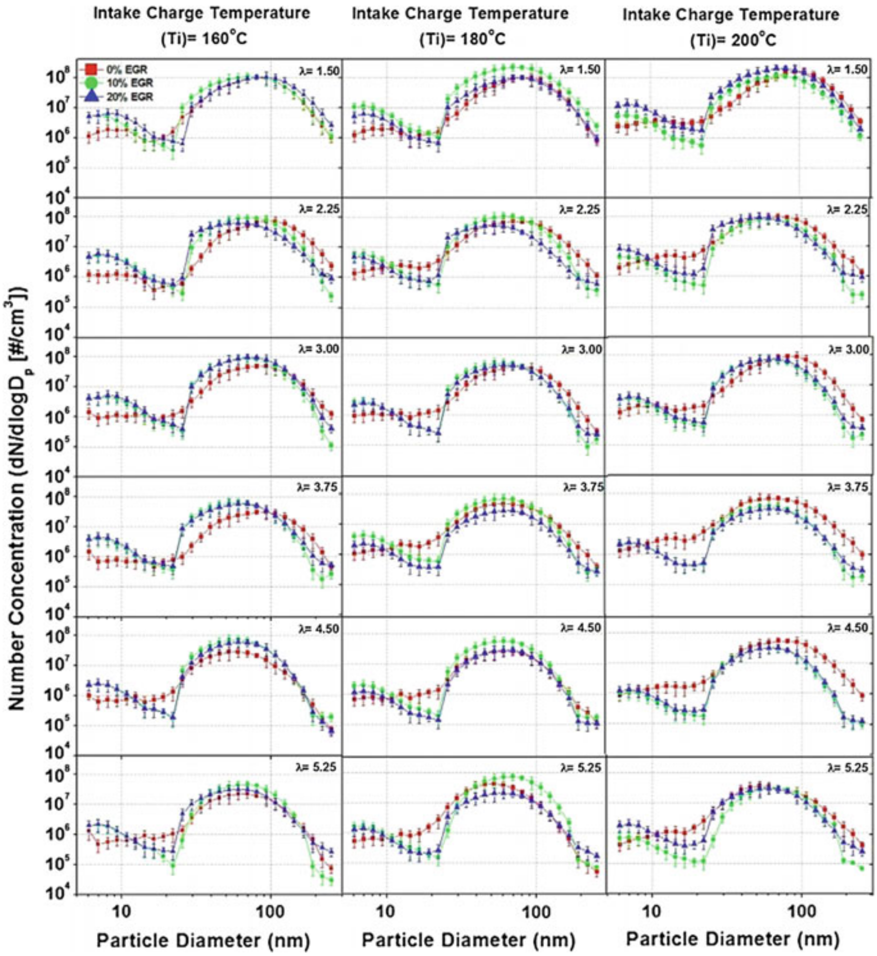


Fig. 15.9 Number size distribution of particulate emitted from B20-fueled PHCCI engine at different engine loads, EGR, and intake charge temperatures (Singh and Agarwal 2016)

15.4.3 PCCI Combustion

Alcohols, biodiesel, dimethyl ether (DME), etc., are less polluting and are produced at lower costs from renewable resources. Mohammadi et al. (2005) performed PCCI combustion in single-stage and split injection modes using ethanol-blended mineral diesel. In single injection strategy, ethanol-blended fuels offered better reductions in NO_x and PM emissions compared to mineral diesel. However, reduced power output puts a limitation on its use. The split injection strategy resulted in further reduction in NO_x emissions without significantly affecting the thermal efficiency of the engine. Emissions were further reduced by employing cooled EGR along with split injection strategy (Fig. 15.10).

Mancaruso and Vaglieco (2010) performed PCCI experiments using ethanol/air/mineral diesel mixtures. They observed three-stage combustion under varying premixed ratios of in-cylinder charge and suggested ethanol addition to the premixed charge to be responsible for this behavior. Park et al. (2013) investigated the reductions in HC and CO emissions from a PCCI engine fueled by bio-ethanol-blended diesel by employing a narrow angle injector (70°). It was observed that use of narrow angle injector with bio-ethanol resulted in low and stable HC and CO emissions with much higher IMEP compared to baseline diesel.

Biodiesel blends were used in diesel PCCI engines by Fang et al. (2009; Fang and Chia-fon 2009). Although biodiesel has higher CN, however, relatively higher boiling point of biodiesel resulted in longer ignition delay compared to mineral diesel. Moreover, spray impingement and longer penetration length (for all test cases) were observed for biodiesel blends (Fig. 15.11).

These issues were tackled by Lahane and Subramanian (2014) by modifying the injector nozzle (from 5 to 6 holes and a slight reduction in nozzle diameter). The modified nozzle resulted in reduced spray penetration and significant reduction in soot and NO_x emissions compared to mineral diesel. Kitano et al. (2003) investigated the effect of CN and distillation characteristics on the PCCI combustion. They found that lower CN fuel increased the ignition delay under high load conditions, which resulted in lower NO_x emissions. They also reported that lower distillation characteristics of fuel promoted faster mixture formation and combustion, resulting

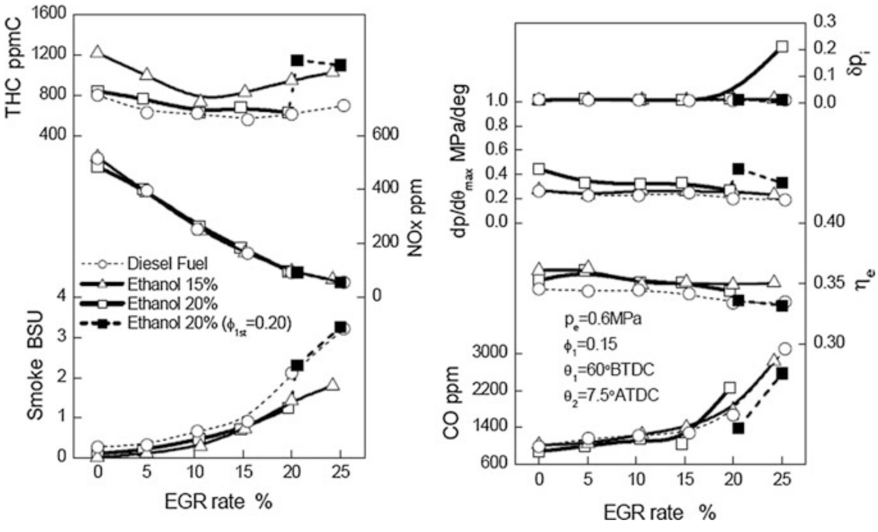


Fig. 15.10 Effects of ethanol blending on engine performance and emissions with varying EGR rate for early pilot injection (Mohammadi et al. 2005)

ISFC (gm kW^{-1} hr^{-1})				
Case 1	426	442	461	487
Case 2	239	261	287	294
Case 3	219	232	257	306

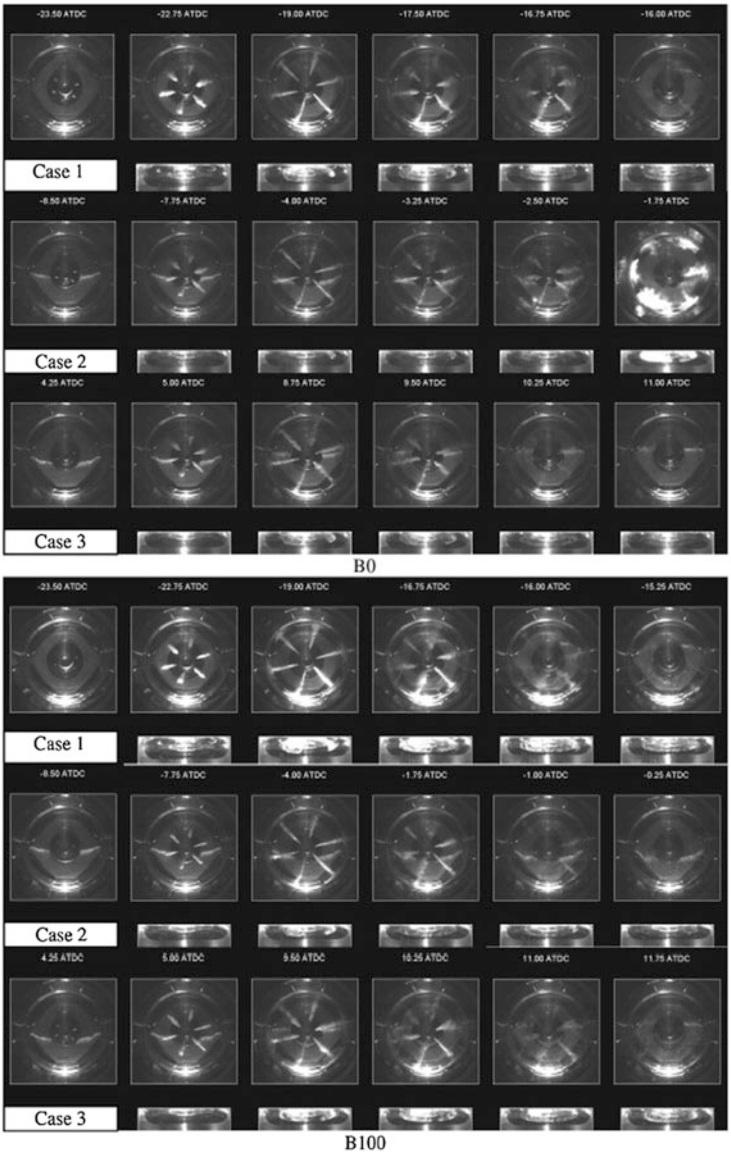


Fig. 15.11 Mie scattering images of B0 and B100 at different crank angles for the three start of injection timings in an engine cylinder (Fang et al. 2009)

in lower soot formation. Therefore, it was suggested that PCCI engine fuel should have optimal CN and distillation properties for optimal emission control.

In retrospect to the above-mentioned issues with ethanol, biodiesel, etc., fuels such as dimethyl ether (DME) and JP-8 are currently being explored by several researchers. Zhao et al. (2014) carried out PCCI combustion using blends of DME and mineral diesel. They observed significant reduction in NO_x and soot emissions with increasing percentage of DME in the mineral diesel. However, brake specific fuel consumption (BSFC) increased along with an increase in HC and CO emissions due to this intervention. Yoon et al. (2010) studied combustion, performance, and emission characteristics of a PCCI engine using DME and narrow cone angle injectors (60°, 70°, and 156°). For all injection timings, NO_x emissions were lower for DME compared to mineral diesel. However, HC and CO emissions were higher for narrow angle injectors compared to conventional injectors. Jeon and Bae (2013) compared PCCI combustion using two test fuels and used double injection strategy with DME as reference case (first condition) and replaced DME main injection by hydrogen in the second condition. To investigate the effect of hydrogen, they varied the hydrogen quantity. In the experiments, they observed stable combustion for 100% DME PCCI combustion; however, hydrogen–DME PCCI combustion resulted in relatively higher IMEP (Fig. 15.12).

Odaka et al. (1999) used a gasoline-type injector for mineral diesel manifold injection in order to investigate premixed mineral diesel-fueled HCCI in combination with a normal DI system. They used methyl tert-butyl ether (MTBE) in mineral diesel as an additive for delaying the auto-ignition of the premixed charge.

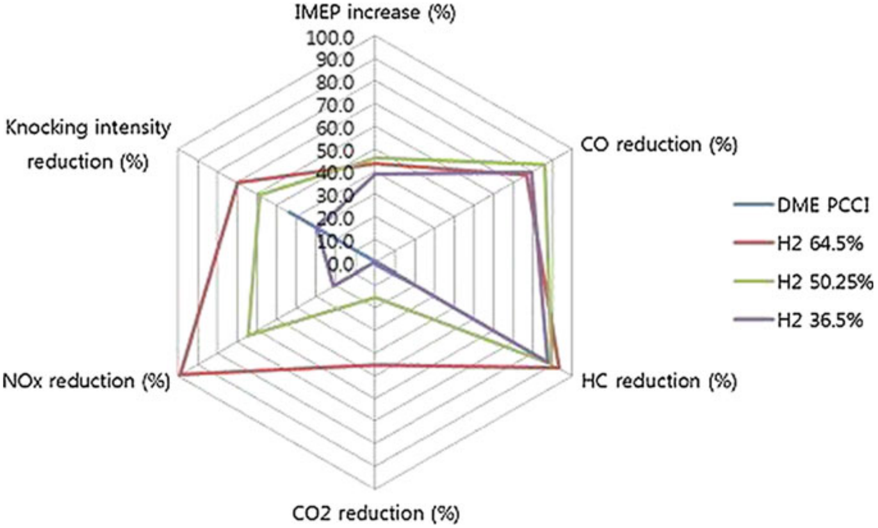


Fig. 15.12 Comparison of IMEP increase, and reduction in exhaust emissions, and knock intensity for each strategy, at 1200 rpm, 30 MPa DME injection pressure, and 0.5 MPa hydrogen injection pressure (Jeon and Bae 2013)

Similar work was also reported by Milovanovic and Chen (2001). JP-8 was tested in a single-cylinder PCCI diesel engine by Park et al. (2010). The fuel showed lower NO_x and smoke emissions under low load conditions due to its lower aromatic content, lower CN, and higher volatility, compared to baseline mineral diesel. However, under conventional combustion strategy, NO_x emissions were higher than baseline mineral diesel because of its more dynamic premixed combustion phase.

Sakai et al. (2005) successfully demonstrated PCCI combustion using low distillation temperature fuels. Heptane and iso-octane were blended with diesel to resolve issues related to lower volatility of diesel. It was observed that mixture homogeneity improved significantly using high-volatility fuels, which resulted in leaner mixture formation in the squish area near the end of the compression stroke. It was also observed that regardless of the fuel volatility, a large fraction of fuel adhered to the piston bowl. However, the rate of evaporation in case of low distillation temperature fuel was much faster compared to baseline diesel; thus, thermal efficiency got significantly improved in the former case. Ishiyama et al. (2005) explored natural gas PCCI direct injection combustion with the main incentive to resolve the issue of combustion control in the natural gas. They figured out that by reducing the dissemination of fuel–air mixture, higher combustion efficiency could be obtained in leaner conditions but at the expense of the engine knock.

15.4.4 Dual-Fuel Strategy for RCCI Combustion

In recent years, dual-fuel technique for LTC has gained importance due to its capability to operate at higher engine loads. RCCI combustion is mainly affected by fuel properties, fuel quantities and their ratio, EGR, and fuel injection parameters; therefore, these parameters can be used to optimize the engine power output (fuel efficiency) and engine emissions (by controlling the combustion temperature and equivalence ratios) (Fig. 15.13).

Such dual-fuel combustion is commonly referred to as ‘RCCI combustion’ and has been explored using different pair of fuels such as mineral diesel–gasoline (Kokjohn et al. 2011), mineral diesel–ethanol (Gao et al. 2013). Previous results indicate that moderate to high engine loads are achievable using RCCI combustion (Kokjohn et al. 2011; Asad et al. 2013), while retaining or exceeding mineral

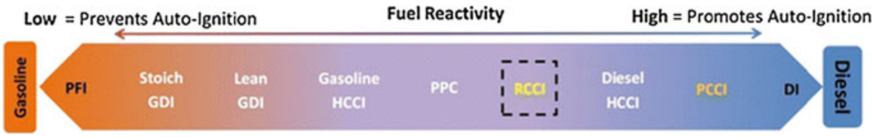


Fig. 15.13 Advanced combustion strategies converging on the hardware and the test fuel (Loaiza et al. 2016)

diesel-like thermal efficiencies. Use of low to moderate levels of EGR maintains ultralow NO_x and soot emissions, which are practically negligible. The dual-fuel RCCI combustion seems to be a viable option for achieving clean combustion; however, requirement of additional fuel injection and storage system restricts its commercial application. In dual-fuel type controls, two fuels with different auto-ignition properties are used. The system will use a main fuel with a high octane number and a secondary fuel with low octane number (Olsson et al. 2001). Different auto-ignition properties of dual-fuel systems are used to control combustion phasing in HCCI since blending two fuels in different proportions changes their auto-ignition properties. Use of commercial fuels or mixtures of single-component and commercial fuels and PRFs have been investigated in several studies (Shimasaki et al. 2004; Aldawood et al. 2012; Ma et al. 2008). For better understanding of dual-fuel mode operation of CI engines, Mancaruso and Vaglieco (2010) performed PCCI experiments using ethanol and mineral diesel. In these experiments, ethanol was injected into the intake manifold; however, mineral diesel was injected directly into the cylinder. The experiments were performed at different premixed fuel ratios, and it was reported that the LTC governing parameter (OH radicals) was significantly controlled by premix fuel ratio. Ma et al. (2013) investigated the effects of different diesel injection strategies on combustion, emissions, and fuel economy of a modified single-cylinder diesel engine, fueled by gasoline/mineral diesel dual-fuel. This gasoline/diesel dual-fuel combustion mode proposes port fuel injection of gasoline and direct injection of mineral diesel with rapid in-cylinder fuel blending. Fang et al. (2015) developed a response surface methodology (RSM) to optimize complex dual-fuel RCCI combustion with reduced need for experimentation.

RCCI experiments were performed in a single-cylinder research engine using hydrous ethanol as the low reactivity fuel and mineral diesel as the high reactivity fuel. They found unburned ethanol as the main source of HC emissions at low engine loads however in-cylinder injection of mineral diesel as the major source of HC emissions at higher engine loads. They reported that CO emission was mainly affected by physical parameters namely intake air pressure, intake air temperature, and fuel injection pressure (Fig. 15.14).

Park and Yoon (2016) carried out RCCI experiments using dual-fuel combustion (DFC) strategies. They used diesel–biogas and diesel–gasoline in order to simultaneously reduce emissions, while maintaining the engine performance similar to conventional CI combustion. They reported that DFC strategy can be used to maintain engine performance using advanced fuel injection timings and increasing the port fuel injection ratio, which results in higher IMEP. They compared the emission characteristics of DFC strategy and reported that HC and CO emissions in DFCs were higher than single injection conventional diesel combustion; however, it was lower than early injection diesel combustion (Fig. 15.15).

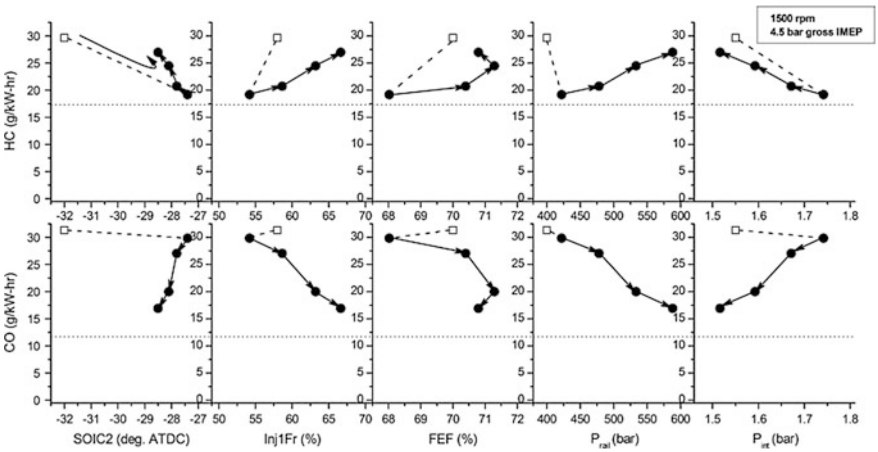
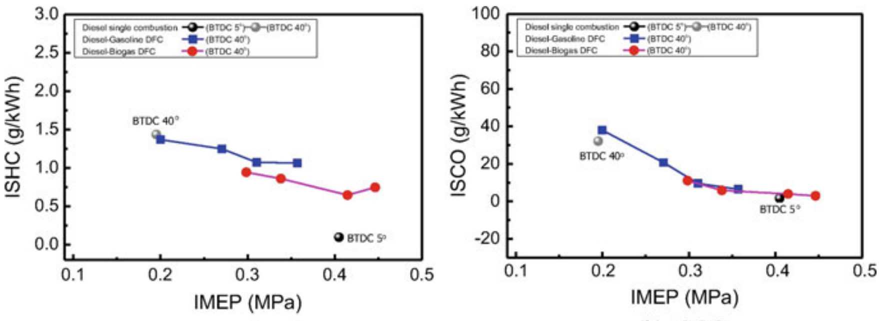


Fig. 15.14 HC and CO emissions at starting point (open squares) and on optimization path (closed circles) versus active factors for the low load condition. The horizontal dotted lines denote target emission values (Fang et al. 2015)



(a) ISHC

(b) ISCO

Fig. 15.15 ISHC and ISCO emissions in dual-fuel combustion strategies (Park and Yoon 2016)

Researchers also focused on natural gas as a potential alternative to conventional liquid fuels (i.e., gasoline and diesel) for automotive applications. Relatively higher octane number of natural gas compared to gasoline makes it more appropriate for RCCI combustion. Kakaee et al. (2016) carried out computational modeling to investigate the natural gas/diesel RCCI combustion. They reported that higher engine speed led to lower in-cylinder pressure and temperatures, which resulted in delayed combustion phasing. This led to reduced ringing intensity (RI) and increased UHC and CO emissions. Study by Splitter et al. (2011) on a heavy-duty

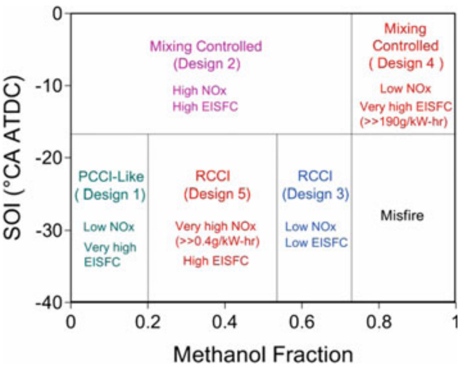
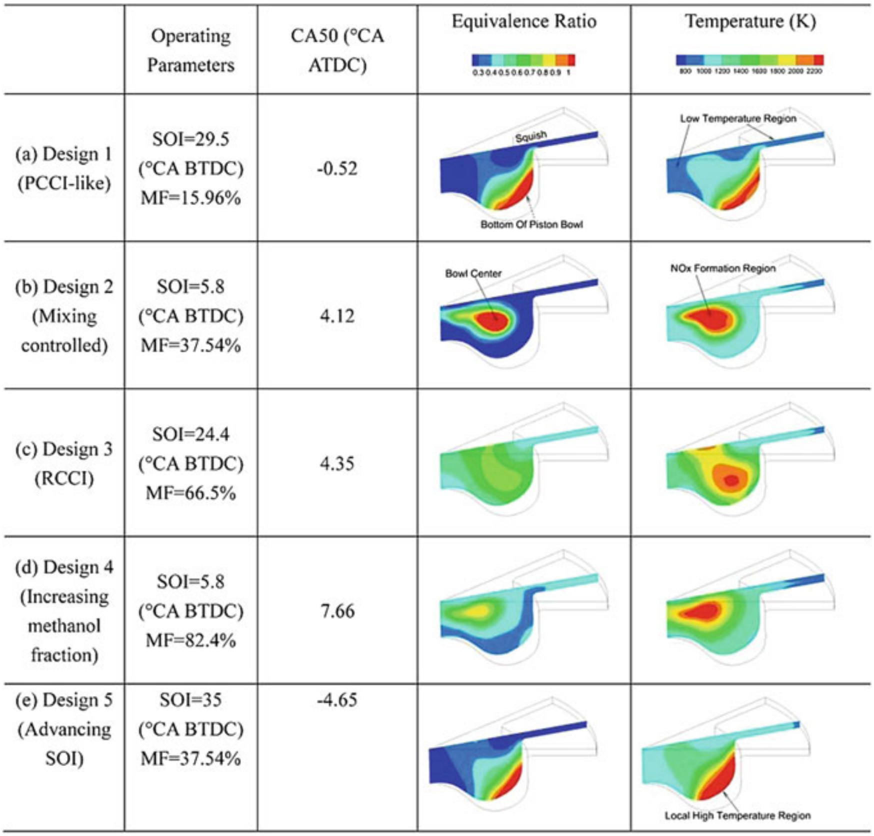


Fig. 15.16 Characteristics of different combustion modes with varying SOI timings and methanol fractions (Li et al. 2014)

engine showed that in RCCI combustion using combinations of ethanol (E85/diesel and gasoline/gasoline + Di-tert-butyl peroxide (DTBP) cetane improver) leads to high gross indicated thermal efficiencies, (well over 50%) cleaner and quieter combustion, NO_x and soot emissions well below US 2010 HD regulations, and PPRR values between 5 and 10 bar/CAD at all engine loads. Li et al. (2014) carried out detailed investigations of methanol/diesel-fueled RCCI combustion and suggested that efficient and stable combustion without the loss of power and fuel economy could be achieved by methanol/diesel RCCI combustion. They reported that variations in different parameters significantly affect the chemical kinetics of the in-cylinder fuel–air mixture and combustion characteristics (Fig. 15.16).

Figure 15.16 clearly shows that variations in SOI timings and premixed ratio affected the engine performance and emission characteristics. The RCCI combustion with high energy fraction of methanol ($\sim$70%) and advanced SOI timings exhibit higher fuel efficiency and lower emissions compared to other optimum solutions (Fig. 15.16). They reported that initial temperature and EGR rates are the most important operating parameters for the overall engine performance and emissions due to their significant influence on the in-cylinder temperature. Methanol fraction and SOI timings affected NO_x and soot emissions significantly by influencing the locally fuel-rich and high-temperature regions (Fig. 15.17).



	Operating Parameters	CA50 (°CA ATDC)	Equivalence Ratio	Temperature (K)
(a) Design 1 (PCCI-like)	SOI=29.5 (°CA BTDC) MF=15.96%	-0.52		
(b) Design 2 (Mixing controlled)	SOI=5.8 (°CA BTDC) MF=37.54%	4.12		
(c) Design 3 (RCCI)	SOI=24.4 (°CA BTDC) MF=66.5%	4.35		
(d) Design 4 (Increasing methanol fraction)	SOI=5.8 (°CA BTDC) MF=82.4%	7.66		
(e) Design 5 (Advancing SOI)	SOI=35 (°CA BTDC) MF=37.54%	-4.65		

Fig. 15.17 Variations in equivalence ratio and in-cylinder temperatures of the four-fuel strategy designs for LTC at CA_{50} (Li et al. 2014)

15.5 Summary

This chapter shows that advanced combustion techniques such as HCCI, PHCCI, PCCI, and RCCI have significant potential to reduce harmful exhaust emissions from IC engines. These combustion techniques can be easily employed with alternative fuels, which make these techniques better suited for future transportation needs. Alcohols have great potential to improve engine efficiency, reduce GHG, regulated emissions, and particulate matter especially while using advanced combustion techniques. Biogas can also be utilized in advanced combustion concepts since they reduce GHG potential of exhaust gas by converting methane to CO_2. Alternative fuels in advanced combustion techniques have shown significant potential to resolve some of the control issues, which are difficult to resolve by other techniques. Recent developments in RCCI combustion attracted researchers due to its stable combustion characteristics as well as potential for utilization of alternative fuels. Therefore, massive research efforts are underway worldwide to promote these combustion techniques for production grade engines; however, there are several practical issues which need to be resolved before their commercialization.

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Chapter 16
Fuel Injection Equipment (FIE) Design for the New-Generation Alternative Fuel-Powered Diesel Engines

Gaurav Tripathi, Sarthak Nag, Atul Dhar and Dhiraj V. Patil

Abstract Most widely acceptable, new-generation alternatives to the fossil (diesel and gasoline) fuels are alcohols, biodiesel, hydrogen, dimethyl ether, and natural gas. Current supply situation of these alternative fuels does not allow for a full replacement of the fossil fuels. For achieving the stringent emission norms (i.e., beyond EURO V or Bharat Stage V), engine manufactures are facing challenges in terms of engine technology upgradation while simultaneously controlling the cost for design and modification of the engine and fuel injection equipment for blending as well as using alternative fuels. This chapter reviews the fuel injection equipment technology employed worldwide for the alternative fuels (or its blend with the fossil fuels) and suggests important modifications. The injection strategy optimization, which includes understanding the fuel injection systems' requirements and the interplay between various injection parameters for different fuel blends, is also discussed.

Keywords Fuel injection · Alternative fuel · Atomization · Injection timing

16.1 Introduction

Current scenario of energy requirement mainly depends upon fossil fuels (Fig. 16.1). Approximately 80% global energy requirement is fulfilled by fossil fuels. This dependency over fossil fuels will increase by approximately 40% in 2035 (Global 2014). Sources of fossil fuels are limited, and nuclear energy has limitation because of safety concerns, so we have to look forward to renewable energy sources. India, currently ranked fifth in the energy consumption, is expected to be ranked third by

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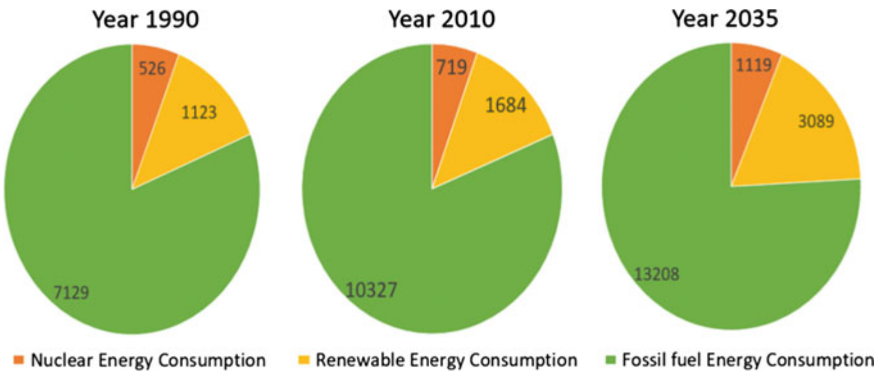

Fig. 16.1 Energy consumption in million tons of oil equivalent (Olejarnik 2013)

2030. Therefore, there is an indication by the Indian government to use 20% biofuel blending (biodiesel and bioethanol blending) by 2017 (Patni et al. 2011). Hence, there is a need to develop and modify the design of the fuel handling and fuel injection equipment (FIE) to deal with the proper blending of fuels.

Fuel injection process plays vital role in reducing emission. By adjusting injection timing, injection pressure, and adapting different fuel injection techniques such as pilot injection, post-injection, and multiple injections, emissions can be controlled (Johnson 2002). There are different European exhaust emission standards implemented for engine emission reduction.

The main purpose of FIE is the supply of fuel into the combustion chamber. Performance of fuel injection equipment affects the engine performance as well as engine out emissions. The fuel injection system approximately has one-third cost of engine (Khair and Jaaskelainen 2013). The main elements of fuel injection system are fuel pumping and metering element, fuel injection timing, and fuel–air mixing element.

Figure 16.2 describes main functional operations of the fuel injection equipment. Fuel pumping is the operation in which fuel is supplied from fuel tank to engine cylinder through piping. In fuel metering operation, according to engine load and speed fuel quantity is controlled. In fuel distribution operation, fuel is distributed among number of cylinders. In timing section, fuel is injected at correct time and fuel injection is stopped at correct time. In mixing operation, fuel distribution takes place inside the cylinder.

Among these elements, there are some basic requirements of fuel injection equipment. Such as, fuel should be injected at correct time and fuel should be injected sharply (no dribbling). Fuel injection amount should be measured correctly, and distribution should be uniform. Performance of injection system is dependent upon atomization, mixing, and utilization of air. If fuel is metered properly and injected timely, then engine performance enhances. During the atomization process, the fuel droplets break into small droplets. These small fluid droplets then vaporize rapidly. Improvement in the rate of vaporization of the fuel

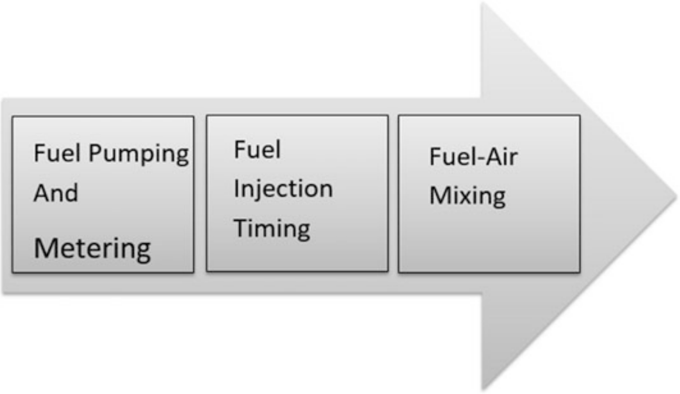

Fig. 16.2 Elements of injection system

droplets enhances the combustion. Non-vaporized droplets come out as unburnt hydrocarbon emissions. Better functional operation of fuel injection equipment impacts on spray characteristics such as uniform spray of fuel droplets in cylinder, proper utilization of oxygen available in cylinder, fast and complete vaporization of fuel droplets (Khair and Jaaskelainen 2013; Reif et al. 2014).

16.2 Types of CI Fuel Injection Systems

Based on the position of fuel injection system inside the combustion chamber, there are two main methods of fuel injection in compression ignition (CI) engines that are direct fuel injection system and indirect fuel injection system. In the direct injection system, fuel is directly injected into the cylinder, and in the indirect injection

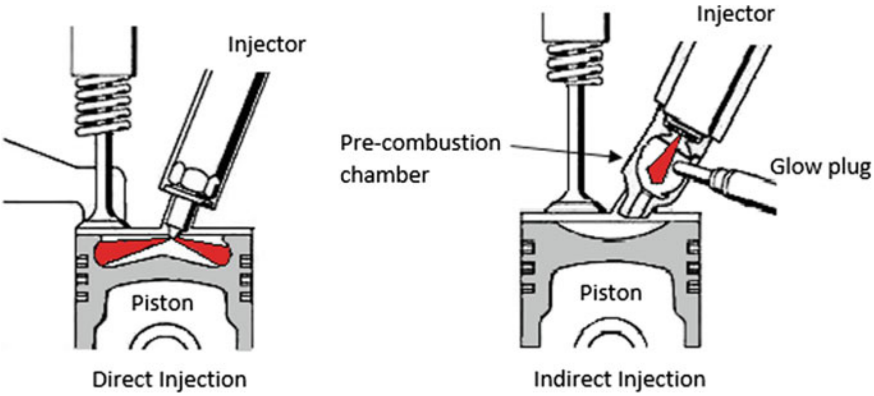

Fig. 16.3 Direct injection system and indirect injection system (Heywood 1988)

system, fuel is first injected into the precombustion chamber where fuel attains certain temperature and then injected into main cylinder (Fig. 16.3). In the indirect injection system, the flame front expands in precombustion chamber which pushes fuel in cylinder. Precombustion chamber or swirl combustion chamber results in better mixing and atomization. In the direct injection system, fuel is injected at higher pressure, which results in better mixing and atomization. In indirect injection system because of precombustion chamber, there is continuous combustion due to which higher speed of engine is obtained. Indirect injection (IDI) system has simple design and involves simple production process. IDI system uses small diesel engine and has less cost. IDI system causes lower stress on various parts of engine. While direct injection (DI) system has better fuel efficiency than IDI system because there is high pressure and less heat loss in DI. In IDI system, there is requirement of glow plug for cold starting problem, while there is no such requirement of glow plug in DI system. DI system is suitable for turbocharging, while IDI system is not suitable for turbocharging case because in IDI system pressure and heat release on small area of piston. There is more distortion and cracking in IDI system with increase in pressure and temperature. In IDI system, glow plug is not suitable for starting fuel. Because of these reasons, there is more detonation and wear in IDI engine. Overall, indirect injection system is old and complex technique, while direct injection system has shown lower emission and higher thermal efficiency (Heywood 1988).

Further, there are mainly three types of injection systems depending on fuel pressure generation and control: pneumatic injection system, mechanical injection system, and electronic injection system.

In pneumatic injection system, pressurized air is used to supply fuel in cylinder and metering of fuel is controlled by varying the pressure of air. Multistage compressor is used for creating high pressure air that controls closing and closing of valve according to injection timing with the help of cam shaft (Fig. 16.4). Air injection system is able to operate with high viscous fuel and provides better atomization. Its size becomes bulky because of the use of various linkages and multistage compressor, and hence, operating at high pressure becomes dangerous.

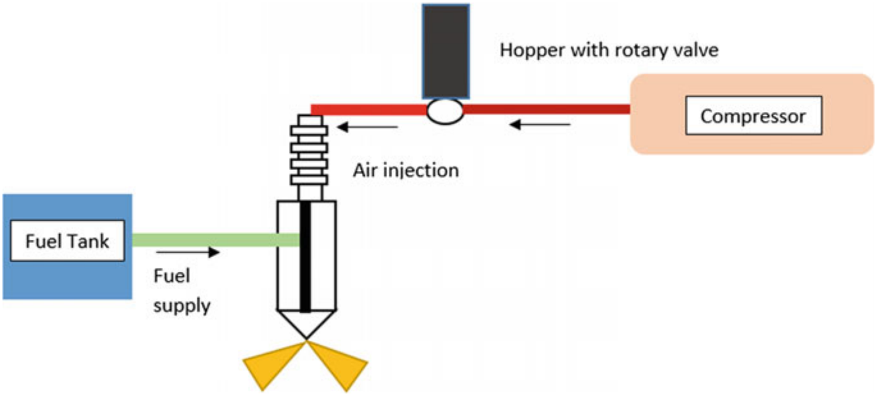

Fig. 16.4 High-pressure air-assisted injection system

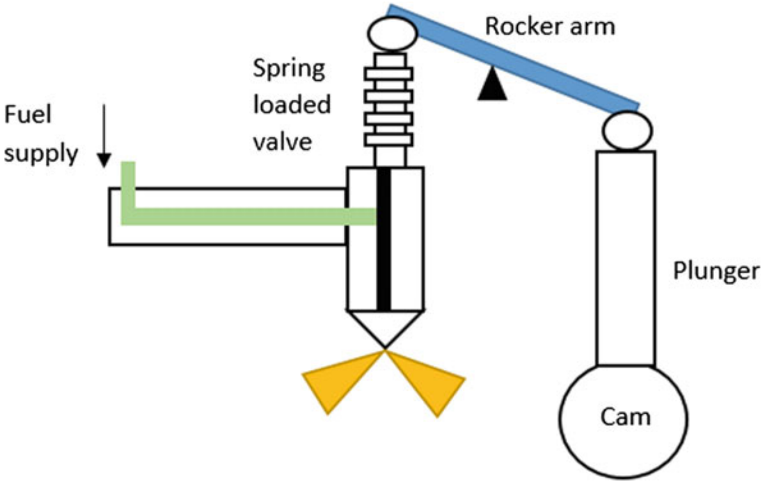

Fig. 16.5 Unit injection system

Here, the closing and opening of valves is actuated with air pressure, which is fairly a complicated process.

In mechanical injection systems (also known as solid injection system), high pressure air is not required for initial atomization. The fuel is directly pressurized and injected into the combustion chamber. Based on method of control of fuel injection parameters, solid injection systems are further classified in mechanical and electronic fuel injection systems. Unit injection system, common rail injection system, and individual injection system are main types of advanced fuel injection systems. Unit injection system is formed by combining pump and injector in same housing. Each cylinder contains separate unit fuel injection system. Pump supplies fuel to the injector. From injector to the cylinder, the fuel is supplied with the help of plunger, cam, and rocker arm (Fig. 16.5). Main parts of unit injection system are solenoid valve, pump, plunger, barrel, and nozzle.

In the unit injection system, injector and pump are combined in single housing, while in the individual injection system pump and injector are mounted separately. Pump is placed on the engine side, and injector is placed on the cylinder side. With the help of cam and plunger, pump supplies fuel at a high pressure that is able to open the intake valve.

In the common rail injection system, fuel is accumulated at a constant pressure in the accumulator with the help of pump. From accumulator (referred as common rail), fuel is supplied to the metering, timing elements, and injectors of different cylinders (Fig. 16.6).

Above advancements in fuel injection systems have resulted in big improvement in engine efficiency and considerable reduction in the particulate matter and other pollutants from the engine. Design of fuel injection equipment is also highly tuned with respect to the fuel (e.g., diesel) properties. Due to supply constraints and some

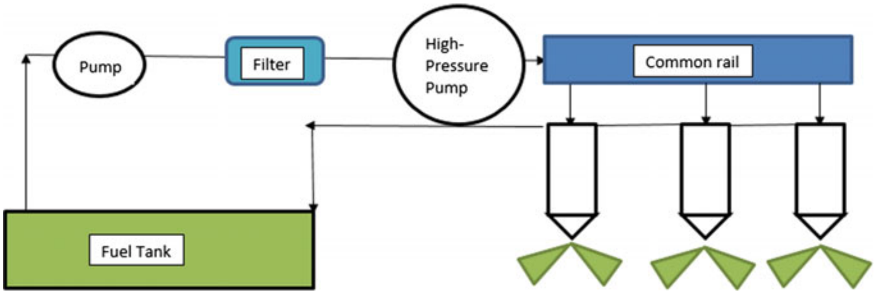

Fig. 16.6 Common rail injection system

other property advantages, efforts are also going on for large-scale implementation of various alternative transport fuels. US Department of Energy has stated that biodiesel, ethanol, hydrogen, natural gas, propane, and electricity as the futuristic alternative fuels and advanced vehicle technology fuels are alcohols, biodiesel, hydrogen, dimethyl ether, and natural gas (US Department of Energy 2017). In the next section of this chapter, important fuel-related properties and requirement of fuel injection system for ethanol, biodiesel, hydrogen, DME, and natural gas are discussed.

16.3 Fuel Properties and Fuel Injection System for Alternate Fuels

Important fuel properties of alternative fuels (ethanol, biodiesel, hydrogen, DME, natural gas) are compared with the diesel in Table 16.1. Hydrogen has the widest flammability limit; however, its auto-ignition temperature is high when compared with other discussed fuels. Minimum energy required to ignite hydrogen is very low. It also burns rapidly with very high flame velocity. DME has the lowest auto-ignition temperature among the discussed alternate fuels. But it has high minimum ignition energy. The cetane number value of DME is better than neat diesel; however, it has a lower viscosity which is a problem for the fuel injection system. Ethanol and biodiesel have comparable auto-ignition temperatures; on the other hand, the lower viscosity and lubricity of ethanol wear the injection equipment rapidly when compared to biodiesel. Natural gas has high heating values comparable to diesel. High auto-ignition temperature of natural gas makes it safer to use in engines.

Table 16.1 Properties of fuels

Property	Diesel	Biodiesel	Ethanol	Hydrogen	DME	Natural gas
Formula	C_8 to C_{25}	$RCOOCH_3$	C_2H_5OH	H_2	CH_3O CH_3	CH_4
Molecular weight (g/mol)	~96	250–300	46.06	2.02	46.07	16–19
Density (kg/m^3)	800–840	~870	789	0.08	2.11	0.7–0.9
Minimum ignition energy (mJ)	–	–	–	0.02	0.29	0.28–0.3
Flammability limit in air (% vol.)	0.6–7.5	–	3.3–19	4–75	3.4–18	5–15
Auto-ignition temperature (K)	410	705–840	636	858	508	853
Lower heating value (MJ/kg)	42.6	36.5	26.95	120	28.8	47.13
Higher heating value (MJ/kg)	45.56	40.2	29.84	142	31.67	52.21
Cetane number	40–55	47–65	5	–	55–60	–
Octane number	15–25	–	107	>130	–	~120
Viscosity @ 25 °C (cSt)	2–4	4–6	1.074	–	0.185	–
Vapor pressure @20 °C (kPa)	<1	<1	5.95	–	530	–
Boiling temperature @1 atm (°C)	150–380	315–330	78	−253	−24.825	−161.5

16.4 Ethanol

Ethanol (C_2H_5OH) is a renewable alternate fuel, which can be made from many natural materials like sugarcane, molasses, corn, barley, sorghum, biomass by using fermentation processes and various other technologies. Ethanol has been seen as a potential replacement for the diesel fuel due to its ability to reduce emissions in compression–ignition engines. The first introduction of ethanol in India as fuel in automobile engines goes back to 1930s when alcohol blends were used in Bangalore city buses (Murthy 2011). In 1970s, the oil crisis hit the world and Brazil government promoted the use of ethanol as a fuel for automobiles. Brazil was able to replace 14% of the countries' transportation fuel consumption by 2003 with ethanol (Fichera and Kueter 2006). USA is the top producer of ethanol fuel (Balat and Balat 2009). Presently, most car manufacturer's engines can be run on flexible fuels with 51–83% ethanol content in gasoline in USA and Brazil (Moriarty and Yanowitz 2015). Many other European and Asian countries have followed footsteps in the use of ethanol as a fuel for transportation.

Ethanol is an oxygenated fuel; hence, it has a great potential to reduce the emissions from diesel engines. This one property has pushed the use of ethanol in the automobiles. Ethanol has very low cetane number of 5–8 (Hansen et al. 2005) which leads to the reduction in the cetane number of diesel fuel blend. It has been reported that with every 10% volume addition of ethanol, the cetane number of resultant blend decreases by 7. Lubricity is an important property of the fuel as it plays a vital role in lubrication and retards wear in the system. Ethanol has lower viscosity and lubricity when compared to diesel. Addition of ethanol lowers the viscosity of the blended fuel. Ethanol also has low energy density due to which it lowers the energy density of the blend in the proportion of its content. The diesel ethanol blends also show reduction in surface tension with proportion to the amount of ethanol added. Stability of the blend depends on the two factors, temperature and water content of the blend. Blend is stable if blended with dry ethanol at warm ambient temperatures. Stability can be improved by addition of emulsifier and cosolvents. Due to the lower viscosity and lower boiling point as compared to diesel, the current fuel injection equipment can be used for the fuel delivery to the combustion chamber. Addition of 1% isopropanol to 10–15% ethanol diesel mixture prevents phase separation.

Fumigation is one method of injecting ethanol into the intake airstream for combustion and reducing the share of diesel (Chauhan et al. 2011). Some additional components required during fumigation of ethanol are carburetor, injector for injecting ethanol in manifold, separate fuel storage tank, and fuel line. The main advantage of fumigation is minimal modification of the engine, since only alcohol injector is to be placed in the air intake manifold. Since alcohol is not mixed with diesel directly, hence there is no problem of stability of the blend. Other added advantage is the switch ability between fuels. A minor modification is required on the intake manifold of the engine to allow the mounting of ethanol injector either at each intake port of the cylinder or in the common rail of the intake system (Abu-Qudais et al. 2000). Some researchers have also reported installation of injector in the pre-extension pipe of the air intake manifold to allow maximum interaction between air and ethanol for an even mixture for combustion with diesel. Use of injector at each port gives even supply of ethanol at each cylinder; however, the mixing time is low. In this case, it is expected that the ethanol will get the vaporization heat from the cooling jacket of the engine wall. The positioning of the injector should be such that ethanol is injected in the direction of the airflow (Shropshire and Goering 1982). In case of more than one injector, there is an additional requirement of distributor valve. Rotary vane pump is required for the even flow of ethanol to the engine and back. Figure 16.7 shows the schematic diagram of ethanol fumigation.

16.5 Biodiesel

Biodiesel is an alternate fuel which can be produced from vegetable oil, waste cooking oil, or animal fats. It is very similar to conventional diesel fuel. Although straight vegetable oils can be used as a substitute for conventional diesel, it has other problems like high viscosity, which causes chocking of fuel injectors and low

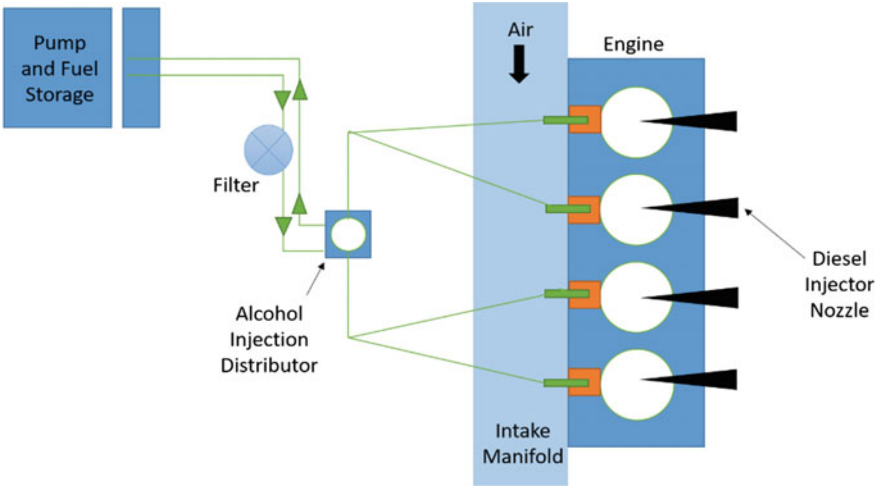

Fig. 16.7 Schematic diagram of the injection system for ethanol fumigation

atomization when sprayed. Hence, oils are converted to biodiesel by the process called transesterification in which the oils react with alcohols in the presence of catalyst and esters and glycerol is produced (Meher et al. 2006; Fukuda et al. 2001). This lowers the viscosity of oils and makes them easy to use in engines.

Biodiesels can be used unblended (B100) or can be blended with conventional diesel. Blended biodiesel is more common due to high pricing of B100 fuels (U.S. Department of Energy 2014). Also, B100 has a cleaning effect on fuel equipment and may cause clogging of fuel filters (Ge et al. 2009). The energy content in biodiesel is low when compared to conventional diesel. Hence, maximum car manufacturing companies allow blending till 20% (B20) (U.S. Department of Energy 2013). B20 and lower fuels can be used in the conventional diesel engines without any major modification in the fuel injection system. B20 fuels have same performance (fuel economy, torque) when compared to conventional diesel (Edwards et al. 2008). The advantage of B20 fuel is the reduction in greenhouse gas emissions by nearly 20% (U.S. Department of Energy 2014).

High levels of blended fuels may cause erosion of the gaskets and leakages (Ge et al. 2009). Hence, fuel storage and handling is an issue with high blended fuels. The fuel tank should be made from stainless steel or aluminum. Biodiesels have a rapid rate of degradation, and it is recommended that they should be consumed within 6 month of manufacturing. Biodiesels also have a problem of cold flow; hence, stabilizers and cold flow improvers are required. Cold temperatures lead to precipitation of wax and water present in biodiesels. Biodiesels can easily hold dissolved water, which may lead to the corrosion of fuel systems or microbial growth. Fuel filters need to be designed in such a way that they remove water from the fuel.

Biodiesels have high viscosity (about 25–30% higher than diesel). During injection of biodiesel and its blends, the droplet diameter is greater than the droplets produced by the conventional diesel (Chen et al. 2013). Larger droplet size leads to an incomplete or inefficient combustion. It was found that droplets at the periphery of the spray were larger in diameter than the droplets at the center. Study also found that B100 had the greatest penetration due to higher density of the fuel. Biodiesels also have a problem of injection delay due to high viscosity. It was noted that the higher viscosity leads to poor atomization and mixture penetration with air during the ignition delay period (Hwang et al. 2014).

Pertaining to the above-mentioned problems, blends up to B20 are recommended. Since most of the vehicles run on common rail injection where injection pressure is very high, using blends of biodiesel and diesel does not require any major modification in fuel injection equipment except for initial change of fuel filters.

16.6 Hydrogen

The first hydrogen internal combustion engine was built in 1807 by Issac de Rivas, but its application in internal combustion engines as a potential fuel has been studied recently (Gillingham 2007). Many researchers believe that hydrogen-based CI engines should be the ultimate goal of the automotive sector (Verhelst and Wallner 2009; Edwards et al. 2008; Sharma and Ghoshal 2015). As the hydrocarbon-based fuels cause many harmful emissions, hydrogen has the potential to replace them due to the need for enforcement of stringent EURO VI or Bharat Stage VI pollution norms. Hydrogen-fueled vehicles are seen as the ultimate solution to reduce exhaust emissions and energy crisis.

Hydrogen has a wide flammability limit of 4–75%. This helps in high fuel economy owing to its high flammability limit. It also has a high diffusivity, which is an advantage for uniform mixing. Hydrogen has a very high flame velocity of 1.85 m/s, high heating value (119.7 MJ/kg), and high heat of combustion (3.37 MJ/kg of air). All these factors suggest that the engine will be stable and controlled at dilute conditions, implying high fuel economy but low power output. But due to high auto-ignition temperature of 858 K, there is a requirement of the initiation of combustion, a spark. Although it has a high auto-ignition temperature, the energy requirement for the ignition is of the order of 0.2 mJ. This ensures burning of hydrogen at very lean mixtures. However, this leads also to the preignition of hydrogen (Natkin et al. 2003). This preignition leads to the advance start of combustion which eventually leads to high pressure rise rate, more acoustic emissions, and high in-cylinder surface temperatures which serve as further advance start of combustion, and leads to engine failure if left unchecked (White et al. 2006). Hence, there is a need to avoid preignition in the engine.

The peak power of hydrogen-based CI engines is determined by volumetric efficiency, fuel energy, and preignition (White et al. 2006). For the above three factors, the preignition is the limiting factor for peak power output. The use of port fuel injection for injecting hydrogen in the intake air channel leads to the loss in volumetric efficiency due to the replacement of air by hydrogen. However, the high power density of the hydrogen as a fuel compensates for some loss in volumetric efficiency.

The mode of fuel injection plays a pivotal role for the hydrogen-based engines. Hydrogen can be used as a secondary fuel in dual fuel engines with diesel being the primary fuel (Saravanan et al. 2008; Rao et al. 1983) or as the only fuel in the engine (e.g., HCCI) (Ibrahim and Ramesh 2014; Sharma and Dhar 2016). The former is the most popular, whereas the latter is not a convenient method due to high auto-ignition temperature of hydrogen where preheating or an external initiator is required (Saravanan et al. 2008). There are various strategies for the injection of hydrogen in CI engines (Das 2002). Carburetion leads to an uncontrolled combustion and preignition of hydrogen in the cylinder which is undesirable. Fumigation of hydrogen in the air manifold can be an effective way of inducing hydrogen in the cylinder, but it needs to be timed in such a way that injection occurs once the maximum air is inside the cylinder. This leads to cooling of the cylinder due to fresh air. Also, the hydrogen is injected just before the inlet valve closes, and hence, the preignition can be avoided. Direct cylinder injection is another strategy which is not very common due to the harsh conditions for hydrogen injector in the engine (Das 2002). However, it has some added advantage of elevated levels of shaft power from the engines, enhanced engine control, and no chances of air manifold backfire (Antunes et al. 2009). Hydrogen may cause embrittlement of the injection components due to its small size and high mass diffusivity. Along with this, the time allowed for mixing inside the chamber is less, thus leading to incomplete combustion. Port fuel injection (PFI) is a favored way of injection in the duel fuel engines. The PFI injects hydrogen in the intake manifold toward the end of air intake.

Hydrogen is highly inflammable gas. It also has a very low density. These factors add up to the safe and efficient storage of hydrogen. The modes of storage of hydrogen are as follows: compressed hydrogen gas, liquefied hydrogen gas, metal hydrides, and slush storage (Das 1996). Hydrogen is readily produced in gaseous state; hence, it may be feasible to store it in compressed gaseous form. It may be stored at a pressure of about 700 bars (type IV carbon composite tanks). It can also be stored in glass microspheres in gaseous form. In the cryogenic tanks as liquid hydrogen, it needs to be kept at 20 K which requires extremely insulated storage system. Rechargeable metal hydrides are more feasible way to store hydrogen for automotive application. Metal hydrides emit hydrogen gas when heated. FeT_iH_2, $LaN_{1.5}H_7$, MgH, Mg_2NiH_4 can be used for the storage of hydrogen.

Figure 16.8 shows a typical hydrogen fuel system. A non-return valve has to be installed at the storage tank so that under no circumstances does hydrogen go back out of the tank. Multiple safety valves are also required for enhanced safety. Since the density of hydrogen is very low, high-precision hydrogen regulators are also required to regulate its flow toward the engine.

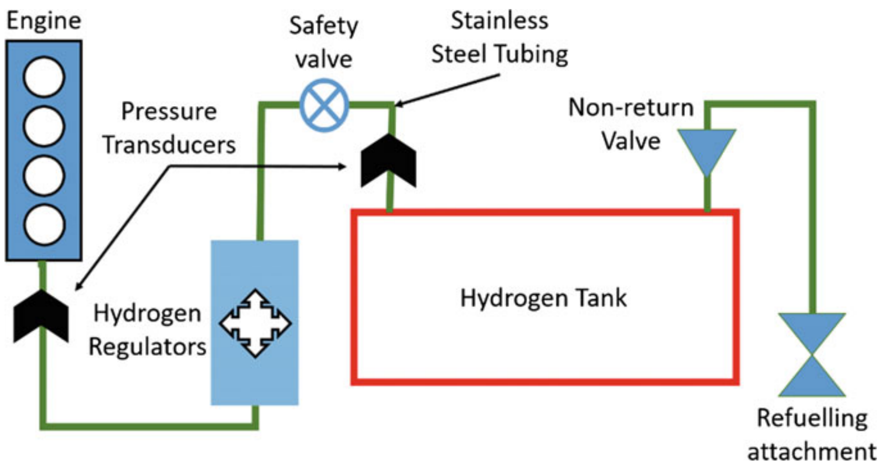

Fig. 16.8 Schematic of typical hydrogen fuel supply system

16.7 Dimethyl Ether

Dimethyl ether (DME; CH_3OCH_3) has shown a great potential as an alternative fuel for the use in compression ignition engine. DME is considered to be as one of the high efficiency compression ignition fuels, which is clean due to reduced NO_x, SO_x, and particulate matter (Semelsberger et al. 2006). The major promotion of DME as a substitute for diesel began in the 1990s. DME when compared with diesel on stationary engine showed that the basic specific fuel consumption for both to be almost same at same load conditions, but the advantage of DME comes with emissions where it produces only around 1/4th of HC, half of CO, 1/6th of NO_x, and no smoke as compared with diesel engine. The acoustic behavior of DME is also good when compared with diesel. Demonstrations of vehicles with DME as a fuel have been done in USA and some parts of Europe. Pennsylvania State University along with Volvo and Oak Ridge National Laboratory tested DME truck, which performed similar to diesel truck with comparable efficiency. The test also concluded that the exhaust emissions from DME could meet the standards without using diesel particulate filter (Szybist et al. 2014). There are various proposals of building low compression ratio DME engines with superior thermal efficiency, exhaust emissions, and engine noise. Lower CR may lead to lighter, less robust engines and hence cheaper engines. Hence, DME has a great potential for a clean alternate fuel to be used in CI engines.

The properties of DME are quite similar to liquefied petroleum gases. Table 16.1 shows some physical properties of DME. The major advantages of using DME as a fuel are its high oxygen content, low boiling point, high cetane number, and clean emissions. However, when it comes to the fuel injection, it has a disadvantage due to the low viscosity and lubricity. Low viscosity leads to an accelerated wear in the fuel injection equipment. It also has low modulus of elasticity, which increases the compression work of the fuel pump. DME has a very low penetration depth due to smaller droplet diameter and high rate of evaporation. It could work on a conventional diesel engine with improvements relating to fuel injection equipment and installation of a storage tank. DME has a high vapor pressure (nearly of the order of LPG). This high vapor pressure leads to major issue: cavitation in the fuel injection system. Due to the cavitation problem, fuel injection systems' operations are tampered. It has been suggested that when DME is pressurized to 0.5 MPa in storage, the fuel supply pressure must be kept between 1.2 and 3 MPa to restrict cavitation (Edgar et al. 1997; Arcoumanis et al. 2008). DME also has a lower lubricity when compared with diesel which leads to enhanced wear in the components. Accelerated wear is highly undesirable for a stable fuel injection equipment operation. Various additives need to be added to enhance the lubricity. DME when blended with Ethyl H4140 (1000–5000 ppm), soybean oil, Ethyl H580, Lubrizol 539 N, and diesel has shown an enhancement in lubricity (Arcoumanis et al. 2008; Bhide et al. 2003). Due to the low boiling point, DME vaporizes suddenly during injection. Hence, DME can be injected at a low pressure in the order of 20–35 MPa (Tsuchiya and Sato 2006). Due to the low calorific value (28.1 MJ/kg; diesel—43 MJ/kg) and low density, a higher amount of DME is required to be injected into the cylinder to produce similar engine output. Hence, fuel injection system to have longer injection duration (Arcoumanis et al. 2008) is needed. DME requires to be pressurized in a closed system due to its low boiling point. DME is stored in liquid state at a pressure of 0.5 MPa. Under the standard temperature conditions, it exists as a gas, and hence, there is a requirement of a closed system to store it as a liquefied gas (Sorenson 2001). DME, being a less viscous fuel, has leakage problems. DME can even leak through small tolerances. Moreover, DME can chemically react with fuel injection system components. Improved sealants, sealing materials, special elastomers, and PTFE are required for sealing fuel line and systems (Yu et al. 2002).

DME injection has many other challenges. DME has low modulus of elasticity. This has a direct effect on needle lift profile of the injector. Due to higher compressibility, the stage where nozzle opens is slower for DME (Egnell 2001). Also, due to high compressibility, there is a loss of pressure while injection, which leads to lower spray velocity. Also, there are pressure fluctuations in the injection line due to the compressibility of DME. One can see ripples in the fuel pressure line trace due to this phenomenon. This leads to the residual pressure in the line. Hence, there is a need for the improvement of fuel injection equipment for DME-fueled CI engines.

Fuel injection methods using DME as fuel can be developed using two methods: (1) modification of the conventional fuel injection systems or (2) common rail injection systems (Arcoumanis et al. 2008). Modification of existing systems can be done for light-duty vehicles; however, there are still many uncertainties pertaining to its operation. Major focus is on the common rail system development for deployment on the vehicles for DME-fueled engines. Common rail injection unit specifically built for DME fuel is the best option. It has been reported that DME

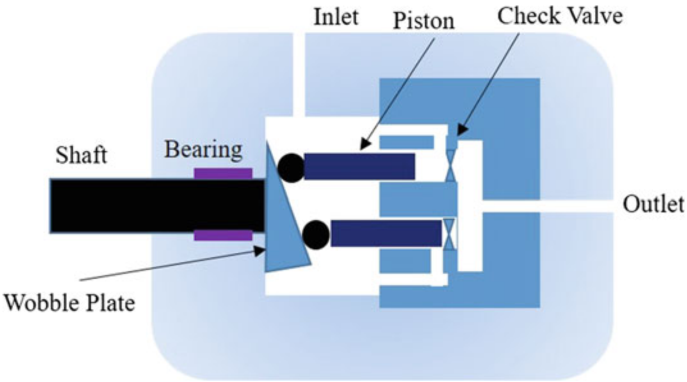

Fig. 16.9 Schematic diagram of wobble plate-type fuel pump

when injected by the common rail system at high pressure has smaller droplet diameter than diesel at the same pressure (Kajitani et al. 2000). Low-pressure common rail systems for DME injection have been proposed since it can be injected at low pressure when compared to diesel. Other than these two methods, modifications have been proposed for the fuel pumps. Wobble plate-type fuel pump has also been developed for the stable supply of DME fuel, which comes with additional benefits like enhanced durability, easy manufacturing, and high pressure capabilities (Suh 2015). Figure 16.9 shows the schematic diagram of wobble plate-type fuel pump. All the pistons of the pump are actuated by single wobble plate instead of separate cam shafts. The fuel is discharged by the virtue of reciprocating movement of the pistons. Major advantages of this fuel pump are high pressure capability and durability. Injection strategies of DME with pilot and split injections are important to study the spray atomization, reduction of exhaust emissions, and effect on *Sauter mean* diameter. Multiple injections lead to poor atomization due to its influence on spray density at each measuring point but controlled the NO_x emissions as compared to single injection (Godavarthi 2015). Other than this, a liquid DME fuel tank needs to be designed for the storage. Tank can be made from steel, which is cheaper than stainless steel or carbon graphite used for LNG and CNG, with Isolast and EPDM as sealing materials (Szybist et al. 2014).

16.8 Natural Gas

Natural gas is mainly composed of methane (CH_4, up to 98%) with other components like ethane (C_2H_6, 0.6%), propane (C_3H_8, 0.2%), butane (C_4H_{10}, 0.2%), pentane (C_5H_{12}, 0.1%), nitrogen (N_2, 0.8%), and carbon dioxide (CO_2, 0.1%) (Papagiannakis and Hountalas 2004). Combustion of natural gas produces low level of CO_2 emissions due to single carbon molecule in CH_4. It is also known to reduce particulate matter, nitrogen oxides, and CO emissions. The auto-ignition temperature of natural gas is higher than that of gasoline, and hence, natural gas is considered as comparatively safe fuel. Natural gas has a high octane number, and engine efficiency can be increased by high compression ratio. Natural gas has a low flame velocity. This results in prolonged combustion and reduced engine efficiency.

Natural gas is a cleaner alternate fuel and is expected worldwide (Unich et al. 1993). Presently, there are 23 million natural gas vehicles (NGVs) and nearly 29,000 refueling stations in the world (NGV Global 2017). There is a prediction of over 30 million NGVs worldwide by 2024 (NGV Global 2017). The reason for the popularity of NGVs is the cleaner emissions as compared to other fossil fuels (Weaver 1989). Any conventional vehicle can be easily converted to NGV by addition of new head with spark plug or by using dual fuel mode with diesel. Gasoline vehicles can be retrofitted with fuel change over switching where a driver has a flexibility to choose the desired fuel for operation. Commercial conversion kits are available in the market for both gasoline and diesel engines.

CNG can be used as a single fuel with spark plug or as a dual fuel with diesel as initiator in CI engines. Old injection strategies used mechanical carburetion of natural gas for combustion, but it sometimes led to unwanted *A*/*F* ratio. Electronically controlled direct in-cylinder fuel injection is also being attempted. But there also some difficulties are encountered due to compressibility and low density of natural gas. The normal plunger-type pump which simultaneously pressurizes and meters liquid fuel cannot be used due to the compressibility of fuel. Literature states that fuel pressurization and metering must be done individually (Chehroudi 1993). The amount of fuel to be injected depends on the orifice area and valve opening. Direct injection of CNG maintains the efficiency of diesel engine with a huge 40% decrease in NO_x and reduction in particulate matter (Harrington et al. 2002). Figure 16.10 shows the schematic diagram of DI CNG in CI engine (Harrington et al. 2002). CO_2 content is also lowered by around 20% by DI of CNG in the CI engines (Chiodi et al. 2006). The efficiency of DI CNG engine is high owing to the throttle-less operation (Harrington et al. 2002). Fumigation is the most common method for using natural gas in CI engines (Chehroudi 1993; Nwafor 2007). Natural gas is injected in the air manifold, and diesel is used to initiate combustion inside the engine. Engine idles on diesel fuel and natural gas is injected as the load on engine increases. Preheated air is mixed with natural gas in gas mixer to avoid the ignition delay and increases flame velocity as compared to cold air.

Natural gas requires robust storage system. Natural gas can be stored as compressed natural gas (CNG) and liquefied natural gas (LNG). CNG requires a robust storage tank that can sustain a pressure of around 25 MPa. This adds up to the cost and weight of the storage tank. LNG requires a highly insulated storage tank that can maintain the temperature below −160 °C. CNG is the more popular in transport sector with LNG mainly used in large trucks, high torque applications, and marine engines.

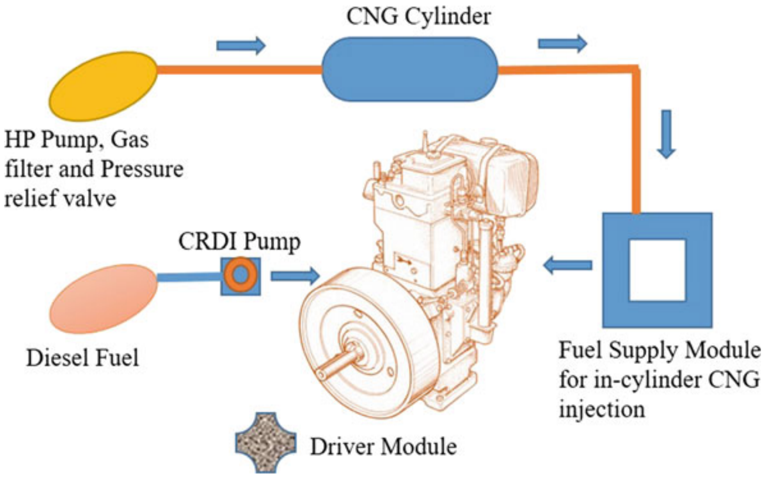

Fig. 16.10 Schematic diagram of DI CNG in CI engine

16.9 Summary

With the maximum dependency of transportation sector on diesel and petrol, there is a need to develop technologies to implement alternate fuels due to depleting fuel reserves. Exhaust emissions are also a major concern, and there is a need to shift to alternate less polluting fuels. Fuel injection equipment's development is essential as different fuels have different properties, and there is a need to develop compatible injection system based on fuels properties. There are already many existing injection systems for CI engines: direct and indirect injection, high-pressure air-assisted injection system, unit injection system, common rail injection system, etc., which have been discussed in the chapter. Common rail injection system is the most commonly used injection system in diesel vehicles. Injection system requires a very precise control on fuel injection timing and amount of injected fuel, which further requires tuning of the finest level. With different fuels, this precise control is the major concern owing to fuel properties. Ethanol, biodiesel, hydrogen, DME, and natural gas have been discussed as alternate fuels for engine operation. The fuel injection equipments for these fuels are discussed. Ethanol can be either blended with diesel or can be fumigated. Fumigation requires minimum engine modifications, whereas ethanol–diesel blends have blend stability issues. Biodiesel has high viscosity and can be used with existing fuel injection equipment for diesel, but fuel filters need to be changed due to the cleaning effect of biodiesel. Hydrogen's injection is through port fuel injector in the intake manifold, while diesel acting as pilot fuel for combustion is suitable for hydrogen addition in CI engines. DME has low lubricity which accelerates wear in the fuel injection equipment. Low-pressure common rail injection specifically built for DME is the best-known method for injection of DME in CI engine. Injection of natural gas can be in-cylinder, electronically controlled, due to the high efficiency of throttle-less operation. In a nutshell, the transfer from conventional fuels to alternate fuel is challenging. Apart from the fuel injection equipment, many hurdles like availability, refueling stations, cost still stand in the way of broad term implementation. But sooner or later, there will be need and strong push for such fuels for cleaner emissions.

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