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Alternative Fuels and Their Utilization Strategies in Internal Combustion Engines

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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 energy availability because it touches every facet of human life and activities. Transportation and power generation are two major examples. Without 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 International Society for Energy, Environment, and Sustainability (ISEES) was founded at Indian Institute of Technology Kanpur (IIT Kanpur), India, in January 2014 with an aim to spread knowledge/awareness and catalyze research activities 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 create awareness about the environmental challenges, which the world is facing today. The unique way adopted by the society was to break the conventional silos of specializations (engineering, science, environment, agriculture, biotechnology, materials, fuels, etc.) to tackle the problems related to energy, environment, and sustainability in a holistic manner. This is quite evident by the participation of experts from all fields to resolve these issues. The ISEES is involved in various activities such as conducting workshops, seminars, and conferences. in the domains of its interests. 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.

Third International Conference on "Sustainable Energy and Environmental Challenges" (III-SEEC) was organized under the auspices of ISEES from December 18–21, 2018, at Indian Institute of Technology Roorkee. This conference provided a platform for discussions between eminent scientists and engineers from various countries including India, USA, Norway, Finland, Sweden, Malaysia, Austria, Hong Kong, Bangladesh 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 resource for sustainable development and cleaner environment. The conference presented five high-voltage plenary talks

from globally renowned experts on topical themes, namely "The Evolution of Laser Ignition Over more than Four Decades" by Prof. Ernst Wintner, Technical University of Vienna, Austria; "Transition to Low Carbon Energy Mix for India", Dr. Bharat Bhargava, ONGC Energy Center; "Energy Future of India", By Dr. Vijay Kumar Saraswat, Honorable Member (S&T) NITI Aayog, Government of India; "Air Quality Monitoring and Assessment in India" by Dr. Gurfan Beig, Safar and "Managing Large Technical Institutions and Assessment Criterion for Talent Recruitment and Retention" by Prof. Ajit Chaturvedi, Director, IIT Roorkee.

The conference included 24 technical sessions on topics related to energy and environmental sustainability including five plenary talks, 27 keynote talks, and 15 invited talks from prominent scientists, in addition to 84 contributed talks and 50 poster presentations by students and researchers. The technical sessions in the conference included advances in IC engines, solar energy, environmental biotechnology, combustion, environmental sustainability, coal and biomass combustion/gasification, air and water pollution, biomass to fuels/chemicals, combustion/gas turbines/fluid flow/sprays, energy and environmental sustainability, atomization and sprays, sustainable transportation and environmental issues, new concepts in energy conservation, waste to wealth. One of the highlights of the conference was the Rapid Fire Poster Sessions in (i) engine/fuels/emissions, (ii) renewable and sustainable energy, and (iii) biotechnology, where 50 students participated with great enthusiasm and won many prizes in a fiercely competitive environment. Two hundred plus participants and speakers attended this four days conference, which also hosted Dr. Vijay Kumar Saraswat, Honorable Member (S&T) NITI Aayog, Government of India, as the chief guest for the book release ceremony, where 14 ISEES books published by Springer, Singapore, under a special dedicated series "Energy, environment and sustainability" were released. This was the second time in a row that such significant and high-quality outcome has been achieved by any society in India. The conference concluded with a panel discussion on "Challenges, Opportunities and Directions for National Energy Security," where the panelists were Prof. Ernst Wintner, Technical University of Vienna; Prof. Vinod Garg, Central University of Punjab, Bhatinda; Prof. Avinash Kumar Agarwal, IIT Kanpur; and Dr. Michael Sauer, Boku University for Natural resources, Austria. The panel discussion was moderated by Prof. Ashok Pandey, Chairman, ISEES. This conference laid out the roadmap for technology development, opportunities and challenges in energy, environment and sustainability domain. All these topics are very relevant for the country and the world in the present context. We acknowledge the support received from various funding agencies and organizations for the successful conduct of the Third ISEES Conference III-SEEC, where these books germinated. We would, therefore, like to acknowledge NIT Srinagar, Uttarakhand (TEQIP) (Special thanks to Prof. S. Soni, Director, NIT, UK), SERB, Government of India (Special thanks to Dr. Rajeev Sharma, Secretary); UP Bioenergy Development Board, Lucknow (Special thanks to Sh. P. S. Ojha), CSIR, and our publishing partner Springer (Special thanks to Swati Meherishi).

The editors would like to express their sincere gratitude to large number of authors from all over the world for submitting their high-quality work in a timely manner and revising it appropriately at a short notice. We would like to express

our special thanks to Dr. Atul Dhar, Dr. Pravesh Chandra Shukla, Dr. Nikhil Sharma, Prof. V. S. Moholkar, Dr. Vikram Kumar, Dr. Dev Prakash Satsangi, and Prof. V. Ganesan, who reviewed various chapters of this monograph and provided their valuable suggestions to improve the manuscripts.

Currently, IC engines are facing many challenges related to fuel supply, energy efficiency, and emissions, which require serious research efforts. This monograph is based on the production and utilization aspects of different liquid and gaseous alternative fuels. In the last few years, methanol and DME have gained significant attention of energy sector because these fuels can be easily utilized in all kinds of engines with very less modifications. Few sections related to alcohols especially methanol are an important aspect of this book. We hope that the book would be of great interest to the professionals, postgraduate students involved in fuels, IC engines, engine instrumentation, and environmental research.

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Varanasi, India   Yogesh C. Sharma
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Dr. Akhilendra Pratap Singh is working at IIT Kanpur. He received his Masters and PhD in Mechanical Engineering from Indian Institute of Technology Kanpur, India in 2010 and 2016, respectively. His areas of research include advanced low-temperature combustion; optical diagnostics with special reference to engine endoscopy and PIV; combustion diagnostics; engine emissions measurement; particulate characterization and their control; and alternative fuels. He has edited seven books and authored 21 chapters, 40 research articles in international journals and conferences. He has been awarded with "ISEES Best Ph.D. Thesis Award (2017)," "SERB Indo-US Postdoctoral Fellowship," (2017) and "IEI Young Engineer Award" (2017). He is a member of numerous professional societies, including SAE, ASME, and ISEES.

Prof. Yogesh C. Sharma is a full Professor in Department of Chemistry, Indian Institute of Technology (BHU) Varanasi, India. He is Fellow of the Royal Society of Chemistry (FRSC), UK, and a Fellow (Elected) of the Biotech. Research Society of India (FBRS). His areas of interest include adsorption and diffusion, water remediation, renewable energy, biodiesel production, and synthesis of heterogeneous catalysts for biodiesel production. He authored four books and published more than 150 research papers in reputed international journals.He is a highly cited research author and has ~ 8000 citations with h-index of 41.

Dr. Nirendra N. Mustafi received his PhD on particulate emissions from a dual fuel engine operated on alternative gaseous fuels (NG and biogas) from The University of Auckland, New Zealand in 2008. Then, he joined back to the department of mechanical engineering at Rajshahi University of Engineering & Technology (RUET), Bangladesh. He was appointed Professor at RUET in 2013, where he teached different courses of mechanical engineering such as heat transfer, thermodynamics and applied thermodynamics, internal combustion engines, automobile engineering, and renewable energy. He also served as the Head of mechanical engineering department, Dean of faculty of mechanical engineering, and Director of Institute of Energy and Environmental studies at RUET. His research experiences and interests lie on engine particulate matter emissions measurement and characterization, dual fuel engines, alternative fuels for IC engines, simulation analysis of SI engine performance and emissions, sustainable and renewable energy engineering energy conversions, and waste-to-energy. Currently, he is staying at Indian Institute of Technology, Kanpur, India, as a visiting Fellow in mechanical engineering. He has authored and co-authored more than 30 papers in journals and conferences.

Prof. Avinash Kumar Agarwal joined IIT Kanpur in 2001. He worked at the Engine Research Center, UW@Madison, the USA, as a PostDoctoral Fellow (1999 – 2001). His interests are IC engines, combustion, alternate and conventional fuels, lubricating oil tribology, optical diagnostics, laser ignition, HCCI, emissions and particulate control, and large bore engines. He has published 270+ peer-reviewed international journal and conference papers, 35 edited books, 63 books chapters and has 7850+ Scopus and 11900+ Google Scholar Citations. He is an associate editor of ASME Journal of Energy Resources Technology. He has edited "Handbook of Combustion" (five Volumes; 3168 pages), published by Wiley VCH, Germany. He is a Fellow of SAE (2012), Fellow of ASME (2013), Fellow of NASI (2018), Fellow of Royal Society of Chemistry (2018), Fellow of ISEES (2015), and a Fellow of INAE (2015). He is a recipient of several prestigious awards such as Clarivate Analytics India Citation Award-2017 in Engineering and Technology; NASI-Reliance Industries Platinum Jubilee Award-2012; INAE Silver Jubilee Young Engineer Award-2012; Dr. C. V. Raman Young Teachers Award: 2011; SAE Ralph R. Teetor Educational Award -2008; INSA Young Scientist Award-2007; UICT Young Scientist Award-2007; INAE Young Engineer Award-2005. He received Prestigious Shanti Swarup Bhatnagar Award-2016 in Engineering Sciences.

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Part I
General

Chapter 1
Introduction to Alternative Fuels and Their Utilization Strategies in Internal Combustion Engines

Akhilendra Pratap Singh, Nirendra N. Mustafi, Yogesh C. Sharma and Avinash Kumar Agarwal

Abstract Increasing global demand of fossil fuel and harmful pollutant emitted by petroleum-fuelled internal combustion (IC) engines are two major concern for Indian transport sector, which require an immediate action to explore the alternative fuels such as biofuels, biodiesel, alcohols, etc. This book is based on such alternative fuels and covers different aspects of alternative fuels such as production and utilization. This book is divided into four sections. First section is based on introduction of alternative fuels and their utilization strategies in different type of IC engines. Second section deals with biofuel production from different sources such as agricultural waste, organic waste, microalgae, etc. Third section of this book is based on utilization of alternative fuels in engines. This section shows the potential of different alcohols and ethers to be utilized in engines. Last section of this book is based on advance topics related to alternative fuels. Overall, this book presents an overall picture of alternative fuels and shows the potential of alternative fuels for sustainable transport sector.

Keywords Alternative fuels · Alcohols · Biofuels · Methanol · Electrical vehicle · Emissions

Internal combustion (IC) engines are the essential part of our life because they contribute in various sectors such as transport, power generation, construction, agriculture, etc. However, availability of petroleum based fuels and harmful exhaust emissions are two major issues involved with IC engine, which need to be resolved. In last few decades, IC engines are considered as the main source of air pollution.

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Therefore, researchers have explored many solution to resolve this problem in which utilization of alternative fuels is the important one. Use of alternative fuels in transportation sector can solve both issues namely energy availability and air pollution simultaneously. This book is based on different alternative fuels and discusses various aspects of alternative fuels such as production and utilization. First section of this book introduces different alternative fuels and their potential to reduce the dependency on fossil fuels as well as reduction in pollutant emission.

Second section of the book is mainly based on biofuel production from different sources. First chapter of this section describes the production of 2nd generation ethanol from agricultural residues, which are accessible, abundance and comparatively inexpensive biomass. Different challenges and limitations such as biomass transportation and handling, effective pre-treatment methods, high costs based on current technologies are comprehensively discussed in the chapter. Second chapter is based on production of alcohols and esters from different renewable resources. This chapter is focussed on conversion of biomass into liquid and solid fuels via thermal, light-induced, catalytic and bio-based techniques. This process is a sustainable solution because this process delivers the useful product recycling of waste materials. These products can be used as fuel as well as in various other applications such as precursors, reagents, solvents or additives in perfumes, essential oils, food flavourings, cosmetics, etc. This present chapter reviews various green methods reported for the production of alcohols and esters from renewable energy sources. Third chapter of this section is based on bioethanol production from rice paddy straw. Rice paddy straw is an attractive lignocellulose material for bioethanol production since it has several features such as elevated content of cellulose and hemicellulose, which can readily be hydrolysed into fermentable sugars. This chapter also presents the challenges involved in this process in which pre-treatment (physical or chemical pre-treatment) and fermentation are important ones. Fourth chapter of this section deals with different ways in which biofuels can be produced using agricultural waste thereby making entire process cost effective and economical. Last chapter of this section is based on fuel production from microalgae, which is a potential source of several other value added products. This chapter provides an overview of microalgae based bio-refinery concept aimed at economical and efficient product formation. The integrated approach of different processes such as CO_2 sequestration, waste water treatment and biomass accumulation of microalgae result in fuel production and pollution reduction.

Third section of this book is focussed on utilization aspects of alternative fuels in IC engines. First chapter of this section discusses about the methanol economy versus electric vehicles, which is a burning topic for transportation sector. Electric vehicles (EVs) are considered as a clean and economical option for transport sector, however, there are several issues related to the availability of resources to produce battery for electric vehicles, including surplus electricity and batteries. In such conditions, methanol seems to be a better option for transportation sector in India because India has plenty amount of resources by which methanol can be produced economically. Methanol-powered vehicles have higher power density, the comparable cost

to benefit ratio, cleaner emissions from its production to its burning vis-à-vis to battery equipped vehicles which would help India to change its economic status from developing country to developed country. This chapter discusses the possible strategies to utilize methanol in existing engines. Second chapter is also based on alcohol utilization in IC engines. This chapter presents the advantages of alcohol utilization in IC engines and shows the path forward for alcohol in transportation sector. Next chapter is based on the unregulated pollutants emitted from engines fuelled with oxygenated fuels. This chapter discusses about the importance of fuel-bound oxygen in combustion process, which improves the combustion and reduces the formation of intermediate species. Next chapter of this section presents the influence of oxygenate additive diethyl ether (DEE) on entropy generation, exergy performance coefficient, emission, and performance characteristics of direct-injection (DI) diesel engine fuelled with WCO (waste cooking oil) biodiesel. Results showed that addition of DEE enhances the engine performance from the energy and exergy point of view. Last chapter of this section discusses about the engine experiments, which were performed in a DI diesel engine with an ignition improver (DEE) by fumigation technique. This chapter showed addition of DEE resulted in slightly lower brake specific nitric oxide (BSNO) and smoke emissions however brake specific carbon monoxide (BSCO) and brake specific hydrocarbon (BSHC) emissions were found to be slightly higher.

Fourth section of this book discusses about different alternative and gaseous fuels, which can be utilized in IC engines. First chapter of this section is based on natural gas (NG), which is considered as one of the most influential alternative fuels for transport sector. This chapter presents the advantages of NG-fuelled vehicles in which low photochemical reactivity, zero evaporative emissions, minimized cold-start and low-temperature emissions, and suitability for lean-burn operations are important. This chapter reviews the state-of-the-art in NG-fuelled vehicles and presents typical combustion and emission characteristics of NG-fuelled vehicles. This chapter also covers the recent progress in the area of hydrogen and CNG (HCNG) blends-fuelled engines, which is an innovative part of this chapter. This chapter was ended with the discussion on challenges and future R&D required for CNG fuelled vehicles. Second chapter of this section is based on biogas as a sustainable alternative fuel option, which can be produced from waste materials such as agricultural wastes, municipal solid wastes, food wastes and vegetable market waste, in addition to human and animal excreta. This chapter explores the state-of-the-art technologies associated with the biogas generation, biogas upgradation, storage, and utilization. Inclusion of several case studies on assessing performance of biogas fuelled vehicles make this chapter very relevant for this book. Next chapter of this section is a review of the current state of knowledge regarding CO_2 and shale interactions and their potential impacts on shale properties and groundwater quality in the context of CO_2 enhanced shale gas recovery. The chapter first introduced the characterization of shale and CO_2 followed by the major interaction mechanisms between CO_2 and shale. This chapter is ended with the list of remaining question and path forward in this direction. Next chapter of this section is based on bio-GTL technique, which is a potential technique to utilize the enormous amount gas. This chapter proposes the biological route for

methane-to-methanol conversion, which can be operated at ambient temperature and pressure conditions. Last chapter of this section is based on the biodesulphurization (BDS) because conventional hydrodesulphurization (HDS) process suffers from various disadvantages such as severe and hazardous operation conditions, inefficiency, high capital and operating costs, generation of the hazardous H_2S end product etc. Biodesulphurization (BDS) is one of these emerging nonconventional technologies that can be merged with other desulphurization technologies to produce S-free fuels. This chapter reviews research findings of utilization of mesophilic, thermophilic and Gram-negative bacteria for desulphurization of gasoline, jet and diesel, which are the most used transportation fuels.

Overall, this monograph presents the production and utilization aspects of alternative fuel, which can reduce the rate of petroleum consumption and lower the exhaust emissions. Specific topics covered in the monograph include:

- Introduction of Alternative Fuels and their Utilization Strategies
- Agricultural Waste Derived 2nd Generation Ethanol Blended Diesel Fuel in India: A Prospective
- Production of Alcohols and Esters from Renewable Energy Resources: A Promising Green Energy Carrier for Clean and Sustainable Development
- Second Generation Bioethanol Production from Organic Waste
- Biofuel Production from Agricultural Waste—An Economical Approach
- Sustainable Production of Green Fuels and Chemicals using Microalgae as Feedstock
- Methanol Economy versus Electrical Vehicle Economy—Indian Context
- Alcohols as Fuels in Compression Ignition Engines
- A Comprehensive Review on Oxygenated Fuel Additive Options for Unregulated Emission Reduction from Diesel Engines
- Influence of DEE on Entropy Generation and Emission Characteristics of DI Diesel engine Fuelled with WCO Biodiesel
- Bioethanol Operation in a DI Diesel Engine with DEE Fumigation
- Review of Combustion, Exhaust Emissions and Controls of Natural Gas (NG) Fueled Vehicles in the Transportation Sector
- Biogas as a Transportation Fuel—Current Status and Future Perspectives
- A Review of Coupled Geo-Chemo-Mechanical Impacts of CO_2-Shale Interaction on CO_2 Enhanced Shale Gas Recovery
- Bio-GTL: Recent Advances of the Potential Technique
- Microbial Desulphurization of Refractory Organic Sulphur Compounds from Transportation Fuels.

The topics are organized in four different sections: (i) General, (ii) Biofuel Production, (iii) Biofuels for Engine Applications, and (iv) Advancements in Alternative Fuels.

Part II
Biofuel Production

Chapter 2
Agricultural Waste Derived 2nd Generation Ethanol Blended Diesel Fuel in India: A Perspective

Rabinder Singh Bharj, Gurkamal Nain Singh and Rajan Kumar

Abstract The Ministry of New and Renewable Energy announced the National Biofuels Policy in 2009 to promote biofuels in India, and the Union Cabinet approved the National Biofuels Policy–2018 to succeed the existing policy from 2009. Biofuels have attracted worldwide attention over the past decade and it is imperative that biofuels be noticed to accelerate developments. It is noticed that the conversion of agricultural waste into 2nd generation ethanol has opened the door to unused resources and has promoted environmental sustainability. The 2nd generation ethanol, made from agricultural residues, offers significant prospective due to the extensive accessibility, abundance and comparatively inexpensive biomass. The use of agricultural waste to produce 2nd generation ethanol is proving to be a substitute source of energy for a narrow range of nonrenewable energy and food crops. Although this process has many challenges and limitations which are discussed in the chapter e.g. biomass transportation and handling, effective pretreatment methods, high costs based on current technologies that enable high efficiency and high process costs. The use of ethanol blended with diesel fuel has recently attracted the attention of many researchers. The usage of 2nd generation ethanol blended in diesel fuels will develop the agricultural commodity markets and create additional returns from 2nd generation ethanol derived from crop residues. The announcement by the Government of India on stringent emission regulations and the increased use of biofuels may lead to the use of 2nd generation ethanol blended with diesel fuel as a marketable fuel. This chapter highlights agricultural waste, its sources and various practices that include the processes undergone to produce 2nd generation ethanol economically, it also provides insight and suggests a renewable alternative fuel for diesel engines which will help in meeting the stringent emission standards.

Keywords Air pollution · 2nd generation ethanol · Diesel engines · Emission norms

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2.1 Introduction

The 21st century is seeking a shift towards alternating industrial feedstock from renewable biomass resources and recent strategies for energy and climate change encourage renewable energy such as bioenergy to be developed and used. Biomass obtained from unused resources i.e. municipal waste, agricultural and forest waste, whereas biomass from crops i.e. grasses, wood, plants, and aquatic plants, is a multipurpose and vital renewable feedstock for various industries as shown in Fig. 2.1 (Naik et al. 2010). Biomass is a composite material consisting of organic elements containing oxygen (lignin, cellulose, hemicellulose, and organic minerals) and inorganic minerals.

Over the years, biofuels have been keenly explored, produced and used in solid, liquid and gaseous forms. Biofuels produced from renewable resources could help minimize the burning of fossil fuel and the production of CO_2. Biofuels prepared from biomass such as crops or organic waste could help to decrease oil dependence and CO_2 production worldwide. Biomass-produced biofuels and bio-products would lessen global warming. In addition, the development of biofuels and bio-products can offer new possibilities for revenue and jobs in rural regions.

2.1.1 History

A time ago, biofuel was a primary fuel. Biofuels and bioenergy are as ancient as civilization. Since the discovery of fire, solid biofuels such as wood, dung, and
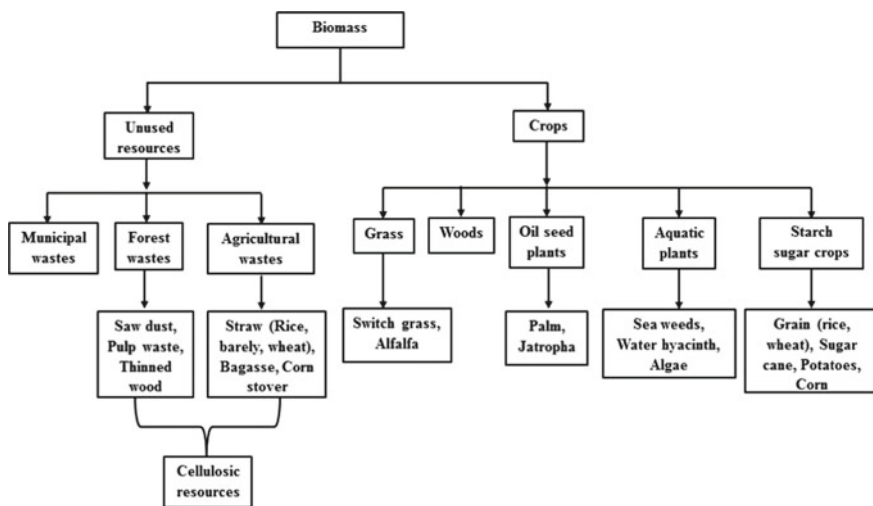
Fig. 2.1 Biomass: as a renewable feedstocks

charcoal have been used and are still used in numerous communities of emerging nations for cooking and heating. At least since the early ancient times, even liquid biofuels such as whale oil and olive oil were used. In the mid-1700s and early 1800s, whale oil was extensively used and was the fuel option for illuminating houses. Whaling was a large scale trade, and around this time the whale population was in severe decline. As a result, whale oil prices rose and people ultimately began consuming inexpensive, fossil-fuel kerosene in the mid-1800s. Fortunately, before whales became extinct, the whaling business ran out of customers. Ironically, at this time it could be fossil fuels, which protected the whale. Similarly, wood fuel was mostly substituted by fossil fuels after 1900 (Webb and Coates 2012). This also assisted to decrease the unsustainable use of timber assets at the time, which during the century had risen dramatically in price. Biofuels were our primary transport fuels. The initial wagons ever manufactured were made to work on biofuels rather than fossil fuels: the primary automobile to be patented in the United States in 1826 was made to run on a blend of ethanol and turpentine (from pine trees). Henry Ford designed his 1908 Model T to run by ethanol.

In 1925, Henry Ford predicted, "*The fuel of the future is going to come from fruit like that sumac out by the road, or from apples, weeds, sawdust – almost anything. There is fuel in every bit of vegetable matter that can be fermented*" (Ford 1925).

Biofuels get back on track when there was (fossil) oil shortage during the First World War, and thus ethanol was in high demand since it became known that ethanol could be mixed with gasoline for an appropriate motorized fuel. This led many countries to start modern large-scale biofuel production, such as the US and Brazil. Biofuels have been embraced over the past 10 years as a way to help solve some of the biggest challenges in the world: decreasing supplies of fossil fuel, the high price of oil, and climate change.

2.1.2 Eminence of Biofuels

Energy is the fundamental supporter of advancement, particularly among developing nations. To continue the advancement procedure, the supply of energy must be enlarged. The present instability of petroleum price and limited petroleum reservoirs threatens the overall development. Consequently, in both developed and developing nations, the search for alternative energy, including biofuels, is being sought aggressively. Biofuels are observed among the most encouraging elective alternatives, as they can be produced in the vicinity and can be replaced for diesel and gasoline to encounter the transportation part's necessities. Internationally, nations have been mounting fluctuating targets, extending from 5 to 20% for the transportation of fuel products to be delivered from sustainable sources, to be met at different occasions inside the period 2010–2030 (Koonin 2006; Wiesenthal et al. 2009; Eisentraut 2010). The enthusiasm for biofuels in the industrialized nations, aside from advancing energy security, is likewise gone for assisting agriculture and rural growth

Table 2.1 Classification of biofuels according to the feedstock, production processes and products (NNFCC & Low CVP 2010; DENA 2006; IRENA 2016)

Classification	Feedstock's	Production	Products
First generation biofuels	Sugar crops Starch crops Vegetable oils	Transesterification Fermentation Hydrogenation Fischer-Tropsch Gasification Pyrolysis Hydrolysis	Bioethanol Biodiesel Methanol Butanol Mixed alcohols Jet fuels Vegetable oil
Second generation biofuels	Agricultural residues Forest residues Sawmill residues Wood waste Municipal solid waste		
Third generation biofuels	Algae		

and alleviating the danger of environmental change by supplanting petroleum powers with sustainable bases (Lapola et al. 2010). Biofuels have a huge prospective to diminish GHG emissions in the transport sector (IPCC 2007). Whereas rural development and energy security are the most imperative drivers for biofuels all around the globe. The biofuels can be classified according to their feedstock as shown in Table 2.1.

During the previous decade, the enthusiasm for biofuels continued to expand with the improvement of environmental change relief arrangements and methodologies to reduce GHG outflows from the vehicle zone. Since then, more than 60 nations have been driving biofuel projects and setting targets for mixing biofuels into their fuel pools (IRENA 2016). As a result, the segment of biofuels has developed impressively and contributes around 4% to the transportation capacity around the world (REN21 2016). A few universal and national associations have made mid-and long haul predictions of the worldwide creation of biofuels. These predictions give wide-running evaluations on a future increment in fluid biofuels for transportation comprehensively. Some gauge that as much as 33% of all transport fuel by 2050 could emerge out of biofuels, whereas others anticipate increasingly unassuming increments. For instance, the International Energy Agency (IEA) 'innovation guide' on transportation biofuels proposes that biofuels may establish around 27% of worldwide transportation fuel supply in 2050 (IEA 2011). It assumes that most production will come from second-generation feedstocks grown on marginal soil that are not suitable for food crops.

2.1.3   National Prominence of Biofuels for India

India is one of the rapidly rising markets in the world and the progress aims, emphasis on financial development, equity, and social wellness. At the same time, India also stands among one of the biggest producers of ozone-depleting substances (GHG),

and its vehicle segment represents 13% of the nation's vitality related CO_2 discharges (MoEF 2010). As the conventional fuel assets are limited, polluting and non-renewable, thus, must be used sensibly. Alternatively, renewable energy assets are non-polluting indigenous and essentially are everlasting. India is gifted with ample renewable energy assets. Thus, their usage must be motivated in a potential manner. India's energy security would continue to be unprotected until alternative fuels are developed on the basis of indigenously produced renewable feedstocks to replace/supplement petro-based fuels. The nation has a ray of expectation in providing energy security in biofuels. Biofuels are environmentally friendly and their use would address universal worries over carbon emissions. In any case, India's developing transport sector can turn out to be progressively supportable and atmosphere compatible by adjusting advancement and environmental change plans. As expressed in India's National Action Plan for Climate Change (NAPCC), transport discharges can be diminished by embracing a sustainability tactic, which incorporates measures such as expanded public transportation use, the higher entrance of biofuels, and upgraded vehicle efficiency. Consequently, the use of biofuels has become considerable due to stringent emission standards of automotive vehicles to control pollution. India, in the same way as other different nations, is setting focuses on the substitution of oil-based goods by biofuels (GOI 2003; MNRE 2009). The aim of biofuel expansion in India will be to use waste for the production of biofuels. It would also be ensured in the future that the next-generation technologies will be focused on non-food feedstock so that the issue of fuel versus food security is obsolete. For numerous end-use applications, research, development, and demonstration must be supportive in covering all aspects of feedstock production and biofuel processing. Insertion must be made in the development of biofuels of the 2nd generation and further novel feedstocks for biofuels production.

2.1.3.1 Government Biofuel Policy

National Biofuels Policy was approved by Union Cabinet in 2018 to encourage biofuels in the country. Biofuels are strategically important in India since it boosts well by ongoing government policies such as Skill Development, Make in India, and Swachh Bharat Abhiyan. Furthermore, it provides a great prospect to integrate with ambitious objectives of augmenting import reduction, job creation, farmer's income, wealth creation waste.

The policy's goal is to allow biofuels to be available on the market, thereby improving its proportion of blending. Presently, the proportion of ethanol blending in gasoline is about 2.0% and the proportion of biodiesel blending in diesel is less than 0.1%. A goal of 20% ethanol blending in gasoline and 5% biodiesel blending in diesel is proposed by 2030. The policy categorizes biofuels to allow each category to extend suitable fiscal and financial incentives. Basic Biofuels: 1st Generation bioethanol and biodiesel. Advanced Biofuels: 2nd Generation ethanol, Municipal Solid Waste (MSW) to drop-in fuels, 3rd Generation biofuels, bio-CNG, etc. (National Policy on Biofuels 2018).

Incentives for advanced biofuel are initiated by the government as feasibility gap funding scheme indicated in 6 years for US$72 crore 2nd generation ethanol Bio refineries are given as special importance to progressive biofuels (FIPI 2018). Also, it offers extra tax incentives, higher buying price than biofuels of the 1st generation. The policy encourages the establishment of mechanisms for the supply chain for the production of bioethanol from various kind of agricultural waste. To synergize efforts, it predefines the roles and duties of all the government departments and ministries concerned about biofuels. The supply of ethanol will help in decreasing the dependence on crude oil on imports, resulting in forex savings. Moreover, the emissions of greenhouse gas will be reduced by decreasing the crop burning and by converting the agricultural residues and waste into biofuels. The addition of 2nd generation bio refineries throughout the nation will stimulate venture in rural infrastructure. Establishing a 2nd generation bio refinery will contribute a large number of jobs in plant operations. The transformation of additional agrarian biomass can also assist farmers in price equilibrium.

2.2   Potential of 2nd Generation Biofuels

The concern about the competition of feedstocks among the food and biofuel industries have threatened the food safety and influenced economically, the use of food produces for fuel production. The debate initiated by the worldwide food crisis of 2008 emphasized that the feedstocks for 1st generation biofuels need huge quantities of soil, water, and chemical fertilizers, with significant ecological and financial costs and significantly uncertain results for GHG mitigation. Therefore, various companies are aggressively developing and marketing a number of advanced 2nd generation biofuels made from non-food feedstocks, including municipal waste, algae, perennial grass, and wood chips. The potential of 2nd generation biofuels from agrarian residues relies largely on the whole quantity of annual crop residues produced, their present rates of use, and the potential excess supply for energy use. There is a large variation in the reported agrarian residue market price(s) in India.

It is practically feasible to obtain rice husks from a range of up to 100 km in Chhattisgarh at $74 per vehicle (Pandey et al. 2012). Rice mill owners will earn about $9 per ton of rice husks in this scenario. Rice husks were sold in Punjab in 2010 for $55 per ton, compared to $46 per ton in 2009. The price even reached $74 per ton (Sharma 2010). In total, rice husk prices ranged from $18 to $74 per ton in 2010, while rice straw prices ranged from $11 to $13 per ton (Sharma 2010). According to estimates from CSE (2010), $92 to $111 per ton is the normal rate at harvest time for wheat or bajra straw anywhere in Rajasthan. The cost of rice husks in Uttar Pradesh is between $37 and $46 per ton while the cost of coal is between $83 and $92 per ton (Yadav and Singh 2011). Dairy animal owners have purchased chaffed sorghum stalks at prices as high as $102 to $120 per ton in urban areas, especially around Hyderabad and Bangalore (Hegde 2010). Even wheat straw was

purchased between $37 and $55 per ton, while paddy straw was sold between $28 and $37 per ton.

India, with a total area of ~329 Mha, uses ~141 Mha for agriculture, which is one of the highest at 42.8% compared to a global average of ~11%. The residues produced in the largest amounts are rice straw (152 MMT), wheat (136 MMT), sugar cane (145 MMT), corn (41 MMT), cotton stalks (68 MMT), and other coarse cereals (29.01) (MoA 2014). These accounted for nearly 90% of the agro-residues produced together. Other important residues included pulses (21 MMT) and oilseeds (62 MMT) (Pandey et al. 2009). Alone, soybean contributed approximately 50% of the predicted "oilseed" residues. Most cereals and pulse residues enter the basket of animal fodder and are inaccessible for bioethanol applications as feedstock (MoA 2014). The use of agro-residues as fodder also relies on the preferences of the geographic region and the farmer. Despite a big portion that has been diverted to distinct end uses, a big amount of agro-residues continues excess and can be used as feedstock for bioethanol. With more than 650 MMT of agricultural residues produced annually, this is undoubtedly the most plentiful feedstock accessible in the nation for biofuel conversion. Municipal and industrial waste would be another potential feedstock for the production of biofuels. Due to a population boom, industrial development and urbanization, the increasing amount of waste have led governments and international organizations to take a stronger stand in reducing waste generation. In an attempt to reinforce this notion, several developed countries have already taken stern measures to hugely decrease their waste by enforcing heavy taxes on non-biodegradable goods packaging. Figure 2.2 shows the production of 2nd generation biofuels from biomass (Naik et al. 2010). The 2nd generation biofuels obtained from lignocellulosic feedstocks can resolve the feedstock accessibility problem, allowing a much
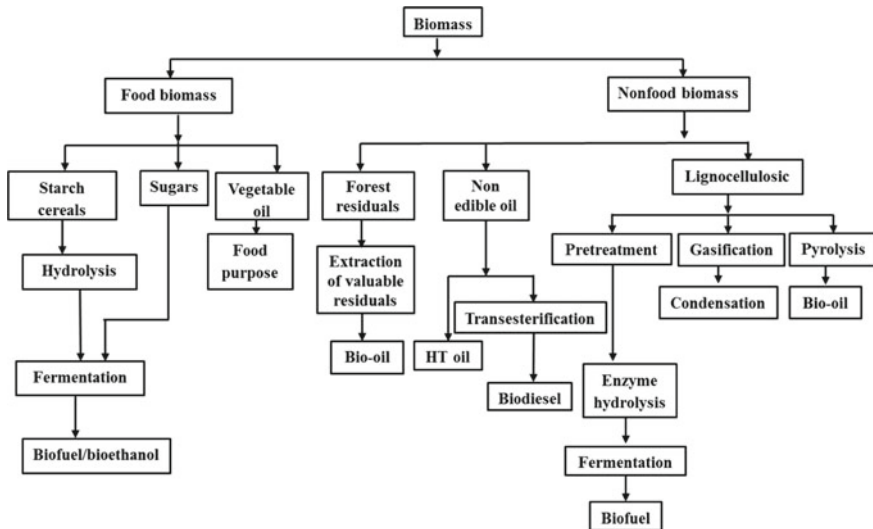
Fig. 2.2 Second generation biofuel production from biomass

wider range of biomass sources can be used as feedstock (Zabaniotou et al. 2008). In recent years, 2nd generation biofuels which are obtained from renewable biomass has gained higher consideration; it is one way of reducing the use of fossil fuel and greenhouse gas emissions. Out of these fuels, 2nd generation ethanol has arisen as a thriving transportation fuel which has the potential of abating global warming and environmental pollution. Most researchers have tended to emphasis on developing an efficient and environmentally friendly process of ethanol production over the past decade.

The fermentation of raw materials based on sugar is referred to as bioethanol 1st generation, while the usage of raw materials for lignocelluloses is commonly referred to as bioethanol 2nd generation as classified in Table 2.1. Algal bioethanol's 3rd generation is at an initial phase of research. Furthermore, the cellulosic plant material is a source of fermentable sugar for substantial use. In particular, non-food agricultural waste products such as rice straw, wheat straw, rice husk, bagasse, etc. The 2nd generation biofuels can be derived through various processes. The flow chart of biomass conversion processes is shown in Fig. 2.3 (Naik et al. 2010). The biochemical procedure depends on enzymatic hydrolysis of the lignocellulosic material, utilizing an assortment of enzymes that breakdown the cellulosic material into sugar. The sugars are fermented into alcohol, which is then refined into ethanol in the 2nd step of the biochemical method. The thermochemical procedure utilizes high temperatures to change feedstock into synthesis gas. After that, the synthesis gas is converted into various types of gaseous or liquid fuels, termed as "synthetic fuels".
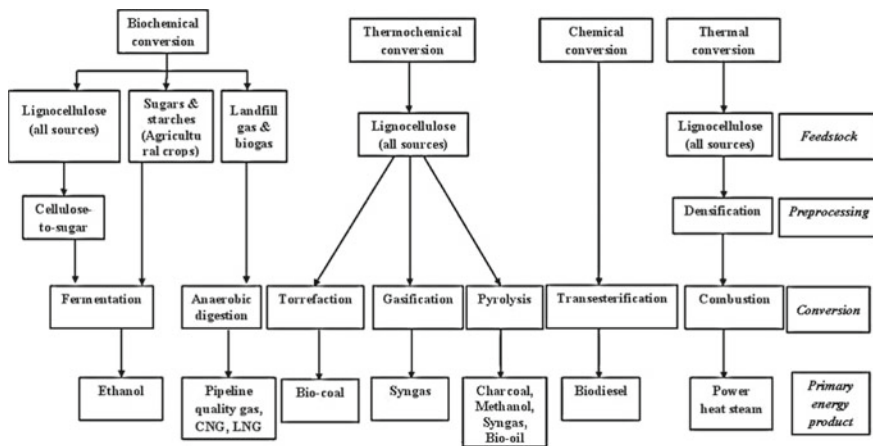
Fig. 2.3 Biomass conversion processes

2.2.1 Production of 2nd Generation Ethanol

The 2nd generation ethanol is one of the advanced biofuels which is produced from various type of non-food biomass and agricultural waste due to which it does not compete against food supplies. Molasses, a by-product of sugar production, are usually used in the production of alcohol and ethanol in India. Estimation indicates that only bio-ethanol derived from sugarcane will not be able to achieve India's mandated blending condition (Shinoj et al. 2011). At the same time, over half of India's land is used for farming, with huge crop residue production and crop wasting. Lignocellulosic biomass typically produces 2nd generation ethanol as the production process is shown in Fig. 2.4. In many plant raw materials, lignocellulose is considered a renewable and sustainable source of carbon (Kim et al. 2010). The available amount of lignocellulosic biomass relies on climatic conditions. Other sources of lignocellulosic biomass are agricultural waste such as cereal, wheat straw, rice husk, corn cob, and sugar cane bagasse. Another research has focused on wood waste and forest biomass (sawdust, bark), softwood chips (pine) and hardwood chips (oak) whereas park and gardens waste (leaves, grass, branches). Industrial waste, such as spent grains from the brewer and spent grains from distilleries, and municipal solid waste such as cellulose-containing food waste, kraft paper, and paper sludge are also considered. Lignocellulosic biomass from vegetable waste has great prospective for usage in bioethanol production, however, owing to its complex structure; pretreatment is essential to improve the output of cellulose and hemicellulose sugar reduction in hydrolysate during enzymatic hydrolysis. The existence of almost non-biodegradable lignin in lignocellulosic material without pretreatment during the enzyme saccharification stage and the low digestibility of crystalline cellulose and hemicellulose hinder the usage of complicated lignocellulosic biomass (Maurya et al. 2015). Pretreatment makes hydrolytic enzymes e.g. cellulases and hemicellulases that make simple sugars more readily accessible for cellulose and hemicellulose. However, the usage of complex pretreatment technologies raises the cost of producing ethanol. Pretreatment decreases the crystallinity of cellulose, leads to anamorphic cellulose, eliminates

Fig. 2.4 Production of 2nd generation ethanol from lignocellulosic biomass

or degrades lignin (delignification) and involves complete or partial hydrolysis of hemicellulose (Cardona and Sánchez 2007).

The aim of hydrolysis is to release monosaccharides in the plant cell wall from polysaccharides. Polysaccharide hydrolysis, e.g. cellulose and hemicellulose, yields fermentable sugars that can be transformed during fermentation into ethanol. The amount of hydrolysate sugars relies on the type of lignocellulosic waste used and the techniques used for pretreatment. The fermentation aim is to efficiently 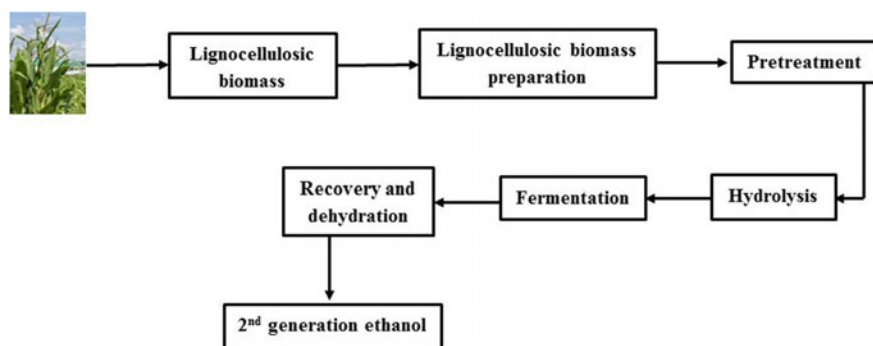convert hexose and pentose sugars into ethanol by fermenting microorganisms e.g. yeasts. Depending on their strain and fermentation circumstances, ethanol-producing microorganisms are prone to lignocellulosic hydrolysate (Olsson and Hahn-Hägerdal 1996). Typically, traditional distillation systems are based on vapor/liquid mass transfer countercurrent. Distillation makes it possible to recover diluted volatile products, such as ethanol, from impure biomass streams (Madson and Lococo 2000). Ethanol obtained through fermentation is contaminated and in fractions of low volume. Ethanol is separated from the other components in the mixture during distillation. Rectification enables ethanol to be concentrated and purified. Extremely high purity (99.7% by volume) ethanol can only be attained after drying due to dehydration (Bioethanol Zeitz). Lignocellulosic bioethanol produces lower greenhouse gas levels than bioethanol in the 1st generation and causes less air pollution (Hahn-Hägerdal et al. 2006). However, lignocellulosic bioethanol production requires the preparation of feedstock before fermentation and the finding/development of ethanol producers capable of fermenting cellulose and hemicellulose breakdown sugars.

Ethanol obtained from lignocellulosic materials is 2nd generation ethanol. Lignocellulosic biomass relates to agricultural residues such as wheat straw, rice straw, bagasse, maize stover and residues from plants. These biomasses are the world's most valuable and sustainable raw materials and are the appealing feedstock for bioethanol extraction because their use as bioenergy raw materials does not deplete food and feed sources. The extraction of ethanol from these raw materials is more complex than the starchy raw material. It is necessary to hydrolyze lignocellulosic biomass to fermentable monosaccharide, hexoses, and pentoses, but there are issues with this method. In general, lignocellulosic material can be split into three primary parts: cellulose (30–50%), hemicellulose (15–35%) and lignin (10–20%) (Girio et al. 2010). Cellulose and hemicellulose are tightly packed with lignin layers that safeguard cellulose and hemicellulose from enzymatic hydrolysis. Therefore, the pretreatment is necessary to break the layers of lignin to expose cellulose and hemicellulose by reducing the crystallinity of cellulose, increasing the surface area of biomass, removing hemicellulose, and breaking the seal of lignin to facilitate subsequent enzyme action. Consequently, an effective, quick and complete enzymatic hydrolysis for the pretreatment of biomass is one of the main technical and economic tailbacks in the lignocellulose to bioethanol bioconversion cycle (Ishizaki and Hasumi 2014).

The polysaccharides, cellulose, and hemicellulose in the plant cell wall are closely associated with lignin in the waste products. The lignin component acts as an obstacle and should be removed in order to provide the carbohydrates for further processes of transformation. Bioconversion of biomass from cellulose to fermentable sugar for

ethanol production using microorganisms, especially cellulose-degrading fungi, creates bioethanol economically, environmentally pleasant and also renewable (Koshy and Nambisan 2012; Patel et al. 2006; Kang et al. 2004). The sustainably derived agricultural residues have the potential to be used in the production of biofuels. Biofuels of 2nd generation cost estimates show significant differences depending on the complexity of plants and the efficiency of biomass conversion (Cherubini 2010; Sims et al. 2010; Shie et al. 2011). Important considerations include annual full-load plant operating hours, feedstock expenses and requirements for capital. Biofuel crops with a greater manufacturing ratio of biomass to biofuel can therefore generally recognize greater expenses of supplying biomass compared to less effective crops (de Wit et al. 2010; Eisentraut 2010). With oil at $60/bbl, the cost of production for BTL-diesel and lignocellulosic ethanol is currently within $0.84–0.91/lge and therefore, fossil fuels and most biofuels of the first generation are not competitive (IEA 2009). However, with increased plant capacity and enhanced conversion efficiencies, both BTL-diesel and lignocellulosic ethanol could be generated at considerably lower expenses over the long term. In this case, production costs of lignocellulosic ethanol are projected to be approximately $0.62/lge and BTL-diesel $0.58/lge (IEA 2009). The estimated prices of production for rapeseed biodiesel are lower than those, but still more costly than gasoline and other biofuels of the 1st generation. With oil at $120/bbl, the cost of production for BTL-diesel is $1.07/lge and for lignocellulosic ethanol is $1.09/lge. In the long term, BTL-diesel prices are projected to drop to $0.73/lge and lignocellulosic ethanol to $0.72/lge. Thus, with lower overall costs and oil prices at $120/bbl, 2nd generation biofuels could be produced at lower costs than petrol and rapeseed biodiesel and close to the cost of corn ethanol (IEA 2009).

There are some developments that propose interest for bioethanol may increment significantly more than for biodiesel. The diesel motor and diesel vehicles, specifically, have been under expanding investigation attributable to control of the discharges homologation process by some vehicle producers and the inability to recreate expected NO_x outflows in genuine driving conditions. Real estimations have shown that normal tailpipe NO_x emanations from diesel autos are multiple times the certified discharge limit for Euro 6 vehicles (Franco et al. 2014). This issue is causing significant concern, especially in urban conditions, where air quality issues and related human wellbeing impacts are accepting expanding political attention (Laybourn-Langton et al. 2016; Howard 2015).

2.3   2nd Generation Ethanol Blended Diesel Fuel as an Renewable Alternative Fuel for Diesel Engines

The concept of blending diesel-ethanol is not new. Ethanol blends with diesel fuel are frequently referred to as "E-Diesel" or "eDiesel". Research studies from the 1980s have shown that these blends can be used in compression ignition (CI) engines (Hansen et al. 1982; Hashimoto et al. 1982). Improvements in pollutant emissions

connected with the use of E-Diesel blends in CI engines (without any changes) are heavily dependent on the corresponding engine's working circumstances. Different physical and chemical properties of diesel and ethanol affect the properties of the resulting blend. Ethanol solubility in diesel fuel is mainly affected by two factors: the ambient temperature and the water content of the mixture (Hansen et al. 2005; Lapuerta et al. 2007). Percentages of up to 15% v/v anhydrous ethanol can be mixed with diesel at temperatures above 30 °C without phase separation. However, phase separation can be observed at temperatures below 10 °C and without the use of additives (Torres-Jimenez et al. 2011). Another factor that can influence the stability of the blend is the aromatic content of diesel fuel, which acts as a bridging agent and co-solvent to some extent (Gerdes and Suppes 2001). The water content of the blend impacts not only the stability of the blend but also the properties of combustion and the durability of the parts of the fuel injection system (Armas et al. 2012). In addition, due to an enhanced hygroscopic trait of ethanol, unique steps must be taken when storing E-Diesel blends for longer periods. Due to variations in the homogeneity of E-Diesel blends, accurate control of the quantity of injected ethanol can be challenging and problems with injection and combustion can arise. Two techniques are suggested to stabilize the blend: (1) Adding an emulsifier—suspending tiny droplets of ethanol in diesel fuel; (2) adding a co-solvent—acts as a molecular bridge agent (Letcher 1983). In order to allow the concurrent use of diesel and ethanol in diesel engines, various techniques have been assessed. Some of these techniques include alcohol fumigation, alcohol-diesel emulsions, double injection, and alcohol-diesel blends. Only alcohol-diesel emulsions and blends are well-suited with the majority of commercial diesel engines among these techniques. Because emulsions are hard to achieve and tend to be unstable, blends-either as micro-emulsions or using co-solvents, are the most common approach as they are stable and can be used in engines without any kind of engine modification.

In e-diesel blends, standard diesel fuel is typically blended with various percentage of ethanol (by volume) using a co-solvent that helps to maintain the blend stability. Singh and Bharj (2019) studied the importance of chemical and physical properties of blended diesel fuel with different concentration (7, 13 and 19% by volume) of 2nd generation ethanol. The measured fuel properties i.e. kinematic viscosity, density, calorific value, cetane number, sulphur content and a flash point of the prepared blends were compared with standard diesel fuel. The addition of 2nd generation ethanol led to marginally decrease in the density and kinematic viscosity of the prepared blends but the values were within the standard limit of diesel fuel. The minimal reduction in kinematic viscosity may cause less filter damage, less pump resistance, and will lead to form a decent fuel spray pattern. In addition to that, sulfur content and cetane number were also decreased for prepared blends. The decrement in sulfur content in the blended fuel will create less toxic pollutants during the process of combustion. The authors suggested that the blended diesel fuel with different concentration (7, 13 and 19% by volume) of 2nd generation ethanol can be used directly in a diesel engine without any kind of modification as the examined fuel properties of the fuel blends were in standard range of diesel fuel, further a minor tunings in fuel injection will result in a low level of emissions. More stringent

emissions regulations and government announcements to increase the use of biofuels should reinforce the importance of overcoming unresolved barriers to the adoption of 2nd generation ethanol blended diesel fuel as a commercial fuel as suggested by Singh and Bharj (2019). The use of 2nd generation ethanol in diesel fuel will enlarge the agricultural commodities and will produce additional income through 2nd generation ethanol derived from crop residues.

2.4 Conclusions

Transformation of agrarian waste to bioethanol has paved the method for unused assets and strong ecological stability, with which the ethanol-from-cellulose has shown tremendous potential due to mass availability, abundance and comparatively low price of cellulosic biomass resources. At the same time, the potential to use available agricultural residues to produce 2nd generation biofuels underlines the essential for technology development. As accessible technologies are updating commercially, therefore, the developing countries can revive rural economies by investing in agricultural production, rural infrastructure, and refining energy supply. In this regard, various bioenergy systems can play a vital role by providing access to inexpensive and fresh national energy with noteworthy prospective for improvement in productivity and global living standards in rural societies. Investment to help build feedstock supply and handling capacities in the field can create favorable conditions for the establishment of a biofuel industry of 2nd generation. Thus, countries that are currently unable to produce biofuels of the 2nd generation could take advantage of fresh technologies and new market prospects as soon as the technologies are commercially available. Another salient point is to strengthen collaboration with both developed and developing countries in order to build capability in the field of 2nd generation biofuels and ensure access to technology. It is apparent that under the influence of current policies on renewable energy and climate change, global bioenergy consumption will continue to rise. In the near future, bio power, lignocellulosic bioethanol will be the most prosperous bioenergy and renewable markets with the highest growth potential. There is a durable sign that by 2050 bioenergy will meet 30% of the world's energy demand. Presently, there is no policy system to encourage farmers to collect and deliver residues of biomass to an ethanol plant of the next generation. Therefore, a reliable supply chain for biomass covering the collection, transportation, and handling of biomass feedstock is important. If governments seek to nurture an industry for the longer term, they could generate a mechanism by which farming communities or cooperatives societies could participate in the process of collecting, storing and delivering residues. A supply chain should be designed and operated to maximize economic potentials and social benefits and minimize environmental impact in order to reduce supply chain uncertainties and high market risk associated with the 2nd generation biofuel industry. India can take advantage of its population segment and should be tackled through training and integrated into larger national programs if skill discrepancies exist.

Biofuels transport sector requires separate infrastructure. However, these separate biofuel infrastructures are either capable of being limited or unavailable. Biofuel integration would require a scale of biofuels, and retail outlets essential to be encouraged to sell blended fuels to accelerate biofuel adoption as a transport fuel. Biofuels can grow faster and reach an economic scale if it is possible to address the vehicle limitations in the use of biofuels. In this way, the new different fuels can be proposed significant prospective to stimulate rural growth and augment in financial conditions for developing regions.

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Chapter 3
Biofuels from Renewable Biomass Resources: An Overview of Technologies for Production, Environmental and Economic Impacts

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Abstract In recent years, there is a great deal of social obligation involve with scientists to common people that a sustainable chemical processes having industrial importance which is associated with greener concept and environmentally benign methodology is the need of the hour. This trends of technology driven greener process will continues to roll on for next few decades. With this aspects in mind, biomass, a sustainable alternative feedstock, can be processed into liquid and solid fuels via thermal, light-induced, catalytic and bio-based techniques. Conversion of biomass materials into value added products and energy can address environmental sustainability and recycling of waste materials. Utilization of bio-based energy has not been explored fully. We continue to rely on fossil fuels, nuclear energy and hydroelectricity to meet our energy demands. Alcohols and its derivatives are the important source of bioenergy that are hidden in biomass. In this context, the production of alcohols or esters is an extremely important industrial process as they are useful as precursors, reagents, solvents or additives in perfumes, essential oils, food flavorings, cosmetics, etc. Even though there have been numerous methods available for the production of alcohols and esters, designing non-hazardous methods to generate chemical products that limit the usage of hazardous substances is highly required. The present chapter aims at the analysis of various green methods reported for the production of alcohols and esters from renewable energy sources. Also provide a broad overview of the environmental and economic impacts of biofuels. The major environmental impacts are conceived under two headings, viz. direct emissions those that are expelled during the biofuels production and consumption and indirect emissions those that are associated with their land use.

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3.1 Introduction

Evaluation of data from various quarters indicate that USA can sustainably generate roughly one billion tons of biomass from non-edible biomass per year. Bio-based fuels can substitute roughly 1/3 of the conventional fuels which are chiefly used in automobile sector. Currently about 2 million barrels per day vehicular fuels are generated from biomass. By 2030, it is expected to increase nearly 6 million barrels per day. This is roughly six percent increase in fuel consumption. Hence, it is convincing that there is a trend toward decreasing the reliance on conventional source of fuels and meeting the future requirements for transportation fuels by an amalgamation of non-conventional source of electricity and bio-based fuels. To exemplify the inspiration for sustainable strategy in the bio-energy creation, it is important to look into the property parameters of biomass and those of the fuels one would like to generate. Bio-fuels can be generated from edible and non-edible sources as shown in Table 3.1. Predominantly, edible source mainly comes from corn crops. On the other hand, non-edible source is mainly from lignocellulosic biomass.

Lignin, hemicellulose and cellulose are the important ingredients of lignocellulosic biomass. Within this, hemicellulose and cellulose are carbohydrate based polymers having five and six carbon sugars. Carbohydrates, monosaccharides nor disaccharides, produced from enzymatic or acid catalyzed hydrolysis of bio-mass are not considered as appropriate fuels. This is mainly due to elevated level of oxygen content and reduced energy density (15–20 MJ/kg versus 42 MJ/kg for hydrocarbon fuels). Figure 3.1 describes the types of bioenergy.

Furthermore, fuels that are routinely used in automobile sector need low volatility and appropriate combustion properties, viz. octane number, cetane number and lubricity. Thus, generation of fuels from biomass should exclude most, if not all, oxygen content level and generation of carbon molecular framework with five to twenty two carbon atoms holding branched network of carbon skeleton for gasoline fuels and linear carbon backbone for diesel. An additional limitation on any procedure for

Table 3.1 Biomass feedstock based on edible and non-edible source

First generation biomass feedstock	Second generation biomass feedstock
Based on the food crops	Based on the non-food crops
Bioethanol and vegetable oil from corn crop and sugar cane	Lignocellulosic materials
	Homogeneous—wood chips Quasi homogeneous—agriculture and forest residue Non-homogeneous—municipal and industrial solid waste
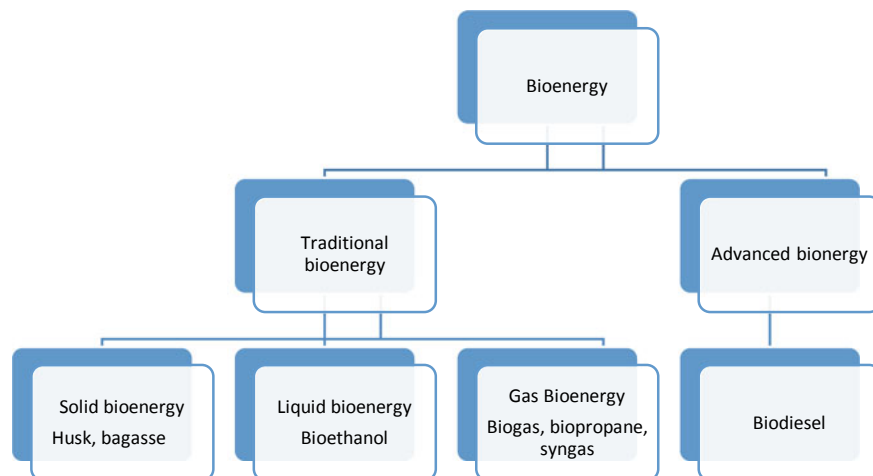
Fig. 3.1 Classification of bioenergy

the conversion of biomass to fuels is the entire hydrogen demand for oxygen conversion. By adopting steam reforming method of methane, industrial methods of fuel generation is achieved for a fossil fuel for generation of hydrogen, and while every carbon dioxide generated in the reforming reaction produces four moles of hydrogen. The endothermicity of the chemical transformation and the elevated pressure at which reduction processes (hydrogenation) are normally carried out to facilitate additional energy inputs from fossil sources.

3.1.1 Biomass to Bio-chemicals—An Alternate Source of Bioenergy Additive

Annually, twenty five billion gallons of bioethanol is manufactured from biomass. It is the most versatile chemical method adopted to generate alcohol. Despite the fact most of the bioethanol is mixed with gasoline, it is construed as an important feedstock for generating multiple chemicals like unsaturated non-aromatics, aromatic hydrocarbons and oxygenates. For example, annually about one hundred and forty million tons of ethane is produced by adopting chemical dehydration of ethanol. On the other hand, new and more sustainable pathways utilizing ethanol and other three-carbon to five-carbon alcohols as feedstocks can be utilized to generate different kinds of aldehydes, treasured chemical intermediates to be useful as plasticizers and detergents. Aldehydes can be synthesized by hydroformylation reaction of alkene as well as dehydrogenation of alcohols by non-oxidative pathways. Later method is specifically fascinating because it produces hydrogen as a byproduct. It was also

revealed that nanoparticles from gold can act as acid-base supports such as hydrotalcite (Au/HT) and hydroxyapatite (Au/HAP) initiate this reaction very efficiently. By taking ethyl alcohol or three-carbon to five-carbon alcohols, the corresponding carbonyl compounds (aldehydes or ketones) are generated at 473 K with an excellent selectivity of more than 90%.

Generation of alkenes and ethers from alcohols can be achieved by utilizing powerful acidic supports like silica-alumina (Si–Al), which can catalyze the dehydration of two carbon to five carbon structures. Similarly, basic supports, such as magnesium oxide, generate substantial yields of Guerbet products.

Globally, organic chemicals are produced from bio-based sources like cellulose, hemicellulose, lignin and pectin which covers roughly 10% of world production. These chemicals are highly useful in various sectors. These hydrocarbons are highly diverse in nature. Moreover, these chemicals require low technological utility. Many of these hydrocarbons are important intermediates valuable in multi-step process. Eventually, these chemical intermediates are believed integrate with ultimate consumer utility products.

From a commercial point of view, chemicals that are derived from biomass are extremely valuable in international market as a result of greener methods involved in the production. Generation of optically active highly pure amino acids from natural sugar components or demonstrated cost-competitive with their conventional counterparts.

With regard to market potential of high utility chemical products, specifically, this sector is well recognized due to its importance. These products include functionalized high-value but low volume chemicals cosmetics, therapeutic agents and extremely useful polymers. Basic chemicals derived from biological sources have the limitation of reaching out broader market utility. This is primarily due to higher price range which are consistently well-adjusted to exceptional market prices. Chiefly motivated by consumer expectations, a rapidly expanding growth market for bio-based polymeric material has to supersede a market share of three percent in 2020. Nevertheless, the learning curve in fuel-bio refineries in blend with the creation of improved catalytic components derived from biological sources would enhance the price component for sustainable chemicals as well and hence a constant exponential growth to a bio-based share of twenty two percent by sales in 2020. The production volume of bio-based chemicals is smaller than bio-based fuels, the more market for bio-based chemicals are not popularized by government subsidies.

3.1.2   Features of Bioenergy

Combination of several large varieties of numerous hydrocarbons constitutes petroleum based fuels. Bio-based fuels chemically consist of pure single component substances such as H_2, CH_4 and CH_3CH_2OH. On the other hand, chemical constituent of biofuels are chiefly consist of a mixture of typically 5–6 esters of fatty acids. The relative ingredients of which may vary depending upon the source of raw materials. This comparatively fixed number of fatty acid esters in bio-based diesel

divergences with the much wider and more intricate varieties of hydrocarbons that occurs in petroleum. Apart from this, fossil fuels are mixed with bio-based fuels. The existence of oxygen content within the hydrocarbon molecular framework can differentiate alcohol fuels from bio-based diesel and petroleum-based fuels. This is important parameter that discriminates the types of fuels that are available for day to day use.

By utilizing multidimensional spray technique and combustion modelling, a recent investigation demonstrated the changing the fuel's properties on the spray and combustion specific of diesel-engines when fuels are functioned by multiple bio-diesel fuels. The normal properties of biodiesel fuel that are used in the investigations and the simulation studies outcome, are correlated with those of traditional diesel fuels.

The sensitivity of the computational outcomes to selected physical properties is also studied by varying one parameter at a time. Taking advantage of selected studies outcome, it offers a standard on the acceptable properties of combined fuels. The analyzed properties are; (i) density measurement of liquid; (ii) vapor pressure; (iii) surface tension; (iv) fluid viscosity; (v) thermal conductivity of liquid sample; (vi) liquid specific heat; (vii) latent heat; (viii) vapor specific heat; (ix) vapor diffusion coefficient; (x) vapor viscosity; and (xi) vapor thermal conductivity. The outcomes of the studies advocate that the intrinsic physical properties of each of these fuels ominously effect spray structure, ignition delay and combustion rates in a broad range of engine specific to functional parameters.

Furthermore, the interpretation that substantiates the prediction that ignition delay between diesel and bio-based fuels is not governed by single physical properties. Nevertheless, liquid fuel density, vapor pressure and surface tension properties have profound effects on fuel. There is a strong correlation exists on the atomization, spray and mixture preparation methods of fuels which contributed to the prominence of aforementioned properties.

With regard to cold weather conditions, diesel fuel has the capabilities hold liquid characteristics. This is very significant characteristics of diesel fuels. However, when optimal temperatures are low enough, a few hydrocarbons in diesel fuel start to become solid, thus, preventing the flow of fuel from the storage tank to the fuel injection pump through the filter system. This parameter is characterized by the cloud point and cold filter plugging point (CFPP), for which bio-based diesel fuels normally have elevated temperatures; this keeps them vulnerable to obstruction of the fuel system and hindering the engine being started when cold. The presence of relative levels of saturated and unsaturated fatty acids in bio-based fuels has direct correlation with liquid characteristics of fuels. Higher the level of the saturated component, the greater the cloud point and CFPP temperature. Chemical additives such as malanstyrene esters and polymethacrylate can effectively address these limitations.

Energy density is a degree of quantum of energy a fuel holds; this property has a straight effect on quantity of energy an engine generates by burning this specific fuel. The energy content for wider varieties of fuels is attributed to the lower heating values. Ethyl alcohol has about thirty percent reduced energy content than gasoline on a per unit volume basis; this transforms into a reduced distance travelled per tank

of fuel compared to gasoline. By the same token, biodiesel shows an energy content that is roughly nine percent lower than that of conventional fossil-based diesel. One important chemical behavior of ethyl alcohol is its resistance to auto-ignition, as echoed by its elevated octane number. The octane number of a fuel is a vital property to reveal whether the given fuel will knock the engine under given operating conditions. In order for a fuel to resist knocking, it is preferred to have fuel with higher octane number. To improve the fuel properties, ethyl alcohol is added as an enhancer for gasoline. The reason for this property variation is due to ethyl alcohol is relatively having high heat of vaporization. The elevated level of heat of vaporization results in cooler fuel-air composition, which in turn slows down the burning and offers a higher resistance to knocking. Further, the significance of increased octane number can burn ethyl alcohol at a higher compression ratio. In a similar way, the cetane number offers a degree of compression ignition. The greater the centane number is, the higher the ignition parameter of a fuel and reduced ignition delay. This is a critical parameter since extended ignition delay results in most of the fuel being injected before ignition happens. In turn, this results in rapid combustion rates and very high rates of pressure rise once ignition starts such that, in some cases, diesel knock can happen. This article covers in detail the thermochemical, biochemical, and chemical routes for biofuel production. Further, this study highlights the environmental and economic impacts of biofuels. Thus the chapter outlines on the efforts to progress for sustainably transforming biomass-based materials to additive fuels (alcohol and ester) to selected useful chemicals mainly used in the transportation sector.

3.2   Overview of Transformation Methods

Numerous biomass resources (Owusu and Asumadu-Sarkodie 2016) have been used to convert them to fuels (liquid, solid, and gaseous) with the help of chemical, thermochemical, biochemical routes (refer Fig. 3.2). Other processes related to biomass conversion reported are physical extraction, electrochemical, direct liquefaction and indirect liquefaction.

3.2.1   *Thermochemical Conversion Process*

Thermochemical conversion can be classified into three subcategories: pyrolysis, gasification, and liquefaction as shown in Fig. 3.3 (Appell et al. 1971).

The conversion of biomass materials into fuels having physico-chemical characteristics facilitates the transferability through pumping routes and economic storage. In general, gasification at the first stage is partial combustion of biomass to yield gas and char and subsequent reduction of the gases produced CO_2 and water; useful CO and H_2 as major products and CH_4 and other hydrocarbon fractions as minor
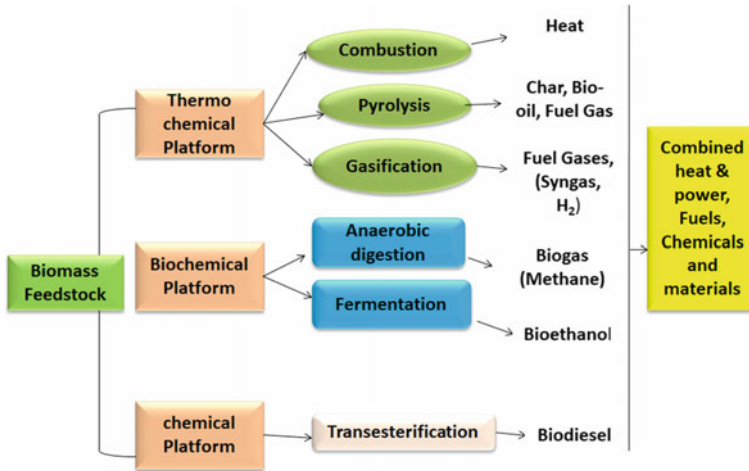
Fig. 3.2 Various routes for the production of value added products from biomass
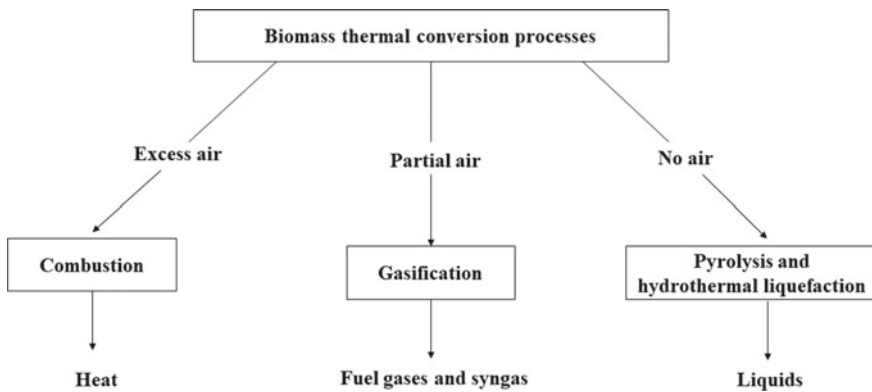
Fig. 3.3 Thermal conversion processes reported for biomass conversion

products by charcoal. The conversion efficiency in this process is affected by the design of the reactor and operating conditions (Balat 2008).

Pyrolysis is an incomplete gasification process with the source of both gasification and combustion of solid fuels, by facilitating the chemical changes of a material at elevated temperatures in the absence of oxygen. The flash pyrolysis of biomass directly converts small dried biomass particles in the absence of oxygen into a liquid fuel. The vapor phase of char catalyzes the secondary cracking. Plasma arc processes provide very high heat from electricity to produce a discharge converting the surrounding gases to an ionized gas. But the mechanistic aspects in the formation of various products have been regarded as complex systems. Thermochemical conversion is known for their faster rate of reactions under the extreme conditions. The rate

of conversion is influenced by the strength of oxidizing or reducing media, process temperature, and pressure.

Various fluids have been employed including water for the biomass conversion processes: hydrothermal upgrading (HTU) and supercritical water gasification (SCWG). In order to design the efficient biomass conversion processes, both phase equilibria and phase behavior in the reactor and separators are extremely important (Feng et al. 2004). HTU (or direct liquefaction) is a favorable technology to treat waste from various sources and to produce valuable bio-products such as bio-crudes.

Mechanistic aspects of thermal decomposition of biomass

Liquefaction takes place through the systematic structural and chemical changes of carbonaceous materials, which involve any one or more following steps (Chornet and Overend 1985; Demirbas 2000).

1. Cracking/reduction of polymers (*e.g.* lignin and lipids)
2. Conversion of cellulose and hemicelluloses by hydrolysis to glucose
3. Hydrogenolysis of the matter in the presence of hydrogen gas
4. Reduction of amino acids
5. Dehydration and decarboxylation reactions for molecular rearrangements
6. Hydrogenation of active functional groups.

As per the studies, the reactions in biomass de-polymerization process are remarkably complex.

Hydrothermal Liquefaction of Bio-renewable Feedstocks

Direct hydrothermal liquefaction and further rapid pyrolysis produce condensable organic vapors, oils and tars in liquid form (Goudriaan and Peferoen 1990). The catalysts are used in indirect liquefaction to convert the non-condensable products of gasification or pyrolysis into liquified products. Figure 3.4 shows the block scheme of commercial HTU plant.

Hydrothermal reaction is one of the effective methods for the treatment of organic wastes under supercritical or subcritical reaction conditions (Jomaa 2001). This is classified into two broad categories: (a) oxidative process in the presence of oxidants, and (b) non-oxidative process in the absence of oxidants. Subcritical temperatures provide the production of huge quantities of dissolved organic matter along with volatile fatty acid including acetic acid. In general, the efficiency of combustion is based on the temperature of flue gas and the air (Jomaa et al. 2003).

The calculations on combustion efficiency assuming the complete fuel combustion mainly depend on three following factors:

(1) the properties and chemistry of the fuels
(2) the net temperature of the corresponding stack gases and
(3) the volume percentage of oxygen/CO_2 after the combustion

The efficiency of combustion remarkably increases with increasing contact time and the temperature of the reactants which leads to enhanced vapor pressures, improved surface areas, and increasing stored chemical energy. The liquid ethanol is called as
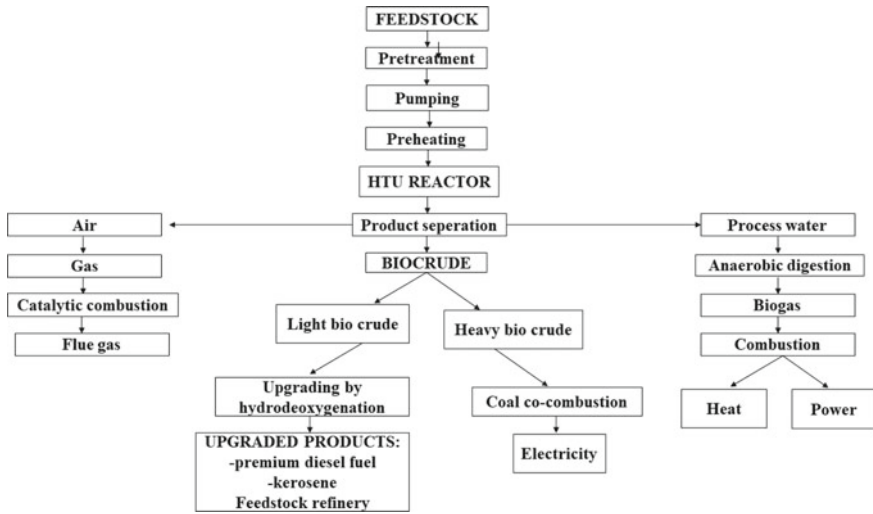
Fig. 3.4 Block diagram of a commercial HTU plant

oxygenated fuel and it has significantly low combustion heat than those of petroleum-based fuels. Figure 3.5 shows the procedures for isolation of aqueous liquefaction products. Direct liquefaction involves hydrothermal route to produce liquid tars and oils including condensable organic vapors (Demirbas 2007). Indirect liquefaction can have successive production of synthesis gas or ethylene intermediates, and the
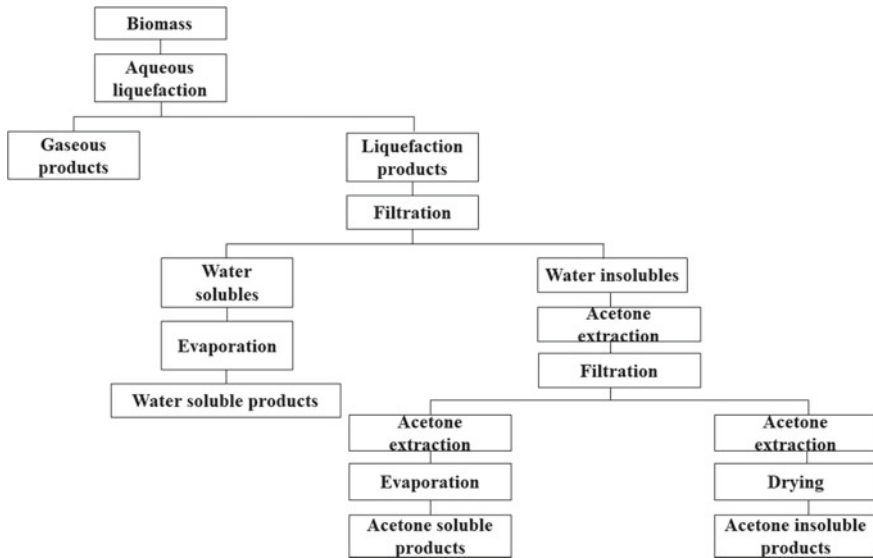
Fig. 3.5 Procedures for separation of aqueous liquefaction products (Demirbas 2009a, b)
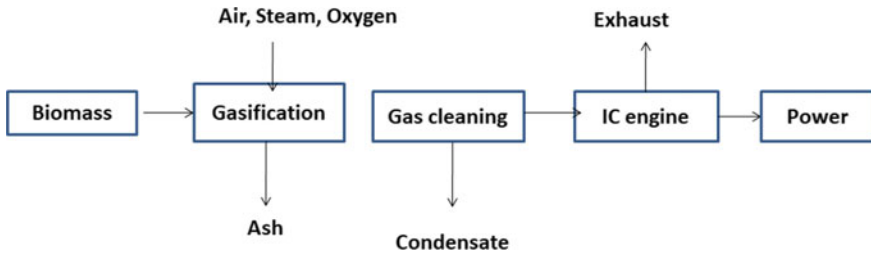
Fig. 3.6 Flow-chart for biomass gasification process

formation of liquid fuels through Fischer–Tropsch processes in the presence of catalysts. In this context, the degradation of biomass proceeds through depolymerization and deoxygenation to produce smaller products.

Biomass gasification technologies are based upon the partial oxidation or partial combustion principles, resulting in the production of hot, dirty, low heating value containing gaseous products (Chen et al. 2004; Warnecke 2000). Biomass integrated gasification combined cycle cogeneration technology is not yet commercially available as this process has several limitations including the source of insufficient energy and release of unwanted gaseous products into the atmosphere (Stevens 2001). The system for power production by means of biomass gasification is given in Fig. 3.6 (Demirbas 2009a, b).

3.2.2 Catalytic Conversion Processes of Biomass to Bioenergy

There has been significant interest continuously to produce sustainable energy, fuels for transportation, and valuable chemicals from renewable resources (Hao et al. 2005). This interest stems from the sincere efforts of researchers to address the problems associated with climate change, job creation, sustainability, energy independence and national security. Among the processes those are envisioned for the conversion of biomass into value added products are strongly dependent upon nature of catalysts. The stability, activity, and selectivity of the catalysts play a critical role in the process economics of biomass conversion methodologies.

In general, there are three types of feedstocks recognized from biomass that are suitable for the generation of renewable fuels (Yung 2016): (i) starch related (including sugars), (ii) triglycerides, and (iii) lignocellulosic materials. As shown in Fig. 3.7, the representative chemical structures for triglycerides and starches are compared to that of cellulose (lignocellulosic biomass). Starchy feedstocks contain glucose polysaccharides linked by aglycosidiclinkages (amylaseandamylopectin). Trigylderide feedstock consist of fatty acids and glycerol derived from the sources of both plants and animals, various vegetable oils, waste oil products, and algal
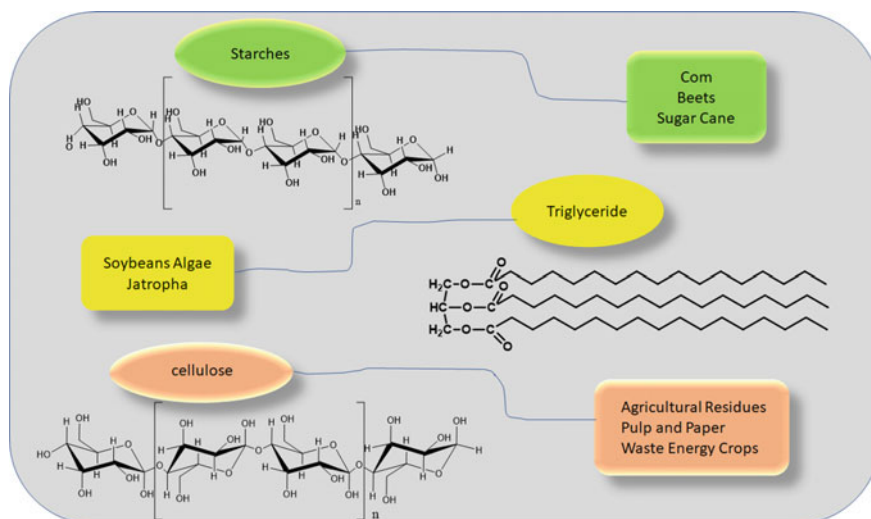
Fig. 3.7 Chemical structure of biomass feedstocks

sources. The most abundant lignocellulosic biomass is a combination of three different fractions: lignin, hemicellulose, and cellulose (Alonso et al. 2012).

First generation biofuels (i.e. alcohols-bioethanol and oils-biodiesel) are readily available and can be derived from the well-refined conventional technologies using food crops. The main challenge in current research for the generation of biofuels is the optimization of processes to reduce cost, but not the development of new technologies. The production of bioethanol begins with the pre-treatment of biomass to produce sugar monomers, such as glucose, that can be converted into ethanol by fermentation using various microorganisms (e.g., yeast, bacteria etc.). The purification of ethanol obtained is done by distillation for the further use as an additive or a direct fuel. The second generation bioethanol is derived from the feedstocks of lignocellulosic biomass. The limitation in the utilization of lignocellulosic biomass is pre-treatment and hydrolysis for the production of sugars. These steps are regarded as the greatest disorder to economic feasibility of various strategies involved in the production of sugars from lignocellulosic biomass. Algae crops have been considered as third generation biofuels as they possess a sustainable source of feedstocks for bioethanol and biodiesel. The second most abundant renewable liquid fuel is biodiesel prepared by using a variety of basic (Kim et al. 2004; Di Serio et al. 2006; Granados et al. 2007) or acidic catalysts (Lotero et al. 2005; Melero et al. 2009), and has been used in current engines with a wide range of blends the preparation is outlined schematically in Fig. 3.8. Normally canola. sunflower, palm, soybean and rapeseed oils are useful as food oils, but they are expensive. Currently the biodiesel research is mainly focused on the development of new catalytic processes that makes the use of low quality or waste oils (used oils), such that biodiesel production becomes less expensive and does not directly involve with the food supply (Liu and Zhang 2016).
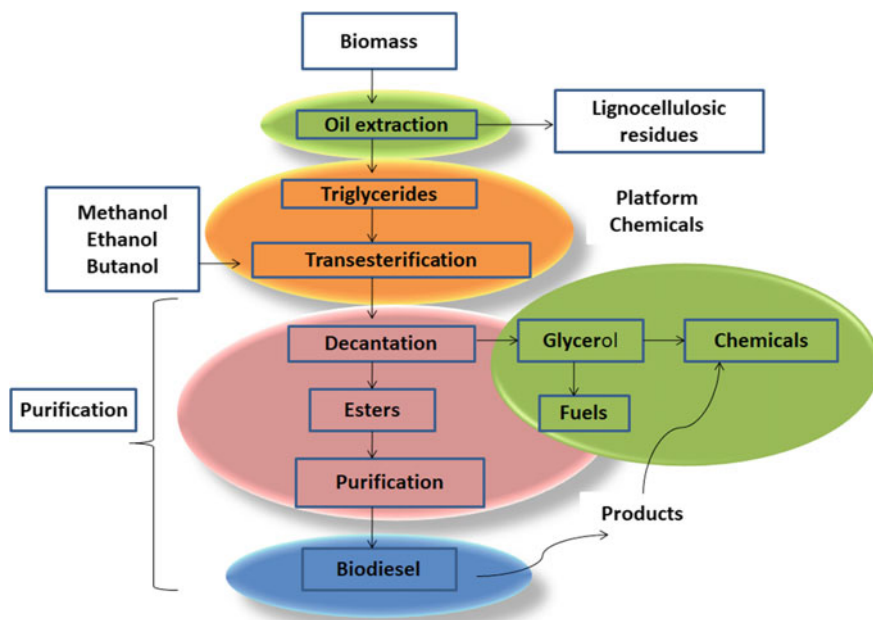
Fig. 3.8 Process schematic: biodiesel production

3.2.3 Biochemical Processes

It is well-known that micro-organisms are regarded as biochemical "factories" and can convert the biomass to ethanol. Further, the microbial technology has been developed different fermentation processes (aerobic and anaerobic) to produce biogas and fertilizers (Bisio et al. 1997). The production of methane from manure (human and animal) can be achieved by anaerobic reactors and the crop residues by employing mixed methanogenic bacterial cultures at optimal temperature ranges for the appropriate growth. Under the suitable conditions, about 90% of the feedstock energy content can be converted by the bacteria into biogas (around 55% of methane) and the sludge produced is absolutely non-toxic and odourless. Anaerobic digesters of various types were widely used in the form of biogas plants as ideal candidates for rural villages. The efficiency of bio-conversion processes strongly depends on construction defects, the rate of bacterial growth, the digesters requirements for water, mixed nature of the bacterial population and maintaining the optimum nitrogen ratio of the medium. Modern designs in the recent past have solved many of these problems associated with the digesters. Methane gas can be produced through anaerobic digestion in landfills by the microbial decomposition of the organic matter in refuse. Landfill-generated gas is on average half methane and half carbon dioxide and the production does not require high pressure.

The production of ethanol by well-developed fermentation technologies has been remarkable as a petroleum substitute and fuel enhancer, and beneficial in view of both economic and environmental fronts. The most common feedstock is sugarcane by "Biostil" process in developing countries, due to its high production value. The following section comprehends the techno-economics of biofuels and is further categorized into three sub sections, wherein the first section comprises the effect of biofuels on direct emission followed by the second section bears the impact on greenhouse gases and the last section outlines the economics of biofuel market.

3.3 Environmental and Economic Impacts of Biofuels

In 1997, an international summit held in Kyoto, Japan identified combustion of hydrocarbon fuels as the dominant factor enhancing the concentration of Greenhouse gases (GHG) which induces global warming. Till date numerous measures have been taken by various governments and protection agencies to control emissions. However, the environmental impacts of biofuels have been a growing concern around the world. For these reasons, it is important to clearly understand the environmental and also the economic impact of biofuels. The direct emissions, which are incurred due to the production and consumption of the biofuels, would be discussed here.

3.3.1 Direct Emissions

In last three decades, there have been extensive investigations carried out to evaluate the emission characteristics of biodiesel fuel in different types of compression ignition engines vis-a-vis fossil diesel. Usage of biodiesel in a conventional diesel engine substantially reduces the emissions of unburned hydrocarbons (UBHC), carbon monoxide (CO), and smoke emission. However, biodiesel generally tends to increase the oxides of nitrogen (NO_x) emissions. Similar trends are reported by McCormick et al. (2001) and Anand et al. (2009) in their investigations. Biodiesel operated diesel engines significantly lowers the soot/particulate emissions due to the presence of fuel bound oxygen and absence of sulfur and aromatic constituents. Table 3.2 provides the detail of investigations concerning the variety of neat biodiesel and/or their blends with fossil diesel using single and multi-cylinder engines.

Graboski and McCormick (1998) identified the following important causes for biodiesel-NO_x formation, changes in spray and ignition characteristics, absence of soot particles and variation in fuel chemistry. It can be summarized that the NO_x emission with neat biodiesel remains higher than fossil diesel, and composition of biodiesel plays a significant role in altering fuel property characteristics affecting the NO_x emission. Various strategies such as optimization of the injection parameters, recirculation of exhaust gases, blending methanol/ethanol in biodiesel, water-in-oil emulsions, hydrogenating biodiesel, etc. are used for mitigating the biodiesel-NO_x

Table 3.2 Impact of biodiesel and their blends on diesel emissions

Investigator(s)	Fuels	Engine type	Remarks
Ali et al. (1995)	Soybean, 10, 20, 30, 50 and 75% blends	Detroit 206 kW and Cummins 298 kW diesel engine	Exhaust emissions except NO_x reduced with increase in biodiesel blend percent for both the engines
Monyem and Van Gerpen (2001)	Soybean and 20% blend	Four cylinder, DI, turbocharged	Exhaust emission such as HC, CO and smoke reduced, NO_x increased up to 14%
Dorado et al. (2003)	Waste olive oil	Three cylinder, DI, 34 kW @ 2250 rpm	8.5% lower fuel consumption with 58.9% lower CO, 37.5% lower NO
Silva et al. (2003)	5 and 30% blends of oleic sunflower	Six cylinder, turbocharged, 180 kW @ 2200 rpm	Decrease in CO at full load and idle condition, a slight increase in NO_x and lower smoke opacity
Canakci (2005)	Soybean and 20% blend	Four cylinder, DI, turbocharged, 57.1 kW @ 2100 rpm	Neat soybean resulted in 42.5% lower HC, 18.3% lower CO, 11.2% higher NO_x, 61.5% lower smoke
Haas (2005)	Neat Soybean oil soap-stock and 20% blend	Six cylinder, turbocharged, DI, 257 kW @ 1800 rpm	50% lower HC, 45% lower CO, 10% higher NO_x, 70% lower PM for neat biodiesel, 20% blend results in similar HC, CO, 20% lower PM, 1.5% higher NO_x
Usta (2005)	10, 17.5 and 25% Tobacco seed oil blends	Four cylinder, IDI, turbocharged	Lower CO emissions and slightly higher NO_x at full load
Lin and Lin (2006)	Soybean	Four cylinder, NA, DI	Lower CO and higher NO_x emissions
Szybist et al. (2007)	Soybean, 20% blend, 10% methyl oleate and 80% diesel	Single cylinder, naturally aspirated, DI	Biodiesel-NO_x penalty is attributed to the inadvertent advance in injection timing (0.9 deg.CA)

<div align="right">(continued)</div>

Table 3.2 (continued)

Investigator(s)	Fuels	Engine type	Remarks
Dudaa et al. (2018)	swine lard and turkey lard with mixtures of rapeseed oil/diesel	Turbocharged, CRDI engine with Euro 4 complaint	A significant reduction in exhaust gas emissions such as CO and HC was observed with an increase in NO_x emission (~7%) for both the animal origin biofuels
How et al. (2018)	B20 and B50 of coconut oil biodiesel blends	Four cylinder, turbocharger CRDI diesel engine	Significantly lower NO_x level (<100 ppm) is claimed by retarded start of injection (SOI) for both the fuel blends with triple injection strategy
Rajkumar and Thangaraja (2019)	Diesel, karanja, coconut biodiesel and their blends, hydrogenated karanja samples	Four-cylinder, turbocharged diesel engine	NO emission is found to decrease with increasing fraction of coconut in the biodiesel binary blends

penalty. Blending alcohols namely methanol, ethanol and butanol with biodiesel helps biodiesel-NO_x control due to their cooling effects because of high latent heat of vaporization. Several investigations on multi-cylinder engines using biodiesel-methanol blends reported reduction in NO_x with penalties in fuel consumption, CO, UHC, aldehyde emissions (Cheng et al. 2008). Research works concerning alcohol blending with biodiesel are summarized in Table 3.3.

As discussed, the favorable physicochemical properties result in lowering the engine exhaust emissions. For a compression ignition engine, the oxygenated diesel fuel blends have a potential to decrease the PM generation during the combustion process. The presence of fuel bound oxygen (refer Fig. 3.9) in biofuels enhances the oxidation process and thus relatively lowers the hydrocarbon, carbon monoxide and soot emissions than the fossil fuels.

Meanwhile, for a spark ignition engine, the blend of alcohol assist in reducing knock tendency, carbon monoxide and unburned hydrocarbon emissions (Yusri et al. 2017). A considerable amount of literature highlighted that the emissions of methanol or ethanol blends in internal combustion engines have yielded a considerable reduction in NO_x, Smoke, HC and CO emissions with an increase in BSFC. Thus it can be concluded that aliphatic alcohol family (methanol, ethanol, propanol and butanol) are capable of reducing harmful engine exhaust emissions, however, at the expense of lower engine performance characteristics.

Table 3.3 Investigations on biodiesel-NO_x control using alcohol blends

Authors	Engine and fuels	Merits	Demerits
Cheng et al. (2008)	Four-cylinder, naturally aspirated diesel engine. Waste cooking biodiesel blended with methanol (10% by vol.)	The brake specific CO_2 drops by 2.5% and 5% reduction in NO_x with methanol addition	Higher fuel consumptions with methanol blends
Cheung et al. (2009)	Four-cylinder, naturally aspirated diesel engine. 5, 10 and 15% by vol. of methanol in waste cooking oil biodiesel	With increase in the proportion of methanol, NO_x and PM emissions decreased and are less than those of the diesel	Higher fuel consumptions, CO, HC, formaldehyde and acetaldehyde emissions with methanol blends
Qi et al. (2010)	Single-cylinder, naturally aspirated diesel engine. Soybean biodiesel 50%+ diesel 50% (BD50) as baseline fuel. 5 and 10% vol. of methanol in BD50 (BDM5 and BDM10)	At higher loads, the combustion parameters of BDM5 and BDM10 are higher than BD50.BDM5 and BDM10 reduced the smoke	The performance characteristics of BDM5 and BDM10 are slightly lower than BD50. NO_x and HC emissions are almost similar for BDM5 and BDM10 compared to those of BD50
Yilmaz (2012)	Two-cylinder, naturally aspirated DI Diesel operated with blends of waste cooking biodiesel 85 and 15% alcohols (methanol and ethanol)	The biofuel blends reduced the NO emission compared to fossil diesel, however increased the CO and HC emissions	Ethanol blended biofuel is prominent than methanol blends for enhanced engine performance and lowering the emissions
Yilmaz and Sanchez (2012)	Two-cylinder, naturally aspirated DI Diesel, waste cooking biodiesel, ethanol, methanol and diesel blends	Methanol blends are effective in lowering the CO and HC emissions, whereas NO is controlled via ethanol blends	Biodiesel-methanol diesel blends show a higher brake specific fuel consumption than biodiesel ethanol diesel blends

It is also important to recognize the greenhouse gas emissions (GHG) of biofuels during its life cycle period. European council has proposed a 35% reduction in GHG emissions as the sustainability criterion for biofuels relative to fossil fuels. Carbon dioxide being one of the primary greenhouse gases is produced not only during consumption/combustion of a biofuel, but also during cultivation, processing and transportation. This indirect CO_2 production is associated with energy inputs in these processes and inherent nature of the processes involved. During its life cycle biodiesel
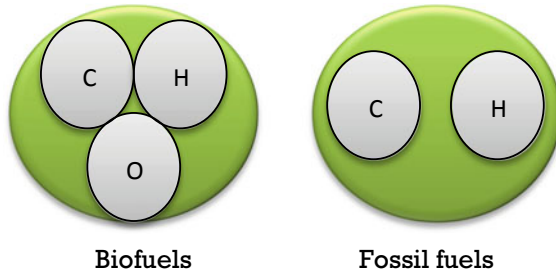
Fig. 3.9   The chemical composition of biofuel and fossil fuels

possess a significant GHG reduction potential relative to fossil diesel. The values of GHG reduction potential arrived by various authors are provided in Fig. 3.10. The result variation could be attributed to the choice of feedstock, selected region for cultivation and the co-product allocation or displacement methods adopted. However all the samples abide by the sustainability mandate of European Union as seen in Fig. 3.10.

GHG emissions are not always produced directly from the process but released during the upstream of energy transfer processes. For example, electricity used by mechanical stirrer in the transesterification process is acquired from thermal or hydro-electric power plant, thus the electricity consumed can be related to the amount of CO_2 released in the particular plant. Also the oil extraction method, esterification process and the fertilizer production are the major source of GHG emissions. Ethanol production from sugarcane is energy efficient than from sugar beets, sweet sorghum, palm or vegetable oils, especially when bagasse is used in the process of generating
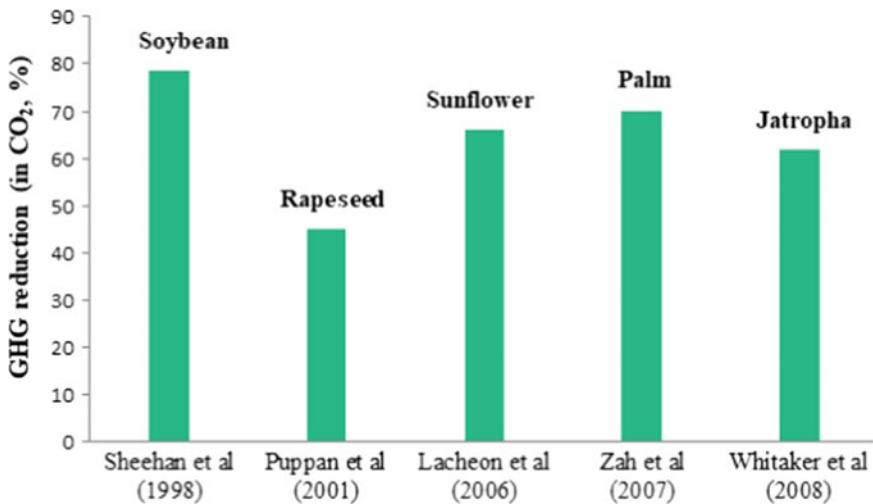
Fig. 3.10   Maximum reduction in greenhouse gas with various biodiesel fuels

heat and power. A study conducted by Khatiwada et al. (2016) has analyzed the sustainability of ethanol production from sugarcane molasses in Indonesia and reported a reduction of greenhouse gas emission (~67%) compared to the fossil fuels, whereas Brazilian sugarcane bioethanol exhibits some of the highest greenhouse gas (GHG) savings. To summarize the direct emissions, namely, the emissions associated with the biofuel production and its consumption is less carbon intensive than their counterpart viz. fossil fuel. It is crucial to consider the indirect emissions, which refer to emissions from changes induced during cultivation of energy crops and to emissions from changes induced in the oil market. One such potential effect is the indirect land use change (ILUC) and will be discussed briefly to rate the overall emission perspective of biofuels.

3.3.2   Indirect Emissions

Indirect land use change (ILUC) emissions occur when forest and grass lands are converted to cropland to meet the demand for goods displaced by the production of biofuel feedstock (Plevin et al. 2010). Thus alternate field of arable land has to be looked for to meet the rising demand for food and animal feed. The associated change of land use causes an increase in the monetary value of agricultural land and CO_2 emissions, a process known as indirect land use change. Further, this process will cause the conversion of non-cultivable land that tends to be carbon-rich into relatively carbon-poor agrarian land (Rajagopal et al. 2011). Table 3.4 provides the ILUC estimates by California Air Resources Board (CARB 2009).

Hence, ILUC is one of the primary potential greenhouse gas (GHG) sources in life cycle analysis of biofuels and also has become a central issue in the ongoing food-versus-fuel arguments. In countries like Brazil and Malaysia where palm oil is a major biodiesel feedstock, plantations are being grown through deforestation. This has raised major concerns around the world about these practices. Such plantations destroy local ecosystems and endanger many species of flora and fauna. Tough the direct emissions from biofuel are claimed to be advantageous; the overall scenario considering the indirect emissions is alarming. Although biofuels present an opportunity for renewable energy production, significant land-use change resulting from biofuels may contribute to negative environmental, economic, and social impacts (Transport & Environment 2016).

Table 3.4 Indirect land use change for biofuel production (CARB 2009)

Biofuel feedstock	ILUC (gCO_2/MJ)
Corn ethanol	30
Sugarcane ethanol	46
Soybean biodiesel	62

3.3.3 Economic Impacts

It is also important to study the economic potential of biofuels, which demands techno-economic analysis on their production method and refinery process. Further, economics plays a major role in promoting a biofuel for its application and sustenance. The production costs of biofuels tend to vary widely based on the chosen feedstock, adopted conversion process, scale of production and also the area of cultivation. Among these parameters, the cost of feedstock (up to 90% of the total costs) plays a major factor in determining the overall costs of the biofuel.

3.3.3.1 Ethanol Fuel

Ethanol is the low cost, high octane fuel additive available to gasoline operated systems. Environmental protection agency has approved the usage of E15 and concomitantly the auto makers are extending their warranty coverage for the new vehicles. Minimum ethanol selling price (MESP) is the cost of ethanol required for a zero net present value for the project when the cash flows are discounted at 10% real-after tax (Eggeman and Elander 2005). The National Renewable Energy Laboratory (NREL) projected a representative MESP value of 0.57 US$/L in 2011. A study conducted by Gubicza et al. (2016) has claimed the MESP value ranging between 0.50 and 0.62 US$/L. Some of the significant contributors to the MESP of ethanol include the cost of the feedstock (23–28%), capital cost (40–49%), the ethanol yield, and the cost of enzymes (Chovau et al. 2013). Also the production costs of ethanol from sugarcane in Brazil have declined continuously over the last three decades. Inclusion of co-products like the excess power generated could be sold to the main power grid for further cost benefits.

3.3.3.2 Biodiesel Fuels

Several research works have been carried out to analyze the economic requirements of producing biodiesel fuels (Zhang et al. 2003; Marchetti et al. 2008; Apostolakou et al. 2009). In general the production cost of biodiesel is higher than diesel and most of the studies has emphasized that the higher cost of source material/feedstock is creditworthy for the biodiesel production, with waste cooking biodiesel being an exception. Graboski and McCormick (1998) recommended accounting for the credit benefits from glycerol to reduce the production cost of biodiesel. The distribution of production cost of palm biodiesel for a plant capacity of 143 million liters is provided in Fig. 3.11.

Explicitly, the feedstock cost is predominant and with an economic return on glycerol, the choice of larger plant has lowered the price to 0.82 $/liter.

Fig. 3.11 Production cost of palm biodiesel Demirbas (2009a, b)

- Capital costs
- Feedstock
- Methanol
- Other
- Glycerol credit
- Distribution & blending
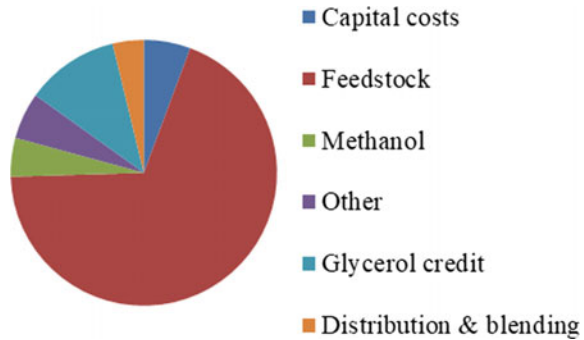
3.4   Conclusions and Future Scope

This chapter presented the various production process of biofuel from renewable biomass resources and touched upon the economics of biofuel and their environmental impacts. In conclusion, biofuel production is set to rise in a drastic manner, considering the rise in human population and demand for energy security. While these favor the government revenues as an indigenous resource and create jobs, consequently there are a number of environmental concerns. Like the indirect or non-regulated emissions need to be monitored carefully and assessed precisely for biofuel sustainability. Sustainability plays a major role in ensuring advanced biofuels are available for end-users. Biofuels are measured against the broad claims of sustainability "to meet the requirements of the existing populations without negotiating the ability of future generations to satisfy their own requirements". These claims constitute to the following;

 (i)   Climate safety and proper land usage,
 (ii) Societal subjects such as jobs and community well-being,
 (iii) Economical profitability in the existing and future viable environment,
 (iv) Advancement in technology along with sustainable standards and
 (v)   Reassuring government plan for offering a smooth legislative agenda.

Apprehensions over the effect of GHG emissions on the climate change have encouraged looking for long-term approaches for producing biofuels from sustainable sources. In many countries biofuels are being produced from their major agricultural products. For example, Malaysia's biofuel policies are biased towards palm biodiesel production. In a long run, this scenario has adverse effects on the environment and sharp rises in food prices especially edible oils. Thus the chances and options relating to biofuel production vary considerably between different countries. Thus the future scope is to regulate the biofuel production process, explore for alternative feedstock, flex crops and adopt multi-functionality of lands. The capability to reduce greenhouse gas emissions by limiting the carbon capacity of biofuels can also be pursued. Further only through the mutual effect of various government agencies and biofuel industries, the market price of biofuel could be affordable in par with the fossil fuels.

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Chapter 4
Second Generation Bioethanol Production from Organic Waste

Tomesh Kumar Sahu, Satyajit Gupta and Pravesh Chandra Shukla

Abstract Increasing global urge to decrease fossil fuel dependency, and better control of pollution needs the development of alternative energy resources like biodiesel, alcohols etc. Use of organic waste as feedstock for biofuel production is an innovative approach to solve the waste management problems, fossil fuel dependence, greenhouse gas (GHG) emissions and most importantly prevent the nation's economy from global oil price fluctuations. Rice paddy straw is an attractive lignocellulose material for bioethanol production since it has several features, such as elevated content of cellulose and hemicellulose, which can readily be hydrolysed into fermentable sugars. Further fermentation can be done to produce ethanol from the hydrolysed intermediate product. The ethanol production process using rice paddy straw involve mainly the preparation of raw material which is known as pre-treatment (physical or chemical pre-treatment) and fermentation. One of the key challenges in implementing bioethanol production from rice paddy straw is the choice of a suitable pre-treatment method. Moreover, India is an agricultural based country where rice is one of the major product. Utilization of rice paddy straw as a biofuel may result in saving of significant foreign exchange for the country and also reduce environmental concerns.

Keywords Bioethanol · Lignocellulose · Organic waste · Rice paddy straw · Pre-treatment · Fermentation

4.1 Introduction

The global fuel crisis in 1973 and 1979 give rise to awareness amongst many nations for the development of alternative fuel sources for its utilization in compression ignition (CI) engines (Hansen et al. 2005). Biodiesel and alcohol-based fuel were

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considered as the potential alternative fuel for mineral diesel and gasoline. These fuels are derived from biomass and have inherent oxygen content. Alcohol-based fuels has emerged as a strong alternative, which are derived by fermentation of organic materials. It can be used as a full or partial replacement of gasoline and diesel both. Due to the technological difficulties, these are being used as blend at present. Ethanol and diesel blends were thoroughly investigated and found suitable for engine application, however production cost of alcohol was higher compared to gasoline and diesel which limited its application in past. Major advances in engine technology have occurred over the last couple of decades, leading to greener fuel economy, reduction in engine emissions and manufacturers are trying to meet regulatory requirement has become a major factor (Thipse 2010). As a result of above development, alcohol-based fuels showed a great potential in current scenario. This chapter review about the production of ethanol from organic waste, feedstock availability and methodology involved for production. Also, ethanol yields for different substrates by various microorganisms as a fermenting agent has been compared.

4.2   History of Ethanol as a Fuel

Henry Ford has devised an engine in 1908 capable to run with pure ethanol named as Model T, and he quoted it as 'The fuel of the future'. During 1920 and 1930s, US Ethanol program promoted to use ethanol in motor vehicles however this attempt failed due to certain reasons. Increased environmental concerns and sudden limitation in the crude oil supply during 1980s led to the research and utilization of ethanol in transportation (Thipse 2010). Also, concerns of hazardous effect of Lead (Pb) booted the it further (Thipse 2010). A blend of 10% ethanol in gasoline E10 was commercially introduced in the Midwestern state of US (Hansen et al. 2005). U.S. government also increased tax exemptions for ethanol-gasoline blend utilization in vehicles during 1982 and 1984. During the time, Research and development are promoted to develop the E85 vehicle which will use the 85% ethanol and 15% gasoline. In 1990, amendments to The Clean Air Act required the inclusion of fuel oxygenates that promote efficient and cleaner combustion in gasoline propelled vehicles (Saunders 2015). Under the Act, methyl tert-butyl ether (MTBE) was chosen in place of Lead (Pb) which again found to be toxic and infectious (Saunders 2015). Further, MTBE has been replaced with ethanol, which creates an immediate demand for ethanol close to 3.5 billion gallons (Saunders 2015). This caused an ethanol price hike and greatly accelerated investment in ethanol production capacity. It resulted in ethanol production in the U.S. grew from 175 million gallons in the 1980s to 1.4 billion gallons in 1998 (Thipse 2010). Nowadays the use of ethanol with different blend ratio into diesel was a subject of research for its effective utilization. E10 and E15 and M15 are some alcohol bend in diesel, which are mostly in their optimized stage for its utilization in compression ignition engine.

In context of India, Indian government has already introduced 10% blend of ethanol in commercial gasoline available at outlets. It has been reported that Bureau

Table 4.1 Physico-chemical properties of mineral diesel and ethanol (Xing-Cai et al. 2004; Zhang et al. 2011)

	Diesel	Ethanol
Chemical formula	$C_{10.8}H_{18.7}$	C_2H_5OH
Mole weight (g)	148.3	46.1
Density (g/cm^3 at 20 °C)	0.84	0.789
Boiling point (°C)	180–330	78
Heat of evaporation (kJ/kg)	280	856
Lower heat value (MJ/kg)	42.5	27.0
Liquid viscosity (cP at 20 °C)	3.03	1.20
Surface tension (mN/m at 20 °C)	34.1	28.9
Flash point (°C)	78	13.5
Stoichiometric air-fuel ratio	14.4	9
Cetane number	45	5–8
Auto-ignition temperature (°C)	235	363
Carbon content (wt%)	87.4	52.2
Oxygen content (wt%)	0	34.3

of Indian Standards is also finalizing the scope for 20% ethanol utilization as a blend in gasoline (Sakthivel et al. 2018). There are attempts to use pure alcohol in ED95 engine also which run for a long time as passenger buses in Brazil and Sweden. Several researchers are currently working on the development of CI engines which be run with pure alcohols (Scania Group, https://www.scania.com/group/en/scania-is-ready-for-the-rise-of-ethanol/; Janssen 2010).

4.3 Fuel Properties of Diesel and Ethanol

Table 4.1 shows the physico-chemical properties of mineral diesel and ethanol. It should be noted that ethanol has much lower calorific value and higher auto-ignition temperature compared to diesel fuel. Concerning to the application of ethanol in compression ignition engines, auto-ignition quality is an important parameter which affects the combustion and increases the ignition delay. Also, ethanol tends to show the cooling effect during combustion as it have high heat of evaporation.

4.4 Generation of Biofuels

In recent decades, exponential growth in the transport sector has significantly increased fossil fuel use. This led to research and commercial use of alternative fuel resources, mainly for the motor vehicle industry. As liquid fuels like gasoline and mineral diesel are the basis of the transportation sector, global attention
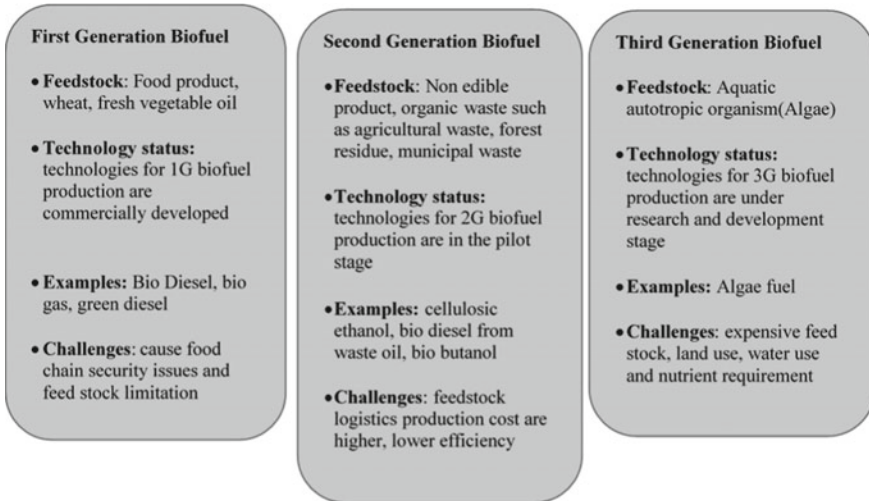
Fig. 4.1 Generations of biofuel (Stephen and Periyasamy 2018)

has gained from liquid biofuels. Biofuel uses provides a solution for energy security, emission control and improvement in society. Biofuel evolution can be divided into three generations. First generation biofuel production includes raw materials like corn, wheat, cassava (Edible food sources), etc. (Bhojvaid 2006). Which are in direct relation to food security issues and feedstock limitations. The biofuel of the second generation includes non-edible sources of food, Lignocellulose material such as agricultural residue, forest residue, and municipal solid waste. Advantage of Lignocellulose materials are, it is renewable, low cost of feedstock and it is abundantly available. Most of the technologies for second-generation biofuel production is in the research stage. Third generation biofuel production includes its production from sea-based plants like algae. Global bioethanol production from organic waste is approximately 1391 million liters per year out of around 118 billion liters per year of total global production (Howe et al. 2017). Figure 4.1 Shows a generation structure and relevant techniques and issues for biofuel generation.

4.5 Feedstocks Availability

There is a broad range of organic waste materials used to produce biofuels that shows sustainable biofuel potential opportunities. Organic waste material includes waste from the kitchen, garden, forest, lignocellulosic materials, agricultural waste, farm, animal waste, and municipal organic waste, etc. (Mahmoodi et al. 2018).

The availability of organic waste can differ from location to location. Feedstocks consisting of organic fractions of municipal waste are economical and easily available options in metropolitan regions, while agricultural waste and other green waste are appropriate for the production of biofuels in village areas. Forest and other lignocellulosic residues are significant choices in areas where the production of wood is common due to their easier accessibility and reasonable costs. Availability and costs of feedstock are therefore key factors in the production of biofuels in different regions of the world. The Four major agricultural waste which is rice straw, wheat straw, corn straw, and bagasse are most favorable feedstocks for bioethanol production due to their high cellulose and hemicellulose content and its availability. Chemical composition of agricultural waste are given below in Table 4.2.

Table 4.3. shows the worldwide availability of agro-waste, Asia is the main producer of rice straw and wheat straw, while bagasse and corn straw are mostly produced in America. The worldwide potential of ethanol production from these four agro waste is about 419 billion liters annual, rice straw can produce about 205 billion liters annual, which is highest among other agricultural waste and 104 billion liters is from wheat straw (Fig. 4.2) (Sarkar et al. 2012).

India is a major rice producing country and rice straw is one of the abundant source available throughout the country for the production of ethanol which can be a potential candidate for alternative fuel source as biofuel. Paddy cultivation in India is happening over 43.95 million hectares producing about 106.54 million tons of rice and approximately 160 million tons of straw with a ratio of 1:1.5 for rice grain produced to straw produced (Chandra et al. 2017). The yielding potential of ethanol from rice paddy straw is about 300 L for 1000 kg of paddy. On the other hand, the burning of rice paddy straw is a major problem which can be reduced by using it for ethanol production (Chandra et al. 2017).

Table 4.2 Chemical composition of agricultural waste (Sarkar et al. 2012)

Substrate	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Protein (%)	Ash (%)
Rice-straw	32–47	19–27	5–24	–	12.4
Wheat straw	35–45	20–3-	8–15	3.1	10.1
Corn stover	42.6	21.3	8.2	5.1	4.3
Bagasse	65 total carbohydrate		18.4	3	2.4

Table 4.3 Quantities of wasted crop and lignocellulosic biomass (million tons) potentially available for bioethanol (Kim and Dale 2004)

Crop waste	Africa	Asia	Europe	America
Rice-straw	20.9	667.6	3.9	37.2
Wheat straw	5.34	145.20	132.59	62.64
Corn stover	0.0	33.90	28.61	140.86
Bagasse	11.73	74.88	0.01	87.62

Fig. 4.2 Worldwide ethanol potential from agricultural waste in billion liters (Sarkar et al. 2012)
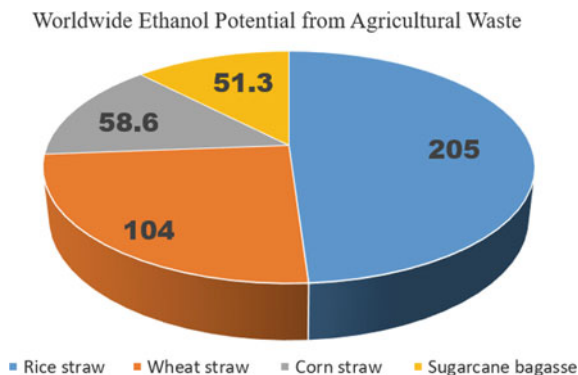
4.6 Bioethanol Production from Lignocellulose Material—Pre-treatment, Hydrolysis, Fermentation

Lignocellulose material includes primarily cellulose, hemicellulose, and lignin. Cellulose is linear and crystalline, hemicellulose is a short and highly branched polymer, and lignin is hydrophobic and it binds tightly to carbohydrate polymers (Sarkar et al. 2012). Bioethanol production from lignocellulose material mainly performed through three major operations pre-treatment, which is essential to release cellulose and hemicellulose before hydrolysis. Further hydrolysis of cellulose and hemicellulose is performed to produce fermentable sugars, which includes glucose, xylose, etc. and fermentation of reducing sugars is performed, to convert it into ethanol (Sarkar et al. 2012). Once the fermentation is completed, a distillation of fermented juice is performed to separate ethanol, for the complete process it will take 6–7 days.

Rice straw has a number of features, making it the potential feedstock for the production of fuel ethanol. There is a high content of cellulose and hemicelluloses which can easily be hydrolysed into fermentable sugars. The theoretical ethanol yield for rice straw is shown in Table 4.4 with respect to the chemical composition Cellulose (38%), and Hemicellulose (19.7%) (Zhu et al. 2006).

Table 4.4 Carbohydrate composition and theoretical ethanol yields of rice straw (Binod et al. 2010)

Component	Percentage
Cellulose	38.6%
Hemicellulose	19.7%
Theoretical ethanol yield (L/kg dry)	0.42

4.6.1 Pre-treatment

Pre-treatment of lignocellulose biomass is essential as it contains cellulose and hemi-cellulose that are tightly packed with layers of lignin that prevent them against enzymatic hydrolysis. For enzymatic action, pre-treatment of biomass is needed to break the lignin seal to expose cellulose and hemicellulose (Fig. 4.3). Pre-treatment is aimed at reducing the crystallinity of cellulose and hemicellulose, increasing the surface area of biomass and breaking the seal of lignin. Pre-treatment makes cellulose more available to enzymes so that the conversion of carbohydrate polymers to fermentable sugars can be accomplished more expeditiously and more efficiently (Mosier et al. 2005).

Pre-treatment of rice straw is most challenging and improvement needs to increase the sugar yielding which converts into ethanol subsequently. It can broadly be divided into two categories, mechanical and chemical pre-treatments. Mechanical pre-treatment include grinding, milling, electron beam irradiation, microwave pre-treatment, etc. whereas chemical pre-treatment includes acidic, alkali, ammonia treatment, etc. (Yoswathana et al. 2010). Yoswathana et al. (2010) have experimented for bioethanol production from rice paddy straw, while experiment they compared various pre-treatment method which includes, acidic, alkali, subcritical water treatment with or without ultrasound combination at the different operating condition. They performed acidic pre-treatment with dilute sulfuric acid, where its concentration was varied from 1 to 9% for its optimization and found that less concentration gives more sugar yielding. Also they conducted experiment for pre-treatment by varied its concentration form 1 to 5%, for that they found that very less sugar yielding compared to acidic pre-treatment shown in Fig. 4.4. They stated that dilute acidic pre-treatment
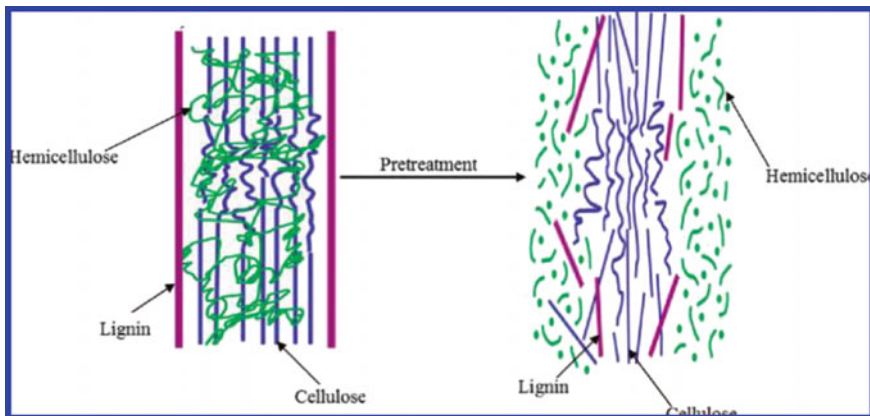
Fig. 4.3 Schematic of the role of pre-treatment in the conversion of biomass to fuel (Kumar et al. 2009)
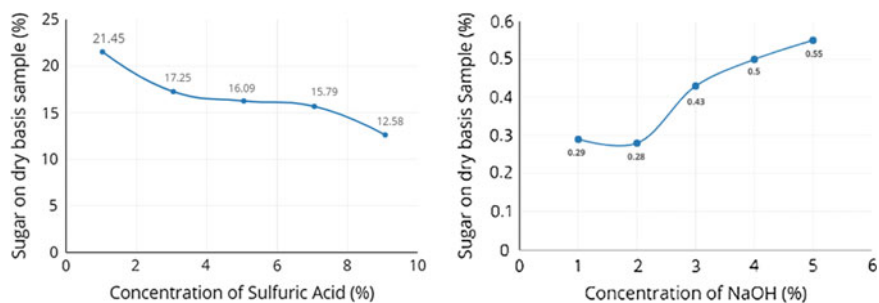
Fig. 4.4 Sugar content in acid pre-treated and alkali pre-treated rice straw (Yoswathana et al. 2010)

with ultrasonic and subsequent enzyme treatment will give better ethanol yielding after 6 days fermentation with *S. cerevisiae yeast* (Yoswathana et al. 2010).

Pre-treatment of shredded rice straw with 2% NaOH with 20% solid loading at 85°C reduces the lignin by 36% (Zhang and Cai 2008). The main effect of NaOH pre-treatment on lignocellulose material is delignification by disintegration the ester bonds cross-linking lignin, thus results in the porosity on biomass. Pre-treatment at an ambient temperature of lignocellulose with acids enhances anaerobic digestibility. Dilute acid pre-treatment predominantly affects hemicellulose with a small impact on lignin degradation (Tarkow and Feist 1969). Zhu et al. (2006) have performed microwave alkali pre-treatment, rice straw 8% (w/v ratio) is pre-treated with 1% NaOH aqueous solution in boiling condition for 30 min and followed by microwave frequency (2450 MHz) at 700 W for 30 min. They claim that it reduces lignin by 76% due to alkaline pre-treatment and crystallinity of rice straw also reduced (Zhu et al. 2006) (Fig. 4.4; Table 4.5).

Trinh et al. (2016) have investigated the effect of acidified glycerol pre-treatment for bioethanol production enhancement from rice paddy straw, they performed pre-treatment at 130–210 °C for 1–24 h with 5% solid loading they found that 190 °C for 10 h is the optimal condition for pre-treatment shown in Fig. 4.5. Furthermore, it was observed that glycerol pre-treatment with the addition of HCL to improve digestion

Table 4.5 Lignocellulose conversion to sugar and sugar yield of differently treated rice straw (Yoswathana et al. 2010)

Pre-treatment	Sugar %
Acid 1%	21.45
Acid 1%/enzyme 0.8% v/w	36.95
Acid 1%/enzyme 4% v/w	39.10
Alkali 5%	0.55
Alkali 5%/enzyme 0.8% v/w	24.60
Enzyme 0.8%	3.40
Acid 1% + ultrasonic + enzyme 4% v/w	43.93
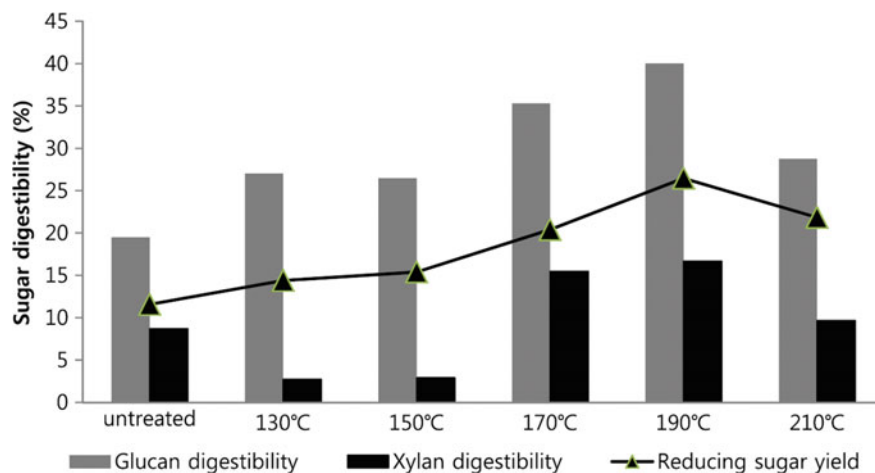
Fig. 4.5 Effect of pre-treatment temperatures on biomass conversion from rice straw Pre-treated for 10 h (Trinh et al. 2016)

of sugar. They concluded that acidified glycerol is one of the good candidates for the pre-treatment of organic waste and ethanol yield of 0.44 g/g of sugar was observed (Trinh et al. 2016).

Khaleghian et al. (2015) have investigated the effect of sodium carbonate for pretreatment of ethanol production from rice paddy straw. The optimized pre-treatment condition was 0.5 M Na_2CO_3 and 1:20 solid loading for 3 h. They found that pretreatment remove more than 90% silica from straw and improve enzymatic hydrolysis, they claim that ethanol yield was improved from 39.8 to 83.2% using Na_2CO_3 Pre-treatment shown in Fig. 4.6. They concluded that ethanol yield was improved by

Fig. 4.6 Ethanol yield of untreated and treated rice straw with 1:10, 1:15, and 1:20 g/g solid loading, with 1 M Na_2CO_3 (■) and 0.5 M Na_2CO_3 (■) (Khaleghian et al. 2015)
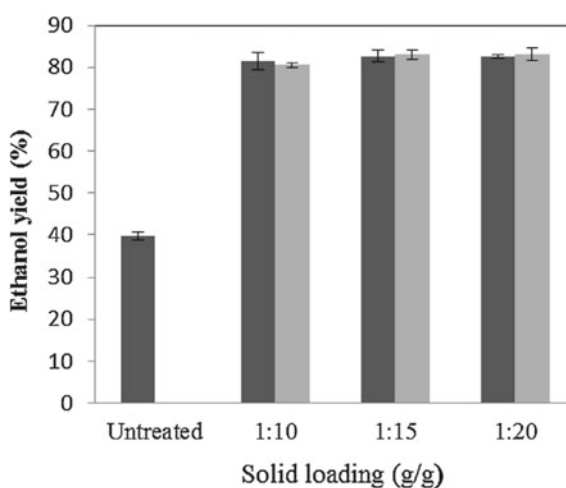
40% using *m. hiemalis* under optimum condition (Khaleghian et al. 2015). Abedinifar et al. (2009) have experimented ethanol production from rice straw using three different yeast and compare the result of hydrolysis and fermentation. For pre-treatment, they used dilute sulfuric acid which results 0.72 g/g sugar yielding during 48 h, which is comparatively higher compare to steam pre-treatment which gives 0.60 g/g sugar yielding and untreated straw which gives 0.46 g/g sugar yielding, however, increase in acid concentration decreases the sugar yielding (Abedinifar et al. 2009).

Oberoi et al. (2010) have performed an experiment to enhance ethanol production with hydrolysis and fermentation using candida trolicalis. Separate acidic and alkali pre-treatment is performed, for alkali treatment rice straw at 10% (w/v ratio) is treated with 1–5% NaOH solution in a shaker at 150 rpm, 40 °C for 1 h and autoclaved at 121 °C for 30 min they found that lignin is decreased by 47%. And for acidic pre-treatment, rice straw 10% (w/v ratio) is treated with 2% dilute sulfuric acid at 132 °C which reduces its crystallinity and makes this more suitable for enzymatic hydrolysis. (Oberoi et al. 2010).

4.6.2 *Enzymatic Hydrolysis*

After pre-treatment, Enzymatic Hydrolysis is the second step in the production of ethanol from lignocellulose biomass material. This includes cleaving of cellulose and hemicellulose polymers by enzymes. Sugar present in cellulose and hemicellulose is extracted in the solution which can be converted into ethanol through fermentation (Singh et al. 2016). Cellulose generally includes glucans, whereas hemicellulose includes several polymers of sugar such as xylan, glucan, and galactane. The primary hydrolysis product of cellulose is glucose, whereas hemicellulose leads to several pentoses and hexoses. (Taherzadeh and Niklasson 2004).

Production of ethanol also depends on the percentage of sugar recovery and type of sugar (pentose or hexose). Cellulose and hemicellulose enzymatic hydrolysis can be done by a highly specific enzyme called glycosyl-hydrolases. A complete cellulase system consists of 3 types of enzymes: 1,4-β-D-glucan cellobiohydrolases, endo-1,4-β-D-glucanases and 1,4-β-D-glucosidases. Here the first and the second enzyme breaks out the cellulose to cellobiose than the third enzyme further split it to glucose. Along with this several species of bacteria Cellumonas, Bacillus, Thermomonospora, Bacteroides, Acetovibrio, Microbispora, etc. and fungi including Trichoderma, Pénicillium, Fusar are able to produce cellulase and hemicellulases (Taherzadeh and Niklasson 2004). enzymatic hydrolysis is performed under moderate condition, temperature require for hydrolysis is 40–60 °C and the solution is to be maintained at a pH of 4.0–5.0 for its optimum enzymatic action (Taherzadeh and Niklasson 2004). Yoswathana et al. (2010) have performed hydrolysis after pre-treatment it with acid or alkali solution. Pre-treated juice is separated and the remaining pulp is mixed with distilled water (10 times of rice straw w/v ratio) containing 0.8% enzyme (with respect to rice straw w/w ratio) for its enzymatic hydrolysis. Hydrolysis is performed at 55 °C for 12 h for both acidic and alkali pre-treated biomass. After hydrolysis, they
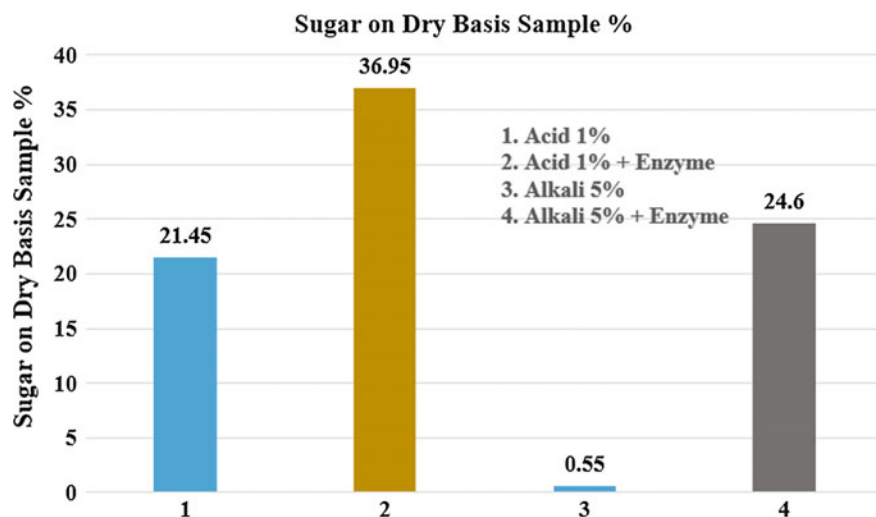
Fig. 4.7 Effect of acid and alkali pre-treatment with or without subsequent enzyme treatment to the sugar content of rice straw (Yoswathana et al. 2010)

found that sugar content present in the acid pre-treated solution is 36.9% whereas it is 24% for alkali pre-treated solution shown in Fig. 4.7 (Yoswathana et al. 2010).

Trinh et al. (2016) have performed enzymatic hydrolysis of the pre-treated and untreated rice straw in a conical tube, containing 5% biomass (w/w ratio) in buffer of sodium nitrate 0.05 M (pH 4.8), Using an enzymatic cocktail of cellulase 17.5 FPU/g, β- glucosidase 6.25 CBU/g and xylanase 25 FXU/g with 2% sodium azide. The operation was performed at 50 °C, 150 rpm for 72 h (Trinh et al. 2016). Chen et al. (2012) have performed hydrolysis of solid residue after pre-treatment it with dilute sulfuric acid. The solid residue is transferred to the hydrolysis reactor until 1% dry Matter. Over this enzyme, loading was done at 6.5 FPU/g of dry matter using a commercial cellulase, 1.5 L celluclast with filter activity of 60 FPU/ml. Hydrolysis was performed at a constant temp of 50 °C for 72 h. After hydrolysis to separate hydrolysates from lignin residue, the mixture was centrifuged at 5000 rpm for 30 min. therefor hydrolysate are kept at 4 °C before fermentation (Chen et al. 2012). Han et al. (2019) have experimented for the utilization of waste cake for ethanol production by hydrolysis and fermentation. They investigated the effect of volume of alpha-amylase enzyme on hydrolysis performance, 0.8 mL alpha-amylase per liter gives optimum result, and after 80 min of hydrolysis 44 g/L reduced sugar was obtained. They observed that 46.6 g/L ethanol produced with an ethanol yield of 1.13 g/g of reduced sugar after fermentation (Han et al. 2019).

4.6.3   Fermentation

For ethanol production from the lignocellulose material, fermentation is the third important process in which ethanol is directly produced through the metabolic activities of a fermenting agent (i.e. microorganisms, usually either bacteria, yeast or fungi). Theoretically, one kilogram of glucose and xylose may produce 0.49 kg of carbon dioxide and 0.51 kg of ethanol.

$$3C_5H_{10}O_5 \rightarrow 5C_2H_5OH + 5CO_2 \tag{i}$$

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 \tag{ii}$$
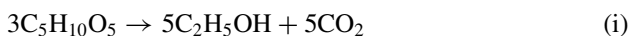
Fermentation requires specific digestive conditions, a specific temperature and pH were needed. Typically, a pH of 6.5–7.5 are essential to sustain the growth of the bacteria for fermentation types of bacteria (Hamelinck et al. 2005). The fermentive agent used to digest sugar is primarily Zymomonas, Saccharomyces cerevisiae, which converts to ethanol glucose, sucrose, pentose, and fructose. However, for their ability to convert pentose sugars (xylose), Candida shehatae, Pichia stipitis, and Pachysolen tannophilus are also recognized (Mosier et al. 2005).

Lin et al. (2012) have performed an experiment for ethanol production from rice paddy straw using Pichia-stipitis as a fermenting agent. They have performed ammonia and NaOH Hydrolysis and corresponded ethanol yield was 0.39 g/g and 0.34 g/g respectively for both cases Pichia stipitis is used for fermentation (Lin et al. 2012). Tiwari et al. (2015) have investigated ethanol production from rice- bran and comparative study has been performed for ethanol production from three different bacteria. They also experiment for process optimization by varying temperature and pH of sample for B. Cereus strain McR-3, they found that pH- 5 and Temperature 37 °C is an optimum condition for maximum Bioethanol Production (Tiwari et al. 2015).

Yoswathana et al. (2010) have experimented for bioethanol production from rice paddy straw, the yeast S. cerevisiae was used for fermentation. The initial yeast count in fermentation sample was $2–8 \times 10^8$ CFU mL-1. They concluded that dilute acidic pre-treatment with ultrasonic and subsequent enzyme treatment will give better ethanol yielding after 6 days fermentation with S. cerevisiae yeast (Yoswathana et al. 2010). Abedinifar et al. (2009) have experimented ethanol production from rice straw using three different yeast and compare the result of hydrolysis and fermentation. They also investigated the effect of variation of temperature and variation of pH during enzymatic hydrolysis, they found that best performance obtained at 45 °C and pH 5.0, For pre-treatment they used dilute sulfuric acid which results 0.72 g/g sugar yielding during 48 h, which is comparatively higher compare to steam pre-treatment which gives 0.60 g/g sugar yielding and untreated straw which gives 0.46 g/g sugar yielding, however, increase in acid concentration decreases the sugar yielding. Anaerobic digestion of the hydrolysed sugar gives 0.36–0.43 g/g ethanol

and 0.11–0.17 g/g biomass using Mucor indicus yeast and 0.33–0.41 g/g ethanol and 0.06–0.12 g/g biomass obtained using R. oryzae yeast (Abedinifar et al. 2009).

Haung et al. (2009) have experimented to enhance ethanol production from rice straw using the new strain of Pichia stipitis, initially, they dried rice straw at 105 °C to reduce moisture content and hydrolysate was performed in a twin-screw conveyer connected high-pressure reactor. 3% concentrated sulfuric acid was used for pretreatment with 50% solid loading in it and it squeezed at 40 rpm, 145 °C for 20 min to reduce solid content. Further fermentation of hydrolysate was performed using Pichia stipitis, ethanol production is about 0.44 g/g of sugar which is 87% of the maximum possible ethanol conversion (Huang et al. 2009). Table 4.6 compares the ethanol yield from various agricultural organic waste by using a different fermentive agent.

Apart from agricultural waste, industrial food waste also has the potential for ethanol production Arapoglou et al. (2010) have experimented for ethanol production

Table 4.6 Ethanol yields from various substrates by various microorganisms (Sarkar et al. 2012)

Substrate	Fermentive agent	Yield of ethanol	Feature of microorganism
Rice straw	Candida shehatae NCL-3501	0.45 and 0.5 g/g of sugar utilized produced from auto hydrolysate by free and immobilized cell in 48 h	Co-ferment glucose and xylose and utilizes ethanol in the absence of sugar
	Saccharomyces cerevisiae ATCC 26603	Maximum ethanol production achieved 4 g/L	Ferment only glucose
	Pichia stipitis NRRL Y-7124	Maximum ethanol production achieved 6 g/L (78% of theoretical maximum)	Ferment glucose first and then xylose from the mixture
Wheat straw	Pichia stipitis NRRL Y-7124	0.35 g_p/g_s Calculated as final ethanol	Adapted at increased concentration of hydrolysate
	Pichia stipitis A	0.41 g_p/g_s concentration divided by total sugar in the fermentation medium	Adapted at increased concentration of hydrolysate
Sugarcane bagasse	Pichia stipitis BCC15191	0.29–0.31 ethanol/g available fermentable sugars (glucose and xylose) after 24 h	Can ferment both glucose and xylose
	Recombinant Escherichia coli KO11	31.50 g of ethanol/L in 48 h equivalent to a theoretical maximum yield of 91.5%	Utilizes xylose and glucose present in hydrolysates
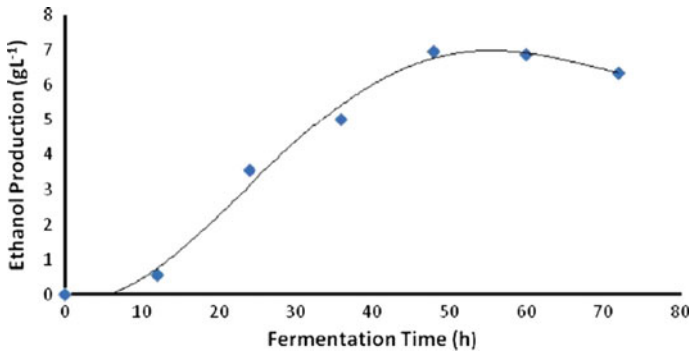
Fig. 4.8 Ethanol production (g/L) of soluble fermentable sugar from the acidic hydrolysis of PPW (Arapoglou et al. 2010)

from potato peel waste as PPW is available in a large scale from the potato processing plant, which has the potential for ethanol production as it has lignocellulose in it. For ethanol production potato peel is initially hydrolysed with enzyme than fermented with S. cerevisiae yeast. For enzymatic hydrolysis combination of three enzymes is used which is Ternamyl 0.24KNU + Viscozyme 12 FBGU + celluclast 1%. they claim that using these enzyme sugar yielding of 18.5 g/L is obtained and ethanol production after fermentation is about 7.6 g/L (Arapoglou et al. 2010) (Fig. 4.8).

4.7 Conclusion

The development of bioethanol is a potential solution to overcome global concerns about the future energy scenario in which fossil energy is constantly depleted. Bioethanol of the second generation can be produced from a wide variety of feedstocks. Bioethanol production from organic waste is very promising while maintaining minimum environmental effects and overall production costs for sustainable and economic growth. One of the primary resources for economically appropriate bioethanol production is expected to be the use of lignocellulose biomass (agricultural waste). Theoretical yields of ethanol from lignocellulose are higher. And agricultural wastes are abundantly available in nature, it is less costly and it does not require separate land, energy, and water requirements.

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Chapter 5
Biofuel Production from Agricultural Waste—An Economical Approach

Elsa Cherian and Harikrishnan Hariharan

Abstract Biofuel is an important solution to the fuel crisis which may affect the future generation. Also production of biofuel will greatly reduce the need and dependency of fossil fuels. It also can greatly reduce the environmental pollution. Different types of biofuels include bioethanol, biodiesel, biogas and biobutanol. Biodiesel is a very good replacement fuel for petroleum and also produce less toxins and a biodegradable one. Thus bioethanol is a clean gas produced through fermentation technology. High energy biofuel, biobutanol can also be produced by the fermentation of agricultural residues. All these energy rich high value fuels can be produced from agricultural wastes, which are getting wasted as such in the nature. The current chapter mainly deals with different ways in which biofuels can be produced using agricultural waste thereby making entire process cost effective and economical. This can make every country independent for biofuel production making the nature stable for future generation.

Keywords Biofuel · Agricultural waste · Bioethanol · Biodiesel · Biogas · Biobutanol

5.1 Introduction

Bio fuels are generally produced from biomass. They are strong alternatives as well as a viable source of renewable energy in contrast to overall adverse effects of fossil fuel. They include chemicals obtained from biological processes alongside chemical conversion of biomass. They were synthesized mainly using microorganisms such as photosynthetic bacteria, micro as well as macro-algae. The major types of biofuels are in liquid as well as solid form. These products are convertible by means of physical and chemical methods. Biofuels are generally grouped into primary and secondary. The primary biofuels are directly generated by burning dried green plant material. The secondary biofuels are classified into three generations which are developed

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indirectly from plant and animal sources. First generation includes ethanol derived from food crops rich in starch as well as biodiesel taken from animal fats. The second generation is bioethanol from non-food cellulosic biomass and biodiesel from oil seeds. The third generation is the biofuels from cyano bacterial, micro algae and other microorganisms.

In current decades, the energy devastation and environmental concerns have become a key problem. Industrialization caused the depletion of the fossil fuels and increase in pollutant emissions. Research has been done profusely to find an alternative fuel to satisfy the energy demand. Conventional fuels are non-sustainable and currently having various issues such as demise of natural reserves and the substantial environmental impacts. A transformation arised now to displace conventional fuels with renewable energy sources. Biomass-derived energy appears to be the most promising one (Lucian et al. 2007; Klass 1998).

5.2 Overview of Biofuels

Biofuel production widely varies depends on the type of raw material, efficiency level, production volume, surrounding situation and end-users requirement. A potential research area is clean and sustainable technologies to develop biofuels (Tilman et al. 2009). Biomass involves the vegetable matter from photosynthesis. Biomass has been used from a wide range of materials that can be converted into biofuels using conversion processes (Carlos and Khang 2008). Transportation fuels derived from bio mass can be produced from agricultural crops, ligno cellulosic crops and micro organisms (Alexander et al. 2012; Berndes et al. 2003). Conversion of biomass into liquid fuels is a major element of supply chain. A biorefinery is a facility that integrates conversion processes in converting biomass into biofuels. The bio refinery can reduce environmental impact and consume less fossil energy. The major conversion technologies can be grouped as biochemical and thermo chemical (Anex et al. 2010).

5.3 Importance of Bio Fuel

Biofuels are considered as relevant technologies by both developing and industrialized countries due to energy security reasons, environmental issues and socioeconomic issues. Various countries use biofuels due to its sustainability, less greenhouse gas emissions and biodegradability (Unal and Alibas 2007; Ilkilic and Yucesu 2008; Arisoy 2008; Lv et al. 2008; Mushrush et al. 2007). Biofuels such as bioethanol, biomethanol, biohydrogen and biodiesel generally results lower emissions. Performances and emissions studies of compression ignition engines fuelled with biodiesel performed well (Laforgia and Ardito 1994; Cardone et al. 1998).

5.4 Types of Biofuels

The term bio renewable fuel (refuel) is referred to as fuels that are produced using biomass (Chhetri and Islam 2008; Konwer et al. 2007; Najafpour et al. 2006). The production of biofuels is expected to rise steadily in the next few decades (Wen et al. 2009). Liquid biofuels were segregated into bio alcohols (Hacisaligoglu 2009), vegetable oils (Demirbas 2008) biodiesel (Demirbas and Karslioglu 2007) and biocrude oils (Balat 2009). They offer a promising alternative (Gercel and Gercel 2007; Demirbas 2008). Wood, straw and household wastes can be used to produce bioethanol in facile manner. It can be done through alcoholic fermentation of simple sugars. Methanol is produced by chemical process involving catalytic steam reforming of natural gas (Demirbas 2008; Zinoviev et al. 2010).

Bioethanol showed greater potential for energy protection and environmental security. Now a day, natural resources have been studied for bio ethanol production, which can broadly be classified into sugars and starch. Conversion of biomass into ethanol varies depends upon the nature of source and composition (Zabed et al. 2017). Butanol is an oxygenated fuel that can be blended with gasoline for use in vehicles. Fermentation results in an isomer as the major product (Bunting et al. 2010).

Biodiesel is an ecofriendly fuel mainly used in diesel engine. Usage of vegetable oils for biodiesel production is a cheaper way (Demirbas 2008). Currently, biodiesel has been introduced as an economical renewable and sustainable fuel which is quoted as an environment friendly one (Seyed and Mazlan 2012). The fatty ethyl methyl esters (FAME) are used extensively as a diesel enhancement for its resemblance towards diesel (Dajun et al. 2014). Bioethanol seems to be a potential and successful fuel in the market. Hence, various liquid biofuels, in particular C3–C8 fuels, are recently under exploration. n- Butanol is a linear C4 alcohol is used as transportation fuel due to its lower volatility and low hygroscopicity (Demirbas 2005).

5.5 Bioethanol

In the present situation the bioethanol is one of the most extensively used fuels in various vehicles in international level (Gil and Maupoey 2018). Not only in transportation side but also it can even be used for power generation. But the major hindrance in the production of bioethanol is the cost of production which will even go beyond that of fossil fuels. This can be reduced to a great extent by the use of agricultural waste as the source for bioethanol production. The fuel, bioethanol can be used both alone and in blended form with gasoline. Ethanol in pure form is difficult to vaporize which may result in difficulty in stating of vehicles in cold weather. In such conditions it is advantageous to blend with small amount of petrol. The bioethanol can be produced from many different types of agricultural waste which may include algae waste, vegetable and fruit waste, sugarcane bagasse, rice straw, wheat straw etc.

5.6   Bioethanol Production from Fruit and Vegetable Waste

Bioethanol can be produced from different vegetable and fruit wastes like peels etc.
Segui and Fito (Erman et al. 2017) elaborated a work on the production of bioethanol
from pineapple waste obtained from juice and canning industry. Different methods
were proposed for the production of bioethanol which include direct fermentation,
consecutive saccharification and fermentation and simultaneous saccharification and
fermentation. Out of the three methods simultaneous saccharification and fermen-
tation produced more bioethanol (5.4% v/v) when compared to other two methods.
1.38 and 1.57% of bioethanol was produced after 24 and 48 h of fermentation, when
sugar rich fruit processing waste was hydrolyzed utilizing dilute acid pretreatment
and fermentation using *E. coli* FBR5 strains. In the study, fruit processing waste
acted as a carbon sources with 3.6% (w/v) fructose (Chintagunta et al. 2017).

Pineapple leaf waste was also converted to bioethanol with a concentration of
7.12% (v/v) in 24 h from delignified biomass. Here the bioethanol production was car-
ried out by simultaneous saccharification and fermentation using cellulase-xylanase
concoction and yeast. Even the residual biomass was fortified with NPK by means
of cyanobacteria in 4–5 weeks (Choi et al. 2015). Citrus fruit peel waste produced
from agricultural processes was converted to bioethanol using enzymes produced
from Avicel. Around 90% of the substrate was converted to fermentable sugars in
48 h of incubation. Further the inhibitory compound like limonene was removed
and the remaining was fermented for the production of bioethanol. It resulted in an
ethanol concentration of 14.4–29.5 g/L and yielded around 90.2–93.1% (Widmer
et al. 2010).

Yusuf and Inambao (2019) converted Citrus processing waste which was pre-
treated at 160 °C for more than 4 min with steam purging to bioethanol. It yielded
a bioethanol concentration ranging from 76 to 94%, after 48 h of simultaneous sac-
charification and fermentation. The bioethanol yield of 71.54 g/L was obtained for
Mbwazirume variety of matooke species when fermented with *Saccharomyces cere-
visiae*. The properties of the produced bioethanol were in accordance with ASTM
standards (Raman and Gnansounou 2014).

Empty fruit bunches (EFBs) is also considered as one of the prospective biomass
wastes, which can be used effectively as a raw material for bioethanol production.
EFBs are rich in lignocelluloses but have o be pretreated before fermentation for
bioethanol production due to its rigid cellulosic structure combined with lignin and
hemicelluloses (Sangwichien and Duangwang 2013). In many countries the avail-
ability of the EFBs are at a higher side. This can be converted to a wealth if properly
managed. Separate hydrolysis and fermentation of EFBs released an ethanol yield
of 8.49 g/L at the end of the fermentation period of 3 days with 1.5 g of baker's yeast
(Cui et al. 2014) (Table 5.1).

Table 5.1 Bioethanol production from lignocellulosic waste

S. No.	Substrate	Fermentation process	Yield	Reference
1	Empty fruit bunches	Simultaneous saccharification and fermentation	83.6	Kim and Kim (2013)
2	Empty fruit bunches	Simultaneous saccharification and fermentation	37.8	Duangwang and Sangwichien (2015)
3	Empty fruit bunches	Separate hydrolysis and fermentation	6.23–8.49	Duangwang and Sangwichien (2015)
4	Banana rachis	Simultaneous saccharification and fermentation	$103\ Lt^{-1}$	Guerrero et al. (2018)
5	Banana peel	Simultaneous saccharification and fermentation	45.088%	Gebregergs et al. (2016)
6	Energy cane clone	Simultaneous saccharification and fermentation	9.11–0.68 g/L	Thammasittirong et al. (2017)
7	Sago pith waste	Microwave assisted acid hydrolysis and fermentation	80%	Thangavelu et al. (2019)

5.7 Bioethanol Production from Algae

Industrial algae waste is also considered as a very good and potential source of bioethanol. Algae are considered as very good sources of sugars which can be converted to biofuel. Alfonsín et al. (2019) indicated that bioethanol yield of 11.6 g EtOH/g algae was acquired at 70 min, H_2SO_4 concentration of 9% and acid to dried algae ratio of 7. For bioethanol production, industrial waste of *Eucheuma spinosum* was used. The conversion efficiency was found to be 75% of that of the theoretical one. Extracts of Laminaria hyperborean like laminin, mannitol were converted to bioethanol under oxygen stringent conditions with *Zymobacter palmae*. Under the above circumstances, the bacteria grew and yielded ethanol of 0.38 g ethanol/ (g mannitol) (Horn et al. 2000). Around 0.4 g ethanol/g of sugars was released when *E. coli* KO11 acted on Laminaria japonica hydrolysates which mostly contain sugars like mannitol (Kim et al. 2011).

Further bioethanol was produced from microalgae, spirulina. The algae was grown by providing sufficient amount of phosphates, nitrates etc. The fully grown algae was dried, grinded and pretreated by acid hydrolysis and then fermented with *Saccharomyces cerevisiae* to produce ethanol. Around 5.2 g/L of reducing sugar was obtained from hydrolysate, which then yielded an ethanol percent of 0.85–1.0 (Hossain et al. 2015). Ashokkumar et al. (2017) converted *Padina tetrastromatica* which is brown algae to liquid biofuels. In the study lipid was extracted and used for biodiesel

production and further the residual biomass was converted to bioethanol by anaerobic fermentation process. Yield of bioethanol was found to be 83.4%. Thus production of bioethanol from algae is further proved.

Bioethanol was produced also from *Nannochloropsis gaditana* in different munic-ipal waters. Microalgae was cultivated and used for bioethanol production. Yield of bioethanol was found to be in the range of 70.3–94.3 mg/gbiomass. Thus even algae in waste water can also be used for the production of value added goods like bioethanol (Onay 2018).

Even the fresh water macroalgae can also be used for the production of biofuel. Kumar et al. (2018) produced biodiesel and bioethanol from fresh water macroal-gae. After the extraction of lipid which was used for the production of biodiesel, the leftover biomass was hydrolyzed for the release of sugar for fermentation. The theoretical yield of bioethanol was estimated to be 61%. The blends of biofuels were also found to be effective.

5.8   Bioethanol Production from Bagasse and Straw

Bioethanol production can be made economical by the use of lignocellulosic mate-rials from starch rich and sugar rich crops. The process can be made much more economical by the usage of non edible crops. Sugar can be squeezed out of bagasse which can be converted to bioethanol. Khalil et al. (2015) converted sweet sorghum bagasse to bioethanol. Bioethanol was produced using two microorganisms, *Saccha-romyces cerevisiae* ATCC 7754 and *Zymomonas mobilis* ATCC 29191. Bagasse was pretreated and then hydrolyzed thermo-chemically utilizing 2% (v/v) sulfuric acid (98%) at 120 °C for 60 min and filtered. This was neutralized and added with nutri-ents for bioethanol production. After the fermentation 10.5 mL L^{-1} of bioethanol was produced from bagasse.

Also bioethanol was produced from sweet sorghum juice with the help of *Saccha-romyces cerevisiae* DBKKUY-53 which was immobilized in alginate-loofah matrix. In the study the bioethanol production efficiency was compared between free and immobilized yeast. It was confirmed that ALM-immobilized cell containing media produced more bioethanol when compared with free one. The bioethanol produc-tion was found to be 97.54 g/L for immobilized and 1.36 g/L for free one. Even the immobilized cell was repeatedly used in the bioethanol production study and the efficiency was proved up to six consecutive experiments (Nuanpeng et al. 2018). Kataria et al. (2019) also proved the production of bioethanol from sweet sorghum juice which was concentrated by membrane filtration techniques. The amount of ethanol produced at fifth batch fermentation by Saccharomyces cerevisiae BY4741 was around 113.7 ± 3.1 g/L. Around 98.7% of ethanol titer was obtained in the first batch of batch fermentation in sequential way. Thus the entire process was proved to be economical.

5.9 Biobutanol

Biobutanol is also considered as an ideal substitute for existing fuel due to several of its properties like high energy content, less hygroscopic nature, low volatility etc. (Sasaki et al. 2015). It can be used as an alternate to gasoline since it doesn't need any modification for use as an engine fuel and also it can be used as industrial solvent (Rakopoulos et al. 2011). Even though butanol production seems to be very useful, the major hindrance is the cost of production. This can be reduced by the usage of lignocellulosic raw materials for the production (Lee et al. 2008). In many agriculture dependant countries, amount of agricultural waste getting deposited is increasing. This can be effectively converted to biofuel through fermentation process either in sequential or in simultaneous way. So biobutanol can be produced as a result of a anaerobic digestion reaction called acetone butanol ethanol fermentation. Commonly used organism for the fermentation belongs to Clostridium family.

Alikaline pretreated rice straw and sugarcance bagasse were hydrolysed using cellulases produced using *Pseudomonas* sp. CL3 and *Clostridium* sp. TCW1. The sample was then converted to biobutanol by SHF and SSF. The amount of butanol produced was found as 1.95 and 2.93 g/L for bagasse and rice straw respectively. Thus authors confirmed that the process was feasible for the conversion of agricultural waste into value added products like biobutanol (Kumar et al. 2012). Again pea pod waste was also converted to butanol using *Clostridium acetobutylicum* B 527 by following a sequence of steps. This was a rich source of carbohydrate with more content of cellulose and hemicelluloses. Saccharification released large quantity of sugar, from which phenol compound and acetic acid content was detached by activated charcoal detoxification. Further fermentation resulted in the production of 4.3–5.9 g/L with the consumption of around 50% sugar. Thus it was proved that waste of pea pod also can be converted to butanol (Cheng et al. 2012). Further some of the research works for the production of butanol from agricultural waste are listed in Table 5.2.

5.10 Biodiesel

Depletion of fuel sources and high price of currently using fuels have forced researchers to work more towards the production of another important biofuel, biodiesel. It is a very good alternate fuel which satisfies the criteria or ASTM standard. By transesterification process the raw materials can be converted to either methyl or ethyl esters with the help of either homogenous or heterogeneous catalyst. These catalysts can even be prepared using agricultural waste. The main advantages of biodiesel are its cleaner production strategies, lesser amount of environment harmful emissions and its ease of degradability (Khedkar et al. 2017).

Different types of oils and animal fats can be converted to biodiesel in an effective way. For the conversion, catalyst plays a major role. Some of the waste biomass like

Table 5.2 Biobutanol production from lignocellulosic waste

S. No.	Raw materials for butanol production	Microorganism used for fermentation	Butanol yield (g/L)	Reference
1	Rice straw	*C. acetobutylicum* NRRL B-591	2	Nimbalkar et al. (2018)
2	Rice straw	*C. acetobutylicum* MTCC 481	2.07	Moradi et al. (2013)
3	Sugarcane bagasse	*Clostridial species*	2.29	Ranjan and Moholkar (2013)
4	Corn cob	*C. acetobutylicum* ATCC 824.	18.54	Cheng et al. (2012)
5	Corn cob	*C. beijerinckii* NCIMB 8052	9.90	He and Chen (2013)
6	Corn cob	*C. acetobutylicum* SE-1	18.20	Zhang et al. (2012)
7	Wheat bran	*C. beijerinckii* ATCC 55025	11.80	Zhang et al. (2013)
8	Cassava bagasse hydrolysate	*C. acetobutylicum* JB200	76.40	Liu et al. (2010)
9	Empty fruit bunch of palm	*C. acetobutylicum* ATCC 824	2.75	Lu et al. (2012)
10	Pineapple peel waste	*C. acetobutylicum* B-527	5.23	Ibrahim et al. (2015)

vegetable oil asphalt was effectively used for the conversions of waste oil to biodiesel (Ma and Hanna 1999). Also the catalyst prepared from sulfonated palm seed cake was also used for the production of biodiesel from palm fatty acid distillate (Shu et al. 2010). Further the catalyst prepared from agricultural wastes like corn straw was used for the transesterification of oleic acid and methanol (Akinfalabi et al. 2017). Also catalyst synthesized from rice husk after pyrolysis reaction was efficiently used for the synthesis of biodiesel from waste cooking oil (Liu et al. 2013). The solid acid catalyst prepared from micro algal residues can even be used for the production of biodiesel (Li et al. 2014). In a similar way green sulfonated carbon based catalyst consequent from coffee residue was also used resourcefully for esterification reaction (Fu et al. 2013). Thus the utilization of waste biomass for catalyst synthesis reduces the cost of synthesis of catalyst to a large extent.

Different types of waste cooking oil can be converted to biodiesel in a resourceful way. Many researches are available in this category. Waste palm oil was converted to biodiesel by many scientists (Ngaosuwan et al. 2016; Thushari et al. 2019; Harahap et al. 2019; Ahmad et al. 2019; Vargas et al. 2019; Farid et al. 2017; Lam, in press; Inayat et al. 2019; de Almeida et al. 2015; Matinja et al. 2019; Márcio de Almeida et al. 2017). Also it is proved that not only waste palm oil, but many kinds of waste cooking oil can be converted to highly valued biodiesel with the help of different

types of catalyst (Roschat et al. 2018; Sadaf et al. 2018; Zhang et al. 2018; Kataria et al. 2019; Aghel et al. 2019; Abed et al. 2018; Dhawane et al. 2018; Soegiantoro et al. 2019; Pikula et al. 2019; Rabie et al. 2019; Borah et al. 2019; Mansir et al. 2018; Badoei-dalfard et al. 2019; Xiong et al. 2019; Jung et al. 2019). Even though so many researches are going on this field amount of edible oil from agriculture as a feedstock for agriculture is limited. So another source for biodiesel is micro and macro algae.

Microalgae are considered to have higher amount of lipid and has a rapid growth rate. This makes microalgae a significant producer of biodiesel. So great efforts have been put for the betterment of productivity and oil percentage of microalgae in a profitable way. Oil content different types of microalgae have been converted to biodiesel using variety of catalyst (Raj et al. 2019; Arcigni et al. 2019; Felix et al. 2019; Aghilinategh et al. 2019; Abinandan et al. 2019; Raoufi et al. 2018; Kadir et al. 2018). So algae is considered as one of the important source of biodiesel. It can be cultivated easily in discarded and infertile land. By using the available nutrients algae can grow in an efficient way. Macro algae can also be converted into oil which then can be transformed into biodiesel. Many researchers have focused their work in the conversion of macroalgae into biodiesel some of the prominent work include the conversion with the help of novel catalysts (Abomohra et al. 2018; Kalavathy and Baskar 2019; Ramola et al. 2019; Ashokkumar et al. 2017; Xu et al. 2014; Yin et al. 2019; Kumar et al. 2018; Suganya et al. 2014; Silitonga et al. 2019; Suganya et al. 2013; Bai et al. 2015).

There are many aquatic plants which are highly problematic invasive species in many parts of the world. These plants can also be treated for the released of oil which then can be transesterified to biodiesel. One such weed is Eichhornia crassipes. The oil extracted from the weed was transesterified to biodiesel. This was found to be more efficient when blended with diesel. Thus it was proved that novel source can also be used for the sustainable production of biofuel (Alagu et al. 2019). Further researches happening in this field is listed in Table 5.3.

5.11 Conclusion

In the current scientific research, many techniques are getting evolved for the synthesis of biofuels. Thus production of biofuel like bioethanol can be effectively carried out from lignocellulosic resources. But there are many hindrances that need to be overcome before getting the product commercialized. The biofuel production from lignocellulosic waste will not affect forest resources harmfully when we are depending on the wastes. Also many types' wastes can be still exploited for the production of different types of biofuel. The growing economy with increase in competition in different areas will result in fuel crisis in the near future. So to make the life of the next generation secure, environment friendly sources of energy should be depended most. Also it should be cost effective so that economic economic development will be stable.

Table 5.3 Biodiesel production from waste

S. No.	Raw materials for butanol production	Biodiesel yield (%)	Reference
1	Waste pepper seed	94.1	Lee et al. (2017)
2	Chicken manure biochar and waste cooking oil	95.6	Jung et al. (2017)
3	Biochar derived from chicken manure as a porous media and catalyst	95	Jung et al. (2018)
4	Biomass-derived waste date pits	98.2	Ala'a et al. (2018)
5	Wet spent coffee grounds waste	131.1 mg biodiesel/g dried SCGs	Tong cumpou et al. (2019)
6	Mesua ferrea oil	95.5	Bora et al. (2018)
7	Palm oil using catalyst derived from coconut shell	88.15	Endut et al. (2017)
8	Waste cooking oil	89.6	Tran et al. (2017)
9	Fish oil	97	Papargyriou et al. (2019)

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Chapter 6
Sustainable Production of Green Fuels and Chemicals Using Microalgae as Feedstock

Jayati Trivedi and Neeraj Atray

Abstract The most crucial challenges faced by our society today are energy security, uncertainty in fuel prices and the environmental impact due to the harmful emissions. The last decade has seen intensive research efforts in exploitation of microalgae as a potential source of fuel and other value added products. This chapter provides an overview of microalgae based biorefinery concept aimed at economical and efficient product formation. The integrated approach of carbon dioxide sequestration and wastewater treatment along with biomass accumulation of microalgae provides dual advantage of reducing pollution load and simultaneously generating biomass for valorisation. The commercialization potential of microalgal fuels and chemicals has also been highlighted in this chapter.

6.1 Introduction

Microorganisms classified under the kingdom protista are termed as microalgae. These resemble single plant cells in many ways. These are eukaryotic, unicellular organisms, photoautotrophic and contain chloroplasts like plant cells. Every cell is a unique organism which can sustain life on its own.

Algae have been recognised as a valuable resource exploited by humans as a source of food and feed over the last century. Extensive efforts have been made to use algae both micro and macro for energy requirements, biomaterials as well as for waste water treatment. As the algae cultivation utilizes Carbon dioxide from the environment, it is treated as a potential source for its sequestration and conversion to different compounds naturally. Algal lipids are very similar to many plant lipids, with

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the notable exception that algal lipids are more likely to contain fatty acid components having higher degrees of unsaturation (Hu et al. 2008). The other advantages of microalgae are its ability to grow in non-cultivable land, short doubling time, capability to utilize brackish water or waste water, high carbon fixing efficiency than terrestrial plants, and potential to produce high value compounds such as biofuel, proteins, pigments and pharmaceutical products (Rawat et al. 2013).

Although the technology for production of microalgae is still in its nascent phase, efforts for its successful commercialization have on peak during the last decade. Presently, the main challenges are scale up, reduction of production costs and attaining stable and reliable processes. Also, more concerted push towards understanding the algal metabolism and regulation mechanism is required. Economic considerations and principles of green design suggest that if algae-to-fuel technology is to be successful, biofuels must be produced simultaneously with value-added co-products (Patrick et al. 2011).

6.2   Algae Based Biorefinery

Microalgae are considered to be potential feedstock for successful establishment of a biorefinery because of their ability to produce numerous compounds. Biorefinery can be defined as a system where numerous products such as biofuels, energy and high value products can be obtained through biomass transformation. Biorefinery is also expected to provide utilization of products, co-products and energy generated through one industry into the other industries for maximization of resources and reducing the carbon emissions. The Proposed schematic flow sheet for a microalgae biorefinery is shown in Fig. 6.1. The products obtained from Biorefinery can be divided into fuel and non-fuel products (Trivedi et al. 2015). The fuels mainly consist of Biodiesel, Bioethanol, Biobutanol, Biogas and Biohydrogen. Algae have high biomass productivity as compared to other oil producing trees and can accumulate significant concentrations of high value products or over 50% of dry weight as lipid in the form of triglycerol (TAG) under stress conditions. The non-fuel products consist of carbohydrates, pigments, proteins, biomaterials, and other bioproducts. These products have high value in the market and provide greater profit margins (Chandra et al. 2019). The carotenoids for example astaxanthin, lutein/zeaxanthin, and B-carotene produced from *Nannochloropsis* have a surging demand as natural additives in food and feed industry (Spolaore et al. 2006; Nobre et al. 2013). Table 6.1 shows the major products which can be produced from algae and their potential applications.

Gouveia (2014) has reported, different production routes in the biorefineries using number of microalgal species. For example production of oil, pigments and Biohydrogen production can be done successfully using *Nannochloropsis* as feedstock for biorefinery. *Anabaena* sp. biorefinery is most suited for the production of Hydrogen through autotrophic fermentation route. Campenni et al. (2013) have described a biorefinery which can produce significant quantities of lipids and carotenoids using
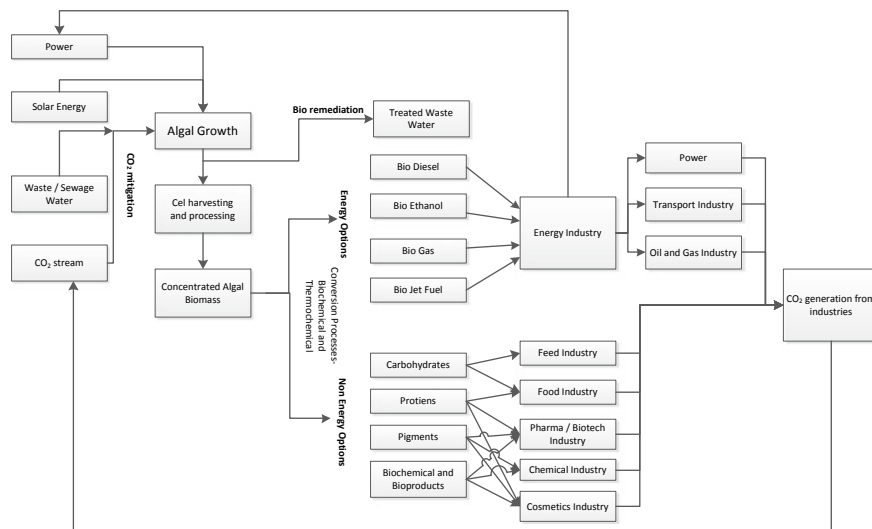
Fig. 6.1 Proposed schematic flow sheet for a microalgae biorefinery (Trivedi et al. 2015)

Table 6.1 Main products obtained from Algae and its potential industrial application

Class	Product	Potential use in industry
Polysaccharides	Agar, Alginates, Carrageenans	Food industry—Gelling and Thickening agents
Pigments	Carotene	Colourant, Additive for feed and food supplement, anti inflammatory, Chemopreventive
	Astaxanthin	Feed additive and food supplement, antioxidant
	Phycocyanin	Phycobili-protein
PUFA (Poly unsaturated Fatty Acids)	Eicosapentenoic acid (EPA)	Nutritional supplements
	Linoleic acid (GLA)	Infant formula for full term infants
	Docosahexaenoic acid (DHA)	Infant formula for full term/pre term infants and aquaculture
Antibiotics	Laxaphycins, Calophycin, Ambiguines, Tanikolide	Antibacterial and Antifungal activity
Vitamins	Essential vitamins—A, B1, B2, B6, B12, C, E, folic acid	Nutritional supplements for vegetarian individuals
Antioxidants	Alkaloids, Terpenopids, Phycobiliprotein	Cosmetics, sun protection

Chlorella protothecoides as a source of lipids and carotenoids. Under illumination stress and salinity stress conditions chlorella produces high value chemicals. In the *Chlorella* biorefinery the biomass after lipid extraction is used for hydrogen and bioethanol production making use of the residual sugar present in the chlorella strain.

However, the formation of bioproducts in the biorefinery context is dependent on the composition of biomass which varies according to the strain characteristics and the growth conditions of the algae (Laurens et al. 2014; Gatenby et al. 2003). The major drivers behind successful biorefineries are focused on identifying means to achieve targeted levels of algal biomass productivity and composition and conversion efficiencies, all identified as critical factors for economic development of algal biofuels. According to Chew et al. (2017) the major bottleneck of a biorefinery approach is the separation of different fractions without effecting the quantity and quality and to the other fractions. This hindrance can be overcome by deployment of a cost efficient and scalable separation processes.

Along with the production of spectrum of products, microalgae is also used in treatment and recycling if waste water streams. Enhanced biomass generation at lesser cost without extra input of nutrients can be done by utilizing waste water streams (Kothari et al. 2012). The potential of algal species such as *Scenedesmus obliquus*, *Arthrospira pcrtenix*, *Botryococcus braunii*, *Azolla microphylla*, *Chlorella vulgaris*, and *Chlorella pyrenoidosa* as an effective tool for wastewater treatment is shown in Kothari et al. 2013. In a report by Wang et al. (2010), nutrient removal rate using green microalgae was found to be 100%, 75.7–82.5%, 62.5–74.7%, 27.4–38.4% for ammonia, total nitrogen, total phosphorus and COD (Chemical Oxygen Demand) respectively when digested dairy manure was used as a nutrient source. Microalgae are also capable of sequestering CO_2 from the environment. In that many researchers have used industrial flue gas for enhanced growth of algae such as *Scenedesmus* and *Botryococcus braunii* (Li et al. 2011). Ho et al. (2011) have reported *Nannochloropsis* sp. and *Chlorella* sp. which are tolerant to high temperature, high CO_2 concentration and presence of toxic gases such as SO_x and NO_x. Therefore, an integrated system of waste water treatment and CO_2 sequestration has been proved to be economically more efficient due to savings in supply of nutrients and has environmental benefits also (Mallick 2002).

Thus, the combination of outstanding properties of microalgae with the increasing market demand of natural products, it is worth exploring for utilization in the future in feed, food, cosmetic and pharmaceutical industry.

There have been many attempts at commercialization of microalgae all over the world. Table 6.2 shows the commercial food products from microalgae. Although, microalgae have many positive factors such as fast growth, carbon dioxide sequestration potential, waste water treatment etc., the successful commercialization of microalgae based biofuel will depend on development of methods and techniques for enhancing biomass accumulation and easier harvesting and energy efficient extraction of compounds. For establishing economically sustainable and profitable microalgae based business enterprises to grow, the production cost is essential to be reduced. Biofuels also have a bright future for the defence applications but the research is still required on various aspects of cultivation and extraction.

Table 6.2 Commercial food products from microalgae (Gouveia et al. 2008)

Microalgae	Producer	Product	Production (ton/year)
Spirulina	Hainan Simai Pharmacy Co. (China) Earthrise Nutritionals (USA) Cynotech Corp. (USA) Myanmar Spirullina Facto	Powders, tablets, dan extract Tablets, powders, drinks Extract, Tablets, chip, liquor, liquid extract	3000
Chlorella	Taiwan Chorella Manufacturing Co. (Taiwan) Klotze (Jerman)	Tablets, Powders, nectar	2000
Dunaliella salina	Cognis Nutrition and health (Australia)	Powders of β-caroten	1200
Aphanizoenon flos-aquae	Blue Green Foods (USA) Vision (USA)	Capsules, Crystal powders, capsules	500

6.3   Conclusion

The limitations of the first and second generation of biofuels indicate that there is a urgent need for a more reliable and greener source of feedstock for fuel and energy production. Microalgae require lesser resources and inputs as compared to other oil bearing crops used for biofuel production. The key problems which need to be addressed for developing a sustainable model of algal biorefinery are to reduce the operational costs during drying and extraction of value added products. Also, to increase the productivity of algae, genetically engineered robust strains will be required along with the development of new reactors. However with the increased R&D efforts all over the world in this field and development of new processes and products the commercialization of algae based product is likely to happen in the next decade.

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Part III
Biofuels for Engine Applications

Chapter 7
Future Automotive Powertrains for India: Methanol Versus Electric Vehicles

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Abstract Oil and gas demands in India are growing at an alarming rate and gap between demand and supply has emerged as a great concern for the country's economy. Globally, petroleum reserves are depleting rapidly, and may not sustain beyond 2050. Therefore, finding alternative, renewable and eco-friendly fuels is an absolute need for the age, not only due to petroleum resource scarcity but also due to adverse impact of combustion generated emissions on human health and environment. Electric vehicles (EVs) are emerging into the transport sector globally as well as in India because apparently they are marketed to be producing zero tailpipe emissions. EVs are also expected to reduce dependence on imported petroleum fuels, if electricity is produced from indigenous energy resources or from renewable resources. However, there are several critical issues associated with EVs such as storage batteries, driving range, total weight of the vehicle, lack of recharging facilities, and their high costs. On the other hand, fuels derived from stray carbon in waste biomass, municipal solid waste (MSW) or low grade high ash coal are considered to be superior alternative fuels for transport sector. Among different alternative fuels, methanol has been given greater attention in recent times. Methanol fuelled vehicles (MFV) are quite practical, economical and eco-friendly and can contribute significantly to the transport sector. Methanol fuelled vehicles have higher power density, comparable cost-benefit ratio, and relatively cleaner emission spectra compared to conventional petroleum fuelled vehicles. In this chapter, possible strategies to adopt methanol in existing IC engines are discussed and current national and global status of methanol fuelled vehicles is presented. Next section discusses different types of EVs and their current national and global status, including their historical evolution and risks involved in their mass penetration. The reasons why MFV are a reliable future option for Indian transport sector on a large scale, while EVs seem impractical for large scale implementations are also discussed at length.

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7.1 Emerging Powertrains Solutions

India has achieved considerable economic growth via industrialization and urbanization in the last decades. Its transport sector is expanding and the vehicle population is increasing exponentially. Indian automotive sector is one of the leading automotive sectors in the world, which contributes 7.1% to GDP and 13% excise revenues, while employing ~29 million people (Society of Indian Automobile Manufacturers). At present, transport sector mostly relies on petroleum fuels such as gasoline and diesel, which are usually imported fuels hence they have a negative impact on the national economy. On the other hand, human health and local environment are under threat due to toxic pollutants generated from the combustion of conventional fuels. Combustion of petroleum fuels are responsible to increasing levels of greenhouse gases (GHG) emissions in the atmosphere, which adversely affects vegetation growth, ice core thickness in glaciers, structure of buildings, earth surface temperature and climate change. Ten major cities of India have been suffering from seriously deteriorating air quality, primarily due to uncontrolled tail-pipe emissions from vehicles. Vehicular emission species such as CO_2, CO, NO_x, SO_2, and particulate matter (PM) affect the environment and people's health adversely, leading to serious diseases such as emphysema, bronchitis, asthma, cardio-vascular dysfunction and cancer. In a mega city like Delhi, $PM_{2.5}$ level is more than six times the safe prescribed limit by World Health Organization (WHO). Therefore, it is warranted to control the vehicular emissions to desired levels urgently. India is signatory to the Conference of Protocol in October 2016, known as 'Paris Climate Agreement'. As per this agreement, India is obligated to reduce its carbon footprint by 33–55% compared to the levels recorded in 2005, in next 12 years (Environment Updates 2014–2016). This certainly requires implementation of stringent emission norms. Government of India (GoI) has implemented stringent emission norm Bharat Stage (BS)-VI, which is equivalent to Euro-VI standards with a view to protect human health and environment. These norms are effective from April 1, 2020. These norms will affect entire Indian automotive Industry, motivating use of low carbon fuels in the existing vehicles, in addition to implementation of exhaust gas after-treatment systems. Conventional petroleum fuels contain long chain hydrocarbons, thereby producing high GHG and heavy hydrocarbon emissions. In this context, India has to develop and implement low carbon alternative fuels urgently, which can potentially reduce the consumption of conventional petroleum fuels, while complying with existing BS-VI emission norms using existing after-treatment technologies. This would require substantial R&D efforts to adopt selected alternate fuels for the transport sector before its large scale implementation. Automobile sector in India includes different types of vehicles such as passenger vehicles, commercial vehicles, 2-wheelers, and

3-wheelers. All segments are rapidly growing. Sales of passenger vehicles, commercial vehicles, 3-wheelers, and 2-wheelers have increased to 191.53%, 100%, 100%, and 162.10% respectively in FY-2017 compared to FY-2006 (Two-wheeler Industry Research). Indian 2-wheeler market became the largest in the world recently by displacing China from the top.

GoI previously took steps to promote alternative fuels usage via a notification made by Ministry of Petroleum and Natural Gas (MoPNG) on 20th September 2006, which mandated the oil marketing companies (OMCs) to sell 5% ethanol blended gasoline (EBG) from the petrol stations in 20 States and 4 Union Territories (UTs) effective from 1st November 2006 (Standing Committee on Petroleum & Natural Gas 2008–09). Additional ten states of Delhi, Himachal Pradesh, Madhya Pradesh, Chandigarh, Kerala, Rajasthan, West Bengal, Odisha, Bihar, and Jharkhand were included later on in this list. However, North-Eastern States, J&K, Andaman & Nicobar Islands and Lakshadweep Islands are still not covered under this program. Availability of ethanol has been a major bottleneck to implement this mandate successfully and policymakers have to rethink about sustainability as well as further extension of the EBG program. An important lesson learnt is that the alternate fuel must be derived from renewable sources to support the transport sector sustainably. Therefore appropriate alternative fuel selection is highly desirable for developing countries like India. Exploration of possible alternate fuels was started with hydrogen, CNG and now, India is concentrating on two primary options: MFV and EVs because of several advantages they offer over other possible options as discussed below and these will also be compared among themselves.

7.1.1 Methanol

Methanol can be used as a fuel for both spark ignition (SI) engines and compression ignition (CI) engines. It has a great potential to substitute traditional fuels such as gasoline and diesel, which can contribute significantly in reducing emissions from transport sector. Methanol being a low carbon fuel produces lesser GHG and other pollutants compared to those emitted by conventional fuels. Relative merits and demerits of methanol utilization are summarized below:

Merits

- Methanol can be produced from low grade coal (with high ash content), MSW, low-value biomass, natural gas, and atmospheric CO_2.
- Methanol fuelled vehicles produce fewer emissions, especially CO, HC and PM compared to baseline conventional fuelled vehicles because it has oxygen in its molecular structure, which leads to a greater degree of completion of combustion.
- Methanol has ~245% and ~190% higher latent heat of vaporization compared to diesel and gasoline respectively, which gives relatively extra charge cooling effects (Fuel Properties).

- Methanol has ~82% and ~71% lower molar mass compared to diesel and gasoline respectively. Thus its burning results in relatively lower emissions due to the fact that methanol has lower diffusion rate compared to heavier hydrocarbon fuels (Fuel Properties).
- Methanol has ~34% and ~32% higher auto-ignition temperature compared to diesel and gasoline respectively, which underscores that methanol is a safer transportation fuel compared to conventional fuels (Fuel Properties).
- Methanol combustion products are free from sulfur compounds since it does not contain any sulfur.

Demerits

- Methanol has ~53% and ~54% lower heating value compared to diesel and gasoline respectively, which warrants increased fuel quantity injection into the engine cylinder for the same power output. This further requires necessary modifications in the existing fuel supply systems (i.e., fuel injector and carburetor) so that they can deliver additional fuel quantity in each combustion cycle (Fuel Properties).
- Methanol has ~73% lesser and ~23% higher kinematic viscosity compared to diesel and gasoline respectively. Therefore, additives are required to be added to make it compatible with CI engines (Fuel Properties).
- Methanol has poor lubricity properties compared to conventional fuels, which may lead to faster wear in the engine components.
- Methanol is corrosive to most materials therefore its use requires that engine components should be made of methanol resistant materials or they should be coated with methanol resistant coatings.

7.1.2 Electric Vehicles

Since stored electrical energy is used to energize the powertrain of EVs, they exhibit zero tailpipe emissions however emissions of pollutants takes place at the generation points of electricity. Relative merits and demerits of EVs in transport sector are summarized below:

Merits

No Fuel requirement: EVs are powered by electricity, thus it apparently does not require any fuel combustion on-board to operate. In some cases, electricity is cheaper compared to conventional fuels. However if the electricity is produced from fossil fuels such as coal or natural gas, the pollutants are emitted into the environment.

No Emissions: As far as on-board emission generation is concerned, EVs by and large remain free from tail-pipe emissions thus have negligible impact on urban ambient air quality.

Cost Effective: EVs can become cost effective, if government provides tax incentives and other financial incentives in order to promote their mass productions.

Low Maintenance: EVs are powered by electrical motors and battery, and they do not have as many complicated mechanical parts like IC engines. Hence, EVs require very low or no lubrication and warrant lower maintenance compared to IC engine-powered vehicles.

Noise Pollution: EVs cause relatively lower noise pollution since they do not include parts having constrained relative motions, which are found in IC engines. Electric motors are commonly referred to as smooth drives, which is practically soundless.

Demerits

Recharge Points: Charging infrastructure for EVs is still in the nascent stage of development in developing countries as well as developed countries and is grossly inadequate for large scale adaptation of EVs. Lack of charging infrastructure severely affects the driving range of EVs.

Type and Cost of Electricity: EVs are pollution free only if it consumes green electricity, which is not the case for most countries. If the electricity is mostly produced from coal such as in India, its claim of being a clean mode of transport is a farce. Cost of electricity may also be a concern if it is produced from fossil fuels. Moreover, electricity is the most superior grade of energy, which has various other applications hence it is a costly energy resource for transport sector.

Driving range and speeds: EVs are limited by low driving range and low speeds compared to their IC engine counterparts.

Suitable for light-duty vehicles: Most EVs available in market are made for light-duty applications. Even under this category, they provide less on-board space, and they are grossly unsuitable for heavy-duty vehicles.

Low Battery Life: Typical battery replacement time is approximately 3–5 years, which is a discouraging factor for the consumers, who are used to drive engine operated vehicles. The cost of batteries is roughly 50% of the cost of the vehicle, if not more, and this money has to be invested after every 3–5 years, and is a major recurring capital expense.

Expensive: EVs are considerably more expensive. They are at least twice or more as expensive as IC engine based vehicles.

Safety issues: EVs are quieter than engine operated vehicles, which may sometimes lead to accidents on the road, since the fellow commuters would have no sound to warn them of the incoming vehicle.

7.2 Methanol Fuelled Vehicles

Methanol fuelled vehicles are similar to conventional vehicles because they use methanol or methanol blended conventional fuels for powering their engine. Methanol can be utilized as a stand-alone fuel in compression ignition (CI) engines and spark ignition (SI) engines by suitably modifying these engines.

However, methanol blended fuels can power these particular engines without significant hardware modifications. Different strategies that are generally employed for methanol injection are discussed in following sub-section and required critical components for methanol fuelled compression ignition engines, and methanol fuelled spark ignition engines are also discussed.

7.2.1 Methanol Induction in Conventional Engines

Methanol induction in conventional engines can be done by three ways: Induction through conventional carburetor, direct injection and port fuel injection. These techniques are explained briefly in the following sub-sections.

7.2.1.1 Methanol Induction Through Carburettor

Blending with gasoline is the first choice for introducing methanol in SI engines because it doesn't require any additional devices or modifications in the fuel delivery system. Methanol and gasoline are mixed in a fuel tank to make desired blends, which are then inducted into the engine combustion chamber using existing carburettor. Gasoline can be easily blended with methanol since both fuels are completely miscible at Normal Temperature and Pressure (NTP).

7.2.1.2 Port Fuel Injection of Methanol Blended Conventional Fuels

In port fuel injection method, methanol or methanol-gasoline blends are injected into engine's intake manifold to prepare a homogeneous fuel-air mixture before inducting into the combustion chamber. This technique can be applied for both, SI and CI engines. In case of CI engines, two injectors are required; one injects methanol in the intake port and the other injects diesel into the combustion chamber as usual but with reduced diesel quantity.

7.2.1.3 Direct Injection

In case of CI engines, methanol and diesel are mixed together in a fuel tank and prepared blend is injected into the combustion chamber using existing fuel injector. Different additives are used to prepare diesel-methanol blends since the blends face phase-separation issues, if more than 10% v/v methanol is blended with diesel. In case of GDI engines, methanol or methanol-gasoline blends are injected directly into the combustion chamber using an injector. This method opens up an avenue to inject higher concentrations of methanol in existing engines. An extra injector is used to inject methanol and conventional fuels separately. This method increases the weight

of the system because it requires an additional injector for induction of methanol in the combustion chamber (Abedin et al. 2016).

7.2.2 Methanol Emulsions

Limited solubility of methanol with conventional fuels, especially diesel has led to extensive R&D efforts for finding ways to utilize high concentration of methanol via emulsion route. By using emulsions, it is possible to add a 30% methanol on volume basis into the diesel fuel. However this method results in a poor combustion quality in CI engine since cetane number of test fuels reduces with increasing methanol content in the emulsion.

7.2.3 Glow-Plug Concept

Methanol suffers from non-firing or misfiring events during cold starting due to its higher latent heat of vaporisation and slower flame propagation speed compared to conventional fuels. Using a glow plug can overcome this problem, which helps initiate combustion in cold climatic conditions.

7.2.4 Critical Issues with Material Compatibility and Exhaust Emissions

Methanol generally attacks aluminium material and corrodes them easily. Thus, components made of suitable material having methanol compatibility should be used for both methanol fuelled SI and CI engines. Similarly, fuel lines, high pressurized fuel pump and fuel tank also needs to be made of methanol compatible materials in order to avoid corrosion problems.

Methanol fuelled CI engines produce variety of nanoparticles, which have adverse health hazards. Diesel particulate filter (DPF) can be employed to remove such nanoparticles. In order to comply with BS-VI emission norms, NOx emissions also need to be controlled. Using selective catalytic reduction (SCR) technology, NOx emissions from the engine can be reduced. SCR system injects a reducing agent through a special catalyst into the exhaust stream. These agents chemically convert NOx into nitrogen, water, and small amounts of CO_2 as shown in Eqs. (7.1) and (7.2) (Partridge and Choi 2017) in presence of vanadium/tungsten oxides coated titanium substrate catalyst.

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O \qquad (7.1)$$

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \tag{7.2}$$
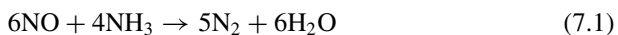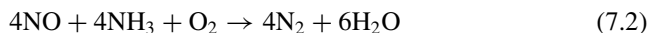
Methanol fuelled SI engines produce toxic pollutants such as NO_X, CO, and HC. Two-way or three-way catalytic converters (TWC) could be employed to reduce these emissions to desired levels. Two-way converter reduces HC and CO emissions by converting them into water and CO_2, and a three-way catalytic converter additionally reduces NO_X.

7.3 International Status of Methanol as Transport Fuel

Globally, methanol is used as a fuel in transport sector. China, USA and EU are leading countries in the world, which use methanol mainly in the form of methanol-gasoline or methanol-diesel blends in existing IC engines in transport sector. Few studies involving prototyping of dedicated methanol engines have also been reported. These are discussed comprehensively in the following sub-section.

7.3.1 China

China is world's largest methanol producer and consumer, especially in transport sector. Availability of enormous coal reserves, waste biomass and natural gas has motivated China to strongly go for methanol based transport system. Global methanol production capacity was 103.2 million metric tons in 2015, of which China alone produced 65.7 million metric tons, mainly from coal (70% of total production) (Asiachem Report 2016). Moreover, China's fast-growing automotive industry, in addition to evolving stringent emission norms also act as motivating factors for utilizing methanol as fuel for transport sector.

In 2015, China converted 35.5% methanol to olefins, 9.2% to DME, 3.4% to MTBE, 3.8% to MTG, 2% to methylamine, 3.1% to methane chloride, 24.4% to formaldehyde, 4.5% to acetic acid and 11.2% was utilized as additive in gasoline for transport fuel (Asiachem Report 2016). Apart from coal-to-methanol conversion, China had setup a facility which treats 500,000 tons of waste and 450,000 tons of sewage sludge wastes per year respectively for generating 100,000 tons (30 million gallons) of alcohol-based fuels and an electrical output of 20 MW (Methanol as an alternative transportation fuel in the US: Options for sustainable and/or energy-secure transportation).

Shanghai and thirteen other provinces have prepared special fuel standards for methanol blended gasoline (MBG), especially for M15 and M85. M5, M10, M15, M85, and M100 are available at private fuel stations in Shanxi and Shaanxi provinces (New methanol fuel standards for China). Last year, China used ~12 million metric

tons of methanol to power their SI engines and CI engine based vehicles using blending or port injection techniques (News report).

Several Chinese automotive industries are involved in manufacturing methanol fuelled vehicles such as Chery Automobiles, which demonstrated twenty methanol flex-fuel vehicles, Shanghai Maple Automotive produced 50,000 methanol cars in 2008 and Chang' an Auto Group introduced methanol fuelled Ben-Ben car (Methanol as an alternative transportation fuel in the US: options for sustainable and/or energy-secure transportation). Due to keen global interest in methanol utilization in transport sector, several researchers investigated performance of methanol-fuelled engines vis-à-vis baseline fuels to demonstrate advantages of methanol utilization in traditional engines, which are summarised in Table 7.1.

Tabulated emission data revealed that methanol blends can be used as a fuel in existing IC engines. In general, researchers found that the presence of –OH radicals enhanced combustion hence NO_X emissions decreased and CO, HC emissions increased for methanol blends in diesel engines compared to baseline fuels. An opposite trend was observed in case of gasoline engines, where both CO and HC emissions mostly decreased and NO_x increased for methanol-gasoline blends.

Table 7.1 Effects of methanol fueling on emissions from IC engines

S. No.	Researcher	Fuel used	Concluding remarks
1	Zhao et al. (2010)	G100 G85M15	CO and NO_X decreased by ~8% and ~1% respectively for G85M15 fueling and HC increased by ~175% compared to baseline fuel
2	Peipei et al. (2013)	G100 G85M15	CO and HC decreased by ~6% and ~16% respectively for G85M15 fueling, but NO_X increased by ~84% compared to baseline fuel
3	Li et al. (2015)	G100 G85M15	HC and CO decreased ~11 to ~34.5% and 63–84% respectively for G85M15 fueling, but NO_X increased by ~77–108% compared to baseline fuel
4.	Crowley et al. (1975)	G100 G95M5 G80M20	CO decreased by ~40%, but HC and NO_X increased by ~6% and ~32% respectively for G95M5 fueling compared to baseline G100 CO and NO_X decreased by ~55% and ~8% respectively for G80M20 fueling, HC increased by ~12% compared to baseline G100
5	Johnson and Riley (1976)	G100 G90M10	Both CO and NO_X decreased by ~9% and 19% respectively for G90M10 fueling, but HC increased by ~41% compared to G100

(continued)

Table 7.1 (continued)

S. No.	Researcher	Fuel used	Concluding remarks
6	Huang et al. (2004)	D100 D80M20 D60M40 D40M60	CO decreased, and NO_X increased for methanol-diesel blends compared to D100. However, methanol and diesel are miscible up to only 10% v/v blending
7	Cheng et al. (2008)	D100 BD100 D90M10	CO_2 and NO_X decreased by 2.5% and 5% respectively for methanol-diesel blends compared to baseline fuel
8	Zhu et al. (2010)	D100 BD95M5 BD90M10 BD85M15 WCO Biodiesel	Both HC and CO decreased by 10% and 15% at 5% blends of methanol and diesel compared to baseline fuel
9	Yao et al. (2008)	D100 BD100 D70M30 BD70M30	Using port injection, NO_X and smoke opacity decreased by 50% for blends compared to baseline fuel
10	Zhang et al. (2011)	D100 D80M20 D60M40 D40M60	Using methanol fumigated, NO_X decreased, CO and HC increased with an increase in methanol fumigation ratio
11	Canakci et al. (2009)	D100 D95M5 D90M10 D85M15	Using methanol concentrated blends, NO_X decreased, and CO, HC, and smoke increased with increasing mass fraction of methanol compared to baseline fuel, where fuel injection pressure (FIP) was 180 bar Using methanol concentrated blends, smoke, HC and CO decreased, and NO_X increased with increasing fraction of methanol compared to baseline fuel, when FIP was 200 bar Using methanol concentrated blends, smoke, HC and CO decreased, and NO_X increased with increasing fraction of methanol compared to baseline fuel, when FIP was 220 bar
12	Ciniviz (2011)	D100 D95M5 D90M10 D85M15	Nitrogen Oxide (NO) increased, and CO and HC decreased for methanol-diesel blends compared to baseline fuel
13	Sayin (2010)	D100 D94M05DO1 D89M10DO1	CO, HC, and smoke decreased, but NO_X increased for methanol-diesel blends compared to baseline fuel. Here dodecanol was used as an emulsifying agent to avoid phase separation

G Gasoline; *D* Diesel, *M* Methanol, and *DaMbGc* Diesel a % (v/v), Methanol b% (v/v), and Gasoline c% (v/v)

7.3.2 USA

In 1976, lead (Pb) was used as an additive in gasoline for SI engines, which was banned. Consequently, researchers started exploring another octane booster. Methanol was identified to be an alternative sustainable octane booster, because of its higher-octane number compared to gasoline. As a result, several methanol programs were initiated by the government between 1980 and 1990, aiming to convert existing vehicles to operate on M85. However a converted vehicle could not be operated on gasoline, which resulted in consumer dissatisfaction since only a few fueling stations delivered M85 at that time. Afterwards, US government declared that M85 would be available in specific regions such as California, where dedicated vehicles could operate on M85.

Later, ten automakers participated and produced 16 different models of 900 methanol fuelled vehicles ranging from light-duty to heavy-duty vehicles. For direct comparison, 40 vehicles were operated by Department of Energy (DOE) laboratories between 1986 and 1991 using gasoline and methanol blends. After a successful demonstration in California, New York State also demonstrated a fleet of dedicated methanol vehicles with dedicated refueling stations, located along the New York Thruway. The high-power capability of methanol also attracted bike/car racers to use methanol fuelled engines for racing purposes.

7.3.3 European Union

Methanol utilization in the transport sector in EU was limited to lower blends. In 1960s, Federal Republic of Germany introduced 4% methanol and solvents in traditional fuels however; general use started in the late 70s. In 1988, an agreement was signed between member countries of the EU to allow methanol blending with gasoline with specific labelling at the petrol stations. France implemented methanol program and installed a few refueling stations. Sweden allowed a maximum blending of 2% methanol with traditional fuels (Alcohols et al. 1986). Additionally, Sweden started field testing of twenty-two methanol fuelled light-duty vehicles including seven different cars, which were supported and financed by Swedish Motor Fuel Technology Co. and Swedish National Board for Technical Development. All vehicles were fitted with carburettors except one, which used an injector for fuel induction. Main motto of the project was to figure out the effect of fuel supply system (carburettor and/or injector) on engine performance under Swedish conditions and report it to the government so that oil companies and car manufacturers could realize the positive/negatives effects of methanol fueling on vehicles. They concluded that wider fleet trials were required to assess the effect of methanol use in the existing engines. However, evaluation of this project suggested that comprehensive engine design and development work was required for reducing warm-up time suitable for low ambient temperature conditions with specific lubricating oil adaptations. In 2004, curtailing greenhouse

gas (GHG) emissions as per the levels of US environmental protection agency (EPA) further drove EU countries to increase methanol blending in conventional fuels for vehicular applications.

EU mandated that at least 10% of its transport fuel should come from renewable resources such as biofuels by 2020. Furthermore, in Sweden during chemical wood pulping process, methanol forms as a by-product (chemically identical with coal based methanol), which after purification can be used in vehicles, hence contribute to GHG emission reduction (Energy Details). Azerbaijan produced 250,000–300,000 tons of methanol whereas Turkey, Italy, Romania, and Slovenia are its biggest partners.

7.4 National Status of Methanol as Transport Fuel

India's energy demand is increasing sharply and would continue to rise at a rate of ~3.5% on a compounded annual growth rate (CAGR) base until 2040 (India Energy Security Scenarios IESS). Crude petroleum and natural gas import dependence of India increased to 81% and 40% in 2015–16 from 73% and 17% in 2005–06 respectively. Table 7.2 presents petroleum import scenario of India for the last five years (Various Industry sources—India's Leapfrog to Methanol Economy).

In order to reduce dependence on imported petroleum products and to improve energy security, India is planning to introduce 'Methanol Economy'. India is in nascent stage of commercial methanol production for fuel use since currently only five domestic companies are producing methanol for the country, primarily for commodity chemical usage: Gujarat Narmada Valley Fertilizer & Chemicals limited, Rastriya Chemicals and Fertilizers, Assam Petrochemicals, National Fertilizers Limited and Deepak Fertilizers.

As per a GoI report, methanol plant of 1600 tons/day capacity costs ~175 million US$ capital investment, which can provide methanol at INR 17–19 (0.25–0.28 US$)

Table 7.2 Crude oil imports of India (Petroleum Import Scenario)

Year	Import crude oil (MMT)	% Growth in import of crude oil	Average crude oil prices (US$/bbl)	% Growth in average crude oil prices
2011–12	171.73	4.97	111.89	31.50
2012–13	184.80	7.61	107.97	−3.50
2013–14	189.24	2.40	105.52	−2.27
2014–15	189.43	0.10	84.16	−20.25
2015–16	202.85	7.08	46.17	−45.14
2016–17	213.93	5.46	47.56	3.02
2017–18 (P)	220.43	3.04	56.43	18.65

Where, *P* Provisional

Table 7.3 Performance tests of methanol blended fuels

Year	Researcher	Fuel used	Concluding remarks
2016	Agarwal et al. (2016)	D100 D95BD5 D80BD20 D95M5Biodiesel (Karanja)	CO and HC decreased at higher engine loads, but HC increased at lower engine loads, and NO_x decreased for methanol blended fuels compared to baseline fuel
2016	Bharadwaz et al. (2016)	BD100 BD95M5 BD90M10 BD85M15 Biodiesel (Pure Palm Oil)	CO, HC, NO, and smoke decreased for methanol blended fuels compared to baseline fuel

D Diesel, *M* Methanol, *BD* Biodiesel, and *DaMbBDc* Diesel a % (v/v), Methanol b% (v/v), and Biodiesel c% (v/v)

per Liter (Various Industry sources—India's Leapfrog to Methanol Economy). However, at present, indigenous methanol production cost in India is INR 25–27 (0.37–0.39 US$) per liter because it uses natural gas as feedstock. India is planning to produce ~0.7 million ton of methanol from its abundant low grade (high ash content) coal, which cannot be used otherwise for any other commercial application.

India is preparing a road map for methanol introduction in its transport sector, aimed at reducing 20% diesel consumption in next 5–7 years, which can potentially save ~3.77 billion US$ annually. Niti Ayog is planning to make M15 fuel use mandatory for vehicular applications, which can help GoI cut down its crude petroleum import bills substantially. Currently, field tests are going on with M15 for existing vehicles in India. Several researchers have already investigated the potential of methanol-fuelled engines for transport sector and these findings are summarised in Table 7.3.

Tabulated emission data demonstrates that lower methanol blends lead to reduction in CO, HC, and NO_x emissions. Therefore lower methanol blends can be utilized as fuel on the Indian roads.

7.5 Electrical Vehicles

An electrical vehicle powered by electricity uses a large battery to store electricity and then power the propulsion 'motor'. It needs to recharge the batteries after getting discharged. Entire system of EVs can be divided into four sub-systems for understanding, namely (i) Energy source, (ii) Electric propulsion, (iii) Body design, and (iv) Auxiliaries. Energy source includes batteries and battery charger required for energy supply; electric propulsion includes electronic controller, power converter, electric motor, transmission and wheels for propulsion; body design includes body structure, frame, bumpers and suspension; while auxiliaries include brakes, steering,

temperature control, and energy management. All these subsystems interact with each other to drive the vehicle using electrical energy. EVs can be designed to drive solely on stored electricity or by using both electrical energy and fuel energy. EVs can therefore be categorized based on the source of energy used to power the vehicles (Un-Noor et al. 2017):

- Battery Electric Vehicles (BEVs)
- Hybrid Electric Vehicles (HEVs)
- Plug-in Hybrid Electrics Vehicles (PHEVs)
- Fuel cell Electric Vehicles (FCEVs)

7.5.1   Battery Electric Vehicles (BEVs)

BEVs are solely powered by electricity supplied from batteries. Battery provides power to the motor via converter circuits for driving the wheels (Grunditz and Thiringer 2016). Mileage of EVs depend on the battery capacity as well as on vehicle driving conditions, road conditions, air resistance, climatic conditions, and vehicle configuration. Typically it can run 100–250 km with fully charged batteries before recharging, whereas an advanced BEV model can run for larger range between 300 and 500 km (Grunditz and Thiringer 2016). However BEVs require significantly longer recharging time compared to refueling time for traditional IC engine powered vehicles. Depending on the size of BEVs, recharging time can vary from 2 to 8 h or sometimes as long as 36 h (Standard SAE 2010; Yilmaz and Krein 2012). Charging time also depends on charger configuration, battery's power capacity, and available charging infrastructure. BEVs exhibit following advantages over IC engine powered vehicles.

- Simple in construction and operation
- Do not produce tailpipe emissions
- Do not create noise
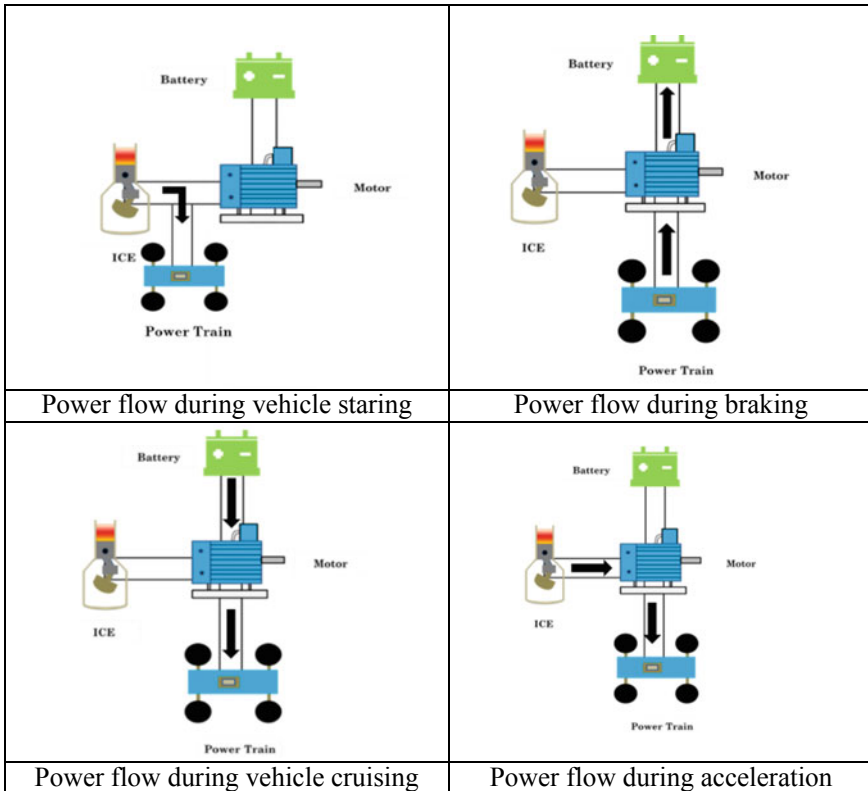- Provide high torque at low speeds

7.5.2   Hybrid Electric Vehicles (HEVs)

HEVs use both conventional fuel energy and electrical energy to drive the vehicles. HEVs can work sequentially on one drive train, or simultaneously on both drive-trains for powering the wheels. It uses an electric propulsion system during low power demand and switches to an IC engine based propulsion system for catering to high power demand. Generally, hybrid system is used extensively to remove the turbo lag in IC engine based turbocharged vehicles. Simultaneously working of two drives improves vehicle's performance. It also improves performance by reducing

the residence time for gear shifting and provides an instant speed boost as per vehicle requirements. During vehicle starting, IC engine runs the motor as a generator to generate electricity, which is stored in the battery. Also, during braking, it runs the motor as a generator to charge the batteries by regenerative braking. Necessary energy flows of HEVs for different operating conditions of the vehicle are shown in Table 7.4 through the direction of arrows. Relative advantages of HEVs over the BEVs are listed as follows:

- Mode switching facility provides better drivability, especially in urban areas where vehicles are often required to operate in variable speeds.
- It has provision to charge the battery even when the vehicle is in operation thus enhances the driving range compared to BEVs.
- It improves vehicle's performance as it uses both powertrains: electrical and IC engines.

Table 7.4 Driving conditions for HEVs

Power flow during vehicle staring	Power flow during braking
Power flow during vehicle cruising	Power flow during acceleration

7.5.3 Plug-In Hybrid Electric Vehicles (PHEVs)

PHEV concept was developed to further extend the range/mileage of HEVs (March-esoni and Vacca 2007; Schaltz et al. 2009; Kramer et al. 2008; Williamson 2007; Wirasingha et al. 2008; Gao and Ehsani 2009). Component wise, it is similar to HEV, but its working pathway is quite different from the HEV. PHEV uses electric propulsion as its main power plant instead of IC engine. Therefore, these vehicles require a normal capacity battery pack. It starts and runs using an electrical propulsion system, and it calls on IC engine only to power the vehicle/charge the battery, when the battery is drained out after a certain vehicle travel distance. PHEV provides flexibility to charge the batteries directly from the grid (during night time, when parked in the garage) and also utilized regenerative braking. Nowadays, automotive market is dominated by PHEVs compared to HEVs due to following advantages they offer:

- They run on electrical propulsion system most of the times, resulting in lower carbon footprint, which makes them preferable over HEVs. Typical daily office commutes on a routine basis do not require IC engine operations.
- They are economical because they use relatively less conventional fuel and they do not have very large battery pack therefore they are not as heavy and as expensive as BEVs.

7.5.4 Fuel-Cell Electric Vehicles (FCEVs)

An electric vehicle equipped with a fuel cell as the source of power is known as Fuel Cell Electric vehicle. Generally, Hydrogen is used as fuel to generate electricity due to its high calorific value; thereby this type of vehicle sometimes is called hydrogen fuel cell electric vehicles (HFCEVs). HFCEVs use a highly pressurized tank to store hydrogen and atmospheric oxygen is also needed to generate electrical power. Generated electricity is consumed by the electric motor for the vehicle driving, and in case for excess electricity generation. Batteries/super-capacitors are used to store the surplus electricity (Camacho et al. 2014; Camacho and Mihet-Popa 2016; Miller et al. 1997; Rodatz et al. 2003; Thounthong et al. 2005). Schematic of a FCEV is shown in Fig. 7.1 to demonstrate schematic of motor, hydrogen-oxygen fuel cell, and pressurized hydrogen tank. These vehicles may have a large market share shortly (Chan 2002; Samuelsen 2016) due to the following advantages they offer:

- Their utilization leads to a zero-carbon footprint because they produce only water as a by-product in the power generation process.
- They use onboard self-generated electricity rather than using separately generated electricity as in case of BEVs.
- These types of vehicles consume lesser time to fill the hydrogen cylinder compared to the battery charging time in case of BEVs.
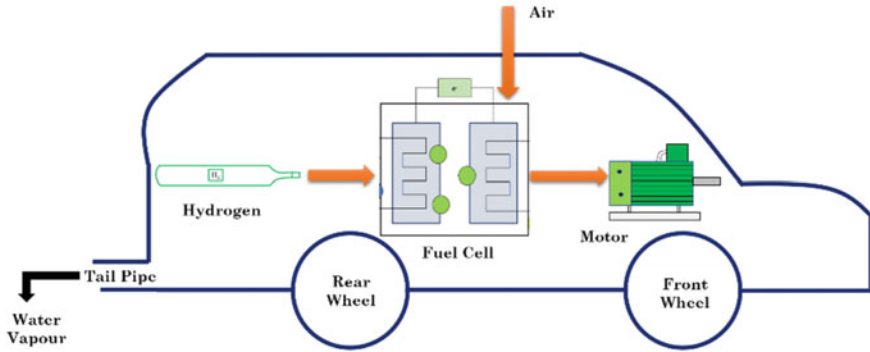
Fig. 7.1 FCEVs configuration

7.6 International Status of Electric Vehicles

Electric vehicles are not a new development, and its seeds started growing in nine-teenth century as shown in Table 7.5 (Global EV outlook 2018). The first electric car was developed in the late 19th century. However the interest faded away due to cheaper availability of petroleum products and limitation in battery storage capacity.

In 2009, sixteen of world's leading governments established Electric Vehicles Initiative (EVI) with a common challenge of spreading 20 million electric cars by 2020 in their territory. Due to national incentive programs of several governments, production costs of EVs, especially battery prices decreased and as a result, by 2014/15, more than 550,000 EVs were sold globally, which was an overall increase of 70% from the previous year as shown in Fig. 7.2 (International Energy Agency 2016).

Table 7.5 Historical evolution of EVs (Global EV outlook 2018)

Year	Country	Remarks
1832–39	Scotland	Robert Anderson developed the prototype of electric carriage
1834	USA	Thomas davenport invented the first electric motor for cars, which operated on a circular electrified track
1888	Germany	Anderson Flockern built the first four-wheeled electric car
1897	USA	Introduction of first commercial electric vehicle and Pope manufacturing company became the first large-scale EV manufacturer
1899	France	First electric vehicle developed, which travelled over 100 km/h
1900	USA	Electric powered cars had the best-selling vehicles with a market share of 28%
1908	USA	Petrol powered vehicles were introduced to replace electric powered vehicles

(continued)

Table 7.5 (continued)

Year	Country	Remarks
1909	USA	US president William Taft bought first automobile-a baker electric
1912	–	An electric starter was invented by Charles Kettering to replace required manual hand cranking in petrol-powered cars
1935	–	Electrical vehicles are almost obsolete due to cheap petrol prices.
1947	Japan	Tama released a 4.5 hp electric car, which requires a 40 V lead-acid battery
1966	USA	US Congress prepared legislation, which recommended utilization of EVs to reduce air pollution
1973	–	OPEC increased oil prices due to which fuels were not available at petrol station. Hence interest in EV was renewed
1976	France	French government launched PREDIT program to accelerate research and development of EVs
1996	USA	GM produced an electric car to comply with zero-emission vehicle requirements in California
1997	Japan	Toyota started selling world's first commercial hybrid car and 18,000 cars were sold in the first year
2008	–	Oil prices increased rapidly
2010	–	Nissan LEAF was launched
2011	–	Autolib launched an electric car with a stock of 3000 vehicles
2011	France	French government committed to buying 50,000 EVs in the coming four years as the global stock of EVs reached to ~50,000
2012	–	Global stock of EVs reached to ~1,80,000
2014	–	Autopilot equipped Tesla Model S introduced
2015	–	One leading Car manufacturer were found cheating the emission regulations, hence making EVs more reliable for emission reduction and reducing the petroleum consumption
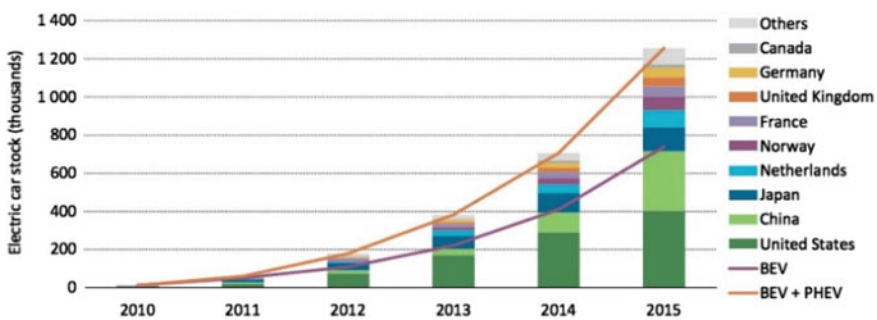
Fig. 7.2 Evolution of the electric car stock worldwide between 2010–15 (International Energy Agency 2016)

China and USA are leading markets for present day on-road EVs. In 2015, China took over the global electric car sales leadership and outperformed the USA by registering highest number of EVs in the world in a year. However, USA possesses the most significant EV stock globally, and China is in the second position by having more than 404,000 cars and 312,000 EVs on their roads. Japan has 126,000 electric cars and is on the third spot. Other significant EVs enthusiast countries are the Netherlands, Norway, France, UK, and Germany.

7.7 National Status of Electric Vehicles

To meet the commitments of Paris Accord, India unveiled 'National Electric Mobility Mission Plan (NEMMP)-2020' to address the issues related to national energy security, tail-pipe emissions, and growth of new era electric vehicles (The Economic Times 2017; India Wants To Become First Country With 100 Percent Electric Vehicles 2016). However, electric vehicles constitute less than 1% among 24 million vehicles sold in 2017–2018. Therefore, the GoI think tank, Niti Ayog declared 'Faster Adoption and Manufacturing of Electric Vehicles (FAME)' program for promoting electrification of transport sector in India. States such as Karnataka, Telangana, Andhra Pradesh, Maharashtra, Goa, and Uttar Pradesh are participating in instituting policies, which would ensure seamless adaption of EVs. GoI and OEM's are working together for boosting the technology. Reva Electric Car Company (RECC), Uber and Ola cabs are working on adoption of electric cars so that EVs can become commercially viable in next two decades in India (The Times of India 2017; Marketers of Electric Vehicles in India). Many leading companies have launched EVs in different segments of transport sector, such as in Cars, Motorcycles, Buses, Mini-trucks, and Rickshaws, as shown in Table 7.6. Investment details of two leading companies for development of EVs are shown in Table 7.7.

7.8 Risks Associated with Battery Electric Vehicles

The most crucial factor in favour of EVs is that they reduce the harmful emissions from mobile transport sector. Thus, their application in transport sector has apparently high potential.

Kjosevsk et al. performed tests of hundreds of EVs under European New Car Assessment Programme (NCAP) and found only one case of an accident of a small fire due to electric shock, which burned plastic foam insulation near the radiator (Risks and safety issues related to use of electric and hybrid vehicles 2017). Accidents revealed that special care should be taken during testing/operating the vehicle, and these are listed in Table 7.8.

Table 7.6 List of Indian companies and Models in EV space

Electric car models	Motorcycles		Buses
Eddy Current Controls, Love Bird	SVM Bikes by Srivaru Motors Pvt. Ltd. (SVM, Srivaru Motor)	Ultraviolette Automotive (The Hindu BusinessLine)	Ashok Leyland
Mahindra e2o Plus	Earth Energy EV (to be launched) (Earth Energy)	Darwyn	Tata Motors
Atom Motors, Stellar	Tork Motors (to be launched) (Economic Times)	Orxa Energies (to be launched) (https:// orxaenergies.com)	Goldstone Infratech
Mahindra e-Verito (2016)	Emflux Motors (to be launched) (http://www.emfluxmotors.com; https://www.financialexpress.com/ industry/sme/electronic-vehicles-company-emflux-motors-raises-rs-2-crore-from-fabian-brian- crain-samar-singhla-and-others/1134413/)	Ather Energy	Mahindra (Electric Truck)
Tata Tigor Electric	Menza motors	Rexnamo	
Mahindra e-KUV 100	Ok Play		
Tata Tiago Electric			

(continued)

Table 7.6 (continued)

Mini-trucks	Auto-rickshaws	Hybrid cars
Tata Motors	Dilli Electric Auto Pvt. Ltd.	Toyota Prius
Ace Electric	Entice Impex Pvt Ltd (Gatti E-Rickshaw)	Toyota Camry Hybrid
Ashok Leyland	Ceeon Indi	BMW i8 test
Dost Electric pick-up truck	Adapt Motors Pvt. Ltd.	Honda Accord Hybrid
OK play	Atul Auto Ltd.	Toyota Prius
	Go Green BOV	
	Mahindra electric	
	Infinite e-solutions	

Table 7.6 (continued)

Scooters			
LightX Motors Pvt. Ltd.	Sincero B6 (https://sinceroautomobiles.wordpress.com)	BSA motors (discontinued) (http://www.evfuture.com/products/view/?product_id=118)	Okinawa Autotech Pvt. Ltd. (http://okinawascooters.com)
Atom Motors (Atom Motors Pvt. Ltd.) (http://atommotors.in)	Ampere vehicles (Electric Vehicle Market in India (PDF) 2018)	Thunder wind	YoBykes (Electrotherm (I) LTD.) (http://yobykes.in)
Avan Motors	Ather Energy Pvt. Ltd. (https://www.atherenergy.com)	BPG	Lohia Auto Industries
Hero electric (Hero MotoCorp) (https://heroelectric.in)	Ceeon India	Rexnamo	BSA motors (discontinued)
Greendzine Tech (http://greendzine.in/)	Palatino (Xxplore Automotive Pvt Ltd.)	Shema E-Vehicle and Solar Pvt. Ltd.	Twenty-Two Motors (kymco) (https://www.moneycontrol.com/news/business/startup/ather-energy-raises-51million-from-sachin-bansal-others-ather-energy-raises-51mn-from-sachin-bansal-others-4032861.html)
Ampere vehicles (Electric Vehicle Market in India (PDF) 2018)	Avera New & Renewable Energy MotoCorp Tech Pvt. Ltd.	Nds eco	Yo Bikes (Electrotherm India Ltd.)
Ather Energy Pvt. Ltd.	Sincero B6	Ether	Ved Motor
Ceeon India (http://www.ceeonindia.co.in)	Okinawa Autotech Pvt. Ltd.		

Table 7.7 Investments made by OEMs in EV manufacturing

Companies	Investments (Crores)	Purpose
Ather Energy	130	6500 Ather Grid fast charging points across India (https://www.moneycontrol.com/news/business/startup/ather-energy-raises-51million-from-sachin-bansal-othersather-energy-raises-51mn-from-sachin-bansal-others-4032861.html)
Mahindra and Mahindra	900	To setup new R&D facility for EV Vertical (https://auto.economictimes.indiatimes.com/news/industry/mm-invests-rs-200-cr-for-ev-power-train-plant-in-chakan/69665724)

Table 7.8 Risks involved with BEVs

Risk	Reduction	
Electric shock 1	DC supply system	Risk
	High Voltage	Electrical arcing
	Low voltage	Electrical shock
	Extra-low-voltage	Low risk
Electric shock 2	High voltages are present in complex electric circuits. Therefore the earth leakage trip should be used in vehicles to avoid probable risks	
Battery acid	Sulfuric acid is corrosive. Hence suitable personal protective equipment/rubber gloves should be used during replacing/working with batteries	
Running battery equipped vehicles	Loose clothing should not be worn by the driver to avoid unexpected accidents since EVs uses complex belt drive mechanisms for powering the drive	
Short circuits	Very high current can flow from the battery, which can burn the driver also. Therefore jump lead with inline fuse should be used to prevent damage while changing/testing the battery	
Person with pacemaker	If a person having a pacemaker system is driving the vehicle, a complex electrical circuit may affect its controller. Therefore, a person with a mentioned condition should avoid using EVs	
Battery damage or incorrectly modified	Potential for release of explosive gases and corrosive liquids are very high	
Presence of magnetic forces	Due to presence of magnetic forces, vehicle may move by itself even when standing in the parking. Additional controller or circuits should be designed to avoid such problems	
Battery storage	Electric energy storage may lead to explosion in the vehicles	

7.9 Methanol Versus EV Powertrains

Large-scale BEV implementation in the Indian transport sector seems to be an impractical solution in the current scenario. Whereas bio-based renewable alternative fuels such as methanol can potentially contribute to the transport sector, since it can be used in the existing vehicles thus reduce petroleum consumption and national import demand. Implementation of BEVs in India is quite challenging due to the following reasons.

7.9.1 Resource Availability

The primary requirement for BEVs is the availability of surplus electricity that can power these vehicles. In India, majority of electrical power is produced by coal-based thermal power plants. Power from other non-polluting sources is relatively insignificant. Power generation on a commercial scale from renewable energy sources, in particular, is in a nascent stage in India. In January 2018, the total installed capacity in India was 334.4 GW, which was predominantly thermal power-based generations (~66%) and contribution of other sources included renewable sources (~19%), hydropower (~13%) and nuclear energy (~2%) (India Population). Electricity production in India follows an increasing trend with some fluctuations. For instance, in 2010, total electricity production was 771.6 billion units, which increased to 1160.1 billion units in 2017 but reduced to 1003.5 billion units in 2018 (India Population; India is now the world's third-largest electricity producer).

According to geological survey of India, the nation had 315.149 billion tons of coal reserves as on April 2017 (Indian Coal Reserves estimate). Indian coal is quite different from American coal due to its drift origin, which has high inorganic inclusions thereby has high ash content. Petrographic analysis indicates the presence of semi-fusinites and fusinites in Indian coal, which are low reactive constituents that cause negative impact on combustion performance in large capacity boiler furnaces. 80% of this coal cannot be used for power generation or for Industrial applications in furnaces due to such a high ash content. However such a high ash content coal can be used for methanol production which is definitely a superior way of coal utilization. It can become a jackpot for India to utilize this high ash coal as raw material for methanol production on an industrial scale and operate the national transport system based on Methanol. Methanol can also be produced from renewable resources and non-renewable resources as mentioned previously.

Two important eco-friendly routes for methanol production are shown in Fig. 7.3: (i) MSW/Biomass where, GHG emissions are reduced by producing energy from wastes (Valera and Agarwal 2019) (ii) catalytic hydrogenation of atmospheric CO_2, which promotes CO_2 sequestration and capture.

Realizing the huge gaps between the demand and supply of electrical energy in India, there exists a big question about 'How the additional electricity demand can be raised by new consumer BEVs (if they are implemented on a large-scale) will be fulfilled?'. On the contrary, India can easily satisfy entire raw material needs for methanol production even if the entire Indian transportation system is 100% dependent on methanol.

The second important concern with BEVs is the manufacturing of batteries, which require rare metals such as Lithium, Cobalt and Nickel. India does have these resources at all and they have to be imported to support the BEV program. The reserves of these rare materials are located in some specific regions of the world, which may leap to global political issues and will limit the BEVs nationwide implementation on an aggressive scale. Hence, BEVs seem to be an impractical solution also for India as far as the availability of required resources are concerned.
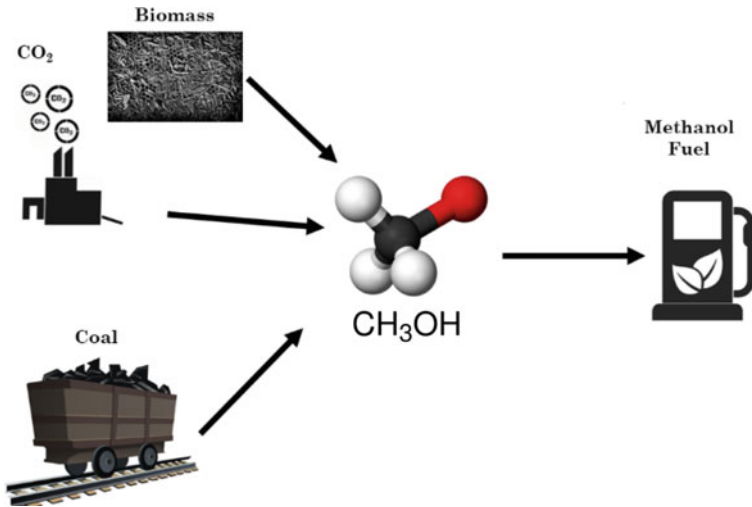
Fig. 7.3 Methanol production routes

- Democratic Republic of Congo, China, and Bolivia are the countries, which have these mineral resources and rare earth deposits, through which they can have monopoly and solely control the market prices of EVs and battery manufacturing materials. Most of these mines have been leased by China globally and they enjoy the monopoly on these resources.

Unfortunately, India will have to depend on China for supply of the required resources for BEVs production, which obviously would increase the market price of BEVs in India, when the demand for these materials exceeds the supplies, which is expected to happen by 2022.

7.9.2 Energy Density

BEVs are not powered as efficiently as conventional ICE based vehicles. To attain similar energy density as that of conventional ICE vehicles, it requires a huge battery pack. In other words, the battery pack should be plentiful in energy storage capacity similar to traditional petrol or diesel tank for supplying an equal amount of energy to the vehicle. Figure 7.4 shows the gravimetric and volumetric energy density of different fuels.

Researchers of Argonne National Laboratory, USA carried out a comparative analysis of overall powertrain energy density between BEVs and gasoline-fueled cars and found that the energy density of gasoline was about 100 times higher than the battery (Fischer et al. 2009). Therefore it is clear that for a similar driving range, BEVs would require a significantly larger space just to make room for the huge battery
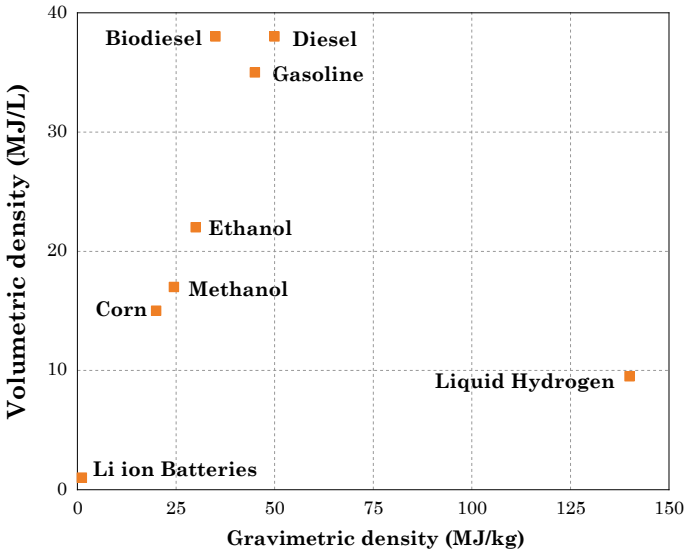
Fig. 7.4 Gravimetric and volumetric energy density of different fuels
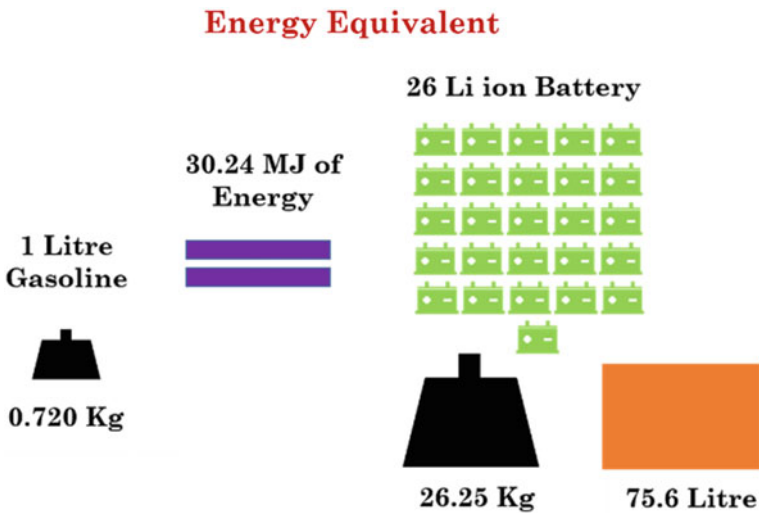
Fig. 7.5 Energy equivalency of current generation batteries vis-a-vis gasoline

pack. It would not only occupy spaces but also increase the total vehicle weight, thus reducing its load carrying capacity, as shown in Fig. 7.5 (Energy Density of EV and Gasoline Powertrains will converge).

On the other hand, methanol has a drawback of lower energy density, about half of that of gasoline or diesel, but still it is far better than batteries in terms of energy

density. To ensure same driving range as traditional fuels, one has to have a relatively larger fuel tank for methanol fueled vehicles.

7.9.3 Emissions and Environmental Impact

Methanol has inherent oxygen in its molecular structure, which helps accomplish more complete combustion and reduces CO, HC, PM and NO_x (depending on engine operating conditions) emissions. Methanol contains zero sulfur; hence its utilization in engines results in zero emission of SO_2 and SO_3, which are toxic pollutants and responsible for acid rains. BEVs, on the other hand, are not at all clean, as long as they use electricity produced from coal and other non-renewable energy sources. In India, coal-based power plants produce majority of electricity and these plants operate at very low thermal efficiency in the range of 25–30% only therefore use of coal based electricity for BEVs propulsion cannot be claimed as being pollution free and is a true eye wash. Indian coal contains high sulfur, mercury and other heavy metals hence coal firing in the power plants produces hazardous pollutants, which adversely affect human health and the ecosystem. Coal-fired power plant emissions can be more dangerous than vehicle tailpipe emissions. As per the report published in Dec-2012 by the GoI, coal emissions resulted in 80,000 to 1,15,000 pre-mature deaths and more than 20 million asthma cases due to exposures to the air pollution generated by them (India's Dirtiest Energy Source). Additional health impacts such as a large number of cases of heart attacks, emergency room visits, hospital admissions, and loss of workdays were also reported in large numbers due to these emissions. The study revealed that the cost associated with the air-pollution related health impacts exceeded Rs. 16,000–23,000 crores per year. If the transport sector shifts to EVs, the pressure will be transmitted to the thermal power plants to produce surplus electricity for powering this sector. As a result, coal-burning emissions will further increase in India, worsening the already grim situation. Therefore, implementation of BEVs may reduce the tailpipe emission apparently, but it will increase the coal-fired emissions with significantly greater magnitude, which are more hazardous compared to emissions from methanol/gasoline fuelled engines. BEVs are also associated with some other relevant sources of dangers that they would pose, some of which are mentioned below:

- Lithium-ion batteries have no recycling value, which will damage the environment extensively. Used Lithium batteries are a hazardous waste.
- Mining and smelting of nickel and cobalt generates immense water, soil, and oil pollution.
- Battery manufacturing company would emit 74% more CO_2 than producing a popular car to run on fossil fuels (Battery Data).

7.9.4   Fueling Outlets

Existing vehicle refueling infrastructure can be used for methanol supply because it has physico-chemical properties comparable to those of conventional fuels. Modest changes may be required in the fuel supply infrastructure for handling methanol because it absorbs moisture from the atmospheric air. It is possible to convert existing outlets into the ones compatible with methanol blends at a small cost. However, in addition to governmental support, India would require the involvement of independent fuel distributors, methanol suppliers, and oil companies to develop desired infrastructure for methanol fuel production and distribution. GoI can also impose regulation by mandating methanol (similar to ethanol mandate) and launch different financial supporting schemes in order to promote methanol adaptation in the transport sector.

On the other hand, recharging stations are quite crucial for BEVs, which warrants a completely new infrastructure development. BEVs based transports would need a very high number of recharging facilities since they have a limited driving range. Customers can only go for BEVs if they are assured that the battery charging stations are densely located around the region. However, there always exists a dilemma, whether BEV manufacturing and marketing should come first or the development of required infrastructure should come first. Some of the important aspects related to BEVs recharging stations are mentioned below.

- Replacement of batteries or required recharging time may create chaos at these stations. Some of this is already being experienced in Bangalore.
- Ample space is required at the charging stations and space availability is a big issue in cities.
- A large number of plug-in slots are needed to charge the batteries, which is associated with the risks of electrical hazards including electrocution, more so during rainy season, putting the occupants of the car in grave risk.
- Apart from public charging stations, charging stations are also required at workplaces and at parking towers, the development of which would require huge investments.

7.9.5   Economics

A case-study was done in the UK, California, Texas, and Japan to assess the total cost of ownership (TCO) of conventional, plug-in hybrid, hybrid, and battery-electric vehicles. In the study, TCO of the Toyota Prius, Prius Plug-in, and Nissan LEAF was compared to the Toyota Corolla in Japan, California, and Texas, and to the Ford Focus in the UK. TCO was calculated on an average annual mileage of region, and average annual maintenance cost. EVs were found to be slightly cheaper compared to conventional ICE vehicles due to less wear of the brakes and existence of fewer

Table 7.9 Comparison table for conventional, methanol and battery vehicles

Factors	Conventional Vehicles	Electric Vehicles	Methanol vehicles
Resources	Poor	Poor	Excellent
Energy Density	Excellent	Poor	Good
Emissions	Good	Good	Excellent
Fueling Infrastructure	Excellent	Poor	Excellent
Price	Good	Poor	Excellent
Status	Excellent	Good	Poor

moving parts. Another study by Arthur D Little revealed that BEVs are 45–60% more expensive in terms of TCO, compared to IC engine vehicles.

However, Indian scenario is different since all the necessary materials for EVs production are needed to be imported from abroad and eventually it will make EVs more expensive compared to the conventional vehicles. The price of Indian cars used by masses is also much lower than the rest of the world therefore making a decent EV at those price-points will not be possible.

On the other hand, India is currently producing its entire methanol from imported natural gas. It is now possible to use indigenous high ash coal, MSW and Agricultural waste as a raw material for Methanol Production, which is an economically viable route for methanol production in India to cater transport sector. Investment of ~INR1200 Cr is required to produce 1600 tons of methanol per day with a price of INR17–19 per kg, which is comparable with the cost of imported methanol. At present, per liter methanol production cost in India is INR 25–27, which can vary depending on price volatility of imported natural gas (Various Industry sources—India's Leapfrog to Methanol Economy).

Even if the present value is considered as a reference price; it is approximately one-third the gasoline price, which makes methanol fuelled vehicles more economical compared to EVs. Based on the above discussion, Table 7.9 compares conventional petroleum fuelled vehicles with Methanol fuelled vehicles and battery electric vehicles.

7.10   Conclusions

Indian automotive sector is one of the world's largest sectors, where passenger vehicles, commercial vehicles, 2-wheelers, and 3-wheelers are the four important segments. Vehicles in each segment are driven by conventional fuels such as gasoline and diesel. These vehicles emit harmful pollutants such as NOx, SO_2, CO_2 and PM. As a result, India's ten major cities figure in world's most polluted cities. India signed the Paris Climate agreement to reduce vehicular tailpipe emissions therefore there

is need to take urgent step to meet these obligations. There is continuous depletion of conventional fuels in India and we are resource limited country with burgeoning appetite for energy due to our growing economy. Stringent emission norms are pushing researchers to find alternative fuels, which can reduce tail pipe emissions and helps the country to comply with the Paris Climate agreement. However conventional fuel prices are continuously rising due to high demand and global politics. Fossil fuel combustion is one of the significant factors, which are worsening the ambient air quality of Indian cities. Methanol economy is one of the best ways to salvage this situation.

A comprehensive review of methanol-fuelled vehicles and electric vehicles with their national and international status has been covered in this chapter. Potential and limitations of electric vehicles and methanol fuelled vehicles have been comprehensively discussed. Methanol fuelled vehicles seem to be an economical/eco-friendly solution compared to electrical vehicles due to following reasons: (i) Existing electricity production in India does not support large scale adaptation of EVs in the transport sector, (ii) Unavailability of necessary resources for EVs production is a big concern, (iii) Methanol can be economically produced from Indian high ash-coal and its utilization in transport sector can reduce India's petroleum import bill, (iv) Low methanol blends with conventional fuels can be used as fuel in existing engines without any major modifications.

On the EV front, China and US are the market leaders for on-road EVs. US Congress prepared legislation for utilization of EVs to prevent the air pollution. Japan-based Toyota company sold the first commercial hybrid car in 1990s. In India, National Electric Mobility Mission Plan was unveiled to increase the market share of Electricity driven vehicles. Faster Adoption and Manufacturing of Electric (FAME) Vehicles program was declared by GoI for complete electrification of transport sector. Reva electric car company, Ola and Uber are working together for the viability of electric cars. However the fact remains that EVs suffer from the driving range anxiety and low battery life. There is lack of public charging infrastructure in the country. EVs have high vehicle procurement costs and operating cost, high batteries charging/swapping time compared to ICE fueling time, unavailability of material resources for EVs production, and severe electrical hazards due to complex electrical circuits.

China on the other hand, is producing millions of gallons of alcohol fuels using sewage sludge waste. Their production of methanol is higher compared to other alcohols. M5, M10, M15, M85, and M100 are officially available at private fuel stations. US car/bike racers are utilizing methanol to power their vehicles. Sweden is working on bio-methanol production plants, which is going to produce 5000 tons of methanol per year. European Union has targeted 10% of transport fuel to be biofuels by 2020. India has plenty of high ash coal, which can be used as a raw material for methanol production. Indigenously produced methanol can be utilized to power the vehicles, which can make India energy self-dependent for transport fuels. Methanol has ~50% inherent oxygen, which improves the combustion and produces relatively higher power compared to conventional fuels. Methanol contains zero sulphur and its combustion does not produce SO_2 and SO_3. Existing refueling stations can be

retrofitted for methanol supply without significant investment. Hence no additional investment is required for constructing new refueling infrastructure. In India, Gujarat Narmada Valley Fertilizer & Chemicals limited, Rastriya Chemicals and Fertilizers, Assam Petrochemicals, National Fertilizers Limited and Deepak Fertilizers are the main methanol producing companies. Niti Ayog is preparing a road map for making M15 as mandatory for existing vehicles. Experimental tests are going on with M15 fuel for the existing vehicles.

In summary, it will be wiser for India to promote Methanol fuelled vehicles and methanol economy and shun the EV program, which is ill conceived and poorly implemented. Let the customers decide, which technology they would like to use. The government should be technology agnostic and it should leave the choice of technology to market forces, which is a sign of matured economy.

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Chapter 8
Engine Parameters Assessment for Alcohols Fuels Application in Compression Ignition Engines

Sam Shamun, Giacomo Belgiorno and Gabriele Di Blasio

Abstract An increasing interest of governments on alternative fuels for internal combustion engines (ICE) as a possible route to reduce pollutant and CO_2 emissions has been shown. Advanced combustion concepts combined with alternative fuels have the potential to improve efficiency and emissions levels. In this framework, the compression ignition (CI) engines have a higher brake thermal efficiency compared to the spark ignition (SI) engines and therefore lower efficiency related CO_2 emissions. High research octane number (RON) fuels can be used in CI engines to realize premixed combustion thus reducing the soot emissions, and to a certain extent also NO_x. Thus, alternative alcohol fuels such as methanol and ethanol represent a valuable option for further reducing the CO_2 footprint of CI engines. In this chapter, the main advantages and drawbacks of using alcohols as primary fuel or additive in diesel are evaluated in terms of performance, combustion characteristics and emissions, with particular reference to energetic analysis.

Keywords Alcohols · Methanol · Ethanol · Partially premixed combustion

8.1 Analysis of the Main Calibration Parameters of Alcohol Fuels in Compression Ignition Engine

In this chapter, a short review about the combustion calibration parameters that most influenced the combustion process, emission and efficiency of a compression ignition engines fuelled with methanol and ethanol has been carried out. The main results comes from activities performed at Lund University and Istituto Motori respectively using methanol and ethanol (Shamun 2019; Belgiorno et al. 2018; Shamun et al.

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Table 8.1 Engines geometrical characteristics

	Light duty	Heavy-duty
Displaced volume (cc)	477.5	2100
Stroke (mm)	90	160
Bore (mm)	82	130
Compression ratio	16.5	15.3
Number of valves	4	4
Diesel injection system	Common rail	Common rail
Injector	Solenoid 7 holes microsac	Solenoid 10 holes
Fuels	Ethanol blends, Diesel	Methanol, Ethanol, Diesel

2018). In particular, the experimental activities were conducted on compression ignition engines test rigs for heavy duty and light duty engine application. The activities regarding the methanol in CI engines were performed on a heavy duty single cylinder engine (SCE), while the ethanol blends activities on light duty SCE. The main engine geometrical characteristics are reported in Table 8.1.

The in-cylinder pressure traces were detected by means of a Kistler piezo-quartz transducer with a resolution of 0.1 CA deg. Starting from pressure signal, the indicated mean effective pressure (IMEP), the apparent heat release (HR) and heat release rate (HRR) have been calculated. The heat release analysis is based on the first law of thermodynamics as reported by Heywood (1988). The engine-out gaseous emissions in terms of THC, MHC, NO_x, CO, CO_2 and O_2 are measured using the emissions test bench.

The chapter focuses on how the engine calibration parameters impact on its reduction by preserving or improving the engine performance and emissions. The parameters analysed are injection pressure, injection strategy (single and double injection), EGR and the ethanol blend ratio. The aim is to provide general statements of the engine parameters effects on combustion characteristics, emission and efficiency when fuelled with alcohols fuels.

The fuel property differentiating alcohol fuels from conventional high cetane number compression engine fuels is the charge cooling effect. This property affects the whole cycle from the start of injection event until the exhaust valve opening. Commonly, the charge cooling effect depends on the heat of vaporization, ΔH_{vap}, of the fuel, measured in kJ/kg. However, this measure is not very relevant in internal combustion engine applications since it does not take o account the stoichiometric air-fuel ratio and energy density, Q_{LHV} (Shamun et al. 2018). In order to compare the charge cooling effect of the different fuels, for each fuel the ΔH_{vap} should be normalized with its Q_{LHV} to be relevant. From Table 8.2, relevant fuel properties from selected fuels can be observed, including the ΔH_{vap}, Q_{LHV}, and ΔH_{vap} normalized with Q_{LHV}, in this chapter termed $\Delta H_{vap}/Q_{LHV}$.

Table 8.2 Selected fuel properties for diesel fuel, methanol and ethanol (Heywood 1988; Yates et al. 2010; National Center for Biotechnology Information 2018)

	Diesel	Methanol	Ethanol
RON (–)	–	~109	108–109
MON (–)	–	92	89
Molar mass (g/mol)	170	32.0	46.07
H/C (–)	1.8	4	3
O/C (–)	0	1	0.5
Q_{LHV} (MJ/kg)	42.9	19.9	26.9
$(A/F)_s$ (–)	14.5	6.45	9.0
Viscosity (mPa/s)	3.91	0.544	1.36
Density (kg/m^3)	810	792	785
Boiling point (°C)	180–360	64.7	78
Heat of vaporization (kJ/kg)	270	1103	840
ΔHvap/QLHV (kJ/MJ)	6.29	55.43	31.23
Specific heat (kJ/kgK)	2.2	2.6	2.5

From Table 8.2, it is evident that charge cooling effect of ethanol and methanol are ~5 and ~8 times higher than that of diesel, contributing to a significant difficulty to ignite these fuels when using conventional compression ignition intake temperatures and compression ratios. Several studies have shown that to achieve methanol or ethanol ignition with a single injection event, it is required to inject the fuel into a hot combustion chamber ambient or alternatively using a continuous activated glow plug (Kaiadi et al. 2013; Shen et al. 2013; Mueller and Musculus 2001). To give the reader a comprehension of the required intake temperature for an engine using 15:1 compression ratio; ethanol needs an intake temperature of approx. 105 °C while methanol requires approx. 155 °C to obtain satisfactory igniting conditions (Shamun 2019). More details regarding the effects of charge cooling effects on the combustion, performance and emissions are further discussed later on.

As a result, from the charge cooling effect, the combustion occurs at a lower temperature than that of gasoline and/or diesel combustion, given that the load and other control parameters are held constant. This means that the temperature difference between the burning charge and the combustion chamber walls is smaller, which in turns means that a lower amount of heat will be lost during combustion and will instead be utilized to exert pressure on the piston, increasing the overall efficiency (Caton 2012).

8.1.1 Injection Pressure

In modern compression ignition engine utilizes a common rail fuel injection system, which enables the use of very high injection pressures keeping the soot emissions,

combustion noise under control achieving high specific power density (Di Blasio et al. 2017).

When running a compression ignition engine on commercial diesel fuel, the general strategy is to have different injection pressures at different loads: the injection pressure is generally reduced at lower loads while it is kept higher at higher loads (Di Blasio et al. 2017).

At lower loads, a high injection pressure is avoided to reduce the mechanical losses originating from the high-pressure fuel pump. Instead, a lower injection pressure in combination with a regulated duration of the injector needle lift is utilized to regulate the load. Higher loads and injection pressures do not cause a significant deterioration of the mechanical efficiency as it does at the lower loads. Meanwhile, a higher injection pressure limits the soot emissions due to improved air entrainment and thus oxygen availability in the fuel jet, which helps to oxidize soot at the end of the combustion process (Gallo et al. 2017).

When using alcohols, or alcohol-diesel emulsions as fuel, the trade-off between mechanical losses and soot emissions plays a less significant role. This is because the combustion of neat alcohols does not produce soot in the same manner as the heavier diesel fuels due to the lack of formation of polycyclic aromatic hydrocarbons (PAH), thus less attention needs to be paid to reduce the emissions at the cost of mechanical efficiency (Shamun et al. 2016). Soot emissions will be discussed in further detail in Sect. 1.6.

The injection pressure, when utilizing alcohols, or blends of alcohols, can instead be used to further optimize the combustion in terms of emissions, performance and engine noise (Shamun 2019).

8.1.2 Single Injection

Double injection strategies in modern compression ignition engines, with pilot and main injections, are generally used to reduce the maximum pressure rise rate, PRR_{MAX}, which is the major factor affecting engine noise (Selim 2003). When the fuel is injected into the hot ambient of the combustion chamber, the first process is the fuel atomization followed by evaporation. As earlier mentioned, the evaporation of the fuel draws a significant amount of energy from the air trapped inside the cylinder, which cools down the charge. This leads to a long ignition delay resulting in a positive mixing period which is a separation of the end of injection from the start of combustion (Abu-Qudais et al. 2000). The higher level of premixing generally causes a hear release rate which only consists of a premixed flame mode (Pucilowski et al. 2017). Depending on the intake temperature, injection timing, fuel properties, the end of the heat release rate can sometimes be seen to have a vague diffusion tail. This can be observed in Fig. 8.1.

The combustion strategy, in which the charge is burning in several combustion modes simultaneously—homogeneous and diffusion flames—is commonly defined as partially premixed combustion, PPC. It is not necessarily defined by a single

Fig. 8.1 In-cylinder
pressure and heat release rate
of diesel and ethanol blends
at 2000 rpm and 4 bar of
IMEP net with single
injection strategy
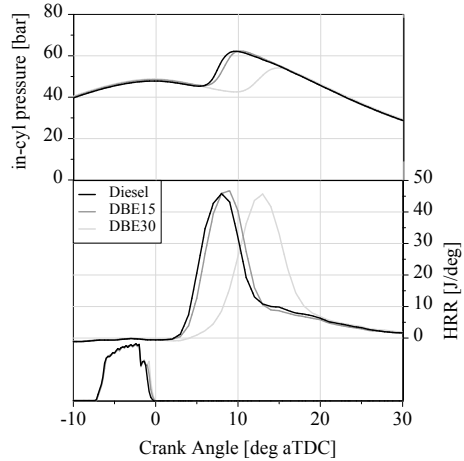
injection strategy of a high octane fuel, since several authors claim that PPC can be achieved with a double injection strategy as well (Kaiadi et al. 2013). This combustion strategy is generally characterized by lower heat transfer, reduced NO_x emissions, while using fuels with higher octane number in a CI engine to achieve more premixing and lower soot emissions. The general "recipe" for this combustion mode is the heavy use of exhaust gas recirculation (50%), EGR, and lambda = 1.5 (Yin et al. 2016; Solaka et al. 2012).

This separation means that the charge will be less stratified due to the longer time frame for charge homogenization while simultaneously be more premixed. The higher level of combustion premixed is advantageous in the sense that it reduces overall heat losses. First and foremost, the combustion duration is reduced. This shortens the timeframe in which heat transfer can occur during the combustion process itself. Assuming that the faster combustion is phased at an optimal crank angle, there will be more time to expand the hot exhaust gases and thus extracting more energy from the heat to be converted into torque (Shamun et al. 2018). The faster combustion of methanol and ethanol also contributes to the reduced heat losses due to the faster combustion at similar operating points (Sayin 2010; Veloo et al. 2010).

The issue, as mentioned earlier in the beginning of this Subsection, is the charge cooling effect. The charge, at the time and location of the ignition, must still be maintained above the autoignition temperature of the used fuel. This is done either by increasing the intake temperature, compression ratio or a continuously active glow plug.

Moreover, the colder combustion of ethanol and methanol can tend to decrease combustion stability, increasing the coefficient of variation of the indicated mean effective pressure, COV_{IMEP} (Shahir et al. 2014). The increased instability of the combustion can in its turn increase the emissions of CO and THC due to increased under-mixing and over-leaning (Heywood 1988). However, it should be mentioned that if an appropriate in-cylinder temperature is applied prior to the combustion,
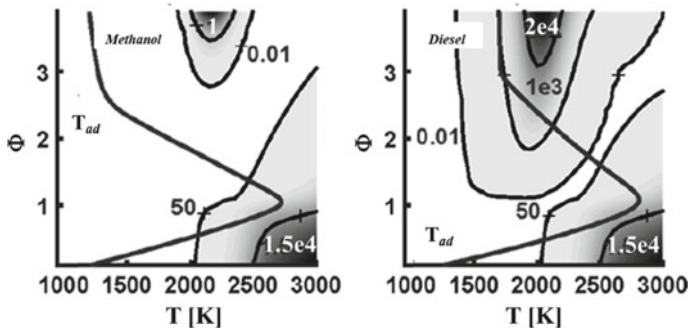
Fig. 8.2 Φ-T diagram comparing methanol (left) and diesel (right) soot and NO$_X$ levels

the instability, as well as the CO and THC emissions, can be remedied. The higher intake temperature also reduces the ignition delay, which will result in a lower amount of fuel impingement on the combustion chamber walls, leading to further reduced THC emissions. However, the remedial action of reducing the CO and THC will come often come with the cost of increasing the NO$_X$ emissions due to the resulting higher combustion temperature, given otherwise similar combustion characteristics and constant control parameters (Shamun et al. 2016; Manente 2010).

It is well established that there are three main factors affecting the NO$_X$ formation in an internal combustion engine: temperature, equivalence ratio and time. The lower exhaust gas NO$_X$ emissions for methanol- and ethanol-PPC can be explained by illustrating the path of combustion in terms of equivalence ratio and temperature over the soot and NO$_X$ islands, observed in Fig. 8.2.

1-D and computational fluid dynamics simulation studies conducted by Svensson et al. and Pucilowski et al. showed that the combustion of methanol starts in the lean regions of the charge, in contrast to diesel fuel where the ignition is initiated in the rich regions (Pucilowski et al. 2017; Svensson et al. 2016). This phenomenon can possibly be explained by the long ignition delay of methanol, which grants more time for the charge to lean out. Another reason for the lower NO$_X$ emissions—apart from the generally colder combustion—is that a portion of the combustion takes place in the lean region, in which the temperature is low and therefore does not contribute to the NO$_X$ formation despite the higher peak pressures and temperatures of the PPC strategy.

8.1.3 Double Injection

Using methanol and ethanol, a double injection strategy is very different from that of a single injection strategy in several aspects. The injection event is divided into a small first injection, generally called pilot injection, and a larger main injection. The heat release rate resembles very much that of conventional diesel combustion, CDC,

Fig. 8.3 In-cylinder
pressure and heat release rate
of diesel and ethanol blends
at 2000 rpm and 4 bar of
IMEP net with double
injection strategy
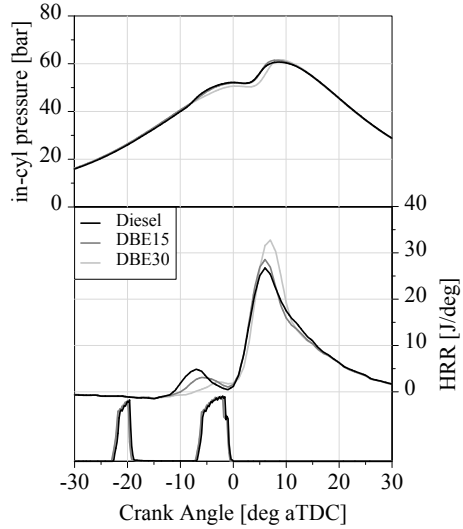
consisting of a small premixed flame, followed by a large diffusion tail. Alcohols
heat release rate when combustion occurs in PPC and CDC, can be seen in Fig. 8.3.

This combustion mode is superior to single injection mode in terms of stability,
when using methanol and ethanol. This does not mean that a low COV_{IMEP} cannot
be achieved with a single injection strategy, however, that the COV_{IMEP} of a dou-
ble injection strategy is less sensitive to varying control parameters, such as intake
temperature, intake pressure, EGR, to mention a few (Shamun 2019). The lower
sensitivity of the double injection strategy comes from the pilot injection. The pilot
is, as earlier mentioned, a significantly smaller injection, which does not contribute
much in cooling the charge. Instead, the pilot starts the combustion event. The hot
gases from the pilot are then partially pushed back towards the injector, at the timing
which the main injection is initiated (Knox et al. 2015). Then, the temperature is then
high enough to start the combustion as soon as the main injection occurs, without
the need of a premixing period. It is of importance that the pilot injection is small
enough to not cool down the charge below the autoignition point of the utilized fuel
when the main injection takes place. The advantage of the double injection strategy
is the ability to be able to use a lower intake temperature—due to the pilot increasing
the in-cylinder temperature—which could eventually be beneficial from a cold start
perspective.

In terms of overall efficiency, this injection strategy performs slightly worse than
that of a single injection strategy. The combustion event has a significantly longer
duration due to the occurrence of the longer diffusion tail. The longer combustion
duration gives more time for heat transfer from the charge to the combustion chamber
walls to occur, which increases the heat transfer losses (Chang et al. 2012). Moreover,
since the combustion duration is longer, a higher amount of fuel will inevitably
burn further into the expansion stroke, leaving less potential for expansion and thus

increased exhaust gas losses due to the higher exhaust temperature (Knight et al. 2010).

Since the combustion has a smaller ignition delay and no mixing period if measured from the main injection event, the fuel impingement on the combustion chamber walls is significantly reduced when compares of those of single injection strategy. The fact that the combustion is stable, with reduced occurrences of undermixing and over leaning, also contributes to reduce the CO and THC emissions for this injection strategy (Kaiadi et al. 2013).

The peak pressure, and thus the combustion temperature, when running CDC with methanol or ethanol, is not as high as that of PPC owing to the reduced PRR_{MAX} of CDC which could potentially decrease NO_X emissions for this combustion strategy (Nehmer and Reitz 1994). On the other hand, the longer combustion duration of CDC can cause a significant amount of the time spent at a lower temperature, in comparison to PPC, which could be considered a trade-off. Considering a constant equivalence ratio and temperature, the relation between the NO_X concentration and time is of an exponential type, meaning that even a slight increase in combustion duration can have the potential to cause a significant increase in NO_X formation (Heywood 1988).

In Fig. 8.3, the premixed part of the CDC combustion can play a role in the formation of NO_X. If the premixed portion of the flame—generally caused by the pilot or any of the pre-injections—is larger, the temperature at that part will be increased more in comparison to a smaller premixed flame. A larger premixed flame will, in turn, be a set-up for a maintained high temperature as well during the diffusion combustion for a longer period and thus increase the NO_X emissions (Shamun 2019). In this sense, even though the peak pressure and temperature can be lower for CDC than those of PPC, a lower concentration of NO_X in the exhaust when utilizing CDC cannot be established as a general conclusion.

8.1.4 Effect of EGR on Alcohol Combustion

Many modern compression ignition engines utilize EGR, which is a way to reduce the NO_X emissions by increasing the specific heat ratio, γ, of the intake air. By having a higher γ of the intake air, the inducted air is able to absorb a larger portion of the energy produced by the combustion and thus reducing the maximum temperature during the combustion event (Murayama et al. 1995).

The use of EGR, however, does not come without drawbacks. In compression ignition engines running on diesel fuel, the reduced concentration of oxygen in the charge promotes the formation of soot emissions, due to a deteriorated oxidization process. For gasoline, the trend is similar to that of diesel, however, the produced soot at a given EGR rate, or intake oxygen concentration, $O_{2,IN}$, is slightly lower. A further increase in EGR deteriorates the combustion to the level at which the fuel itself is poorly oxidized and thus the emissions of CO and THC are increased to
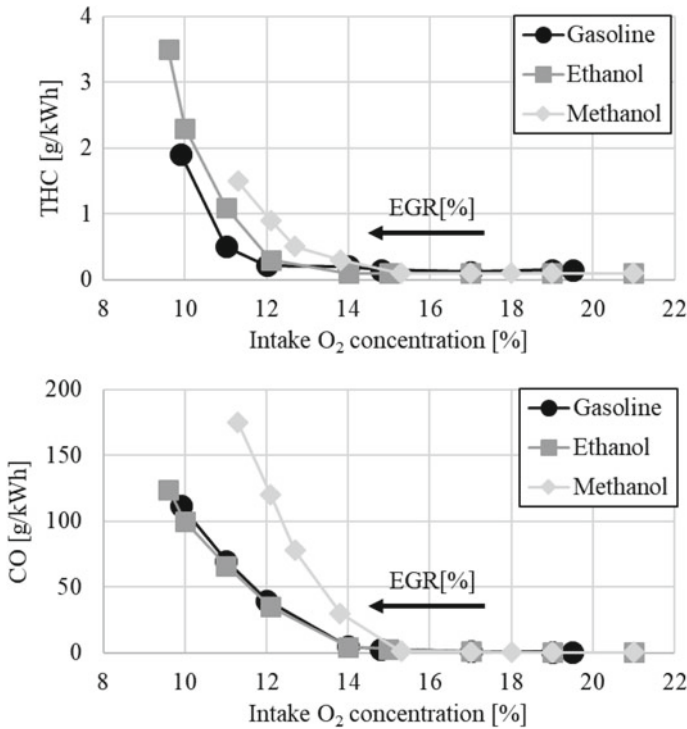
Fig. 8.4 THC (above) and CO (below) as a function of intake oxygen concentration for different fuels tested at 1200 rpm and 6 bar of IMEP gross

unacceptable levels (Shamun et al. 2016; Murayama et al. 1995). This can be seen in Fig. 8.4.

Apart from the effects of EGR on emissions, there are also effects on the combustion characteristics as well. Due to the high CO, THC and soot emissions, the combustion efficiency drops significantly, reducing the overall efficiency of the engine. Meanwhile, the COV_{IMEP} is reduced due to the deteriorated combustion efficiency and the inadequate concentration of O_2 in the charge (Shen 2013).

In the case of methanol and ethanol combustion in CI engines, the trends are similar. However, due to the fact that these fuels have a high $\Delta H_{vap,}$ they tend to be more sensitive to EGR in terms of a reduced COV_{IMEP}. As mentioned earlier, this combustion instability, as well as the elevated CO and THC emissions, can be circumvented by increasing the intake temperature or the compression ratio while keeping the NO_X emissions under control. The major advantage of running methanol or ethanol, with high levels of EGR, is that the well-established NO_X-soot trade-off, can be avoided altogether since these fuels do not have the issue of producing soot (Shamun et al. 2016).

A study conducted on a methanol-fuelled CI engine using a compression ratio of 27:1, have shown that an EGR rate of 50% can be used while maintaining CO, THC
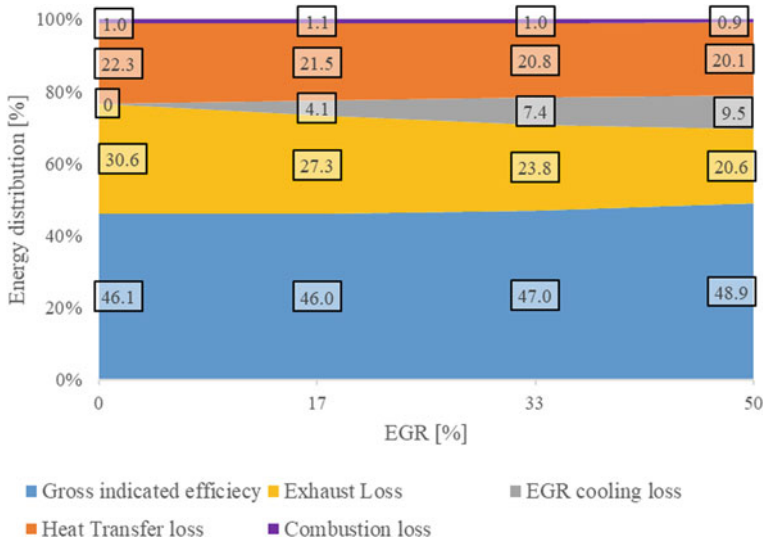
Fig. 8.5 Energy distribution on methanol combustion at different levels of EGR at 1200 rpm and 6 bar of IMEP gross

and, in particular, NO_X emissions on a low level (Shamun et al. 2017). The relatively low CO and THC was a result of high pressure and a good oxidization process while the near-zero NO_X was due to reduced combustion temperature. Moreover, the study—using a Box-Behnken design of experiment—also measured a higher gross indicated efficiency, η_{GIE}, at 50% EGR. It was shown that the increased η_{GIE} was due to the lower combustion temperature and heat transfer which in turn decreased the heat losses. The effect of EGR on methanol combustion in a CI engine with a high compression ratio can be seen in Fig. 8.5.

Moreover, several studies have also shown that a slight decrease in $O_{2,IN}$—or a slight increase in EGR—reduces the THC emissions in particular (Shamun et al. 2016). It is reasoned that this slight decrease occurs due to the existing THC in the exhaust gases are combusted twice once the exhaust gases are reintroduced into the intake manifold (Shen et al. 2013; Shamun et al. 2016, 2017; Jacobs et al. 2003).

8.1.5 Ethanol Diesel Blends

Until now, the chapter has presented the effects on combustion characteristics, performance and emissions of methanol and ethanol utilization in CI engines. However, there is a possibility to blend alcohol and diesel, given that there is a presence of an emulsifier. An emulsifier is necessary since the chemical structure of alcohols tend to have a polarity that is exponentially increased with a reduced carbon chain length, which arises due to the position of the oxygen atom in the molecule. In contrast,

diesel fuel consists mainly of long hydrocarbon chains in the range of 18–21 carbon atoms (Collins 2017).

It is not possible to generalize the trends observed from the utilization of alcohol-diesel fuel blends, since some engine parameters can show completely opposite effects depending on the emulsifier used. Several studies have been conducted on this matter, and the results differ significantly due to different combustion chamber geometry, emulsifier type, operating conditions etc. Two studies conducted by Belgiorno et al. and Shamun et al. on the same experimental setup and using similar operating conditions, however, with two completely different emulsifiers: gasoline and soybean fatty acid methyl ester (FAME or biodiesel) (Belgiorno et al. 2018; Shamun et al. 2018). Gasoline, being a fuel dedicated to spark ignition engines, show different results from FAME in terms of combustion characteristics, performance as well as emissions. It can be mentioned briefly that the diesel fuel content in the blends eases the ignition significantly in comparison to neat methanol or ethanol. In this Subsection, however, mainly the effects of the different fuel blends on soot formation will be discussed.

A higher ethanol concentration in an alcohol-diesel fuel blend will reduce the soot emissions drastically. Although methanol and ethanol both burn with a virtually smokeless flame and has a very small contribution to the particle number (PN) and particulate matter (PM), there are also other factors affecting the soot formation inside the cylinder (Shamun et al. 2017). In Fig. 8.6, it is possible to observe the particle size distribution (PSD) curves and black carbon soot emissions respectively, comparing diesel with diesel-gasoline-ethanol in the ratios of 68:17:15 and 56:14:30 as well as diesel-biodiesel-ethanol utilizing the same ratios. In this work, they are referred to as DGE15, DGE30, DBE15 and DBE30.

As can be seen from Fig. 8.6, an addition of 15 vol.% of alcohol reduces the PN and soot emissions significantly. Of course, a consideration has to be taken to the fact that both the emulsifiers used, reduce the PM emissions when compared to diesel fuel. Gasoline reduces the PM emissions mainly due to its constituents have a shorter average carbon chain, while FAME has an ester group which contains an oxygen atom (Belgiorno et al. 2018; Shamun et al. 2018).

The reduction of soot concentration in the exhaust gas, is not proportional to the concentration of ethanol in the fuel. In fact, the reduction of the soot concentration is larger than the addition of ethanol, or any emulsifier, in the fuel blend. The reduction of the exhaust PM emissions is very much influenced by the combustion itself. In the case in which gasoline is used as an emulsifier, the higher level of premixing also helps to reduce the soot formation due to the earlier mention oxygen availability in the charge. Also, the high oxygen content in the ethanol, works in synergy with the premixing, since the oxygen availability increases the oxidation process significantly. In the case of biodiesel, the premixing period is decreased, in comparison with the DGE fuels. However, the oxygen content of biodiesel, still aids in increasing the oxygen availability, which in turn decreases the PM emissions (Sison et al. 2007).

Fig. 8.6 Particle size
distribution function for
diesel and ethanol blends at
different engine speed and
load conditions
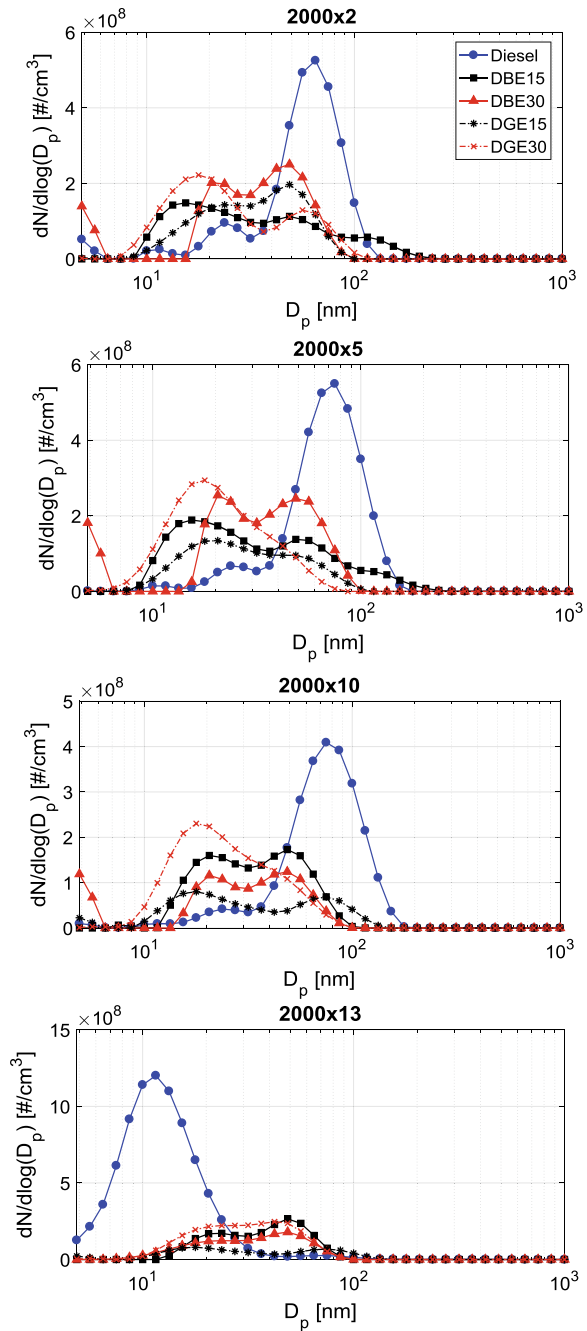
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Chapter 9
A Comprehensive Review on Oxygenated Fuel Additive Options for Unregulated Emission Reduction from Diesel Engines

Vijayashree and V. Ganesan

Abstract Compared to petrol and diesel engines, higher fuel economy along with higher power output is obtainable from diesel engines. Further, it has better thermal efficiencies and torque characteristics. On the negative side, the diesel engines are a major source of both regulated and unregulated emissions causing deterioration in air quality causing greater health hazard. Therefore, there is an urgent need to mitigate the society from this peril. From the authors' point of view compared to regulated emissions unregulated emissions should be tackled with greater zeal. There are three possibilities

 (i) to get rid of IC engines and to use electric vehicles,
 (ii) to discard present day petro diesel and go for hydrogen as a fuel,
 (iii) to use alternate source of energy like biodiesel and oxygenated additives to diesel.

The third one is relatively easy, quick and viable since no major change to be incorporated to the millions of existing engines. In this chapter, a review on the option of using oxygenated fuel additives such as biodiesel, acetone–butanol–ethanol (ABE) solution and water-emulsion as additives to reduce unregulated emissions is carried out. From this review, it becomes clear that more systematic research is absolutely essential to come to a definite conclusion on unregulated emissions such as polycyclic aromatic hydrocarbons (PAHs), persistent organic compounds (POPs) and carbonyls. When biodiesel and/or ABE solution in the diesel blends is used emissions such as particulate matter (PM), CO, PAHs and POPs do reduce. However, in most cases, the NOx emission increases. Further, through this review, a combination of factors such as higher oxygen content, more complete combustion and cooling effect could be brought out. Unregulated pollutant emissions can be reduced considerably if diesel blend, which contains proper amount of biodiesel, ABE solution and

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a small amount of water (0.5%), is employed appropriately. This means that such green fuels exhibit excellent performance in both brake thermal efficiency (BTE) and NOx–PM trade-off and in significant emission reductions for PAHs and POPs. This chapter proposes a green diesel fuel blend not only for scientific study but also for future practical application.

Nomenclature

ABE	Acetone–butanol–ethanol
BaPeq	Benzo(a)pyrene-equivalent
BEAM	Butanol, ethanol, acetone, methanol
BSFC	Brake specific fuel consumption
BTE	Brake thermal efficiency
CO_2	Carbon dioxide
CO	Carbon monoxide
cm	Centimeter
DOC	Diesel oxidation catalyst
EGR	Exhaust gas recirculation
Gt	Gigaton
H_2	Hydrogen
HC	Unburnt hydrocarbons
HMW	High molecular weight
HRR	Heat release rate
IC	Internal combustion
IARC	International Agency for Research on Cancer
KOH	Potassium hydroxide
LMW	Low molecular weight
LTC	Low temperature combustion
MMW	Medium molecular weight
MAHs	Mono aromatic hydrocarbons
MTBE	Methyl tertiary butyl ether
NaOH	Sodium hydroxide
NOx	Nitrogen oxides
OH	Hydroxyl radical
PAHs	Polycyclic aromatic hydrocarbons
PBDD/Fs	Polybrominated dibenzodioxins and furans
PBDEs	Polybrominated diphenyl ethers
PCBs	Polychlorinated biphenyls
PCDD/Fs	Polychlorinated dibenzodioxins and furans
PM	Particulate matter
POPs	Persistent organic compounds
PPM	Parts per million

SCR   Selective catalytic reduction
SOx   Oxides of sulfur
UNFCC   United Nation's Framework Convention on Climate Change
VOCs   Volatile organic compounds

9.1 Introduction

Before 1900 AD, man was using horses for his mobility and after 1900 AD, he started using engines for the same. The transition from 'horse power' to 'horsepower' took place because of the unbearable problem of pollution caused by horses. By late 1800, the increase in horse population outstripped the human city dwellers population. By 1894 the situation went to an alarming stage. The 'Times of London' reported that every major city will be buried under 10 feet of horse droppings. It became a public health and sanitation problem of unmanageable level. In those days' horses were absolutely essential for functioning of nineteenth century city. The situation was such that without horses the cities will almost starve. Man, somehow wanted to get rid of the horses from the transportation sector and no possible solutions could be devised. There came the ingenuity of two great scientists, viz. August Otto and Rudolf Diesel who invented gasoline and diesel engines respectively by which 'horse power' problem could be solved. Again, similar situation is faced today where 'horsepower' problem due to pollution from automobiles is a great headache. By 2020, it is estimated that the increase in vehicle population will outstrip the human city dwellers population as happened earlier. A similar situation has arisen again and researchers are at the cross roads to find a way out.

Global warming due to engine emissions is a real threat for cities close to coastal area of all the continents, due to sea level rise and therefore this problem should be addressed immediately. Climate changes associated with rise in global temperature can ruin the energy security of the entire world (EPE USEPA 2002; Abu-Zaid 2004; Acharya et al. 2009; Agarwal 2007). Because of the ever-increasing energy demand, it is feared that in the near future there will be scarcity for fossil fuels (Agarwal et al. 2008). It is predicted that this century will witness the peak extraction of fossil fuel with increased cost (Ahmed et al. 2010; Akihama et al. 2001). Therefore, there is an urgent need to focus on alternatives (Al-lwayzy and Yusaf 2013). However, it is to be noted that oil producing countries will try to extract more and more fossil fuel to avoid market competition from alternatives even at a risk of global warming. Thus, there is a critical position due to depletion of fossil fuel and increased environmental degradation and should admit our folly in not realizing the consequences degradation of the environment (Altın et al. 2001; Ballesteros et al. 2008; Baranzini et al. 2003). The entire ecosystem habitat is under great strain (Agarwal 2007; Altın et al. 2001; Baranzini et al. 2003; Baruch 2008; Beatrice et al. 2014).

It is always the point of contention that, industrialized countries, are mainly responsible for the high CO_2 emissions (Ahmed et al. 2010; Bertola et al. 2003; Borrás et al. 2009). Therefore, It is necessary to cutback in energy production to combat global warming. There is an immediate need for alternative modes of energy production, alternative fuel sources and investment on more energy efficient equipment to reduce the problem due to cutback in energy production and to offset the trade imbalance between oil producing and non-oil producing countries. This imbalance is due to the rising prices of dwindling oil reserves (Brunt and Platts 1999; Buyukkaya 2010; Campos-Fernández et al. 2012, 2013). From the authors' point the possible alternative energy sources that get favorable consideration are: (i) biofuels, (ii) biomass (iii) nuclear, (iv) solar, and (v) geothermal, hydroelectric and wind (Agarwal 2007; Chang 2010).

As of now, of the five mentioned above, geothermal, hydroelectric and wind contributes less than 5% of the energy demand of the world. Contribution from Nuclear power is around 10%. Positive aspect about nuclear power is it is CO_2 free and is considered as a CO_2 free technology (Agarwal 2007), which provides around 10% of the world energy requirements. However, there is lot of concern about safety especially after 2011 Fukushima disaster. This disaster has made some counties to decommission nuclear power plants (Chang 2010). Thus, the world's 85% energy demand is met from fossil fuels (Agarwal 2007; Chang et al. 2013). At this rate of energy consumption, it is feared that one day one may face the extinction of fossil fuels in the near future but nobody is able to say how near that future is. However, the authors' have a different perspective. The authors are of the opinion that the earth has enough fossil reserve and as long as mankind exist the fossil fuel will be available. It is because, over the last 50 years there is unprecedented increase in the vehicle population and are still able to meet the demand. This is made possible by drilling deeper and deeper these oil wells. But the difference between 1970 and 2020 is that the fuel was costing 1 Indian rupee per liter in 70's whereas we will be paying 100 Indian rupees by 2020's in India. Therefore, when it becomes 1000 rupees per liter it will become uneconomical to use this fuel. Further, when drilled very deeper to get this fuel, the amount of energy input to drill will be more than the energy that is obtained out of this fuel. On this count, and not out of fear, an alternate source of energy has to be found. In this, biofuels is considered as promising alternative fuel sources especially for transportation sector.

9.1.1 Transportation Sector

It is the fact that major contributor to the global warming is the transportation sector, especially road transport (Alriksson et al. 2005; Chang et al. 2014a, b). It is due to direct emissions of carbon dioxide (CO_2) and indirect emission of greenhouse gases such as carbon monoxide (CO) oxides of nitrogen (NOx), and volatile organic compounds (VOCs) into the atmosphere. Moreover, the oxidation–reduction capacity of the atmosphere is also affected by the emissions of aerosols and particulate matter

(PM) (Chang et al. 2014c). It is to be noted that transportation sector is the major consumer of fossil fuels like gasoline, diesel, natural gas, etc. (Chen et al. 2006, 2010; Chiari and Zecca 2011).

It is estimated that in the United States, transportation sector consumes more than 90% of its petroleum supply (Acharya et al. 2009). The studies by Skeie et al. (2009) and Wallington et al. (2013) have revealed that in worldwide the road transport contributes around 16% of the anthropogenic CO_2. This means that out of about 30 Giga tons (Gt) of total global CO_2 emissions, approximately 5 Gt are from road transportation sector compared to other transport sectors such as aviation, rail and shipping. It may be noted that greenhouse gases emissions are proportional to fossil fuel consumption. With the increasing population, the vehicles will increase on the road to satisfy the quest of the quality of life (Chuang et al. 2010a, b, Chisti and Yan 2011; Chang et al. 2014c).

The emission of greenhouse gases deteriorates air quality in the urban areas. However, the transportation sector is blamed as one of its sources. This emission is a major risk factor to human health and it will become the highest source of air pollution in the near future (Chang et al. 2011, 2014c). Nelson et al. (2008) have proved a correlation between adverse human health problems and exposure to air pollutant emissions from vehicles.

9.1.2   The Advantages and the Disadvantages of Diesel Engines

The credit of inventing an internal combustion engine goes to August Otto when he invented his famous spark ignition engine in 1873. Rudolf Diesel closely followed Otto's invention and invented a self-igniting engine in 1894, and was called diesel engine. Diesel underwent lot of difficulties in patenting his engine. His engine was better than Otto's engine in three aspects. It had (i) higher thermal and fuel efficiency, (ii) lower carbon-di-oxide emissions and (iii) greater power output compared and also had longer durability and better torque (Acharya et al. 2009; Correa and Arbilla 2006; Cotana et al. 2014). Hence, this engine became the best option for on-road and off road operations and mostly used for heavy duty operations such as, transportations, trains and ships (Campos-Fernandez et al. 2013). This invention found applications in agriculture, mass transportation and power generation (De Ojeda et al. 2011). Diesel engines, compress air to attain high pressure and temperature followed by fuel injection to deliver power. The injected fuel evaporates, mixes with air and burns using the oxygen in the compressed air. During combustion, the chemical energy is released and the combusted gases expand. The power is produced during this expansion process. Hence, this engine is called as compression-ignition engine, as the ignition happens due to high temperature of the compressed air. Higher efficiency of diesel engine is due to higher compression ratios and operates on leaner mixtures. Further, there is rapid combustion and the less throttling losses (Acharya et al. 2009).

The diesel engine operates on a mixture of hydrocarbons, which is known as diesel fuel with carbon number C6 to C20 aliphatic alkanes, namely, major components of tetra-, penta- and hexa-decane, branched alkanes in small quantities and aromatic alkanes (Demirbas 2007a, b, 2008). It emits hundreds (Demirbas 2009) of species both, regulated and unregulated. The regulated species are gaseous and particulate matters, PM (Demirbas 2007a, b; DeOliveira et al. 2006), and other emissions such as COx, SOx, NOx, (Chuang et al. 2011). The unregulated emissions are dioxins, dioxin like compounds, PAHs and VOCs. These are produced whether the combustion is complete or incomplete. It should be noted that the unregulated emissions are potentially dangerous to the ecology and environment (Dogan 2011; Dutta and Radner 2009). The non-homogeneity of fuel-air mixture and its subsequent combustion are the principal cause for pollutants formation.

Moreover, the conditions prevailing during the combustion process play a very important role. The operating conditions such as temperature, humidity and air–fuel ratios, composition of lubricating oils and diesel fuel, type and age of the engine, and the type of emission control devices used are some of the factors of the pollutant formation. It is to be noted that, the diesel engine emits hundreds of gaseous or particulate forms of compounds. However, the ones that have potential impact on human health are classified as pollutants (Dyke et al. 2007; Egnell 2000; Ema et al. 2013). This is proven through measurements and modeling studies (Chuang et al. 2010a, b). It is an established fact that pollutants are toxic and pose health problems. They cause mainly respiratory complications. Further, it is a cause for cardiovascular and carcinogenic and mutagenic diseases (Cotana et al. 2014; Fahd et al. 2013; Fernando et al. 2006).

Stringent regulations have been enacted to control and reduce diesel engine emissions (Campos-Fernández et al. 2012; Claassen et al. 2000; Demirbas 2007a, b; Franco et al. 2013). A lot of research is being conducted in this direction and to achieve a remarkable balance between maximum power output and energy efficiency (Fraioli et al. 2014). From the above discussion, it is clear that it is very important to find alternate fuels. In the following sections, the possible alternatives and their impact will be dealt with. The objective of this review is to make the reader understand the possibilities of using oxygenated fuels in reducing unregulated emissions so that an easy and quick solution can be found.

9.2 Possible Alternatives for Conventional Diesel Fuel

Possible green fuel alternatives along with reformation of conventional diesel fuel for reducing pollution are reviewed in the following sections.

9.2.1 Oxygenated Fuels

The name, oxygenated fuels, imply the oxygen bonding in the chemical structure of the fuels which is different from conventional fossil fuels. If such a fuel is to be used in diesel engines then they must have following characteristics.

(i)   must be miscible with diesel fuel,
(ii) must have a good cetane number with minimum volatility when mixed with diesel (Geueke et al. 1999).

In this category, alcohols, biodiesel, ethers and water-emulsions can be classified as oxygenated fuels. A typical example is acetone (a ketone), with about 28% of oxygen content (Ghannam and Selim 2009). Similarly, about 10% in biodiesel, 36% in diglyme, an ether and 35% in ethanol, an alcohol (Franco et al. 2013). Diethyl adipate, diethyl carbonate, ethyl glycol monoacetate and diethyl succinate (Dutta and Radner 2009), dimethoxymethane, dimethyl carbonate, among others (Geueke et al. 1999; Gill et al. 2012) are some of the good oxygenated additives.

These fuel additives, which have oxygen content in itself play an important role in soot and PM reduction and also reduce CO, PAHs, HC, other POPs, and unregulated carbonyls emissions. This is mainly due to oxygen enrichment that enhance premixed combustion phase and better diffusive combustion phase (Brunt and Platts 1999; Franco et al. 2013; Guarieiro et al. 2008). It is to be noted that these reductions are at the expense of considerable increase of NOx emissions (Hagos and Tan 2011; Haik et al. 2011; Han et al. 2009; Hariram and Kumar 2013; He et al. 2009).

9.2.2 Biomass-Derived Fuels

As discussed, it is clear that more sustainable sources of fuels have to be developed at the earliest (Campos-Fernández et al. 2012; Heeb et al. 2008). Economically viable and sustainable contenders are bio-hydrogen, syngas, biogas, vegetable oil, biodiesel, bio-oil, bio-alcohols and bio-char fuels that can be produced from the abundant biomass. They are collectively referred to as biofuels (Chen et al. 2006, 2010; Heeb et al. 2005). The above fuels have good oxygen content that makes them to stand apart from petro-fuels. From the authors' opinion, biofuels are the promising candidates, especially for the transportation sector. The most important ones among them are called BEAM (Butanol, Ethanol, Acetone and Methanol). Of course, propanol and biodiesel can also be considered because the modifications required on the existing diesel engines (Heeb et al. 2007) will be minimal.

These fuels have a good possibility to replace the petroleum-based fuels because they have greater potential to reduce greenhouse gases. Heeb et al. (2013) have estimated in their study that by 2050, at an average of at least 50% of the world's energy demand will be met, especially in transport sector by these fuels. Further, by using Fischer–Tropsch Synthesis to give off hydrocarbons (Hernández et al. 2012)

bio-oil can be produced from pyrolysis, bio-syngas from biomass gasification and bio-hydrogen from catalytic thermal cracking of bio-oil.

Moreover, producing fuel from biomass is more environmentally friendly than petroleum processing. Chen et al. (2010), Chiari and Zecca (2011) have stated that use of bio-fuels can usher economic, environmental and energy security. Further, the advantages that can be derived are listed below.

 (i)   easily available and exploitable from biomass,
 (ii) environmentally friendly, and
(iii) better economic and sustainable potential specially to countries, which import oil.

9.2.3   Vegetable Oil

Vegetable oils are being tried from the day of invention of diesel engines (Al-lwayzy and Yusaf 2013; Hoekman and Robbins 2012; Hountalas et al. 2008) especially during the second World War when there was a scarcity for diesel (Howe and Leiserowitz 2013). Because of the oil crisis in 1970s interest started developing again in this area (Chuang et al. 2010a, b). This is mainly due to the following three reasons: (i) renewability (ii) availability and (iii) lower sulfur and aromatic contents compared to petro-diesel.

Vegetable oils are extracted through cold/hot pressing or straining, filtering or decanting the oil rich seeds such as coconut, castor, groundnut, karanja, cotton flax, jatropha, palm, olive, linseed, rapeseed, sunflower and soybean (Al-lwayzy and Yusaf 2013). Raw forms of these oils are biodegradable and contain free fatty acids, phospholipids, triglycerides and waxes. Their physio-chemical properties depend on the biomass source (Chuang et al. 2010a, b). These oils lead to reduction of CO_2 emissions and also have characteristics close to those of diesel fuels. Hence, can be used without any major modifications in conventional diesel engines (Hsieh et al. 2011). Further, the cost of production is relatively high compared to fossil diesel (Hountalas et al. 2008; Huo et al. 2014). However, the drawbacks in using these oils are:

 (i)   particulate deposition in the combustion chamber walls
 (ii) clogging of fuel nozzles,
(iii) excessive engine wear on a long run
(iv)   operational difficulties
 (v)   durability
(vi)   storage problems.

The other disadvantages from these vegetable oil run engines are its (a) lower calorific values slightly lowers the power output, (b) less volatility and higher viscosity increases the specific fuel consumption (c) longer ignition delays worsens the combustion characteristics and also lowers the thermal efficiency, (d) higher CO and

HC emissions. However, the blessing in disguise is reduced smoke opacity and lower NOx (Heeb et al. 2007; Hoekman and Robbins 2012; Hountalas et al. 2008). The advantages of using these oils are they can be preheated or pretreated to blend easily with diesel oil before using in the engines. Hence, to use these fuels efficiently, engine combustion strategy should be altered by exhaust gas recirculation, modifying the injections systems and attempting dual fuel.

Vegetable oils, which are miscible with diesel (Hountalas et al. 2008), can be blended with it to reduce the viscosity problems. To reduce the poor atomization and subsequent incomplete combustion (Heeb et al. 2013), solvents like alcohols or BEAM (Butanol, Ethanol, Acetone, and Methanol) can be used to form micro-emulsions (Hariram and Kumar 2013; Howe and Leiserowitz 2013). Vegetable oil can be considered as alternate source of energy in diesel engines since they are amenable for easy adaptation and conversion to biodiesel.

9.2.4 Biodiesel

Biodiesel are nothing but fatty acid methyl/ethyl esters (Heeb et al. 2008). They are biodegradable, tranesterified and nontoxic vegetable oil (Chen et al. 2010; Howe and Leiserowitz 2013; Huo et al. 2014). Biodiesel can be produced from vegetable oil either by transesterification, pyrolysis and alcoholysis, thermal cracking or micro-emulsion and hydrodeoxygenation (Alriksson et al. 2005; Huo et al. 2014; Hwang et al. 2013).

Feedstock for biodiesel can be classified as first, second and third generation (Hwang et al. 2013). Biodiesel that are produced from edible sources such as coconut, olive, rapeseed, soybean, and sunflower are considered as first generation and from non-edible sources are the second generation. The non-edible seeds like castor, corn, cottonseed, jatropha, jojoba, karanja, linseed, rice husks, and palm fiber form the second generation. Animal fats, microalgae, water emulsions and waste cooking oil form the third-generation sources. However, these promising sources of fuels are unattractive due to the multitude of problems they face. Transesterification and pyrolysis processes are material demanding and energy intensive.

Moreover, the first-generation sources, if used for biodiesel production will threaten food security status of the global population. Further, biodiesel production will face high cost of feedstock, problem of oxidation, storage and comparatively lower heating values. Transesterification is not a simple process. It involves the reaction of vegetable oils containing triglycerides with an alcohol especially excess methanol. Further, there must be an involvement of a catalyst, either NaOH or KOH, to form glycerol and esters (Izquierdo et al. 2012). These processes produce large amounts of glycerol (10% by mass) (Heeb et al. 2005). It is not economically viable because of low market value and problems involving disposal (Campos-Fernández et al. 2012).

In addition, saponification (Huo et al. 2014) is a problem during transesterification. The process yield is mainly dependent on the catalyst which can be either base or acid

and reactive conditions (Ithnin et al. 2014). The temperature, molar ratio of alcohol to the vegetable oil and the reaction time play a very vital role (Huo et al. 2014). However, secondary pollutants caused from the transesterification processes, cost of pretreatment and purification processes are some of the other issues. However, combustion process is improved due to its higher cetane number as it is an oxygenated fuel (Campos-Fernández et al. 2012; Jacobs et al. 2003) and the emissions, namely CO, HC, PM, PAHs and POPs, namely PCBs, PCDD/Fs, PBDEs and PBDD/Fs get reduced (Heeb et al. 2008; Johnson 2009; Kagawa 1994). It is evident from the published work (Kessel 2000; Hwang et al. 2013) that neat biodiesel used in diesel engines cause higher NOx emissions than the conventional diesel engines.

Biodiesel as biodiesel blends, in its neat form or as fossil diesel can be used in the diesel engine (Alriksson et al. 2005; Chuang et al. 2010a, b). However, it has the following disadvantages,

(i) cold start problems
(ii) injector choking,
(iii) high viscosity,
(iv) higher cloud and pour points, and
(v) lower energy content compared to fossil diesel (Jacobs et al. 2003).

During pyrolysis process, vegetable oils and animal fats are heated with or without a catalyst (Chen et al. 2006; Huo et al. 2014) at higher temperatures to thermally crack them into simpler molecules to convert biomass to fuel (Howe and Leiserowitz 2013). Linear and cyclic paraffins such as alkanes, alkenes and aromatics (Alriksson et al. 2005) are the products obtained during this process and the undesirable oxygenated compounds such as carboxylic acids, ketones and aldehydes are the byproducts from this process. These can be segregated by fractionation and the desirable fractions can be used with the fossil diesel to make blends and can be used in diesel engines (Kessel 2000).

Microalgae oil, a third-generation source is the emerging biodiesel fuel. Due to its biological photocatalyst process, it reduces the CO_2 levels in the atmosphere (Knibbs et al. 2011). It is not a threat to food crops and for the cultivable lands. Therefore, microalgae can be considered as one of the sustainable sources and promising fuel (Koebel et al. 2000; Kreso et al. 1998).

Mwangi et al. (2009) used B2 (98% fossil diesel + 2%-microalgae biodiesel) blends with butanol and with addition of water and found reductions in regulated pollutant emission. Similar studies also state that the use of microalgae biodiesel reduced HC, CO and PM pollutant emission (except for NOx). However, fuel consumption increased when compared to conventional fossil diesel (Hagos and Tan 2011; Kumar et al. 2002; Labeckas and Slavinskas 2006; Ladommatos et al. 1997).

9.2.5 Alcohols and Bio-Alcohols

Recently, one of the most important alternate fuels under consideration is bioethanol. It is a bio-alcohol produced from fermentation of sugars. The source is either barley, cassava, sugar beets, sugarcane, corn, sorghum or other agricultural wastes (Campos-Fernández et al. 2012; Lapuerta et al. 2008). By hydrolysis, enzyme invertase found in yeast convert the sucrose in sugar to fructose and glucose. The obtained fructose and glucose are further converted to ethanol by zymase (Chen et al. 2010).

9.2.6 Diesohol Blends

Mixing of alcohol with diesel lowers cetane number. Hence, biodiesels are added as cetane value improvers and heating value enhancers. However, viscosity also increases. (Li et al. 2009). To overcome this problem ethanol as a solvent can be used which can reduce the viscosity of biodiesels (Heeb et al. 2008). The diesohols or bio-diesohols, are oxygenated fuel blends, which consists of biodiesel, alcohol (mostly ethanol) and diesel. These are used in diesel engines and found to have remarkable improvement in engine combustion and emission reduction (Campos-Fernandez et al. 2013; Ghannam and Selim 2009). However, the cost involved is much higher.

9.2.7 Blends of Acetone, Butanol and Ethanol

The problems experienced with straight biodiesel get reduced by adding solvents and additives like acetone, ethanol and butanol to these blends (Lif and Holmberg 2006; Lim et al. 2014; Lin and Huang 2003). These blends are found to decrease the emissions from IC engines (Demirbas 2007a, b). Acetone, butanol and ethanol can be produced using the acetone–butanol–ethanol (ABE) fermentation process developed during the First World War.

Acidogenesis and solventogenesis are the two stage processes involved in this method. Acido-genesis produces aceric and butyric acids and the solventogenesis process produces acetone, butanol and ethanol (Lin et al. 2010a, b). The fermentation process yields volumetric percentage range of acetone 20–30%, butanol 60–75% and ethanol 1–5% (Lin et al. 2012). Further, blends have, reduced viscosity and calorific value (Lin et al. 2010a, b). Ethanol being attempted infrequently in diesel engines due to low cetane number problem.

Butanol is the main product of the ABE process (Hariram and Kumar 2013). It has superior qualities such as easier miscibility, less hydrophilicity, lower volatility, higher cetane and heating values compared to other alcohols. Its energy density is also similar to gasoline (Lin et al. 2008). However, butanol is used in the food, plastic

and specialty industries (Lin et al. 2008). Acetone has higher oxygen content and better solubility and is considered as good for oxygenated additive to diesel blends (Demirbas 2007a, b). The ABE fermentation process depends on cellulosic sources as substrates. Carbohydrate rich feedstock, namely bagasse, beets, cassava, domestic waste, molasses, maize, palm fiber, rice straw and potatoes are some of the substrates (Lin et al. 2006a, b, 2008). In the ABE fermentation process (Haik et al. 2011; Lin et al. 2006a, b) the solventogenic activity is driven by anaerobic Clostridium bacteria strains.

The drawbacks in using ABE are its production costs are quite high and removal of water content and separation of acetone, ethanol and butanol from the fermented mixture demands high energy and are prohibitive (Lif and Holmberg 2006; Lin et al. 2011a, b). Hence, in engine studies to save energy and cost and also to ensure its applicability and viability, it is appropriate to use ABE directly without separation (Lapuerta et al. 2012). However, only very few studies have been reported on ABE in the open sources (Lin et al. 2009, 2012).

9.2.8 Water–Diesel Emulsion

A number of research studies are being conducted since 1970's on water–diesel emulsions in engines (Liu et al. 2011). Some studies are being conducted to find the effect of addition of a small quantity of water in the biodiesel blends. It is found that compared to using straight biodiesel, there could be a trade-off between reductions of CO, NOx and PM emissions (Ma and Hanna 1999; Machado Corrêa and Arbilla 2008; Maddox et al. 1995). Alahmer (2013) has stated that a significant effect on the physical and chemical kinetics of combustion was found due to the presence of small amounts of water in the fuel. Further, it provides OH radicals, which can control NOx formation and further oxidizes soot, in the combustion environment and also reduces combustion temperatures. Hence, it has both the advantages of reducing NOx and PM emissions.

Further, there are possibilities for micro-explosions of water droplets. These micro-explosions will induce higher turbulence and enhance the mixing of fuel and oxidants, which causes better combustion. Hence, there is a significant reduction in pollutants emissions. Water–diesel mixtures are stabilized by adding surfactants in the emulsions to minimize the coalescence mechanism of the water phase. These surfactants will reduce the surface tension between the diesel and water phases (Maiboom et al. 2007, 2008). Ghannam and Selim (2009) have brought out the following points in their study on water diesel emulsions. They are: (i) surfactants are essential for water–diesel emulsions stability (ii) water–diesel emulsions stability is inversely proportional to water fractions (iii) addition of surfactants is directly proportional to water fraction (iv) the density of water–diesel emulsions is also directly proportional to water fractions.

It is well known that water addition is one of the well-known techniques in reducing diesel emissions. The various strategies that can be adopted are: (i) Steam induction to mix water with air at inlet; (ii) simultaneous injection of water and diesel and (iii) stabilized or non-stabilized diesel water emulsions (Maiboom et al. 2009). A detailed study was conducted by Subramanian (2011) on water–diesel emulsion and timed injection of water into the intake manifold. From these studies, it is found that the emulsion method has a good promise in NOx and smoke control and the injection method can control CO and HC emissions. It may be due to better diffusion combustion phase.

It becomes clear that water-diesel emulsions is one of favoured techniques to reduce pollution in general. As mentioned earlier, water emulsions result in micro-explosion phenomena. However, diesel having lesser volatility plays a controlling role in the overall boiling temperature during combustion (Maiboom and Tauzia 2011). Water evaporates faster than diesel due to differences in boiling points (Marklund et al. 1990) and creates a vapor expansion, which makes water to reach its superheated stage much earlier than diesel. Thus, micro-explosions occur by which bigger droplets disintegrate into smaller droplets, where air-fuel mixing is enhanced and becomes an advantage in emission reduction (Mayer et al. 2008). This is considered as secondary atomization. Ithnin et al. (2014) established in their study that water in diesel emulsions can reduce NOx and PM concurrently. They found that the presence of water increases the amount of OH radicals, which in turn reduces soot formation by oxidizing the soot precursors and also combustion efficiency improved without engine modifications.

The results of various studies on the use of water addition technique in engines will be reviewed in the following sections. Attia and Kulchitskiy (2014) have concluded in his study that the emulsion droplets should be as fine as possible for higher HC and CO reductions and larger droplets for higher reduction in NOx emissions.

9.2.9   Polycyclic Aromatic Hydrocarbons (PAHs) and Other Persistent Organic Pollutants (POPs)

Aromatic content of fossil diesel fuel and the nature of additives (Wen et al. 2013) play a vital role in the emission of PAHs (Wang et al. 2012; Wen et al. 2010, 2013; Winter 2014) from diesel engines. The PAHs are formed mainly from pyrosynthesis of aromatic compounds during the combustion process, unburned fuel and lubricating oil (Dogan 2011). PAHs can be classified into (i) low molecular weight (LMW), (ii) medium molecular weight (MMW) and (iii) high molecular weight (HMW) categories. PAHs can exist in both particulate and gas phases in the atmosphere as they are semi-volatile organic compounds. It is to be noted that the major contributors of total-PAH masses are LMH PAHs and HMW PAHs. They are associated with the particulate phase making and toxic (Dogan 2011; Han et al. 2009). PAHs are

immunosuppressive, carcinogenic and mutagenic and can cause cancer of the lung and skin (Wen et al. 2010, 2013; Winter 2014; Wu et al. 2014a, b).

Persistent organic pollutants (POPs) are dioxins and dioxin like compounds. They are acutely and chronically carcinogenic and toxic and cause lot of health hazards to human beings (Wu et al. 2014a, b). In 2012, Dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), polybrominated dibenzo-dioxins, polychlorinated dibenzo-p-dioxins and polybrominated diphenyl ethers (PBDEs) are categorized as POPs by International Agency for Research on Cancer (IARC). These species are found in the exhaust of diesel engines in gas and particle phases (Wurzel 2005). It is due to incomplete combustion (Kagawa 1994; Machado Corrêa and Arbilla 2008). Only very few studies are done in this direction throughout the world (Yang et al. 2012a, b). One consoling factor is that the overall emissions of above toxins is too small by the transportation sectors (Yang et al. 2012a, b).

Persistent organic pollutants (POPs) are generated due to the presence of organic and inorganic halogens in the combustion system (Kadota and Yamasaki 2002). The major formation mechanisms of dioxin and dioxin like POPs include aromatic precursor pathway (between 200 and 400 °C), De Novo synthesis (between 200 and 400 °C) and homogeneous or gas-phase mechanisms (between 350 and 800 °C). This is mainly due to crankcase lubricating oil, chlorine or bromine contents in the fuel, or halogenated lead scavengers (Johnson 2009; Yao et al. 2010a, b; Yilmaz et al. 2014; Yuan et al. 2009a, b). It is important to note that formation and destruction of POPs occurs simultaneously. A suitable mechanism involving dechlorination/or debromination, oxidation, or pyrolysis should be used for POP destruction (Tompkins et al. 2014). The POP emissions from the diesel engine can be reduced by employing any of the following mechanisms:

(i)   using ABE blended diesel
(ii) water addition to fossil diesel fuel (Machado Corrêa and Arbilla 2008),
(iii) using catalysts (Maddox et al. 1995),
(iv) employing diesel particulate filters (Wang et al. 2013).

Biodiesel Blends and Their Effect on the Emission of PAHs and POPs: Lee et al. (2011) have found in their studies that increased blending of biodiesel decreased the total mass and total benzo(a)pyrene-equivalent (BaPeq). This, they attributed to increased oxygenation that oxidize PAH forming precursors, improved combustion and the reduction in fuel PAH content due to dilution effect (Topare et al. 2011).

Tsai et al. (2010, 2014a, b) reported in their study that diesel reformation reduces emissions of total PAHs by 6–42% (mean 24%) and the total BaPeq by 17–75% (mean 46%). Borrás et al. (2009) stated that reformulation using biodiesel addition in diesel fuel modifies the aromatic and sulfur content. This helps to reduce the PAH emissions sufficiently. Correa and Arbilla (2006) conducted studies with 2%, 5% an 20% biodiesel blends and found that PAH emission was reduced by approximately 3%, 6%, 17% and mono aromatic hydrocarbons (MAHs) emissions were reduced by 4%, 8%, 21% respectively. Yuan et al. (2009a, b) in their findings report 61–98% reduction in PCDD/Fs emission by adding biodiesel and paraffinic fuel with diesel.

Alcohol addition and its Effect on the Emission of PAHs and POPs. Molecular weight PAHs was lowered resulting in significant reduction in the total PAHs emission when higher amount of butanol was added to fossil diesel. Further, the increased oxygen content results in complete combustion which inhibits the formation of lower molecular PAHs (Fraioli et al. 2014). According to Leong et al. (2002), use of ethanol in fossil diesel can greatly reduce aromatic compounds due to its dilution effect, higher oxygen content and higher-octane rating. However, it is to be noted that these aromatic compounds are the precursors for PAHs and POP formation. But, Song et al. (2007, 2010) have reported in their studies that increase in ethanol content in fossil diesel increased PAH emissions. They found that addition of 5% and 20% ethanol in diesel increased PAH emissions by 19% and 39%, respectively. They attributed the reason for this trend to high latent heat of vaporization of ethanol and the lower combustion temperature that enhances soluble organic fraction formation and hence higher PAH emissions.

Influence of Water Addition on the Emission of PAHs and POPs. Lin et al. (2010a, b) researched with addition of different amount of water and found a decrease in PAH formation due to the reduction in medium molecular and higher molecular weight PAHs by 7 to 23% and 7 to 1.5%, respectively.

Chang et al. (2013) reported that 2% biodiesel with 10% and 20% water containing butanol reduced the POP emissions compared to normal biodiesel-blend (2% biodiesel + 98% diesel). He used the two blends, WBT10 (0.25% water, 9.75% butanol and 90% B2) and WBT20 (0.5% water, 19.5% butanol and 80% B2) for this study. He found that the POP emission factors for PCDD/s, PCBs, PCDEs, PBDD/Fs, PBBs, and PBDEs decreased by amounts in the range of 23–42% and 38–66% on a mass basis, as well as 19–78% and 51–85% on a toxicity basis for WBT10 and WBT20 respectively.

Chang et al. (2013) stated POP emissions reduced due to water addition and water-containing butanol. They have reported that significant reduction in the POP emissions can be obtained by the formation of a lower number of aromatic compounds that lead to better combustion.

ABE-blends and their Effects on the Emission of PAHs and POPs. Chang et al. (2014c) has stated that the fuel mixture with 50% biodiesel and 25% ABE solution resulted in about 35–50% reduction of PAH toxicity and of about 40–50% reduction in total PAH. Aromatic content, the precursors for PAH formation, in the diesel fuel blends is found to be reduced by biodiesel and ABE solution. The oxygen content also increased that led to complete combustion. The emission factors of total PAHs reduced by about 4.5–37% and the total BaPeq reduced by about 2–14% while varying the rate of a H2/O2 in the mixture from 10 to 70 l/min Chang et al. (2014c). This again is attributed to the increased oxygen content in the air fuel mixture.

9.2.10 Carbonyls

Carbonyls are basically ketones and aldehydes. When hydrocarbons react with OH radicals, acetone, acetaldehyde, benzaldehyde and formaldehyde are formed (Zhang et al. 2008). Aldehydes and ketones are the key players of ozone formation in the troposphere, which is responsible for photochemical smog (Demirbas 2008); Kessel 2000); Zhang and Boehman 2007) and are potential hazard for human health (Zhou et al. 2014a, b). It is well known that formaldehyde and acetaldehyde are carcinogenic and mutagenic (Wen et al. 2010). The emission of carbonyls is controlled by engine operating conditions such as the fuel properties and load (Zhou et al. 2014a, b).

Biodiesel Blends and Their Effects on the Emission of Carbonyls. Again, there is an increase of carbonyls emission due to higher oxygen content of biodiesel (Kessel 2000). Formaldehyde is the major carbonyl emission from diesel engines whether biodiesel (47%) or diesel (63%) (Zhou et al. 2014a, b) is used. Similar values of carbonyl emission were reported by Peng et al. (2008). From their study, it is reported that B20 and fossil diesel fuel emit carbonyls in the form of formaldehyde and acetaldehyde and the values are around 41–56% and 27–45% for B20, compared to 49–57% and 24–29% for diesel fuel. An interesting study in 2008 by Machado Corrêa and Arbilla (2008) indicate a correlation of around 0.95 between the carbonyl emissions and biodiesel content. Ester molecules and formaldehyde are reported as major compound. It was followed by acetone, propion-aldehyde, acetaldehyde, benzaldehyde, butyraldehyde and acrolein. If there is a lack of benzene and aromatic content in biodiesel benzaldehyde emissions gets reduced.

Formaldehyde emissions were found to reduce by about 10–50% by biodiesel–ethanol blends. However, an overall increase in total carbonyl emissions by 1–20% was found due to acetaldehyde, acetone and propionaldehyde (Demirbas 2008). Guarieiro et al. (2008) have observed that with 10 and 20% biodiesel blends, the reductions in carbonyl emissions compared to original value was almost nil. However, B100, which is no more a blend, showed an increase in carbonyl emissions. However, there was a distinct reduction with B50 and B75. They came to a conclusion that the biodiesel contents play a vital role in carbonyl formation. But from another study with biodiesel addition (Demirbas 2008) showed an increase in acetaldehyde emissions and decrease in formaldehyde emission.

Lin et al. (2012) found that fuel compositions have significant effect on the carbonyl emissions. They have reported that 20% and 100% biodiesel blend increased carbonyl compounds by about 10% and 3% respectively and a reduction of carbonyl emissions around 30% and 24% respectively when they used 20% and 5% biodiesel blends with paraffinic fuel as the base fuel. In addition, Yuan et al. (2009a, b) also have reported a reduction of formaldehyde around 17%, and 10% and acetaldehyde around 62%, 39%, when they used 100% and 20% biodiesel blends. Further, in their same study they found an increase of formaldehyde by 21% and 31%, and acetaldehyde increase of about 1% and 20% respectively for 20% and 5% biodiesel blends along with paraffinic fuel as a base was used.

Alcohol Addition and its Effects on Carbonyls Emission. Yang et al. (2012a, b) have reported higher emissions of aldehydes 3% ethanol addition such as acetaldehyde, benzaldehyde, formaldehyde and propionaldehyde emissions by 41%, 19%, 37%, and 20% respectively. The increase of carbonyls emission with alcohol addition is attributed to the increase in OH radicals from the hydroxyl structure of alcohols. Further, the higher oxygen content aids this increase during combustion process as well. Pang et al. (2008) from their study report that biodiesel–ethanol blends with diesel fuel, increases acetaldehyde emission by 20 to 80% because of the presence of ethanol. In continuation of their previous study Pang et al. (2008) further report that when biodiesel ethanol blends were used, acetaldehyde accounted for 28–38% of the total carbonyl emissions in which formaldehyde was the dominant component. It was noticed that further addition of ethanol increases acetaldehyde and reduced formaldehydes as well as other aromatic based carbonyls. It is due the dilution effect of the aromatic hydrocarbon content in the fossil diesel. When tests were conducted at varying engine loads, with ethanol–diesel blends the brake specific emission of acetaldehyde and formaldehyde were increased by about 430% and 143%, respectively (Pang et al. 2006). It may be due to formaldehyde helping as an intermediate step for partial oxidation of ethanol and fuel. From a similar study (Zhou et al. 2014a, b), it is reported an increase in acetone and acrolein emissions by 20–220% and 5–90% respectively, when the engine was operated on ethanol–diesel blends.

In their study, Guarieiro et al. (2008) used 10% ethanol and 90% diesel and found an increase in acrolein, butanone, formaldehyde, hexaldehyde + heptaldehyde, hexaldehyde + heptaldehyde + octaldehyde, isovaleraldehyde, propionaldehyde, valeraldehyde, 2-ethylhexaldehyde, and decanaldehyde by varying proportion. Further, 8–15% ethanol in diesel blends increased acetaldehyde emission by 25–140%. By adding H2/O2 mixture to fossil diesel at the rate of 10–70 l/min the total carbonyl emissions were found to reduce by 5–32% (Wen et al. 2014).

9.3 Summary and Conclusions

Right from its invention, diesel engine is found to command large market share as source of power both on-road and off-road applications. It is due to its inherent advantages of having high output power, better fuel efficiency, durability, and stability. Even though it has many positive points, the major negative point with diesel engine, especially in transportation sector, is emissions of large volume of CO_2 and other greenhouse gases, which are largely responsible for global warming.

They are the major source of mutagenic and carcinogenic persistent organic pollutants. Hence, taking into account its excellent energy efficiency, it is very important to reduce these emissions. Reduction in emissions from such an engine can be done by (i) design change and (ii) using fuel additives.

The second one is more attractive since there will be minimum modifications to the existing engines. Hence, biodiesel has become more attractive due to its environmental benefits and renewable vegetation resources. However, due to its higher

viscosity and low calorific value compared to fossil diesel, the injection timing for biodiesel combustion has to be advanced and also higher amount of NOx is emitted. These shortcomings can be addressed by using solvents such as alcohols and water in biodiesel–diesel blends.

The following points are summarized along with findings and recommendations, after carefully reviewing more than one hundred and fifty published literature with respect to green-fuel strategy and emission reductions from diesel engines by using diesel–biodiesel–alcohols–water blends with additives.

It is evident from the research papers published that biodiesel used in diesel engines is a very promising renewable fuel alternative. It is clear that engines without any major engine modifications can be operated with neat biodiesel or blends of biodiesel with fossil diesel.

Microalgae biodiesel seems to be an attractive alternative. Since, it as a third-generation source and does not compete with food crops or other crop-based sources. However, microalgae biodiesel also emits higher amount of NOx with reduced amount of CO, PM, HC, and PAHs just as other biodiesels.

In this review, the main emphasis is on filling the gap regarding the part played by different fuel additives in reducing unregulated emissions.

For example, the results obtained by various studies using ABE-diesel blends and water addition techniques are not conclusive. This is the situation for other existing green fuels on the emission patterns of persistent organic pollutants such as PAHs, VOCs, PCDD/Fs, and PBDEs among others. Though the contribution of POP emissions from diesel engines are not that significant these unregulated pollutants, it is the considered view of the authors that, it should not be neglected. It is because they are very toxic and therefore health implications and environmental impact will be great over a period of time. Thus, there is an urgent need for further investigations on their emission from diesel engines.

More attention should be given to precisely bring out the effect of ABE to reduce most of the emissions. From the present review it is clear that acetone (carbonyl compound) and also ethanol increases acetaldehyde emissions. Therefore, more insight is required to categorically recommend the feasibility of using ABE as a fuel alternative.

Further, it is found that not enough data on unregulated emissions is available in the literature to come to a definite conclusion. It is to be noted that these unregulated emissions will pose great risk to humankind due to lack of stringent laws.

Finally, the authors are of the opinion that, further investigations under controlled conditions are a must regarding the use of oxygenated additives, namely water emulsion and ABE blends to arrive at the unregulated emissions, viz, carbonyl, PAH and POP emissions.

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Chapter 10
Influence of DEE on Entropy Generation and Emission Characteristics of DI Diesel Engine Fuelled with WCO Biodiesel

Veena Chaudhary and R. P. Gakkhar

Abstract This study present the influence of oxygenate additive DEE on entropy generation, exergy performance coefficient, emission, and performance characteristics of direct-injection (DI) diesel engine fuelled with WCO (waste cooking oil) biodiesel. Experiments are conducted at constant speed of 1600 rpm for full load condition. DEE is mixed with WCO biodiesel blend in the proportion of 5, 10, and 15%. Performance and exergy parameters for WCO biodiesel blend are compared with that of diesel fuel. It is found that addition of DEE enhance the engine performance effectively from the energy and exergy point of view. Reduction in NOx emission is also observed with the addition of DEE. The exergetic efficiency is increased by 8.5% for 15%DEE addition and NOx emission is reduced from 1900 ppm to 420 ppm with the addition of DEE. Lower entropy generation and improve exergy performance coefficient is also observed.

Keywords WCO biodiesel · Entropy generation · NOx emission · DEE additive

Nomenclature

DI	Direct injection
DEE	Diethyl ether
WCO45	45% WCO biodiesel + 55 diesel
NOx (ppm)	Nitric oxide
CO (%vol)	Carbon monoxide
UHC (ppm)	Unburned hydrocarbon
$\dot{Q}_{in}$ (kW)	Rate of heat input
$\dot{m}_{fuel}$ (kg/s)	Mass flow rate of fuel
LHV (kJ/kg)	Lower heating value
N (rpm)	Engine Speed

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T (Nm)	Torque
$\dot{E}x_{unacc.}$ (kW)	Exergy associated with heat losses
$\dot{Q}_{cv}$	Rate of heat at control volume
$\dot{E}x_{cw}$	Exergy Associated with cooling water heat
$\dot{m}_{cw}$	Rate of cooling water flow
h_{wo}	Specific enthalpy at outlet temperature
h_{wi}	Specific enthalpy at inlet temperature
T_o	Ambient Temperature
s_{wo}	Specific entropy at outlet temperature
s_{wi}	Specific entropy at inlet temperature
$\dot{E}x_{eg}$	Exhaust gas exergy
$\dot{Q}_{eg}$	Exhaust energy
$\dot{m}_{eg}$	Mass flow rate of exhaust gas
$c_{p,eg}$	Specific heat of exhaust gas
T_{eg} K	Exhaus gas temperature
P_{eg}, bar	Exhaust pressure
P_0, bar	Ambient pressure
$\dot{Q}_{eg}$, kW	Exhaust Energy
A/F	Air fuel ratio
$\dot{E}x_{Dest.}$	Exergy destruction
$\dot{E}x_{shaft}$	Shaft exergy
$\dot{E}x_{cw}$	Exergy associated with cooling water heat
$\dot{E}x_{eg}$	Exhaust exergy
$\dot{E}x_{unacc.}$	Exergy unaccounted heat loss
η_{II}	Second law efficiency

10.1   Introduction

The main driving force of the present era is energy. Around 80% of energy demand is met by utilization of fossil fuels such as mineral diesel, coal, natural gas and electricity. According to the International Energy Outlook the world energy demand would increase at rate of 1.4% per year resulting in an increase of 49% from year 2007 to 2035 (Misra et al. 2013). Increase in industrialisation, transportation, and population are the prime causes of the higher energy consumption. India has become the second biggest energy consumer in Asia since 2008. In India, transport sector consumes the largest share of energy demand and around 95% of transport energy is delivered by crude oil (Conti et al. 2016). Mineral diesel fuel shares the largest part of oil consumption in India and around 57% of diesel is utilized by automotive sector (Bp-Energy-Outlook-2018.Pdf). Diesel engines are extensively used in the power, automotive and transportation sectors due to their high effectiveness and consistency, although, they are the major cause of hydrocarbon emissions and particulate matter. Emergent concerns about the global climate change, and enhanced consciousness

about the fast reduction of oil reservoirs, have enforced the community of scientists (i) to investigate environment friendly fuels for diesel engines. Biodiesel is one of the replacement since it is biodegradable, non-toxic, sulfur-free and clean-burning fuel (Agarwal and Das 2001). It can be used in the diesel engine without any major modifications which reduces the dependency on the petroleum diesel oil (Ozsezen and Canakci 2011; Usta et al. 2005). Biodiesel production from the non-edible and edible oil, for example, sunflower, soybean, jatropha, neem, waste cooking oil and karanja are gaining attention among the researchers (Agarwal 2007; Kareem et al. 2017; Agarwal et al. 2015; Deore and Jahagirdar 2013; Yamık et al. 2015). However, biodiesel has higher density and viscosity as compared to diesel oil. These differences in properties affect the combustion process of diesel engines when fuelled with biodiesel. A significant result is the increased NO_x emission from such engines (Basha et al. 2009). Therefore, there is a need to improve the physicochemical properties of biodiesel, which could be done by using additives. DEE is one such additive. Blending of biodiesel with DEE helps to reduce the high viscosity of biodiesel (Iranmanesh et al. 2008). The oxygen content of DEE is 21.6% (Rakopoulos et al. 2016).

Unstable operation of engine and heavy smoke limited the amount of DEE up to 24% (Bridjesh et al. 2018; Zhang et al. 2011; Das et al. 2018; Górski and Przedlacki 2014). Kapilan et al. (2008) investigated the influence of 5%DEE with diesel fuel at full load condition. Higher thermal efficiency is reported with the addition of DEE. Das et al. (2018) examined the 10%DEE with the Karanja biodiesel blend B30 at 1500 rev/min. Reduction in NO_X emission is observed with the addition of DEE. Iranmanesh et al. (2008) reported the impact of DEE with the Karanja biodiesel at a constant speed from the performance point of view. They reported that 15%DEE enhance the thermal efficiency and lowers the NO_x emission. Patil and Thipse (2015) investigated the various proportions of DEE with kerosene and diesel fuel. They reported lower NOx emission, improved diesel engine performance with the usage of DEE. Mohebbi et al. (2018) investigated the blend of ethanol, DEE and diesel fuel in reactivity controlled diesel engine. They reported that mixing of 40%DEE, drops the pressure rise during the combustion by 33%, 14% rise in mean effective pressure reduction, and, low emissions. The earlier mentioned studies on diesel engines have conducted from the energy analysis point of view. However, energy analysis tells about only the quantitative energy losses, and it does not give information about the irreversibilities and their location in engine process (Heywood 1988; Ferguson and Kirkpatrick 2016). The detailed information about the irreversibilities (exergy destruction), and their causes in engine operation given by exergy analysis (Caton 2000; Rakopoulos and Giakoumis 2004, 2006). Exergy analysis is the combination of first and second law of thermodynamics that gives the magnitudes of losses associated with the various energy flow and also, identifies the causes of irreversibilities and their locations (Moran 1999; Bejan 2002; Moran and Shapiro 2000). The exergy destruction indicates the irreversibilities in system. Various researchers have applied exergy analysis to identify the irreversibilities of different biodiesel fueled diesel engine (Bahoosh et al. 2017; Çakmak and Bilgin 2017; Caliskan and Hepbasli 2011; Caliskan et al. 2010; Khoobbakht et al. 2016; López et al. 2014). Calisken et al. (2010) carried out the exergy analysis of diesel engine fueled with various biodiesel

blend. It was reported that high oleic soybean biodiesel blend gives the better energy
and exergy performance. Aghbashlo et al. (2015) conducted the exergy analysis and
emission measurement of diesel engine fuelled with blend of 5% biodiesel, diesel, and
additive expanded polystyrene. Exergy analysis is a useful method for maximizing
the benefits and using resources efficiently for sustainable development (Aghbashlo
et al. 2015).

The objective of this study is to present the influence of DEE on emissions charac-
teristics and entropy generation of small single cylinder, direct injection (DI) 4-stroke,
engine fueled with WCO45. Due to the lower viscosity of diethyl ether, it is blended
up to 15% only. If more than 15% is used then it may cause leakage problem in fuel
line. DEE used as an additive since it have higher latent heat of vaporization, and
cetane number, as compared to that of diesel fuel. Experiments were carried out at
fixed speed 1600 rpm, for variable load conditions. Engine performance parameters,
emission characteristics and entropy generation are computed with the recorded
experimental data. The entropy generation is computed by performing the exergy
analysis. The full factorial approach has been used for carrying out the experiments.

10.2   Test Set up

Test engine specifications are given in Table 10.1. A single cylinder, small direct
injection, water cooled, and naturally aspirated diesel engine was used to carry out
the tests. AVL Dycon 201 dynamometer panel performed load variation. Air box
method was used to compute the air flow rate. Type K thermocouples were used
for temperature measurement. AVL Ditest Gas 1000 five gas analyzer was used to
measure the engine out emissions. AVL 480 smoke meter was used for smoke mea-
surement. The specification of exhaust gas analyzer is given in Table 10.3. Figure 10.1
shows the test engine with all coupled equipment. Table 10.2 present the measured
fuel blend properties

The input energy is given by:

$$\dot{Q}_{in} = \dot{m}_{fuel} \times LHV \text{ (kW)} \tag{10.1}$$

S. No.	Engine manufacturer	Greaves cotton
1	Model no.	GL 600 WII
2	Cooling	Water
3	Cylinder	1
4	Bore	92 mm
5	Stroke	92 mm
6	Displacement (cm^3)	611
7	Compression ratio	18

Table 10.1 Test engine specifications (Chaudhary and Gakkhar 2018)
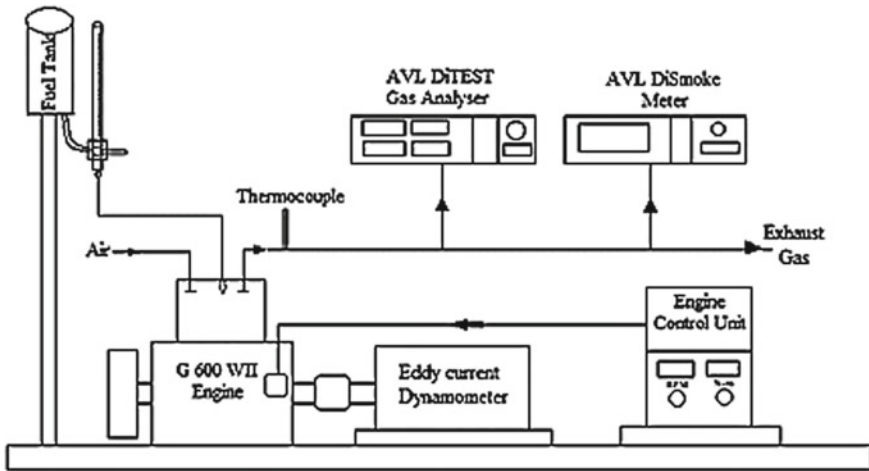
Fig. 10.1 Experimental set-up

Table 10.2 Fuel blends properties

S. No.	Blends	Calorific value (kJ/kg)	Viscosity (cSt)	h/c	o/c	s/c
1	WCO45+5%DEE	41,702	3.24	0.155	0.0792	–
2	WCO45+10%DEE	40,713.1	2.90	0.157	0.0863	–
3	WCO45+15%DEE	39,918.3	2.54	0.1583	0.09382	–

Table 10.3 Technical specification of AVL DiGas 1000 (Chaudhary and Gakkhar 2018)

S. No.	Measurements	Range	Resolution	Precision
1	CO	0%–15% vol	0.01% vol	±0.02% vol
2	CO_2	0%–20% vol	0.01% vol	±0.3% vol
3	HC	0–30,000 ppm	≤2.000: 1	±4 ppm vol
4	NO	0–5000 ppm	1 ppm vol	±5 ppm vol

The brake power or work exergy is given by.

$$BP = 2 * 3.14 * N * T / 60 \, \text{kW} \tag{10.2}$$

Input exergy is computed by equation

$$\dot{Ex}_{in} = \dot{m}_{fuel} \times LHV$$
$$\times \left\{ 1.04 + 0.17\left(\frac{h}{c}\right) + 0.04\left(\frac{o}{c}\right) + 0.21\left(\frac{s}{c}\right)\left[1 - 2.06\left(\frac{h}{c}\right)\right] \right\} \tag{10.3}$$

Exergy transfer by unaccounted heat loss is given by

$$\dot{E}x_{unacc.} = \left(1 - \frac{T_o}{T_w}\right) \times \dot{Q}_{unacc.} \tag{10.4}$$

where T_o = temperature of ambient; unaccounted heat losses are computed by energy balance

Exergy transferred to cooling water is given by:

$$\dot{E}x_{cw} = \dot{m}_{cw}[(h_{wo} - h_{wi}) + T_o(s_{wo} - s_{wi})] \tag{10.5}$$

where h_{wo}, h_{wi}, s_{wo} and s_{wi}, are the specific enthalpy and entropy at water outlet and inlet temperature respectively.

Exergy associated with exhaust gases are computed by (Al-Najem and Diab 1992)

$$\dot{E}x_{eg} = \dot{Q}_{eg} + \dot{m}_{eg} T_o \left[c_{p,eg} \ln\left(\frac{T_0}{T_{eg}}\right) - R\left(\frac{P_0}{P_{eg}}\right)\right] \tag{10.6}$$

where $m_{eg} = m_a + m_{fuel}$; and exhaust heat $= \dot{Q}_{eg} = \dot{m}_{fuel} c_{p,eg} \left(1 + \frac{A}{F}\right)(T_{eg} - T_0)$

Exergy destruction is given by

$$\dot{E}x_{dest.} = \dot{E}x_{in} - \left(\dot{E}x_{shaft} + \dot{E}x_{cw} + \dot{E}x_{eg} + \dot{E}x_{unacc.}\right) \tag{10.7}$$

where Ex_{in} = Fuel input exergy; Ex_{shat} = Work exergy; Ex_{cw} = cooling water exergy; Ex_{eg} = Exhaust Exergy; $Ex_{unacc.}$ = Exergy associated with unaccounted heat losses.

Entropy generation is computed by;

$$\dot{S}_{gen} = \frac{\dot{E}x_{dest.}}{T_0} \tag{10.8}$$

The second law efficiency is the ratio of work exergy to exergy supplied or input is given by equation

$$\eta_{II} = \frac{Work\ exergy(BP)}{Exergy\ input\left(\dot{E}x_{in}\right)} \tag{10.9}$$

10.3   Result and Discussion

Figures 10.2 and 10.3 show the influence of different percentages of DEE on BSFC and brake thermal efficiency of WCO45 at five load levels. It is observed from figures
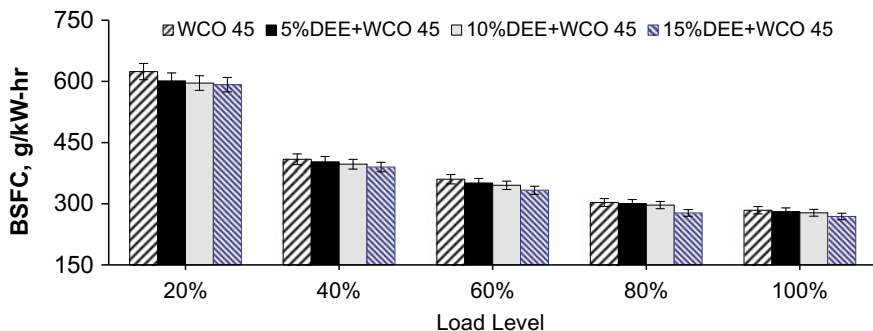
Fig. 10.2 Influence of DEE on brake specific fuel consumption (BSFC)
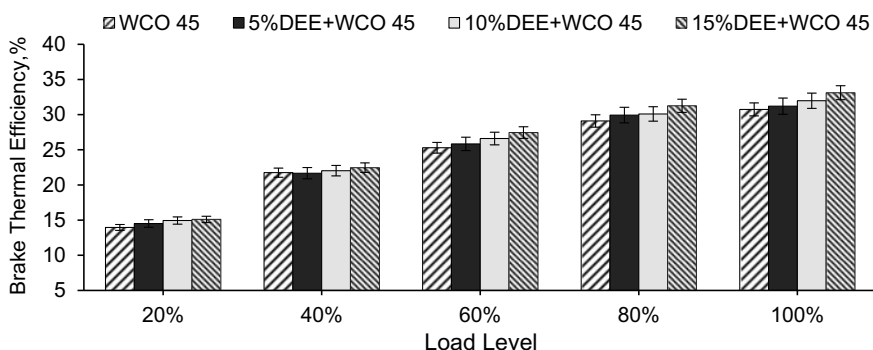
Fig. 10.3 Influence of DEE on bake thermal efficiency

that BSFC is the highest for biodiesel blend (WCO45) without the blending of DEE at any load level. As load increases, BSFC decreases and is minimum at 100% load. As percentage of DEE increases, the BSFC decreases at all loads. With the blending of DEE, the viscosity and density of the biodiesel blend reduce, which result in improved atomization and better spray characteristics, consequently better combustion of fuel, leading to lower BSFC and higher thermal efficiency. The presence of DEE, results in an increase in the brake thermal efficiency as a consequence of better combustion. As the percentage of DEE increases at any load the brake thermal efficiency increases. Higher thermal efficiency is observed with 15%DEE addition 33.13% at full load while for the biodiesel blend (WCO45) without DEE, it is 30.25% only.

Figure 10.4 represents the influence of different percentages of DEE on CO emission at different load levels. With the blending of DEE as an additive, the combustion process improves, due to high oxygen content of DEE, therefore complete combustion and less CO emission. 15%DEE+WCO15 gives the lowest CO emission at any given load level. At full load, it is of the order of 0.014, 0.012, 0.011 and 0.01, respectively for WCO45, 5%DEE+WCO45, 10%DEE+WCO45 and 15%DEE+WCO45.
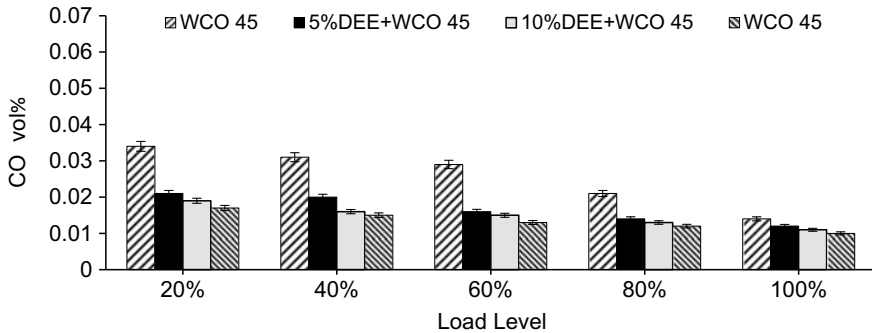
Fig. 10.4 Influence of DEE on CO emission
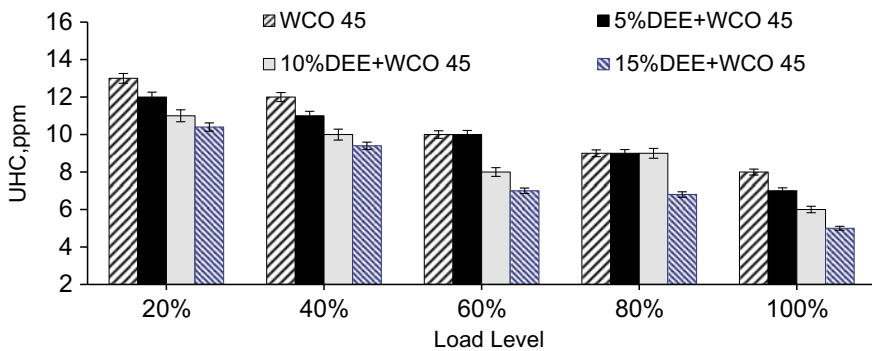
Fig. 10.5 Influence of DEE on HC emission

Figure 10.5 represents the influence of DEE on unburned HC emission at different load levels. It is observed that blending of DEE reduces HC emission for all load levels. Increasing DEE content in WCO45 gives the lower HC emission at any load levels as compared to WCO45 without DEE blending. Blending of DEE increases the oxygen content in the blend, which gives the complete combustion. 15%DEE gives the 5 ppm HC, while the WCO45 gives the 8 ppm at full load.

Figure 10.6 represents the influence of DEE on NO emission at varying load levels. With increasing the content of DEE, the in-cylinder temperature during the combustion process (Barik and Murugan 2016) reduce hence low NO_x emission emits at any load level as compared to that of WCO45. With increasing the content of DEE, the NOx emission reduces as shown in Fig. 10.5. Blending of 15%DEE emits 309 ppm NOx while the WCO45 without DEE emits higher NO 1410 ppm. At full load, the NOx emission is reduced by 48%, 37% and 24% by using 15%DEE, 10%DEE and 5%DEE, respectively as compared to that of WCO45. This is because of their high latent heat of vaporization, leads to low in-cylinder temperature and cools down the charge for all loads.
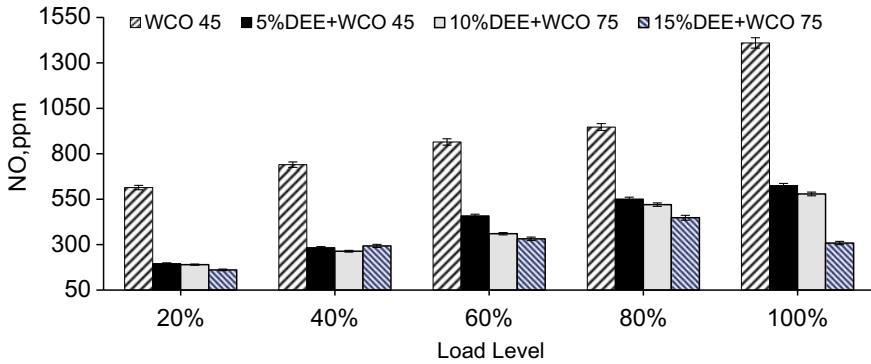
Fig. 10.6 Influence of DEE on NO emission

10.3.1 Influence of DEE on Exergy Destruction, Entropy Generation and Exergetic Efficiency

Figure 10.7 shows the influence on the magnitude of exergy destruction. It is observed that the blending of DEE reduces the exergy destruction at any load level. It is due to the proper utilization of fuel input exergy in engine operation in terms of brake power exergy or work exergy. 15%DEE gives the lowest exergy destruction by 9.1% as compared to biodiesel blend (WCO45).

Figure 10.8 shows the influence of DEE on entropy generation at different load conditions. It follows the similar variation trend of exergy destruction since it depends on it and represents the irreversibilities hence higher exergy destruction gives the higher entropy generation. 15%DEE gives lowest entropy generation due to low exergy destruction. It is of the order of 0.0194 kW/K, 0.0204 kW/K, 0.0213 kW/K and 0.0226 kW/K for 15%DEE + WCO45, 10%DEE+WCO45, 5%DEE+WCO45 and WCO45, respectively at full load.
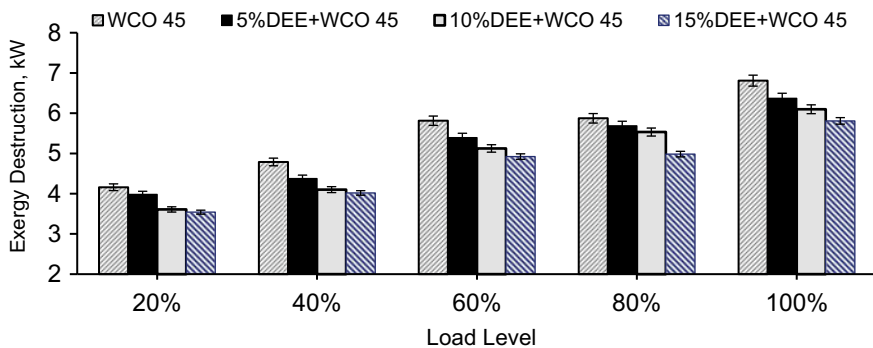
Fig. 10.7 Influence of DEE on exergy destruction
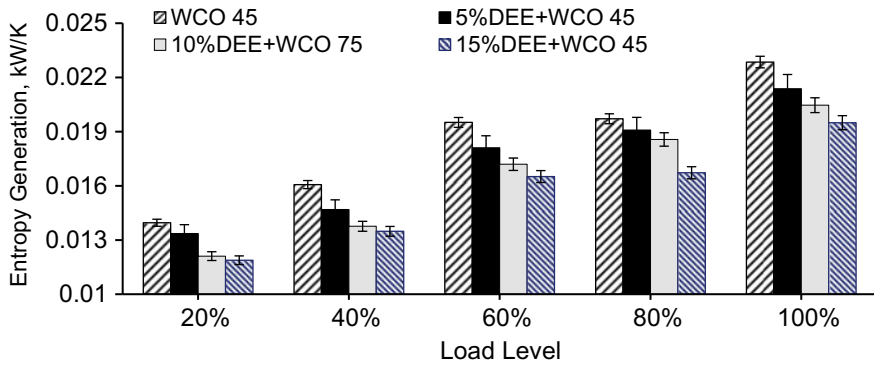
Fig. 10.8 Influence of DEE on entropy generation
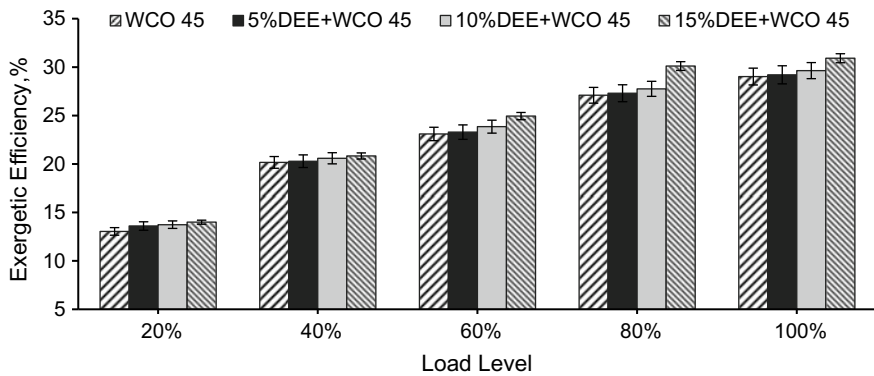
Fig. 10.9 Influence of DEE on exergetic efficiency

Figure 10.9 shows the influence of DEE on exergetic efficiency at different load conditions. It is observed that variation trend is similar to brake thermal efficiency (Fig. 10.2) however, the magnitudes are different. Blending of DEE enhance the exergetic efficiency at any load level as compared to that without DEE blending. 15%DEE blending gives the highest exergetic efficiency of the order of 32.10%, while the WCO 45 without DEE, gives the 28.45% exergetic efficiency at full load.

10.4 Conclusions

Addition of DEE improves the engine performance from the emission and exergy point of view by reducing the entropy generation and harmful emissions. DEE significantly affects the NOx emission and entropy generation of WCO45 fueled diesel engine. Following are the main conclusions.

- NOx emission is reduced by 48%, 37% and 24% by using 15%DEE, 10%DEE and 5%DEE respectively, as compared to that for WCO 45. Reduction in CO and HC emission levels are recorded by 37% and 20%, respectively, using 15%DEE blend.
- 15%DEE with WCO45, reduction the exergy destruction which leads to low entropy generation. Exergetic efficiency is mproved by 8.9%, 9.9% and 12.56% using 5%DEE, 10%DEE and 15%DEE, respectively compared to that for WCO45.
- 15%DEE blending with WCO 45 biodiesel improve the brake thermal efficiency of order of 5.8%, 8.9%, and 10.26% compared to 10%DEE, 5%DEE and WCO 45.

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Chapter 11
Bioethanol Operation in a DI Diesel Engine with DEE Fumigation

Dulari Hansdah, Prabha Chand and S. Murugan

Abstract Engine experiments were conducted with bioethanol in a direct injection (DI) diesel engine with the help of an ignition improver by fumigation technique. The diethyl ether (DEE) was fumigated along with the air in the suction at four different flow rates of 60, 120, 180 and 240 g/h. The results were compared and found to be good agreement with diesel data. The overall heat release rate and useful work for the bioethanol and DEE operation was observed to be higher compared to that of diesel at full load. There was a simultaneous reduction of brake specific nitric oxide (BSNO) and smoke emission with these fuels at every load. But, the brake specific carbon monoxide (BSCO) and brake specific hydrocarbon (BSHC) emission were found to be increased with the higher flow rates of DEE compared to diesel at full load.

Keywords Bioethanol · *Madhuca indica* flower · Diesel engine · DEE fumigation

11.1 Introduction

Use of bioethanol in compression ignition (CI) engines is gaining importance today, as it is a renewable and offers lower pollutants. More emphasis is given to explore bioethanol from new feed stocks and its application in automotive vehicles. It plays a key role in life-cycle greenhouse gas savings (Croezen and Kampman 2008; Beer et al. 2002) which is a major cause of global warming and climate change. *Madhuca indica* seed is already proved to be one of the feed stocks for biodiesel production and its application in diesel engine. Also the bioethanol is obtained from *Madhuca indica* flower and utilised in engine by many researchers (Swain et al. 2007; Mohanty et al. 2009; Hansdah et al. 2013).

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Literature revealed that bioethanol-diesel blend/emulsion can reduce diesel demand up to 25%. The fumigation and dual fuel operation of bioethanol can replace up to 50 and 90% of the diesel demand (Ecklund et al. 1984). Generally, the lower limit of Cetane number for diesel fuel is 30, but bioethanol has the Cetane number in the range of 8–15. It is reported that the ignition can be improved when a high Cetane fuel is added with low Cetane fuel either in the form of blending or in dual fuel mode in diesel engines. Fumigation is one of the types of dual fuel operation in which bioethanol is injected as a main fuel, while an ignition improver is inducted in little quantities along with air in suction. The fumigation technique offers the advantages of easy conversion of the diesel engine to work on dual fuel mode (Hariharan et al. 2013). Dual fuel mode also offers increased thermal efficiency and reduced smoke emissions. Many papers have been documented with diesel, vegetable oils, biodiesel and low Cetane fuels in dual fuel/fumigation mode with induction of high-Cetane fuel or gaseous fuels at intake manifold (Hariharan et al. 2013; Yadav et al. 2012; Namasivayam et al. 2010; Sahoo et al. 2009; Sankaranarayanan et al. 2005; Purushothaman and Nagarajan 2010; Edwin Geo et al. 2009). Ignition improvers such as dimethyl ether (DME), diethyl ether (DEE) and diglycol methyl ether (diglyme) have Cetane numbers higher than diesel. Considering the availability, production method and cost, DEE found to be a better ignition improver than DME and diglyme.

Alcohols can directly burn inside the cylinder with the pilot injection of diesel in dual fuel mode. This leads to smooth combustion with minimal smoke and particulate emission (Mohanty et al. 2009). Researchers have attempted to fumigate 3% of diethyl ether (DEE) in diesel engines with neat ethanol and found that the brake thermal efficiency was higher and the ignition delay was longer with the ethanol-DEE operation compared to that of diesel. The carbon monoxide (CO) and hydrocarbon (HC) emissions were found to be higher and the NO and the smoke emissions were lower with the ethanol-DEE operation (Nagarajan et al. 2002). It was reported that the engine was operated smoothly and with less noise when DEE fumigation is done in ethanol fueled Volvo AH10A245 bus engine. Cylinder pressure was found to be increased and ignition delay was shorter compared to that of diesel operation (Gjirja et al. 1998).

In this present study, bioethanol produced from *Madhuca indica* flower was used as an injected fuel in diesel engine with fumigation of DEE through suction at four different flow rates of 60, 120, 180 and 240 g/h. Results obtained at different loads were compared with diesel and presented in this paper.

11.2 Materials and Methods

The different production methods and factors which affect the bioethanol production from *Madhuca indica* flower were documented by some researchers (Swain et al. 2007; Mohanty et al. 2009). Figure 11.1 illustrates the schematic diagram of the bioethanol production process. For the present study, the fresh flowers of *Madhuca*
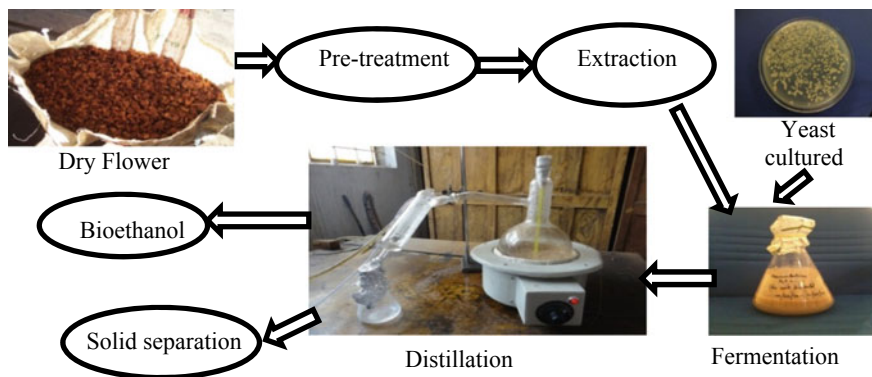
Fig. 11.1   Production process of bioethanol from feed stock

indica were collected from the village people, cleaned properly to remove the adhering soil particles, and dried in the sun. The yeast (*Saccharomyces cerevisiae)* was cultured on YENB (Yeast Extract Nutrient Broth) having 5% glucose and 1% of yeast extract, for 48 h. The *Madhuca indica* flowers were pre-treated for the extraction of sugars. The flowers of *Madhuca indica* and distilled water in a 2:1 ratio were autoclaved, at a pressure of 68.947 kPa for 15 min. For the fermentation process, a starter culture was added at the rate of 10% (v/v) to the *Madhuca indica* extract taken in a 1000 ml Erlenmeyer flask, and fermentation was carried out in a batch on the laboratory bench at a temperature of 30 °C ± 2 °C for 96 h. After the fermentation process, the first distillation was carried out to get the crude extract and further, fractional distillation was done for the removal of water. The purity of bioethanol was checked by an alcoholmeter.

Also the conversion efficiency from sugar to bioethanol in the fermentation can be given as overall ethanol yield (%).

Overall bioethanol yield

$$= \text{(concentration of bioethanol produced/initial concentration of sugar added)}$$
$$* (1/0.51) * 100 = (5.067\text{g}/10\text{g}) * (1/0.51) * 100 = 99.35\%$$

where 0.51 indicates the theoretical ethanol yield (0.51 g-ethanol/g-sugar). Bioethanol yield is the ratio of amount of bioethanol produced divided by the amount of sugar consumed during fermentation.

Table 11.1 Comparison of physical properties of diesel, bioethanol from *Madhuca indica* flower

Properties	Diesel	Bioethanol	DEE
Density (kg/m^3)	870	800	713
Lower heating value (MJ/kg)	43.8	29.4	33.89
Cetane number	50–55	5–18	>125
Kinematic viscosity at 40 °C (cSt)	2.58	1.73	0.224
Auto-ignition temperature (°C)	210	329	160
Boiling point (°C)	180–330	80	34.4
Latent heat of vaporisation (kJ/kg)	260	820	465
Oxygen content (wt%)	0	35	22
Molecular weight	170	42	74.12

11.2.1 Fuel Properties

The physical properties of bioethanol produced from the *Madhuca indica* flower were tested in a standard fuel testing laboratory, i.e. ITA lab, Kolkata. Table 11.1 gives the comparison of physical properties of diesel, bioethanol and DEE.

11.3 Experimental Set up and Procedure

The test engine used for the experiment was a single cylinder, four-stroke, and air cooled, DI diesel engine with the maximum rated power of 4.4 kW, at a constant speed (1500 rpm). Figure 11.2 shows the schematic representation of the experimental set up and the technical specifications of the engine are given in Table 11.2.

Two fuel tanks were used in the study, where fuel tank 6 stores bioethanol while tank 6A stores DEE. An automatic solenoid controlled type burette was used for fuel consumption readings of bioethanol. But, for DEE fumigation, a manually operated stopper was used which was connected with pipe line of fuel tank and injection valve to the intake manifold. The stopper was also regulated for fuel supply of different flow by adjustment. The injection was in the form of droplets, 10 cm from the intake manifold.

To accumulate sufficient air, an air box was fitted with the engine intake manifold. A manometer fitted in the air box showed the reading of the water head in terms of pressure difference, which was used to calculate the air consumption of the engine. A temperature sensor was fitted in the exhaust pipe indicating the temperature of the exhaust gas. A gas analyser was used to measure the HC, CO, NO emissions in the exhaust. The gas analyser was inserted and kept in the exhaust pipe for a few minutes to measure the emissions. The HC and CO, CO_2 emissions were measured with the help of the gas analyser that worked on the NDIR principle. The NO emission was measured by the photochemical sensor. A diesel smoke meter was used to measure the
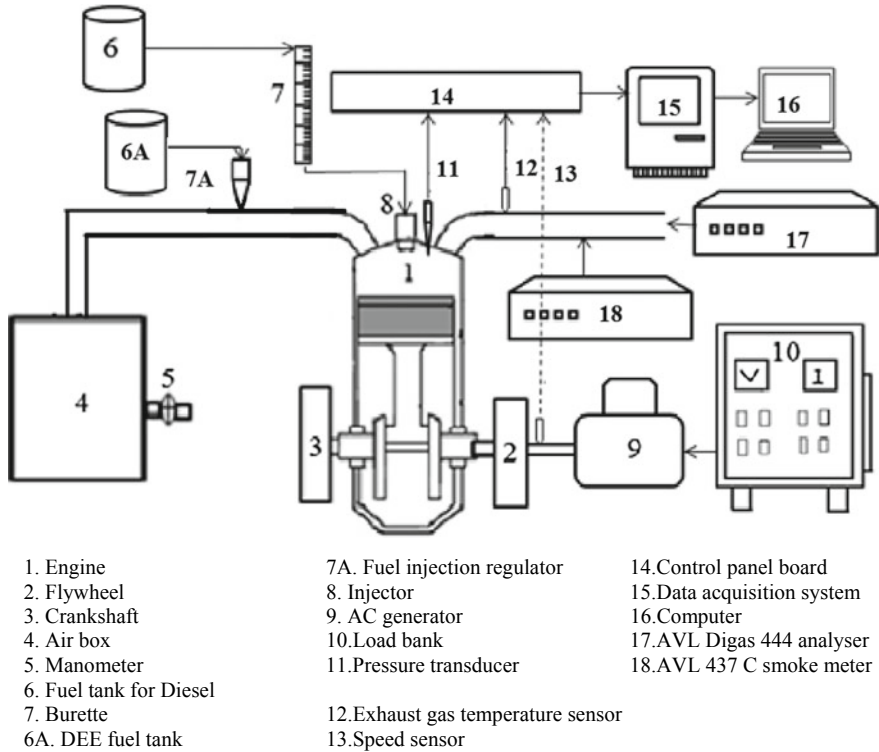
Fig. 11.2 Schematic diagram of the experimental set up

1. Engine	7A. Fuel injection regulator	14.Control panel board
2. Flywheel	8. Injector	15.Data acquisition system
3. Crankshaft	9. AC generator	16.Computer
4. Air box	10.Load bank	17.AVL Digas 444 analyser
5. Manometer	11.Pressure transducer	18.AVL 437 C smoke meter
6. Fuel tank for Diesel		
7. Burette	12.Exhaust gas temperature sensor	
6A. DEE fuel tank	13.Speed sensor	

Table 11.2 Technical specifications of the diesel engine

Type	Kirloskar TAF1 vertical diesel engine
No. of cylinder	1
Type of fumigation	Direct
Rated power at 1500 rpm (kW)	4.41
Bore (mm)	87.5
Stroke (mm)	110
Compression ratio	17.5
Method of cooling	Air cooled with radial fin
Displacement volume (L)	0.662
Fuel fumigation timing bTDC (°)	23°
Number of injector nozzle holes	3
Nozzle-hole diameter (mm)	0.25

smoke density of the engine exhaust. Smoke is measured using Hatridge smoke meter in percentage opacity which adopt the light extinction principle. The measurements of smoke are compatible with Hatridge Smoke Units (HSU). The cylinder pressure at a particular crank angle was measured with the help of a Kistler made quartz piezoelectric pressure transducer (Model Type 5395A), mounted on the cylinder head in the standard position. A crank angle encoder was fitted to the output shaft to measure the crank angle. The data acquisition system in conjunction with pressure transducer and crank angle encoder will record the pressure and crank angle values.

Initially, the engine was operated with diesel to obtain the reference data at different loads ranging from 0 to 100% for 1 h to complete one set of measurement. Later experiments were conducted with bioethanol and fumigated DEE at flow rates of 60, 120, 180 and 240 g/h. The quantity of the DEE was progressively adjusted in such a way that the minimum and maximum level of the DEE was determined by the onset of unstable operation or misfiring and knocking observed from the pressure–crank angle diagram. In every set of experiment, at every load condition, the emission readings were taken at three times. Then the average value of emission measurements was considered for the analysis. Finally, the engine was allowed to run with diesel to flush out the bioethanol in the fuel line. The engine was able to produce the designed power. **The bioethanol is injected to the engine through fuel injector at 23° bTDC and DEE is fumigated along with air**.

11.4 Combustion Analysis

11.4.1 P–θ Diagram

Figure 11.3 depicts the variation of cylinder pressure with crank angle of diesel and neat bioethanol operation with the help of an ignition enhancer. DEE fumigation
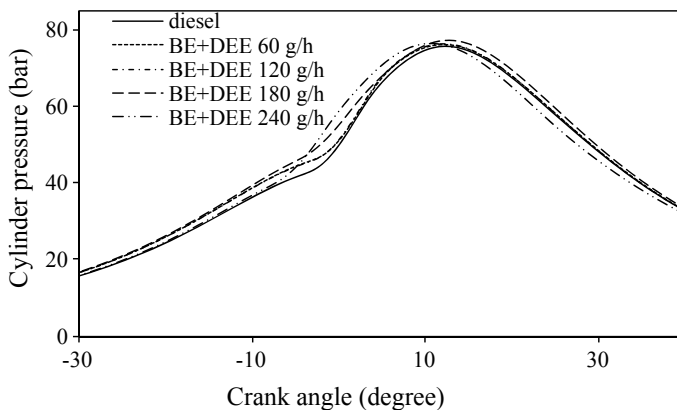
Fig. 11.3 Variation of cylinder pressure with crank angle

enhances the combustion process of a neat bioethanol fueled diesel engine. As the DEE is oxygenated and low boiling point fuel, it evaporates quickly and mixes with air properly and creates a rapid flame front propagation, which may ignite the bioethanol easily. With a lower proportion of DEE, the cylinder pressure is more, but with higher induction of DEE, it is found to be lower due to charge cooling. The over cooled and over rich mixtures can be formed with higher percentage of DEE and bioethanol operation. Some liquid droplet impinges on cylinder wall and remains unburnt due to charge cooling. Hence, result in low cylinder pressure in expansion stroke (Huang et al. 2015).

The peak cylinder pressure of 180 g/h is found to be more, followed by 120, 60, 240 g/h and diesel, which is achieved at the crank angles of 0.2–0.8 °CA variations.

11.4.2 Ignition Delay

The variation of ignition delay with respect to load for diesel and bioethanol, with DEE fumigation at four different flow rates of 60, 120, 180 and 240 g/h, is shown in Fig. 11.4. It is inferred from the figure that the bioethanol operation with 60 and 120 g/h of the DEE fumigation at the intake manifold, exhibited a longer ignition delay compared to that of diesel at every load. The values of ignition delays vary from 0.5 to 1 °CA, from the diesel data. The DEE fumigation at the intake manifold generally lowers the intake charge temperature due to its cooling effect and hence, a longer ignition delay is achieved. But, the ignition delay is found to be shorter by about 1–2 °CA with bioethanol and DEE fumigation at 180 and 240 g/h flow rates,
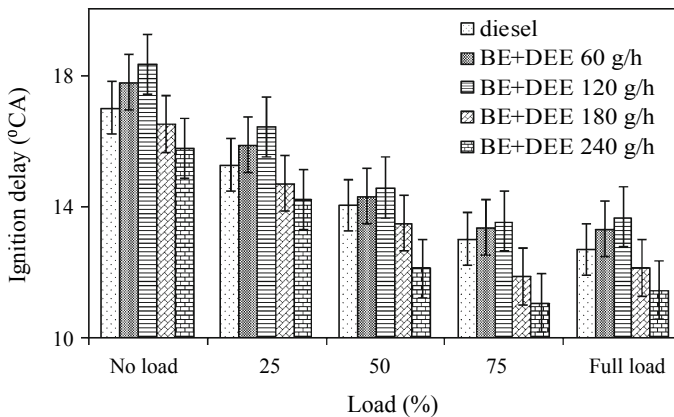
Fig. 11.4 Variation of ignition delay with load for diesel and bioethanol operation with DEE fumigation

in comparison with diesel at every load. When high cetane fuel is introduced at a higher percentage, the cetane number of bioethanol also increases and the fuel may ignite better.

The delay period is also shortened due to the mixture homogeneity. The DEE mixes properly with the air when it is inducted at the intake manifold, and the time required for the physical and chemical delay is reduced. The ignition delay for all the tested fuels in this study shows a declining trend from no load to full load, due to a higher cylinder gas temperature.

11.4.3 Heat Release Rate (HRR)

Figure 11.5 illustrates the variation of the heat release rate with respect to the crank angle for diesel and bioethanol operation at full load. The effect of changes in engine design, fuel injection systems, fuel types and engine operating conditions on combustion and performance of engine can be analyzed by heat release rate. The first law thermodynamics analysis by Sorenson et al. is used to calculate the HRR, which is given by the following equation,

$$\frac{\partial E}{\partial \theta} = \vartheta \frac{\partial P}{\partial \theta}(1/\gamma - 1) + P\frac{\partial \vartheta}{\partial \theta}(\gamma/\gamma - 1) \tag{11.1}$$

where,

$\frac{\partial E}{\partial \theta}$ = rate of heat release (J/°CA)
ϑ = gas volume (m^3)
P = cylinder pressure (bar)
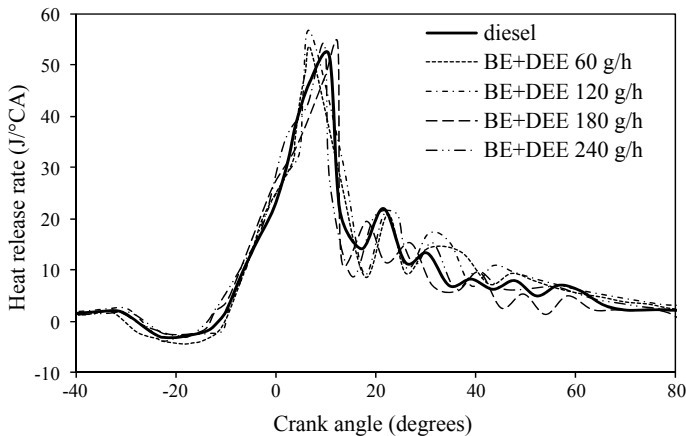
Fig. 11.5 Variation of heat release rate with crank angle for diesel and bioethanol operation with DEE fumigation

θ = crank angle (°)
γ = ratio of specific heats, C_p and C_v.

The bioethanol operation with the DEE fumigation at the flow rates of 60, 120, 180 and 240 g/h shows a higher heat release rates compared to that of diesel at full load. It varies by about 2–3 J/°CA from diesel data at 9–14 °CA aTDC. The maximum heat release rate for diesel is 51.8 J/°CA which occurs at 10.7 °CA aTDC at full load. With 60 and 120 g/h, the ignition delay is longer compared to that of diesel; hence, more accumulation of fuel in the delay period is achieved. The boiling temperature of DEE is 34.4 °C. So, it can vaporise and mix with air easily. DEE burns faster compared to bioethanol, and it helps the bioethanol to ignite as it has a higher auto ignition temperature. Both DEE and bioethanol are oxygenated fuels; the fuel in the local region can get oxygen to burn easily. With the higher induction of DEE, the heat release rate is also found to be higher with a little shift of the crank angle towards the TDC compared to that of diesel. Due to the lower auto ignition temperature and higher cetane number of DEE compared to those of bioethanol, more heat release is achieved in the premixed phase by the DEE, which will burn the bioethanol, and this results in higher maximum heat release rates and peak cylinder pressure.

There is an abrupt combustion with an audible knock with at higher induction of DEE, beyond 240 g/h. Hence, the engine was not operated with the flow rate of DEE higher than 240 g/h.

11.4.4 Maximum Cylinder Pressure

Figure 11.6 portrays the variation of the maximum cylinder pressure of diesel and neat bioethanol with DEE fumigation, at the flow rates of 60, 120, 180 and 240 g/h
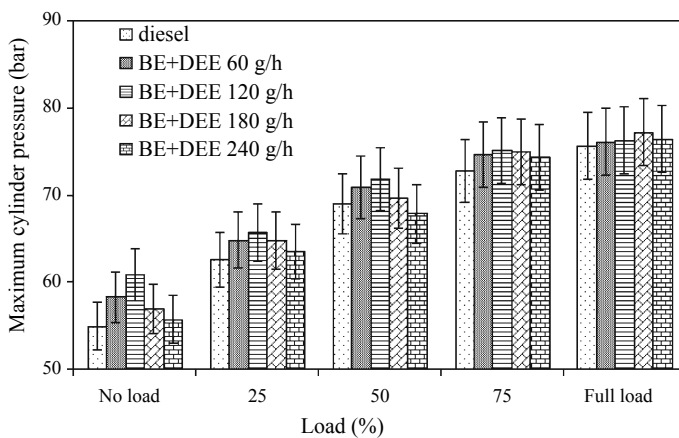
Fig. 11.6 Variation of the maximum cylinder pressure with load for diesel and bioethanol operation with DEE fumigation

with respect to the crank angle at different loads. Generally, the performance and knocking characteristics of the engine with a specific fuel can be better clarified with the help of cylinder pressure and crank angle history. The occurrence of the maximum cylinder pressure with diesel and neat bioethanol operation is observed to vary from 10 to 12 °CA aTDC, at full load.

From the figure, it is noticed that all the flow rates of DEE with neat bioethanol have higher cylinder pressure compared to that of diesel at full load. The values of the maximum cylinder pressure for bioethanol and DEE fumigation varies from 1 to 3 bar compared to that of diesel at full load. The reason may be the high cetane number and oxygen content of DEE, which ignites bioethanol easily. With the higher induction of DEE, the premixed combustion is accelerated with the higher burning velocity of DEE in neat bioethanol operation. The lower viscosity and higher volatility of bioethanol results in more accumulation of bioethanol in the delay period, which may also be the reason for the higher cylinder pressures.

11.4.5 Maximum Rate of Pressure Rise

Figure 11.7 depicts the variation of the maximum rate of pressure rise for diesel and bioethanol, and DEE operation with respect to load. It can be observed figure, that the maximum rate of pressure rise for the flow rates of 60 and 240 g/h is found to be higher compared to that of diesel at full load. For all the flow rates of DEE in the bioethanol operation, the maximum rate of pressure rise ranges from 0.5 to 2 bar/°CA in comparison to diesel, at full load. At 240 g/h flow rate of DEE, the delay period gets shortened, and rapid combustion is achieved with audible knock.
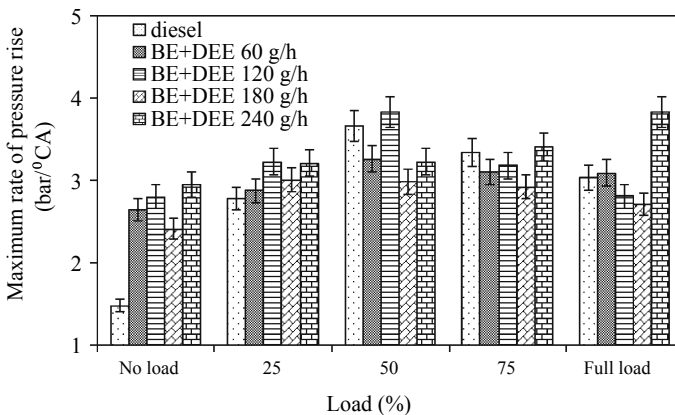
Fig. 11.7 Variation of the maximum rate of pressure rise with load for diesel and bioethanol operation with DEE fumigation

11.4.6 Combustion Duration

Figure 11.8 depicts the variation of the combustion duration of diesel and bioethanol operation with the DEE fumigation with respect to load. The combustion duration for all the tested fuels in this study, shows an increasing trend with respect to load. When the load is increased, the fuel consumption is also increased to overcome the friction and generate the required power. And the fuel undergoes the oxidation process with the help of the entrapped residual gases in the previous cycle in the early stage of combustion. The combustion is very rapid, which minimises the premixed combustion phase; all the fuel may not burn in this phase, and hence, takes part in the post oxidation process. So, the combustion period gets prolonged. At full load, the combustion duration data are observed to be shorter by about 2–4 °CA and longer by about 1–3 °CA according to the lower and higher values of DEE fumigation with bioethanol operation compared to that of diesel respectively. As discussed earlier, DEE fumigation at the flow rates of 60 and 120 g/h allows more injection of bioethanol due to the longer delay period. All the injected fuel gets a sufficient time for ignition, and the combustion is also faster, due to the faster burning velocity of the DEE. So, the combustion duration is reduced with these two flow rates. But, the higher flow rates of DEE reduce the premixed combustion phase, and some fuel gets combusted with the help of the local oxygen in the diffusion combustion phase.
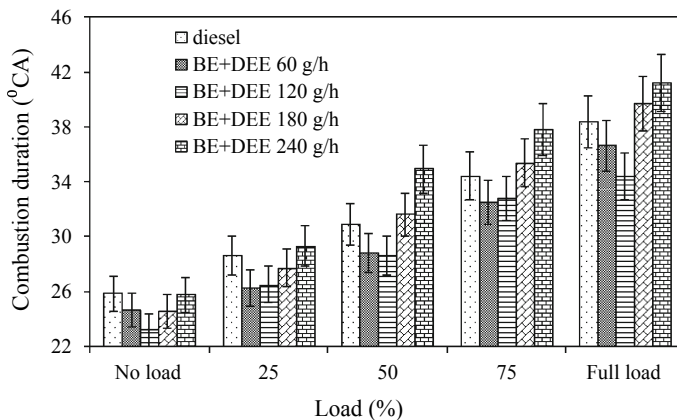
Fig. 11.8 Variation of combustion duration with load for diesel and bioethanol operation with DEE fumigation

Table 11.3 Energy share of DEE in bioethanol operation

Flow rates	No load	25% load	50% load	75% load	Full load
BE + DEE 60 g/h	13.9	12.2	8.3	6.7	5.6
BE + DEE 120 g/h	26.7	20.9	16.5	13.8	10.7
BE + DEE 180 g/h	34.4	26.7	18.7	14.8	11.3
BE + DEE 240 g/h	45	39.2	29.4	23.7	19.5

11.5 Engine Performance Analysis

11.5.1 Energy Share

The energy share of DEE in the bioethanol operation is shown in Table 11.3.

The energy share is found to be increased with the higher flow rates of DEE. The reason is that a large amount of air is displaced by the DEE due to more flow rates of DEE. From no load to full load, the DEE energy share shows a decreasing trend, due to the higher gas temperature of the cylinder. When the energy share of DEE increases, the performance of the engine is also found to be increased, due to the combustion of fuel achieved closer to TDC. As it is an oxygenated fuel, the fuel gets combusted easily, due to good mixture formation.

11.5.2 Brake Specific Fuel Consumption (BSFC)

The variation of BSFC for diesel and bioethanol with DEE fumigation at four different flow rates with respect to load is shown in Fig. 11.9.
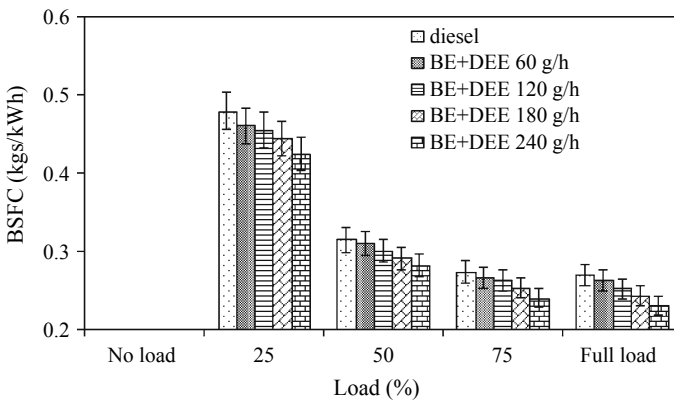
Fig. 11.9 Variation of BSFC with load for diesel and bioethanol operation with DEE fumigation
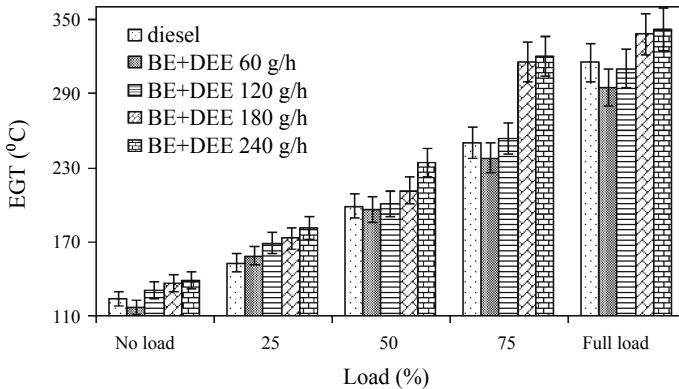
Fig. 11.10 Variation of EGT with load for diesel and bioethanol operation with DEE fumigation

It is observed from the figure, that the BSFC is found to be low for the bioethanol operation with DEE fumigation in comparison with diesel at full load. This is due to high oxygen content of the fuel. The energy share of DEE is found to be increased with load and it enhances the combustion, due to which BSFC reduces.

11.5.3   Exhaust Gas Temperature (EGT)

The variation of EGT for diesel and bioethanol operation with DEE fumigation at four different flow rates is shown in Fig. 11.10. It is apparent from the figure that, the EGT is found to be more with a higher flow rate of DEE at full load. At higher flow rates of DEE, the combustion is closer to TDC, hence some amount of heat is available as a waste at the exhaust. Also the combustion is faster due to oxygen availability in the delay period. At a lower flow rate of DEE, the heat is converted to useful work.

11.5.4   Volumetric Efficiency

Figure 11.11 depicts the variation of the volumetric efficiency of diesel and bioethanol operation with the DEE fumigation with respect to load.

The volumetric efficiency of a CI engine pertains to the breathing ability of a four stroke engine. Generally, a gaseous fuel displaces air and, therefore, the breathing capacity of the engine is reduced. Usually, the volumetric efficiency of diesel is between 85 and 90%. With the induction of DEE at the intake manifold of the engine, the molar mass of the fuel-air mixture reduces, lowering the density of the intake mixture. This may be due to the supply of more DEE at higher load, which
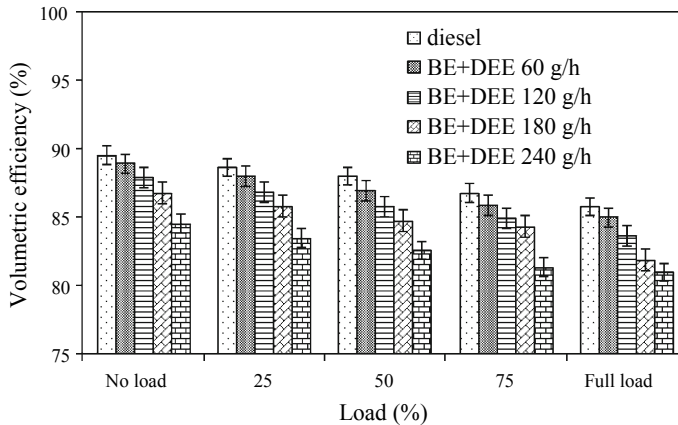
Fig. 11.11 Variation of volumetric efficiency with load for diesel and bioethanol operation with DEE fumigation

reduces the air consumption. The bioethanol operation with DEE fumigation at four different flow rates at the intake manifold reduces the air consumption and volumetric efficiency of the engine is found to be reduced. The volumetric efficiency of the engine fueled with diesel and the bioethanol operation at 60, 120, 180 and 240 g/h is found to be 85.7%, 84.9%, 83.6%, 81.8% and 80.9% respectively, at full load.

11.5.5 Thermal Energy Balance

Figure 11.12 shows the variation of the thermal energy balance for diesel and bioethanol operation with DEE fumigation. At full load, the useful work for bioethanol with DEE fumigation is found to be higher compared to that of diesel. This may be due to better combustion and lesser heat loss compared to that of diesel.

The unaccounted losses are minimised, and hence, more useful work is obtained. It is also observed that the heat carried by the lubricating oil is increased with the bioethanol and DEE operation compared to that of diesel. Generally, bioethanol and DEE have less lubricity properties in comparison with diesel. The temperature of the lubricating oil is increased in overcoming the friction.
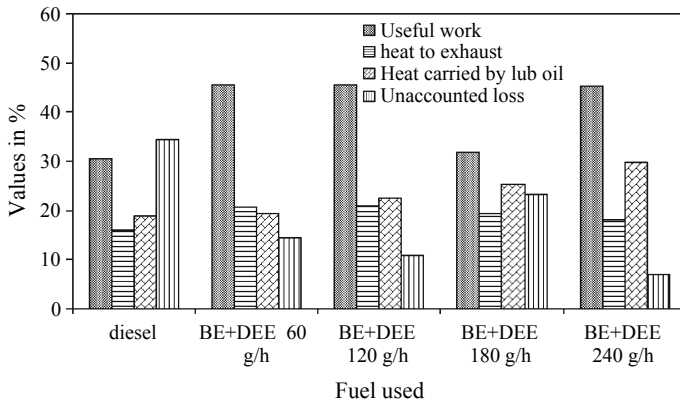
Fig. 11.12 Variation of thermal energy balance for diesel and bioethanol with DEE fumigation at full load

11.6 Mission Analysis

11.6.1 BSHC Emission

The variation of BSHC emission for bioethanol operation with DEE fumigation at flow rates of 60, 120, 180 and 240 g/h from diesel is given in Fig. 11.13. There is a reduction of BSHC emission for the bioethanol operation with the DEE fumigation at the flow rate of 60 g/h at every load, and at full load it is found to be lower by about 9.6% compared to that of diesel. At this flow rate, the fuel gets combusted by the faster burning velocity of the DEE and mixture homogeneity without flame
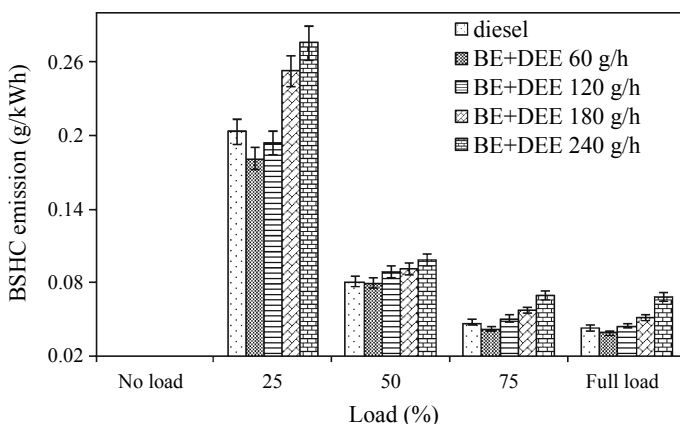
Fig. 11.13 Variation of BSHC emission for sole bioethanol operation with DEE and diesel at different loads

quenching. The percentage increase with the DEE fumigation at the flow rates of 120, 180 and 240 g/h is found to be about 3.2%, 5.6% and 11.3% respectively, compared to that of diesel at full load. With these flow rates, though the heat release is more, the BSHC emission is also found to be more compared to that of diesel. Due to the increased admittance of DEE, some fuel would not have burnt because of the quenching effect. Flame quenching affect the combustion process near the wall due to heat loss from the flame. The burning velocity may be rapid, which will not combust the fuels close to the cylinder wall, which is also a fuel rich zone surrounded by the cooled DEE (Gutkowski and Santos 2014).

11.6.2 BSCO Emission

Figure 11.14 shows the variation of BSCO emission for the bioethanol operation with the DEE fumigation at flow rates of 60, 120, 180 and 240 g/h, from the diesel data.

The BSCO emission for the bioethanol operation with 60 and 120 g/h flow rates of DEE is found to be lower by about 8.8 and 2.6% respectively, compared to that of diesel at full load. This is due to the more complete combustion achieved by the presence of oxygenated fuels and formation of homogeneous mixture. The figure portrays that the BSCO emission percentage for bioethanol is increased with the flow rates of 180 and 240 g/h by about 17.5% and 25.4% respectively at full load. With a higher induction of DEE, the mixture of air and DEE may be rich and some of the mixture is nearer to the wall and the crevice volume, where the flame cannot propagate properly. When this mixture gets in contact with the hot combustion gases during the latter part of the power stroke, and also in the exhaust manifold, oxidation
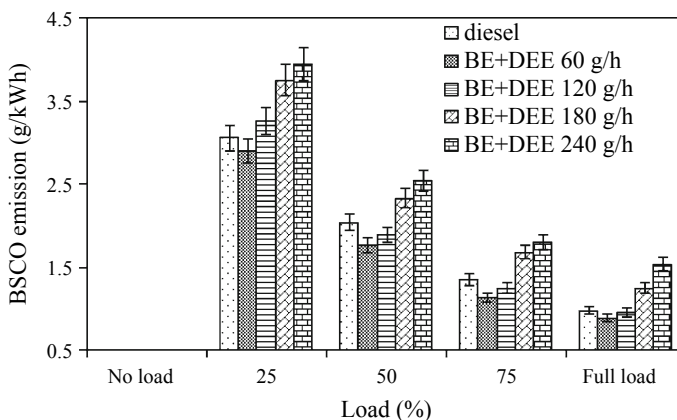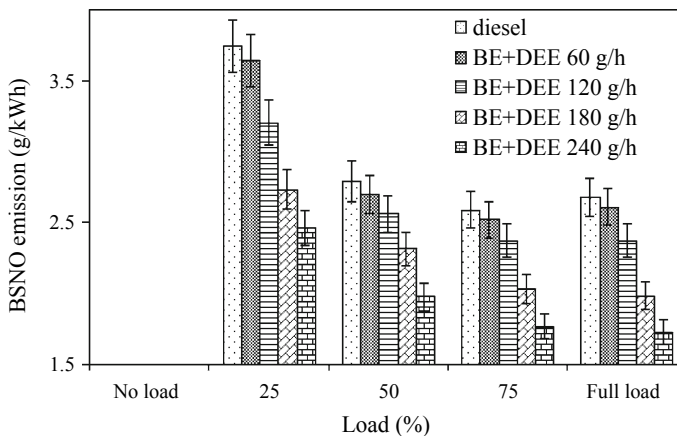

Fig. 11.14 Variation of BSCO emission for sole bioethanol operation with DEE and diesel at different loads

reactions occur, but do not have time to undergo combustion. Another reason may be the over cooled effect experienced with higher percentage of bioethanol direct injection into the engine (Huang et al. 2015). The fuel rich and over cooled zone lead to incomplete combustion and hence, increases the BSHC and BSCO emission.

11.6.3 BSNO Emission

The variation of BSNO emission for the bioethanol operation with the DEE fumigation at the flow rates of 60, 120, 180 and 240 g/h, from diesel with respect to load is given in Fig. 11.15. It can be observed from the graph, that the percentage of the BSNO emission with the bioethanol operation, is found to be lower compared to that of diesel with respect to load. At full load, the BSNO emission is found to be lower by about 2.6, 11.5, 26.2 and 35.6% with DEE fumigation of 60 g/h, 120 g/h, 180 g/h and 240 g/h respectively, compared to that of diesel.

The BSNO emission is due to the premixed combustion phase. High cetane fuels have the advantage of reducing the BSNO emission. Also, the latent heat of vaporisation of bioethanol is higher compared to that of diesel. It requires more energy to ignite; so, the heat liberated due to the DEE is utilized to ignite the bioethanol and hence a lower BSNO emission is achieved. The nitrogen available in the air gets less time to react with oxygen in the shorter ignition delay with higher flow rates of DEE.

Fig. 11.15 Variation of BSNO emission for sole bioethanol operation with DEE and diesel at different loads
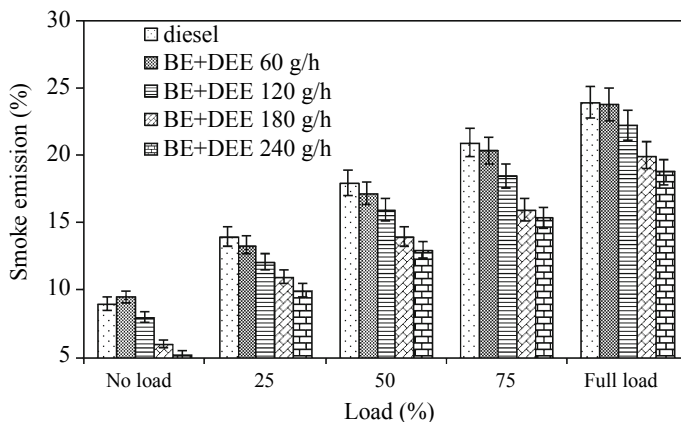
Fig. 11.16 Variation of smoke emission for sole bioethanol operation with DEE and diesel at different loads

11.6.4 Smoke Emission

Smoke is predominantly affected by the type and quantity of fuel used its carbon content, C/H ratio, and aromatic content. Figure 11.16 depicts the variation of smoke emission for bioethanol and diesel operation with respect to load. At full load, the percentage reduction in smoke opacity for bioethanol with the DEE fumigation at flow rates of 60, 120, 180 and 240 g/h is found to be about 1%, 7.1%, 16.6% and 21.6% respectively, compared to that of diesel. The molecular weight of bioethanol and DEE is 42 and 74.2. But for diesel, the molecular weight is 170. Generally, a fuel with a high molecular weight is a complex compound; it is difficult to break, and requires more oxygen in the combustion period. This results in more smoke emission. Both the bioethanol and DEE have low molecular weights and are oxygenated fuels. With the higher induction of DEE, the diffusion combustion phase is prolonged and more oxygen reacts with hydrogen. As a result, less smoke is observed at the exhaust in the bioethanol operation in comparison with diesel operation at any load.

11.7 Conclusion

The experiment was conducted successfully with neat bioethanol with little quantities of DEE fumigation at intake manifold in a small capacity DI diesel engine. From the results, it was concluded that the ignition delay for lower flow rates of DEE is found to be shorter, but it is longer with the higher flow rates. The useful work is increased with an increase in the flow rates of DEE. The BSCO and BSHC emissions are found to be higher with the flow rates of DEE. But, there is a simultaneous reduction in the BSNO and smoke emissions with neat bioethanol and the DEE operation. The flow

rate of 180 g/h, of DEE provides better combustion, useful work, less heat loss, and lower emissions, compared to that of diesel and other flow rates of DEE.

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Part IV
Advancements in Alternative Fuels

Chapter 12
Combustion and Emission Characteristics, and Emission Control of CNG Fueled Vehicles

Nirendra N. Mustafi and Avinash Kumar Agarwal

Abstract Natural gas (NG) is considered as one of the most attractive alternative fuels for vehicles due to its clean-burning characteristics. Rapid growth of urbanization and industrialization has multiplied transport fuel demand worldwide. Vehicle population particularly in metropolitan cities has grown exponentially. Adverse effects of vehicular emissions on the environment and human health have forced regulatory bodies to impose increasingly stringent emission legislations. This has necessitated use of cleaner alternative fuels such as NG in the transport sector. NG fuelled vehicles (NGV) have several advantages such as low photochemical reactivity of the exhaust, zero evaporative emissions, minimized cold-start and low-temperature emissions, and suitability for lean-burn operations. Compressed NG (CNG) vehicles have been used since 1960s and have proven safety record. The most important advantage of NGV is that NG is readily available at low cost worldwide, including many developing countries and technologies exist for its transportation, storage, and distribution systems are well matured. This chapter reviews the state-of-the-art in the NG fueled vehicles, focusing on engine combustion and emissions characteristics of NGVs. Worldwide prospects and challenges of NG as a transport fuel are also included. Technical aspects such as CNG properties, and their effect on engine performance, and emissions are discussed. Hydrogen enriched CNG (HCNG) significantly improves mixture flammability limit thus contributing to lean-burn operation of NG fueled spark ignition (SI) engines. Hence, HCNG has shown to be advantageous over traditional SI engines in terms of fuel economy and pollutant emissions. This chapter provides an overview of recent progress on HCNG fueled engines as well. An overview of the emission control strategies for NGVs is presented towards the end. Finally, main challenges and future R&D required for NGVs are identified.

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12.1 Introduction

Transport sector is energy-intensive but a crucial industry for a nation's economic
growth. It mostly relies on petroleum based fuels such as gasoline and diesel, hence
demand for such fuels will continue to grow exponentially in future for moving
people and goods globally. According to EIA 2017, global annual transport energy
consumption can climb up to 151 quadrillion BTU by 2040, an increment of 44
quadrillions BTU from 2015 (Fig. 12.1) (U.S. Energy Information Administration
(EIA) 2017). This heavy reliance of transport sector on petroleum based fuels has
already created great havoc on earth's ecosystem and human health by emitting GHGs
and harmful pollutants in the ambient environment. Global warming as a consequence
of greenhouse effect has appeared as a severe threat to human civilization, which at
the moment seeks sincere attention of energy producers and consumers. Substantial
reduction in GHG emissions, especially from transport sector is an absolute essential.
Other leading concern is the toxicological effects of transport-related pollution on the
human health. Now-a-days, urban air quality in medium and low income countries
has deteriorated, and transport sector origin pollutants play a major role in this. Traffic
congestion, small-distance urban trips, use of vehicles without appropriate fitness and
after-treatment devices, ineffective catalytic converters—all together cause a high
degree of ambient air pollution in these urban areas. Transport-related air pollutions
normally includes gaseous pollutants (such as carbon monoxide (CO), oxides of
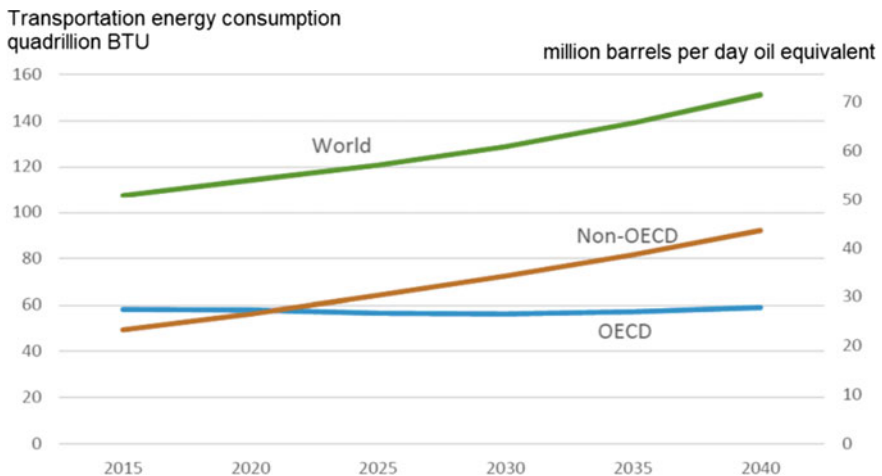
Fig. 12.1 Global transport energy consumption trend (Reference case: International Energy Outlook 2016) (U.S. Energy Information Administration (EIA) 2017)

nitrogen (NO_x), hydrocarbons (HC), sulfur dioxide (SO_2), ozone (O_3) and suspended particulate matter (PM) of various sizes and compositions. Especially $PM_{2.5}$ and Nano-particles are major concerns since they can easily penetrate deeper into the human respiratory system and beyond. Research studies have confirmed that long-term exposure to air pollution can cause several life threatening diseases such as respiratory infections and inflammations, cardiovascular dysfunctions and cancer. Hence millions of premature deaths per year globally are linked to air pollution (Hajbabaei et al. 2013).

Children are most susceptible to the health hazards of air pollution. As per World Health Organization (WHO) reports, 4.2 million premature deaths occurred due to the exposure to outdoor air pollution in 2016; out of which, ~300,000 were children under the age of 5 years (Ghorani-Azam et al. 2016; World Health Organization 2016).

On the other hand, petroleum reserves are depleting rapidly, which has led to price volatility in global fuel market. Emission regulatory agencies are implementing ever stringent legislations in order to address these critical issues, aimed at improving urban air quality and minimize GHG emissions from transport sector by reducing dependence on petroleum products (World Health Organization 2018).

Along with engine design modifications, innovative engine combustion controls, and after-treatment systems, use of low carbon or carbon-neutral alternative fuels has been given top priority. Among various alternative fuels, natural gas (NG) is considered as one of the most attractive fuel for automotive sector due to its multiple benefits, namely vast reserves, availability at lower price, and cleaner combustion characteristics due to its lowest C/H ratio amongst fossil fuels, and compatibility with conventional SI and CI engines (Ma et al. 2007; Khan et al. 2015). NGVs offer several technical advantages such as low photochemical reactivity of exhaust gas, zero evaporative emissions, minimized cold-start and low-temperature emissions (i.e. CO and HC), and suitability for lean-burn operations (Khan et al. 2015; Weaver 1989). Realizing multiple benefits of using NG, many governments around the world are currently expanding NG infrastructure in order to adopt NG as fuel for passenger vehicles as well as for stationary engines (Park et al. 2019). For instance, in the US, share of NGVs has increased significantly in captive heavy-duty fleets including refuse trucks, transit buses, school buses, and delivery trucks (Lounici et al. 2014). In a developing country like Bangladesh, mostly light vehicles are fueled by CNG in urban areas, which accounts for 5% of country's total NG consumption (Thiruvengadam et al. 2018). Engines powered by NG emit far less CO and non-methane hydrocarbons (NMHC) compared to a gasoline engine, but NO_x emissions may not be low enough to meet increasingly stringent emission norms (Khan et al. 2015). PM emissions from NG vehicles are generally quite low because of nearly homogeneous premixed charge combustion, and non-existence of heavy hydrocarbon chains and aromatics in the fuel (McTaggart-Cowan et al. 2006). However, particulate number-size distributions can be important to monitor since it is reported that NGVs emit smaller (Nano-range; 10–30 nm) size particles compared to diesel engines (Jayaratne et al. 2012; Lanni et al. 2003).

At NTP, unit volume of NG usually possesses substantially lower energy content compared to the same volume of gasoline or diesel, hence NG must be compressed to increase its weight or total energy content in a given container of certain volume on a vehicle (Final Report 2017). Natural gas for vehicular applications is usually compressed to very high pressures (200–250 bar), thus reducing its volume by ~99% compared to NTP conditions, in order to facilitate fuel storage in small volume cylinders and to increase driving range between refueling events (CNG 2009). NG is distributed either through underground pipe network (gas grid) or storage cylinders and NGVs require extra onboard spaces for carrying the storage cylinders. NG can fuel all types of vehicles, including motor- bikes, cars, vans, light and heavy-duty trucks, buses, lift trucks, and locomotives.

12.1.1   Global Status of NG Vehicles

Though it is understood that the population of NGVs is increasing rapidly worldwide, actual statistics is not available readily. According to NGV Global statistics, the number of NGVs operating worldwide exceeds 27 million as of 2019, and more than 32,000 NG refueling stations serve these vehicles. Though Iran seemed to be the leading country with more than four million NGVs in 2013 (slightly higher than China), currently China has the highest number of NGVs (more than 6 million) followed by Iran (more than 5 million) (Kalghatgi 2018). Trend of rapid growth of NGVs worldwide is presented in Fig. 12.2, which shows an annual growth rate of
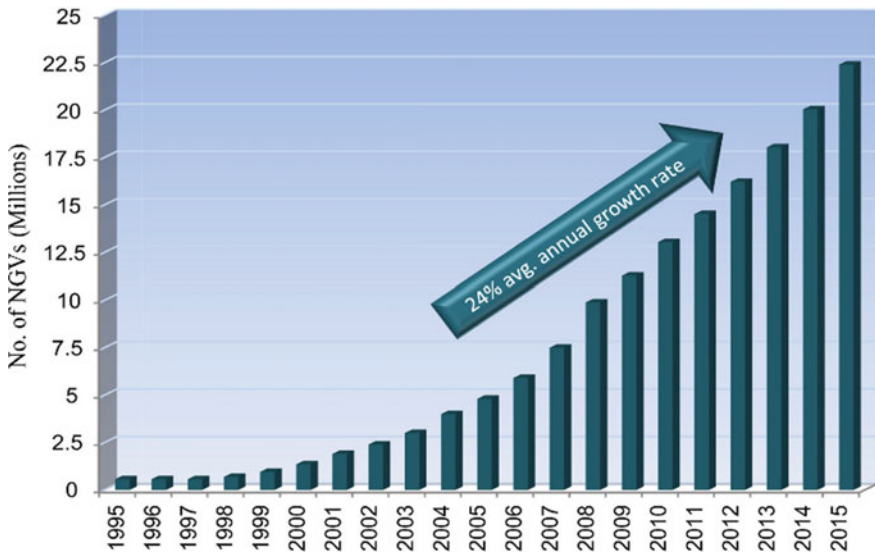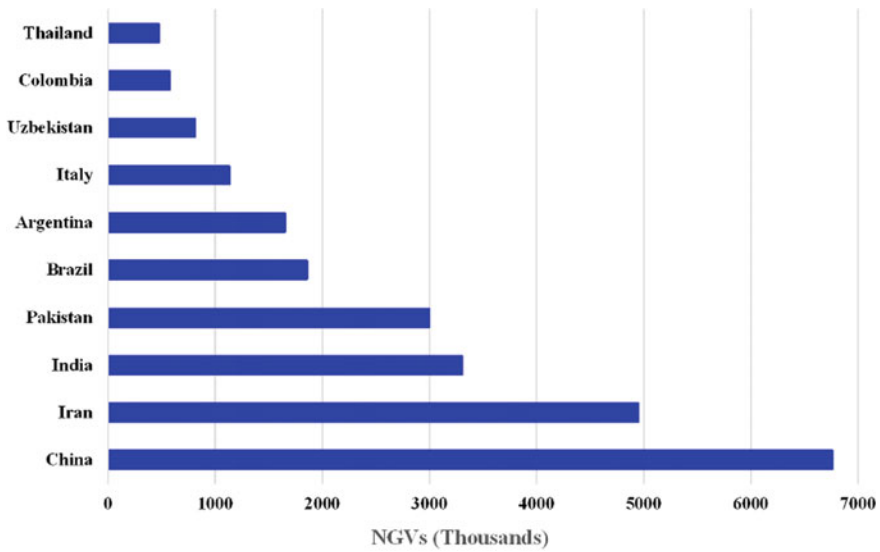

Fig. 12.2   Global NGV growth rate between 1995 and 2015 (Khan et al. 2015)

Fig. 12.3 Top ten countries with the highest population of NGVs (http://www.iangv.org/current-ngv-stats/)

NGVs ~24% between 1995 and 2015. As far as regional growth rate is concerned, the most significant contribution comes from the Asia-Pacific and Latin America regions. Figure 12.3 presents world's top ten countries with the highest number of NGVs in their transport sector (http://www.iangv.org/current-ngv-stats/).

12.1.2   Physico-Chemical Properties of NG

Natural gas is extracted from gas wells or from crude oil production. NG is a mixture of gases, primarily consisting of methane (CH_4) and trace amounts of other higher hydrocarbons such as ethane, propane, n-butane, iso-butane, and pentanes and some other gases including nitrogen, helium, carbon dioxide, hydrogen, hydrogen sulfide, and water vapor (Thiruvengadam et al. 2018; Lijiang and Peng 2016). However, composition of NG extracted from these reserves can vary significantly (mainly the CH_4 content) based on the geographical location of the gas reserves, which ultimately results in variation in the energy content of the NG. As per a report of Shell, CH_4 content can vary between 76 and 90% by volume for gas extracted from 12 different wells (Thiruvengadam et al. 2018). Vehicle engines require certain compatibility with NG compositions (i.e. minimum methane content). For instance, Cummins Westport designated a minimum methane content of 75% by volume for their engines (Westport 2018). Typical physico-chemical properties of NG/CNG in comparison to conventional gasoline and diesel are presented in Table 12.1.

Table 12.1 Physico-chemical properties of CNG in comparison to gasoline and diesel (Khan et al. 2015; Thiruvengadam et al. 2018)

Properties	CNG	Gasoline	Diesel
Octane/Cetane number	120–130	85–95	45–55
Molar mass (kg/mol)	17.3	109	204
Stoichiometric $(A/F)_s$ mass	17.2	14.7	14.6
Stoichiometric mixture density (kg/m^3)	1.25	1.42	1.46
L.H.V. (MJ/kg)	47.5	43.5	42.7
L.H.V. of stoichiometric mixture (MJ/kg)	2.62	2.85	2.75
Calorific value (MJ/m^3)	24.6	42.7	36
Flammability limit in air (vol.% in air)	4.3–15.2	1.4–7.6	1–6
Flame propagation speed (m/s)	0.41	0.5	–
Adiabatic flame temperature °C	1890	2150	2054
Auto-ignition temperature °C	540	258	316
Wobbe index (MJ/Nm^3)	51–58	–	–

Due to its high resistance to auto-ignition, NG in gasoline engines can be operated at relatively higher compression ratios but in diesel engines, it requires an ignition source such as pilot diesel injection. Such arrangement is usually termed as dual-fuel combustion. However, it can directly be fed to SI engines with a little intake manifold modification. NG exhibits relatively lower flammability limit on the lean side compared to gasoline, which assists lean burn in SI engines (Cho and He 2007). Although NG has a lower heating value higher than gasoline, its feeding through intake system reduces engine's volumetric efficiency, which leads to lower heat release and lower power output. As presented in Table 12.1, NG requires more air for stoichiometric combustion compared to gasoline or diesel, resulting in cleaner combustion. However, the flame propagation speed of NG is somewhat slower than gasoline, which affects engine combustion, heat transfer as well as engine performance. Blending of a high flame speed fuel such as hydrogen (H_2) with NG can significantly improve this situation.

12.2   Types of NG Vehicles

There are three basic types of NG engines or vehicles based on operating mode or fuel supply system: (i) pure/dedicated NG engines/vehicles (either CNG or LNG fueled), (ii) gasoline/NG bi-fuel vehicles (basically retrofitted SI engines), and (iii) diesel/NG dual fuel (DF) vehicles based on diesel engines.

12.2.1 Dedicated NG Vehicles

Dedicated NG/CNG vehicles works on SI engines fueled by NG. However, as mentioned before, such engines usually operate at relatively higher compression ratios (16:1–19:1) compared to gasoline (typically 9:1–11:1) to enable them to harvest the benefit of higher octane rating of NG and thus exhibit enhanced thermal efficiency (Ouchikh et al. 2019). Dedicated NG vehicle require a simple engine modification to feed NG into the engine either in the intake port (i.e. port fuel injection mode) or directly into the engine cylinder (i.e. direct injection mode). A typical NG fueling system consists of high pressure gas cylinder, control valve, CNG regulator, filter, and fuel rail feeding injectors (Cammalleri et al. 2013). Compared to port fuel injection mode, direct injection mode of operation provides better volumetric efficiency, thus improving cycle efficiency significantly. Fuel injection timing optimization is important to achieve better engine performance of these vehicles.

12.2.2 Bi-Fuel Vehicles

Bi-fuel vehicles employ a conventional SI engine, which has two fuel feeding systems and thus can operate on either NG or gasoline. The driver can simply switch over from NG mode to gasoline mode as per his/her choice. An existing gasoline engine can easily be converted to a NG/gasoline bi-fuel engine by incorporating a NG storage and injection system and usually termed as retrofitted gasoline engine. Most of the NGVs running today on the roads of developing countries like India, Bangladesh and Pakistan are in bi-fuel category retrofitted gasoline engines (Jahirul et al. 2010). Unlike dedicated NGVs, bi-fuel vehicles cannot have high compression ratios as it is limited by the gasoline knocking. It also requires optimization of spark timing (usually more advanced) since CNG operation causes a relatively longer ignition delay as well as combustion duration due to lower flame propagation speed of NG.

12.2.3 Dual Fuel Vehicles

Dual fuel vehicles are powered by CI engines and like bi-fuel vehicles, the engines have two fuel supply systems. However, the basic difference between them is the fact that unlike bi-fuel system, two fuels (NG and diesel) simultaneously take part in combustion and also the main target of dual fuel system is to use as low as possible diesel (thus termed as pilot fuel) while the major energy release is from the gaseous fuel (termed as primary fuel). NG is usually supplied into the intake air of the diesel engine forming a homogeneous NG-air mixture during the intake and early compression stroke. Despite high compression ratio of the diesel engine, homogeneous gas-air mixture cannot be auto-ignited because of high auto-ignition

temperature of NG and hence an injection of pilot diesel into the hot gas-air mixture is essential near the end of the compression stroke to initiate combustion. Pilot diesel acts as an ignition source, which typically accounts for ~10–15% of the total energy release. The engine is initially operated in diesel mode at low load conditions and is gradually switched over to the dual fuel mode by increasing the gas feed rate to the engine. However, the engine enjoys fuel selection flexibility and can be switched over to either mode even under high load conditions. Dual fuel combustion energy release can include three overlapping components: pilot diesel combustion, followed by gaseous fuel combustion in the immediate vicinity of the ignition and combustion centers of the pilot; and eventually turbulent flame propagation within relatively leaner mixture (Mustafi et al. 2013). An important feature of dual fuel operation is the diesel substitution rate, which can be estimated by the following formulae (Mustafi and Raine 2008):

$$DR(\%) = \frac{(DCR)_d - (DCR)_{df}}{(DCR)_d} \times 100$$

where, $(DCR)_d$ is the diesel consumption (kg/h) under diesel operation and $(DCR)_{df}$ is the diesel consumption rate under dual-fuel operation. The diesel substitution rates vary according to the operating engine loads. Typical diesel substitution rates can vary between 60% to a maximum of 90% for modern dual-fuel engines (Khan et al. 2015). Both the engine performance and emissions are affected significantly by diesel substitution rates. Increased BSFC, higher CO and HC emissions with increasing diesel substitution rates have been reported in the literature (Egúsquiza et al. 2009). However, NO_x emissions decreased with the corresponding increase in substitution ratio. Another study revealed that dual-fuel vehicles provided higher efficiency compared to diesel mode (Volvo Trucks 2014).

12.3 Overview on Combustion in NG Engines

12.3.1 Lean Burn Technology

Generally, lean burn technology refers to a type of combustion, in which the combustible charge is intentionally made leaner than stoichiometric conditions by diluting the inlet charge with excess air, and is aimed at achieving lower emissions and lower pumping/throttling losses. Heavy-duty spark ignited CNG engines often use lean burn technology to control emissions. For instance, NO_x emissions can be reduced in lean burn engines as a result of low burnt gas temperature. Hence prime objective of using such technology in both light-duty and heavy-duty NG engines is to meet stringent emission legislations without employing an expensive catalytic converter or another after-treatment device. Besides, specific heats ratio increases for lean mixtures, which provide improved thermal efficiency (Manivannan et al. 2003). It is to

be noted that lean burn NG engines can achieve diesel like efficiencies at full load condition, which motivates engine developers to convert diesel engines to SI mode of operation using lean-burn concept. As relative A/F increases in lean burn conditions, combustion is normally characterized by longer ignition delay and longer combustion duration. In reality, using lean burn mixtures can exhibit several difficulties during combustion including lower flame propagation, misfire, poor charge distribution particularly in multi-cylinder engines and increased HC emissions. However, these problems can be alleviated by using (Manivannan et al. 2003):

- Higher compression ratio,
- Higher energy ignition system,
- Increasing swirl and turbulence at the end of the compression stroke, and
- Catalytic coating on the combustion chamber.

The third approach demands for careful design and modification of the combustion chamber, including geometry of the piston crown to ensure faster burning without affecting the volumetric efficiency. Research investigations on the combustion chamber design for such lean burn operation revealed that using squish motion, generating a series of jets directed towards the center of the chamber could improve the combustion, which was reflected in the results of faster burn rate, lower BSFC, higher BMEP and enhanced lean burn limits. This type of combustion chamber also resulted in 20–50% lower brake specific total hydrocarbons (BSTHC) and brake specific oxides of nitrogen ($BSNO_x$) emissions (Evans and Blaszczyk 1998). Another way to attain faster combustion was to use a pre-chamber, which commonly increased mixture turbulence significantly, leading to higher burn rates and shorter combustion duration in the main combustion chamber (Zuo and Zhao 1998).

Though lean burn operation can reduce NO_x emissions largely, it may result in higher cyclic variations and combustion instability (Cho and He 2008; Bartolucci et al. 2016; Reyes et al. 2015). The issues of cyclic variability and combustion instability was handled by using a different combustion strategy termed as partially stratified charge (PSC) combustion, in which, a small quantity of fuel was injected in the vicinity of spark plug, resulting in combustion stability (Reynolds and Evans 2004). Both experimental and numerical studies confirmed that after the flame kernel development in locally rich mixture, successive flame propagation developed more smoothly along with extended flammability limits (Bartolucci et al. 2015a; b). Research studies showed that lean burn heavy-duty vehicles (i.e. buses) emitted higher CO and formaldehyde, which required use of oxidation catalysts to control these emissions effectively (Ayala et al. 2003). Lean burn NGVs also suffered from unwanted CH_4 emissions, which was roughly 35 times more potent heat trapping GHG over 20 years compared to CO_2 (Wang et al. 2014) hence required to be controlled by using suitable CH_4 oxidation catalysts. However for lean burn NG vehicles, oxidation of CH_4 to CO_2 and H_2O at low temperatures by employing appropriate catalysts still remains a challenge.

12.3.2 Stoichiometric Combustion

Stoichiometric combustion involves supply of chemically correct amount of air to combust a given quantity of fuel completely. Theoretically it refers to an exact quantity of air that mixes with a given quantity of fuel to burn the mixture completely to produce heat, leaving only CO_2 and H_2O in the exhaust.

Stoichiometric operation of NG engines generally leads to higher heat release and thus higher heat losses, higher pumping work at low to medium loads, higher thermal stress on the engine and higher knock tendency (Einewall et al. 2005). However, at this operating condition, higher NO_x emissions are evident due to higher in-cylinder temperature compared to lean-burn operation. That is why in the stoichiometric combustion NG engines, using three-way catalysts (TWC) is a common practice to minimize the exhaust emissions. Lean burn NGVs with oxidation catalysts are generally considered older technology, while stoichiometric combustion NGVs equipped with TWC and water cooled exhaust gas recirculation (EGR) is treated as modern technology. Cho and He (2007) concluded that stoichiometric combustion NG engines equipped with TWC and EGR system can meet the most stringent emission regulations. However, stoichiometric combustion NGVs with TWC show higher CO emission in the exhaust than lean-burn counterparts (Lanni et al. 2003). To achieve high performance of catalytic converters, it is recommended to control the A/F ratio precisely in such engines. If the CNG engine is developed from a diesel engine, controlling detonation and exhaust gas temperature becomes crucial to maintain admissible durability (Corbo et al. 1995). On the other hand, to control the exhaust gas temperature, and knocking tendency, charge dilution by EGR is often required. This also improves the engine efficiency, possibly due to operation at higher compression ratio (Vávra et al. 2017). Since EGR prolongs the combustion duration, it requires a fast combustion chamber under high EGR operating condition.

Research showed that engine operation under stoichiometric condition with EGR and a three-way catalyst, NO_x emissions could be effectively reduced by 99.9% and HC emissions by 90–97% compared to lean burn strategy (Einewall et al. 2005). Vávra et al. (2017) experimentally investigated the performance and emissions of a diesel-NG dual fuel engine with stoichiometric mixtures and obtained 11% higher power density than pure diesel operation without noticeable smoke. Even under high load conditions, smoke opacity and filter smoke numbers showed extremely low values. However, particle numbers were measured to be above legislative limits hence particulate filters should be used. Composition of NG used in vehicles is important since it influence the formation of emissions. Hajbabaei et al. (2013) concluded that stoichiometric combustion NG vehicles showed greater acceptability to variations in NG composition without impacting emissions compared to lean burn vehicles. Researchers reported that in case of lean burn engine powered buses, lower CH_4 content NG exhibited relatively higher NO_x and NMHC emissions than higher CH_4 content NG.

12.3.3 Direct Injection System

Direct injection (DI) strategy refers to a specific fuel supply system, which delivers NG directly to the engine cylinders instead of delivering in the intake system. While in case of spark ignited NG engines (both gasoline and diesel engines adapted for NG fueling) are based on premixed combustion, DI natural gas engines can be based on either premixed combustion, or diffusion combustion, or both (i.e. partially premixed and partially diffusion nature) (Zhang 2010). Although SI NG engines exhibit higher efficiency than gasoline engines, they cannot attain diesel like efficiencies, mainly due to knock limited lower compression ratio compared to diesel engines. Thanks to DI NG engines, they exhibit the potential to attain diesel like efficiencies, while maintaining lower NO_x and PM emissions compared to those emitted from diesel engines. Research studies have confirmed that DI NG engines can have higher power output and higher thermal efficiency compared to conventional SI NG engines due to their higher compression ratios and lower intake air pumping losses at part load conditions. Since designing and manufacturing a new engine dedicated to use NG may not be feasible in current vehicle/engine market, conversion of existing gasoline and diesel engines appears to be a viable option.

Conversion of gasoline direct injection (GDI) engines to DI NG engines is rather simpler than the conversion of a conventional SI gasoline engine. It would be required to develop NG supply system to supply NG directly to the engine cylinder and necessary modifications are required in the engine electronic control unit/module (ECU/ECM). Incorporation of a turbocharger in such vehicles to enhance power output and efficiency has become a common practice. A simplified schematic is presented in Fig. 12.4.
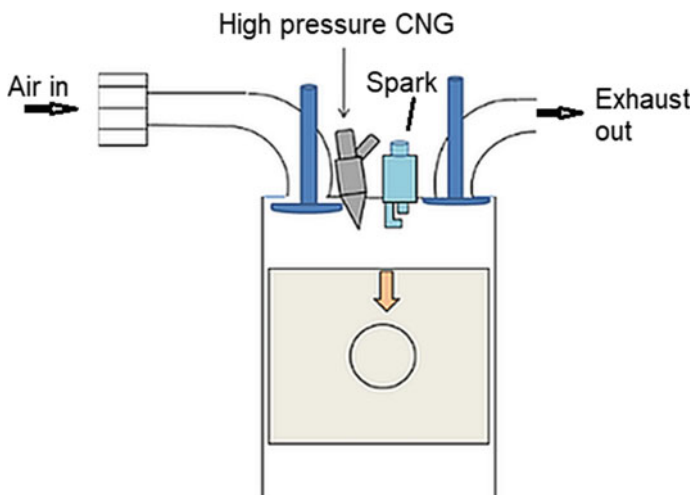
Fig. 12.4 Spark ignited CNG DI engine technology

In case of conversion of a diesel engine to DI NG engine, fuel storage, injector, ECU, all have to be redesigned/re-tuned. It is to be noted that DI NG engine converted from conventional diesel engine would require an ignition source (i.e. spark plug, glow plug or laser) to initiate combustion due to very high auto-ignition temperature of NG. DI NG engine converted from a diesel engine can also run without an additional ignition source, but has to be operated in dual-fuel mode, where a pilot diesel can do the task of initiating the combustion. However it would require a dual-fuel injector (see Fig. 12.5) in place of conventional diesel injector. The efficiency of spark ignited DI NG engine will be obviously lower than that obtained from compression ignition DI NG engine due to higher compression ratio that can be tolerated in the latter type.

Introduction of CNG directly into the combustion chamber produces a significant improvement in the volumetric efficiency and reduces pumping losses. Exclusion of diesel spray permits reduction of unburned hydrocarbon emissions. Ikeda et al. (1995) reported that a heavy-duty 8-cylinder CNG DI engine developed twice the BMEP compared to conventional SI CNG engine. DI of NG permits engine operation with stratified mixture, providing relatively higher combustion efficiency (Liu et al. 2014). The same advantage is also obtained for CNG-diesel DI dual-fuel engine. NG jet is quite different from liquid fuel jet and slower fuel-air mixing takes place in the DI NG engines compared to conventional diesel engines. Slower mixing then leads to slower combustion. Another issue is the air requirement for such engines. It requires ~ 4% more air compared to conventional diesel engines to produce same power output. Therefore boosting the engines ensures sufficient air supply to the engine for smoother and efficient combustion. To summarize the above discussion, it can be pointed out that combustion and emissions of DI NG engines (diesel conversion particularly) are basically influenced by formation and quality of mixture, which mainly depends on a number of parameters such as injection timing, injection pressure, nozzle geometry, combustion chamber and piston crown shapes and turbulence inside the combustion chamber (Hajialimohammadi et al. 2004).

The experimental studies of Li et al. (2015) on pilot ignited DI NG engine revealed that advancing NG injection timing increased both the peak cylinder pressure and
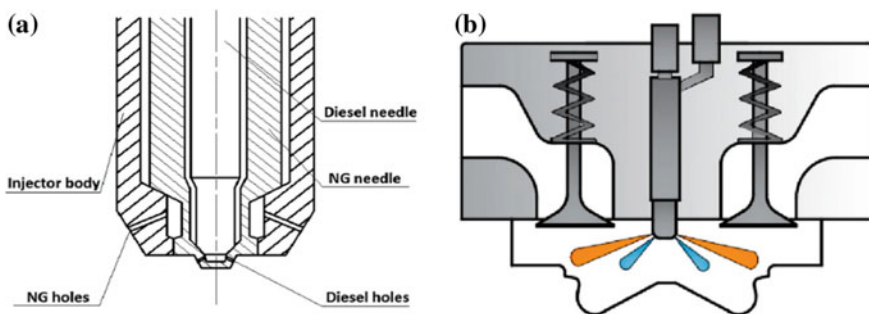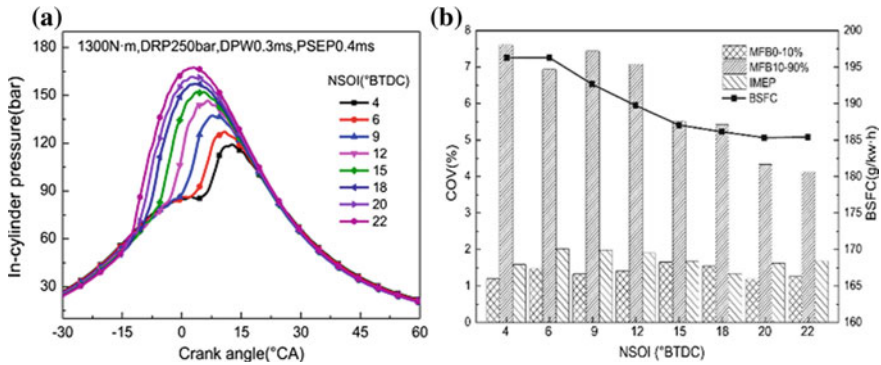

Fig. 12.5 Schematic of a typical dual fuel injector for DI application (Li et al. 2019)

Fig. 12.6 a Variations of in-cylinder pressure at different NG start of injection (NSOI) as a function of crank angle degrees; **b** variations in specific fuel consumption and combustion stability as a function NSOI (Li et al. 2015)

maximum rate of pressure rise (Fig. 12.6a), while higher heat release rate was observed at retarded injection timings. Heat release rate was also found to be influenced by changes in injection interval, pilot quantity and injection pressure. Injection timing advancement as well as increasing injection pressure provided relatively better fuel economy and combustion stability (Fig. 12.6b). However, greater engine stability was obtained in this study at lower injection pressures.

Brake specific HC and CO emissions were normally higher for DI NG engines than diesel engines, particularly at higher engine speeds and lower loads due to slower burning rate of NG. Effective measures to tackle these problems could be: improving mixture quality (avoiding the existence of over-lean or over-rich zones), and increasing burning rate by increasing ignition energy, increasing flame propagation speed, optimizing combustion chamber design etc. (Zhang 2010).

Li et al. (2019) investigated the effect of partially premixed combustion on emissions of a DI NG engine and reported that soot and CO emissions reduced significantly without compromising on NO_x emissions and engine performance by optimizing NG pre-injection, injection timing and EGR ratio.

### 12.3.4 Combustion of NG with H_2 Addition

Because of slower flame burning velocity of NG (laminar burning velocity: 0.38 m/s), CNG fueled engines suffer from combustion instability issues hence reduced performance and increased emissions, particularly under lean burn conditions. In order to enhance the flame speed of NG, traditionally a fuel with fast burning velocity was mixed with the NG. Among different options, mixing with hydrogen (H_2) can be the most attractive one since H_2 exhibits highest flame speed (laminar burning velocity: 2.9 m/s) amongst test fuels, along with wide flammability limits (equivalence

ratio Φ: 0.1–7.1) (Swain et al. 1993). On the other hand, H_2 being a carbon-free fuel, produces zero emissions. Research studies have identified the followings for H_2 enriched CNG (HCNG) engines:

- Turbulent burning velocities can be significantly improved even by a small amount of H_2 addition to CH_4. With increasing H_2 fraction in HCNG mixture, laminar burning velocity of HCNG mixture can increase exponentially (Huang et al. 2006). Prasad et al. (2017) compared the combustion phenomenon between CNG and HCNG fueling using a laser, instead of a conventional spark plug in a constant volume combustion chamber (CVCC). They observed that the primary flame kernel development and its propagation became faster and combustion duration shortened, as H_2 fraction increased in the HCNG mixture. These results were attributed to the effect of notably lower ignition energy requirement of H_2 and its wider flammability range.
- A small blend of H_2 can effectively reduce quenching distance for lean air/fuel mixtures.
- Ignition delay can be reduced significantly with HCNG fueling.

All of these aspects help enhance thermal efficiency of the HCNG engines. Because of explosive nature of H_2, careful design and development of safe HCNG handling and supply system is crucial. Instead of using conventional solenoid injectors, customized high volume solenoid injectors was recommended by the researchers. Also a safety device such as a flame arrester can be incorporated in the fuel system to prevent backfire issues. Instant mixing of desired proportions of H_2 in CNG can also be an issue and a dynamic HCNG mixing system can be helpful in getting the desired HCNG composition instantly, as reported by Sagar and Agarwal (2017). Spark ignited CI engine for HCNG operation generally requires a few engine modifications, including lowering compression ratio and installation of a spark plug in the cylinder head, since HCNG mixture has very high auto-ignition temperature. Since HCNG-air mixtures require relatively lower ignition energy and have wider flammability range compared to conventional fuels, it can lead to an extremely uncontrollable combustion. Any hot spot therefore present inside the combustion chamber can potentially risk occurrence of undesired spontaneous ignition.

Adequate research studies are available in open literature on engine's combustion, performance, and emissions, which explore the potential of using HCNG mixtures in existing vehicles/engines. Enhanced engine performance such as increased brake power and enhanced fuel economy along with reduced emissions are mostly reported in those studies of HCNG. Optimization of H_2 fraction in HCNG is crucial to ensure best engine performance. While experimenting on a prototype SI engine fueled with different HCNG mixtures (H_2 content varied between 0 and 100%), Sagar and Agarwal (2017) observed that 30HCNG (30% H_2 and 70% CNG) mixture provided the best efficiency (~44%) amongst all other test fuels (see Fig. 12.7a). Higher H_2 fractions in CNG (>50%) increased engine's knocking tendency particularly at high load conditions. Optimization of ignition timing for HCNG engines is equally important and with H_2 fraction increase in HCNG mixtures, ignition timings needs to
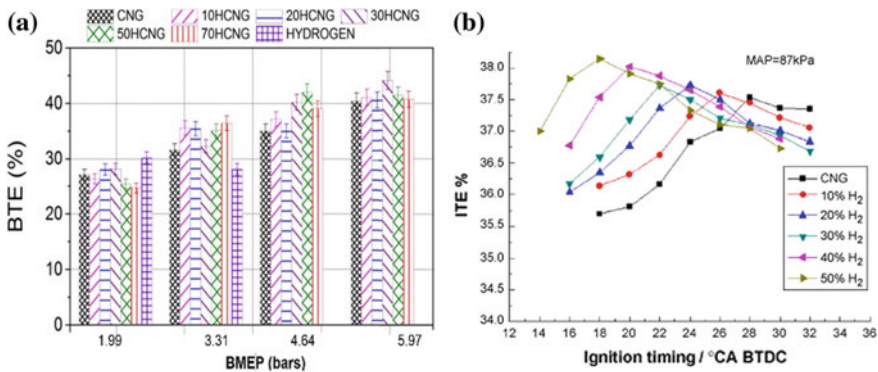
Fig. 12.7 a Variations in brake thermal efficiency (BTE) with brake mean effective pressure (BMEP) (Sagar and Agarwal 2017); **b** Variations in indicated thermal efficiency with ignition timings for different HCNG mixtures (Ma et al. 2008)

be retarded proportionately (close to TDC for HCNG mixtures) for optimum engine performance and reduced emissions as shown in Fig. 12.7b (Ma et al. 2008).

Ma et al. (2007) experimentally investigated effect of H_2 enrichment of CNG in a SI NG engine and reported that combustion duration reduced irrespective of the operating A/F ratio, while the lean burn limit greatly extended (from lean limit of $\lambda = 1.7$ for CNG to $\lambda = 2.4$ of HCNG with 50% H_2, i.e. >40% increment), as the H_2 content in HCNG increased. Optimization of spark timing can further extend the lean burn limit (Ma and Wang 2008). Ouchikh et al. (2019) reported that H_2 enrichment of CNG in a dual fuel engine improved the combustion, resulting in higher peak in-cylinder pressure, and heat release rate with reduced combustion duration and coefficient of variation (COV$_{IMEP}$) compared to baseline CNG-diesel dual fuel operation. Part load or low-load operation difficulties in dual-fuel engine can be alleviated by using H_2 as an additive to CNG. Lounici et al. (2014) claimed that at high load condition (70% load), highest BTE was obtained for 10HCNG (10% H_2; 90% CNG) mixture, which was ~12% higher than baseline CNG operation and even somewhat higher than diesel operation. Exhaust emissions such as CO, THC and NO$_x$ were found to reduce for HCNG compared to either CNG-diesel dual fuel or diesel operation. However, among the three blends (10HCNG, 20HCNG and 30HCNG), 10HCNG showed the most desirable performance in this study.

NO$_x$ emissions generally increased for SI HCNG fueled engines compared to only CNG operation and the level of emissions increased further with increased H_2 fraction in the HCNG mixtures. Ma and Wang (2008) added that NO$_x$, and other emissions such as CO and THC decreased as the ignition timing retarded. The level of NO$_x$ emissions from either CNG or HCNG vehicles may not comply with current emission regulations therefore application of EGR can be effective in reducing emission level further. When the HCNG engine operation was optimized in terms of H_2 content, EGR percentage, and ignition timing, not only NO$_x$ emissions decreased substantially but also engine efficiency improved by a few percentage (1–3%) (Dimopoulos et al.

2007; Dimopoulos et al. 2008). Fortunately the presence of H_2 in CNG can tolerate high percentage of EGR (even 40% EGR) without affecting engine's combustion stability (Huang et al. 2009).

Ma et al. (2012) also investigated the effect of compression ratio (CR) on 20HCNG (20% H_2, 80% CNG) mixture in a six cylinder engine running at 1200 rpm and constant excess-air ratio of 1.6 at different ignition timings. Advanced ignition timings exhibited higher BTE and ITE for increased CR in this study. However, maximum brake torque (MBT) timing retarded for higher CR operations. Hora and Agarwal (2016) added that exhaust emissions such as CO, HC and NO_x emissions increased as the CR of the engine increased.

12.3.5 Factors Affecting the Performance and Emissions Characteristics of HCNG Fueled Engines

The key factors that influence HCNG engine's performance and exhaust emissions include excess air ratio (λ), ignition timing, compression ratio, and engine speed.

As the fuel-air mixture gets leaner (i.e. at higher λ), cyclic variability and combustion stability generally deteriorated in CNG engine. With H_2 enrichment of CNG, these problems are alleviated to a great extent and engine's performance and emissions improve significantly. However, there exists an optimum value of λ, which exhibits maximum power output along with the best fuel economy, while emitting lower pollutants for a given engine operating condition.

Ignition or spark timing greatly influences engine's performance and emissions behavior. In general, addition of H_2 in CNG reduces the requirement of ignition advance. Advanced ignition timing can cause increased maximum cylinder pressure and can reduce the COV_{IMEP} for a CNG engine. Furthermore, lean burn limit extends for advanced spark timings. Strategy of retarding spark timing is an effective way to minimize NO_x emissions, however it can cause combustion instability and thus deteriorate the engine performance. Therefore, like other parameters, ignition timing also needs to be optimized in a HCNG engine since either the over-advanced or over-retarded condition would result in deteriorated engine performance and increased emissions. Research studies also identified that employing MBT spark timing can provide minimum COV_{IMEP} depending on the engine operating conditions. Engines operated with EGR require different ignition time setting than engine operating without EGR. For instance, Hu and Huang (2011) achieved maximum engine power output at MBT spark timing for a particular EGR, while optimizing the ignition timing and EGR ratio for a SI engine fuelled with HCNG mixtures.

Engine speed is an important factor for on-road vehicles since any real driving cycle consists of combination of engine speeds. Research studies reported that at stoichiometric condition, slow speed engines with low H_2 content HCNG fueling provided better engine performance. Idle condition (very low speed) is quite common in any driving cycle and engine can operate at high excess-air ratio requiring proper

adjustment of spark timing for improved performance. In idle condition, when the efficiency of a CNG engine normally deteriorates, H_2 enrichment of CNG enhances its performance.

Operating an IC engine at higher compression ratio (CR) is always desirable since it offers high power output and higher brake thermal efficiency. CR of a conventional SI gasoline engine is relatively lower, which is normally knock limited. However, CNG engines can safely operate at higher CR compared to gasoline due to its very high auto-ignition temperature. HCNG engines can also operate at higher CR than gasoline engines (typically 9.5–12) since addition of H_2 in CNG does not affect the auto-ignition temperature of HCNG mixtures. However if a diesel engine is converted to SI HCNG engine, the original CR of the diesel engine needs to be lowered. Enhanced CR in HCNG engines is beneficial since it offers increased brake torque, lower BSFC, higher ITE and lower COV_{IMEP}. Researchers identified that increased CR can exhibit slower flame development and lean burn limit can reduce (Zhao et al. 2013).

12.4 Emissions from CNG Vehicles, Health Impacts and Emission Control

12.4.1 Emissions from CNG Vehicles/Engines

As mentioned earlier, NG has low C/H ratio, hence it is regarded as a low CO_2 emitter (by 20–30%) on unit energy basis compared to conventional liquid fossil fuels (Kakaee and Paykani 2013; Bielaczyc et al. 2016). NG engines also emit lower CO and NMHC emissions compared to gasoline SI engine. In gasoline SI engines, significant CO is produced during cold-start because of poor spray atomization, and partial vaporization of gasoline, leading to inadequate fuel-air mixing and incomplete combustion (Jahirul et al. 2010). In contrast to liquid gasoline, NG does not require atomization or vaporization and can mix directly with air to produce more homogeneous mixture, resulting in more complete combustion and remarkably lower CO emission (50–90%) (Sevik et al. 2016). On the other hand, NGVs operating under leaner conditions (high λ) generally exhibit lower CO and NMHC emissions compared to gasoline engines, which usually operate at either stoichiometric or slightly richer condition. Furthermore, NG fueling does not have any wall-wetting effect either on the intake passage or on the cylinder liner, which lowers the NMHC emissions as well as reduces specific fuel consumption (Cho and He 2007). However CO emission from NG-diesel dual fuel engines are significantly higher than baseline diesel engines due to incomplete combustion caused by slower burning speed of NG (Sun et al. 2015).

NGVs conventionally operate under higher CR and more advanced spark timings, which cause them to emit higher NO_x emissions (by ~33%) than gasoline SI engines (Aslam et al. 2006). Spark timing optimization in terms of engine performance and

emissions can help to a great extent in this context. NG-diesel dual fuel engines however emit lower NO_x emissions compared to their diesel counterparts since they usually operate at relatively lower equivalence ratios and only a pilot quantity of diesel is burnt (Korakianitis et al. 2011).

Methane emission from NGVs is another great concern since it is a more dangerous GHG than CO_2. This is mainly attributed to the lower flame speed of NG, which leads to incomplete combustion and relatively higher unburned methane emissions in the exhaust. Other difficulties remain with handling of unburned methane by after treatment devices such as TWC because of slower reactivity to the catalysts. Significantly higher HC emissions are commonly observed in the case of diesel-NG dual fuel engines compared to baseline diesel engines, particularly at low load conditions, which are influenced by lean operating conditions and slower flame speed of the NG (Sun et al. 2015; Korakianitis et al. 2011). Because of high CR, charge could be trapped in the crevices, and may survive the combustion process, and eventually escape along with the exhaust gas. However operating at high load or using relatively high pilot quantity of diesel can reduce these emissions.

Fortunately, PM emissions from NGVs are significantly lower than either gasoline or diesel engines (by 70–95%) since aromatics, C = C and cyclic molecules are absent in the chemical structure of NG (Mustafi et al. 2013; Semin 2008). PM emissions from NGVs are principally influenced by unburned hydrocarbons and lubricating oil, while partial combustion of lubricating oil and its pyrolysis post-combustion increases the particle numbers (Sagar and Agarwal 2017). NGVs can easily comply with Euro-VI emission regulations related to PM emissions. However recent research studies have confirmed that NG engines emit very high number of particles in the range of 8–10 nm (Hajbabaei et al. 2013; Sagar and Agarwal 2017; Jayaratne et al. 2009; Hallquist et al. 2013), which may potentially have adverse health impact.

12.4.2 Health Impacts

Epidemiological studies have been conducted to explore potential health hazards, caused by inhalation of vehicle exhaust. Toxicological level of any vehicle's exhaust depends on the engine type and its physical condition, operating condition, fuel and lubricating oil type, ambient conditions etc. Research evidences show that there exist a correlation of increased human morbidity and mortality with the level of exposure to vehicular emissions. Particularly, PM emissions (and its particle based PAH), volatile and semi-volatile organic compounds (composed of PAH) from vehicles are of great concerns since they are cytotoxic, mutagenic and carcinogenic. Fortunately, CNG based transport system is cleaner and less harmful compared to gasoline or diesel based transport system. It was reported that shifting of public transportation system from petroleum based liquid fuels to CNG would reduce urban $PM_{2.5}$ emissions by 229 t/year in Santiago, Chile with notable health benefits monetized to the tune of 9130 US$/year for each diesel bus replaced by CNG bus (Mena-Carrasco et al. 2012). Research studies have confirmed that CNG fuelled heavy-duty vehicles emit

substantially lower PAHs compared to gasoline (Gao et al. 2015) and diesel vehicles (Sabin et al. 2005). Sabin et al. (2005) measured significantly lower black carbon, particle based-PAHs and NO_2 but somewhat higher formaldehyde from CNG buses compared to diesel buses. Turio-Baldassarini et al. (2006) experimentally investigated the existence of carcinogenic compounds and genotoxic activity of pollutants from diesel and CNG buses. Authors claimed that CNG buses emitted more than 30 times lower PM, 20 times lower formaldehyde, and nearly 50 times lower carcinogenic PAHs compared to diesel buses. About 20–30 fold reduction in genotoxic activity of exhaust from CNG buses was estimated in this study. Seagrave et al. (2005) reported that mutagenic potencies of emissions from CNG buses were similar to the range estimated for gasoline and diesel emissions, but lung toxicity potency factors for CNG sample was found to be lower than other samples. Similar results of highly reduced genotoxicity for CNG heavy-duty vehicles compared to diesel vehicles were also reported by Jalava et al. (2012), which were attributed to very low level PAH emissions (PAHs reduced by ~92% compared to diesel bus) from these vehicles. However, PM samples from CNG bus exhibited higher cytoxicity and high potency to cause oxidative stress in macrophages, which could be attributed to high metal content of the PM samples as reported in this study.

12.4.3   Emission Control

Lean Burn and Stoichiometric Engines. Spark ignited NG engines can operate under lean burn as well as stoichiometric conditions. Lean burn NG engines generally produce lower NOx, but relatively higher CO and HC emissions. The emission control strategies for such engines commonly include optimization of relative A/F ratio (λ) and use of suitable oxidation catalysts. However, accurate control of λ is not an easy task, and a small change in λ value significantly affects engine performance and emissions. A wideband oxygen sensor (i.e., λ sensor) is commonly employed to achieve close loop control of λ in NG engines, which tries to optimize the fuel supply as well as ignition-timing by measuring the residual-oxygen availability (Alkemade and Schumann 2006). In contrast to lean burn, stoichiometric combustion NG engines emit notably low levels of HC and CO emissions with a little compromise in fuel economy but relatively higher NO_x emissions. In order to alleviate and control of emissions, generally, EGR along with a TWC system is employed in such engines (Hajbabaei et al. 2013; Bartolucci et al. 2015a; Karavalakis et al. 2016).

EGR application. Application of EGR to control NO_x emissions from IC engines is a common technique, which can also be applied in NG engines. However in the case of lean burn engines, application of EGR can only be effective if H_2 is added to the fuel. Combustion deterioration with EGR under lean burn condition can mostly be compensated by addition of H_2 in CNG, which significantly enhances the combustion efficiency, resulting in more complete combustion and reduced HC and CO emissions.

Spark timing adjustments. Accurately determined spark/ignition timings are crucial for NG engines. Generally, NG engines need to advance the spark timing as NG shows reduced flame propagation speed compared to baseline gasoline operation. Spark timing advance may be in the range of 2–10° bTDC in NG engines compared to conventional gasoline engines (Evans and Blaszczyk 1997; Ji and Wang 2009). Higher spark advance can be used for lean burn NG engines. However, unburned HC and CO emissions can rise due to low combustion temperature and relatively shorter combustion, which are evident for advanced spark timings. The strategy of employing MBT spark timings can be possible for NG engines but depending on NG quality and engine operating conditions.

After-treatment systems. Although NG vehicles/engines exhibit relatively lower emissions compared to conventional gasoline or diesel engines, they would certainly need after-treatment systems in order to comply with prevailing stringent emission regulations such as Euro-VI emission norms. A combination of oxidation catalyst based on platinum or palladium oxides and the selective catalytic reduction with ammonia as reducing agent (NH_3–SCR) can effectively control emissions from lean burn heavy-duty vehicles to desired level. Adouane et al. (2013) achieved ~40% CH_4 conversion at 415 °C, 99% CO, and 70% NO_x conversions using combined catalytic system in a lean burn engine. However, compared to TWC technology, this combined catalytic system is more complex and expensive, and that is why stoichiometric combustion NG engines with TWC system are preferred over the lean burn engines in modern NG vehicles (Cho and He 2007). Stoichiometric NG engines are generally equipped with TWC system, which can effectively control emissions from the engine but with a compromise on the engine performance resulting from relatively higher heat losses and pumping work at stoichiometric condition, particularly at low to medium loads. Using water-cooled EGR with this TWC system has shown better fuel economy while maintaining low emissions (Einewall et al. 2005, Karavalakis et al. 2016).

NG-Diesel Dual Fuel Engines. In case of NG-diesel dual fuel engines, application of EGR can effectively control HC, CO and NO_x emissions, particularly at low loads. At high loads, this might not be helpful since HC emissions remain unaffected, while CO and PM emissions may increase mainly due to a oxygen deficiency (Abdelaal and Hegab 2012). Diesel pilot quality and quantity also play a role in dual fuel combustion and pollutant formation. Compared to low pilot quantity, a high pilot quantity has shown to be far more effective in controlling CO and HC emissions at low engine loads. At high engine loads however, increasing pilot quantity increases NO_x and PM emissions since at this condition, the in-cylinder temperature remains high, and diffusion combustion of diesel dominates (Alla et al. 2000; Liu et al. 2013). Compared to retarded injection timings, a moderately advanced timing was effective for controlling emissions from diesel pilot-ignited NG engine (Alla et al. 2002; Sahoo et al. 2009; Zhou et al. 2013). However, injection timing optimization was essential since too advanced injection timings could eventually deteriorate results (Zhou et al. 2013). Use of alternative liquid fuel to pilot diesel such as rapeseed oil methyl ester (RME), dimethyl ether (DME) has shown positive reduction in NO_x emissions from the dual fuel NG engines. RME having a relatively higher cetane number than diesel,

reduces ignition delay and premixed combustion, which leads to lower in-cylinder temperatures and thus NO_x formation. DME on the other hand reduces combustion temperature due to its cooling effect, leading to reduced NO_x emissions. However, it may adversely affect HC and CO emissions.

12.5 Challenges and Direction of R&D for CNG Vehicles

Despite high potential of using CNG as a transport fuel, its current worldwide contribution in the transport sector is not up to the desired level. Significant efforts have been put in developing NGVs as well as their markets globally in the last few decades. However, share of NGVs in the current transport sector still remains quite insignificant (~1%) compared to conventional vehicles operated on liquid petroleum fuels. Several technical and policy-related factors can be identified as challenges in NGV adaptation, which need to be addressed appropriately in order to exploit its full potential:

- Driving range is often considered as one of the critical limitations of NGVs, especially for heavy-duty transport. Because of lower volumetric energy density of NG compared to gasoline or diesel, it generally requires either more frequent refueling or carrying extra-large storage cylinders. This, in many cases appears to be a discouraging factor.
- Arrangement of onboard storage of CNG cylinders is another important issue to bother about. Cargo space is quite important for light-duty vehicles and generally large CNG cylinders occupy majority of cargo space available in these vehicles and add extra weight to the vehicle too.
- CNG fueling and combustion in IC engines is still based on retrofitting of gasoline and diesel engines. Therefore more R&D efforts is required for developing dedicated CNG engines/vehicles. Though DI technology looks promising, design and development of fuel system and combustion chamber is rather complicated. On the other hand, CNG-diesel dual fuel technology for diesel engines is mature. However, there exists no global standard for such engines.
- Unlike gasoline or diesel, NG does not undergo fuel evaporation therefore there is no opportunity of cooling the intake passage, which affects durability of the intake manifold, particularly for port fuel injection engines.
- Effective control of NGVs is very crucial in order to harness their full potential of offering better engine performance with fewer emissions. Key parameters such as excess air ratio, injection timing, and spark timing are required to be controlled and optimized appropriately. However, design and development of effective and reliable controls for NGVs still remain great challenges.
- High safety requirement for both the NGVs (i.e. onboard storage tank) as well as the fueling stations since they deal with very high pressures.
- Existing fuel and vehicle market strictly relies on gasoline or diesel. To enter and sustain in the existing market remains a great challenge for NG and NGVs.

- Availability of spare parts, after-sales service, technical support for repair and maintenance etc. are also big concerns for the customers.
- Composition of NG is a factor to consider since CH_4 content of NG greatly influences engine's combustion and pollutant formation. Therefore, local, regional as well as global NG standards compatible to gasoline or diesel engines should be prepared and implemented. Development of either engine controls or dedicated engine compatible to NG's composition variability therefore remains a challenge.
- Reliable and sustainable supply of NG is the most vital concern from consumer's point of view. Though NG is considered as one of the most available fuel worldwide, it cannot be produced from renewable source in large scale as of now. Therefore, Renewable natural gas (RNG) production via anaerobic fermentation of organic wastes and its incorporation into the existing NG grid should be promoted. However, development of techno-economically feasible technology remains a challenge.
- Development of CNG supply and distribution infrastructure remains a great concern for establishing CNG as alternate transport fuel. It requires substantial investment. Government has to take necessary steps to arrange sufficient financial supports. Engine manufacturers and companies are always in a dilemma whether infrastructure development should be prioritized first or the engines and refueling stations. Installing sufficient number of gas fueling stations in a given region is crucial to ensure better accessibility and less refueling time for the vehicles.
- Several R&D areas can be identified for promotion, development and implementation of NGVs at a global scale:
  - NGV engine development and optimization for desired performance
  - Easy and efficient use of NG in the existing vehicles
  - Hybrid vehicle technologies
  - DI NG engine development and controls for optimum engine performance and minimum emissions
  - Onboard NG storage system
  - Development of refueling infrastructure
  - Environmental impact of NGVs (LCA studies)
  - Use of alternative renewable source for NG production such as from biogas.

12.6 Closure

Use of greener alternative fuels in the transport sector is now an ultimate need of the day since pollutants generated by vehicles contribute significantly to deterioration of the earth's ecosystem and human health. Natural gas as a vehicle fuel is conventionally considered as one of the most promising solutions to these problems. This chapter reviews the current status of NGVs worldwide and different technologies associated with NGVs. Research studies have been reviewed to explore engine performance and emission characteristics of NGVs. Finally, challenges for NGV

implementation globally are identified along with future R&D directions. Based on the above discussion, following conclusions can be made:

- Due to growing concerns about urban air quality and environment and health, CNG application in the transport sector can be identified as one of the most promising alternative fuel. All types of vehicles can be operated on CNG.
- Growth of NGVs worldwide seems to be phenomenal over the last few decades. This has been observed in most NG producing countries. This has contributed significantly to the environment and health protection at lesser costs.
- CNG vehicles are based on existing IC engine technologies. Retrofit systems for adopting NG as fuel on these existing vehicles are well established and commercially available for all type vehicles. SI gasoline engine and CI diesel engine can be converted easily to operate on CNG. In both cases, port fuel injection system and DI systems are available. Bi-fuel and dual fuel technologies also exist for gasoline and diesel engines respectively, where fuel flexibility is an attractive feature. However, various technical issues are associated with these technologies, which required further R&D efforts.
- Lean burn NGVs with oxidation catalysts are generally considered as older technology while stoichiometric combustion NGVs equipped with TWC and water-cooled exhaust gas recirculation (EGR) system are considered as modern technology that has potentials to comply with prevailing stringent emission regulations.
- Because of slower flame speed of NG, CNG fueled engines suffer from cyclic variability as well as combustion instability issues, which eventually affect engine performance and pollutant formation, particularly under lean burn conditions. H_2 enrichment of CNG or the use of HCNG can improve the situation significantly. HCNG mixtures have extended lean burn limits and wider flammability range.
- Several challenges exist both from technology view point and policy view point for large scale implementation of NGVs worldwide. These challenges have to be overcome to ensure NGVs are used in large number in current and future transport markets globally.

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Chapter 13
Biogas for Transport Sector: Current Status, Barriers, and Path Forward for Large-Scale Adaptation

Nirendra N. Mustafi and Avinash Kumar Agarwal

Abstract Global demand for conventional petroleum fuels for powering transport vehicles is enormous and is increasing sharply with time. However, depleting petroleum reserves, and negative impacts of vehicular emissions on human health remain the most important concerns, which motivate researchers to look for alternative and eco-friendly fuels for the transport sector. On the other hand, emerging stringent regulations are forcing engine researchers and manufacturers to develop appropriate and newer engine technologies to comply with these emissions regulations in addition to improving the fuel economy. Among different alternative fuel options, biogas certainly can be regarded as one of the most attractive options since it is mainly produced from waste materials such as agricultural wastes, municipal solid wastes, food wastes and vegetable market waste, in addition to human and animal excreta, which are unlimited resources. Though biogas technology is considered as a matured technology, its full potential is yet to be explored globally. Raw biogas contains some impurities hence it cannot be used directly in engines/vehicles, therefore it must be upgraded for these applications. This chapter explores the state-of-the-art technologies associated with the biogas generation, biogas upgradation, storage, and utilization. Biogas-to-useable fuel conversion techniques are also discussed. An estimate of biogas generation potential worldwide is explored, and techno-economic feasibility is addressed. Recent case studies on assessing performance of biogas operated vehicles are reviewed. Finally, the main barriers in biogas adaptation for vehicular applications are identified, and necessary recommendations are made.

Keywords First biogas · Anaerobic digestion · Biogas purification · Biogas upgradation · Vehicular fuel · Urban transport · GHG emissions · Barriers

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Abbreviations

AD	Anaerobic digester
AM	Accumulation mode
BGV	Biogas vehicles
CBG	Compressed biogas
CBM	Compressed bio-methane
CHP	Combined heat and power
CSTR	Completely stirred tank reactor
ETC	European transient cycle
FM	Fresh matter
GHGs	Greenhouse gases
GoI	Government of India
GST	Goods and services tax
HRT	Hydraulic retention time
LBM	Liquefied bio-methane
LIP	Local Investment Program
LNG	Liquefied natural gas
MIDC	Modified Indian driving cycle
MMT	Million metric tons
MSW	Municipal solid waste
Mtoe	Million ton oil equivalent
NIER	National Institute of Environmental Research
NM	Nucleation mode
NMHC	Non-methane hydrocarbons
O&M	Operations-and-maintenance
PAHs	Polycyclic aromatic hydrocarbons
PM	Particulate matter
PSA	Pressure swing adsorption
PWS	Pressurized water scrubbing
R&D	Research and development
RNG	Renewable natural gas
SATAT	Sustainable alternative towards affordable transportation
STP	Standard temperature and pressure
TFC	Total final energy consumption
THC	Total hydrocarbons
TS	Total solid
VOC	Volatile organic compounds

13.1 Introduction

Transport sector being world's second-largest energy consuming sector (IEA 2018), is commonly regarded as one of the most vital sectors for any nation's economic growth. Worldwide the transport sector is heavily reliant on fossil fuels. Current global demand for conventional petroleum fuels in this sector is enormous and is increasing rapidly with time. Global transport energy consumption has significantly increased from ~976 Mtoe in 1971 (23% share of total final energy consumption, TFC) to ~2770 Mtoe in 2015–2016 (29% of TFC) (IEA 2018). This has been further projected to reach 151 quadrillions Btu in 2040, an increase of 44 quadrillions Btu from 2016 (Reference case) as shown in Fig. 13.1a (EIA 2017). The improved understanding of earth systems has reflected that petroleum reserves are rather limited and pollutants generated by petroleum consumption affect the ecosystem and the human health severely. Figure 13.1b presents the increasing trend of global transport CO_2 emissions in 1990 and 2016 (IEA 2019). Hence the extraction of fossil petroleum based fuels and their consumptions must be reduced in order to meet the new environmental and climate challenges and to minimize human health hazards. It has also been understood that the gap between the demand and supply of petroleum products needs to be filled by sustainable alternative and eco-friendly fuels. International treaties such as Agenda 21, Kyoto Protocol or Paris Agreement have already emphasized the urgency of development and utilization of renewable energy sources that can potentially bridge this gap, while protecting the environment and human health (Nizami et al. 2017). Worldwide, this is being addressed at different levels, and renewable energy sources are successfully penetrating various energy markets to accomplish this mammoth challenge. The EU has already put a target that at least
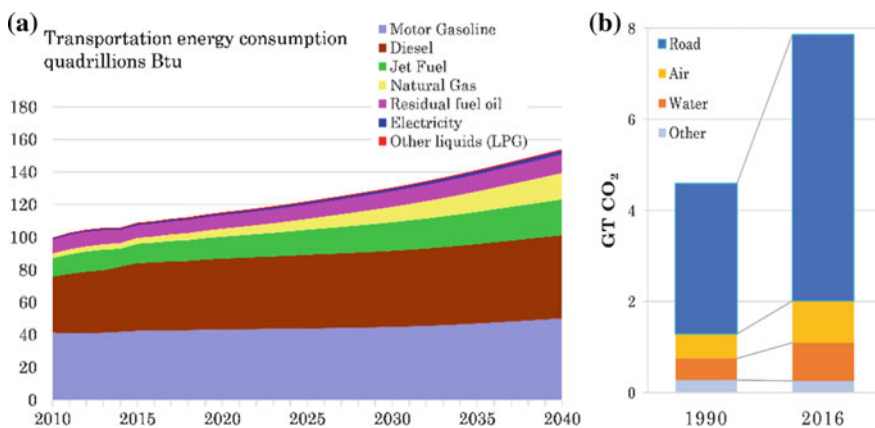
Fig. 13.1 **a** Projected world transport energy consumption, fuel-wise (Ref. year 2015–2016); **b** global transport CO_2 emissions in 1990 and 2016 (U.S. Energy Information Administration (EIA), https://www.eia.gov/analysis/studies/transportation/scenarios/pdf/globaltransportation.pdf.; IEA 2019)

10% of transport fuels should be from renewable resources (with 6% less carbon-intensive fuels than fossil diesel and gasoline baseline fuels) by 2020 (EU 2018).

Among different renewable energy resources, biomass has the highest potential to shoulder demand for transport fuels globally. Biomass resources are abundant, omnipresent and versatile, and currently biomass accounts for 10% of world's primary energy supply (World Energy Resources 2016). Biofuels (biomass-derived transport fuels) such as biodiesel, biogas, and bio-alcohols are currently being used as transport fuels worldwide in niche markets. It is quite complex to decide, which alternative fuel is the best choice to substitute fossil fuels in the transport sector under local context. Biogas clearly emerges as an alternative fuel for vehicular applications globally and has attracted increased attention. Main driving forces for biogas adaptation in transport sector are (Papacz 2011):

- stricter regulations and taxes on waste disposal, health risks and methane (CH_4) emissions from the wastes,
- increasing demand for renewable fuel resources,
- obligation for the use of low carbon intensity transport fuels, and
- obligation to improve the urban air quality using clean/green transport fuels.

Biogas technology is a dual-purpose technology since it reduces the volume of the solid organic wastes as well as converts them to useful gaseous fuel, thus avoiding direct emission of methane (CH_4) to the atmosphere. As per an estimate, one metric ton of organic solid waste can potentially emit 50–110 m^3 of CO_2 and 90–140 m^3 of CH_4 into the atmosphere, if not treated and results in an energy loss equivalent to ~400 kWh (Cecchi et al. 2011).

Biogas is primarily produced from any organic waste, which is broken down by micro-organisms and enzymes in an oxygen-free environment, by a process called anaerobic digestion (Viking Strategies 2013). Typical feed-stocks include a variety of waste materials such as sewage sludge, manures (pig, poultry, cattle, and human excreta), energy crops (maize, sweet sorghum, sugar beet etc.), agricultural wastes (rice and wheat straw, cassava rhizome, sugarcane residues, corn cobs etc.), organic solid waste from industries, food waste from homes and restaurants, waste from vegetable markets, wastes from food processing industries, sugar mills, fish processing and slaughter houses, organic fraction of municipal solid waste (MSW) (Viking Strategies 2013; World Bioenergy Association 2013; Sarker et al. 2018). Biogas is produced by anaerobic fermentation and the overall production process follows successive biochemical processes, including hydrolysis, acidogenesis, acetogenesis and methanogenesis (as shown in Fig. 13.2).

The gas yield is generally influenced by the type of feedstock used, temperature range (for mesophilic: 30–40 °C), pH (7–8.5) and inoculum concentration (World Energy Resources 2016). Biogas thus produced is a mixture of gases, mainly consisting of methane (CH_4), and carbon dioxide (CO_2). Typical composition of biogas is given in Table 13.1. Methane yield from different biomass feed-stocks is given in Fig. 13.3 (IRENA 2018).
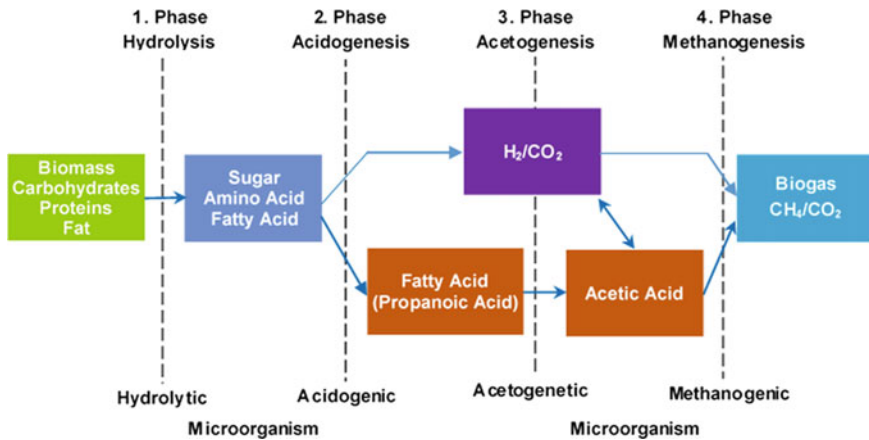
Fig. 13.2 Stages of organic material breakdown by micro-organisms for biogas production under anaerobic conditions (Strippel et al. 2016)

Table 13.1 Typical composition of biogas (World Energy Resources 2016; Viking Strategies 2013)

Constituents	(%)
Methane (CH_4)	50–75
Carbon dioxide (CO_2)	25–45
Water vapor (H_2O)	2.0–7.0
Nitrogen (N_2)	<2.0
Oxygen (O_2)	<2.0
Ammonia (NH_3), Hydrogen (H_2), Hydrogen sulfide (H_2S), other trace gases	0.1–3.0
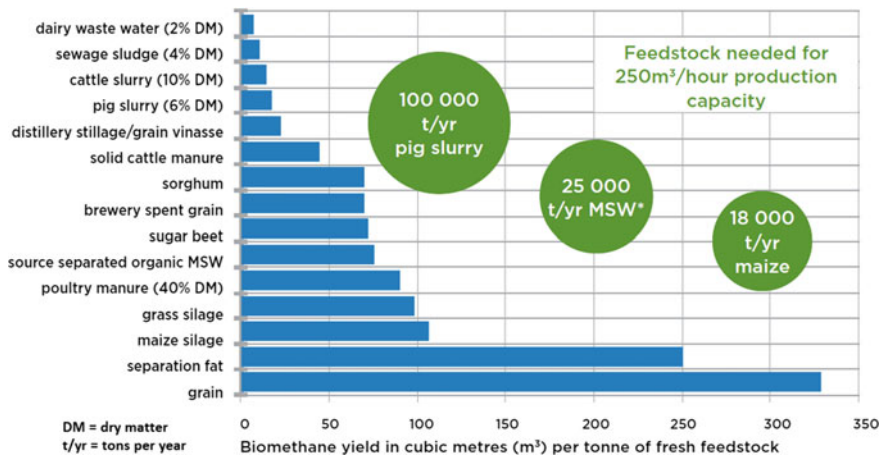
Fig. 13.3 Typical bio-methane yield from different biomass feed-stocks (IRENA 2018)

Table 13.2 Typical energy content (LHV) of biogas and bio-methane (Viking Strategies 2013)

	kWh	MJ
Biogas (avg.) (1 Nm^3)	6.0	21.6
Bio-methane (1 Nm^3)	9.97	35.9
Bio-methane (1 kg)	13.9	50.0

Biogas as a renewable energy resource, which can have multiple applications including electricity and heat generation and cooking energy and as fuel for gas-powered vehicles. Besides these applications, it also provides highly nutrient and humus-rich organic fertilizer for agriculture, which can potentially replace the energy-intense factory-made chemical fertilizers. Though raw biogas can be utilized directly for heat and power generation, an upgradation is essential in order to increase its energy density and heating value and to make it corrosion-free by removing impurities such as CO_2, H_2O, and H_2S, making it suitable for vehicular application or natural gas (NG) grid applications. The upgraded biogas is often referred as "bio-methane" (at least 90%, but typically 96–99% CH_4) or renewable natural gas (RNG), which has an enhanced energy value compared to raw biogas, as shown in Table 13.2 (Viking Strategies 2013).

Biogas as transport fuel can potentially reduce greenhouse gas (GHG) emissions from the transport sector (60–80% reductions are possible compared to gasoline operations) (IRENA 2018). In most developing countries, raw biogas is directly combusted in household stoves and gas lamps, whereas in industrialized countries, CHP applications have become standard technology. Biogas based CHP generation is dominating in Europe. Largest producers of biogas for transport applications were Germany, Sweden, Switzerland, UK, and US in 2016. Inspite of this, contribution of biogas in the transport sector globally remains quite insignificant (<1%) (IRENA 2018), which does not truly reflects its potential.

13.2   Global Potential of Biogas Production

Leading countries in the world producing biogas include USA, UK, EU, Russia, China, Thailand, and India (World Energy Resources 2016). Global production of biogas energy increased from 0.28 EJ in 2000 to 1.28 EJ in 2014 (equivalent to 59 billion m^3 biogas or 35 billion m^3 bio-methane). Notably, the biogas production growth rate was the highest in the EU, which alone produced half of global bio-methane (18 billion m^3) in 2015 (World Bioenergy Association (WBA) 2017). As per an estimate, globally ~500 plants produced biogas and upgraded it to NG quality, which was equivalent to ~50 PJ/year. (IRENA 2018). Recent data showed that nearly 160 million m^3 of bio-methane was consumed by the transport sector in EU alone in 2015, of which Sweden shared the highest fraction (113 million m^3), followed by Germany (35 million m^3), Norway (10 million m^3), Iceland (2 million m^3), Finland (0.2 million m^3) and Italy (28,000 m^3) (Scarlat et al. 2018). It is therefore

expected that the biogas/bio-methane market for the transport sector will develop and grow worldwide in near future. Several countries around the world have significant potential of biogas/bio-methane production for vehicular applications because of vast availability of waste biomass, and existence of infrastructure related to NG fueled vehicles and NG distribution for transport sector. Because of diverse nature of biogas feed-stock and lack of data, exact estimation of global bio-methane production potential is difficult. Nevertheless studies of global biomass energy sources (Viking Strategies 2013; World Bioenergy Association 2013; IRENA 2018) have shown that there exists significantly high potential for biogas/bio-methane production from energy crops, MSW, sewage sludge and animal manure worldwide, particularly in EU, Latin America, North America and Asia, including India and China (IRENA 2018). A summary of global potential is presented in Table 13.3, which indicates that biogas would have sufficient contribution to the global primary energy supplies (Viking Strategies 2013). According to Table 13.3, organic wastes and energy crops as biogas feedstock materials have the largest potential for biogas production. However biogas production from energy crops may be controversial since they require arable land and water, and thus compete with food crops. Without any doubt, biogas production from organic wastes would remain an ever-increasing trend, and is therefore regarded as a highly sustainable means of providing renewable and clean alternative fuel for vehicular applications.

Global population is expected to increase in coming decades [from 7.6 billion currently to 9.8 billion in 2050, and 11.2 billion in 2100 (United Nations 2017)]. On top of it, rate of urbanization will also continue to grow, hence the MSW generation worldwide would also grow to be enormous. As per an estimate, ~4.3 billion urban residents will generate ~2.2 billion tons MSW/year by 2025 (Hoornweg and Bhada-Tata 2012), which can provide enough organic feed-stock, suitable for large-scale biogas productions. Biodegradable urban wastes will be ~70 kg/person/year soon (Tabatabaei and Ghanavati 2018). Besides, effluents and by-products of large agro-industrial plants will also increase and can be potentially used as biogas feed-stock.

13.3 State-of-the-Art of Biogas Generation Technologies

Biogas or bio-methane production chain involves several steps including feedstock management (collection, storage, transportation of feed-stock to plant, etc.), pretreatment of feedstock materials and input to anaerobic digester (AD) or biogas reactor, biogas production, collection and storage, biogas purification or upgradation to bio-methane and finally usage, digestate or effluent storage/usage/disposal as bio-fertilizer as shown in Fig. 13.4. Every step of the entire plant processes requires careful design and evaluation, according to the final target of the project and its constraints. Many different combinations of equipment, methods, and techniques are available for application, but their optimization can only result in a successful project implementation. The best practice includes design expertise for the specific area mentioned above; for the process equipment and a good understanding of the

Table 13.3 Potential for biogas production (in PJ and billion m^3 CH_4 equivalent) for EU27, China and world

Type of resource	EU 27 PJ	EU 27 Billion m^3 CH_4	China PJ	China Billion m^3 CH_4	World PJ	World Billion m^3 CH_4
Manure	738	20.5	2591	72		
Residues (straw from grain, corn, rice, landscape cleaning)	407	11.3	1152	32		
Energy crops	978	27.2	1799	50		
Total from agriculture	**2123**	**59**	**5542**	**154**	**22,674**	**630**
Urban waste (organic fraction of MSW)	360	10	2591	72		
Agro-industry waste (organic fraction)	108	3	1152	32		
Sewage sludge	216	6	576	16		
Total waste, billion m^3 CH_4	**684**	**19**	**4319**	**120**	**13,316**	**370**
Total (agriculture and waste)	**2807**	**78**	**9861**	**274**	**35,990**	**1000**
Total in EJ	**2.8**		**9.9**		**35.9**	

Note The bold in the table refers to the summation of the previous figures in the same category
1.67 Nm^3 biogas $= 1$ m^3 bio-methane (Viking Strategies 2013; Paolini et al. 2018)

parameters influencing production processes, and overall plant performance etc. For instance, adequate mixing of the ingredients is vital for all digester types to ensure good contact between the raw materials and microbes and maintaining a constant temperature, and homogenous quality throughout the digester contents is also crucial for high gas yield (Luostarinen et al. 2011).

Biogas yield for a given feedstock depends on its physicochemical properties such as moisture content, total solids (%TS) content, volatile solids (%VS) content and the quantity of fresh matter (FM) fed into digesters. Biomass contains complex structures of carbohydrates, proteins, fats, cellulose, and hemicellulose, and microbial actions
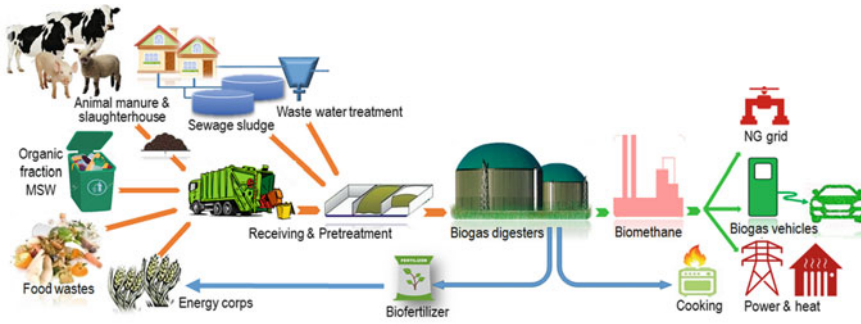
Fig. 13.4 Schematic of biogas/bio-methane production and utilization with material cycle

are generally required to facilitate hydrolysis of these structures for biogas production. Carbohydrates and proteins show faster conversion rates than fats. However, fats provide higher biogas yield (Luostarinen et al. 2011). Short HRT is always preferred in biogas production, and different feedstock pretreatment procedures (i.e., mechanical, chemical or thermal) can reduce HRT significantly by enhancing hydrolysis or feedstock decomposition reactions and can increase the biogas yield as shown in Fig. 13.5 (Achinas et al. 2017).

In recent times, use of co-substrates or co-digestion (simultaneous digestion of more than one substrate with complementary characteristics) has become quite common, which increases the organic content of the mixture, resulting in a high biogas/bio-methane yield compared to the gas yield from the substrates treated individually. Further-more, a large number of different substrates can be converted to biogas using this technique (Pagés-Díaz et al. 2011, 2015).

Biogas plants vary in size (scale) and technology: small capacity and locally-made simple technology (floating-dome, fixed-dome plant, balloon plants)-based plants are commonly used in developing tropical countries, which feed waste mainly from household/farming, and gas is used for cooking and lighting. In industrialized

Fig. 13.5 Effect of pretreatment on anaerobic digestion or biogas yield (Achinas et al. 2017)
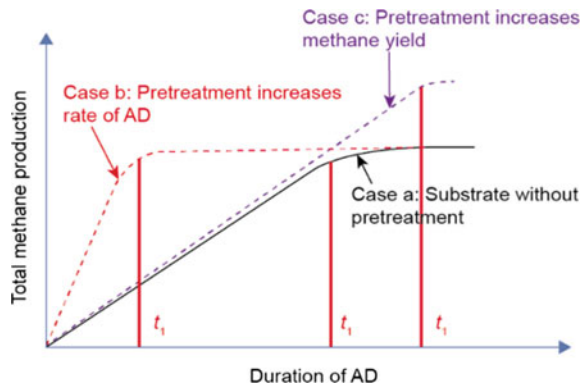
countries, biogas plants are significantly larger with modern equipment and advanced technologies for enhanced digester capacity and with process control applications for stable operation. These can be farm-scale type, cooperative farm type, and centralized type biogas plants. In case of farm-scale plants, the technology is more elaborated, but still not very complicated, therefore easy-to-use. On the other hand, a centralized scale biogas plant can be quite large, may integrate several different processing units including many digesters, which increase the system complexity and usually requires more monitoring, sophisticated controls and operator's skills, and knowledge. For instance, the centralized biogas plants built by NAWARO® BioEnergie AG at Güstrow Penkun in Germany (the world's largest biogas park at present) consists of tens of digesters and produces 46 million m^3 of bio-methane per year. This is equivalent to ~160 million kWh/year of power and 180 million kWh/year of heat energy, sufficient to meet the total energy demands of a city with more than 50,000 households. Besides this, renewable natural gas (RNG) at a rate of ~5000 m^3/h is fed into adjacent NG network (Güstrow GmbH https://www.nawaro. ag/en/company/guestrow-bioenergy-park/).

Biogas plants being strictly case-specific, are usually selected and designed according to the availability and characteristics of feedstock materials, investment and operational costs available, subsidy available, work force available, and end-use goals. Biogas digester or reactor is the heart of the plant. Anaerobic digester can be classified based on the following technical parameters (Luostarinen et al. 2011):

- Solid content of the feedstock (wet or dry digestion process)
- Digestion temperature: psychrophilic type (<20 °C and 70–80 days HRT; mesophilic type (30–42 °C and 30–40 days HRT), or thermophilic type (43–55 °C and 15–20 days HRT)
- Technology (Batch process, Continuous process e.g., Plug-flow, Completely stirred tank reactor (CSTR), Upflow anaerobic sludge blanket reactor (UASB), Lagoon, etc.)
- Number of stages/phases (single-stage, two-stage, multiple stages)
- Loading strategy (batch, continuous, semi-batch).

Biogas digester types or its operating mode may also depend on the dry matter content of the feedstock as shown in Fig. 13.6. Wet continuous digestion process
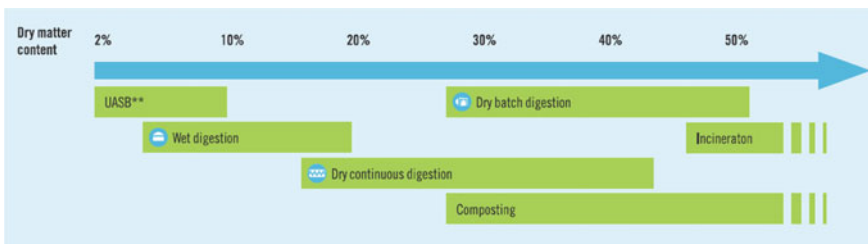
Fig. 13.6 Overview of the selection of digester technologies or the mode of operation based on the feedstock's dry matter content (Strippel et al. 2016)

(CSTR or hydraulic digester) accepts diluted solid feedstock (fed in certain intervals such as a few times per day or hour with simultaneous withdrawal of digestate) made into slurry by either process water or liquid biomass. Liquid digestate can either be used as fertilizer directly or can be used to dilute the solid feedstock. CSTR is the most commonly used digester technology and is suitable for any size/capacity of biogas plant. The technology is simple but robust and can digest a wide range of possible feed-stocks with high gas yield because of efficient mixing of feedstock and microbes. Dry continuous digestion (plug-flow digester) on the other hand is suitable for feedstock with high dry matter content. The feedstock is generally mixed with already digested material to provide necessary microbial inoculum and is slowly transported from the inlet to the outlet of the digester. Even though a robust stirrer is employed to provide mixing, adequate mixing remains a significant challenge of the dry process and the digestate often requires post-treatment such as composting. Under the batch digestion type, high TS content feedstock with digestate are fed to the digester (garage type digester), where the feedstock remains for a definite HRT and emptied after that period and refilled with the next batch. Since the biogas production in this process depends on the operational cycle, usual practice is to have at least three parallel digestion systems with three batches at different stages of operation: one being filled, one in biogas producing phase and the other being emptied (Strippel et al. 2016; Luostarinen et al. 2011).

Recent research has revealed that methane conversion rates of the organic materials increase by splitting the entire digestion process into multiple stages: acid-formation (hydrolysis and acidogenesis) in one digester and methane formation (acetogenesis and methanation) in another digester. However, high cost of such a complex system can be an impedance for commercial usage (US Environmental Protection Agency (EPA) 2006). A multiple-stage bioreactor system can be beneficial as it enables independent controls of the reactors and permits the application of different process conditions (such as temperature) at different steps of the total system to enhance a particular process reaction controlled by the specific species of bacteria. Physical separation of overall anaerobic digestion process into two or more stages can eventually result in a high biogas and methane yield (Colussi et al. 2013; Marín Pérez and Weber 2013; Park et al. 2008; Kim et al. 2011). High-pressure anaerobic digestion is another option, which can provide increased biogas yield with >95% methane content. This technique integrates biogas production and in situ biogas purification under pressure, producing upgraded biogas (99% methane). Previous research at high operating pressures (starting from 20 bar up to 100 bar) have demonstrated enhanced cleaner gas yields since high pressure influences microbial processes and more CO_2 can be dissolved in water (Lindeboom et al. 2011; Bartlett 2002; Merkle et al. 2017). Since anaerobic digestion process involves microbial actions, micro-biological dynamics has significant influence on gas production and methane yield. However, inadequate knowledge exists regarding different microbes and their respective metabolic activities in the anaerobic digestion process. Microbiology investigations of biogas production processes remain a challenge due to enormous diversity of microbes. Current research efforts are therefore focused on

structures of different microbe species suitable for anaerobic digestion using molecular biology techniques and on development of micro-organisms and/or bio-catalysts aiming to widen the application range with better features and low costs (Achinas et al. 2017).

13.4 Biogas Purification and Upgradation to Transport Fuel

13.4.1 Need for Biogas Cleaning and Upgradation

Biogas being a mixture of gases contains several non-fuel constituents as shown in Table 13.1. Therefore most biogas applications require a high CH_4 content with removal of the non-fuel constituents (termed as biogas contaminants) namely CO_2, N_2, H_2O, H_2S, etc. Biogas as a transport fuel or for bio-methane applications require pipeline NG composition typically consisting of 80–96% or higher CH_4, <2–3% CO_2, <0.2–1% O_2, <5–15 mg m^{-3} H_2S, <3–20 mg m^{-3} NH_3, and <5–10 mg Si m^{-3} methyl siloxanes (Ryckebosch et al. 2011). Even though biogas contains a small amount of H_2S, its presence can be problematic since it severely corrodes pipes, engines, pumps, compressors, gas storage tanks, and valves (Petersson and Wellinger 2009). Moreover, H_2S takes part in combustion to form SO_2 (sulfur dioxide), which further reacts with water vapor to produce H_2SO_4 (sulfuric acid) vapors that cause environmental pollution. Presence of halocarbons and NH_3 also corrodes pipelines and engine parts during biogas combustion (Abatzoglou and Boivin 2009). Siloxanes are not commonly present in all biogas mixtures but can be identified in the gas mixture produced from wastewater treatment and landfill-based biogas plants. Recently, methyl siloxanes contaminants are also gaining attention, since they tend to form silicon oxide deposits during combustion, leading to abrasion, over-heating, and malfunctioning of engines and valves (Sun et al. 2015). However, a high concentration of H_2 in bio-methane can be beneficial for vehicle applications since it enhances engine combustion performance (Wylock and Budzianowski 2017). Primary contaminant CO_2 not only reduces the energy value of biogas (Table 13.2) but also lowers its Wobbe index, flame velocity and flammability limits (Shah et al. 2016). Moreover, if biogas with a high concentration of CO_2 is used as a transport fuel, it occupies additional space in the storage cylinder, which makes the cylinder excessively large, in addition to requiring excess energy consumption for biogas compression, thus resulting in higher operational cost (Persson et al. 2006), with no apparent benefit. Following sections provide an overview of biogas purification technologies for vehicular applications as well as a comparative analysis between different techniques.

Biogas Purification Purification of biogas mainly refers to the removal of contaminants and impurities including H_2S, H_2O, and hazardous trace compounds such as

ammonia, siloxanes, or volatile organic compounds (VOCs) (if present). The concentration of H_2S in biogas can be minimized to acceptable levels either by precipitating it in the digester liquid, or by applying any suitable gas treatment technique, or by simultaneous removal along with CO_2. H_2S can be readily adsorbed by activated carbon. Activated carbon is often impregnated or doped with permanganate or potassium iodide, potassium carbonate, or zinc-containing chemicals [such as Zinc oxide (ZnO), Zinc carbonate ($ZnCO_3$)] as catalyzers to improve its performance (Papacz 2011). Other H_2S adsorbing chemicals include copper compounds such as copper carbonate, hydrogen peroxide, and iron compounds (Wylock and Budzianowski 2017). Sodium hydroxide washing is considered as one of the oldest methods of H_2S removal. However its application is limited since dealing with caustic solution is complicated. Support materials (i.e., pressed minerals, wood chips) coated with iron-oxides ($Fe(OH)_3$ or Fe_2O_3) can also be used to adsorb H_2S. Though this is a commonly used method for sewage sludge treatment plants worldwide, it has regeneration issues. H_2S can be absorbed in a ferric chelate solution, in which Fe^{3+} ions are reduced to Fe^{2+} ions, while H_2S is oxidized to elementary sulfur. Recently, an effective H_2S removal technique was introduced by a Dutch company, which works on precipitation reaction between H_2S and a metal ion in an aqueous solution. The regeneration of metal ion involves oxidation reaction converting it to sulfur dioxide, which can be used to produce Sulfuric acid or gypsum (Papacz 2011). High chemical requirements make H_2S removal processes (as discussed above) expensive as well as they incur energy and disposal costs (Wylock and Budzianowski 2017). That is why, H_2S removal by biological treatment methods can be a superior alternative to chemical treatment. In biological process, a few species of microorganisms such as Thiobacillus and Sulfolobus oxidize H_2S (Papacz 2011). In addition to H_2S, commonly used technologies for removing other impurities including N_2/O_2, water, and siloxanes, which are summarized in Table 13.4.

13.4.2 Biogas Upgradation

Biogas upgradation is a quality enhancement process of biogas after removal of minor compounds, which involves removal of primary component CO_2, drying of biogas, followed by compression. The product is usually known as bio-methane, which is suitable for injection to NG grids and for use as fuel for vehicular applications. Standards for upgraded biogas compositions exist in different countries for NG grid injection or city gas network. For instance, according to Swiss standards, biogas application for engines or city gas network requires the concentration of CO_2 and H_2S to be <6% and <5 mg m^{-3} respectively (Paolo et al. 2017). Sweden has also set national standards for upgraded biogas to be used for vehicular applications, which are given in Table 13.5 (Karim and Fatima 2018; Danish Technological Institute 2012). Biogas upgrading technologies (i.e., CO_2 removal) that have been commonly used both on farm-scale or industrial-scale globally are based on absorption (physical

Table 13.4 Purification of minor contaminants of biogas (Wylock and Budzianowski 2017)

Minor contaminants	Purification technology	Purification capability	Cost	Remarks
H_2S	Biological treatment	<50 ppm	0.1–0.25 EUR/kg H_2S	Most desirable
	Impregnated activated carbon	<0.1 ppm		Commonly used before PSA
	Iron chloride	100–150 ppm		
	Iron oxide or hydroxide	<1 ppm	3.85 EUR/kg H_2S	Used for high H_2S %
	NaOH washing	1 ppm	0.85 EUR/kg H_2S	Regeneration is possible for a limited number of times
	Metal ion in aqueous sol. (precipitation)			Regeneration is not possible Pilot test
Water	Adsorption with silica gel or aluminum oxide	A dew point of −10 to −20 °C at atm. pressure		
	Adsorption of tri-ethylene glycol or glycol	A dew point of −5 to −15 °C at atm. pressure		Regeneration temperature: 200 °C
O_2/N_2	Activated carbon			
	Molecular sieves			
	Membranes			
Siloxanes	Activated carbon	<0.87 ppm	81–113 EUR/kg siloxanes two landfill plants	Carbon cannot be regenerated
	Cooling	−25 °C: 26% removal, −70 °C: 99% removal		The absorption is sensitive to humidity

and chemical), pressure swing adsorption (PSA), membrane separation, cryogenic separation, and biological methods (Swedish Gas Center (www.sgc.se), www.iea-biogas.net/files/daten-redaktion/download/…/10/Swedish-experience.pdf).

Pressurized Water Scrubbing (PWS) Pressurized water scrubbing has been the most widely used biogas cleaning method due to its simplicity in operation and performance reliability (Cozma et al. 2013), but it is an energy-intensive method (Kadam and Panwar 2017).

Table 13.5 Biogas quality standard for vehicular applications (Otto engines) in Sweden (Karim and Fatima 2018; Danish Technological Institute 2012)

Particles	<1 μm
Methane	$97 \pm 2\%$
Water	<32 mg/Nm^3
$CO_2 + O_2 + N_2$	<5%
Oxygen	<1 vol%
Sulfur	<23 mg/Nm^3
N (except for N_2) expressed as NH_3	<20 mg/Nm^3

Odorized and compressed to 200 bar for grid injection: addition of propane (~7 to 9 vol%)

Water requirement for this method is also a major concern. On the contrary, water scrubbing at atmospheric pressure is less energy intensive method, but it is limited to small size plants. High-level purification is challenging to attain (Shah et al. 2016) by low pressure water scrubbing method. Because of higher solubility of H_2S than CO_2 or CH_4 in water, in principle H_2S and CO_2 can be removed together by this method. However since gaseous H_2S is poisonous and dissolved H_2S is corrosive, pre-separation of H_2S from the raw biogas is usually recommended. H_2S-free biogas after compression (6 to 12 bar) and cooling is flown through the bottom of an absorber column, while water is sprayed from its top to attain gas-liquid counter-flow contact (Cozma et al. 2013; Kadam and Panwar 2017; Angelidaki et al. 2018; Yasin et al. 2018). The absorber column generally contains packing material in order to provide a large surface area for gas-liquid contact, which enhances the absorption efficiency. Different types of packing materials have been used such as pall ring, intalox metal, berl saddles, tellerette, tri-packs, raschig ring, and sponge carriers (Noorain et al. 2019; Bauer et al. 2013).

Even though the amount of CH_4 dissolved in pressurized water is quite low as compared to CO_2, CH_4 dissolved in water is considered as CH_4 loss and hence it should be recovered back. Methane recovery is made by de-compressing the CH_4-dissolved water (to 2.5–3.5 bar) in a flash tank and recycling it to the inlet of the second compressor, as shown in Fig. 13.7. Water from the flash tank can be regenerated for recycling through air stripping (desorption) column, where water is decompressed to atmospheric pressure in order to remove CO_2 (and H_2S, if not pre-separated). Recent studies on pressurized water scrubbing focus on reduction in requirement of quantity of water and high-pressure applications (Cozma et al. 2013).

Physical Absorption In principle, physical absorption method and pressurized water scrubbing method are similar. In this method, organic solvents such as mixture of methanol and dimethyl ethers of polyethylene glycol (marketed using the trade names of Selexol® and Genosorb®) are used in place of water. Considerably higher solubility of CO_2 compared to water is the main basis for using organic solvents, which significantly reduces the volume of solvent that must be recirculated in the system thus permitting a more compact upgradation plant for the same capacity.
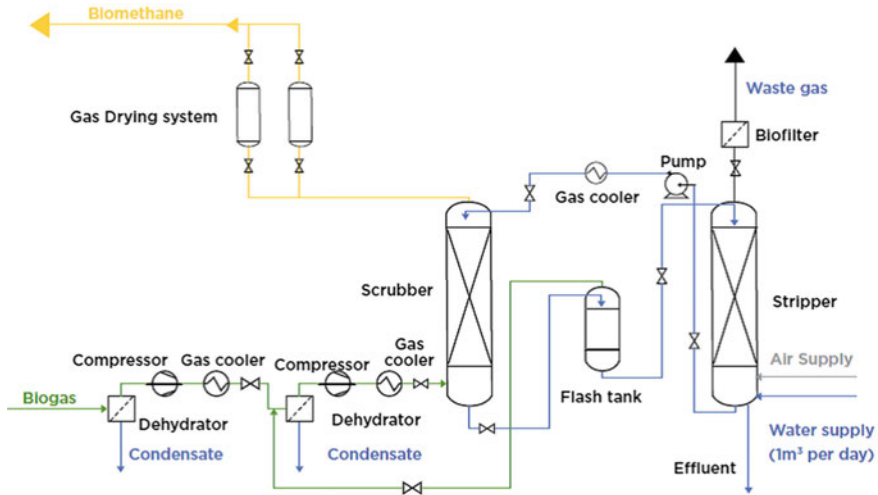
Fig. 13.7 Schematic of a typical pressurized water scrubbing system (IRENA 2018)

However the regeneration of organic solvents is difficult because of their high affinity to CO_2. Moreover, since H_2S is highly soluble in these solvents compared to CO_2, it creates more complexity during regeneration process hence pre-separation of H_2S is recommended before injecting it into the scrubber. Like water scrubbing method, physical absorption cannot remove N_2 and O_2. Raw biogas is compressed (7–8 bar) and cooled (at ~20 °C) before sending it through the bottom of absorption column/scrubber. Afterwards the pressure is reduced to atmospheric level and heating up to 40 °C is required for organic solvent regeneration in the desorption column (Wylock and Budzianowski 2017; Zhao et al. 2010). Upgraded gas obtained by this technique can eventually contain 98% methane (Zhao et al. 2010), while the energy consumption is comparable to PWS.

Chemical Absorption Method Using Amine Solutions In this method, aqueous amine solutions (i.e., mono-, di- or tri-ethanol-amine) capture both CO_2 and H_2S through chemical reaction mechanisms. Like other scrubbing systems, an amine scrubbing system also comprises of an absorber unit and a stripper. As usual, raw biogas is in counter-contact with the amine solutions in the absorber, where gas flows from the bottom and liquid solution is sprayed from the top. The absorber operating pressure however in this case, remains quite low (1–2 bar). After the absorption column, solvent rich in CO_2 and H_2S is taken to the stripper unit for regeneration. The stripper also operates at low pressures (1.5–3 bar) and contains a heat source (i.e. boiler) to provide the necessary heating up to 120–160 °C. Chemical absorption method provides very high separation efficiency and final gas can contain as much as 99% CH_4. Since scrubber operates at near atmospheric pressure, the process requires less electricity for compression compared to PWS. However the solvent regeneration is generally high heat energy-intensive and requires a heat supply at ~160 °C. Besides

the high cost of amine solvents, their evaporative losses and toxicity to human and environment remains major concerns of this method. In addition to amine solutions, aqueous alkaline salts such as sodium, potassium, and calcium hydroxides can also be used as solvents to react with CO_2 chemically (Yoo et al. 2003). Since sodium hydroxide has higher affinity to CO_2 than amine-based solvents, lesser amount of solvent would be required to recirculate through the scrubber for the cleaning of a similar volume of biogas. Alkaline solvents are also more abundant and cost-effective compared to amine solvents (Augelletti et al. 2017).

Pressure Swing Adsorption (PSA) Pressure swing adsorption (PSA) is a dry method in which gases (i.e., CO_2) are separated due to physical interaction between the gas molecules and adsorbent material. The adsorbents are generally porous solid materials having high specific areas for maximizing the gas-adsorbent contact. Common adsorbents are carbon molecular sieves, activated carbon, and zeolites (Zeolite 13x, Zeolite 5A) (Awe et al. 2017). In PSA, initially H_2S is removed to avoid toxicity in the process and also because adsorption of H_2S is usually irreversible. The other constituent H_2O is removed next, in order to avoid potential poisoning of the adsorbent material (Sun et al. 2015). Then clean biogas is fed to the adsorption column, where CO_2 is adsorbed in the adsorbents at elevated pressure (usually 4–7 bar) as shown in Fig. 13.8. Bio-methane is recovered from the top of the column, and almost saturated adsorbent material is passed through desorption process in order to release CO_2.

The released gas mixture may contain significant amount of CH_4 and is recycled (Cavenati et al. 2005) or burnt in a flox chamber to minimize/avoid CH_4 release into
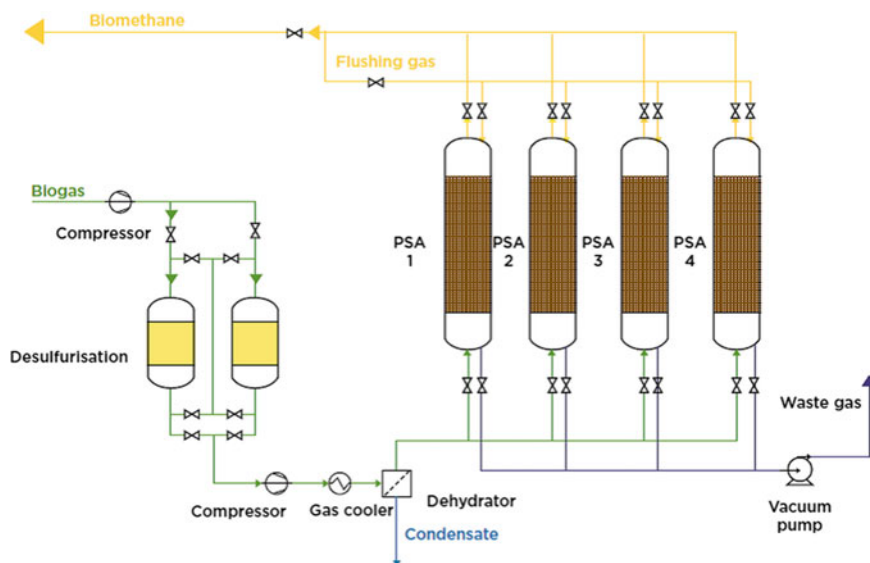

Fig. 13.8 Schematic of the pressure swing adsorption (PSA) method (IRENA 2018)

the atmosphere (Paolo et al. 2017) and eventually the waste gas (i.e., CO_2) escapes to the atmosphere. For a continuous process, multiple adsorption columns (generally four to six) operate simultaneously but each at a slightly different state of overall process (Zhao et al. 2010). Simultaneous removal of CO_2, O_2, and N_2 from raw bio-gas can be considered as a big advantage of this method, which can yield bio-methane containing 96–98% (v/v) CH_4 (Wylock and Budzianowski 2017). However this technology requires substantial process controls, and investment and operational costs are rather high (Harasimowicz et al. 2007).

Membrane Separation Though membrane separation is considered as a new technology for biogas upgradation, it has already secured large market share and become competitor to conventional absorption based upgradation methods due to its low cost, high separation efficiency and ease of operation (EU 2018; Persson et al. 2006; Bauer et al. 2013). The membrane separation works at molecular level and it depends on different solubility and diffusivities of gaseous species in a given membrane material. Most commercially available membranes are of polymeric materials such as polysulfone, polyimide, polycarbonate, polydimethyl siloxane, and cellulose acetate (Miltner et al. 2017). Inorganic membranes are also available such as zeolite, activated carbon, silica, carbon nanotubes, etc. and it is often reported that they provide better mechanical strength, thermal stability and resistance against reactive chemicals compared to conventional polymeric membranes (Khan et al. 2017). Recent developments focus on mixed matrix membranes (MMMs), which are combination of both polymeric and inorganic membranes (Scholz et al. 2013; Makaruk et al. 2010).

Initially the particles, H_2S and other trace elements of raw biogas are cleaned and then the biogas is dried and compressed (typically between 5 and 30 bar) before passing through the membrane. Methane having a larger molecular structure does not pass through the pores of the membrane (remain as retentate), while relatively smaller molecules of CO_2 pass easily onto the other side (known as permeate), and hence the gas gets rid of CO_2, as shown in Fig. 13.9. Other configurations of
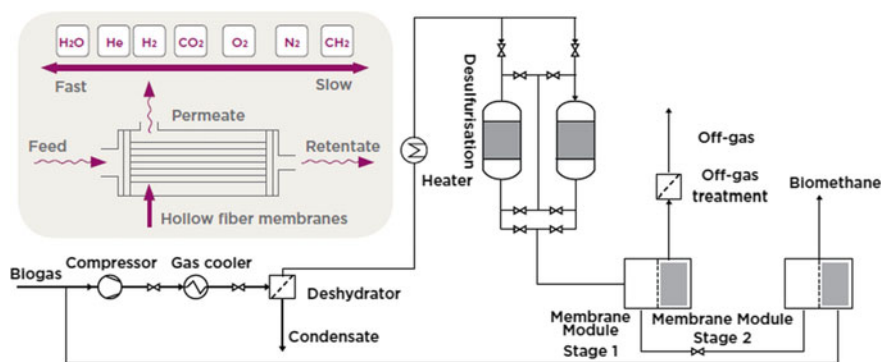

Fig. 13.9 Membrane separation technology for biogas upgradation (IRENA 2018)

membrane technology include single stage, two-stage with a recirculation loop, two-stage with sweep biogas stream and three-stage with sweep biogas stream (Miltner et al. 2016). Single stage is the most straight-forward technology. However, methane enrichment enhances as the number of stages increase (Makaruk et al. 2010). An extensively developed and optimized membrane separation system can provide a very high-quality bio-methane (~99% (v/v) CH_4) (Grande and Blom 2014).

Cryogenic Separation This technology is based on condensation and distillation of different constituents of biogas under high pressure and very low temperatures. How-ever the constituents such as CO_2, CH_4, and the rest liquefy at different low temperatures. This is emerging as an attractive biogas upgradation method since it provides liquid bio-methane in conformity to liquefied NG quality standards (Hosseinipour and Mehrpooya 2019). Successive cooling of raw biogas at relatively lower constant pressure (~10 bar) removes water, H_2S, siloxanes and halogens (at −25 °C) from the biogas, and CO_2 is removed in liquid phase (at −55 °C) and in solid phase (at −85 °C), thus providing CH_4-enriched gas. Further cooling down (to temperatures −120 to −160 °C) at pressure of ~40 bar eventually produces N_2 and O_2-free liquefied bio-methane (LBM) or bio-LNG (Petersson and Wellinger 2009; Cavenati et al. 2005; Patterson et al. 2011).

Major advantages of this technology include: (i) higher energy density (LBM has more than double volumetric energy density compared to compressed bio-methane), which facilitates efficient transportation and refueling at filling stations, (ii) no chemicals required and (iii) almost pure bio-methane (>97%) produced, in addition to recovery of pure CO_2 as a by-product. Though the technology shows high potential for biogas upgrading, such an approach is still under research and development stage, and only few facilities are operating on a commercial scale (Cozma et al. 2013). For instance, Air Liquide Advanced Technologies, France has commissioned their first LBG plant (550 kg/h capacity) in Lidköping, Sweden in 2012, which has been operating successfully, meeting the setup requirements. This cryogenic technology for LBG works on a reverse nitrogen Brayton Cycle and consumes electricity typically at a rate of 1.56 kWh/kg LBG. Other LBG plants commissioned by Wärtsilä are operating successfully in Norway. London-based company Gasrec produces and supplies LBG or bio-LNG facilities commercially, and several plants are in operation in the UK. Cryogenic separation usually requires high investment and has high operation costs, and some issues with operational difficulties have also been reported (Angelidaki et al. 2018).

Biological Method for Biogas Upgrading Major attraction for biological biogas upgrading technologies is the conversion of CO_2 into other energy containing products or value-added products. For instance, chemoautotrophic type of biogas upgradation methods are based on hydrogenotrophic methanogen reaction, in which H_2 reacts with CO_2 to produce CH_4, as shown in the following equation (Song et al. 2017):

$$4H_2 + CO_2 \rightarrow CH_4 + H_2O \quad \Delta G = -130.7 \, \text{kJ/mol} \tag{13.1}$$
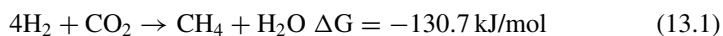
Results have shown that by this upgradation technique, CH_4 content of biogas can be increased from 60 to 96%, while H_2 and H_2S are not detectable (Wylock and Budzianowski 2017). However, H_2 production and storage are big concerns with this technology. Though biological biogas upgradation technologies have been experimentally proven, they are at an early stage of pilot or full-scale implementation.

Future Biogas Upgradation Technology A comparative assessment of the merits and demerits of different biogas upgradation technologies may conclude that rather than using a single technology, a combination of technologies (i.e., hybrid technologies) can result in high CH_4 enrichment at low operating costs, and low energy consumption. Researchers have reported that additional techno-economic benefits could be harvested in case of membrane-PWS or membrane-cryogenic separation hybrid systems (Makaruk et al. 2010; Shao et al. 2012). Shao et al. (2012) reported that using a hybrid membrane–temperature swing adsorption technology for bio-methane production could be beneficial and the techno-economic analysis showed a payback period of 6.8 months on an investment for processing 200 Nm^3/h biogas stream with a yield of 97% methane. It is expected that more R&D efforts will be focused on hybrid technologies, integrating two or more technologies to explore their potentials towards improved techno-economic dimension of biogas upgradation.

Comparative Techno-economic Feasibility of Different Methods Among different biogas upgradation methods, PSA, pressurized water scrubbing, organic physical and chemical scrubbing, and membrane separation are most commonly used commercially. Comparative technical characteristics of these technologies are summarized in Table 13.6. It should be noted that selection of the best upgradation technology depends on a number of factors: raw biogas quality and capacity, desired gas quality for the specific use, energy required to upgrade biogas to bio-methane (i.e., availability of cheap heat and the electricity at reasonable price), required skillset and technical support available for selected technology, capital cost, operating cost etc. (Papacz 2011; Wylock and Budzianowski 2017; Angelidaki et al. 2018). It is always possible to have a system yielding the minimum methane loss, but with increasing complexity in the system at the expense of higher energy consumption and investment. In the EU, pressurized water scrubbing technology for biogas upgradation has the largest share, followed by PSA and chemical absorption technology (Niesner et al. 2013). According to Table 13.6, cryogenic separation, chemical scrubbing (heat and electricity) and physical absorption are the most energy-intensive technologies, while water scrubbing technology demands lesser energy. The efficiency of a particular biogas upgradation method employed mainly depends on methane purity/loss fraction. Today's technological developments have contributed to cheaper and more efficient plants. Table 13.6 shows that chemical absorption delivers the highest purity methane or minimum methane loss. However it is concluded that no definite technology can be ranked as the best one, covering all aspects.

Table 13.6 Comparison of different biogas upgradation technologies (Swedish Gas Center (www.sgc.se), www.iea-biogas.net/files/daten-redaktion/download/ …/10/Swedish-experience.pdf; Kadam and Panwar 2017; Angelidaki et al. 2018)

|	Water scrubbing	Physical scrubbing	PSA	Chemical absorption	Membrane separation	Cryogenic separation
Electricity consumption for raw biogas (kWh/Nm³)	0.25–0.30	0.2–0.3	0.23–0.30	0.05–0.15	0.18–0.20	0.76
Electricity consumption for clean biogas (kWh/Nm³)	0.3–0.9	0.4	0.29–1.00	0.05–0.25	0.14–0.26	
Heat consumption (kWh/Nm³)	None	<0.2	None	0.5–0.75	None	
Heat demand (°C)	–	55–80	–	100–180		–196
Cost	Medium	Medium	Medium	High	High	High
CH₄ losses (%)	<2	2–4	<4	<0.1	<0.6	2
CH₄ recovery (%)	96–98	96–98	96–98	96–99	96–98	97–98
Pre-purification	Recommended	Recommended	Yes	Yes	Recommended	Yes
H₂S co-removal	Yes	Possible	Possible	No	Possible	Yes
N₂ and O₂ co-removal	No	No	Possible	No	Partial	Yes
Operation pressure (bar)	5–12	4–8	3–10	atm.	5–8	80
Pressure at outlet (bar)	7–12	1.3–7.5	4–5	4–5	4–6	8–10

13.5   Bio-Methane Costs

Overall costs for purified and upgraded biogas (bio-methane) supplies as transport
fuel includes three distinct components: capital costs, operational-and- maintenance
costs, and costs for consumables. These are further categorized as costs associated
with biogas production, biogas upgradation to bio-methane, its compression, and
distribution.

13.5.1   Production Costs

The cost of biogas production by anaerobic digestion is strongly influenced by the
type and quality of feedstock materials and plant capacity. It is generally expected
that as the plant capacity increases, the capital and O&M costs decrease propor-
tionately. However costs for the consumables (feedstock supply in particular) may
have an insignificant decreasing effect with increasing plant capacity. In general,
biogas production from industrial organic waste and residues incurs lower capital
costs (difference lies between 25–30%) than that for energy crops due to existing
facilities for handling and storage of feed-stocks in the previous case. Irrespective
of the plant type and capacity, biogas digester shares the most significant fraction of
total capital costs (40–45% for energy crops and 55–60% for agricultural or indus-
trial waste; Fig. 13.10), followed by buildings, feed-stock storage, pre-treatment and
feeding equipment, electrical and control systems and interests on the invested capi-
tal. O&M costs typically include costs for maintenance and repair, labor costs. This
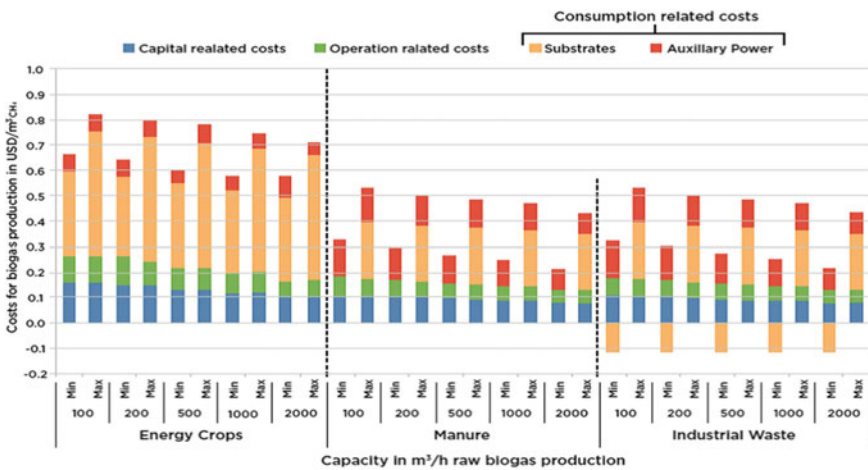
Fig. 13.10   Biogas production costs for different feed-stocks as a function of capital, operation, and
consumption related costs (IRENA 2018)

type of costs are usually slightly higher for biogas production from energy crops compared to that from agricultural and industrial wastes.

Costs for consumables include costs for feed-stock and expenses associated with energy consumption for plant operations. In general, waste materials as biogas feed-stock are cheaper compared to energy crops since wastes can be available at a minimum cost to free of charge to even at a negative price (referred to as tipping fee i.e., plant owners may be paid for waste disposal/treatment; for instance, negative costs USD -20/GJ to USD -9/GJ for MSW or sewage sludge in Central Europe) (IRENA 2018).

Heating is essential to maintain optimal temperature for anaerobic digestion, especially in cold climatic conditions. Heat requirements are generally lower for dry feedstock (e.g., energy crops) and consequently the heat costs, compared to using manure or industrial wastewater. Heat demand further increases if the biogas plant is located in cold climate areas. Besides heat energy, running, monitoring, and control of different plant equipment requires electrical power, and its consumption mainly depends on the technology selected for biogas production. Typically, for production capacities of ~500 to 2000 m^3/h raw biogas, energy crops feedstock based plants account for US$0.55/$m^3$ CH_4 to US$0.81/$m^3$ CH_4; manure based plant accounts for US$0.23/$m^3$ CH_4 to US$0.41/$m^3$ CH_4 and industrial waste products based plant accounts for US$0.12/$m^3$ CH_4 to US$0.52/$m^3$ CH_4 (IRENA 2018).

13.5.2 Upgradation Costs

Biogas upgradation costs depend on plant capacity; upgradation method selected, the specific goal of the project (e.g., bio-methane for NG network injection or vehicular application), raw biogas quality, availability, and price of auxiliary heat and power, environmental regulations (i.e., CH_4 leaks). Like production costs, capital and operating costs for biogas upgradation decrease notably with increasing installed capacity of the plant and typical values based on a survey are presented in Fig. 13.11.

The biogas upgradation costs for small-scale plants can be significantly high (US$1.07/$m^3$ of CH_4 for a 20 m^3/h raw biogas capacity plant; see Fig. 13.11) (IRENA 2018; Yoo et al. 2003). Availability of cheaper heat and electricity can make energy-intensive technology cost-effective and adaptable. For instance, biogas upgradation by chemical scrubbing technology can be more economical than PSA or water scrubbing technology, if cheap heat energy is available onsite as an auxiliary energy supply. If the upgraded gas is planned to be injected into a NG network, upgradation technologies operated with relatively high pressures (e.g., membrane separation) can save injection costs.
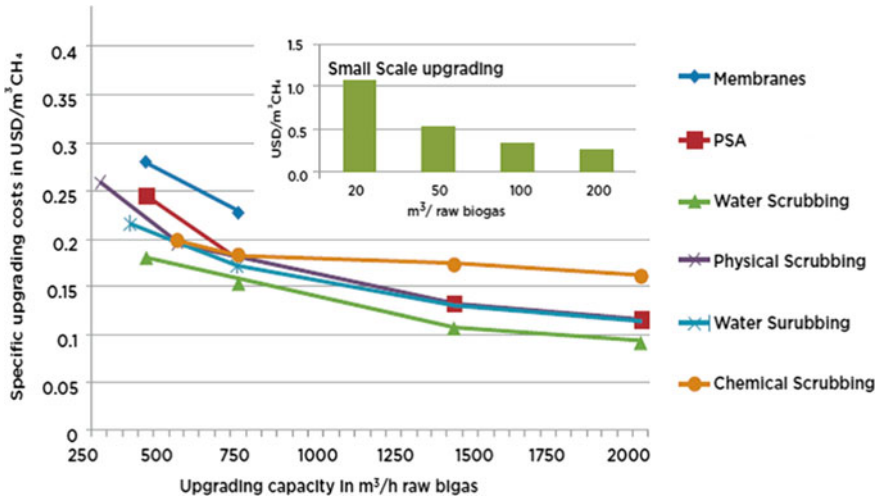
Fig. 13.11 Comparative biogas upgradation costs based on a survey in 2012 (IRENA 2018)

13.5.3 Distribution Related Costs

Bio-methane production plants and consumption points are usually in different locations hence expenditure is incurred in distribution of bio-methane for the end uses. Such delivery of bio-methane can be done either by using an existing NG distribution network or by compressing (at ~200 bar) and filling into cylinders as CBM or liquefying and filling into steel cylinders as LBM and transportation by vehicles to the filling stations. Bio-methane injection to NG grid is regarded as the most common distribution channel, which often shows the most cost-effective solution, if the distance between the NG grid and the gas production plant is within 5 km. Grid injection costs are also influenced by gas injection capacity (decreases with increasing capacity) and the operating pressure of the gas grid. For instance in Germany, the grid injection costs can vary between US$0.06/m^3 CH$_4$ (2000 m^3 gas capacity) and US$0.47 or more per m^3 CH$_4$ (100 m^3 gas capacity). An additional cost, which may be included in the bio-methane transportation costs, if a fee is imposed for using the public gas grid. It is country specific and can vary between regions and the quantity of gas transported. Cost of bio-methane distribution by road transports are generally higher than the grid distribution channel (typically US$0.22/m^3 of CH$_4$). Final cost is related to gas delivery to the consumers, which includes construction and operation of gas filling station. It varies with the capacity and flow rate (fast or slow filling) of the filling station. Typical overall costs for a fast-filling bio-methane fuelling station are about US$0.5/m^3 of gas with a capacity of 3500 m^3/day (IRENA 2018). LBM having much higher energy density compared to CBM can be transported easily to

the distribution points. However its high production cost is a matter of concern and LBM use has been justified for vehicles traveling very long distances non-stop (i.e., trucks or marine ships).

13.5.4 Total Cost of Upgraded Biogas as Transport Fuel

Total cost of bio-methane supply for vehicular applications is the summation of the costs mentioned above, which typically can vary between US$0.28–1.94/m^3 CH$_4$, depending on the type of feedstock material used (see Fig. 13.12). The data presented in Fig. 13.12 are valid for central European countries, where environmental and safety regulations are stricter, labor costs are higher and high-end technology is generally used. These figures may vary in other parts of the world, depending on local conditions. Capacity of biogas plant is found to have a more dominant impact on the total cost for bio-methane as a transport fuel, while the effect of adopted technologies may generally have minor importance. Previous studies have concluded that membrane separation and amine scrubbing technology can be somewhat beneficial for plant capacity below 1000 m^3 STP/h, while pressurized water scrubbing is somewhat economical to some extent for plants with relatively larger capacities (>1500 m^3 STP/h) (Miltner et al. 2017).
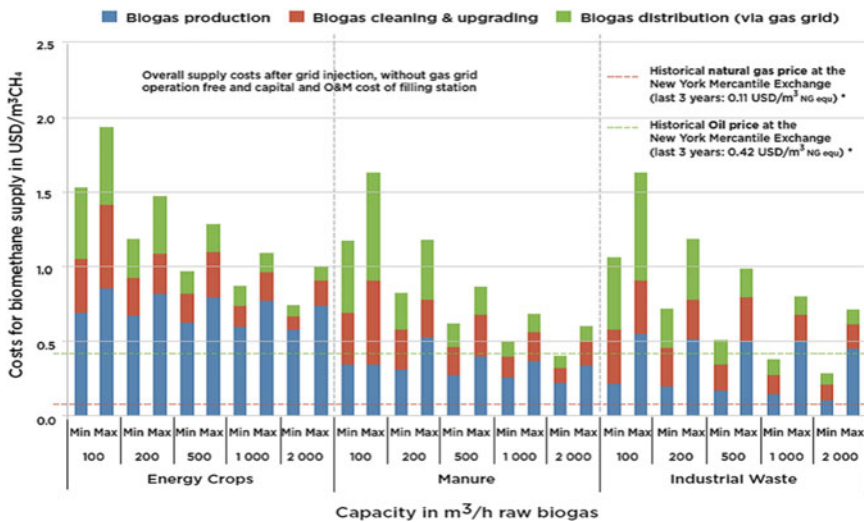

Fig. 13.12 Total production cost of bio-methane as transport fuel as a function of feedstock and plant capacity (IRENA 2018)

13.6 Bio-Methane/Bio-CNG Storage

Bio-methane or bio-CNG storage in compressed form is essential to facilitate easy supply to the consumers for refueling their vehicles operated on bio-methane or bio-CNG. Design and installation of storage systems are quite important since it influences filling efficiency, filling time, charged mass to the consumer's cylinders, safety, and input work of compressors (Farzaneh-Gord et al. 2011). Fortunately, the existing CNG storage systems can quickly be adapted for storing bio-methane preferably in steel air-tight tanks for future usage. Like CNG vehicles, BGV can be fuelled from high-pressure reservoirs at the biogas filling station. Generally, bio-methane or bio-CNG from the distribution pipeline is compressed using a large multi-stage compressor into a high pressure storage system. Either buffer storage or cascade storage systems can be used for storing bio-methane, which are commonly used for storing CNG. The buffer storage system is a single pressure (~20.5–25 MPa) reservoir system and the cascade storage system may include multiple reservoirs of different pressures, typically categorized as low, medium and high-pressure reservoirs (see Fig. 13.13).

In general, the buffer system is characterized by a high mass flow rate, which facilitates fast filling compared to cascade system. Buffer storage system is therefore suitable for light vehicles with fast cylinder filling, while cascade storage system (i.e., slow filling system) is preferable for heavy-duty vehicles (Farzaneh-Gord et al. 2011; Yang et al. 2014; Farzaneh-Gord and Branch 2011). Due to high mass flow rates, the entropy generation in case of a buffer system is higher than that of cascade system, which requires a higher compressor work in the previous case (Farzaneh-Gord et al. 2011). LBM has additional advantages over CBM, since it has three times higher energy density compared to CBM, hence offers extended vehicle autonomy with a much smaller storage space requirement (Annamaria et al. 2018) and can be easily transported via insulated tanker trucks designed for transportation of cryogenic liquids. LBM can be dispensed to either LNG vehicles or CNG vehicles using the existing filling stations.
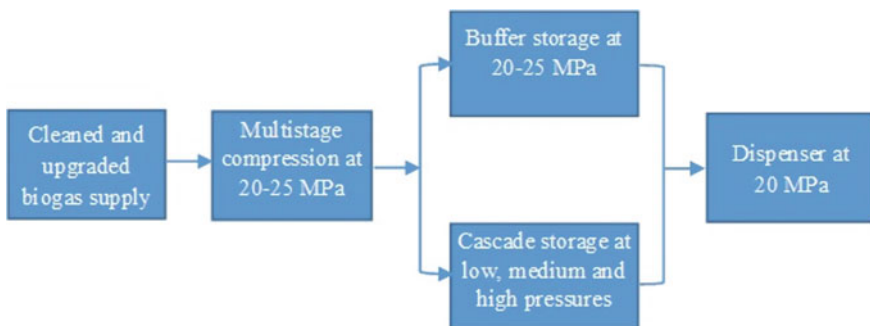
Fig. 13.13 Bio-methane/bio-CNG storage and distribution

13.7 Energy Value of Bio-Methane

It is essential to have an estimation of the energy value of biogas as transport fuel. Since the upgraded biogas has a composition similar to that of conventional NG; it typically has the same or somewhat smaller energy content as compared to NG. Therefore, bio-methane, as a transport fuel provides an equivalent amount of energy, which is more environmentally friendly compared with biodiesel or ethanol (NGVA http://www.ngvaeurope.eu/downloads/fact-sheets/2020). A comparative analysis of the average range of passenger cars fueled by bio-methane in comparison to other biofuels is given in Fig. 13.14. The data of biofuels presented in the figure are from Central Europe and based on an average yield of biofuel per hectare of agricultural land. Figure 13.14 shows that bio-methane sourced from pig manure or MSW or corn has much higher energy value compared to other biofuels such as ethanol or biodiesel.
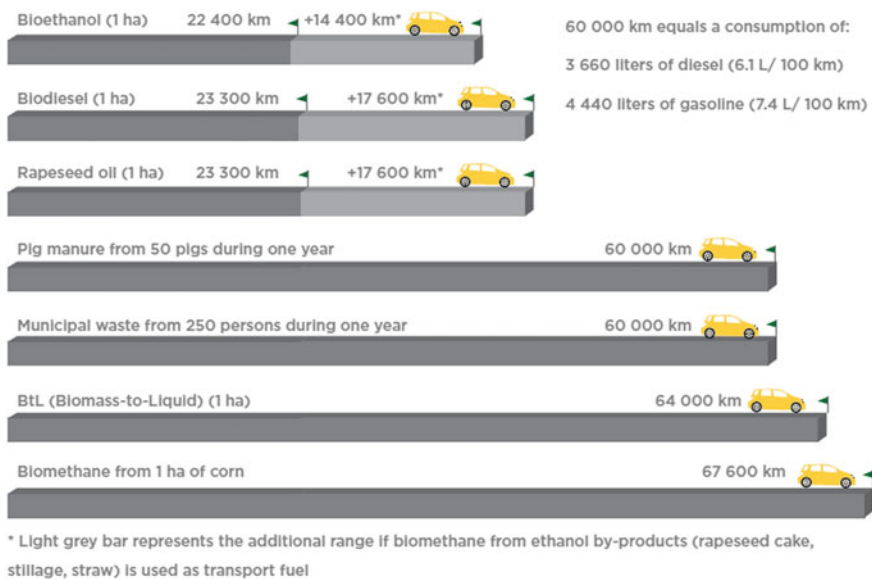
Fig. 13.14 Passenger car driving ranges for different biofuels. Feedstock to biogas conversion rate is estimated as (i) municipal waste: 300 m^3 biogas/ton of dry matter containing 55% CH$_4$ from 350 kg organic waste/capita/year consisting (40% dry matter and 80% digestible); (ii) pig manure: 26 m^3 of bio-gas/ton/year containing 60% CH$_4$ from 6 ton of manure/pig/year. The estimations also considers that the generated biogas is expended for digester heating (15%), meeting electrical energy demand (8%) and methane losses (1%) (IRENA 2018)

13.8   Biogas Utilization to Vehicles

Upgraded biogas, either in the form of CBM or LBM is considered as a renewable alternative to conventional fossil fuels that can suitably fuel different category of vehicles including light-duty vehicles, transit buses, heavy-duty trucks, etc. Use of bio-methane as a vehicle fuel is thus a promising solution to the current environmental issues, since it can potentially reduce GHG emissions compared to conventional transport fuels and can reduce dependency on imported petroleum based fuels (Anderson 2015). Bio-methane possessing a similar quality to NG can operate NG vehicles without specific requirements. However, bio-methane is a low energy density fuel by volume compared to gasoline (1L gasoline is equivalent to 4 L of CBG at 200 bar or 1.7 L of LBM) (Larsson et al. 2016).

Gasoline vehicles can either be operated in bi-fuel mode or only in gas mode. Bi-fuel conversion is simply done by integrating a second fuel supply system for biogas consumption, while the other mode requires a simple conversion to run as a dedicated gas engine. In both cases, storage cylinders for bio-methane are incorporated to the existing fueling system, incurring an additional cost for the vehicles. Current vehicles can be retrofitted for bi-fuel or gas only mode operation for bio-methane applications.

A gasoline vehicle can be easily converted to a gasoline bi-fuel vehicle by using commercially available conversion kit, which usually consists of fuel storage cylinders, fuel lines, a regulator, and a fuel-air mixer. Bi-fuel vehicles can easily switch over between gasoline and natural gas or bio-methane via a switch on the dashboard. Since methane has a higher octane number than gasoline, bio-methane operated engines can be operated at a higher compression ratio, leading to slightly better thermal efficiency than gasoline operation (IRENA 2018). Dedicated bio-methane vehicles can be optimized for superior thermal efficiency. Significant advantage of using bio-methane is that the CO_2 emission can be reduced by up to 99% if electricity is consumed for biogas upgradation and compression, it is generated from biogas or any other green resource. For instance, electricity is almost free of CO_2 emissions in Sweden and Switzerland, which are known as the leading biogas producing and utilizing countries in the world. It has been reported that in addition to CO_2, NO_x and Non-Methane Hydrocarbons (NMHC) emissions also decrease significantly for bio-methane operation (Papacz 2011).

Diesel vehicles, on the other hand can operate in dual-fuel mode for biogas fueling and consume diesel as pilot fuel and biogas as primary fuel simultaneously. Such dual fuel operations mainly at high engine loads hold a promise of diesel-like or somewhat better efficiency. Like gasoline engines, dual fuel system also requires limited engine modifications and the possibility to run on 100% diesel fuel as a backup, which is its major advantage. Typically, in dual fuel operation, 60–65% diesel is replaced by biogas and thus can contribute to GHG emission reduction significantly. Particulate matter emissions from bio-methane fueled vehicles are generally reduced considerably compared with modern diesel engines equipped with particle filters (Papacz 2011; IRENA 2018).

13.9 Research Studies on Biogas Fueled Vehicles

Several research studies confirmed that the use of bio-methane or RNG in vehicles can reduce GHG emissions substantially compared to fossil diesel or CNG operation (Ryan and Caulfield 2010; Bordelanne et al. 2011; Subramanian et al. 2013). For instance, Ryan and Caulfield (2010) examined the effectiveness of using bio-methane (bio-CNG) and CNG for part of the bus fleet in Dublin, Ireland aiming to reduce both GHG emissions and exhaust pollutants. Bio-CNG showed a similar trend of emissions reduction obtained for CNG operation, except CO_2 emissions. CO_2 emissions reduced by ~64 and ~60% for bio-CNG operation compared to diesel and CNG operations respectively. For a gasoline hybrid vehicle (Toyota Prius CNG Hybrid prototype; a natural gas thermal engine with hybrid electric motorization), Bordelanne et al. (Bordelanne et al. 2011) reported that GHG emission levels reduced by ~87%, when fueled by bio-methane in comparison to gasoline baseline operation. This study also showed that with dedicated CNG engines and using lean CNG combustion technology, raw biogas (up to 70% CH_4 v/v) can be used directly if it is blended with NG without major difficulties. However, as it has already mentioned that though it is possible to use raw biogas for fueling stationary engines, it is not suitable for vehicular applications, since it has several issues including compression and storage in the cylinders, low energy density (unsuitable for long distance travels), low flame velocity (because of diluent CO_2), longer ignition delay, and very high HC emissions (Mustafi et al. 2013). GHG emissions from passenger vehicles operating on bio-methane and other biofuels, and conventional petroleum fuels in order to realize the potential of bio-methane in reducing GHG emissions is shown in Fig. 13.15.
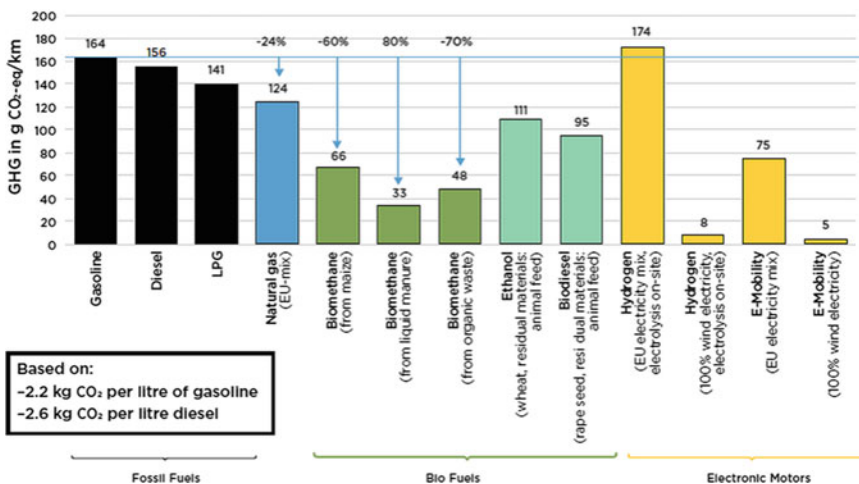

Fig. 13.15 GHG emissions from passenger cars running on bio-methane compared to other fuels (IRENA 2018)

Subramanian et al. (2013) concluded that enriched biogas (bio-methane, 93% CH_4) exhibiting similar performance and emissions levels to those of CNG vehicles could be suitably used as fuel for SI engine powered vehicles. The transient emissions measurements on a chassis dynamometer under MIDC revealed an insignificant difference in fuel economy and the concentration of CO, CO_2 in the exhaust from CNG and bio-methane operations, but a slightly higher NO_x and HC emissions in the latter case. Since CNG or bio-CNG contains almost zero sulfur, generally no SO_2 was present in the exhaust. Bio-methane operated vehicles were also free from heavy metal emissions. Substantial reduction (>80%) of both NO_x and PM emissions from CNG or bio-CNG operation compared to baseline diesel operation were reported in previous studies except non-methane VOC emissions, which increased by ~60% compared to baseline diesel operation (Ryan and Caulfield 2010). Similar results of lower NO_x but higher VOCs emissions were also reported by Lim et al. (2015), when a city bus fueled with upgraded biogas (97% CH_4) and different natural gases (CH_4 content varied from 81 to 91%). The bus was tested on a chassis dynamometer under the ETC and the NIER-6 cycles for investigating fuel economy and exhaust emissions, as shown in Fig. 13.16a–d.

Though bio-methane has somewhat lower heating value than CNG (91% CH_4 along with other large hydrocarbons), bio-methane fueled vehicle show insignificant variations in fuel economy compared to CNG operation but a relatively higher UHC
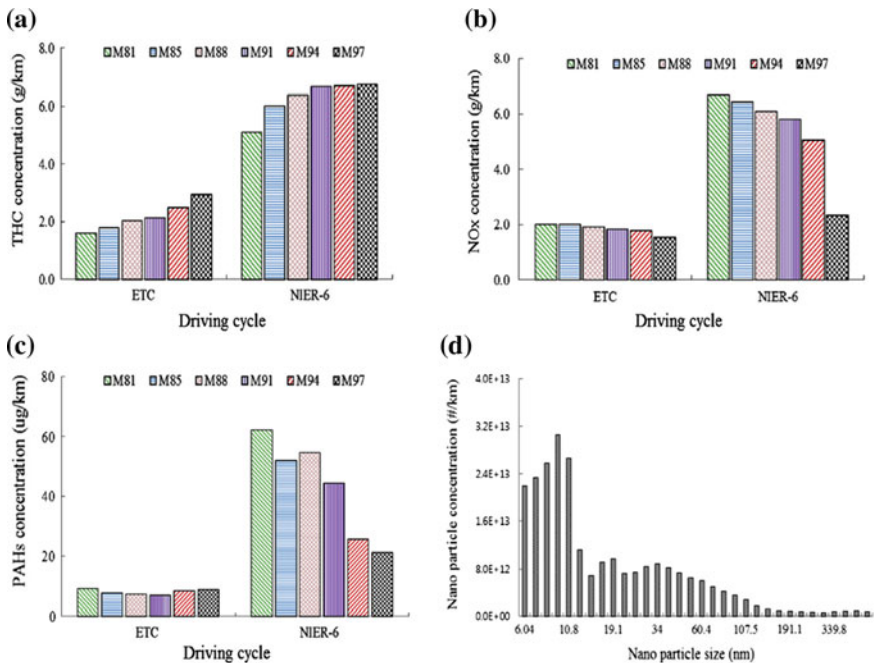
Fig. 13.16 a–d Emissions of THC, NO_x, PAHs, and Nano-particles number-size distribution for bio-methane and different CNG fuels under different driving cycles (Lim et al. 2015)

emissions (Fig. 13.16a) due to relatively lower combustion heat energy release and inferior completeness of combustion compared to low methane content NG. Lim's study (Lim et al. 2015) confirms that bio-methane (usually containing >95% CH_4) can effectively reduce NO_x emissions from a diesel/CNG bus. In this study, it was observed that as CH_4 content in the test fuel increased, NO_x emissions decreased proportionately for both test cycles. Fuels with lower CH_4 content had higher contents of other hydrocarbons (C_2H_6 and C_3H_8), leading to higher heat release during combustion and as a result, it produced more thermal NO_x. Figure 16b showed that vehicle speed may have impacts on NO_x emissions too; slower vehicle speeds (~19.9 km/h for NIER-6 cycle) increased residence time, resulting in higher NO_x formation compared to higher vehicle speeds (~58.9 km/h for ETC cycle). Figure 16c showed that as the methane content in test fuels increased, PAH emissions decreased significantly, indicating lower health hazards potential in case of bio-methane fueled vehicles. Relatively higher emission of Nano-particles was reported for bio-methane operation compared to CNG operation as shown in Fig. 16d. This was attributed to higher VOC emissions in the case of bio-methane operation as discussed above. Particulate number-size distribution followed a bi-modal distribution with a NM peak at <10 nm and AM peak at ~30 nm (Lim et al. 2015).

13.10 Case Studies

Sweden is a country, which has made substantial progress in the exploitation of biogas and is a leading country in using upgraded biogas as a transport fuel. In 2010, ~44% of total biogas produced was upgraded and used as a vehicle fuel, with capacity increasing at a rate of ~20% per year (Biogas in Sweden 2011). At the end of 2014, ~60% of total bio-methane produced was supplied as fuel for 50,000 vehicles, including >2700 buses (Lowry 2016). During the first half of 2018, statistics revealed that bio-methane had a share of 90.8% in total gas consumed in vehicles (Sherrard 2018).

Biogas as vehicle fuel in Kristianstad—Sweden
Upgraded biogas (containing >97% CH_4) or bio-methane energized cars, lorries, and buses in a town named Kristianstad of Sweden. Biogas was produced from co-digestion of 70,000 tons of wastes (50% liquid manure, 45% food industry wastes and 5% household wastes) annually. All buses moving around the town and some school buses were fueled by bio-methane. In 2005, ~1.2 million Nm^3 bio-methane was consumed as transport fuel in Kristianstad, which saved ~1.3 million liters of petrol (Persson et al. 2006).

100% biogas-fuelled public transport in Linköping, Sweden
The Linköping biogas plant produces 4.7 million m^3 of upgraded bio-gas (>97% CH_4) annually from the treatment of slaughter-house waste and industrial organic waste. Since 2002, urban transport fleet (consisting of 65 city buses) and many heavy- and light-duty vehicles have been operating on bio-methane, leading to a reduction of

CO_2 emissions exceeding 9000 tons/year. In addition to on-road vehicles, world's first biogas train became operational in Linköping in 2005, which had a storage capacity for 530 Nm^3 bio-methane with an operating range of 600 km (IEA bioenergy Task 37. http://www.iea-biogas.net/files/daten-redaktion/download/linkoping-final.pdf).

Bio-methane operated transports in the French city of Lille
The first four city buses fueled by bio-methane were introduced (produced from sewage treatment plants) in 1994. In 2006, the city metropolitan area became the coordinator of the Biogasmax program with an aim of demonstrating biogas derived from wastes as transport fuel. The project resulted in 4 million m^3 of biogas production annually and currently all 430 buses of Lille are fueled by biogas (partially mixed with NG). Some part of the excess biogas is fed into the local gas network and is used for powering waste collection trucks (Lowry 2016).

Indian Initiatives for Compressed Biogas (CBG) for vehicles
Aiming to achieve the target of increasing the contribution of NG in nation's energy mix from existing 6.5–15% by 2022, the Sustainable Alternative Towards Affordable Transportation (SATAT) initiative was launched in October 2018 by the Ministry of Petroleum & Natural Gas (MoPNG), GoI (https://www.businesstoday.in/top-story/5000-compressed-bio-gas-plants-will-be-set-up-by-2023-says-dharmendra-pradhan/story/301346.html). SATAT identified CBG as one of the most promising alternative green fuel for country's transport sector, which can meet its rising demands for petroleum fuels. Under SATAT initiatives, CBG projects are being implemented, which would revolutionize country's transport sector by reducing dependence on imported petroleum fuels as well as reduce the air pollution in urban areas. According to an announcement by the MoPNG, more than 5000 CBG plants are to be built across India by 2023 (http://pib.nic.in/newsite/PrintRelease.aspx?relid=183842). As per an estimate, the total CBG potential in India from various feed-stocks including agricultural residue, municipal solid waste, sugarcane press mud, distillery spent wash, cattle dung, sewage treatment plant waste, and food and vegetable wastes is ~62 MMT (CBG https://www.iocl.com/download/White_Paper_EOI_1.pdf). These CBG plants are aimed to produce ~15 million tons of CBG annually, which can significantly cater to annual national CNG demand. The policy supports for successful implementation of CBG project are presented below (https://www.businesstoday.in/top-story/5000-compressed-bio-gas-plants-will-be-set-up-by-2023-says-dharmendra-pradhan/story/301346.html; http://pib.nic.in/newsite/PrintRelease.aspx?relid=183842; CBG https://www.iocl.com/download/White_Paper_EOI_1.pdf).

- In 2015, Ministry of Road Transport and Highways (MoRTH), GoI, already permitted use of bio-CNG or CBG for vehicles as an alternate composition of CNG. Consequently standards for CBG were adopted.
- GoI has released National Policy on Biofuels-2018, emphasizing the pro-motion of advanced biofuels including CBG.

- The Galvanizing Organic Bio-Agro Resources Dhan (GOBAR-DHAN) scheme was launched by GoI to produce Bio-CNG/CBG and compost from cattle manure and solid wastes in farms. GOBAR-DHAN scheme proposed to cover 700 projects across the country in 2018–19.
- Ministry of New and Renewable Energy (MNRE), GoI has also announced Central Financial Assistance (CFA) for bio-CNG/CBG projects.
- Technology choice for CBG projects will remain free of restriction, and GoI is incurring Rs. 75,000 Crore (~10.5 billion US$) capital expenditure for setting up infrastructure for City Gas distribution network.
- Under the National Policy on Biofuels-2018, the pricing model for CBG is being finalized. Oil marketing companies have to dispense CBG at Rs. 46.00 (~US$0.66) per kg, excluding GST. CBG plant owners would be able to sell by-products, such as bio-manure and pure CO_2 separately.

Under the SATAT initiative, CBG plants would be setup mainly by independent entrepreneurs. To initiate the CBG program, public-sector oil marketing companies namely Indian Oil Corporation Ltd., Bharat Petroleum Corporation Ltd. and Hindustan Petroleum Corporation Ltd. have already sought expression of interest from potential entrepreneurs to setup these plants across the country using already mentioned biomass resources (EOI http://gailonline.com/pdf/others/Invite%20for%20EOI_13.pdf; EOI http://www.hngpl.in/Admin/Attachments/Invite%20for%20EOI_3.pdf). CBG would be delivered to the consumers in two ways: using the existing and/or new city gas distribution networks and by biogas bottles like CNG or LPG cylinders. Producers and/or sellers will deliver CBG (within 25 km) at a public retail outlet and/or at stand-alone selling point, through cascades.

Other bio-methane transportation projects around the world
In the UK, a pilot route for biogas (derived from MSW and sewage wastes) operated buses between Bristol airport and Bath city center was opened in 2015. Other European cities such as Bergen and Oslo in Norway, Tartu, and Tallinn in Estonia, Kaunas in Lithuania, Rzeszow, and Torun in Po-land were involved in Baltic Biogas Bus program between 2009 and 2014 with an aim to clean up the urban transport. In 2015, city authorities of Bergen, Norway launched a first-ever electric-biogas hybrid bus—a 24-m-long combination of a tram and a bus. Besides these cities, biogas operated vehicles also have shares in urban transports in cities of Germany, Denmark, and Switzerland.

Around 33 wastes to bio-methane or renewable NG (RNG) projects for green transportation are currently operating in 15 different states in the US, which can supply RNG transportation fuel in quantities as much as ~480 million Ethanol Gallon Equivalent (EGE) annually (as per 2018 statistics). The applications include on-site fueling of public and private CNG vehicles, fueling NG buses and refuse trucks, long-haul delivery trucks of the farms (Lowry 2016; Tomich 2016).

13.11 Barriers for Biogas Adaptation to Road Vehicles

Although bio-methane as a fuel for vehicular applications has tremendous potential, its adaptation as vehicle fuel faces barriers, which are yet to overcome. There are concerns regarding bio-methane production, its distribution, vehicle conversions for biogas adaptation, consumer behavior, associated economic risks, fuel market, country-specific policies, etc. These are detailed below:

- Although biogas production is attractive due to its manifold benefits, production of bio-methane is a matter of concern as it requires significant investment, use of complex systems, high technological skills for installation, operation and maintenance, and requirement of additional energy supplies.
- Availability of biomass feedstock is generally decentralized, which in many cases can limit biogas production capacity or can raise high transportation needs. Either of these can result in high biogas production costs.
- Bio-methane production costs can be sufficiently high since it depends on biogas quality and quantity, technology adopted for biogas purification and upgradation, plant location, country-specific policies (developing country and developed country cases), etc. Therefore under today's conditions, bio-methane supply as fuel can be relatively more costly as compared to conventional fossil fuels.
- Lack of awareness among politicians and public about the benefits of biogas as a renewable energy source for transportation is a significant impediment for gaining adequate supports from the possible stakeholders.
- The long term economic gains by using NG or bio-methane operated vehicles in comparison to petrol or diesel vehicles are often not known by the costumers.
- Existing infrastructure for NG operated vehicles can potentially be shared by bio-methane operated vehicles. However if such infrastructure (gas grid, filling stations, NG vehicles) does not exist, development of an entirely new infrastructure of biogas fuel adaptation for road vehicles may become challenging.
- Even with existing infrastructure for NG vehicles, lack of appropriate regulations regarding the access to gas grid may hinder biogas fuel adaptation.
- Biogas being a gaseous fuel may not attract the drivers and consumers who use conventional liquid petroleum fuels. Technical limitations including driving range, space in the car occupied by the large size gas cylinder, which may get highlighted in comparison to conventional liquid fuel operation.
- Lacking sustainable and effective regulatory frameworks often fail to convince stakeholders for biogas based project investments.
- Existing structures and stakeholders either in fuel market or vehicle mar-ket often do not authorize a new member to enter.
- Lack of awareness of air pollution problems caused by vehicles, particularly in urban areas that can oblige the customers to look for greener fuels such as biogas for vehicles.

- Lack of awareness of waste management department regarding effective and environment friendly ways of waste disposal as well as waste-to-energy themes often veils the importance of biogas production and its applications.
- Lack of funding, and financial support for the investors and customers to adopt biogas as fuel for vehicles.
- Lack of indigenous technology, skilled labor, and adequate technical support often inhibits the adaptation of new technologies such as bio-gas/bio-methane production and its usage as transport fuel.
- Availability of other alternative solutions for eco-friendly transportation, such as bio-alcohols, and electric vehicles.

13.12   Path Forward for Adaptation in Road Vehicles

Despite currently increasing growth rate of bio-methane fueled vehicles worldwide, exploration of its full potential is yet to be achieved. Although negative impact of using petroleum based fuels are well-understood, they are still much cheaper and readily available compared to alternative bio-fuels. Recent developments in bio-methane application as transport fuel are mainly concentrated in EU countries therefore their valuable experiences and practices should be spread out worldwide. Previous section has identified possible barriers to overcome for adaptation of bio-methane as vehicle fuel. Various approaches including appropriate and effective policy formulation, setting rules and regulations, arranging adequate financial and technological support etc. are required to develop bio-methane based vehicle market worldwide as described below:

- Waste biomass sources are generally scattered (especially for agricultural wastes or animal byproducts) therefore instead of installing source specific biogas plants, co-digestion using a different possible combination of feedstocks must be permitted in order to setup plants for a reasonable gas production capacity. This can not only reduce biogas production cost but also contribute to bio-methane supply at a competitive price. Respective authority can impose necessary regulations for development and implementation of such schemes.
- Cost of biogas as a vehicle fuel is the most critical issue to stimulate fuel market. Government should offer some economic incentives along with short-term subsidies for lowering the fuel cost, which may become essential in today's perspective. Lessons can be learned from EU practices regarding these financial supports for the customers. For instance in Sweden, several financial incentive schemes such as tax exemptions, investment grants under the LIP and subsequent Climate Investment Program (KLIMP) have been provided for biogas based transport sector development. KLIMP program provided significant financial supports (EUR 66 million over six years), where gas production, its infrastructural development, and biogas based transports shared 55, 28 and 12% of the funding respectively (Larsson et al.

2016). The main features of the financial incentives can be summarized as below (IRENA 2018; Ekman 2012):

- no CO_2 or energy tax on biogas for a specific period,
- clean car subsidy (€1100),
- 40% reduction in income tax for the use of company gas vehicles,
- five-year exemption from vehicle tax for clean cars (on average €660 in total),
- free parking benefits in many cities,
- Stockholm congestion tax exemption,
- providing investment grants for new technologies and solutions to biogas based transportation, such as investment support for farm-based biogas,
- climate-investment grant for municipalities towards biogas/bio-methane productions,
- gas stations grant, and
- a fixed financial bonus for biogas production from manure to reduce CH_4 emissions.

- Respective authorities should arrange necessary campaign programs identifying both the short term and the long term benefits of biogas as vehicle fuel via all media types, seminar, symposium, etc. to promote the technology and to convince potential stakeholders and consumers for its development and implementation. Following messages in terms of benefits of biogas applications can be conveyed:

  - possible reduction in GHG emissions including NO_x and PM, and noise for use as vehicle fuel;
  - biogas technology is a wonderful solution to waste disposal problems: utilizes and treats organic wastes and residues and thus prevents ecological damage and closes the material cycle;
  - supply of nutrient organic fertilizer free-of-cost which can substitute mineral fertilizer thus saving energy and environment;
  - substitution of imported petrol and diesel fuels leading to savings of foreign currency as well as reduction in GHG emissions;
  - socio-economic benefits: job opportunities creation, minimizing health risks, income tax, etc. at local and national level.

- Policies and measures should be adopted for stimulating utilization of biogas as vehicle fuel and green transport, which must comprise regulations such as biofuel mandates and/or emission standards; public procurement related (Choice of cars and other vehicles for use in public sector can be controlled under a policy instrument to make a shift towards renewable fuels and green and energy-efficient vehicles. Sweden has successfully utilized such a policy instrument for public procurement of vehicles without any increment in the life-cycle cost of vehicle fleets in the public sector) (Larsson et al. 2016); economic/financial incentives related to biogas/bio-methane production and vehicular applications should be made on a long-term basis that can guarantee for at least 15–20 years as per payback period of the investment.

- Setting up rules and regulations for biogas quality standards and injection of biogas/bio-methane to NG grid is essential. Bio-methane producers should have priority to access the national gas grid with financial dis-charge.
- Comparative but transparent price list (with units comparable to conventional fossil fuels) should be made available at filling stations so that customers are encouraged to go for bio-methane.
- Incorporating private sector entities is essential and therefore must be encouraged for achieving success in scaling up biogas/bio-methane technologies. Private participation or entrepreneurship must be supported for any new and existing solutions of waste-to-biogas production and its use in the transport sector. In this regard, collecting organic waste fractions separately is quite essential and thus should be given high priority in policy formulation. Political and policymakers' supports are necessary to accept the economic risks associated with bio-methane adaptation as vehicle fuel. These supports are crucial to overcoming the chicken-egg di-lemma (filling station is first, or gas vehicles are first) through proposing different attractive financial incentives for establishing gas filling stations and NG/biogas transports.
- If suitable, LBM projects should be encouraged and promoted as LBG has additional benefits over gaseous bio-methane as vehicle fuel.
- Technology transfer at minimum costs from developed to developing nations can play an essential role in developing such projects in other parts of the world, where biogas production potentials are high and NG infra-structures exist.
- Adequate R&D efforts are required to minimize biogas/bio-methane production costs.
- Indigenous technology must be encouraged and developed as it often provides cheaper solutions.
- Formulating national policy to incorporate obligatory biofuel quotas for all companies selling fossil fuels based on minimization of GHG emissions from transport sector and urban air quality improvement.

13.13 Conclusions

Use of upgraded biogas or bio-methane for vehicular applications is highly promising since organic wastes are the feed-stocks for biogas production. Biogas production technology is attractive because it handles organic wastes in an economical way and solves issues such as waste reductions and prevention of GHG (CH_4) emissions to the environment, while providing renewable biogas for multiple applications and nutrient rich organic fertilizer for agriculture. Biogas usage as a vehicle fuel has increased due to environ-mental and health concerns and these vehicles emit potentially low GHG emissions and provide green transport, particularly in cities. Biogas as a vehicle fuel has enormous potentials to substitute fossil fuels such as petrol and diesel and reduce dependence on imported petroleum fuels. Biogas and bio-methane technologies are already matured. However scope is there for further R&D towards minimization

of cost of production. Current technological improvements in biogas upgradation technologies have already made bio-methane cost competitive with fossil fuels for vehicular applications. Use of biogas for vehicular applications has grown in EU countries (such as Sweden, Germany, Denmark, Switzerland, Finland, etc.) due to the availability of various bio-methane support schemes. Many commercial biogas/bio-methane service providers are now available, especially in EU countries. Biogas/bio-methane can be regarded as the most accessible energy resource worldwide since it is derived from wastes. However barriers are there to overcome in terms of cost-effective technology, requirement of significant investments for developing necessary infrastructure, developing biogas fuel as well as gas vehicle market, lack of awareness of advantages of biogas usage as vehicle fuel, etc. Countries which already have NG grids and use NG vehicles are in an advantageous position since bio-methane having desired quality standards can be simply injected into the existing NG grid. Necessary initiatives and efforts are therefore required from the government-private bodies as well as from the waste management organizations to overcome the barriers.

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Chapter 14
CO$_2$ Sequestration in Shale with Enhanced Gas Recovery

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Abstract Shale is an important geological media for carbon capture utilization and storage. On one hand it can be regarded as impermeable caprock to prevent CO$_2$ migration from reservoir, and on the other hand it can also treated as both natural gas and CO$_2$ storage reservoir. CO$_2$-shale reactions within caprock can interfere with the integrity of the rock integrity and compromise the long-term carbon storage safety and stability; however this interaction can also improve the conductivity of the rock to enhance the shale gas recovery from the organic-rich shale. This chapter presents a review of the current state of knowledge regarding CO$_2$ and shale interactions and their potential impacts on shale properties and groundwater quality in the context of CO$_2$ enhanced shale gas recovery. The characterization of shale and CO$_2$ which is critical to the understanding of various interactions between CO$_2$ and shale is first summarized. The major interaction mechanisms between CO$_2$ and shale including CO$_2$-shale-water geochemical reactions, CO$_2$ adsorption induced clay swelling and organic matter extraction with supercritical CO$_2$ and their impact on rock porosity and permeability, and mechanical properties, gas adsorption capacity and groundwater quality are surveyed. Finally, the open questions in this field are emphasized and new research needs are highlighted.

Keywords CO$_2$ enhanced shale gas recovery · CO$_2$-shale interaction · Porosity and permeability · Mechanical properties · Adsorption capacity · Groundwater quality

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14.1   Introduction

Carbon capture utilization and storage, as a critical tool in addressing the global climate and energy issues, can not only significantly reduce emissions from power generation but can also provide a significant emission reduction strategy for key industrial processes including steel, cement and manufacturing (International Energy Agency, https://www.iea.org/topics/carbon-capture-and-storage/). Shale is a low-permeability and low porosity rock containing abundance of oil/gas reserves which has large potential for long term CO_2 storage. It is widely distributed all around the world and is considered as an important geological media for carbon capture utilization and storage.

Shale can be regarded as caprock for long-term CO_2 storage due to its low hydraulic conductivity and its excellent ability to prevent CO_2 leakage from the reservoir. However, the shale with organic-rich gas can be also treated as CO_2 storage reservoir due to its high adsorption affinity to CO_2 relative to CH_4. CO_2 is stored in the shale reservoir by adsorption while CH_4 is replaced and desorbed from the shale matrix and migrates towards the production well simultaneously enhancing the shale gas recovery ratio. Furthermore, the supercritical CO_2 or liquid CO_2 can be used as a fracking fluid. Due to its low viscosity, high diffusivity and anhydrous property, fracturing with supercritical CO_2/liquid CO_2 is much superior to hydraulic fracturing in stimulation of shale reservoir. Due to the win-win advantages of mitigating the CO_2 emissions from the atmosphere through its permanent storage in shale as well as enhancing the shale gas recovery (Fig. 14.1), CO_2 enhanced shale gas recovery technology has attracted a great deal of attention in recent years.

It is well known that the interaction between CO_2 and caprock can affect caprock's integrity and therefore compromise the long-term CO_2 storage security and stability. Reactions among CO_2, brine, and caprock and associated impacts on flow paths and hydraulic properties of the rock have been researched extensively. For example, Shukla et al. (2010) have reviewed the impact of CO_2 injection on caprock integrity by mainly considering the geophysical aspects. They discussed the stability response of the caprock during and after CO_2 injection and systematically analyzed the impact of pre-existing fractures and re-opened cracks. Griffith et al. (2011) presented a review of caprocks across the U.S. considered for pilot and large-scale demonstration projects for CO_2 capture and storage focused mainly on structural, petrophysical, and chemical characteristics. Liu et al. (2012) also conducted a short review on the geochemical aspects of the injected CO_2 on caprock integrity.

The efficiency of the fracking process is dependent on the retention of permeability generated through fracturing. Reaction of the host shale rock with the fracking fluid or brine can cause the formation of new phases such as swelling clays and precipitation minerals. These new phases can block porosity and lead to sudden reductions in production rates. The shale gas enhancing efficiency with CO_2 injection is mainly controlled by the rock preference adsorption capacity of CO_2 over CH_4. The CO_2 interaction with rock can impact the organic geochemical properties of shale so as to interfere with its adsorption capacity to different gases. Thus, CO_2-shale interaction
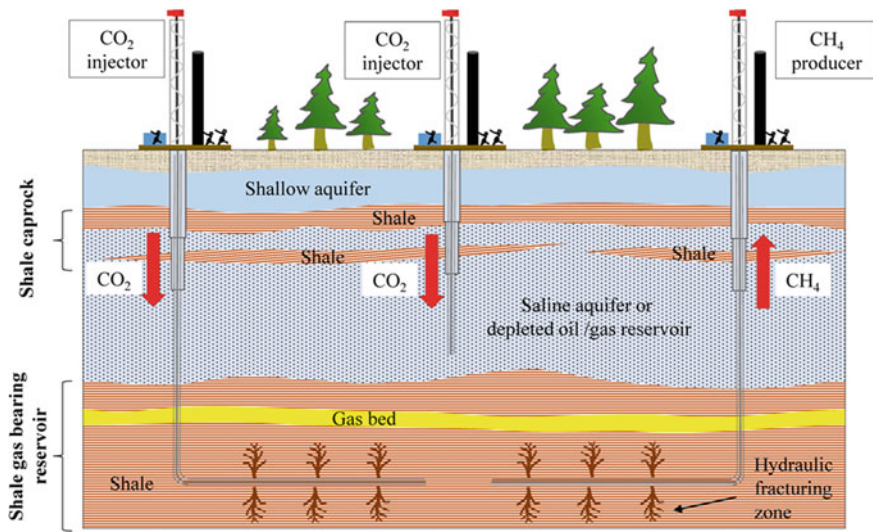
Fig. 14.1 The utilization of shale in the context of CO_2 capture, storage and utilization. Shale, as low permeability rock, is conventionally regarded as the caprock for CO_2 storage in deep saline aquifer or depleted oil/gas reservoir. In shale gas reservoir, CO_2 can be injected to stimulate the reservoir as well as to store it permanently

is critical for CO_2-ESGR (Enhanced Shale Gas Recovery). However, the coupled geochemical-mechanical-adsorption properties change in response to CO_2 injection in the organic-rich gas shale.

This paper reviews the current state of knowledge regarding CO_2 and shale interactions and their potential impacts on shale properties and groundwater quality in the context of CO_2 enhanced shale gas recovery (ESGR). First, we summarize the characterization of shale and CO_2 which is critical to the understanding of different interactions between CO_2 and shale. Then three major mechanisms including CO_2-shale-water geochemical reactions, CO_2 adsorption induced clay expansion, and organic matter extracted by supercritical CO_2 are discussed. The impact of these effects on shale properties such as porosity, permeability, mechanical properties and gas adsorption capacity are surveyed. Finally, we highlight the present research progress on understanding the effect of CO_2-shale interaction on groundwater quality.

14.2 Properties of Shale and CO$_2$

14.2.1 Shale

Shale is a typical sedimentary rock composed of both the organic matter and inorganic matter. Among the organic matter, kerogen and asphaltene are regarded as the major adsorbing medium for the adsorption gas in the shale reservoir (Zhao et al. 2017; Xiong et al. 2017). Among the inorganic matter, clay mineral, quartz, calcite and feldspar all play important roles (Liang et al. 2014; Yang et al. 2015). The total organic carbon content is one of the critical factors that control the gas adsorption ability of shale, while the mineral composition affects the gas containing potential of shale (Ross and Bustin 2009).

Very low permeability and porosity is another prominent characteristic of shale. The particle size of the shale reservoir is quite small and it is mainly made up of silt with size <5 μm and mud or sand with a size in the range 5–60 μm (Tan et al. 2014; Mokhtari and Tutuncu 2015; He et al. 2017). It has been reported that the average porosity of shale is less than 10%. The average porosity of shale in the USA is between 2.5 and 6.6%, while the average porosity of marine shale from the Southern China is less than 4% (Mokhtari and Tutuncu 2015). The permeability of shale is also quite low which varies within the range of nano-Darcy and is two orders of magnitude lower than a typical sandstone reservoir, e.g. the permeability of marine shale from Southern China has been found to be less than 20.2 nano-Darcy (Tan et al. 2014).

The pore structure of shale is the deciding factor of shale gas adsorption properties. Based on the size of pore diameter, the pore in shale can be divided into three types according to the handbook of International Union of Pure and Applied Chemistry (IUPAC): (a) Micropore, diameter <2 nm, (b) Mesopore, 2 < diameter <50 nm and (c) Macropore, diameter >50 nm (Li et al. 2015). The pore in shale can also be classified as mineral pore, organic pore and fracture-typed pore according to its morphology and location as shown in Fig. 14.2. It has been reported that the presence of a large number of organic nanoscale micro-pores is the main controlling factor in shale gas accumulation.
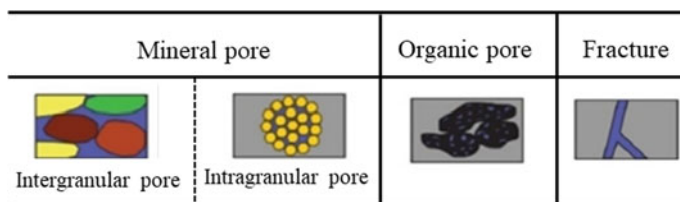
Fig. 14.2 Pore-types of shale: There are mainly three types of pores in shale which include the mineral pores that can be divided as intergranular pore and intragranular pore, organic pore and fracture-type pores
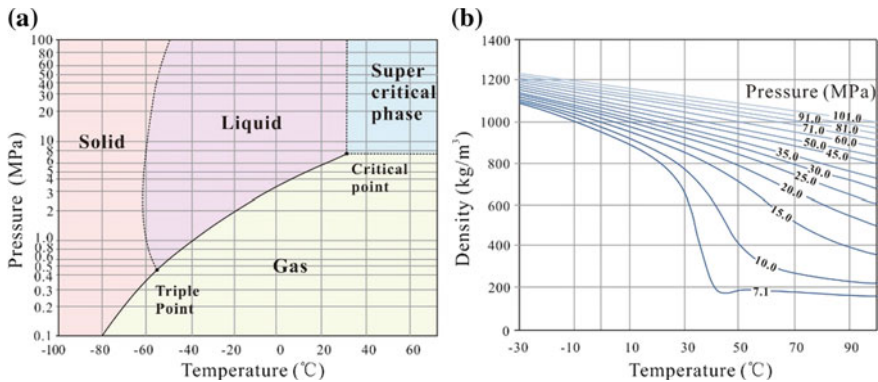
Fig. 14.3 **a** CO_2 phase diagram, the critical point for CO_2 transfer from liquid or gaseous phase to supercritical phase is at temperature of 31.1 °C and pressure of 7.38 Mpa; **b** CO_2 density at different temperatures

14.2.2 CO₂/Supercritical CO₂

As a colorless and odorless gas, the carbon dioxide (CO_2) is ubiquitous in nature, whose content is about 0.03–0.04% in the atmosphere. However, the content of CO_2 in atmosphere is increasing gradually with emissions from burning of fossil fuels in power plants and industry resulting in the global greenhouse effect. The nontoxicity, noninflammability and gaseous state of CO_2 make it a widely used chemical in many industries. With variation of temperature and pressure, it can go through several phase states as shown in Fig. 14.3.

CO₂ exists in supercritical phase when the temperature and pressure exceed the critical value of 31.1 °C and 7.38 MPa. Different from either liquid CO_2 or gaseous CO_2, the supercritical CO_2 has low viscosity and high diffusivity like gas but density similar to liquid CO_2 and has the ability to dissolve certain substances (Zhou et al. 2003). The surface tension of supercritical CO_2 is quite low close to zero, which enables the supercritical CO_2 to penetrate easily into the microstructure in shale. Furthermore, supercritical CO_2 is also a non-polar solvent. It can dissolve lipids, volatile mater, and some other smaller molecular weight substances in the reservoir.

14.3 Interaction of CO₂ and Shale

Due to the reactivity of CO_2 and special properties of shale, the injection of supercritical CO_2 into the gas-bearing shale can induce many reactions not only on minerals but also on organic matters which impact the shale properties. Injected CO_2 is present in supercritical or gas phase in shale for the purpose of fracturing or long-term storage. It dissolves into pore water and creates carbonic acid which interferes with

the mineral reactions. The supercritical CO_2 can interact with the organic matter to reshape the organic microstructure of shale thereby affecting its adsorption capacity. Furthermore, molecular CO_2 can adsorb from its supercritical or water phase onto clay surfaces within the interlayer spaces and can displace water. This process can result in shrinkage altering the inter-granular pore space and possibly the transport flow paths in shale as well as its mechanical properties.

14.3.1 Interaction of Shale with Anhydrous CO_2

As a non-polar solvent, supercritical CO_2 can interact and dissolve smaller molecular weight organic matter in the shale reservoir. The dissolution of organic matter with supercritical CO_2 is an important factor in both CO_2 fracturing and permanent carbon storage in shale reservoir. The dissolution of organic matter by supercritical CO_2 has been systematically studied in the field of chemical engineering (Naik et al. 1989); dissolution of organic matter from oil shale (Bondar and Koel 1998; Akinlua et al. 2008; Allawzi et al. 2011) by supercritical CO_2 has been used to extract hydrocarbons from oil shale and their yield has been found to depend on the inorganic matrix. In order to provide more accurate information on hydrocarbon yield from supercritical CO_2 extraction, Jarboe et al. (2015) have documented the amount of extractable organic matter in the total organic carbon content of shale after interaction with supercritical CO_2. Their results showed that the hydrocarbon yield was a function of matrix size and the supercritical CO_2 was able to extract diesel-range n-aliphatic hydrocarbons from high maturity shale at reservoir conditions. Jin et al. (2017) carried out the hydrocarbons extraction from Bakken shale at reservoir conditions and found that 15–65% hydrocarbons were extracted by supercritical CO_2. Wu et al. (2015) conducted molecular dynamics simulations to determine the effect of supercritical CO_2 on dissolution of kerogen from oil shale and observed that the dissolving capacity of supercritical CO_2 increased with higher pressure as well as temperature.

Recently, some researchers have also studied the effect of solvent/dissolution property of supercritical CO_2 on organic matter in shale on CO_2 geological storage. Scherf et al. (2011) investigated the organic matter type and content extracted by supercritical CO_2 in the process of carbon storage in a deep saline aquifer and showed that the polar lipid fatty acids and low molecular weight organic acids were extracted. In addition, rock porosity, permeability and mineral composition also impact the extraction efficiency of supercritical CO_2. Kolak et al. (2006) explored the extraction effect of supercritical CO_2 on different ranks of coals and found that the supercritical CO_2 has high extraction ability for alkanes and poly-aromatics and the extraction amount was related to coal rank. Okamoto et al. (2005) showed that CO_2 extraction of organic matter can reshape the pore structure of caprock under supercritical condition, which may adversely affect the CO_2 storage security and stability.

Nevertheless, the extraction of organic matter by supercritical CO_2 plays a positive role in the process of CO_2 fracturing. Jiang et al. (2016) have shown that the

shale gas seepage channels widened during CO_2 injection influencing the extraction of organic matter by supercritical CO_2. Zhang et al. (2017a) observed the promotion of seepage-flow pores in shale with significant decrease in compounds with weakly polar functional groups (but seldom changing the strong polar functional groups) of shale after interaction by supercritical CO_2. Pan et al. (2018a; b) compared the interactions between supercritical CO_2 and two shale samples from the marine Longmaxi formation and terrestrial Yanchang formation in China; their results indicated drastic variations in shale nano-pore structures due to supercritical CO_2 treatment in both the shale samples. They claimed that the chemical reactions in the minerals, the swelling in clay and supercritical CO_2 induced extraction of hydrocarbons were the major cause for this phenomenon. Thomas and Clouse (1990) have reported organic pores are reported to be the major conduits for oil and gas within shales. Thus, the extraction of organic matter from shale by supercritical CO_2 can be helpful for generation of organic pores in shale and for promoting the flow of oil/gas towards production well.

14.3.2   CO₂-Water-Rock Geochemical Reactions in Shale

As one of the water-soluble gas, the dissolution of CO_2 into the formation water can result in its acidification and therefore acceleration of the geochemical reaction during geothermal exploitation as well as in CO_2 sequestration in the reservoir (Liu et al. 2016; Cui et al. 2018). With the development of CO_2 enhanced shale gas recovery technology, many more studies have been conducted to focus on the CO_2-water-rock interaction in shale. Alemu et al. (2011) conducted experiments to study the interaction between CO_2, brine and shale including carbonate-rich and clay-rich shale. Their results showed that carbonate-rich shale was more reactive than clay-rich shale, and the temperature had no significant effect on mineralogical changes in clay-rich shale. The presence of more reactive carbonate was consistent with previous study on supercritical CO_2-sandstone interaction ascribing to the fast dissolution kinetics of calcite and dolomite. Study of carbonate-rich shale with CO_2-charged brine by Ilgen et al. (2018) also provides a powerful evidence for carbonate dissolution.

In addition to carbonate dissolution, the clay minerals such as kaolinite, illite, chlorite and quartz as well as feldspar can also dissolve in weak acidic environment. For example, Liu et al. (2012) found the dissolution of feldspar and anhydrite as well as the precipitation of siderite, illite and smectite during shale-brine-CO_2 interaction at 200 °C and 300 bars. Similarly, Rezaee et al. (2017) have documented the dissolution of potassium feldspar and reduction of illite-smectite mixed layer during shale-brine-CO_2 interaction at 66 °C and 151.7 bar. Luo et al. (2019) have also found that the contents of clay minerals and carbonate minerals decrease when reacting with CO_2, whereas the contents of siliceous minerals increase in the system.

14.3.3   CO₂ Adsorption Induced Swelling in Shale

The clay minerals such as smectite, kaolinite, cholorite and illite that make up the shale are reported to have high capacity of sorption due to their wide internal surface area. The naturally occurring clay minerals consist predominantly of stacks of two-dimensional alumino-silicate sheets which carry a negative charge (Chen et al. 2008; Anderson et al. 2010) and a interlayer space with widths in a nanometer scales contains positively charged cations as shown in Fig. 14.4. The cations in the interlayer determine the likelihood of intercalation or exfoliations of molecules into or out of the clay's lattice which cause clays to swell (hydration) or collapse (dehydration) (Anderson et al. 2010).The alumino-silicate sheets include tetrahedral and octahedral structure and are mainly composed of Al^{3+}, Mg^{2+}, Fe^{3+} and Si^{4+} oxides. Between two aluminosilicate layers, there is an interlayer contained exchangeable Na^+, K^+, Ca^{2+}, etc.

Several studies have reported measurements of swelling in clay minerals induced by CO_2 adsorption. The diffusive transport and gas sorption experiments on shale and clay minerals have shown that the high CO_2 adsorption capacity of shale can be attributed to the clay minerals (Busch et al. 2008). Studying the shale from New Albany, Lahann et al. (2013) discovered the phenomenon of swelling in their CO_2 adsorption experiments. Heller and Zoback (2014) measured the adsorption swelling of carbon, kaolinite and illite, and studied the relationship between gas adsorption
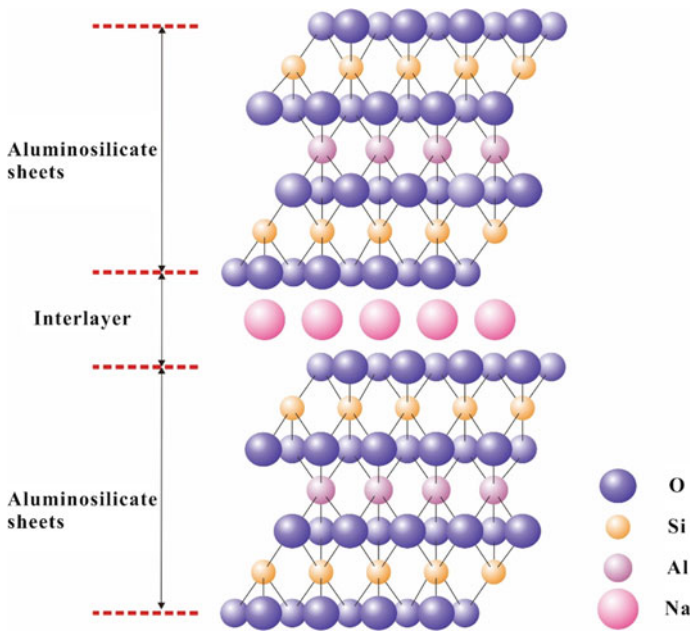

Fig. 14.4 Layered structure and basal unit cell dimension of smectite clay minerals

capacity and the swelling strain of minerals. Schaef et al. (2015) investigated the interaction of hydrated supercritical CO_2 and Na-, Ca-, and Mg-exchanged MMT. Structural volumetric changes were observed; the results indicated that the intercalation of CO_2 was inhibited without the participation of water. The introduction of little water and the partial expansion of the interlayer region could significantly increase the intercalation of CO_2; however it would then gradually decrease with further hydration of clay. Similar observations were also made by Giesting et al. (2012) and Busch et al. (2008).

Many factors impact the swelling effect induced by CO_2 adsorption. Lu et al. (2016) found that the maximum volumetric swelling of shale decreases with temperature and CO_2-induced adsorption is dominant under low pressure while the volumetric swelling under high pressure is mainly affected by the gas pressure. Chen et al. (2018) discussed the relationship of adsorption-induced swelling strain and gas pressure by conducting the shale deformation experiment with helium and methane under constant pressure and at different gas pressures. They also measured the volumetric strain of organic-rich shale with various gas adsorptions and found that the volumetric strain first rose rapidly and then stabilized; it was related to the gas occupying cracks and macropores in the initial stage and filled micropores in the later stage. Bakhshian and Hosseini (2019) built a comprehensive model to study the effect of temperature and pore geometry on CO_2 adsorption of shale. They found that the faster and higher amount of CO_2 adsorption on duct pore compared to slit pore was ascribed to the large attractive surface field and the pore shape as well as temperature had more significant effect on the volumetric strain of mesopores than micropores.

14.4 Effect of CO₂-Shale Interaction on Rock Properties

14.4.1 Porosity and Permeability

Micro-structure of shale can be influenced by CO_2-shale interactions through mineral dissolution and precipitation, adsorption-induced expansion effects as well as organic matter extraction with supercritical CO_2 as shown in Fig. 14.5. Kolak and Burruss (2006) indicated that the extraction of organic matter by supercritical CO_2 was responsible for shale pore volume and increase in specific surface area, and the average porosity enhancements by increase in temperature and pressure were 125.93 and 81.48%, respectively. Similarly, Zhang et al. (2017a) described the extraction of organic matter from Longmaxi shale which was ascribed to the reduction of micropores and fine mesopores. When the ambient temperature and pressure was below the critical point of CO_2, the supercritical CO_2 transformed into subcritical CO_2 resulting in the disparate variation of shale pore structures (Span and Wagner 1996). Pan et al. (2018b) compared evolution of shale pore structures after subcritical and supercritical CO_2 treatment and concluded that different states of CO_2 induce different
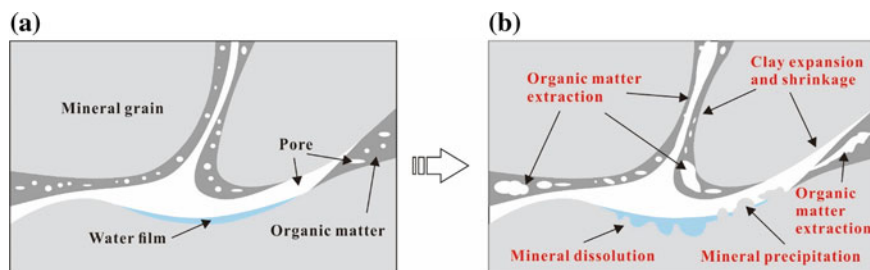
Fig. 14.5 Schematic of the three possible mechanisms responsible for variations in shale microstructure [Revised from Pan et al. (2018a)]. **a** Raw sample and **b** supercritical CO_2-treated sample [Revised from Pan et al. (2018a)]

variations in shale pore structure. Compared to interaction of shale and subcritical CO_2, interaction of shale and supercritical CO_2 can create more pronounced effect on pore structure. Pan et al. (2018a) attributed this phenomenon to greater dissolution, expansion and extraction mechanism associated with supercritical CO_2.

In addition to organic matter extraction with dry supercritical CO_2, mineral dissolution and precipitation can also occur when shale contacts with anhydrous CO_2. Microspore reduction after dry supercritical CO_2 treatment was found by Yin et al. (2016) and Sanguinito et al. (2018). However, in real environment, the injected CO_2 cannot fully displace fluids in the shale reservoir and water always exists in the pores. Research indicates that the shale-CO_2 interaction can be more intensive with water involved in the CO_2-shale system. For example, Goodman et al. (2019) found that the micropores can be completely dissolved during shale-water-CO_2 interaction and generate larger pore volume after reaction compared to anhydrous CO_2 system; it was attributed mainly to the rapid and drastic dissolution of carbonate minerals in water. Furthermore, different mineral compositions of shale result in different types of shale-CO_2 interactions. Zou et al. (2018) found etched pores and cavities on the surface of the shale after shale-water-CO_2 interaction and differences in the mineral composition contributed to various changes in porosity. However, larger dissolved pore of carbonate-poor shale than that of carbonate-rich shale was found after the 168 h treatment, which was related to the high initial porosity and permeability of shale resulting in the easy contact with shale (Yu et al. 2012).

As a key parameter in influencing the mobility of gas flow, the permeability of the reservoir also changes with pore structures after CO_2-shale interaction. Studies have shown that the dissolution of minerals can enlarge the pore volume and increase the rock permeability (Zou et al. 2018; Deng et al. 2015; Soong et al. 2017). However, it has been found that permeability decreases due to the secondary mineral precipitation as well as pore blockage by clay minerals (Yu et al. 2012; Jones and Detwiler 2016). In addition, the asphaltene precipitation and deposition in shale severely decreases its permeability during CO_2 huff and puff injection (Shen and Sheng 2017). The complex composition and pressure change as well as the CO_2 concentration all influence the asphaltenes stability. According to the experiment of Shen and Sheng (2018), 48.5%

reduction in permeability occurred after 6 cycles of CO$_2$ huff-puff injection with 26.8% permeability reduction occurring in the first cycle.

14.4.2   Mechanical Properties

The mechanical properties of shale after exposure to CO$_2$ play an important role in shale gas production and long-term sequestration of CO$_2$. As mentioned before, the injected CO$_2$ can dissolve into water to from carbonic acid which has the ability to dissolve minerals of shale and thereby change its structure and thus affect its mechanical properties. For example, Lyu et al. (2016) measured the variation in uniaxial compressive strength and Young's modulus of shale due to exposure to gaseous and supercritical CO$_2$ and found reduction of 56.43–66.05% in uniaxial compressive strength and 54.21–56.32% in Young's modulus, respectively. Zhang et al. (2017b) also found that reduction in concentrations of Fe, K, Mg, Na, Al, and especially Ca in CO$_2$ saturated and CO$_2$-brine saturated shale resulted in large decrease in its strength and elastic modulus, which demonstrated the relationship between the variations in various minerals in the shale and its mechanical behavior. In addition, the crystal water in shale can combine with CO$_2$ to create acidic environment facilitating the shale-CO$_2$ interaction and influencing the mechanical properties of shale (Liu et al. 2017).

Apart from mineral dissolution, the CO$_2$ adsorption can decrease the surface potential energy of shale and result in its swelling. The supercritical CO$_2$ is more remarkable than subcritical CO$_2$ for reduction in strength and elastic modulus of shale, which is ascribed to the pressure difference for CO$_2$ permeation and CO$_2$ adsorption as well as lower viscosity and negligible capillary force of supercritical CO$_2$ (Lyu et al. 2018). To distinguish the adsorption and gas pressure effects on CO$_2$-induced swelling of shale, Ao et al. (2017) carried out the strain tests on shale with supercritical CO$_2$ and no-adsorption gas (He) and showed that CO$_2$ adsorption was responsible for shale deformation at low pressure, while gas pressure resulted in shale deformation at high pressure. Feng et al. (2019) discussed the relationship between failure behavior and bedding angle of shale after supercritical CO$_2$ adsorption and indicated that the layer direction resulted in the tensile failure as well as shear failure of shale.

Since the organic matter in shale can be extracted by supercritical CO$_2$, the pores dissolution after extraction results in variation in shale's mechanical properties. When interacting with organic rich shale, Yin et al. (2017) noticed that the uniaxial compressive strength and elastic modulus decreased more significantly after supercritical CO$_2$ exposure than subcritical CO$_2$ exposure. Similar results were also found by Lu et al. (2019) when they exposed the Longmaxi shale with gaseous and supercritical CO$_2$. This difference demonstrated that the variations in pore structures of shale were not only affected by dissolution of minerals and precipitation as well as adsorption-induced swelling of CO$_2$, but also due to the extraction of organic matter

by supercritical CO_2. The combination of the above mentioned three mechanisms results in changes in the mechanical properties of shale after shale-CO_2 interaction.

14.4.3 Adsorption Properties

A large number of investigations have shown that the CO_2 adsorption capacity of shale is stronger than that of CH_4, which is really the basis for the development of CO_2 enhanced shale gas recovery technology (Nuttall et al. 2005; Chareonsuppanimit et al. 2012; Duan et al. 2016; Huo et al. 2017; Yang et al. 2018). There is no doubt that the pore structures as well as mineral composition of shale change after CO_2 injection, which affect the gas adsorption capacity of shale. However, only limited research has focused on the cause of variation in adsorption capacity of shale. Zhou et al. (2018) have documented that the adsorption capacity of shale is mainly controlled by the micro- and mesopores, and the organic matter extraction as well as adsorption-induced expansion resulting in decrease in shale's adsorption capacity of CO_2 and CH_4 after supercritical CO_2 treatment. Similar results have been obtained by Hui et al. (2019); they have also ascribed the specific surface area variation to extraction and adsorption-induced expansion rather than mineral dissolution during shale-supercritical CO_2 interaction. However, Yanchang shale exhibited a decrease in adsorption capacity with increase in specific surface area after supercritical CO_2 exposure which has been attributed to the reduction in oxygen-containing species responsible for decrease in CO_2 maximum adsorption in shale. This discrepancy in adsorption behavior of shale after CO_2 exposure indicates that more studies are needed to clarify this problem. Furthermore, the effect of mineral dissolution and precipitation on shale adsorption behavior after CO_2 exposure has been neglected in current research due to the limited interaction period. However, rapid and significant geochemical reactions exist within the timescale of shale gas recovery and their effects on long-term CO_2 storage are not well understood. This is an important issue that needed to be resolved.

14.5 Effect of CO_2-Shale Interaction on Groundwater Quality

The effect of CO_2-water-rock interaction on the elements' migration in shallow aquifers and saline formations has been investigated widely through field monitoring, laboratory experiment as well as geochemical modeling simulations (Viswanathan et al. 2012; Romanak et al. 2012; Rillard et al. 2014; Rathnaweera et al. 2016). A large number of investigations have demonstrated that the injection of CO_2 can dissolve specific minerals such as calcite and dolomite resulting in the groundwater contamination.

Previous studies have shown that the trace elements have different level of affinity for different minerals and organic matter in shale (Glikson et al. 1985; Ripley et al. 1990; Phan et al. 2015). When interacting with CO$_2$ and brine, the dissolution of various minerals results in the release of trace elements. For example, Jean et al. (2015) conducted the shale-CO$_2$-water interaction at 25 MPa and 90 °C for 7 days and found large amount of V, Cr, Co, Cu, and Rb dissolved from shale, while the dissolution of Zn, Se, Mo, and Cd was minimal. Marcon and Kaszuba (2015) indicated that the release contents of Cd, Co, Cu, Cr, Fe, Ni, Pb, V, and Zn from the mixture of limestone and shale were higher than that from limestone only. Similarly, Luo et al. (2019) measured the element mobilization of shale before and after shale-CO$_2$-water interaction and found that the mobility of the trace elements was relatively low compared to major elements. In addition, the research has also indicated that the elements release was not only due to the mineral dissolution, but was also related to the cation exchange.

Many organic compounds such as benzene, toluene and naphthalene have been found in produced water or flowback fluids (Strong et al. 2013; Ziemkiewicz 2013; Cluff et al. 2014; Akob et al. 2015) demonstrating that the organic matter in shale becomes another potential source of groundwater contamination. To clarify the possible contamination of organic matter in shale, Dustin et al. (2018) isolated kerogen from both Green River and Marcellus shales and conducted the experiment on interaction with kerogen-fracturing fluids. Their study showed that organic matter dissolved in both fracturing fluid and hydrochloric acid solution (pH = 2) and dissolution of kerogen contributed to the release of heavy metals. Although the functional group alteration of kerogen had been noticed in this study, analysis of organic components in the solution was not conducted. Since the supercritical CO$_2$ can effectively extract organic matter from shale, it implies its potential release during shale-water-CO$_2$ interaction. Thus, the potential organic contamination during CO$_2$-water-rock geochemical reactions in shale needs further in-depth study.

14.6 Conclusions

Gas shale is mainly composed of clay minerals, quartz, feldspar and plenty of organic matter. The clay mineral is deemed with sorption ability and can expand or contract when contacting the CO$_2$ through adsorption. The organic matter can also be extracted by supercritical CO$_2$ while the geochemical reactions can also occur between shale, water and CO$_2$. Thus, it can be seen that the characteristics of CO$_2$ and shale determine that a series of interaction will inevitably occur once CO$_2$ comes in contact with shale. In addition, as a low-porosity and low-permeability reservoir, small influence on the conductivity of shale may exert huge impact on gas recovery and CO$_2$ storage efficiency. As a result, the interaction between CO$_2$ and shale is critical in the context of CO$_2$ enhanced shale gas recovery.

CO$_2$-water-shale geochemical reactions can cause minerals' dissolution and expansion, CO$_2$ adsorption onto clay inducing the swelling of minerals, and the

extraction of organic matter by supercritical CO_2 leading to the dissolution of organic matter. The aforementioned three mechanisms have the potential to influence the porosity, permeability, mechanical properties and even the adsorption capacity of the shale. However, it is difficult to quantify the relative weight of these mechanisms on changing the shale property. Advanced interdisciplinary methods are necessary to integrate the physical, mechanical and geochemical changes in the shale in order to predict its response at the pore,core, and reservoir scale.

The impact of CO_2-shale interaction on gas adsorption properties of shale needs further clarification. The effect of mineral dissolution and precipitation on shale adsorption behavior after CO_2 exposure is always neglected in the current research due to the limitation on the interaction period in the investigations. However, rapid and significant geochemical reactions exist within the timescale of shale gas recovery, which will also affect the long-term CO_2 storage. As a result, this is also an important issue that needs further investigation. In addition, the CO_2-interaction induced organic contamination in the groundwater is also a critical problem that needs to be further explored.

The ultimate goal of this study on the influence of CO_2-shale interaction on rock properties and groundwater quality is to assess the feasibility and potential of CO_2 enhanced shale gas recovery by considering the shale gas recovery efficiency, CO_2 storage capacity, stability and security as well as its environmental implications. The recent investigations have mainly focused on lab-scale experiments and have explored the micro-structure evolution of shale treated with CO_2; however the relationship between shale gas recovery and CO_2 storage has not been explored in sufficient detail making it difficult to provide straightforward conclusions for policy makers and stack holders. In the future, the coupled organic-geo-chemo-mechanical model should be established and field-scale experiments should be conducted to comprehensively explore the effect of CO_2-shale interaction on enhanced shale gas recovery.

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Chapter 15
BioGTL: A Potential Technique for Converting Methane to Methanol (Waste to Energy)

Aradhana Priyadarsini, Lepakshi Barbora and Vijayanand S. Moholkar

Abstract Methane, the potential fuel, is a major contributor to the global warming chaos due to its heat capturing ability and its increasing release from anthropogenic routes, such as oil and coal mining, as a waste. Owing to technical and economic constraints the methane is flared at the sites, thus preventing the marketing and causing wastage of a potential energy resource. In 2017, for 220 million barrels of oil produced per day, 140 billion m^3 of natural gas was flared per year according to the Global Gas Flaring Reduction (GGFR) report by the World Bank. This enormous amount gas that is wasted can be captured and converted to energy (liquid fuels) through existing chemical and emerging biological routes. Due to the prominent disadvantages associated with chemical route such as energy intensiveness, inefficiency in yield, high-cost, etc., biological route for methane-to-methanol conversion is favourable, which can be operated at ambient temperature and pressure conditions. The methanotrophs, among various groups of methane utilizers, play the key role in biological methane (gas) to methanol (liquid) conversion (*BioGTL*). Besides, Bio-GTL (biological gas to liquid) would prove to be an economically viable technology for capturing the methane released at underrated diffused sites operated by small companies in remote areas. An efficiency (moles of methanol produced per mole methane consumed) of 80% for BioGTL has been reported in 2014. However, the scale-up of this interesting and highly potential technology has been a challenge and hence, demands attention and appropriate R&D measures.

Keywords Methanotrophs · Methane · Biofuels · Methanol · BioGTL · Gas fermentation

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Abbreviations

GTL   Gas to Liquid
BioGTL   Biological Gas to Liquid
U.S. EPA   United States Environmental Protection Agency
GGFR   Global Gas Flaring Reduction
GHG   Greenhouse Gas
MSW   Municipal Solid Waste
NERC   Natural Environment Research Council
IPCC   Intergovernmental Panel on Climate Change
GWP   Global Warming Potential
GWP_{100} Global Warming Potential over a Period of 100 Years
RMI   Rocky Mountain Institute
CNG   Compressed Natural Gas
FT   Fischer–Tropsch
CCE   Carbon Conversion Efficiency
AOB   Ammonia-Oxidizing Bacteria
MMO   Methane Monooxygenase
pMMO   Particulate Methane Monooxygenase
sMMO   Soluble Methane Monooxygenase
CNG   Compressed Natural Gas
LNG   Liquefied Natural Gas
DME   Dimethyl Ether
AMO   Ammonia Monooxygenase
RuMP   Ribulose Monophosphate
ICM   Intracytoplasmic Membrane
PHB   Poly-β-hydroxybutyrate
MBR   Membrane Reactor
MDH   Methane Dehydrogenase
R&D   Research and Development

15.1   Introduction

Ignis fatuus or will-o-the-wisp is the fire moving in the wetlands and thus, perceived as ghosts at night in the folklores by the local inhabitants. When the scientists boggled their heads around the phenomenon, they found that the fire was caused due to the mixture of phosphine (PH_3), diphosphine (P_2H_4) and methane (CH_4) released in the wetlands as a result of decay of organic matter by the inhabitant microbial community. The phosphine (PH_3) and diphosphine (P_2H_4) self-ignite on contact with oxygen in the air and then the methane eventually burns causing the ephemeral fires that appear to move over the water bodies. And in the dark it appears as ghost that scares the people around.

Methane (CH_4) is the lightest member of the alkane hydrocarbon family and is way potent than carbon dioxide as a greenhouse gas (GHG). It is called a short-term enforcer which means that it stays in the atmosphere for shorter time period as compared to carbon dioxide (CO_2) that can prevail in the atmosphere for up to a thousand years but the heating effect of this mischievous gas is much higher than that of carbon dioxide causing huge imbalance in the climate in a very short span of time. It has been reported that methane (CH_4) undergoes chemical reactions in the atmosphere and oxidizes to carbon dioxide (CO_2) and water (H_2O) within a period of around ten years (Le Fevre 2017). This could also be the reason why carbon dioxide persists in the atmosphere for more than thousand years since it adds up from various sources and persists longer. Global warming is the alarming yet subtle issue that is growing day by day. Coherent small efforts to address the GHGs might just help us save our planet.

15.1.1 Sources of Methane

Methane is generated through various sources which can be categorized for study under different heads. The natural sources, also called the **biogenic sources**, of methane include marshes, swamps, bogs, lake basins, methane clathrates, soda lakes, etc. Rice fields also generate huge amount of methane in the water logging stages, trees and the rain forests produce methane in huge quantities. The human activities like transport of coal and oil mining, etc. are categorized as **anthropogenic sources** that also lead to the release of methane as a constituent of natural gas into the atmosphere during the mining operations including natural gas extraction. Figure 15.1 shows the estimated amount of methane emitted by various anthropogenic sources under study. Methane is also emitted as part of *biogas* from the decay of organic matter in anaerobic digesters that process the municipal solid waste (MSW) such as landfills and leachate, some livestock manure storage systems, and agro-industrial and municipal wastewater treatment systems (according to the global methane initiative report). The methane in the biogas serves as an excellent fuel for domestic cooking and heating applications. However, the biogas is a mixture of gases among which carbon dioxide is considered as a major contaminant. The other minor contaminants involve hydrogen sulfide (H_2S), water vapour, etc. The partial burning of biomass also produces methane and is denoted as the **pyrogenic route** (Saunois et al. 2016).

It is surprising to note that the methane that is produced through various sources, does not account for the same amount in the atmosphere, i.e., the amount of methane produced and amount of methane present in the atmosphere differ. This means that all the methane produced does not reach the atmosphere and is captured and converted through various *methane sinks* that could be *chemical sinks* or *biogenic sinks*. The chemical sinks comprise of the chemical reactions that convert the methane to carbon dioxide and water in the atmosphere and the biogenic sinks comprise of the methane-oxidizing microorganisms that utilize methane as a source of carbon for growth and

Fig. 15.1 Estimated Global Anthropogenic Methane Emissions by Source, 2020. *Source* EPA, U.S.A.

metabolism. However, in both cases the end products are carbon dioxide and water. The "bottom-up" estimates, comprising the aggregated inventories of emissions that form the sources of global methane emissions, are usually balanced through methane sinks, which are referred to as the "top-down" budgets, by methane degradation processes and are assessed by direct measurement of atmospheric methane. An ongoing project report on the ***global methane budget*** funded by the NERC (Natural Environment Research Council, the driving force of investment in environmental science in the United Kingdom) shows that both the bottom up and top down budgets are significantly different from one another and the reason for the gap in the estimates is still under research since it is very difficult to track and accurately estimate all the methane emissions.

It has been observed that the natural sources and sinks of methane work hand in hand and keep the troublesome levels under a threshold according to the global methane budget (Le Fevre 2017). However, the atmospheric methane levels have increased considerably in past few years for reasons that are not fully understood and scientists are working relentlessly on it. The issue of global warming is not only a scientific chaos but has also become a political concern of global importance.

Usually the natural gas that comes out of the ground during the coal or oil mining activities, as a byproduct of coal and oil extraction, is considered as waste due to

its marketing constraints and transportation difficulties. Thus, the emitted natural gas is often flared at sites itself to reduce methane emissions into the atmosphere. This leads to the wastage of enormous amount of energy. The phenomena associated are discussed briefly in this chapter in the following sections. The world is leading towards energy crisis in the near future considering the depletion rate of world's fossil fuel reserves and limited efficiency of various renewable and non-renewable resources in producing amount of energy that does not meet the energy demands from all sectors. In the scenario where the world's energy resources are getting depleted rapidly, we can't afford to waste the sources of energy available to us especially this renewable and abundant source of energy. Moreover, the energy harvested from wind, ocean, nuclear power and solar sources has storage difficulties which is a major challenge because the energy produced can't be used all at once. So it needs to be stored for use as and when required. Significant amount of research is required to find better energy storage options as well. The biological gas to liquid (BioGTL) technology is a promising technology that can address most of the issues discussed here.

15.1.2 Global Methane Status

The global methane initiative partnership under its parent organization, United States Environmental Protection Agency (U.S. EPA), in its report on "Global Methane Emissions and Mitigation Opportunities" stated that "methane is the second most abundant anthropogenic greenhouse gas (GHG) after carbon dioxide (CO_2), accounting for about 20% of global emissions" (Fig. 15.2).
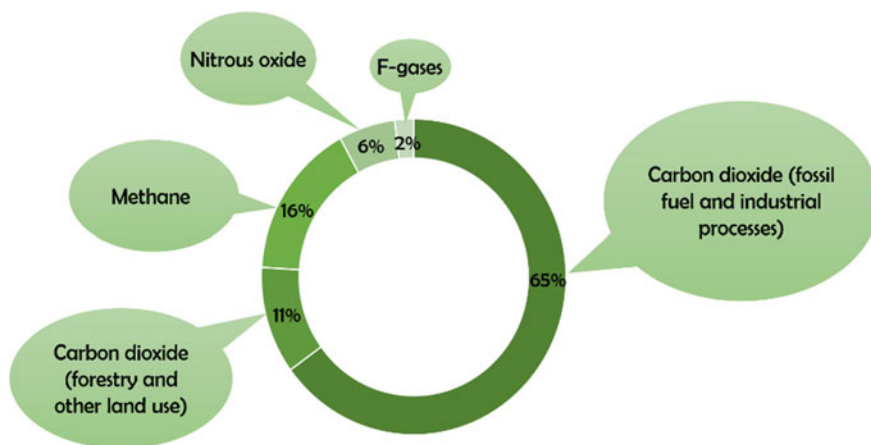

Fig. 15.2 Global GHG emissions by gas. *Source* EPA, U.S.A.

The fifth report of the Intergovernmental Panel on Climate Change (IPCC), released in 2013, reported that despite the short lifespan in the atmosphere and emissions in smaller quantities as compared to carbon dioxide (CO_2), methane (CH_4) has a 28–34 times greater global warming potential over a period of 100 years (GWP_{100}), i.e., methane (CH_4) is more efficient at trapping solar radiation than carbon dioxide (CO_2). As a result, methane emissions contribute to about one-third of today's anthropogenic greenhouse gas (GHG) warming. Evidently, the impact of methane (CH_4) is more than 25 times higher than carbon dioxide (CO_2) over a 100-years period, which is very devastating. All these concerns have urged the researchers to focus their efforts into finding solutions to reduce the greenhouse gas (GHG) emissions and release into the atmosphere.

As evident here, the methane produced during the biogenic, anthropogenic and pyrogenic processes is increasing and efforts are being made to make it available for use. It is predicted that by 2050 the global warming would increase the earth's temperature by 2 °C as compared with the temperature level in the year of 1900 (Intergovernmental Panel on Climate Change 2015).

15.1.3 Flaring and Wastage

In the oil fields where the methane is released as a constituent of natural gas during energy extraction is often flared to reduce its greenhouse effect considering its immense potential as greenhouse gas (GHG). The oils fields do not always belong to huge companies. Most of the oil fields are small scale and usually dispersed in the remote areas where the mode of transportation is very poor due to terrain mostly. Methane is flared because it is considered as waste and uneconomic to bring in the market by the industries due to lack of proper infrastructure and technologies required to make it consumable for the end-user. According to an article entitled, "This Little Think-Tank Goes to Market" by David Labrador, senior writer/editor at Rocky Mountain Institute (RMI), there are more than 16,000 discrete and diffused methane flares around the world and the best business models and technologies for capturing methane and bringing it to market are not widely understood. If we look at the satellite images of the earth at night, these flares can be easily recognized in the areas of oil and coal mines which are very brightly lit up clearly on the map.

However, flaring is an unsafe practice as reports testify various associated accidents in the history of flaring. Simultaneously, flaring leads to the wastage of a potential energy feedstock, carbon monoxide (CO) emission and hazardous black carbon production by incomplete burning (Dong et al. 2017; Gvakharia et al. 2017). Despite the various efforts made to improve the infrastructure for getting the natural gas to market especially through pipelines and other modes of transportation, the topography and terrain of the countries have been the biggest obstacle as far as the transportation is concerned. The compressed natural gas (CNG) cylinders are currently available in the market; however, compressing the natural gas under high temperature and pressure is energy intensive, expensive and risky process.

It was stated in a 2011 World Bank report that flaring is responsible for 1.2% of global carbon dioxide emissions (GGFR). The Global Methane Initiative (GMI) is an international public-private partnership that focuses on managing the recovery of methane and use as source of clean fuel. Thus, capturing and converting this methane to liquid fuels could be a potentially economic method to:

- Capture the wasted energy.
- Obtain a clean and renewable source of commercial fuel.
- Advantageous over cost-ineffective conventional sugar-based fuel production.
- Reduce GHG emissions.
- Mitigate climate change.
- Simultaneously increase energy security.
- Enhance economic growth.
- Improve air quality.
- Worker safety from flaring related hazards.

15.1.3.1 Safety Issues Associated with the Methane Production, Storage and Transport

As mentioned in the earlier section, the flaring is a risky process that has a history of series of accidents associated with it. For example, Piper Alpha Platform, UK (1988); Alexander L. Kielland Drilling Rig, Scotland (1980); Seacrest Drillship, Bangkok (1989); Ocean Ranger Oil Rig, Canada (1982); Glomar Java Sea Drillship, U.S. (1983); Bhn Platform, Mumbai High North (2005); Usumacinta Jack-Up, Gulf of Mexico (2007); etc. to name few as reported in the "Top 10 World's Catastrophic accidents in Oil and Gas Industry" in 2017. Some of the ships caught on fire and some went missing due to storms in the sea.

Since methane is highly flammable, the production, storage and transport of this potential source of energy is associated with some obvious hazards such as risk of fire and explosion, gas poisoning (due to the presence of hydrogen sulfide, ammonia, etc.), explosion due to high pressure, etc. Moreover, methane is naturally odorless and its leakage can't be detected without aid. Therefore, appropriate methane detectors are essentially installed in liquefied natural gas (LNG) and compressed natural gas (CNG) transport systems and also insulated cylinders are used to prevent heating due to friction.

15.1.4 Waste to Energy

The need to monetize the flare gas led to development of technologies to convert this methane to liquid fuel, which is easier to store as a source of energy, through conventional chemical route. Albeit the chemical process has been running on a commercial scale, it has economic viability constraints for the underrated methane sources which

are diffused in remote areas. In nature, methane is converted to methanol as a part of the metabolic process within certain microorganisms. These methane oxidizers can be our solutions to capture the waste energy and tackle climate change issues.

15.2 GTL Versus Bio-GTL Technologies

Gas-to-liquid (GTL) technologies, currently, chemically convert the methane resources into liquid hydrocarbons which can then be readily stored and transported as compared to methane which is gas at ambient conditions (Fig. 15.3). There are two modes of conversion that can convert methane to liquid fuels through chemical route:

(i) direct partial combustion of methane to methanol (DMTM)
(ii) Fischer-Tropsch-like processes (FT)

GTL technology based on the Fischer-Tropsch-like processes is prominent and demands reference since it is the existing chemical route for converting the methane (gaseous fuel) to methanol (liquid fuel) that has been operating at industrial scale. Fischer–Tropsch (FT) process is an important reaction in both coal liquefaction and gas to liquids technology for producing liquid hydrocarbons (Höök et al. 2014). The feedstock for the Fischer–Tropsch process is a mixture of carbon monoxide and hydrogen called syngas which is produced when coal, natural gas, or biomass are subjected to gasification. The syngas is further catalyzed to produce synthetic lubrication and synthetic fuel. Figure 15.4 shows a flow diagram of a typical FT process. Thus, the conversion of natural gas to liquid hydrocarbon takes place in two steps. The FT process requires metal catalysts and the most commonly used ones are cobalt, iron and ruthenium.

However, the first step of the FT process, i.e., the production of syngas from natural gas is associated with notable disadvantages of low yield, poor selectivity, huge capital investment and large energy inputs (Dong et al. 2017), despite of significant efforts that have been applied to make this process economically viable at small scale. Summarily, this two-step process is highly energy intensive and uneconomic. In search of more economic and energy efficient alternatives, various processes for converting natural gas to methanol have been proposed and studied for decades, however it has been observed that all the chemical conversion processes are energy intensive, noneconomic, and environmentally unfriendly (Adebajo and Frost 2012; Foster 1985; Muehlhofer et al. 2002).

Fig. 15.3 General reaction
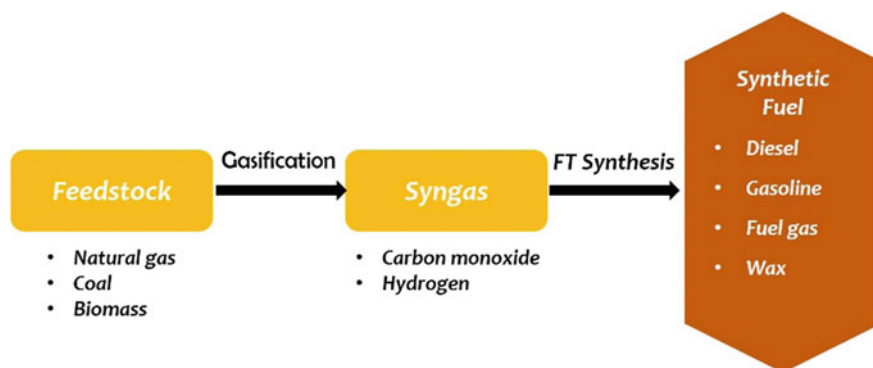
Fig. 15.4 Flowchart of Fischer–Tropsch (FT) process (chemical route)

Since, petroleum reserves are rapidly getting depleted there is a desperate need for alternative fuels that are also sustainable in nature. As compared to the FT chemical process, the biological gas to liquid (BioGTL) conversion is a one-step process and in contrast to FT and DMTM which requires high temperature and pressure conditions, BioGTL operates at mild conditions.

Due to the mild operating conditions the cost of biofuel production can be reduced substantially through the BioGTL process which is extremely energy friendly, cost effective and is based on potentially high carbon conversion efficiency (CCE), good selectivity, low capital investment, and low GHG emissions (Dong et al. 2017). Since thermochemical processes are associated with various disadvantages, the biological route for the gas to liquid fuel conversion stands as a novel and promising alternative. The methane to methanol conversion efficiencies (moles of methanol produced per mole methane consumed) of up to 80% have been achieved so far based on the existing reports (Ge et al. 2014). However, the industrial application of this novel technology is the challenging task.

The biological oxidation of methane to methanol is done through microbial fermentation technique using methane-oxidizing microorganisms. There are different classes of microorganisms that carry out the BioGTL conversion at ambient temperature and pressure conditions as a part of their intrinsic metabolic cycle which is catalyzed by the enzyme system they possess. Among the various classes, the methanotrophs are the methane-oxidizers, also called methane-utilizers that convert methane to methanol in a single-step which is catalyzed by the methane monooxygenase (MMO) enzymes. The various microorganisms that are known to metabolize methane are discussed briefly later in this chapter. This chapter shall focus on the role of methanotrophs in methane oxidation and methanol production (Fig. 15.5).

The MMO enzymes present in the methanotrophic bacteria enable them to utilize methane as the source of carbon and energy (Bjorck et al. 2018). Thus, Bio-GTL is an enzyme catalyzed energy efficient and environment friendly technology that will lead to the production of liquid fuels for future needs. Additionally, well designed bioprocesses can be suitably applied to the small-scale operations that are appropriate

Fig. 15.5 Flowchart showing methane to methanol conversion (biological route)

for remote and diffuse methane sources that need low capital investment. Although the field of Bio-GTL has been discovered and explored since quite some time now, the research in this area has gained momentum to address the alarming issue of global warming and in search for alternate fuels, only in recent years. The technology required for the commercial scale production of liquid fuels through this route stands a mystery unsolved which means the research for its commercial viability is still a work in progress.

15.2.1 Why Go for Methanol Over Methane?

Before we proceed further into the BioGTL process and its details, we would like to discuss why we should go for methanol over methane when methane itself is a fuel. As discussed above methane is currently used as CNG and LNG in transportation sector and heating purposes. Biogas is already used for domestic cooking and heating purposes. However, it is not widely accepted phenomenon.

Methanol is a valuable source of industrial chemicals and over 30 million tonnes are consumed every year (Wogan 2017). The energy density of methanol (15.6 MJ/L) is higher than that of methane (36.6×10^{-3} MJ/L). It can be used as industrial solvent, as feedstock for various chemical processes, fits into current infrastructure as a fuel, has greater energy efficiency due to high energy density and octane number, and is cleaner due to lower emissions of toxic byproducts (Hwang et al. 2014). It can easily blend with gasoline or used directly as fuel. There are five main fuel applications for methanol (Bjorck et al. 2018):

- directly as a transportation fuel;
- blended with petrol;
- converted to dimethyl ether (DME) to be used as a diesel replacement;
- in the production of biodiesel via trans-esterification;
- in fuel cells to generate electricity.

Hence, due to versatile utility profile and easier handling characteristics methanol is more desirable as compared to methane.

15.2.2 Methane-Oxidizing Microorganisms

Metabolic methane oxidation is not restricted to a particular class of microorganisms. In nature, methanotrophs, ammonia-oxidizing bacteria (AOB) and certain acetogens have been found to oxidize methane in their respective metabolic pathways. Some utilize methane as their sole source of carbon and energy, some utilize methane as an alternate carbon source and yet some utilize methane as the major substrate but can also grow using other carbon sources apart from methane.

Ammonia-oxidizing bacteria (*AOB*)

AOBs being chemolithoautotrophs are chemosynthetic organisms that gain energy by oxidizing ammonia (NH_3) to nitrite (NO_2^-) using carbon dioxide (CO_2) as the carbon source in two steps (Ge et al. 2014). One of the steps is catalyzed by the ammonia monooxygenase (AMO) that is also responsible for co-oxidation of methane (CH_4) to methanol under certain conditions. The AMO enzyme also oxidizes other hydrocarbons like methanol, ethylene, and methyl bromide. This provides another option for bio-oxidation of methane (Taher and Chandran 2013). However, AMO enzyme requires additional reducing power for the co-oxidation of methane to methanol.

Acetogens

Acetogens are anaerobic microorganisms that produce acetate as their fermentation product. Drake et al. (2006) defined an acetogen as an anaerobe that can use the acetyl-CoA pathway (also known as the Wood-Ljungdahl pathway) as, (i) mechanism for the reductive synthesis of acetyl-CoA from CO_2, (ii) terminal electron-accepting, energy-conserving process, and (iii) mechanism for the assimilation of CO_2 in the synthesis of cell carbon. However, acetate is the main product of most of the acetogens and not methanol.

Methanotrophs

Methanotrophs, on the other hand, are known to utilize methane as their major source of carbon and energy and produce methanol from methane in a single step. Thus, the role of biocatalysts for this conversion is best suited for the methanotrophs that have been studied intensively since 1970 when Whittenbury tried to isolate, characterize, culture and compare more than 100 strains after Dworkin and Foster (1956) and Leadbetter and Foster (1958) isolated a number of methane-utilizing organisms.

15.2.3 Methanotrophs: The Key Players

Methanotrophic bacteria are ubiquitous and present a good opportunity for biological methane to methanol conversion as they can metabolize and use methane as their carbon and energy source. Methanotrophs are members of a physiological group of

bacteria known as methylotrophs. Methylotrophic bacteria utilize a variety of different single carbon compounds (C1 compounds) like methane, methanol, methylated amines and halomethanes, etc. as sources of carbon (Hanson and Hanson 1996).

The methanotrophs can be categorized into Type I, Type II and Type X based the type of metabolic pathway used for formaldehyde assimilation. The type I methanotrophs utilize the ribulose monophosphate (RuMP) as the primary pathway whereas Type II use the serine pathway. The Type X methanotrophs utilize both and grow at higher temperatures than both the Type I and Type II methanotrophs.

The methanotrophic bacteria have been grouped under two phyla, the *Proteobacteria* and *Verrucomicrobia*. The *Proteobacteria* again consist of *Gammaproteobacteria* and *Alphaproteobacteria*. Since the methanotrophs are very versatile group of microorganisms there is yet so much more to be explored about them. Thus, this classification is not distinct and more members are yet to be included. However, this classification can help us understand the basic nature of the ingenious metabolic mechanisms that convert the methane to methanol at ambient conditions within the cells which would otherwise require high energy input through chemical reactions outside the cells.

The key enzymes that convert the methane to methanol in the first step of their carbon assimilation pathway are the methane monooxygenase (MMO) enzymes. The methanol is further oxidized by methanol dehydrogenase to formaldehyde. The methane to formaldehyde conversion steps are common to all types of methanotrophs. There are two classes of MMO enzymes:

(i)   particulate methane monooxygenase (pMMO) enzyme
(ii) soluble methane monooxygenase (sMMO) enzyme.

The particulate methane monooxygenase (pMMO) are part of the membrane system and thus, the methanotrophs with pMMO possess highly membranous structures called the intracytoplasmic membranes (ICMs) that harbor the pMMO for methane oxidation. In the *Gammaproteobacteria*, the ICMs are arranged in stacks while the ICMs in the *Alphaproteobacteria* are aligned parallel to the cytoplasmic membrane of the methanotrophic cells. On the other hand, the soluble methane monooxygenase (sMMO) are soluble in nature and are present within the numerous vesicles floating in the cytoplasm. So the methanotrophs with only sMMO lack the extensive membrane systems, instead possess large quantities of vesicles associated with the cytoplasmic membrane for methane oxidation (Dedysh and Dunfield 2011).

Also the methanotrophs that prefer methane as the sole source of carbon and energy are called ***obligate methanotrophs*** whereas the methanotrophs that can utilize multiple carbon substrates, can possess sMMO or pMMO and are called ***facultative methanotrophs***. The methanotrophs also produce a range of products apart from methanol such as single-cell protein, biopolymers like poly-β-hydroxybutyrate (PHB), an amino acid called ectoine, etc. As we can infer they are quite versatile and thus efforts are also being made to obtain multiple products from a single bioreactor. It is indeed a fact that the different products discussed here are produced under

different growth conditions. So this gives rise to more research opportunities to integrate the bioprocesses and design a process for industrial scale production of all the products.

15.3 Challenges Associated with Methanotrophic BioGTL Technology

As already discussed the BioGTL technology is an emerging technology which uses gas fermentation techniques for conversion of gaseous substrate to liquid products and other products discussed above as well. There are, however, significant challenges associated with the fermentation process that needs to be addressed before scale-up of the technology. Few of the major hurdles in gas fermentation in methanotrophs are discussed below:

(1) Gas-liquid mass transfer limitations.
(2) Over-oxidation of methane beyond methanol.
(3) Toxicity of source methane impurities.

Few other challenges associated in the Bio-GTL process for methanol production are the transport and delivery of natural gas at the site of fermentation, finding robust strains and attempting optimization of growth media and operating conditions for maximum yields, intensification of methanol production, development and integration of bioprocesses of methanol purification, which need R&D attention to commercialize this potential BioGTL process. The solutions to these challenges can aid the commercialization of BioGTL technology for the production of methanol as transportation fuel for future needs.

According to Hwang et al. (2014), the primary obstruction for the industrial application of BioGTL technology is the failure to express heterologous methane monooxygenase (MMO) in *Escherchia coli*. So other alternatives could be development of a recombinant MMO enzyme for enzyme-based bioconversion of methane to methanol, genetically modified strains are available and under study for enhanced methane to methanol productivity. The development of genetically modified methanotrophs for the higher yields also has its innate challenges. The strains could revert back, the use recombinant strains for multiple products is still not understood well and not to mention the legal formalities and procedures to be followed.

At present, the BioGTL conversion using the wild-type methanotrophic bacteria is limited by slow growth rates and poor specific and volumetric productivities in the range of μmol/mg h. Hwang et al. demand that methanol accumulation, methane mass transfer and reducing power regeneration are the areas that need to be worked upon and can be enhanced by redesigning the metabolic pathway using metabolic engineering and synthetic biology approaches. Additionally, biocatalytic methane transformation to methanol would be especially applicable to countries with small-scale gas fields that are diffused in remote areas and poor infrastructure due to the requirement of low capital investment and flexibility of the bioconversion of methane

over the chemical conversion. The commercial success of biocatalytic methane-to-methanol bioconversion would open up a starting point for a paradigm shift from petroleum-based chemical refineries to gas-based refineries.

15.3.1 Strategies to Address These Challenges

Challenge 1: Gas-liquid mass transfer limitations

Methane is the simplest hydrocarbon and does not dissolve easily in the aqueous medium due to its hydrophobic nature. As in the case of oxygen transfer, methane also must cross the eight barriers to reach the reaction centre within the cells from the gas bubble in the liquid medium. The mass transfer is the limiting step which is common to all fermentation processes. In order to enhance the growth of biomass and cellular productivity, the mass transfer must take place efficiently and few strategies have been discussed below.

Methane vector

Methane being an organic compound has very low tendency to dissolve in distilled water which is inorganic. This factor hinders the availability of methane for consumption by the methanotrophs in the growth medium. This is also the case with the oxygen mass transfer from the sparged bubbles to the cells. Thus, the existing bioreactor designs and gas sparging techniques also need modifications for better mass transfer and are still a work in progress.

The gases oxygen and methane are usually sparged into the medium to maintain a supply for fermentation. The gas molecules must transfer into gas liquid interface and then diffuse through the culture media (aqueous phase) and cross the barriers through the microbial cell surface to reach the reaction centres within the cells where they participate in metabolic reactions. The gas to liquid interface mass transfer is critical for gaseous substrate diffusion especially when the gases are not soluble in the culture medium. Certain steps can be taken to increase the uptake of methane by the methanotrophs like gas sparging reactors, trickle bed reactors etc. (Fei et al. 2014).

Organic compounds have been reported to enhance the mass transfer rate between the gaseous organic phase (methane) and the liquid aqueous phase (culture media). The use of paraffin oil with 5% addition has been reported to increase the cell dry weight of the bacteria in the medium phase which is about 14 g/L, around 7 times higher than without any methane vector. The methanotrophic cells have been reported to align around the surface of oil droplets which might play a role in the enhancement of the uptake of methane by the bacterial cells. The cells cultivated in 5% paraffin were observed to be sticking around the interface of paraffin oil and medium phase trying to draw in methane from the paraffin oil phase while in the 10% paraffin cultures, cells could be observed even in the oil phase by forming irregular agglomerates. This explains that at higher concentrations of paraffin the cells were engulfed into

Table 15.1 Types of membrane reactors

Reactor	Cell density (dry cell in g/L)	Methanol produced (g/L)	Time (hours)	References
Dense silicon tube stirred membrane reactor	17.3	0.95	40	Duan et al. (2011)
Recirculating macroporous membrane reactor (MBR)	–	0.12	24	Pen et al. (2014)
Commercial patented loop reactor	–	–	–	Eriksen et al. (2009)

the large paraffin emulsions where the cells were cut off from the nutrients in the aqueous medium for cells inside the oil (Han et al. 2009).

Reactor design

Membrane reactors have been reportedly employed for the methane oxidation by methanotrophs. The gaseous substrates, i.e., methane and air, are supplied through two porous membranes that apparently fulfills two requirements of (a) separate gas feed and monitoring and (b) helps monitor and prevent the methane and air mixture that is explosive between 5% (v/v) to 15% (v/v) (Bjorck et al. 2018). Few types of membrane reactors have been listed in Table 15.1.

Challenge 2: Over-oxidation of methane

According to the metabolic pathway of the methanotrophs, the methane is converted to methanol in the first step which is catalyzed by the methane monooxygenases and this methanol is further oxidized to formaldehyde by methanol dehydrogenase. The formaldehyde is further metabolized to carbon dioxide through formate and two pathways, such as RuMP and serine pathways that classify the methanotrophs. All the pathways proceed to form cell material at the end leading to growth of the biomass. In order to accumulate methanol, either the formation of methanol needs to be boosted or the oxidation of methanol must be suppressed.

The various methane dehydrogenase (MDH) inhibitors reported are cyclopropane-based inhibitors, salts like EDTA, phosphate, NaCl, $MgCl_2$, NH_4Cl, etc. at high concentrations and carbon dioxide (Sheets et al. 2016; Bjorck et al. 2018). These MDH inhibitors have enhanced methanol production in the methanotrophs. However, the inhibitors also block the primary metabolic pathway since the methanol is supposed to be used to generate cell biomass. Thus, formate is also added in certain cases to help the cells complete their metabolic pathway and accumulate more quantity of methanol.

Challenge 3: Toxicity of source methane impurities

The various targeted sources of methane include natural gas from coal and oil mining fields, landfill sites and biogas from anaerobic digesters. These sources are not purely methane and contain other contaminants such as carbon dioxide, H_2S, water vapour, other hydrocarbon like ethane, propane, etc. These impurities in the methane feedstock hamper the methanotrophic productivity of both methanol and biomass. The R&D on the BioGTL is ongoing with various methane sources to find a suitable technique to utilize the methane from the discussed sources. The removal of contaminants from the methane feedstock can be done by few methods like scrubbing carbon dioxide, H_2S, etc. and other gas purification processes.

Methane is produced anaerobically by groups of bacteria growing in a mixed culture in the anaerobic digesters. The methanotrophs are the aerobic methane utilizers that grow in the anoxic and oxic interfaces as they require oxygen to oxidize the anaerobic product, i.e., methane. Moreover, the methanotrophic concentrations are quite substantial near the natural gas seeps and vents where ethane, propane and butane are also in inhibitory concentration. This indicates that the methanotrophic bacteria exist with other set of bacteria that help the methanotrophs to grow on methane in these harsh environments. So the methanotrophs can also be grown in microbial consortium to address the methane impurity issues from the natural environment.

15.4 Conclusion

Methane is a global warming hazard and at the same time a potential source of energy. Capturing and converting the methane, being wasted at the oil and coal mining sites through flaring, to liquid fuel is not only economic but also essential considering the desperate needs for alternative fuels. As discussed in the chapter, chemical routes are energy intensive and environment unfriendly and also require metal catalysts. So the BioGTL is a lucrative solution as it operates at mild conditions of temperature and pressure. Since the BioGTL is an emerging technology addressing the major challenges discussed here would help the scale up of the process and serve as the foundation for many more future modifications.

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Chapter 16
Microbial Desulphurization of Refractory Organic Sulphur Compounds from Transportation Fuels

Pushpita Das, Lepakshi Barbora and Vijayanand S. Moholkar

Abstract The sulphur content in crude oil ranges from 1000 to 3000 ppm but the environmental regulations require less than 10 ppm sulphur to meet the stringent protocols on reduced SO_2 emission by transportation fuels. Hydrodesulphurization (HDS), which is the most employed technology to reduce sulphur (S) suffers from severe and hazardous operation conditions, inefficiency, high capital and operating costs, generation of the hazardous H_2S end product etc. During the last decades, several advances have been made in developing chemical, physical and biological technologies complementary to HDS to achieve ultra-low sulphur fuel. Biodesulphurization (BDS) is one of these emerging nonconventional technologies that can be merged with other desulphurization technologies, such as the oxidative desulphurization process, to produce S-free fuels. The BDS process involves the use of free or immobilized microorganisms, their enzymes or cellular extracts, as catalysts to remove the S present in fuels. The most extensively studied and utilized microorganisms for BDS processes are Gram-positive bacteria. Gram-negative bacteria with high tolerance to organic solvents and metals, broad metabolic versatility and easy genetic manipulation also make them ideal candidates for the purpose. This chapter reviews research findings of utilization of mesophilic, thermophilic and Gram-negative bacteria for desulphurization of gasoline, jet and diesel fuel to be used as transportation fuel.

Keywords Biodesulphurization · Dibenzothiophene · Diesel oil · Bacteria · Thermophilic · Gram-negative

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16.1 Introduction

16.1.1 Background

The leading source of energy in the worldwide are the fossil fuels such as crude oil (34%), coal (27%) and natural gas (24%), whereas other sources of energy are nuclear energy (4%), hydroelectricity (7%) and other renewable energy (4%) (International Energy Agency IEA 2017). Amongst coal, oil and natural gas, crude oil is the most extensively used transportation fuel. Crude oil is having major chemical constituents of carbon and hydrogen and minor (but important) amounts of hetero elements particularly sulphur, nitrogen and certain metals like vanadium and nickel.

Sulphur, the third most profuse constituent in crude oil not only lowers the yield and quality of the refined products but is also a major concern of pollution. Fuels obtained from crude oil after combustion produces sulphur oxides owing to the presence of the high amount of sulphur in crude oil. This SO_x emission can cause severe environmental pollution problems and menaces to human health. Moreover, the release of highly corrosive H_2S gas during the refining process of crude oil can cause regular damage of transportation steel pipelines, compressors, stove containers, storage tanks, and other metal equipment (Duissenov 2012, 2013). This leads to oil refineries to a high maintenance cost and thus increasing the economic value of fuels.

To resolve the problem arising due to the sulphur content in fuels, stringent legislation on quality of transportation fuel has been introduced by various government across the world. United States Environmental Protection Agency (EPA) has set some strict regulations to incorporate ultra-low sulphur diesel (ULSD) which is having sulphur content less than 15 ppm. However, around the world petroleum refineries are facing a common problem because day by day, the crude oil reserves are becoming heavier with higher sulphur content as they are used as feedstock for the refining process (Bhatia and Sharma 2010). This further results in high sulphur contents in secondary processed diesel oil.

The conventional technique mostly employed to reduce sulphur (S) content in fuels is hydrodesulphurization (HDS). However, HDS, has many limitations such as high operation costs and severe and hazardous conditions, the efficiency of desulphurization of a wide range of refractory S-containing compounds is low, and it releases hazardous environmental air pollutants such as H_2S as the end product (Martínez et al. 2017). Thus to achieve ultra-low sulphur fuel, several advances are made to develop chemical, physical, and biological techniques that are complementary to HDS (Stanislaus et al. 2010).

16.1.2 Sulphur in Crude Oil

The units of sulphur content in crude oil in refineries is expressed in weight per cent (wt%) or parts per million by weight (ppmw). When the sulphur level is less than the

threshold value (e.g., 0.5 wt% (5000 ppmw)), crude oil is called *sweet* (low sulphur) otherwise its *sour* (high sulphur). Due to low-sulphur content in sweet light crude oil, it is commercially more profitable related to sour heavier oil, thus, refining and handling process becomes less (Duissenov 2012, 2013).

The typical refinery process and its products are being illustrated in Fig. 16.1, (El-Gendy and Nassar 2018) where for any given crude oil, with increasing carbon number, sulphur concentration also increases gradually. Thus, heavy crude fractions such as fuel oil and asphalt with a high boiling point (above 1050 °F) are having the highest sulphur content. Jet fuel and diesel oil, in turn, have higher sulphur content than that of gasoline boiling range. Likewise, in the gasoline boiling range, lighter components have lower sulphur content than heavier components.

In crude oil, the organic sulphur compounds present is classified as acidic sulphur compounds including mercaptans and non-acidic compounds including sulphides, disulfides and thiophenic compounds (Duissenov 2012, 2013). The mass of sulphur present in mercaptans is 0.1–15% out of total sulphur content in crude oil is due to the presence of a thiol group (SH). Around 50–80% chemically neutral sulfides are present out of the total sulphur compounds. Disulfides are found in small quantities of about 7–15% of the overall sulphur content of oil (Ryabov 2009). Thiophenic compounds and its derivatives are neutral cyclic five membered-rings with high-temperature resistance. They exhibit similar properties as aromatic hydrocarbons and are insoluble in water (Duissenov 2013). In order to remove the sulphur atom, deep desulphurization processes are incorporated in refineries so that these recalcitrant aromatic sulphur can be desulphurized. The organic sulphur compounds present in petroleum are shown in Fig. 16.2 (Alkhalili et al. 2017).

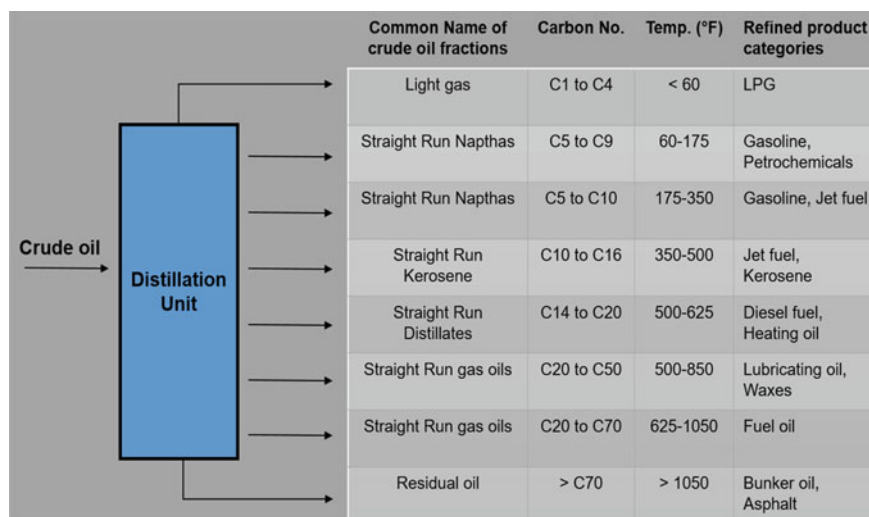| Common Name of crude oil fractions	Carbon No.	Temp. (°F)	Refined product categories
Light gas	C1 to C4	< 60	LPG
Straight Run Napthas	C5 to C9	60-175	Gasoline, Petrochemicals
Straight Run Napthas	C5 to C10	175-350	Gasoline, Jet fuel
Straight Run Kerosene	C10 to C16	350-500	Jet fuel, Kerosene
Straight Run Distillates	C14 to C20	500-625	Diesel fuel, Heating oil
Straight Run gas oils	C20 to C50	500-850	Lubricating oil, Waxes
Straight Run gas oils	C20 to C70	625-1050	Fuel oil
Residual oil	> C70	> 1050	Bunker oil, Asphalt

Fig. 16.1 Typical refinery processes and products (El-Gendy and Nassar 2018)
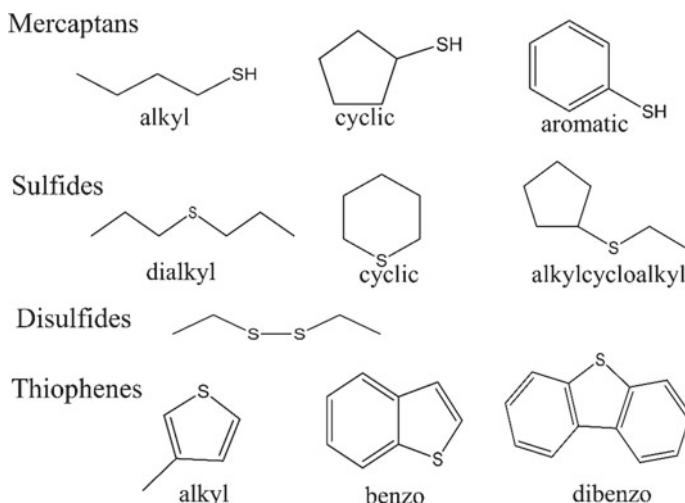
Fig. 16.2 Organic Sulphur Compounds in crude oil (Alkhalili et al. 2017)

16.1.3 Biodesulphurization Process

Biodesulphurization (BDS) is an emerging nonconventional technology to produce S-free fuels that can be combined with other desulphurization techniques such as oxidative and adsorptive desulphurization processes. In order to remove the sulphur content in liquid fuels, the BDS process takes advantage of microbial biodegradation processes. The microorganisms have developed their own mechanisms in which they uptake the organic sulphur from the fuels into their metabolic pathways and thus, removing the sulphur content in the fuel. Either these microorganisms can be used in free or immobilized states, or their enzymes and cellular extracts can be used in the BDS process (Soleimani et al. 2007). BDS is characterised with substrate selectivity and high sulphur removal efficiency and it is because of the use of microbial enzymatic systems. Since the microbial metabolic reactions are substrate specific the generation of undesirable by-products is very low (Ohshiro and Izumi 1999). Mostly Gram-positive bacteria studied and used extensively for BDS processes are, e.g., *Rhodococcus, Gordonia, Paenibacillus, Mycobacterium, Nocardia, Corynebacterium* or *Bacillus* strains (Martínez et al. 2017). However, numerous gram-negative bacteria like *Desulfovibrio* and *Pseudomonas* strains have some features, e.g., organic solvent and metal tolerance is high, easy genetic manipulation and broad metabolic flexibility, which makes them ideal strains for developing recombinant biocatalysts for BDS.
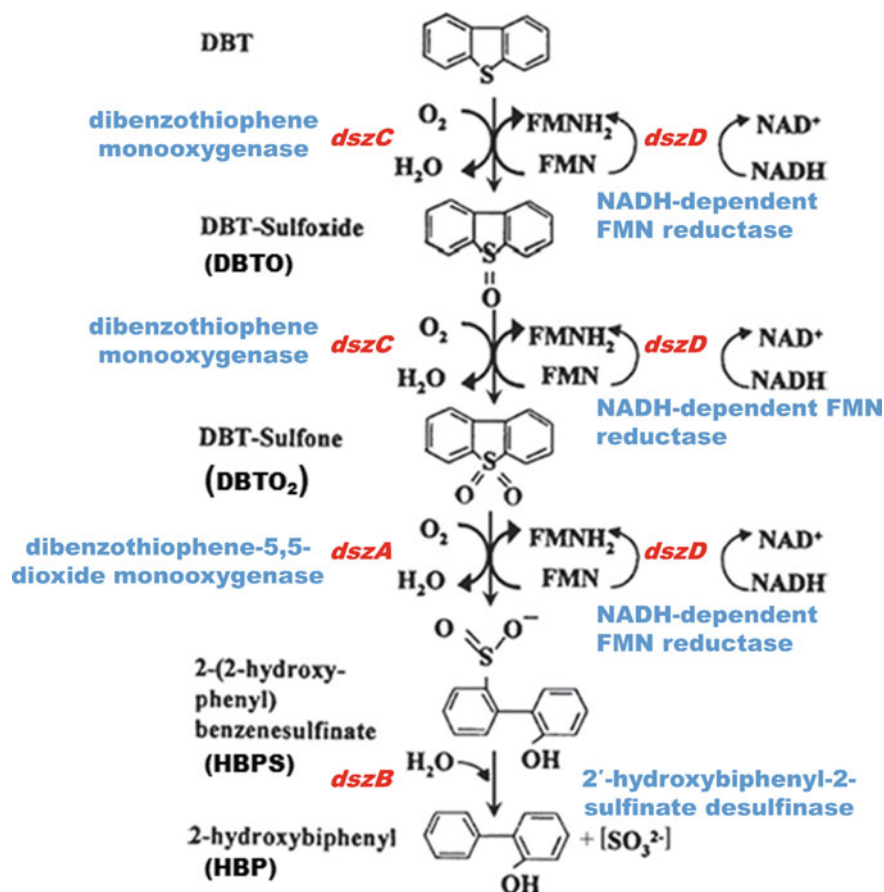
Aerobic desulphurization of dibenzothiophene (DBT) follows mainly three pathways (Klein et al. 1994). Firstly, it follows a complete destructive pathway where DBT is catalyzed to sulfate, water and carbon dioxide. The second pathway is Kodama pathway, a ring-destructive pathway, where there is partial degradation of

sulphur which remains in the organic skeleton. Thirdly, there is a non-destructive pathway called 4S pathway where C–S bond cleaves removing sulphur from DBT and thus does not break the hydrocarbon backbone of the molecule retaining the calorific value of the fuel. The aromatic sulphur compounds like dibenzothiophene (DBT) and its alkylated derivatives are mainly targeted in BDS by the 4S pathway. Thus the 4S pathway is anticipated for the desulphurization of petroleum products in refineries (Monticello 2000). However, the inhibition of the 4S pathway by the toxic end product 2-hydroxybiphenyl (2HBP), leads to a decrease in desulphurization activity, which is the primary reason for failure to develop an exceptional biocatalyst. Genetic engineering approaches targeting the destruction of the toxic and inhibitory end product could be a potential strategy to alleviate/overcome this inhibition and increase desulphurization efficiency.

16.1.4 Genetics of Biodesulphurization

It is reported that there are three genes involved in biodesulphurization designated as *dszABC*. In the biodesulphurization pathway, *dszC* converts DBT directly into DBT-sulfone and that *dszA* and *dszB* work together on converting DBT-sulfone to 2-HBP (Piddington et al. 1995).

In a 4-kb conserved region of a mega-plasmid, the *dsz* genes are arranged in an operon-regulated system (Oldfield et al. 1997). Further investigation of a model organism *R. erythropolis* IGTS8 gave a clearer understanding of the desulphurization genes. The three genes *dszA, dszB* and *dszC* involved in desulphurizing DBT in *R. erythropolis* IGTS8 are clustered on a 120-kb linear plasmid encoding the enzymes DszA, DszB and DszC respectively. DszC is a 45-kDa protein responsible for the conversion of DBT to $DBTO_2$ through two consecutive monooxygenation reactions. DszA is a 50-kDa protein responsible for the second monooxygenation reaction that converts DBT-sulfone ($DBTO_2$) to 2-(2-hydroxyphenyl)benzenesulfinate (HBPS). DszB is a 40-kDa protein encoding the enzyme is a desulfinase that catalyzes the last step in the pathway where 2-HBP and sulfinate are formed as final products. The *dszABC* genes are transcribed in the same direction. The termination codon for the gene *dszA* and the initiation codon for the gene *dszB* overlap. A 13-bp gap separates the genes *dszB* and *dszC* (Ohshiro and Izumi 1999). The fourth desulphurizing gene, *dszD,* is located on the chromosomal DNA and not on the plasmid. This gene code for the protein DszD, a flavin reductase involved in the monooxygenation reactions (Gray et al. 1996). The metabolic pathway for the conversion of DBT to 2HBP is shown in Fig. 16.3 (Alkhalili et al. 2017).

Fig. 16.3 4S Pathway: Metabolic Pathway of Dibenzothiophene desulphurization (Alkhalili et al. 2017)

16.2 Application of Microbial Desulphurization

Biodesulphurization can be used as an alternative process for pre-treatment of crude oil before it enters a pipeline or can be applied to HDS diesel oil while downstream processing in refineries, or refined products like diesel or gasoline can be deep desulphurized. Recent petroleum refineries are generally focusing on refining of sweet and light crude oils which increases reliance and dependency on heavier crude oils. Here, we present an appraisal about the studies of biodesulphurization of not only petroleum compounds achieved from lighter crude oils like gasoline and diesel oil but also review studies on different types of mesophilic and thermophilic and gram-negative bacteria used in biodesulphurization, of crude oil.

16.2.1   Biodesulphurization of Gasoline

Gasoline ranges with naphtha and fluid catalytic cracking (FCC)–naphtha, consists of organosulphur compounds such as thiophene and its alkylated derivatives; benzothiophene and mercaptans (RSH), sulfides (R2S) and disulfides (RSSR) (Song and Ma 2003). The deep desulphurization of gasoline by conventional hydrodesulphurization (HDS) technology decreases the yield of gasoline. Moreover, octane number significantly decreases as the olefins get saturated in naphtha from fluid catalytic cracking and thus, increasing more hydrogen consumption. Biodesulphurization (BDS) follows an alternate 4S-pathway where sulphur removal does not alter the octane value of fuels (Malik 1978). BDS appears to be a promising technology being less expensive and an alternative to HDS that can be effectively applied to the refining of gasoline where the octane value is restored (Li et al. 2005). It is reported that microorganisms such as *Mycobacterium goodii* X7B and *Rhodococcus erythropolis* XP are used in biodesulphurization of gasoline. The total sulphur content considerably decreases, from 227 to 71 ppm when immobilized cells of strain X7B are used to treat Dushanzi straight-run gasoline (DSRG227) for 24 h, at 40 °C. While after using two consecutive cycles of immobilized cells to treat DSRG227 at 40 °C, the sulphur content decreases from 275 to 54 ppm (Li et al. 2005). Using of free whole cells of *R. erythropolis* XP reduces sulphur content in fluid catalytic cracking (FCC) by 30% and straight-run (SR) gasoline oils by 85% (Yu et al. 2006a). Another new method for BDS of gasoline is considered where *R. erythropolis* is supported on polyvinyl alcohol (PVA) and n-hexane as the solvent is used desulphurization of thiophenes. It shows that 97.41% of thiophene is degraded when the reaction is carried out with initial thiophene concentration of 80 ppm, pH 7, biocatalyst concentration of 0.1 g of biocatalyst at 30 °C for 20 h (Fatahi and Sadeghi 2017).

16.2.2   Biodesulphurization of Diesel Fuel

In refinery the ranges of diesel fuel are middle distillate fractions and light cycle oil (LCO) which consists benzothiophenes and its alkylated compounds; dibenzothiophene (DBT) and its alkylated derivatives, 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethydibenzothiophene (4,6-DMDBT). Deep desulphurization of the diesel sulphur (500 to <15 ppm) is dictated mainly by alkylated derivatives of DBT which becomes recalcitrant and difficult to eliminate by HDS due to steric hindrance by substitutions in positions 4 and 6. However, biodesulphurization involving microbial attack of such recalcitrant sulphur compounds is an effective strategy for their removal from diesel oil. Several microorganisms having a high amount of sulphur removal capability are used for biodesulphurization of different middle distillate and LCO. Microbial desulphurization of diesel oil is studied mainly in lab scale batch process either in flask or fermenters with various parameters such as incubation period, temperature, pH, agitation speed, initial sulphur concentration and water to

oil phase ratio. Thus, the sulphur removal rate of various bacteria of different diesel oil in different conditions is reviewed.

16.2.2.1 Biodesulphurization Rate of Various Diesel Fuel by Mesophilic Bacteria

There are several reports on the utilization of mesophilic bacteria for desulphurization of various diesel oil as discussed in Table 16.1.

The resting cells of *Gordonia* strain CYKS1 are used for the treatment of middle distillate unit feed (MDUF) and light gas oil (LGO) for 12 h with initial sulphur concentration of 1500 ppm in MDUF and 3000 ppm in LGO. The total sulphur

Table 16.1 Biodesulphurization rate of various diesel fuel by mesophilic bacteria at different experimental conditions

Oil fraction	Microorganism	Experimental conditions	% Total sulphur removal	References
Middle-distillate unit feed (MDUF) and Light gas oil (LGO)	*Gordonia strain* CYKS1	Batch process (30 °C, 170 rpm, water:oil volume ratio 9:1, 12 h), Initial sulphur conc. MDUF—1500 ppm; LGO—3000 ppm	MDUF—70% LGO—50%	Rhee et al. (1998)
Hydrodesulphurized (HDS) middle-distillate petroleum (MD 1850)	*Rhodococcus erythropolis* I-19	Stirred reactor vessel equipped with controller (30 °C, 1000 rpm, pH-7.5 and dissolved oxygen (DO)—40% air saturation, water: oil volume ratio 3:1), Initial sulphur conc. 1850 ppm	67%	Folsom et al. (1999)
Middle-distillate (diesel range) fraction of Oregon basin (OB) crude oil	*Rhodococcus* sp. ECRD-1 (ATCC 55309)	Batch process (25 °C, 200 rpm, pH-7.0, water:oil volume ratio for undiluted—1000:1 and diluted—100:1, 7 days), Initial sulphur conc. Undiluted-20000 ppm and diluted 10 ppm and 20 ppm	Undiluted—8.1% Diluted—30%	Grossman et al. (1999)

(continued)

Table 16.1 (continued)

Oil fraction	Microorganism	Experimental conditions	% Total sulphur removal	References
HDS-untreated LGO and HDS-untreated MDUF diluted with hexadecane	*Gordonia* sp. CYKS1	Batch process (30 °C, 180 rpm, water:oil volume ratio 20:1, 10 h), Initial sulphur conc. LGO—3000 ppm; MDUF diluted with hexadecane—1500 ppm	LGO—35% MDUF diluted with hexade-cane—60%	Chang et al. (2000)
Low sulphur diesel oil	*Gordonia nitida* CYKS1	Batch process (30 °C, 180 rpm, pH-7, water:oil volume ratio 10:1, 20 h), Initial sulphur conc. 250 ppm	76%	Chang et al. (2001)
Catalytic cracker middle-distillate light cycle oil	*Rhodococcus* sp. strain ECRD-1	Batch process (25 °C, 200 rpm, pH-7.0, water:oil volume ratio: 50:1; 7 days), Initial sulphur conc. 669 ppm	92%	Grossman et al. (2001)
HDS-treated light diesel oil (LDO) and Diesel oil	*Rhodococcus* sp. P32C1	Batch process (30 °C, 150 rpm, water:oil volume ratio: 4:1, 24 h), Initial sulphur conc. LDO- 303 ppm; Diesel—1000 ppm	LDO—48.5% Diesel—23.7%	Maghsoudi et al. (2001)
HDS Diesel oil	*Rhodococcus* sp. IMP-S02	Batch process (30 °C, 180 rpm, 7 days), Initial sulphur conc. 500 ppm	60%	Castorena et al. (2002)
HDS Diesel oil by the BPCL oil refinery	*Arthrobacter sulphureus*, *Rhodococcus* sp.	Batch process (30 °C, 200 rpm, water:oil volume ratio 3:1, 5 days), Initial sulphur conc. 170 ppm in diesel oil I and 70 ppm in high-speed diesel oil II	Diesel I—50% by *Rhodococcus* sp. and 47% by *Arthrobacter sulphureus* Diesel II—72 % by *Rhodococcus* sp.	Labana et al. (2005)

Table 16.1 (continued)

Oil fraction	Microorganism	Experimental conditions	% Total sulphur removal	References
Diesel oil, Fushun crude oil and Sudanese crude oil	*Rhodococcus erythropolis* XP	Batch process (30 °C, 200 rpm, pH 7.0, Diesel oil aqueous:oil volume ratio 9:1, 12 h and Crude oil aqueous:oil volume ratio 20:1, 72 h), Initial sulphur conc. Diesel oil—259 ppm organic sulphur; Fushun crude oil—3210 ppm; Sudanese crude oil—1237 ppm	94.5% in Diesel oil; 62.3% in Fushun crude oil; 47.2% in Sudanese crude oil	Yu et al. (2006b)
HDS Diesel oil	*Rhodococcus erythropolis* FSD-2	Two cycles of batch process (30 °C, 200 rpm, pH 7.0, water:oil volume ratio 5:1, 12 h per cycle), Initial sulphur conc. 198 ppm	97	Zhang et al. (2007)
HDS Diesel oil	*Rhodococcus erythropolis* NCC-1	Batch process (30 °C, 150 rpm, water:oil volume ratio 10:1, 96 h), Initial sulphur conc. 554 ppm	50.5	Li et al. (2007b)
Straight run Diesel oil	*Rhodococcus globerulus* DAQ3	Continuous process in the reactor (30 °C, 600 rpm, O_2 air flow rate—0.2–0.5 vvm, water:oil volume ratio 4:1, 5 days), Initial sulphur conc. 12,600 ppm	12	Yang et al. (2007)
HDS Diesel oil	Mixed cells of *R. erythropolis* DS-3 and *Gordonia* sp. C-6 at 2.2:1 (w/w)	Three cycles of batch process (30 °C, 160 rpm, pH 7.5, water:oil volume ratio 4:1, 24 h per cycle), Initial sulphur conc. 1260 ppm	86	Li et al. (2008)

Notation sp.: species; conc.: concentration; rpm: rotation per hour; ppm: parts per million

content removed is 70% for MDUF and 30% for LGO. Thus, there is a good potential of the newly isolated strain CYKS1 to biodesulphurize diesel oil (Rhee et al. 1998).

A middle distillate (MD) petroleum with initial sulphur concentration of 1850 ppm is treated with *R. erythropolis* I-19. This bacterium is genetically engineered, to have multiple copies of *dsz* genes, which can desulphurize a large range of alkylated dibenzothiophenes (Cx-DBTs). A sulphur amount of 1850 ppm is reduced to 615 ppm resulting in a 67% reduction of total sulphur (Folsom et al. 1999).

Rhodococcus sp. strain ECRD-1 is evaluated for its ability to desulphurize Oregon basin (OB) crude oil which is of middle-distillate fraction range. The maximum level of sulphur removal present in the middle-distillate OB oil by ECRD-1 is of 30% of the total sulphur. The OB oil is diluted 10 times and 20 times in decane i.e. initial sulphur concentration is 20 and 10 ppm respectively. The reduction of 20–10 ppm of sulphur added for biodesulphurization do not increase sulphur removal but it increases the formation of HBP-sultine. It is seen that the final remaining sulphur content for both dilutions is same. This suggests further that sulphur removal gets limited due to the bioavailability and substrate range of the desulphurization enzymes (Grossman et al. 1999).

The harvest time and the highest cell amount (0.12 mg sulphur g^{-1} cell^{-1} h^{-1}) during the early growth phase of resting cells of *Gordonia* sp. CYKS1 intensely supports the rate of desulphurization activity. Sulphur contents of LGO and MDUF are 3000 ppm and 15,000 ppm, respectively. In the case of the LGO, the sulphur content decreases from 3000 ppm to about 1950 ppm in 10 h. When MDUF is diluted with hexadecane to final sulphur concentration of 1500 ppm, its sulphur content reduces to 610 ppm in 10 h. The specific desulphurization rate for diesel oil is higher than DBT containing model oil may be due to the easier removal of other organic sulphur compounds than that of DBT (Chang et al. 2000).

It is observed that *Gordonia nitida* CYKS1 decreases the diesel oil's total sulphur content from 250 to 61 ppm in 20 h. The water-oil volume ratio is 10:1, and the concentration of biocatalyst is 18.6 g l^{-1}. About 180 ppm of sulphur is desulphurized in 4 h and then desulphurization rate sharply decreases. The final sulphur content lowers to about 61 ppm at 20 h. The decrease in desulphurization rate after 4 h, may be due to insufficiency of reducing power for the biocatalytic enzymes to work or accumulation of toxic metabolites in the medium. Thus the biocatalyst implies to have a good potential of deep desulphurizing low sulphur diesel to ultralow-sulphur diesel oils (Chang et al. 2001).

Rhodococcus sp. strain ECRD-1 is used for treatment light cycle oil (LCO) produced by catalytic cracking of middle distillate range whose sulphur content is virtually all substituted DBTs. The sulphur content decreases from 669 to 56 ppm with a total sulphur elimination of 92% in 7 days. After biodesulphurization, the remaining sulphur compounds are present in an oxidized form. This suggests that enzyme monooxygenases DszC and DszA oxidizing the sulphur atom to yield sulfinic acids and sulfones are having broader substrate ranges than the enzyme desulfinase, DszB, that catalyzes the elimination of sulphur from sulfinic acids. Thus the remaining of

oxidized species after biodesulphurization suggests a limitation of the extent of desulphurization due to the kinetic rates and/or substrate range of consequent enzymes in the desulphurization pathway (Grossman et al. 2001).

Resting cells of *Rhodococcus* sp. strain P32C1 a newly isolated strain shows the high desulphurizing activity of organic sulphur compounds in HDS-treated light diesel oil (LDO) and Diesel oil. The final sulphur content of LDO and diesel oil after 24 h of reaction at 30 °C are reduced from 303 to 156 ppm and 1000 to 763 ppm respectively (Maghsoudi et al. 2001).

A deeply HDS diesel oil containing significant amounts of 4,6 dimethyldibenzothiophene with an initial sulphur content of 500 ppm is treated with *Rhodococcus* sp. IMP-S02 cells. After treatment, the total sulphur removed is up to 60% and there is the total removal of all the 4,6-dimethyldibenzothiophene (Castorena et al. 2002).

Desulphurization of dibenzothiophene in diesel oil is reported by two bacteria i.e. *Rhodococcus* sp. and *Arthrobacter sulphureus* that are isolated from soil contaminated with oil sludge. HDS diesel oil named Diesel sample I, with a primary sulphur content of 170 ppm when treated with *Rhodococcus* sp. total sulphur removal rate is 50% and by 47% when treated with *A. sulphureus*. Another HDS diesel oil named diesel sample II, with a primary sulphur content of 70 ppm, when treated with *Rhodococcus* sp. resulted in total sulphur removal of 72%, whereas *A. sulphureus* treatment on this sample had no effect on removal of sulphur content. Though both of the diesel oil samples is HDS, they have different desulphurization activity due to the varying ratio of diverse forms of sulphur compounds such as thiophenes, sulphides, mercaptans etc. (Labana et al. 2005).

The resting cells of an isolated strain *R. erythropolis* after 24 h at 30 °C reduces the sulphur content of diesel oil (initial organic sulphur content, 259 ppm) by 94.5%. Other crude oils like Fushun crude oil (initial total sulphur content, 3210 ppm) and Sudanese crude oil (initial total sulphur content, 1237 ppm) are also biodesulphurized with a total sulphur removal of 62.3% and 47.2% respectively (Yu et al. 2006b).

R. erythropolis FSD-2 is used in desulphurizing HDS diesel fuel where total sulphur removal content is about 97% after two consecutive biodesulphurization (BDS) processes. BDS again. The result shows that the sulphur content in diesel oil with 198 ppm is reduced to 6 ppm within 48 h. Thus *R. erythropolis* FSD-2 is having a good potential of deep desulphurization and can be utilized in producing ultralow sulphur diesel fuel (Zhang et al. 2007).

A newly isolated strain *R. erythropolis* NCC-1 desulphurizes HDS diesel oil having many organic sulphur compounds such as DBT and 4,6-dimethyldibenzothiophene (4,6-DMDBT). In diesel oil, the total sulphur content significantly decreased, from 554 to 274 mg/L which is 50.5% total sulphur removal (Li et al. 2007b).

Rhodococcus globerulus DAQ3 a newly isolated strain has a double reaction rate than that of the commonly used *R. erythropolis* IGTS8. But high desulphurization activity is maintained in a batch reactor for resting cells of DAQ3. Based on continuous bioreactors a novel process is designed where growing cells are used for efficient BDS activity, by using two layers partitioned aqueous–organic phase. The total sulphur content removal from 250 ml straight run diesel oil is 1500 ppm within

a 5-day period which is about 12% total sulphur removal. Though the desulphurizing activity is less the operating conditions of the reactor leads to an improvement on the stability of bacterial conditions and thus maintains the bioactivity for BDS of diesel oils (Yang et al. 2007).

HDS diesel oil is treated with washed cells of mixed bacterial culture of *R. erythropolis* DS-3 and *Gordonia* sp. C-6 with ratio of 2.2:1 (w/w). After three cycles of biodesulphurization the sulphur content from diesel oil was reduced from 1260 to 180 ppm, which is about 86% of the total sulphur (Li et al. 2008).

16.2.2.2   Biodesulphurization Rate of Various Diesel Fuel by Thermophilic Bacteria

Application of thermophilic bacteria for biodesulphurization allows operation at high temperature, which is associated with many advantages such as increase of reaction rate, decrease in oil viscosity thereby leading to increase in efficiency of the process (Le Borgne and Quintero 2003). Table 16.2 discusses studies conducted on thermophilic bacteria for desulphurization of different diesel oils.

Light gas oil with 800 ppm of initial sulphur content was treated with *Paenibacillus* sp. strains A11-1 and A11-2 at 50 °C. The total sulphur removal rate is 83–89% in light gas oil which indicates that at high temperatures both *Paenibacillus* strains are able to desulphurize the light gas oil (Konishi et al. 1997).

Growing cells of *Mycobacterium phlei* WU-F1 at is able to grow at 30 °C to high as 50 °C temperatures, exhibiting high desulphurizing ability towards HDS LGOs. There is 60–70% total sulphur reduction for three types of HDS LGOs- X-LGO (34 ppm S), F-LGO (120 ppm S) and B-LGO (390 ppm S). When the HDS LGOs are treated with resting cells of WU-F1 at 45 °C, with 50% (v/v) oil aqueous phase, the sulphur content reduces from 34 to 15 ppm S in X-LGO, from 120 to 42 ppm in F-LGO, and from 390 to 100 ppm in B-LGO. The bacterium is also capable of a desulphurizing wide range of alkylated DBTs containing 3,4,6-trimethyl-DBT, 4,6-dimethyl-DBT and 4-methyl-DBT as analysed by Gas chromatography. Therefore, M. phlei WU-F1, a thermophilic bacterium which is able to effectively desulphurize not only various sulphur compounds present in HDS-treated LGOs but also over a diverse range of temperature that may be till 50 °C which makes it a favorable biocatalyst for practical use of biodesulphurization of diesel oil (Furuya et al. 2003).

Mycobacterium sp. X7B is able to utilize a wide range of alkylated DBT derivatives such as 4,6-dimethylDBT and as 4-methylDBT. The resting cells after 24 h at 45 °C remove 86% of total sulphur from HDS diesel oil which has an initial total sulphur content of 535 ppm (Li et al. 2003).

Mycobacterium phlei WU-0103 is newly an isolated thermophilic bacteria capable of growing at 50 °C. The bacterium at 45 °C is able to biodesulphurize 12 times diluted straight-run light gas oil by reducing the sulphur content from 1000 to 475 ppm, with a reduction of 52% (Ishii et al. 2005).

Mycobacterium goodii X7B, a facultative thermophilic bacterium, shows improved growth at 40 °C in a fed-batch culture when pH is controlled constantly.

Table 16.2 Biodesulphurization rate of various diesel fuel by thermophilic bacteria at different experimental conditions

Oil fraction	Microorganism	Experimental conditions	% Total sulphur removal	Reference
Light gas oil	*Paenibacillus* sp. *A11–2*	Batch process (50 °C, 50 rpm, 20 h), Initial sulphur conc. 800 ppm	89–93	Konishi et al. (1997)
HDS LGO	*Mycobacterium phlei WU-F1*	Batch process (resting cells at 45 °C, water:oil volume ratio: 2:1, 24 h and growing cells 30–50 °C, 7 days) Initial sulphur conc. B-LGO 390 ppm; F-LGO 120 ppm; X-LGO 34 ppm	60–70	Furuya et al. (2003)
HDS Diesel oil	*Mycobacterium* sp. X7B	Batch process (45 °C, 180 rpm, water:oil volume ratio: 9:1, 24 h), Initial sulphur conc. 535 ppm	86	Li et al. (2003)
Straight-run light gas oil	*Mycobacterium phlei* WU-0103	Batch process (45 °C, 240 rpm, water:oil volume ratio 10:1, 3 days), Initial sulphur conc. 1000 ppm	52	Ishii et al. (2005)
Liaoning crude oil	*Mycobacterium goodii* X7B	Fed Batch culture (40 °C, pH 7.0, aqueous:oil volume ratio 20:1, 3 days), Initial sulphur conc. 3600 ppm	59	Li et al. (2007a)

Notation sp.: species; conc.: concentration; rpm: rotation per hour; ppm: parts per million

Liaoning crude oil is treated for 72 h and there was a total sulphur removal of 59%, from 3600 to 1478 ppm (Li et al. 2007a).

16.2.2.3 Biodesulphurization Rate of Various Diesel Fuel by Gram-Negative Bacteria

Studies reveal that gram-negative bacteria such as *Pseudomonas* strains are more promising for BDS of diesel oil due to their high solvent tolerance capacity than gram-positive bacteria (Table 16.3). Many recombinant *Pseudomonas* strains with higher BDS activity is made by cloning and expressing the *Dsz* genes obtained from *R. erythropolis* IGTS8. There are two reasons for the selection of gram-negative bacteria to carry these desulphurizing *Dsz* genes. Firstly, highly tolerant of the oil

Table 16.3 Biodesulphurization rate of various diesel fuel by gram-negative bacteria at different experimental conditions

Oil fraction	Microorganism	Experimental conditions	% Total sulphur removal (%)	References
Straight run diesel oil	*Pseudomonas delafieldii* R-8	Batch process (30 °C, 170 rpm, water:oil volume ratio 3:1, 24 h), Initial sulphur conc. 1807 ppm	55.2	Mingfang et al. (2003)
Light Gas Oil	*Pseudomonas aeruginosa* PAR41 (Recombinant bacteria)	Batch process (30 °C, 130 rpm, water:oil volume ratio 3:1, 48 h), Initial sulphur conc. 1807 ppm	82.5	Watanabe et al. (2003)
HDS Diesel oil	*Pseudomonas delafieldii* R-8	Two cycles of batch process (30 °C, 180 rpm, water:oil volume ratio 2:1, 20 h per cycle), Initial sulphur conc. 591 ppm	90.5	Guobin et al. (2005)
HDS treated Light gas oil (LGO)	*Sphingomonas subarctica* T7b	Jar fermenter (27 °C, 400 rpm, 0.9 l/min aeration, pH-7, water:oil volume ratio 3:1, 36 h), Initial sulphur conc. 280 ppm	59	Gunam et al. (2006)
HDS Diesel oil	*Pseudomonas delafieldii* R-8	Batch process (30 °C, 180 rpm, water:oil volume ratio 2:1, 16 h), Initial sulphur conc. 591 ppm	47	Guobin et al. (2006)
Light Crude oil	*Pantoea agglomerans* D23W3	Batch process (30 °C, 200 rpm, aqueous:oil volume ratio 10:1, 5 days), Initial sulphur conc. 3800 ppm	71.42	Bhatia and Sharma (2010)
Light Crude oil	*Klebsiella* sp. 13T	Batch process (45 °C, 200 rpm, aqueous:oil volume ratio 10:1, 5 days), Initial sulphur conc. 3500 ppm	53.21	Bhatia and Sharma (2010)
HDS Diesel oil	*Achromobacter* sp.	Batch process (37 °C, 200 rpm, water:oil volume ratio: 9:1, 24 h), Initial organic sulphur conc. 420 ppm	93	Bordoloi et al. (2014)

Notation sp.: species; conc.: concentration; rpm: rotation per hour; ppm: parts per million

in which there is the presence of sulphur compounds and hydrocarbons. Secondly, biosurfactants are released which increases the contact between water and oil phase, which further reduces the limitations of mass transfer and increases BDS rate. Moreover, it is reported that most of the *Pseudomonas* strains are able to metabolize DBT via 4S pathway where the bond of carbon–sulphur (C–S) is not degraded while cleavage occurs at carbon-carbon bonds (Guobin et al. 2006).

The straight-run diesel oil is desulphurized by lyophilized cells of *Pseudomonas delafieldii* R-8 with the water-oil volume ratio of 3:1. Their sulphur content of the diesel oil is reduced from 1807 to 808.9 mg/L after 24 h. The total sulphur content removal is about 1000 mg/L or 55.2% (Mingfang et al. 2003).

Pseudomonas aeruginosa PAR41 is a recombinant strain whose resting cells are used to treat light gas oil (LGO) with a sulphur content of 360 ppm. The resting cells of strain PAR41 are having higher desulphurization activity for LGO when cultivated with *n*-tetradecane (50% v/v) than without *n*-tetradecane (Watanabe et al. 2003).

The cells of *Pseudomonas delafieldii* R-8 in resting condition is used to treat HDS diesel oil having an initial sulphur content of 591 ppm. After two consecutive treatments treatment with water oil volume ratio of 2:1, 90.5% of the total sulphur is reduced. Moreover, analysis by GC-AED (gas chromatography having atomic emission detector) shows that there is approximately 100% reduction for all the C_1DBTs and C_2DBTs, while 94.63% for C_3DBT and 97.09% for C_4DBT. Due to the capability of biosurfactant production by the strain, there is an increase in DBT uptake, resulting in increased BDS activity (Guobin et al. 2005).

Sphingomonas subarctica T7b a newly isolated strain isolated is having the capability of desulphurizing aromatic hydrocarbons such as 4,6-dipentyl DBT and 4,6-dibutyl DBT in light gas oil (LGO). The total content of sulphur removal from LGO is 59% within 36 h (Gunam et al. 2006).

Pseudomonas delafieldii R-8 cells in resting condition are used for biodesulphurization of HDS diesel oil where the total sulphur reduced is from 591 to 313 ppm after 16 h, i.e. 47% total sulphur is removed (Guobin et al. 2006).

Biodesulphurization of model compounds such as dibenzothiophene and its alkylated derivatives are studied by a strain *Pantoea agglomerans* D23W3 which is newly isolated. It is reported that *P. agglomerans* D23W3 are capable of removing sulphur from diverse petroleum crude oils in a range of 26.38–71.42%, among which light crude oil is having highest sulphur removal (Bhatia and Sharma 2010).

Klebsiella sp. 13T a thermophilic, gram-negative bacterium is capable of desulphurizing DBT to 2 hydroxybiphenyl (2-HBP) through 4S pathway at 45 °C. *Klebsiella* sp. 13T is able to remove sulphur from different petroleum oils, with the removal of 22–53% total sulphur and highest removal of sulphur is from light crude oil (Bhatia and Sharma 2012).

The resting cells of *Achromobacter* sp. are used for desulphurization of HDS with total organic sulphur of 420 ppm. The total content of sulphur removal from the diesel oil after 24 h treatment is 83% which is determined to be as 19 ppm. Moreover, DBT and 4-M-DBT are metabolized to an end product of 2-methoxybiphenyl (2-MBP) which does not have a negative inhibition effect on biodesulphurizing activity (Bordoloi et al. 2014).

16.3 Conclusions

Biodesulfurization of fossil fuel utilizing free or immobilized microorganisms has been identified as a potential and sustainable technology and many bacteria (mesophilic, thermophilic and gram-negative) with good desulfurization ability have been recognized. However, more focus should be given to utilization of thermotolerant gram-negative bacteria, which would provide the advantage of high temperature application and high tolerance to solvent. Moreover gram-negative bacteria are easy to be genetically engineered for expression of desulphurizing genes for improved biodesulphurization activity. However, there is the need to conduct biodesulphurization studies with actual oil products to assess the industrial value of the technology.

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