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Application of Clean Fuels in Combustion Engines

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Energy, Environment, and Sustainability

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Preface

Energy demand and pollutants growth are the main concerns due to the increasing population and urbanization. Indeed, modern society significantly depends on energy availability. The transport sector plays a crucial role in energy consumption and CO_2 production. In this regard, the application of cleaner fuels provides a practical alternative toward full decarbonization by 2050. The most common renewable fuels are discussed, and their main effects are assessed.

The International Society for Energy, Environment and Sustainability (ISEES) was founded at the Indian Institute of Technology Kanpur (IIT Kanpur), India, in January 2014 to spread knowledge/awareness and catalyze research activities in the fields of Energy, Environment, Sustainability, and Combustion. Society's goal is to contribute to the development of clean, affordable, and secure energy resources and a sustainable environment for society and spread knowledge in the areas mentioned above, and create awareness about the environmental challenges the world is facing today. The unique way adopted by ISEES 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. Society also recognizes the outstanding works of young scientists, professionals, and engineers for their contributions in these fields by conferring them awards under various categories.

Fifth International Conference on 'Sustainable Energy and Environmental Challenges' (V-SEEC) was organized under the auspices of ISEES from December 19–21, 2020, in virtual mode due to restrictions on travel because of the ongoing COVID-19 pandemic situation. This conference provided a platform for discussions between eminent scientists and engineers from various countries, including India, Spain, Austria, Bangladesh, Mexico, USA, Malaysia, China, UK, Netherlands, Germany, Israel, and Saudi Arabia. At this conference, eminent international speakers presented their views on energy, combustion, emissions, and alternative energy resources for sustainable development and a cleaner environment. The conference presented two high voltage plenary talks by Dr. V. K. Saraswat, Honorable Member, NITI Ayog, on ‘Technologies for Energy Security and Sustainability’ and Prof. Sandeep Verma, Secretary, SERB, on ‘New and Equitable R&D Funding Opportunities at SERB.’

The conference included nine technical sessions on topics related to energy and environmental sustainability. Each session had 6–7 eminent scientists from all over the world, who shared their opinion and discussed the trends for the future. The technical sessions in the conference included Emerging Contaminants: Monitoring and Degradation Challenges; Advanced Engine Technologies and Alternative Transportation Fuels; Future Fuels for Sustainable Transport; Sustainable Bioprocessing for Biofuel/Non-biofuel Production by Carbon Emission Reduction; Future of Solar Energy; Desalination and Wastewater Treatment by Membrane Technology; Biotechnology in Sustainable Development; Emerging Solutions for Environmental Applications’ and Challenges and Opportunities for Electric Vehicle Adoption. 500+ participants and speakers from all over the world attended this three days conference.

The conference concluded with a high voltage panel discussion on ‘Challenges and Opportunities for Electric Vehicle Adoption,’ where the panelists were Prof. Gautam Kalghatgi (University of Oxford), Prof. Ashok Jhunjhunwala (IIT Madras), Dr. Kelly Senecal (Convergent Science), Dr. Amir Abdul Manan (Saudi Aramco) and Dr. Sayan Biswas (University of Minnesota, USA). Prof. Avinash Kumar Agarwal, ISEES, moderated the panel discussion. 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 agencies and organizations for the successful conduct of the Fifth ISEES conference V-SEEC, where these books germinated. We want to acknowledge SERB (Special thanks to Dr. Sandeep Verma, Secretary) and our publishing partner Springer (Special thanks to Ms. Swati Meherishi).

The editors would like to express their sincere gratitude to a large number of authors from all over the world for submitting their high-quality work on time and revising it appropriately at short notice. We would like to express our special gratitude to our prolific set of reviewers, Dr. Ayat Gharehghani, Dr. Burak Zincir, Dr. Atul Dhar, Dr. Harsh Goyal, Dr. Prabakaran Balasubramanian, Dr. Jai Gopal Gupta, Dr. Rudrodip Majumdar, Dr. Luis Felipe Mazadiego, Dr. Farzad Jaliliantabar, Dr. Elumalai P. V., Dr. Saket Verma, Michele Pipicelli, Dr. Roberto Ianniello, Dr. Atul Dhar, Dr. Giuseppe Di Luca, who reviewed various chapters of this monograph and provided their valuable suggestions to improve the manuscripts.

This book is based on the description of the impact of fuels characteristics and their effects on the combustion processes in internal combustion engines. This book includes the analysis of a variety of biofuels (alcohol fuels and biodiesel) and biogases (natural gas, hydrogen, etc.), providing valuable information related to consequent effects on performance and emissions. Chapters include recent results and focuse on current trends of fuel utilization in the transport sector. Few chapters of this book are based on the review of the state of the art of clean fuels application. The book content is oriented to professionals, post-graduate students involved in fuels, IC engines, engine instrumentation, and environmental research.

Naples, Italy	Gabriele Di Blasio
Kanpur, India	Avinash Kumar Agarwal
Turin, Italy	Giacomo Belgiorno
Raipur, India	Pravesh Chandra Shukla

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Editors and Contributors

About the Editors

Dr. Gabriele Di Blasio is currently Research Scientist at the National Research Council of Italy. His main research interest is focused on advanced technologies and fuels for propulsion and energy conversion systems. He has lead various research projects in the field of internal combustion engine technology and fuel development. He has contributed to private and public projects in cooperation with universities, research centres and OEMs. He received his Ph.D. in Mechanical Engineering in 2012. Formerly Dr. Di Blasio worked as R&D responsible engineer in the industry sector leading projects on the development of dual fuel systems for heavy duty engines. He serves as an editor and reviewer for several indexed journals of national and international repute. He has authored over 70 publications in peer-reviewed journals, conference proceedings, books, book chapters and technical reports. He is a member of SAE International and SAE Engine committee.

Prof. Avinash Kumar Agarwal He is joined IIT Kanpur in 2001. He worked at the Engine Research Center, UW@Madison, the USA as a Post-Doctoral 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, 1D and 3D Simulations of engine processes, and large-bore engines. Prof. Agarwal has published 435+ peer-reviewed international journal and conference papers, 70 edited books, 92 books chapters, and 12200+ Scopus and 19000+ Google Scholar citations. He is the associate principal editor of FUEL. He has edited "Handbook of Combustion" (5 Volumes; 3168 pages), published by Wiley VCH, Germany. Prof. Agarwal is a Fellow of SAE (2012), Fellow of ASME (2013), Fellow of ISEES (2015), Fellow of INAE (2015), Fellow of NASI (2018), Fellow of Royal Society of Chemistry (2018), and a Fellow of American Association of Advancement in Science (2020). He is the 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. Prof. Agarwal received Prestigious CSIR Shanti Swarup Bhatnagar Award-2016 in Engineering Sciences. Prof. Agarwal is conferred upon Sir J C Bose National Fellowship (2019) by SERB for his outstanding contributions. Prof. Agarwal was a highly cited researcher (2018) and was in the top ten HCR from India among 4000 HCR researchers globally in 22 fields of inquiry.

Dr. Giacomo Belgiorno is Technology System Engineer in the Department of Advanced Engineering at PUNCH Torino S.p.A., formerly General Motors Global Propulsion Systems, Torino, Italy. He received his M.S. in Mechanical Engineering from University of Campania Luigi Vanvitelli in 2014, and Ph.D. in Energy Science and Engineering from University of Naples "Parthenope" in 2018. During the Ph.D. program, he worked at Istituto Motori as Research Associate and Guest Researcher in Lund University, Sweden. Subsequently, he worked in CNH Industrial. He has authored three book chapters and more than 20 conference and journal articles.

Dr. Pravesh Chandra Shukla is Assistant Professor in the Department of Mechanical Engineering at Indian Institute of Technology (IIT) Bhilai, India. Dr. Shukla received his Ph.D. from IIT Kanpur and has also worked as Senior Research Associate with the institute. He was a Postdoctoral Researcher in the Division of Combustion Engines, Department of Energy Sciences, Lund University, Sweden. He briefly worked in Ecole Centrale de Nantes, France, in the field of dual fuel combustion. He is a recipient of Young Scientist Award from the International Society for Energy, Environment and Sustainability. Dr. Shukla mainly works in the field of internal combustion engines and alternative fuels for transportation. He worked on the development of additives for high compression ratio heavy duty engines fueled with alcohol. He is involved in investigating the emission characteristics for alternative fuels like biodiesel, HVO and alcohols for conventional and advanced heavy duty compression ignition engines. He has published over 28 technical articles in journals of national and international repute and conference proceedings.

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Part I
General

Chapter 1
Introduction to Application of Clean Fuels in Combustion Engines

Gabriele Di Blasio, Avinash Kumar Agarwal, Giacomo Belgiorno, and Pravesh Chandra Shukla

Abstract Energy and the environment are the primary concerns for the transportation sector. Besides, the rapidly shrinking petroleum reserves are already alarming. All these, push the governments to find solutions for alternatives able to reduce the carbon footprint and pollutant emissions. Indeed, recent directives push toward carbon–neutral mobility by 2050. The electrification of the propulsion systems represents the priority. However, the research community has demonstrated as the application of cleaner fuels or zero-carbon fuels in the transport sector represents a valid medium-term alternative for decarbonizing the sector. This accelerates the alternative fuels requirements. In this context, renewable fuels, such as bio-alcohols, biogases are considered promising solutions. In this regard, the chapters of this book are based on aspects related to the technologies, methodologies for improving the combustion process and emissions trends applying cleaner fuels to internal combustion engines.

Keywords Renewable fuels · Biofuels · Biogas · Sustainable mobility · Internal combustion engines

The *first section* of this book includes the present introduction. *The second section* of this book is based on the application of biofuels, mostly alcohol fuels in internal combustion engines. The *first chapter* of this section discusses the use of alcohol fuels in compression ignition (CI) engines. Renewable fuels, such as methanol and ethanol, are studied and considered as a promising solution to mitigate the carbon

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footprint and reduce engine-out emissions. The analyses conducted are based on the type of fuel, the fuel supply method and the engine type, the use of alcohol fuels performs differently in terms of emissions and engine performance. Dual Fuel and blend combustion mode are considered demonstrating significant benefits on NOx-soot trade-offs. Soot reduction levels up to 70% are reached, thus demonstrating as renewable alcohol fuels are an interesting perspective towards sustainable mobility. The *second chapter* of this section analyses the use of alcohol fuels in spark-ignition (SI) engines. Aspects of the intrinsic ethanol and methanol production processes, chemical-physical properties, and their application in SI engines are discussed. Different engine fuelling strategies, dual fuel and blend are analysed in detail. It demonstrates as ethanol and methanol fuels generally have higher thermodynamic conversion efficiencies than conventional gasoline fuel. NOx decreases with alcohol fuels, and significant benefits on particle number emissions are observed independently of the engine fuelling mode. Then, the lower carbon content reduces the CO_2 emissions by up to 10%. The *third chapter* deals with the various fuel injection strategies for alcohol utilization in combustion engines. Their effects on spark ignition and compression ignition combustion characteristics and emissions formations are presented and discussed. Improved performance and emissions characteristics are found in reactivity controlled compression ignition (RCCI) combustion. Additionally, higher efficiencies and lower NO_x and PM emissions are demonstrated with homogeneous charge compression ignition (HCCI) combustion strategies. On the other hand, the integration of technologies as thermal insulation, minimal turbocharger after cooling, and exhaust gas recirculation (EGR) allow higher temperature combustion in the diesel engine, and able to better exert low-cetane and low-soot alcohols in mixing-limited diffusive combustion. Parameters as fuel injection pressure and timing, boosting, and geometrical compression ratio CR must be optimized depending on fuels and engine specifics. The authors state as future fuels will and must meet renewability, scalability, longevity, and affordability requirements. The *fourth chapter* of this section deals with methanol use in compression ignition engines. Methanol is considered a cleaner and carbon neutrally producible alternative to conventional fuels. However, there are challenges with methanol when used as engine fuel. An overall perspective is provided, demonstrating that methanol has better low-temperature combustion characteristics, limited NOx, and soot emission levels. The authors state that suitable additives or modifications in fuel injection systems are required. In general, possible benefits on efficiency, emissions and operating ranges can be achieved by applying alternative combustion concepts (LTC, PPC, RCCI). Further studies and experimental investigations are required to better adapt and exert fuel characteristics in compression ignition engines. The *fifth chapter* examines the potential of bio-butanol as a replacement for conventional fuels such as diesel or gasoline in internal combustion engines. Butanol has a comparatively higher energy density compared to other alcohols. The chapter presents literature and experimental studies about the potential of bio-butanol. The impact of diesel fuel blended in small proportion with butanol is discussed and the results were compared with diesel. The results show as the efficiencies trends strongly depend on the load conditions. However, the clean nature of butanol is highly beneficial for achieving sustainability.

The *sixth chapter* presents an analysis of biofuel combustion generated particles. In this regard, different methods are proposed to control soot emission of diesel engines such as the use of Diesel Particulate Filter which efficiency is characterized by the number of particles and their size. The morphology and microstructure of the soot emission for biofuel are different from diesel fuel, and this causes a higher soot oxidative reactivity. This improves the performance of the diesel particulate filter (DPF) for biofuel. Moreover, the oxygen content of the biofuel leads to a higher oxidation rate compared to diesel fuel. *Last chapter* of this section focuses on an experimental study on the engine performance and emissions of fuels from waste products. Various proportions of these fuels are blended with diesel and tested for solubility. Performance, combustion, and emissions of fully instrumented CI engines are performed by fuelling the chosen blends under various brake powers. Solubility results show that the prepared blends of various proportions of alcohols, recycled plastic oil and pyrolysed waste engine oil are stable up to 20 days under ambient temperature, and these blends are found to be suitable for fuelling engines. Higher thermal efficiency, up to 5% is produced by fuelling these blends. Lower emissions of oxides of nitrogen are produced. Emissions of carbon monoxide are found to be close to diesel fuel. Overall, the sustainability of the land and water quality can be maintained by the recycling of the waste products in a useful and utilizable activity.

The *third section* of this book deals with biogases in internal combustion engines. The *first chapter* is based on the role of renewable gas in mobility emission mitigation strategies. In this regard, second-generation fuels are being developed, such as biomethane, hydrogen and syngas able to reduce GHG emissions. There are still many barriers such as the high price of vehicles, the availability of refuelling points in large cities and transport corridors, the confidence of all stakeholders in these technologies, and the development of low emissions policies to support fleet renew. In this regard, the authors analyse the needed lines of research to efficiently apply renewable gases to sustainable mobility. It concludes that renewable gases are proven a valid solution to achieve GHG objectives. Then, artificial methane and natural methane are fully compatible and could be mixed in tanks or pipelines. Hydrogen is a valid and clean source of energy to produce electricity for transport sectors. Electricity is a valid fuel for vehicle mobility, so the lower GHG emissions in the production process, the lower emissions in the transport sector. In this regard, a large number of vehicles in Europe should be replaced by vehicles powered by renewable gases, and it is necessary promoting research in the areas of methane, hydrogen and syngas feedstocks, storage, capture and transport. The *second chapter* deals with the use of Hydrogen in Spark Ignition Engines. The authors investigate the use of hydrogen as fuel in SI engines. The aim is to improve the combustion and performance characteristics of a single-cylinder spark ignition engine. Hydrogen fuel can be induced in the inlet manifold. The authors assess the combustion, performance and emission characteristics operating with different hydrogen–petrol blends. The results demonstrate as 20% of hydrogen shows greater brake thermal efficiency compared to base fuel. Higher percentages of hydrogen, drastically reduce the hydrocarbon content, carbon monoxide content. Then it was found that hydrogen enrichment beyond 25% lead to unstable engine operation and knocking conditions, and due to partial replacement of oxygen and poor air utilization rate. Moreover, increasing the hydrogen concentration, NOx emission increases due to the high adiabatic flame temperature of hydrogen and higher stoichiometric air–fuel ratio.

The *third chapter* deals with the utilization of biogas in diesel engines. Biogas is a renewable fuel that can be produced from organic waste materials through the anaerobic digestion process. The produced raw biogas contains methane and carbon dioxide in considerable amounts. The auto-ignition temperature of biogas is high enough that it cannot be directly utilized in diesel engines. One of the easiest and flexible ways to utilize biogas in diesel engines is through the Dual Fuel (DF) application. This chapter presents an overview of the effects of biogas operated DF engine and suggests various techniques to enhance the performance of the engine. The performance and emission features of a biogas DF engine depend on various operating parameters. The authors demonstrate as the low load performance of the DF engine is very poor and excessive HC and CO emissions are produced. The composition of biogas is also found to significantly affect the features of the DF engine. Higher CH_4 content in biogas improves the engine performance. It is also shown that fuel injection parameters as pilot injection considerably influence the performance and emission features of the biogas DF engine.

The chapters are grouped into three different sections: (I) General, (II) Biofuels and (III) Biogas for internal combustion engine applications. Specific topics covered in the monograph include:

1. Introduction to Application of clean fuels in combustion engines
2. Alcohol Fuels in Compression Ignition Engines
3. Alcohol Fuels in Spark Ignition Engines
4. Fuel Injection Strategies for Alcohol Utilization in Combustion Engines
5. Methanol Fuel in Compression Ignition Engines
6. Butanol fuel in Internal Combustion Engines
7. Biofuel combustion generated particles analysis
8. Engine Performance and Emissions of Fuels from Waste Products for Sustainable Environment
9. The role of renewable gas in the mobility emission mitigation strategies
10. Hydrogen in Spark Ignition Engines
11. Advances in the utilization of biogas in diesel engines: An exergy based approach

Part II
Biofuels for Internal Combustion Engines

Chapter 2
Alcohol Fuels in Compression Ignition Engines

Michele Pipicelli, Giuseppe Di Luca, Roberto Ianniello, Alfredo Gimelli, and Carlo Beatrice

Abstract The increasing concern of global warming due to the ever-increasing amount of greenhouse gases (GHG) such as carbon dioxide (CO_2) and pollutant emissions induces regulatory authorities to stricter emission legislation in the transportation sector. In this context, renewable fuels, such as methanol and ethanol, are considered a promising solution to mitigate the carbon footprint and reduce engine-out emissions. Based on the several studies published in the specific literature, this work aims to summarise and normalize the main outcomes, highlighting the pro and cons of exerting alcohol fuels in compression ignition engines through a critical literature review for helping the researchers, who start to work on these applications. Both dual-fuel and direct-injection fuelling concepts of diesel and alcohol (ethanol and methanol) in compression ignition engines are discussed. Analyses on the combustion, emissions and performance and CO_2 are carried out. Depending on the fuel supply method and the engine type, the use of alcohol fuels performs differently in terms of emissions and engine performance. Dual Fuel combustion mode, port fuel injected alcohol, and direct-injected diesel emits higher HC and CO, while diesel-alcohol blends perform as diesel. Generally, the blends characterized by lower alcohol concentration than dual-fuel perform higher indicated thermal efficiencies. Significant benefits on NOx-soot trade-offs are observed, independently on the fuelling mode, NOx concentration, and engine type by using alcohols. The soot reduction reaches values up to 70%, and the lower carbon content of alcohols fuel reduces the CO_2 up to 15%.

Keywords Methanol · Ethanol · Compression Ignition Engines · Dual Fuel · Fuel Blend · CO_2 · Emissions

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List of Abbreviations

CDC	Conventional Diesel Combustion
CI	Compression Ignition
COV	Coefficient Of Variation
CR	Compression Ratio
DF	Dual Fuel
DI	Direct Injection
DOC	Diesel Oxidation Catalyst
EGR	Exhaust Gas Recirculation
EGT	Exhaust Gas Temperature
FAME	Fatty Acid Methyl Ester
FFV	Flex-Fuel Vehicle
FSR	Fuel Substitution Ratio
GHG	Greenhouse Gases
GWP	Global Warming Potential
HCCI	Homogeneous Charge Compression Ignition
HD	Heavy Duty
HRR	Heat Release Rate
ICE	Internal Combustion Engine
ID	Ignition Delay
IMEP	Indicated Mean Effective Pressure
ITE	Indicated Thermal Efficiency
LD	Light Duty
LHV	Lower Heating Value
MD	Medium Duty
MPRR	Maximum Pressure Rise Rate
NOx	Nitrogen Oxides
PFI	Port Fuel Injection
PM	Particulate Matter
PPC	Partially Premixed Combustion
TDC	Top Dead Center

2.1 Introduction

Nowadays, great global concert is toward air pollution and climate change. Among the greenhouse gases, carbon dioxide, CO_2 is the most significant. However, other substances have global warming potential (GWP) but with limited emissions and life. Regarding CO_2, most worldwide regulatory authorities have stated the objective of reach carbon neutrality. Most of the worldwide country has been targeted to reach carbon neutrality by 2050 (European Union 2020; Visual Capitalist 2021). The main exception is China which has 2060 as the target to reach carbon neutrality.

The transport sector is responsible for about 23% of the global CO_2 emission (IEA 2021), its reduction toward global carbon neutrality is of great concern. It is widely accepted that the long-term solution is the use of electric-powered vehicles. However, in the short-term period, a variety of powertrain platforms are being developed.

In this context, innovative technologies used for the advanced combustion in diesel engines (Di Blasio et al. 2017a, 2019a, b; Belgiorno et al. 2020; Vassallo et al. 2018; Beatrice et al. 2017a, b; Sequino et al. 2018) and many alternative fuels have been studied and proposed in the scientific literature to reduce carbon footprint and pollutant emissions. Alcohol fuels, ammonia, hydrogen are some examples. Alcohol fuels have been studied intensively in the last decades, resulting in a massive literature production. This chapter aims to be a reference point for those who start to study these alternative fuels. In particular, the chapter focuses on using alcohols, potentially renewables, characterized by suitable properties for engine operation, and cost-effective (Kumar et al. 2020; Coulier and Verhelst 2016). A complex data management of the available literature data was carried out, summarizing them in scatter plots. These are a more immediate way of representing data with respect to the commonly used tables. In authors' knowledge, this type of data representation is unique in literature. Short-chained alcohol as methanol, ethanol, and butanol are the most investigated alternative fuels. According to Fig. 2.1, methanol and ethanol are the most studied alcohol fuels based on the Scopus database, while butanol interest has grown almost exclusively in the last decade. For this reason, in this chapter, only methanol and ethanol as fuel in compression ignition engines are considered. Future review activities will also focus on butanol fuel.

It is worth noting the geographical distribution of the countries in which these two alternative fuels have been studied. Figures 2.2 and 2.3 show it for methanol and ethanol, respectively. The search was carried out on the Scopus database using the chapter keywords. The United States of America are one of the main actors in this field, together with China. However, India has exploited the major interest in the last

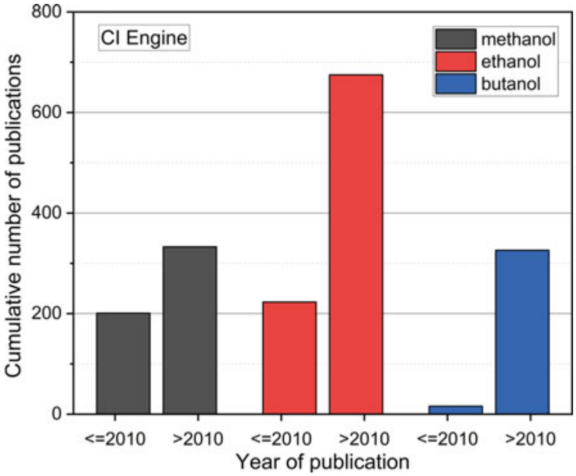


Fig. 2.1 The number of research papers on the use of alcohols (methanol, ethanol, and butanol) in CI engines. *Source* Scopus database

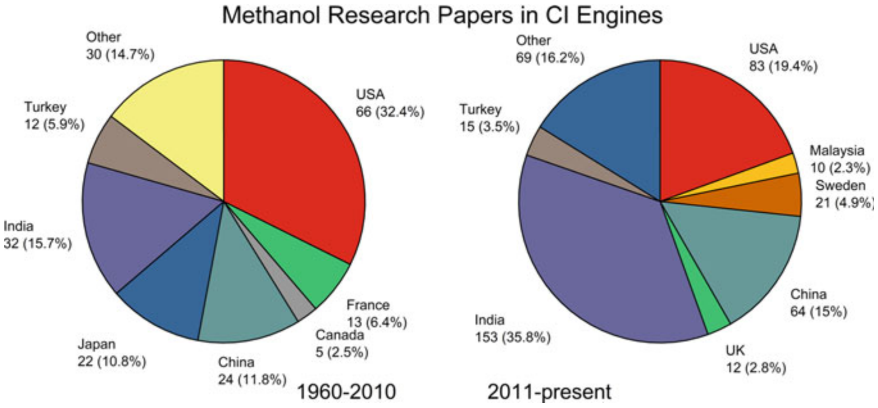


Fig. 2.2 Geographical distribution in two-time frames of the research papers treats methanol use in CI engines. *Source* Scopus database

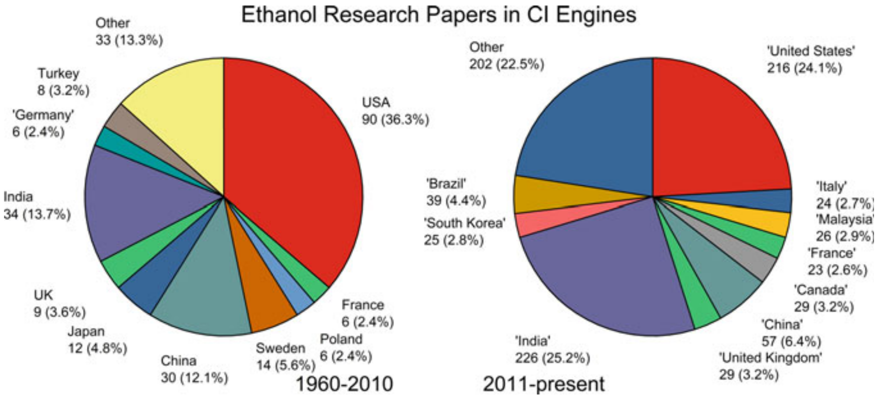


Fig. 2.3 Geographical distribution in two-time frames of the research papers treats ethanol use in CI engines. *Source* Scopus database

decade, producing about one-third of the global papers on methanol and one quarter on ethanol. Brazil, although it is the main producer of ethanol together with the USA (Renewable Fuels Association Focus and Forward 2020) and one of the main users of ethanol as fuel, has only marginal roles in the scientific literature.

This chapter aims to provide to the reader a comprehensive review of the use of alcohol fuels in compression ignition (CI) engines. Over 120 research papers have been studied to present this chapter, and up to 70 papers are selected based on the investigated topic relevance and quality. The main results from the literature presented in this chapter show the main outcomes of CI engines fuelled with methanol or ethanol fuels. First, the production and the properties of methanol and ethanol are discussed. Then, results on various engine fuelling modes are presented with an overview of alcohol fuel effects on compression ignition engines. Combustion processes, looking at in-cylinder pressure and heat release traces, combustion duration, ignition delay, and exhaust gas temperature, are discussed. Emissions trends are merged among different types of fuel, engines and fuelling modes. The conclusions section summarises the main advantage and drawbacks of alcohols application in CI engines.

2.2 Production and Properties of Alcohol Fuels

Among alcohol fuels, ethanol and methanol are the most investigated fuels in the last decade. Great attention is due to the low carbon content, low cost and emission reduction potential (Çelebi and Aydın 2019; Geng et al. 2017). This section provides information about methanol and ethanol fuel production processes and the chemical-physical fuel properties.

Methanol, identified by the formula CH_3OH, is a chemical compound widely used in industries. In 2020, 30% of produced methanol was employed as fuel feedstock (Irena and Methanol Institute 2021). It can be produced by many carbon-containing feedstocks, as from natural gas steam reforming and in recent years, rising interest in sustainable methanol production via CO_2 hydrogenation has been shown (Dalena et al. 2018). Although the methanol produced by different feedstock is chemically identically, the production process influences the true environmental impact. Therefore, a colour-based classification is used to identify the effective environmental impact of the production and use of methanol. The colour used spans from green, which indicates a low carbon intensity process, to brown, which indicates a high carbon intensity process, spanning through blue and grey. The green methanol is usually produced from biomass or through CO_2 hydrogenation with renewable CO_2 and green hydrogen. The blue methanol is also obtained with the CO2 hydrogenation process, but with blue hydrogen and renewable CO_2 or with green hydrogen and non-renewable CO_2. The production of methanol through reforming of natural gas is labelled as grey, while, in the end, the production of methanol from syngas obtained through coal gasification, which is the most carbon-intensive production method, is labelled as brown. Bio-methanol can be produced from biomethane with conventional steam reforming and from converting the bio-syngas from biomasses into methanol (Farsi 2021).

Ethanol, identified by the chemical formula C_2H_5OH, is also produced from different feedstocks such as fermentation processes or catalytic conversion (Susmozas et al. 2020). The widest process used is fermentation, which requires a fermentable sugar or a more complex carbohydrate that can be converted into ethanol (Zabed et al. 2016). Brazil and the USA have been the two major ethanol producers reaching up to 85% of the global production in 2019 (Renewable Fuels Association Focus and Forward 2020) using sugar cane and corn fermentation processes, respectively. The ethanol produced from sugar or starch-containing feedstock is called first-generation (1G) bioethanol (Susmozas et al. 2020).

Table 2.1 Typical fuel properties (Sarıkoç 2020; Epping et al. 2002; Yates et al. 2010; Liu et al. 2015)

Properties	Diesel	Ethanol	Methanol
Research Octane Number [-]	–	108–109	107–109
Cetane Number [-]	≥51	2–12	–
Molar mass [g/mol]	~170	46.1	32.0
Carbon Number [-]	12–20	2	1
H/C [-]	1.8	3.0	4.0
O/C [-]	0	0.5	1.0
LHV [MJ/kg]	43.0	27.0	20.0
(A/F)s [-]	14.5	9.0	6.4
Viscosity (@20 °C) [mPa/s]	3.45	1.21	0.54
Density (@15 °C) [kg/m^3]	820–845	794	796
Boiling point [°C]	180–360	78	65
Heat of vaporization [kJ/kg]	270	840	1160
Specific heat [kJ/kgK]	2.2	2.5	2.6
Adiabatic Flame Temp. in stoichiometric condition [K]	–	2197	2151
Specific CO_2 emissions [g/MJ]	72.2	70.7	68.8

The sustainability of the energy vector production based on food feedstock has been widely discussed, and ever-increasing attention has been directed toward alternative feedstock ethanol production (Susmozas et al. 2020). The bioethanol produced from these alternative feedstocks, like lignocellulosic materials, algal, industrial waste and syngas, is called second-generation (2G) bioethanol (Susmozas et al. 2020; Erdei et al. 2010). Lignocellulosic materials have been the most attractive due to the large availability and the non-edibility of the feedstock.

Table 2.1 reports the main fuel properties of the two alcohols considered in this chapter, including as references the diesel ones.

The hydroxyl group makes alcohol fuels, especially the short-chained ones, hydrophilic and give a dipole moment at their molecular structures (Bae and Kim 2017). The molecular polarity generates a strong intermolecular hydrogen bond that leads to a rise of the boiling point and the heat of vaporization. At the same time, it gives good miscibility with strong molecular polarity substances, such as water (Pearson and Turner 2012). The higher heat of vaporization of the alcohols promotes a cooling effect on the air–fuel charge, leading to a reduction of the in-cylinder temperature (Shamun et al. 2020). The presence of the carbon–oxygen bond tends to reduce the low heating values (LHV) of fuels, compared to the corresponding alkane, raising the fuel consumption (Çelebi and Aydın 2019; Pearson and Turner 2012). Furthermore, oxygen in the fuel lowers the stoichiometric air-to-fuel ratio. It helps to reach complete combustion, achieving likely higher brake thermal efficiency and higher combustion efficiency (Kumar et al. 2020; Çelebi and Aydın 2019).

The polar nature of the considered alcohols is incompatible with the nature of the diesel fuel. It can lead to a phase separation that represents a problem in the blending process (Ianniello et al. 2021). For this reason, ternary blends with biodiesel, gasoline or other additives have been investigated to achieve better fuel stability and miscibility (Shahir et al. 2014). The temperature also influences the diesel blend stability, and for ethanol, phase separation occurs below 10 °C, and so an emulsifier, a cosolvent or iso-propanol must be added to avoid this issue (Shahir et al. 2014). Liu et al. (2010) used as cosolvent 2% v/v of octanol to stabilize a Diesel-ethanol blend up to 30% v/v. Ghosh et al. (Ghosh and Ravikrishna 2021) used a mixture of $C_{64}H_{124}O_{26}$ and $C_{24}H_{44}O_6$ or 1-dodecanol ($C_{12}H_{26}O$) to stabilize the diesel-methanol blend. They verify the emulsion stability up to 1500 bar of injection pressure, highlighting that the surfactant used has sensible influences on spray liquid penetration. The shorter carbon chain than the common hydrocarbon in diesel and gasoline fuel, alcohols effectively reduce particulate matter emissions (Pearson and Turner 2012).

Due to their high-octane number rating, both ethanol and methanol are well suited for SI engines, and therefore not directly usable in CI engines (Kim et al. 2020). Indeed, specific hardware would be necessary to use alcohol as single fuel in CI engines, such as higher compression ratio (CR) till 23:1, or employing an intake electric air heater with a conventional CR of CI engine (Shamun et al. 2017; Zhang and Wu 2016). Siebers et al. (Siebers and Edwards 1987), through combustion vessel experimental tests, showed to achieve a reasonable ignition delay, are needed temperatures of about 1100–1150 K at the top dead centre (TDC) for methanol and ethanol, respectively.

The use of ethanol and methanol as alternative fuels in engines should consider other than performance also characteristics linked to safety, toxicity, tribological properties, storage, and distribution. Moreover, due to higher corrosion and lower lubricant properties, special attention must be done to all the fuelling systems. In addition, high alcohols concentration blends (M85, E85 and similar) have a reduced LHV compared to neat diesel. Therefore, it requires an increase of injected fuel mass for stroke that would be solved by adopting a higher injector nozzle flow number compared to the typical diesel injector one and recalibrate injection energizing time.

Typically, alcohol fuels are blended with gasoline and diesel fuels. For the commercial gasoline fuel, the directive 2009/30/EC (European Union 2009) and the EN 288 (Ente nazionale italiano di unificazione 2003) regulation fix the blending limit volume content of methanol and ethanol to 5 and 10%, respectively. Moreover, they also fix a limit of 3.7% v/v on fuel oxygen content. The actual alcohols content can vary with seasons and fuel producer. This is to guarantee the maximum compatibility of the fuel with the actual vehicle fleets. This blending strategy is effective in making the fuel compatible for as many cars as possible. For traditional diesel fuels, the above-cited directive 2000/30/EC (European Union 2009), together with the EN 590 regulation, does not treat the limit of either oxygen or alcohol. However, they concern about the possibility of blend diesel with fatty acid methyl ester (FAME) up to 7% v/v. This is also referred commonly to as biodiesel, and it is an oxygenated fuel. In the last decades, the flex-fuel vehicles (FFV) concept has been slowly spreading. These vehicles can run indifferently with usually two fuels, generally ethanol-gasoline or methanol-gasoline. Brazil and the USA are the countries with the greatest number of ethanol-gasoline FFV, while experimentation in California is carried out on M85 FFV.

2.3 Fuelling Mode, Combustion, and Emissions of Alcohol Fuels in Compression Ignition Engines

After a brief overview of the methanol and ethanol chemical-physical fuel properties, a detailed analysis of the fuel injection modes used for alcohol fuels in CI engines is exposed. Then specific sections on combustion and emissions analyses have been reported, showing the main outcomes of alcohol fuels compared to conventional diesel fuel.

2.3.1 Fuelling Mode

This section outlines the fuel injection and combustion modes of CI engines fuelled with alcohol fuels. In particular, the fuel injection technologies or modes adopted in CI engines fuelled with alcohol fuels are typically Dual Fuel (DF), blend modes and pure alcohol fuel direct-injected (DI). The first involves installing a second fueling system that injects the alcohol fuel into the intake manifold. In the DF mode, there is port fuel injection (PFI) of alcohol fuel and DI of diesel. The blending mode does not require modification to the fueling system since the alcohol is blended with diesel-fueled in DI mode. The last method involves the complete substitution of the diesel fuel with alcohol without modification of the fueling system schematic. Indeed, modification of the system component can be needed to match the different fuel properties, particularly relevant are the corrosive and lubricant ones. To characterize how much diesel fuel was replaced with alcohols, the fuel substitution ratio (FSR) indicator is used. In this chapter, the FSR on an energy basis is used and defined as:

$$FSR = \frac{m_a \cdot LHV_a}{m_a \cdot LHV_a + m_d \cdot LHV_d}.$$

where m indicates the fuel mass, *LHV* the lower heating value, and subscripts a and d refer to alcohol and diesel, respectively.

As reported, alcohol can be blended with diesel. However, the maximum alcohol fraction is limited by the miscibility (Damyanov et al. 2018). This behaviour can be overcome using specific emulsifiers into the alcohol-diesel blend to prevent the phase separation of liquids (Lapuerta et al. 2009). The diesel-methanol and the diesel-ethanol blends are usually indicated as DE and DM, respectively. Often the abbreviation is followed by a number (i.e. DE30), which indicates the volume fraction of the alcohol fuel. Sometimes, a third letter is interposed in a ternary blend to indicate the emulsifier type, i.e. gasoline (DGE) or biodiesel presence (DBE).

The DF mode can be used to overcome the maximum ethanol or methanol FSR in blend mode, which is limited by miscibility. It allows increasing the FSR since the ethanol or methanol (low reactive fuels) is injected in the intake manifold via port fuel injection (PFI) and the DI diesel fuel (high reactive fuel). In this mode, alcohol is premixed with the intake air, and then the subsequent homogeneous alcohol-air mixture is ignited by DI diesel. DF combustion allows increasing the amount of alcohol fuel involved in the combustion process in the range from 70–90% replacing diesel fuel instead of 30% in blending mode (Beatrice et al. 2020).

Other fuelling modes for alcohols, which are briefly reported in this paragraph, are investigated in literature (Zhang and Wu 2016; Saccullo et al. 2021; Dong et al. 2020; Gainey et al. 2020; Shamun et al. 2016, 2019). In some works, methanol and ethanol have been direct-injected in CI engines without employing diesel fuel. In these cases, a higher compression ratio or a greater intake temperature are required to promote alcohols ignitability and achieve a stable combustion process, avoiding misfiring. Gainey et al. (2020) used wet ethanol (80% ethanol and 20% water) in a CI engine to control the heat release rate. Zhang and Wu (2016) used only methanol to achieve homogeneous charge CI combustion (HCCI). Shamun et al. (2016, 2019) instead has experimented the partially premixed combustion (PPC) of neat methanol and ethanol. Since these strategies are very uncommon, and only a few research papers treat them, they are not discussed in this chapter.

2.3.2 *Combustion*

In this section, the combustion process evolution of alcohol fuels in DF and blend mode has been discussed, comparing to the conventional diesel combustion. In addition, ignition delay and combustion duration indicators are analyzed.

In dual-fuel mode, the combustion starts from the combustion kernel ignited by the diesel pilot injection. Successively, the burning process involves the premixed charge entrained into the diesel spray and after the flame front is propagated through all the combustion chamber, oxidizing all the premixed fuel (Ahmad et al. 2021). The alcohol-diesel blend combustion mode shows high similarity with the conventional diesel combustion. However, since the alcohol fuel is a low reactive fuel compared to the diesel, the blend combustion exhibits a typically partially premixed combustion process with a higher premixed phase and as well as less late combustion versus the diesel combustion (Dimitrakopoulos et al. 2017, 2019; Belgiorno et al. 2017, 2018a; Shamun et al. 2018).

The fuel properties influence the combustion process. For example, the cetane number of fuels mostly influences the ignition delay (ID). Specifically, as reported in Table 2.1, alcohol fuels (ethanol and methanol) have a lower cetane number than diesel. Indeed, the higher is the fraction of alcohol fuel involved in the combustion, and the higher is the ignition delay. Shamun et al. (2018) reported that the ID increases with ethanol fraction in blend mode but decreases with engine load. However, the ID is also influenced by the cooling effect of alcohol of the charge and determined by the higher latent heat of vaporization. This is due to the strong dependence on the temperature of the chemical kinetics of the ignition and combustion reactions (Dunphy and Simmie 1991; Kobori et al. 2000). Ning et al. (2020) showed a linear trend between substitution ratio and ignition delay. Gürbüz and Demirtürk (2020) found a monotonical increase of the ID with both E85 and E100 in PFI, with the highest value for the last.

The higher ignition delay compared to conventional diesel combustion (CDC) and a higher premixed combustion phase have been observed together with higher flame speed, leading to a faster combustion process (Shamun et al. 2018).

The heat release rate, employing alcohol as fuel, the low-temperature heat release is generally lower than CDC, while the premixed phase is more evident than the diffusion phase, which shows higher peak pressure and combustion noise. In Fig. 2.4, the heat release rate is reported for CDC and ethanol–diesel blend obtained from the past experimental activity of the authors' research group. A higher ignition delay can be appreciated by increasing the ethanol fraction keeping constant the fuel quantity and the start of injection. While employing double pulse injection, the blend combustion with higher ethanol fuel content shows a more pronounced premixed phase and a higher peak of HRR compared to the other ones with a lower first-stage ignition released heat. Instead, the combustion duration varies non-monotonically with FSR due to the superposition of different effects by the lower cetane number of alcohols and higher flame speed. A specific calibration activity should be carried out to control these effects on the combustion process, minimize the combustion noise, achieve suitable peak cylinder pressure, and control the NOx levels.

Higher premixed combustion phase showed typically maximum pressure rise rate (MPRR). Figure 2.5 summarises many MPRR values from the literature as

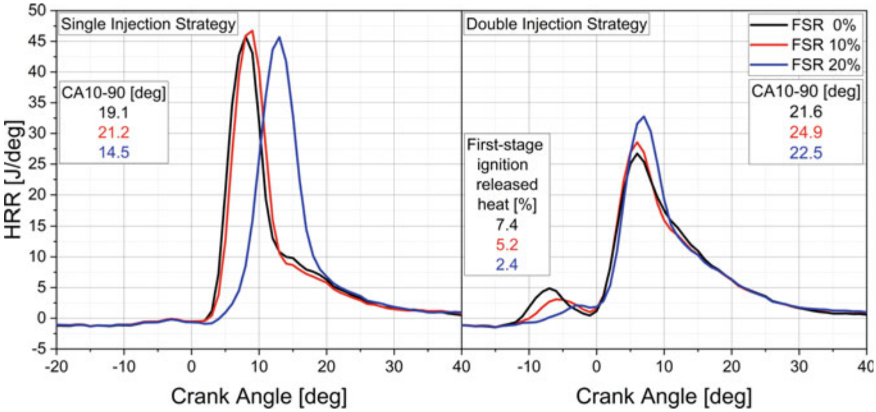


Fig. 2.4 CDC and ethanol blend heat release rates with a single injection (left) and double injection (right) strategies at 2000 rpm and 4 bar IMEP

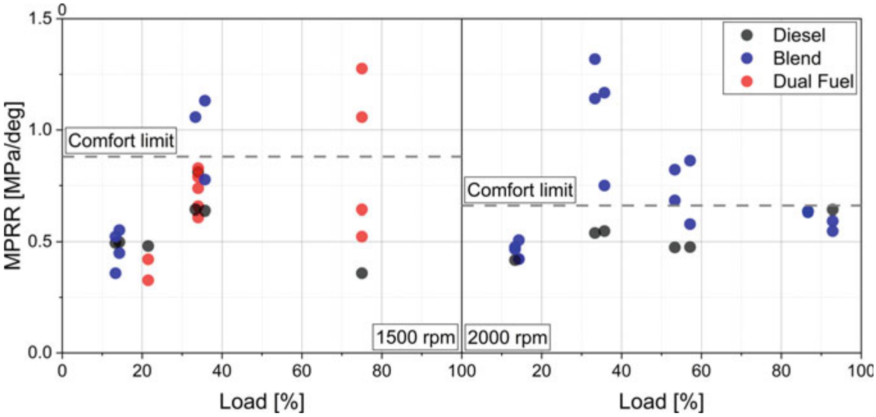


Fig. 2.5 Maximum Pressure Rise Rate (MPRR) for neat diesel and various alcohols fuelling systems as a function of engine load and FSR. 1500 and 2000 rpm. *Source data* (Heuser et al. 2015; Belgiorno et al. 2018b)

a function of engine load for different combustion modes and two engine speed levels. MPRR comfort limit of 0.80 MPa/ms, appropriately converted in MPa/deg, is reported in Fig. 2..5 as a reference value (Di Blasio et al. 2015, 2017b) Alcohol-diesel blends show higher PRR compared to the CDC, especially in the region of medium load condition, moving from 0.5 MPa/deg in diesel combustion up to 1.3 MPa/deg by employing ethanol diesel blend. Dual-Fuel combustion shows typical MPRR values as neat diesel. Gainey et al. (2020) found that wet ethanol split injection can effectively reduce pressure peak and MPRR and reach higher MEP at a fixed MPRR limit.

The combustion stability and repeatability are considered and represented by the coefficient of variation of the IMEP ($\mathrm{COV_{IMEP}}$). Pedrozo et al. (2018) reported that the $\mathrm{COV_{IMEP}}$ increases with the engine load in ethanol–diesel DF combustion. However, Lee et al. (2018) reported the effects of varying the engine parameters in ethanol DF combustion for improving the combustion stability. At low load conditions, higher $\mathrm{COV_{IMEP}}$ values were detected. In Fig. 2.6, $\mathrm{COV_{IMEP}}$ values have been reported at different engine loads, based on data reported in Heuser et al. (2015), Belgiorno et al. (2018b). Alcohol-diesel blend and dual-fuel combustion typically show higher $\mathrm{COV_{IMEP}}$ compared to the CDC at low load conditions. However, increasing the engine load, the combustion stability is aligned to CDC. Besides different trends are found in the literature regarding $\mathrm{COV_{IMEP}}$, which can be explained by different calibrations carried out by the various authors, the absolute values are well aligned with CDC and less than 3% in most cases.

The exhaust gas temperature (EGT) is of great concern for the after-treatment system design functionality and efficiency. Generally, the use of alcohols in both fuelling modes tends to reduce EGT due to a higher cooling effect. The intake air temperature affects the EGT. Due to the high heat of vaporization, alcohols in PFI can achieve a most significant cooling effect, leading to reduced EGT in comparison to

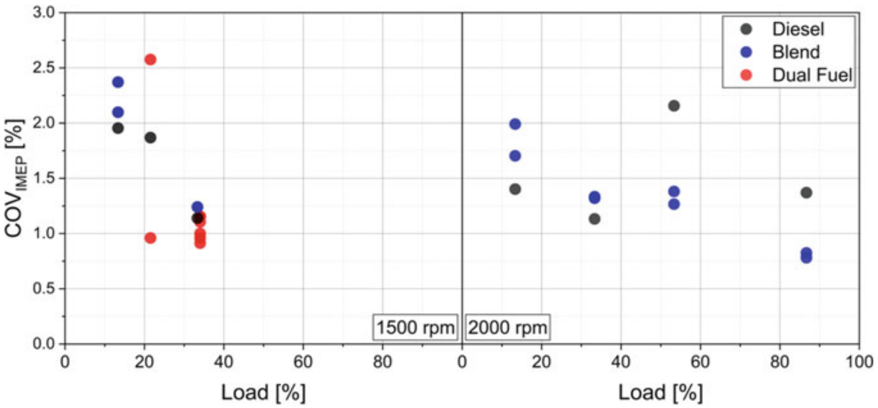
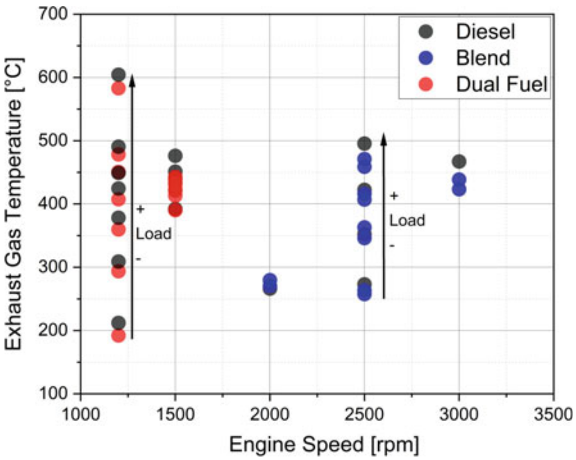


Fig. 2.6 COV$_{IMEP}$ for neat diesel and various alcohols fuelling systems as a function of engine load and FSR. 1500 and 2000 rpm. *Source data* (Heuser et al. 2015; Belgiorno et al. 2018b)

blends mode. Pan et al. (2015) report a decreasing trend of the EGT with an increase of FSR due to the higher heat of vaporization that reduces in-cylinder temperature. Han et al. (2020) found that the FSR influence on EGT is particularly significant at medium load conditions in ethanol-based DF engines. In contrast, less impact is noticed at low and high loads. Agarwal et al. (2020) have also reported a reduction of EGT using both DM and DE blends at different speeds and loads. The afore exposed trend can be seen in Fig. 2.7, where the EGT for different engines at different engine speeds and loads are reported.

Detailed discussion on indicated thermal efficiency (ITE) is reported below. In Fig. 2.8, the ITE as a function of engine load at different combustion modes has been reported. Dual-fuel combustion shows a lower ITE than CDC at low load conditions.

Fig. 2.7 Exhaust Gas Temperature for neat diesel and various alcohols fuelling system as a function of engine speed and load. *Source data* (Kumar et al. 2020; Pedrozo et al. 2018; Pan et al. 2015)



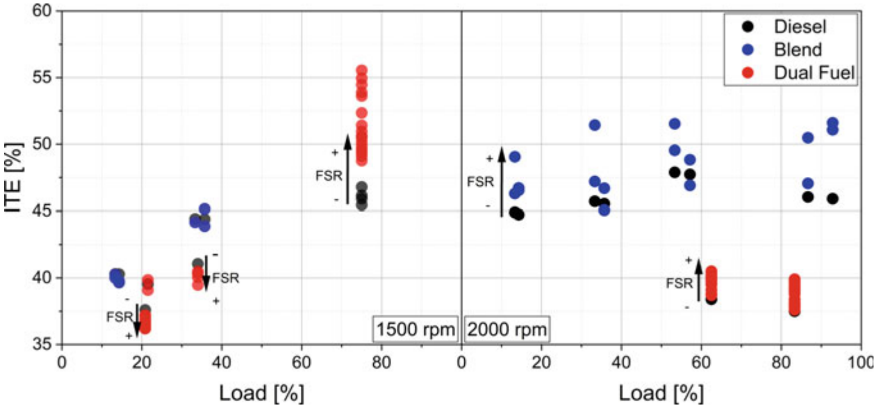


Fig. 2.8 Indicated thermal efficiency for neat diesel and various alcohols fuelling systems as a function of engine load and FSR. 1500 and 2000 rpm. *Source data* (Kumar et al. 2020; Damyanov et al. 2018; Shamun et al. 2018; Heuser et al. 2015; Belgiorno et al. 2018b)

This is due to the higher unburned hydrocarbon (i.e., lower combustion efficiency) and in-cylinder heat transfer losses. While increasing the engine load, the dual-fuel combustion shows an ITE improvement of up to 2% in comparison to neat diesel due to the higher in-cylinder temperature condition that improves the combustion process (Pedrozo et al. 2018).

Alcohol-diesel blend combustion shows higher ITE compared to the neat diesel and up to 3% from low to high load conditions. This effect is mainly related to the alcohol fuels that exhibit a higher premixed combustion tendency, shorter combustion duration, and lower in-cylinder heat losses compared to the neat diesel. The faster combustion tends to approach the actual combustion to a more isochoric process leading to an efficiency improvement due to a potentially higher expansion work. Kumar et al. (2020) investigated the impact of DM10 and DE10 blends at different engine loads for a medium-duty engine application, in comparison to results with the diesel fuel as a baseline. At low load, no differences appreciated on efficiency between the blend fuels and diesel. The maximum efficiency improvement was measured at high load, about 5% for the DE10 and about 6% for the DM10 blend. At full load, He et al. (2018) reported an increase of ITE in the range of about 1–2%, using a blend of 15% (v/v) of ethanol.

2.3.3 Emissions

This section discusses the main engine-out emissions of compression ignition engines fuelled with alcohol in dual fuel and blend modes, showing the potential of alcohol fuel on CO_2 and NOx-Soot trade-off compared to the CDC. However, the HC and CO behaviours are also presented.

Due to the higher heat of evaporation and lower adiabatic flame temperature, alcohol fuels led to reduced in-cylinder temperature and lower NOx emissions compared to conventional diesel fuel. Moreover, the in-cylinder temperature also depends on different engine parameters (equivalence ratio, injection strategy, intake charge temperature, etc.). Furthermore, the oxidation of alcohols produces more hydroperoxyl radicals (HO_2) that enhance the production of NO_2 from NO and HO_2, increasing the NO_2 to NO ratio (Pan et al. 2015). A general reduction of NOx may be expected using alcohol fuels while shifting toward NO_2 the NO_2/NO ratio. Damyanov and Hofmann (Damyanov and Hofmann 2019) reported that in DF mode, NOx emissions increase at low load while at high load reduces with rising of ethanol energy fraction. Dierickx et al. (2021) showed that, although the generally NOx emissions diminishing with increasing methanol mass fraction in DF mode, the NO emissions showed a significant decreasing trend. In contrast, NO_2 emissions tend to increase. This trend is also confirmed by Kim et al. (2020) in a 4-cylinder engine fuelled by a diesel-ethanol blend.

The particulate matter is formed in a relevant manner in a fuel-rich zone and with a lack of oxygen (Mohankumar and Senthilkumar 2017). Due to their short carbon chain (high H/C atom ratio), which helps reduce precursor formations, light alcohols have lower soot emissions than the commonly employed alkenes. Sarathy et al. (2014) attributed no benefit in soot reduction to the fuel oxygen atom. The last statement is also confirmed by Gargiulo et al. (2015) after an analysis of the soot structure of PM emitted by an engine operated both in diesel and ethanol DF mode. However, Wei et al. (2020) reported some differences in soot nanostructure in engines fuelled by methanol blend, probably due to the lack of aromatic compound and the shorter carbon chain. Moreover, oxygen content in the alcohol fuels has a leaner effect while combustion occurs, potentially reducing the particle growth formation. When the alcohol is injected in PFI, a reduction of the equivalence ratio in the diesel spray zone is observed due to the lower oxygen concentration. This causes a rise of ignition delay with the greatest premixed combustion phase, leading to lower PM formation. On the other side, high PFI injected mass can lead to an auto-ignition of the low reactivity fuel that produces a significant reduction of oxygen available with a consequent increment of PM emission, especially at higher loads, as reported by Geng et al. (2014). The DOC effect on the PM size distribution and particle number is also analyzed in their work, reporting similar distribution trace and effective reduction using methanol in DF. As a general trend, a high reduction of PM emission is achievable through the partial replacement of diesel fuel with light alcohols adopting a proper engine parameters calibration.

Kumar et al. (2020) reported PM emission reduction, up to 60%, with DM10 blend at different engine operating conditions. A similar trend is also found for DE10 and DM10 blends, with a greater potential for the latter one. Belgiorno et al. (2018b) carried out tests with diesel, gasoline, and ethanol blends on a light-duty CI diesel engine. They found a reduction of PM emission for all engine speed and load compared to the diesel baseline. Pan et al. (2015), in a 6-cylinder CI engine fuelled with methanol in DF mode, also reported a reduction in specific soot emission from about 20–60%, increasing the methanol mass substitution ratio up to 40%.

They also showed (Wei et al. 2020), for the methanol, an additional particulate matter reduction due to the methanol cooling effect and its oxygen content that promotes the soot oxidation. The nitrogen oxides (NO_x) formation is linked to the achieved local temperature, and its increase exponentially with the adiabatic flame temperature of the considered fuel (Zhang 2010). Partial substitution of conventional fuel with alcohol help to achieve NO_x emissions reduction. The alcohols can reduce PM and NOx emissions, overcoming the traditional trade-off needed in diesel CI engines (Damyanov and Hofmann 2019).

Figure 2.9 reports the NOx–soot emissions trade-off for different combustion strategies at fixed engine speed (2000 rpm). Different engines characterized by different PM baseline levels are identified. The results with higher NOx emissions were obtained without or with a low EGR rate. In this condition, little difference can be appreciated between diesel and alcohol fuels on PM emissions due to lean combustion. The operating points, belonging to engine 1, show the great capability of alcohol-diesel DF to effectively reduce PM level, with low impact on NOx. Increasing FSR, the PM emissions are further reduced. A strong soot reduction of up to 70% in both dual fuel and blend modes can be noticed. The alcohols permit to effectively reduce PM emissions, keeping the NOx ones unaltered, as shown in the zoomed section of Fig. 2.9, where DGE and DBE blends are used. Engine recalibration allows higher exhaust gas recirculation (EGR), lowering NOx emission, keeping the PM at very low levels and below typically CDC.

The use of alcohol in PFI led to the air–fuel mixture in crevices and squish areas due to the mix with combustion air during the intake stroke. As a result, a higher level of HC is generally detected operating in Dual fuel combustion mode (Fraioli et al. 2017; Belgiorno 2018c, 2019; Di Blasio et al. 2017c; Monsalve-Serrano et al. 2020). Several researchers consolidated and confirmed this trend for heavy and light-duty engines (Heuser et al. 2015; Pedrozo et al. 2018; Han et al. 2020). However, also for alcohol-diesel blend, HC emissions tend to increase, especially at low load

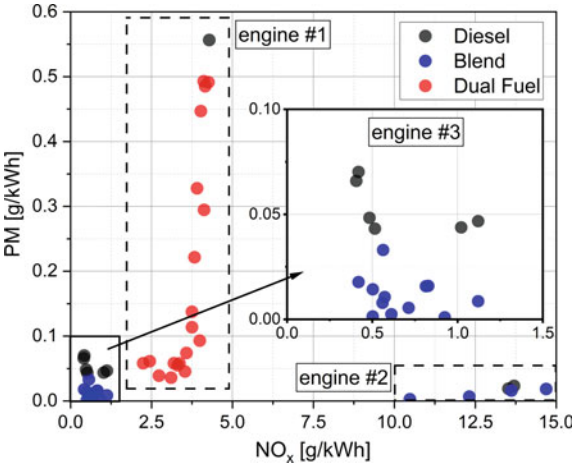


Fig. 2.9 Specific PM emission as a function of specific NO_x emission for ethanol in blend and DF mode. 2000 rpm. *Source data* (Kumar et al. 2020; Damyanov et al. 2018; Shamun et al. 2018; Heuser et al. 2015; Belgiorno et al. 2018b)

conditions, while at high load, the HC level is almost comparable with neat diesel. The different volatility of the alcohols can explain the increment to the diesel baseline.

The CO is formed prevalently in the fuel-rich zone, with a lack of oxygen to oxidize the CO into CO_2. However, this oxidation reaction is also strongly dependent on temperature other than the equivalence ratio (Liu et al. 2010). In dual-fuel ethanol mode, Di Blasio (2015) reported higher CO emissions for all operating points tested, especially at lower loads because of the higher cooling effect. Also, the DGE blend produces higher CO emissions at low loads with similar values as for diesel at higher loads (Belgiorno et al. 2018b). Belgiorno et al. (2018b), testing DM10 and DE10 blend report slighter higher CO emission. Between these two blends, the DM10 led to higher CO emission due to higher heat of evaporation of methanol.

HC and CO emissions are reported in Figs. 2.10 and 2.11, respectively (Kumar et al. 2020; Damyanov et al. 2018; Shamun et al. 2018; Heuser et al. 2015; Belgiorno et al. 2018b). The trend is very similar, of both emissions with increasing with FSR. The DF mode has a further negative effect than the blend one, especially at partial load, where the combustion efficiency is quite low.

The ethanol and methanol have lower specific carbon dioxide (i.e., lower CO_2 emission for energy unit) concerning the standard diesel fuel, as reported in Table 2.1. This property helps to reduce the CO_2, considering that the engine-out CO_2 emissions are also linked to the fuel delivery system, engine operating condition and limitations related to other pollutants emission.

Since the alcohol fuels emit higher HC and CO emissions, their oxidation in the after-treatment systems emits additional tailpipe CO_2, reducing the CO_2 benefits compared to the diesel combustion. Damyanov and Hofmann (2019) reported that assuming the highest efficiency for a diesel oxidation catalyst (DOC), for all ethanol substitution ratios at low engine speed and load, the CO_2 emission is within 1% of the scatter band respect diesel one. For a higher load 2000 rpm and 20 bar, considering the

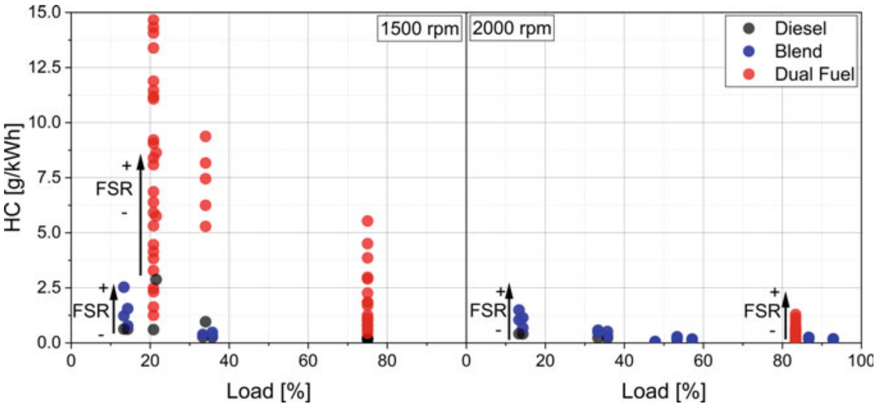


Fig. 2.10 Specific unburnt HC emission as a function of engine load for neat diesel and various alcohols fuelling systems. 1500 and 2000 rpm. *Source data* (Kumar et al. 2020; Damyanov et al. 2018; Shamun et al. 2018; Heuser et al. 2015; Belgiorno et al. 2018b)

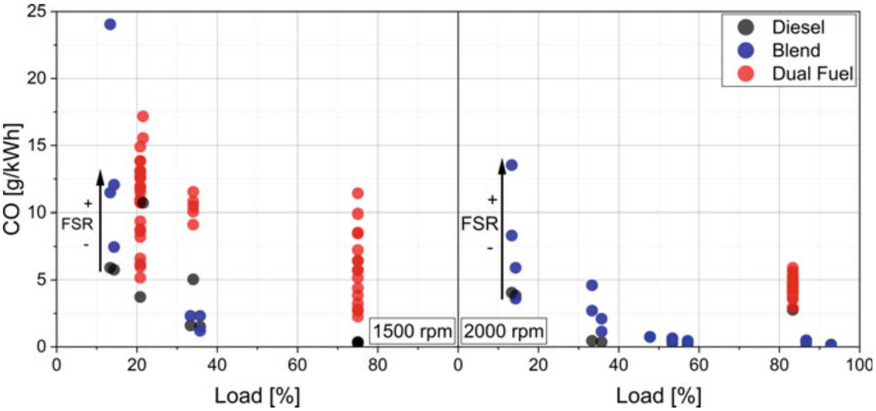


Fig. 2.11 Specific CO emission as a function of engine load for neat diesel and various alcohols fuelling systems. 1500 and 2000 rpm. *Source data* (Kumar et al. 2020; Damyanov et al. 2018; Shamun et al. 2018; Heuser et al. 2015; Belgiorno et al. 2018b)

DOC conversion, the CO_2 reduction respect diesel baseline pass from 7.5% to 6%. In the low load conditions, the CO_2 emissions suffer from the low combustion efficiency typical of the DF mode, leading to a negligible relative difference with respect to diesel fuel. However, the use of renewable alcohols can still lead to beneficial effects on the well-to-wheel carbon intensity.

In an LD engine fuelled by DGE15 and DGE30, Belgiorno et al. (2018b) presented a reduction of specific emissions of CO_2 for all engine load and speed that increase with alcohols content. In Fig. 2.12, the specific CO_2 emissions obtained from literature data (Kumar et al. 2020; Damyanov et al. 2018; Shamun et al. 2018; Belgiorno

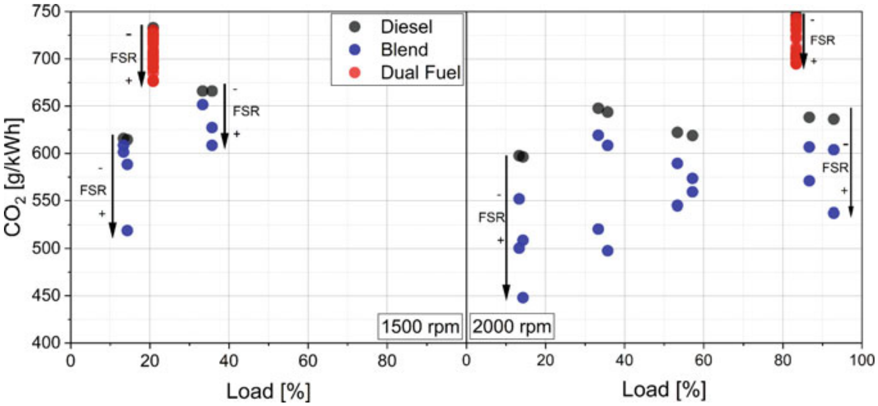


Fig. 2.12 Specific CO_2 emission as a function of engine for neat diesel and various alcohols fuelling systems. 1500 and 2000 rpm. *Source data* (Kumar et al. 2020; Damyanov et al. 2018; Shamun et al. 2018; Belgiorno et al. 2018b)

et al. 2018b) show the above-reported trend. A reduction of about 15% can be achieved both with blend and DF mode compared to the diesel baseline.

2.4 Conclusions

This chapter summarises the main physical and chemical properties, experimental results on alcohol fuels in CI engines in terms of combustion, emissions, and efficiency. The trends are presented through an effective graphical representation able to summarize all data in a single plot merging the main methanol and ethanol effects on engine outputs. The main outcomes from the selected literature papers are listed below.

- It is demonstrated that alcohols are adaptable to CI engine operation due to their chemical-physical properties. Moreover, they can be produced in a renewable manner.
- The alcohol FSR in diesel is limited to about 20% in blend mode, while in DF mode, the FSR can reach values up to 90%. Alcohol-diesel blends require surfactants to guarantee the mixture stability and minimum required lubricity.
- Combustion of alcohol-diesel blends is strongly premixed (due to the higher ID), with a reduced combustion duration and improved thermal efficiency (up to 5%) compared to CDC.
- DF combustion has lower thermal efficiency at low load (up to 3%) and higher at high load (up to 3%) compared to the CDC, consequence of lower combustion efficiencies (higher HC and CO emissions) and higher heat transfer losses.
- Combustion with alcohol-diesel blends exhibits higher MPRR values compared to DF and CDC. The COV_{IMEP} is well below 3% for all fuels and fuelling strategies.
- DF combustion emits higher HC and CO emissions than blends and CDC for all speed and load analyzed, and due to the fuel mixture trapped into the crevice volumes. In the case of blends, the highest values are at lower loads due to the higher fuel volatility. At higher load conditions, the levels are comparable.
- Alcohol fuels improve the NOx-PM trade-offs, especially at low NOx levels or high EGR rates, thanks to the lower carbon chain, higher H/C ratio, and high latent heat of evaporation (combustion temperature drop) compared to diesel.
- The lower carbon dioxide emission of alcohols, together with the generally improved thermal efficiency, reduces the CO_2 emission up to 15% in comparison to CDC and its reduction is proportional to the FSR.

These spots gives the alcohol fuels an interesting perspective towards a more sustainable mobility in a short timeframe. Further work will be conducted by the authors extending the literature-based research to extend the discussion on interesting topics such as storage, toxicity, lubricant properties and unregulated emissions.

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Chapter 3
Alcohol Fuels in Spark Ignition Engines

Giuseppe Di Luca, Michele Pipicelli, Roberto Ianniello, Giacomo Belgiorno, and Gabriele Di Blasio

Abstract Carbon dioxide (CO_2), nitrogen oxides (NOx) and soot emissions are primary concerns and the most investigated topics in the automotive sector. Indeed, recent governments directives push toward carbon–neutral mobility by 2050. In this framework, zero-carbon fuels, as hydrogen, or renewable low carbon alcohol fuels, play a fundamental role. To this aim, in this chapter, the main results on largely used alcohol fuels application in spark-ignition (SI) engines are discussed. Aspects inherent ethanol and methanol production processes, chemical-physical properties and their application in SI engines are presented. Different engine fuelling strategies, dual fuel and blend are analysed. Alcohols have higher enthalpies of vaporisation and research octane number (RON) values as well as excellent anti-knock ability compared to gasoline. This effect enhances in dual fuel mode. Ethanol and methanol have higher thermodynamic conversion efficiencies than gasoline combustion. Cycle to cycle variation is in line with gasoline values. In general, NOx decreases with alcohol fuels, and the best results are achieved in blend mode with a reduction of up to 30% with methanol compared to gasoline. Independently of the fuelling mode, significant benefits on particle number emissions are observed by using alcohol fuels. Carbon monoxide (CO) and hydrocarbons (HC) emission trends strongly depend on fuelling mode and engine operating conditions. Additionally, the lower carbon content of alcohol fuels reduces the CO_2 emissions up to 10% compared to reference gasoline.

Keywords Spark ignition · Methanol · Ethanol · Dual fuel · Fuel blend · CO_2 · Emissions

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Abbreviations

API-GDI	Alcohol Port Injection—Gasoline Direct Injection
BMEP	Brake Mean Effective Pressure
BSCO	Brake Specific CO
$BSCO_2$	Brake Specific CO_2
BSHC	Brake Specific HC
BSNOx	Brake Specific NOx
BTE	Brake Thermal Efficiency
CO	Carbon monoxide
CO_2	Carbon dioxide
COV_{IMEP}	Coefficient of variation of IMEP
CR	Compression Ratio
DF	Dual Fuel
DI	Direct Injection
FSR	Fuel Substitution Ratio
GDI	Gasoline direct injection
GHG	Greenhouse Gases
GPI-ADI	Gasoline Port Injection—Alcohol Direct Injection
HC	Hydrocarbons
IMEP	Indicate Mean Effective Pressure
LHV	Lower Heating Value
NOx	Nitrogen oxides
PFI	Port Fuel Injection
pfp	Peak firing pressure
PM	Particulate Matter
PN	Particle Number
RON	Research Octane Number
SI	Spark Ignition
SOI	Start of Injection
TLV	Threshold limit value
WOT	Wide Opening Throttle

3.1 Introduction

The great concern related to global warming and greenhouse gas (GHG) emissions gives widespread attention to CO_2 reduction. In Europe, in the view of the Green Deal initiatives, most governments have set or are considering net-zero emissions targets (Soest et al. 2021). In this regard, the transport sector is responsible for about 23% of the global CO_2 emission (IEA 2021). Besides, the transition toward a cleaner form of propulsion, such as electric vehicles, is very far to be complete despite the rapid increase of the market share of electric vehicles (Hall et al. 2019) and its growth is expected to rise in the mid-long time frame. The lack of capillary electric fast-charging infrastructures and the production of electricity from renewable sources, especially outside cities, leave room for further developing internal combustion engines in the short-mid timeframe. In this context, SI engines are widely used in modern society in many operative fields such as passenger and commercial vehicles or other kinds of vehicles (Deng et al. 2018). Commonly thermal engines are recognised as a source of pollutant emissions. As a result, stringent regulation limits on CO_2 (EC 2020) and vehicle pollutant emissions push the research communities and industries to develop sustainable and effective solutions. Among the alternatives, in the short-mid timeframe, low carbon fuels, such as alcohol fuels, help to reduce the carbon footprint of the transport sector (Beatrice et al. 2020; Ianniello et al. 2021), especially if alcohols are produced in a renewable manner. Ethanol and methanol have drawn much attention in the last decade since they are considered renewable and cleaner fuels. Figure 3.1 shows a cumulative number of publications on SI engines fuelled with alternative fuels, methanol, ethanol in two different timeframes, based on research in the Scopus database.

Ethanol is a worldwide studied fuel, while interest in methanol fuel increased in the last decade (see Fig. 3.1).

The geographical regions where methanol and ethanol are mostly studied are shown in Figs. 3.2 and 3.3. The United States of America and China are the countries where this topic is most discussed and assessed. In the last decades, the interest is significantly growing in Eastern Asian Nations such as India.

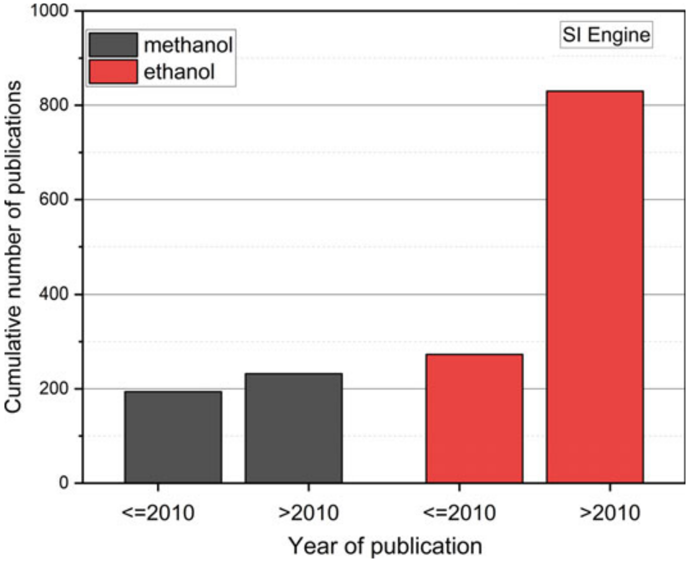

Fig. 3.1 The number of research papers on alcohols fuels (methanol and ethanol) in SI engines. *Source* Scopus database

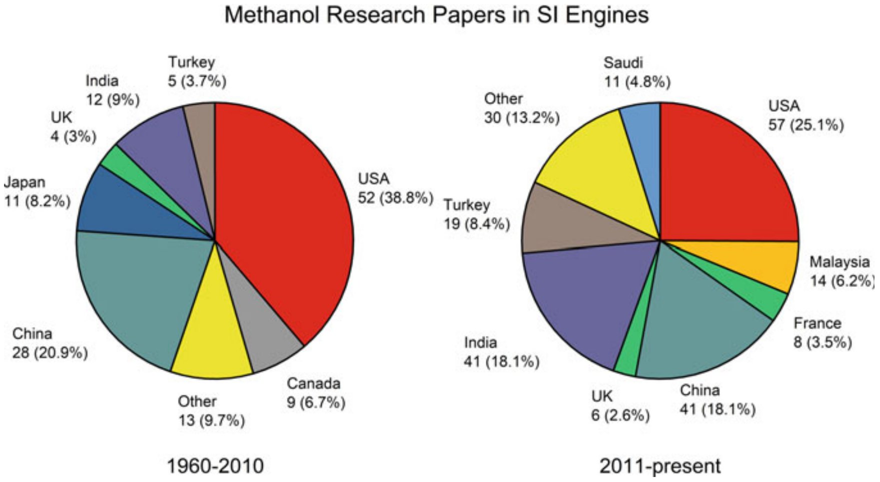

Fig. 3.2 Geographical distribution of the research papers on methanol usage in SI engines. *Source* Scopus database

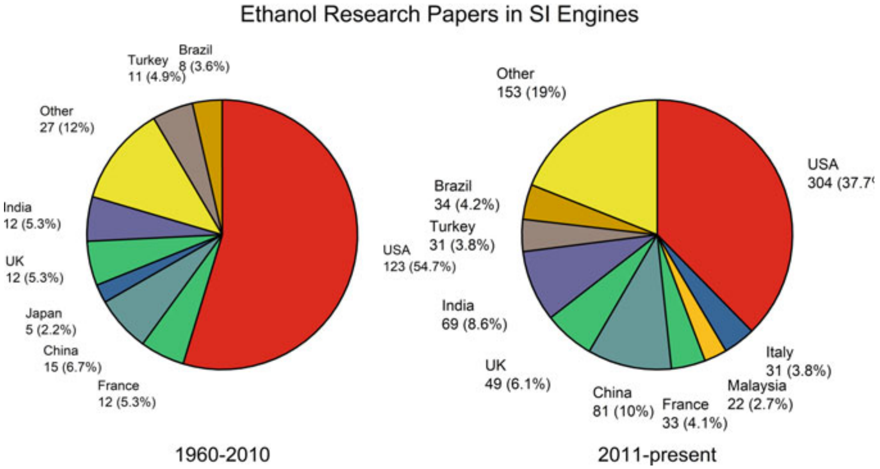

Fig. 3.3 Geographical distribution of the research papers on ethanol usage in SI engines. *Source* Scopus database

In this chapter, the application of ethanol and methanol fuels in spark-ignition engines is discussed. The chapter aims at assessing the use of ethanol and methanol in SI engines covering all fuelling technologies and injection strategies. Specific sections on combustion, emissions and engine performances are reported discriminating the effects of the technologies to those of the fuels.

3.2 Production and Properties of Alcohol Fuels

In this section, an overview on methanol and ethanol production is reported. The main chemical-physical fuel properties are discussed for both fuels and compared to conventional gasoline.

3.2.1 Alcohol Fuels Production

In this section, a brief overview on different fuel production processes for ethanol and methanol is reported below.

As mentioned, the attractiveness of methanol and ethanol fuels is related to the production processes based on renewable sources allowing carbon footprint reduction (Çelebi and Aydın 2019; Geng et al. 2017).

Ethanol can be produced by directly fermenting sugars, including sugarcane, sugar beet, sorghum, whey and molasses with yeast, from lignocellulosic materials, including woody materials, straws, agricultural waste and crop residues and catalytic hydration of ethylene (Çelebi and Aydın 2019). The ethanol produced by starch and sugar-based feedstock is known as first-generation ethanol. However, the increasing concern related to food feedstock production leads to alternative ethanol feedstock production (Popp et al. 2014). As an alternative, lignocellulosic materials seem to be more attractive due to their availability and the non-edibility of the feedstock (Isikgor and Becer 2015). Cellulosic-based ethanol is known as second-generation ethanol (Yun 2020). Recently, the so-called third-generation ethanol emerged as a candidate for future alcohol fuel production from microalgae. This ethanol production system gains increasing attention due to the simple process of converting microalgae into monosaccharides for biofuels production and their high growth rate and short harvesting cycle (Kim et al. 2020). Figure 3.4 shows the global ethanol production by top producer countries per year (2020). Brazil and the US are the two major ethanol producers, reaching about 85% of the world production.

Methanol can be synthesised from several carbon-containing feedstocks, including natural gas, coal, biomass, or CO_2 (Dalena et al. 2018). Methanol can be produced using renewable feedstocks such as forestry and agricultural waste, municipal solid waste, sewage, etc. In recent years, attention has been given to the methanol produced from CO_2. In this case, two different processes for methanol synthesis can be mentioned, a direct and indirect chemical CO_2 conversion. In the former case, CO_2 is directly converted into methanol, while in the second one, it is first converted into synthesis gas. The syngas produced is synthesised in methanol (Samimi et al. 2019). Generally, the primary use of methanol is in the chemical industry as either a feedstock, solvent, or cosolvent. Approximately 65% of the methanol produced worldwide is consumed for this purpose (Dalena et al. 2018). According to the IRENA Innovation Outlook (IRENA and Methanol Institute 2021),

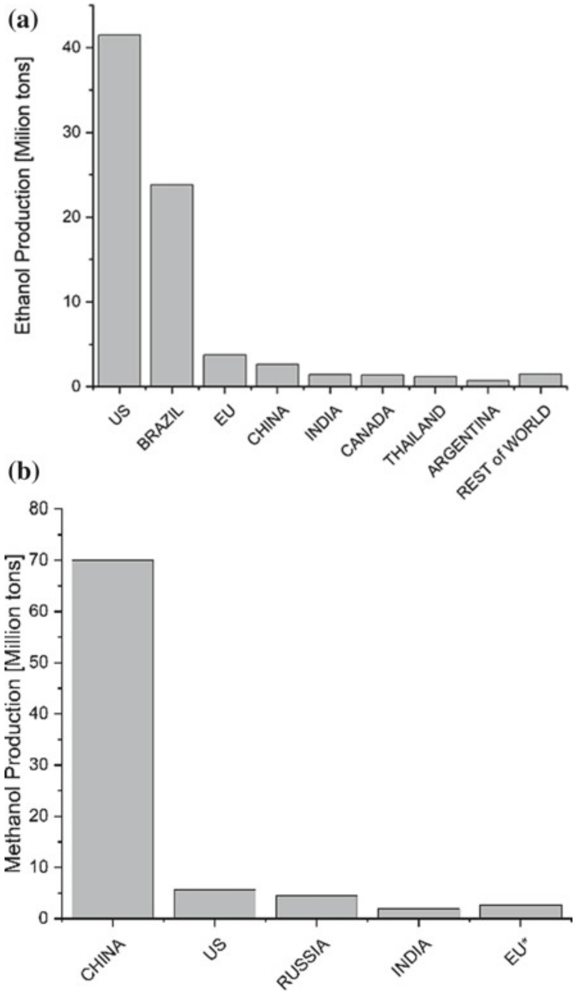

Fig. 3.4 **a** Global ethanol production by main production countries (2020). Sönnichsen (2020). *Source* data was rearranged from Sönnichsen (2020). **b** Global methanol production by different Countries (2018) (*2014)

in 2020, 30% of produced methanol has been used as a fuel feedstock and fuel additive. In Fig. 3.4b, the global methanol production by major Countries is depicted. As can be seen, China is the largest methanol producer in the world (about 70 million tons per year). Other countries produced much less methanol, e.g., the US produced 5.7 million tons per year (2018), and Russia produced 4.46 million tons per year (2018) (Bazaluk et al. 2020). India (2020) (Wikaspedia Domains 2021) and EU (2014) (Galadima and Muraza 2015) produced respectively 2 and 2.6 million tons.

3.3 Fuelling Mode, Combustion, and Emissions of Alcohol Fuels in Spark-Ignition Engines

In this section, a literature-based analysis on combustion process and emissions is carried out. The main alcohol fuels properties and the fuel injection system modes commonly applied for alcohols are also discussed.

3.3.1 Alcohol Fuels Properties

Alcohol fuels belong to the oxygenated family, and as inorganic compounds, a hydroxyl group substitutes a hydrogen atom. Ethanol (C_2H_5OH) and Methanol (CH_3OH) are primary alcohols because the carbon atom bound to the hydroxyl group is bonded with only one other carbon atom. In Table 3.1 are listed the main chemical-physical properties of gasoline, ethanol, and methanol fuels.

The molecular polarity generates a strong intermolecular hydrogen bond that led to a rise of the boiling point and the heat of vaporisation. It gives good miscibility with a substance characterised by a strong molecular polarity, such as water (Pearson and Turner 2012). The high values of heat of vaporisation promote a cooling effect on the air–fuel charge (Shamun et al. 2020).

Furthermore, oxygen content in the alcohol fuel lowers the stoichiometric air-to-fuel ratio. It influenced the combustion process, leading to higher brake thermal and

Table 3.1 Typical fuel properties (Heywood 2018; Ferguson and Kirkpatrick 2015; Noor El-Din et al. 2013; Sarıkoç 2020; Epping et al. 2002; Yates et al. 2010; Liu et al. 2015a)

Properties	Gasoline	Ethanol	Methanol
Research octane number [–]	≥ 95	108–109	107–109
Molar mass [g/mol]	~ 110	46.1	32.0
Carbon number [–]	4–12	2	1
H/C [–]	1.9	3.0	4.0
O/C [–]	0	0.5	1.0
LHV [MJ/kg]	42.6	27.0	20.0
(A/F)s [–]	14.6	9.0	6.4
Viscosity (@20 °C) [mPa/s]	0.6	1.21	0.54
Density (@15 °C) [kg/m^3]	720–775	794	796
Boiling point [°C]	40–200	78	65
Heat of vaporization [kJ/kg]	307	840	1160
ΔHvap/LHV [kJ/MJ]	7.14	31.23	55.22
Specific heat [kJ/kgK]	2.4	2.5	2.6
Adiabatic flame temp. [K]	2266	2197	2151
Specific CO_2 emissions [g/MJ]	75.1	70.7	68.8
Laminar flame speed [cm/s]	38.0	50.0	52.3

combustion efficiencies than conventional gasoline combustion (Çelebi and Aydın 2019; Kumar et al. 2020), but this aspect will be further discussed.

On the other hand, the presence of the carbon–oxygen bonds leads to a lower heating value (LHV) in comparison to gasoline (Table 3.1) and raising the mass fuel consumption at the same load conditions (Çelebi and Aydın 2019; Pearson and Turner 2012). Methanol and ethanol have similar properties, and their high-octane number rating makes them well suited for SI engines.

The material compatibility, density, oxidative stability, and viscosity strongly influence the functioning and life of the engine components. Methanol is more corrosive than ethanol. Aluminum and magnesium are subjected to aggressive corrosion, although with different chemical reaction rates. For these reasons, methanol concentration in blends is limited (Andersen et al. 2010). The EN228 regulation, which regulates the standard gasoline, set the methanol content limit to 3%. The higher methanol ratio tested is 85% v/v (Agarwal et al. 2020). The results show that high methanol concentration in blended fuel promotes engine wear and corrosion (Estefan and Brown 1990). The corrosive properties require modification to a state-of-the-art fuel injection system. Additives can be used with methanol to improve ignition, lubricity, and stability. Methanol is highly toxic in terms of ingestion, skin, or eye contact. According to Methanol Institute (Medina et al. 2017) and European Chemical Agency (ECHA) (van Leeuwenhoeklaan 2018), the threshold limit value (TLV) for time-weighted averaged (TWA) to methanol exposure is 200 ppm for an 8-h day and 40-h per week. The TLV as short-term limit rises to 250 ppm with skin notations. Intoxication by exposure to methanol initially manifests as temporary sickness and drowsiness. Nevertheless, methanol intoxication could have a latent period from 6 to 30 h. Methanol metabolisation could cause vomiting, dizziness, abdominal pain, diarrhea, difficulty breathing, blurred vision, etc. (Moon 2017).

Ethanol is less corrosive. The corrosive potential is in the percentage of water content, which is higher than in methanol and dielectric and conductive properties, leading to galvanic erosion. Matějovský et al. (2017) studied the corrosion effect of different ethanol-gasoline blends on different metallic materials, showing corrosion effect not linear with the ethanol content. According to the analysis conducted by the Royal Society and based on Brazilian experiences (Woods 2008), ethanol concentrations over 25% require an almost complete adaptation of the fuel delivering system.

Another aspect to consider is the cold starting, as one of the main issues affecting countries with average ambient temperature below the standard. Low air temperature influences the combustion process in the first running. The higher viscosity of alcohols determines poorer atomisation and air–fuel mixing. However, this phenomenon is less relevant for port fuel injection (PFI) modes (Gao et al. 2014).

The most commercialized gasoline-ethanol blend is the E10, characterised by 10% ethanol and 90% gasoline on a volume basis. It is commonly used in the US (Awad et al. 2018), and similarly, the EU Directive 2009/30/EC sets maximum ethanol concentration in gasoline to 10% v/v. Additionally, it sets also the maximum oxygen concentration to a 3.7% molar basis. Limited ethanol fractions do not require engine modifications, while neat ethanol requires specific materials to avoid corrosion.

Properties of alcohols strongly influence the combustion process. Indeed, they are characterised by a higher laminar flame rate (Glaude et al. 2010) and a slight increase in flammability limitis compared to gasoline. Methanol is generally safer than gasoline, and it is extinguishable with water thanks to its water solubility (Carpenter and Hinze 2004). On the contrary, ethanol poses significant fire safety concerns due to its solubility in water. Neat ethanol or blends requires custom fire-fighting foams (Naidenko 2009).

3.3.2 Fuelling Mode

This section describes the fuel injection system modes commonly applied for alcohol fuels in a SI engine: port fuel injection and direct injection (DI). The following nomenclatures are adopted in this chapter:

- the blends are reported on a volume basis, e.g., M85 is referred to a blend in which methanol and gasoline are in 85 and 15 v/v, respectively; E instead of M for ethanol;
- PFI-Blend refers to port-injected blend, while DI-Blend refers to direct-injected one. Dual Fuel (DF) mode, when the fuels are both injected in PFI and DI modes; alcohol port injection and gasoline direct injection (API-GDI) and vice versa (GPI-ADI);
- the fuel substitution ratio (FSR) is computed on an energy basis through the following equation:

$$FSR = \frac{m_a \cdot LHV_a}{m_a \cdot LHV_a + m_g \cdot LHV_g}$$

where m is the fuel mass while LHV is the lower heating value. To discriminate the alcohol fuel and gasoline, the *a* and *g* subscripts are utilised.

The most common fuelling approach is the alcohol-gasoline blend, which allows blending in any proportion with few or no modifications on the fuel injection system, notwithstanding cold start problems. Lower FSR, e.g., M85 instead of M100, is utilised to partially mitigate challenging cold starts issues at temperatures under 15 °C, and safety concerns such as in-tank flammability, low flame luminosity and odour (Awad et al. 2018).

The fuel properties cannot be fully exploited over the whole engine operating map at a fixed alcohol and gasoline blending ratio. Thus, a viable solution can be the DF mode, in which alcohol fuels can be injected in the intake manifold or directly into the cylinder depending on the SI engine baseline injection system.

3.3.3 Combustion

In this paragraph, the influence of alcohol fuels on combustion process is assessed. Details on the alcohols impact on knock are also reported.

Alcohol fuels in SI engines influenced the combustion process due to their high oxygen content and lower boiling point compared to gasoline.

The maximum in-cylinder pressure is evaluated as an important combustion control parameter and is limited by structural concerns at maximum engine loads. Figure 3.5 depicts a comparison among maximum peak firing pressure (pfp) as a function of engine speed for the different fuelling modes. The increments of pfp in PFI-Blend and DF modes are up to 5 bar, for DI-Blend up to 3 bar, and due to the higher latent heat and laminar flame speed, while the difference among the modes is related to the cooling effect. Kalwar et al. (2020) reported that increasing FSR in PFI mode further improves the combustion process, leading to slightly higher pfp than gasoline.

In contrast, Cho et al. (2015) investigated intermediate ethanol blends in a DI engine at different engine speeds and partial load. They found that the pfp decreases proportionally with the ethanol blend ratio at the constant energising time because of the reduced lower heating value than the gasoline fuel (Table 3.1). An increase in the combustion duration is observed, as confirmed by Balki et al. (2017).

The use of alcohol can reduce the combustion duration. Indeed, Li et al. reported a comparison among different alcohol-blends in a PFI SI engine at 1200 rpm and 3–5 bar of brake mean effective pressure (BMEP). They found a shorter ignition delay and combustion duration proportional to the FSR. This effect is confirmed by Singh et al. (2016) for different ethanol-gasoline blends (E5, E10, E20) at low engine speeds at wide opening throttle (WOT).

Ethanol and methanol generally increase the volumetric and Brake Thermal Efficiencies (BTE). Figure 3.6 reports the BTE values for the different fuelling modes, engine speeds, and engine types. As seen, a clear trend is not defined in the figures due to the different engine operating conditions. In general, the use of alcohol increases the BTE both in blend modes and in DF. This is partly explained by the higher

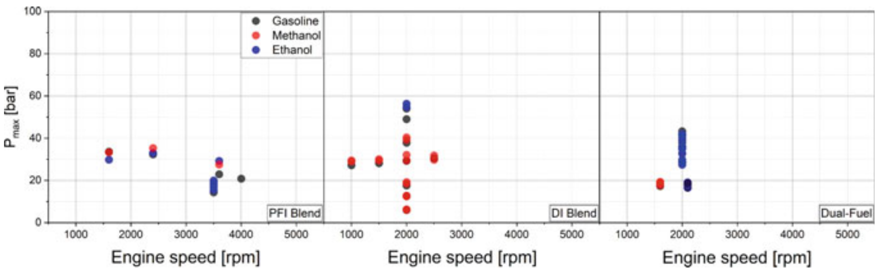

Fig. 3.5 pfp as a function of the engine speed, load, and engine type. Panel division based on PFI, DI and DF fuelling modes. *Source data* Zhang et al. (2014), Balki et al. (2014), Liu et al. (2015b, 2021), Zhuang and Hong (2013), Sharma et al. (2019), Edwin Geo et al. (2019), Qian et al. (2019)

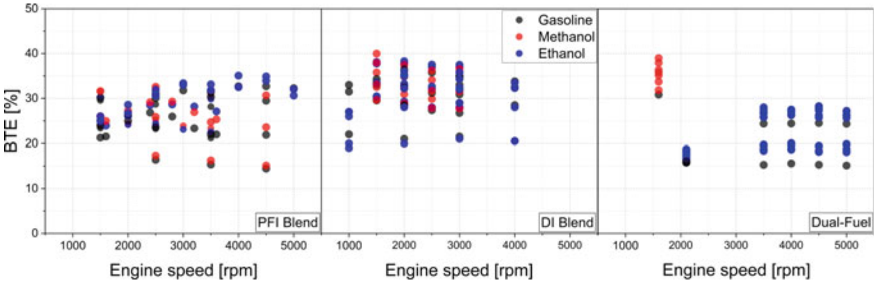

Fig. 3.6 Brake thermal efficiency as a function of engine speed, load, and engine type. Panel division based on PFI, DI and DF fuelling modes. *Source data* Deng et al. (2018), Balki et al. (2014), Liu et al. (2015b, 2021), Zhuang and Hong (2013), Turner et al. (2018), Sileghem et al. (2015), Wallner et al. (2009)

alcohol laminar flame speed and consequently reduced in-cylinder heat transfer losses compared to gasoline operation. In addition, the charge cooling effect with the use of alcohols and the consequent reduction of the exhaust gas temperatures can be considered another contributing factor. Turner et al. (2015) reported that a BTE gains up to 10% compared to gasoline for mid and high blend ratios. Balki et al. (2017) reported an increase of BTE with alcohols due to their oxygen content and higher heat of vaporization. Sileghem et al. (2014) confirmed this trend.

Based on indicated mean effective pressure (IMEP) recorded cycle by cycle, the combustion stability, and repeatability identified by the coefficient of variation of the IMEP (COV_{IMEP}) are discussed. Figure 3.7 reports the COV_{IMEP} values at different engine speeds and fuelling modes. A reference value of 5% has been considered as an acceptable limit for SI engines. Most COV_{IMEP} values are under the acceptable limit in a near stoichiometric operating condition. The outliers relate to ultra-lean conditions characterised by misfiring. In general, alcohol fuels do not influence combustion stability negatively in SI engines.

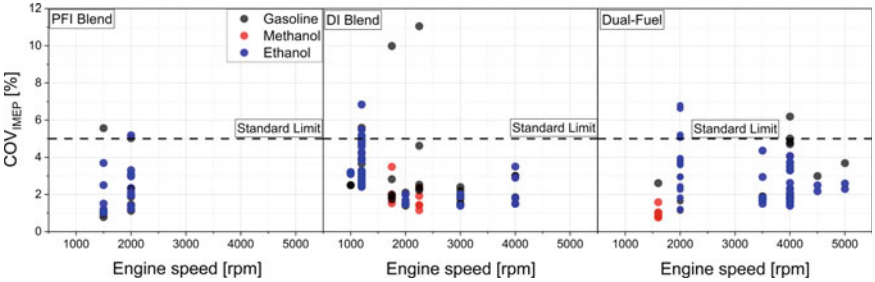

Fig. 3.7 COV_{IMEP} as a function of engine speed, load, and engine type. Panel division based on PFI, DI and DF fuelling modes. *Source data* Liu et al. (2015b), Qian et al. (2019), Wallner et al. (2009), Oh et al. (2010), Zhuang et al. (2018), Ceviz and Yüksel (2005), Nguyen et al. (2019), Ou et al. (2010

SI engine knock is one of the most critical phenomena limiting the efficiency increase. The anti-knock ability of fuel is described by RON number. As shown in Table 3.1, ethanol and methanol have higher RON than gasoline and can be recognised as anti-knock fuels (Wallner et al. 2009; Elfasakhany 2021). DF is the most effective mode to mitigate engine knock (Qian et al. 2019; Al-Muhsen et al. 2019). Liu et al. (Liu et al. 2015b) reported the advantages of the DF strategy in knock mitigation. The authors investigated the knock characteristics of methanol in the API-GDI engine reporting the effectiveness in suppressing engine knock, extending the high-load operating limit and improving fuel economy. Kim et al. (2015) investigated knock mitigation adding ethanol in API-GDI mode engine at different compression ratios (CR), 9.5 and 13.3. They found that at WOT and 1000 rpm, at most critical conditions, the required FSR to mitigate engine knock changes with CR, from 14 to 57%. It is also confirmed by Zhuang et al. (2018) in GPI-ADI mode. Engines operating at high FSR permits more advanced spark timing and higher boosting than gasoline only.

3.3.4 Emissions

In this section, the main engine-out regulated emissions of SI engines fuelled with alcohol in dual fuel and blend modes are discussed and compared to the conventional gasoline combustion.

In general, engine-out hydrocarbons production is related to different mechanisms: incomplete combustion, misfiring, flame quenching, and fuel trapped into crevices. Figure 3.8 shows the brake specific HC (BSHC) emissions as a function of the engine speed, load and fuelling modes. DF mode emits lower BSHC compared to blend ones. This behaviour can be ascribed to the ability to extend the lean burn limit (Huang et al. 2021). In blend mode, a clear trend does not emerge. Since HC emission is related to fuel not involved in the combustion process, the oxygen content of alcohols further improves the unburned fuel oxidation as reported by Silighem (2015). However, if the main mechanism is the charge trapped into crevices, the

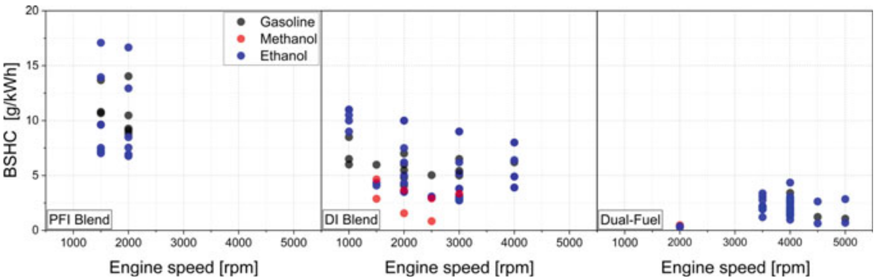

Fig. 3.8 Brake-specific HC emissions as a function of engine speed, load, and engine type. Panel division based on PFI, DI, and DF fuelling modes. *Source data* Kalwar et al. (2020), Sileghem et al. (2015), Wallner et al. (2009), Zhuang et al. (2018), Park et al. (2010)

use of PFI-Blend and DF modes can be worse than DI-Blend. This is confirmed by Kalwar et al. (2020) activities, who detected an increasing BSHC trend with FSR for both ethanol and methanol in DF mode compared to gasoline direct injection (GDI) baseline. Zhuang et al. (2018) found a non-monotonic BSHC trend related in particular to the lower in-cylinder temperature, lean air-to-fuel ratio, speed, and FSR. Park et al. (2010), investigating the effect of air to fuel equivalence ratio, found that E85 emits less HC than gasoline due to ethanol polar nature and its lower interaction with lubricating oil films. Moreover, an increasing trend was showed toward leaner conditions due to the incomplete combustion process. The HC phenomenology is particularly complex, but alcohols for some engine configuration and operation reduce the BSHC.

CO is essentially controlled by the local equivalence ratio (or air to fuel ratio) and temperature in the combustion chamber (Wallner et al. 2009). According to the literature review, using alcohol fuels potentially improves CO emissions, but it depends on the alcohol fuel employed and the engine operating conditions.

Figure 3.9 shows the brake-specific CO (BSCO) emissions as a function of engine speed, load, and fuelling modes. There is a lack of results in the technical literature regarding BSCO trends for the PFI blend. Therefore, no graphs are reported.

BSCO decreases adopting the DI fuelling mode. This trend is marked by adding methanol to gasoline due to the higher reactivity, with stratification in the combustion chamber and improved combustion process. Turner et al. (2018) evaluated the impact on engine-out emissions of blending ethanol at different ratios with gasoline in a DI engine, using a range of spark timings and start of injection (SOI). The greatest CO reduction has been observed adopting higher FSR, SOI advance, and retarded spark timing. The decreasing trend of BSCO emissions is also confirmed by Sileghem et al. (2015).

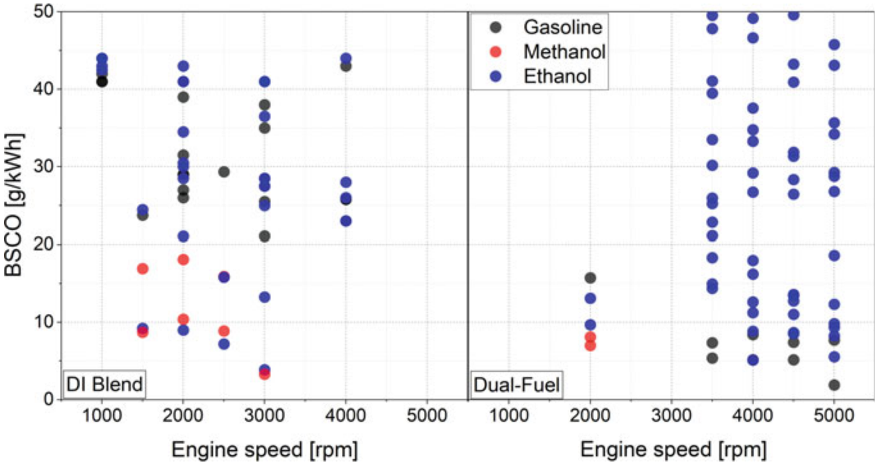

Fig. 3.9 Brake Specific CO emissions as a function of engine speed, load, and engine type. Panel division based on PFI, DI, and DF fuelling modes. *Source data* Kalwar et al. (2020), Zhuang and Hong (2013), Sileghem et al. (2015), Wallner et al. (2009)

Adopting DF mode, an opposite trend in BSCO can be noticed. As depicted in Fig. 3.9, for low engine speeds, the DF mode effectively reduces BSCO. Daniel et al. (2012) investigated engine emissions when ethanol and methanol are fuelled in GPI-ADI mode. The authors also compared the results with both a PFI and GDI baseline. They found for CO emissions a similar trend compared to the PFI baseline at lower loads and engine speeds, while lower CO emissions have been reported compared to the GDI reference. At higher loads, they observed a CO reduction compared to other fuelling modes. The improved oxidation was due to an improvement of the combustion process advancing the spark timing. The authors also estimated that further CO oxidation was related to the better vaporisation of the PFI gasoline, which helped the DI alcohol droplets to burn.

In Kalwar et al. (2020), the authors reported that at 2000 rpm, CO emission from DF engine with ethanol and methanol port-injected was lower than baseline. The oxygen content in the alcohol might be an important factor responsible for this trend due to the improved oxidation of CO in CO_2 in the stoichiometric fuel–air mixture. The authors also reported that increasing the premixed ratio of alcohols showed a different trend of CO emissions. At a higher premixed ratio, with an FSR of 30%, lower CO emissions can be observed employing ethanol/gasoline rather than methanol/gasoline dual-fuel. In this case, the methanol dominant charge cooling effect can be considered the driving factor for this trend.

At higher engine speeds, the DF strategy leads to an increase in BSCO. Particularly, at lower load, the increasing of FSR can cause an overmixing or low in-cylinder temperature, not guaranteeing optimal conditions for the oxidation of CO. This is coherent with the finding by Zhuang et al. (2013), that for FSR value greater than 48% reported an increase of BSCO.

Figure 3.10 shows the brake-specific CO_2 ($BSCO_2$) for blend fuelling mode.

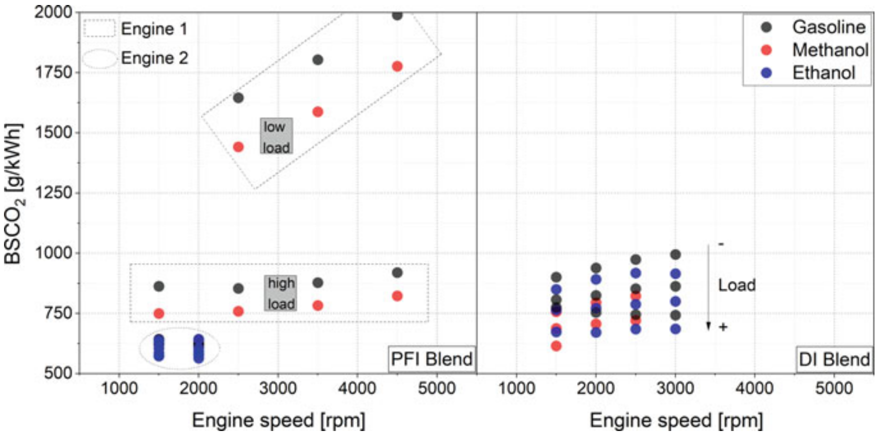

Fig. 3.10 Brake Specific CO_2 emissions as a function of engine speed, load, and engine type. Panel division based on PFI, DI and DF fuelling modes. *Source data* Turner et al. (2018), Sileghem et al. (2015), Park et al. (2010)

Few data are available in DF mode, and therefore no graphs are reported. Different engines characterised by different CO_2 baseline levels are identified. As can be seen, the results show a general decrease of $BSCO_2$ with alcohols. E.g., referring to the PFI-Blend chart, the operating points belonging to engine 1 show the methanol capability to reduce CO_2 at the same FSR, independently of the engine load and speed. In this case, the reduction is up to 10% compared to the baseline. In DI-Blend mode, for both alcohols considered, the CO_2 decreases as the load increases. At constant FSR, the CO_2 reduction is up to 20%.

Turner et al. (2018) reported a reduction of more than 10% in $BSCO_2$ for the gasoline-methanol blend compared to the gasoline baseline. The difference between methanol and ethanol CO_2 emissions is due to the methanol higher H/C ratio (Sileghem et al. 2015).

CO_2 emissions, through a well-to-wheel analysis, could be potentially further lower compared to gasoline due to the renewable nature of the alcohol fuels considered.

The NOx formation is strictly related to the in-cylinder temperature, which depends on the fuel properties and engine parameters, such as engine load and speed, equivalence ratio, coolant temperature, charge composition, etc. As previously discussed, alcohol fuels are characterised by higher heat of vaporisation and lower adiabatic flame temperatures compared to gasoline. Therefore, NOx emissions decrease according to the Zeldovich mechanism. Figure 3.11 shows the ethanol and methanol impact on NOx emissions at different engine speeds and fuelling modes. DI-Blend mode does not show a clear trend. In PFI-Blend one, NOx seems to rise as engine speed increases. However, the brake specific NOx (BSNOx) level is lower compared to the gasoline reference.

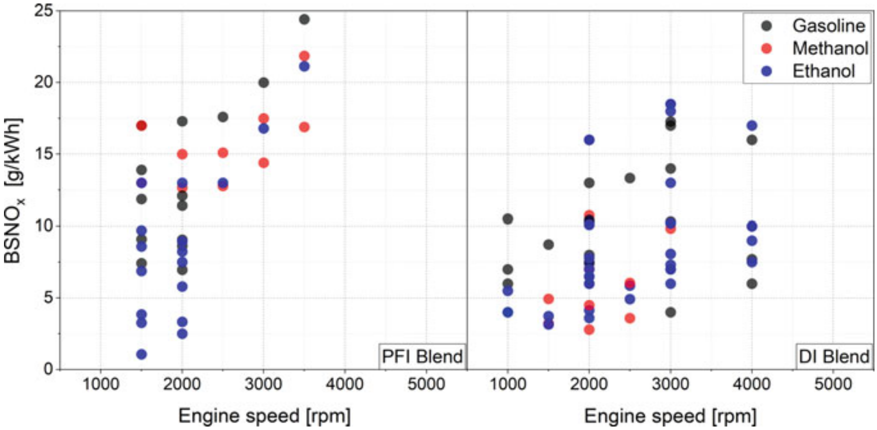

Fig. 3.11 Brake Specific NOx emissions as a function of engine speed, load, and engine type. Panel division based on PFI, DI, and DF fuelling modes. *Source data* Kalwar et al. (2020), Turner et al. (2018), Sileghem et al. (2015), Wallner et al. (2009), Park et al. (2010)

In the blend mode, the NOx emissions decrease as the fuel substitution ratio increases. Saikrishnan et al. (2018) investigated different ethanol blends (from E5 to E20) in a SI engine. The increase of ethanol fraction strongly influences the evaporation phase of the blend, thereby the in-cylinder temperature with a consequence NOx reduction.

The effect of the blending ratio enhances when it is directly injected instead of PFI. Turner et al. (2018) reported NOx emission in a DISI engine at 1500 rpm and 3.4 bar IMEP using ethanol-gasoline blends at different FSR. NOx emissions were reduced proportionally to the ethanol fraction because of the flame temperature reduction, which was corroborated by reducing the exhaust temperature.

In DI-blend mode, the alcohol charge cooling effect becomes the predominant parameter resulting in a further decrease of NOx emissions. In addition, the NOx concentration decreases as the increasing volume percentage of alcohol in the fuel mixture. As a result, the combustion process is more complete at leaner operating conditions, and the concentration of NOx emission is reduced (Thakur and Kaviti 2021).

GDI engines are recognised to emit lower CO_2 emissions, but with the disadvantage to generate more particulate matter (PM) emissions than conventional PFI configuration (Leach et al. 2013; Su et al. 2014). In addition, the particle number (PN) in a GDI is one order of magnitude higher than other ones. The fast fuel evaporation time and the wall impingement strongly influenced the PM emission (Raza et al. 2018), justifying the increase of small-sized particles fraction (Lee and Park 2020).

In Fig. 3.12, the impact of ethanol and methanol on the total PN number for DI-Blend and DF modes is depicted. As previously stated, the PFI data is not reported in this figure due to the lower PN production. As can be seen, alcohol fuel use reduces the total PN number for both injection modes thanks to the oxygen content of the alcohol, which improves the soot oxidation at the end-gas combustion phase.

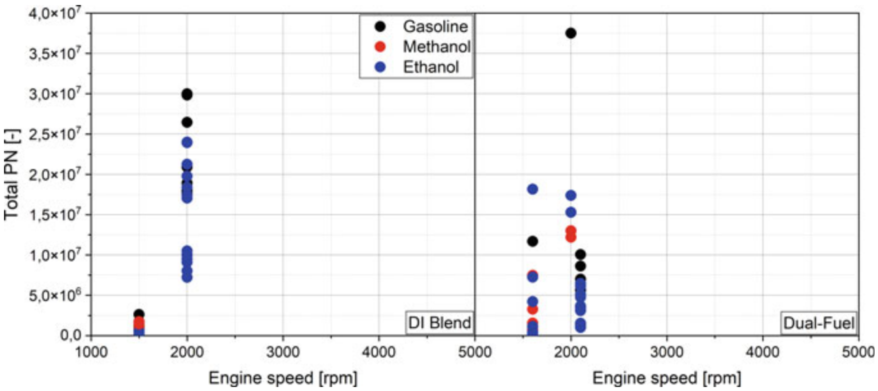

Fig. 3.12 Total particle number emitted as a function of engine speed, load, and engine type. Panel division based on PFI, DI and DF fuelling modes. *Source data* Liu et al. (2015a, 2021), Kalwar et al. (2020), Zhang et al. (2014), Turner et al. (2018)

The PN reduction is proportional to the percentage of alcohol used. This reduction can be observed also for lower FSR values as confirmed by Kalwar et al. (2020). They found that in a GDI-API engine, adding methanol in PFI at low FSR (15% on energy basis) reduced significantly total PN. In the same work, the authors assessed a further decrease of PN adding ethanol via PFI instead of methanol due to the higher oxygen content of ethanol. The increase of the premixed alcohol leads to lower PN emissions as confirmed in Liu et al. (2021). Liu et al. (2015a) found that PN significant reduction can be achieved by adopting DI-alcohol and PFI-gasoline strategy. The authors reported that the PFI-gasoline encourages fuel vaporisation, increases air–fuel mixing, and reduces wall wetting, strongly influencing the particles accumulation mode fraction. The DI-alcohol improves the combustion process leading to a reduction of locally rich regions due to the oxidant action of hydrocarbons by oxygen in the alcohol molecules.

In DI-Blend mode, the PN reduction is related to the FSR. In this case, the enhancement of the oxygen content adding alcohol fuels leads to a better combustion process and a reduction of particle formation. Turner et al. (2018) investigated particulate emissions from a single-cylinder DI engine operating on E85 and M56 fuels, confirming alcohol fuels characteristics to reduce PM emissions.

3.4 Conclusions

In this chapter, an assessment of alcohol fuels in a spark-ignition engine is carried out. This work evaluates the impact of methanol and ethanol fuels on SI engines and their advantages and drawbacks in combustion, emissions, and efficiency. The main outcomes are listed below:

- Ethanol and methanol are considered renewable fuels. Thanks to their physical and chemical properties, they are suitable for SI engines. The blending mode is the most common fuelling approach utilising alcohols. The use of a low FSR ratio in alcohols-gasoline blends needs no engines modifications.
- The alcohol FSR, in blends and DF fuelling modes, is not limited by the combustion process and miscibility issues. However, technical concerns are reported for high FSR blends regarding cold start, corrosion, and wear problems.
- The use of alcohol fuels shows a general increment of pfp in all the fuelling modes investigated and potentially reduces the combustion duration. Ethanol and methanol show better BTE compared to gasoline. According to the technical literature, in blend modes, alcohols lead to a slight increase in BTE. More evident is its increase in dual-fuel mode.
- $\mathrm{COV}_{\mathrm{IMEP}}$ variation, using alcohol fuels is in line with gasoline independently by the fuelling mode and engine type. Alcohols with higher enthalpies of vaporisation and RON have greater anti-knock ability compared to gasoline. This effect is enhanced in DF mode.

- The HC phenomenology is particularly complex. The BSHC emissions are influenced by fueling mode and operating conditions. In blend mode, a clear trend does not emerge. In DF mode a reduction of BSHC is observed due to its ability to extend the lean burn limit.
- Specific CO emissions are lower adopting the DI-Blend mode. The decreasing trend is marked by adding methanol. An opposite trend can be noticed in DF mode depending on engine speeds and loads.
- Specific CO_2 emissions are lower for alcohol fuels due to their lower carbon content. The well-to-wheel CO_2 emissions could be potentially further improved compared to reference gasoline due to the renewable nature of the alcohols.
- Regarding NOx emissions, a clear trend cannot be noticed in DI-Blend mode, while in PFI-Blend one, NOx rises as engine speed increases. However, the BSNOx is lower compared to the gasoline reference.
- Alcohol fuels reduce the total PN number for all the fuelling modes investigated due to their oxygen content, improving the soot precursors oxidation.
- Based on the results above, it can be stated that the use of ethanol and methanol in SI engines can be considered, among the alternatives, a viable solution to reduce pollutant emissions in the short-mid term. Further work will be conducted by the authors extending literature-based research to explore further operating engine conditions adopting alcohol fuels.

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Chapter 4
Fuel Injection Strategies for Alcohol Utilization in Combustion Engines

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Abstract Engine research community and automobile manufacturers are making considerable effort to look for the alternative solutions of conventional diesel and gasoline for internal combustion engines (ICEs) and power production. Several developing technologies including electric vehicles (EVs), fuel cells, hydrogen powered engines, and other technologies are being employed as an alternative to ICEs. Studies suggest that the use of alcohol fuel provides substantial advantages over traditional fuels with lower modifications in existing engine technology. Use of alcohol fuel in ICE is possible through various ways, each has its own advantages over the other alternatives. In this book chapter a thorough review has been conducted of the various strategies for utilization of alcohols in ICEs, their effect on combustion characteristics and emissions formations has been presented and discussed.

Keywords Manifold injection · Dual fuel injection · Ethanol–diesel blends · Diesel engine · Direct injection

Abbreviations

ICE	Internal combustion engine
SI	Spark ignition
CI	Compression ignition
GHG	Greenhouse gases
PM	Particulate matter
EGR	Exhaust gas recirculation
nB	N-butanol
SOI	Start of injection
PPC	Partially premixed combustion

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HC	Hydrocarbon
DI	Direct injection
RCCI	Reactivity controlled compression ignition
HCCI	Homogeneous charge compression ignition
CR	Compression ratio
ABE	Acetone-butanol-ethanol
bTDC	Before top dead center
BSFC	Break specific fuel consumption
GDI	Gasoline direct injection
ECU	Electronically controlled unit
PFI	Port fuel injection
IMEP	Indicated mean effective pressure
NO_x	Oxides of nitrogen
BTE	Break thermal efficiency
PHEV	Plug-in hybrid electric vehicles
ITE	Indicated thermal efficiency
iB	Iso-butanol
SIP	Short injection pulse
RON	Research octane number

4.1 Introduction

Renewable alternatives of fossil fuels (such as alcohols) can potentially support for the development of environment friendly and sustainable fuel for internal combustion engines (ICEs). Some of the critical physical and chemical properties of alcohols (surface tension, viscosity, density, latent heat of evaporation, autoignition temperature etc.) are different compared to conventional fuels which limit its utilization in the existing compression ignition (CI) and spark ignition (SI) engines (Sahu et al. 2021; Vancoillie et al. 2013; Mehta et al. 2010). It is possible to utilize alcohols in existing engines in their blended form, or they may be used in their pure form by making certain modifications to the engines, such as the addition of corrosion-resistant materials (Kameoka et al. 2005) or by increasing the ratio of swept volume and clearance volume of combustion chambers, among other things. Apart from enabling the use of alcohols in IC engines, the engine research community is also working on 2nd and 3rd generation bio-alcohol manufacturing to ensure the availability of these alcohols on a massive scale (Sahu et al. 2020). Methanol and ethanol are the most often utilized alcohols due to the simplicity with which they can be produced and consumed. Both of them have shown outstanding effectiveness in the reduction of automotive emissions of greenhouse gases (GHG) and particulate matter (PM) in the environment. Studying the previous works on utilization of alcohols in ICE, advancements are being observed. Methanol port injection in a turbocharged engine combined with internal exhaust gas recirculation (EGR) improved dilution range of EGR and knock tolerance as compared to gasoline. This was owing to methanol's faster laminar burning velocity and larger dilution tolerance when compared to gasoline, respectively (Randolph et al. 2017). In one of the studies conducted by Behringer et. al (2014) with SI engines, gasoline sprays displayed flash boiling and collapsed more than ethanol sprays under hot engine head and heavy load circumstances, no apparent spray collapse was observed for butanol sprays under the same conditions (Behringer et al. 2014). Increased operability than ethanol was achieved in ICEs by the use of higher order alcohols (n-butanol (nB) and n- pentanol), which primarily resulted from the capacity to operate at lower loads and reduced the partial-burn zone (Pelucchi et al. 2017). As far as particle matter are concerned, methanol and ethanol emitted soot particles are observed smaller when operated in partially premixed combustion (PPC) mode (Shamun et al. 2016). The injection technique adopted for the alcohol injection significantly affect the particle size distribution (Dageförde et al. 2013). It has been observed that cetane number enhancers accelerates the ignition chemically for alcohol fuels, however, combining gasoline with alcohols for higher amount did not allowed a blended cetane improver to attain a given reactivity level (Dempsey et al. 2013). Integrating modern engine techniques with alternative fuels certainly relevant when a CI engine fueled with a low and high reactivity fuel may allow the elevated efficiency and extenuated emissions beyond those of CI or SI engine (Shamun et al. 2020; Belgiorno et al. 2019). However, relative to dual-fuel and conventional diesel combustion, higher ethanol blend and EGR using a multi-injection approach has a better effect on total hydrocarbon (HC) and CO minimization while retaining excellent performance (Ianniello et al. 2021). Adjustment in injection techniques can control the formation of pollutants and resulted in cleaner combustion. This chapter mainly deals with the exploration of various techniques effective utilization of alcohols such as alcohols in the form of blends, fumigation, manifold injection, direct injection (DI), dual fuel injection strategy etc.

4.2 Strategies for Alcohol Utilization in Combustion Engines

Alcohols as fuel for ICEs has been researched vastly, the amount of interest in utilization of alcohols as a transportation fuel has risen and fallen in tandem with phases of fuel shortages and low prices of energy crops throughout the years. Alcohols may be blended directly with diesel or gasoline before pouring into the fuel tank else it may be injected in manifold along with gasoline manifold injection or diesel DI in order to improve engine's performance and emission characteristics. Higher self-ignition temperature, higher latent evaporation energy, corrosive properties, blended mixture separation problems etc. limits the application of pure alcohols in ICEs. Alcohols can be used in ICE by adapting several ways, the most popular ways of utilization of alcohols as fuel are as follows:

(1) Diesel-alcohol/ Gasoline-alcohol blends: Alcohols can be utilized in blended form with raw fuels and can be poured directly in to the fuel tank. Hydroscopic nature of alcohols makes it difficult sometime to use it in this form as it results in layer separation.

(2) Manifold injection of alcohols: Alcohols can directly be fed in the manifold to mix it properly with charge. Precise fuel injection control is one of the advantages of this technique which results in fuel economy. Dual fuel strategy of alcohol injection is also one of the techniques to use alcohols effectively in engines.

(3) Direct injection of alcohols: DI of alcohols in the combustion chamber is also a potential method in which alcohols can mixed with base fuel in the combustion chamber itself for combustion. Alcohols can be used in DISI (lower compression ratio (CR) equivalent to gasoline engine but with provision of spark plug) and DICI (conventional compression engine with sufficient CR to auto-ignite diesel).

4.2.1 Diesel-Alcohol/ Gasoline-Alcohol Blends

Blending form is one of the easier techniques of using alcohols in ICEs. Ethanol and methanol are blended easily with diesel and blend can be created just before the operation, however direct blending quantity is limited to 15% (Liu et al. 2016). Further adding will lead to phase separation in longer run and also having startability issue due to higher auto ignition temperature and its hygroscopic nature (Torres-Jimenez et al. 2011). Blending of fuel may affect fuel properties, so it is essential to measure fuel properties after blending with different proportions. Various research works have been carried out to determine the impact of physical chemical properties alternation due to fuel blending. Torres-Jimenez et al. (2011) studied the influence of ethanol blending with mineral diesel for 5%, 10% and 15% on volumetric basis, they reported that ethanol diesel blended fuels have a tendency of separation at lower temperature condition and suggested the doping of additives to prepare the stable blend. They also reported that water content in the fuel blend kept on increasing with the increase in the alcohol fraction in the blend, leads to deteriorate the fuel quality (Torres-Jimenez et al. 2011). Alcohols possesses higher H/C ratio and inferior cold start cold start capability in comparison to gasoline. Literature based fuel properties shows that the calorific values of alcohols (methanol, ethanol and butanol) are lower compared to the fossil fuels. Thus, blending of alcohols to diesel and gasoline increases break specific fuel consumption (BSFC). Ethanol–diesel blend (upto 20%; v/v) leads to reduced mixing stability, decreased oxidation ability and enhanced cold weather properties (Sahu et al. 2021).

Effect of variation in blending content of alcohol on adiabatic temperature (Tad) and density compensated thermal diffusivity (λ/Cp) at chamber temperature, chamber pressure and equivalence ratio of 363 K, 0.1 MPa and 1.2 respectively have been shown at Fig. 4.1 (Li et al. 2016). A higher order alcohol (such as butanol, which

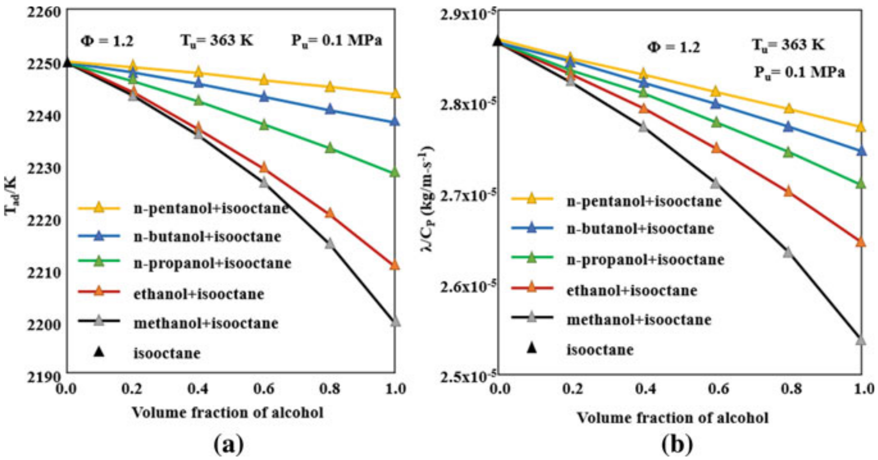
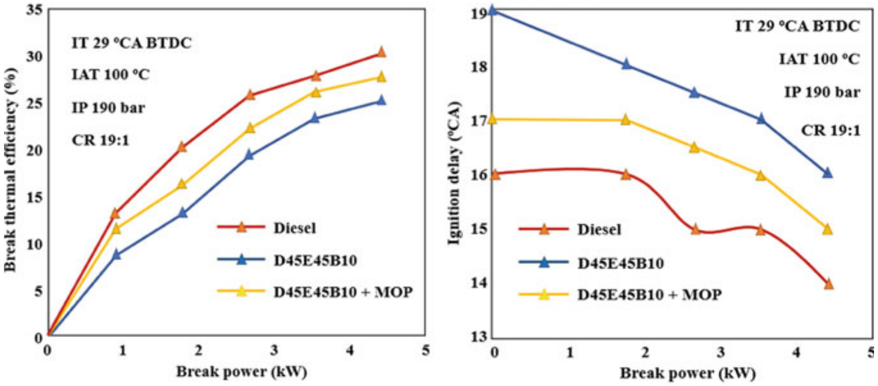


Fig. 4.1 Effect of variation in blending content of alcohol on **a** temperature (adiabatic, T_{ad}) and **b** thermal diffusivity (density compensated, λ/Cp s^{-1}) at chamber temperature, chamber pressure and equivalence ratio of of 363 K, 0.1 MPa and 1.2 respectively (reproduced and adapted from Li et al. (2016))

contains four carbons) have higher calorific value and lower auto ignition temperature and have the potential to enhance biofuel blending in the gasoline beyond the present limits of ethanol and methanol. Precise control over the volumetric yield percentages of acetone, butanol, and ethanol can now be achieved, because of the advancement on better fermentation techniques of acetone-butanol-ethanol (ABE) (Wu et al. 2015). Wu et al. (2015) investigated and analyzed the combustion characteristics of ABE blended diesel with different volumetric ratios (A:B:E; 6:3:1, 3:6:1, and 0:10:0) in a constant volume chamber in order to establish the optimum volumetric ratio for ABE blended diesel. They discovered that increasing the quantity of one component (acetone) significantly advances the combustion phasing, while butanol compensates for the advancing impact (Wu et al. 2015).

McCormick et al. (2017) identified potential biofuels for developing potential biomass-derived blend stocks. 2-butanol, iso-butanol (iB), di- isobutylene and ethanol have the most useful characteristics to blend with conventional gasoline or reformulated E10 gasoline for becoming an advanced fuel with higher octane for SI engine. Prabakaran et al. (2018) demonstrated that a combination of biodiesel based on cauliflower leaves, diesel, and butanol obtained from vegetable waste (40%, 20%, 40%; v/v) achieved comparable performance to diesel (>40% load). On varying the operating conditions, the optimum conditions obtained for running diesel engine with above mentioned blend was 210 bar (injection pressure), of 26 °CA bTDC (start of injection (SOI)), and CR of 19:1 (Fig. 4.2) (Prabakaran et al. 2018). When the two alcohol blends (E10 and M20; 10% ethanol, 20% methanol; v/v in gasoline) were compared on a single cylinder, gasoline direct injection (GDI), E10 produced less soot at high piston temperatures (140 °C), but M20 produced less soot at intermediate piston temperatures (Vedula et al. 2018).



(a) (b)

Fig. 4.2 Break thermal efficiency (**a**) and Ignition delay (**b**) of butanol ethanol blend in diesel (reproduced and adapted from Prabakaran et al. (2018))

Lower emission intensity (spotted OH radicals) caused an increase in the oxidation phase and decreased soot emission as a consequence of the increased nB upto 40% (v/v) in a two-stroke, single cylinder CI engine (Valentino et al. 2015). Further due to the increased resistance to auto ignition of higher volume fraction butanol-diesel blends, an evolution from mixing limited diffusion combustion to PPC was observed in a single injection by Valentino et al. (2015).

4.2.2 Manifold Injection of Alcohols

Figure 4.3 shows the typical alcohol fumigation setup where alcohol was induced to the air intake path with the help of electronically controlled unit (ECU). Fuel is fumigated and infused with air before introducing into the combustion chamber for homogeneous charge compression ignition (HCCI) (Maurya and Agarwal 2015). Combustion begins immediately all across the cylinder in this idea via auto-ignition once the charge is compressed to sufficiently high pressures and temperatures. HCCI causes a low temperature combustion, which is advantageous for break thermal efficiency (BTE), low soot and oxides of nitrogen (NO_x) emissions, although produces higher HC and CO emissions (Maurya and Agarwal 2011). Due to the difficulties associated with low load operations and combustion stability, HCCI has been relegated as a conceptual method and awaited commercial success. However, the available options of changing parameters like CR and intake air temperature, virtually most of the liquid alternative fuels can be utilized in HCCI engines, which is why they are gaining momentum as the next generation of ICEs (Fig. 4.3).

Figure 4.4 shows the feasible range of equivalence ratio and EGR for ethanol HCCI operation to which knocking, misfire and partial burn can be avoided (Bissoli

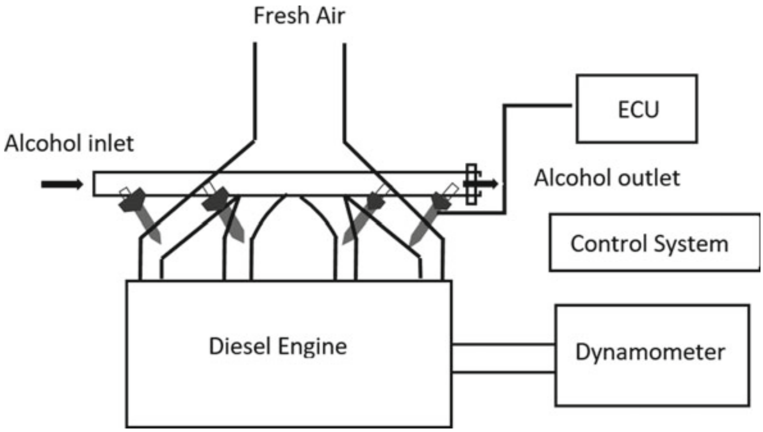
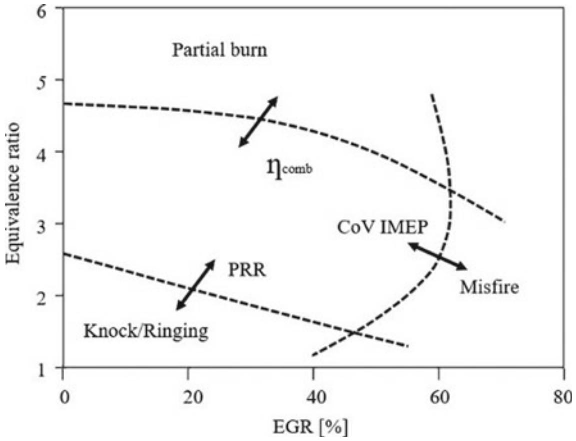


Fig. 4.3 Block diagram showing the manifold injection of alcohol in a diesel engines

Fig. 4.4 An illustrative map equivalence ratio to EGR for operating range of a HCCI engine (reproduced and adapted from Bissoli et al. (2018))



et al. 2018). Randolph et al. (2017) reported that the stability-limited dedicated cylinder equivalence ratio rose by 1.2 points to above 2.67 by applying methanol in a turbocharged port fuel injection engine with internal EGR. Maurya and Agarwal (2014) documented the working range of gasoline and alcohols in terms of indicated mean effective pressure (IMEP) and speed of a modified HCCI engine with port fuel injection (PFI) as shown in Fig. 4.5.

Dual fuel engines utilize two fuels simultaneously, typically one of the fuel with PFI, and another with DI. Further, the DI fuel (with lower auto ignition temperature) injected in combustion chamber and auto-ignited under high temperature and pressure environment, which ultimately combust the port injected fuel. Downsizing is a way of reducing CO_2 emissions in gasoline engines, however it does increase the likelihood of knocking. Pilla et al. (2016) used dual fuel solutions (PFI, lateral DI and

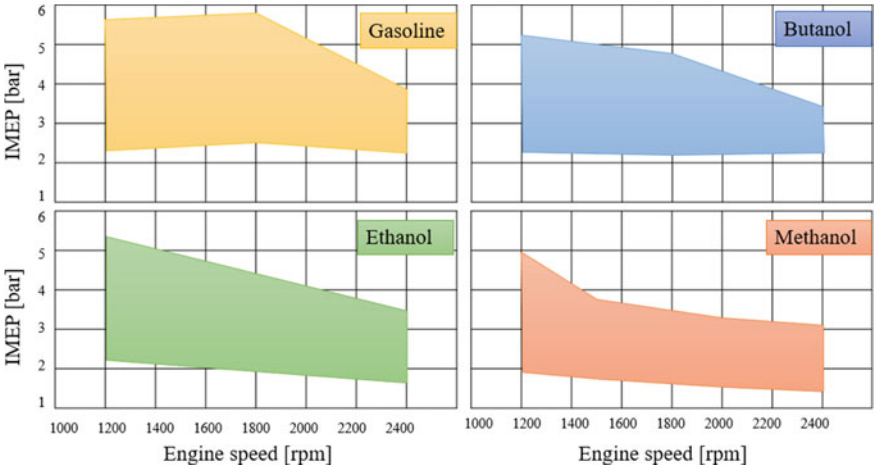


Fig. 4.5 Working range of gasoline and alcohols for HCCI engine operation (reproduced and adapted from Maurya and Agarwal (2014))

central DI) in a single cylinder, SI engine to reduce knock with naphtha fuel (research octane number (RON) 71) and ethanol (RON 107). In another study, Heuser et al. (2016) explored dual-fuel operation under various operating conditions in a light duty diesel engine using ethanol with PFI and DI of diesel. They observed that low-load combustion stability and emissions of unburned hydrocarbons are substantially dependent on the proportion of ethanol injected through the intake duct (Heuser et al. 2016). Dempsey et al. (2013) injected pure methanol with port and injected methanol blended with 2-ethylhexyl nitrate and di-tertbutyl peroxide directly to the combustion chamber. They obtained that injector settings for DI had little effect on combustion phasing since methanol DI caused significant charge cooling (Dempsey et al. 2013).

Reactivity controlled compression ignition (RCCI) combustion concept is another emerging technique (Reitz and Duraisamy 2015). Limited reactivity (low cetane) fuel is inserted through PFI, while greater reactivity (high cetane) fuel is pumped into the cylinder in the RCCI technique (Reitz and Duraisamy 2015). Both fuels are injected in varying proportions for various operating circumstances. Extremely high efficiencies have already been recorded, together with emissions (ultra-low NO_x and particulate emissions) comparable to those of HCCI. RCCI engines are a functional low-temperature combustion (LTC) technology that was further demonstrated by Agarwal et al. (2021) at a fixed speed (1500 rpm) and load (3 bar BMEP). They used primarily used alcohols (methanol, ethanol, butanol) in various premixed ratios (rp = 0.25, 0.50, and 0.75) with mineral diesel. They discovered that the presence of alcohols results in a more consistent combustion process (Agarwal et al. 2021). Benajes et al. (2020) used numerical simulations to estimate the exhaust emissions of the combination of RCCI and plug-in hybrid electric vehicles (PHEV). Their dual-fuel engine ran on diesel, which has a high reactivity, and bioethanol, which

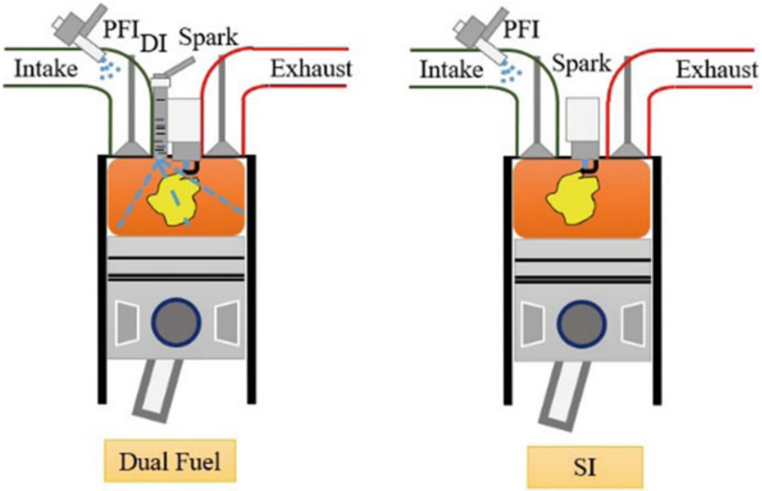


Fig. 4.6 Manifold injection techniques (reproduced and adapted from Tunér (2015))

has a low reactivity. According to their modelling, the combination of RCCI and PHEV engine met the aim of CO_2 as 50 g/km emissions and a moderate size of battery (13 kWh) and NO_x and soot emissions as per European norms (Benajes et al. 2020). Biofuels based on seaweed (ethanol and butanol) do not claim land or compete in the food chain supply for humans. Seykens et al. (2020) achieved gross Indicated thermal efficiency (ITE) of 52% and 51.6% in a single cylinder heavy duty RCCI engine using seaweed-based bio-ethanol and bio-butanol, respectively. Because of the greater fuel reactivity and boiling temperature than the bio-ethanol, increased losses of bio-butanol have been recorded in multi cylinder operations. Han and Somers (2020) experimented three butanol isomers (nB, iB and tert-butanol) with n-heptane (nH) on a diesel engine for heavy-duty applications with RCCI operation. They discovered that tB-nH had the highest ITE (>52%) among tested fuels and negligible soot mass emissions over the entire course of the tests (Han and Somers 2020). Pictorial view of manifold injection combustion methods for alcohols in ICEs have shown in Fig. 4.6.

4.2.3 Direct Injection of Alcohols

The fact that alcohols burns cleanly, without producing soot heavily, enables you to expand the conditional spectrum of the vehicle. The ignition occurrence is, however, dependent on elevated intake temperatures owing to the high latent heat of vaporization of alcohols (Pucilowski et al. 2019). In SI engines, DI of alcohols tends to decrease compression work and in-cylinder temperature. Additionally, it helps to minimise the drawbacks of completely premixing, such as preignition and higher

HC and CO emissions, while also increasing efficiency. These effects enable the SI engine to operate at a greater CR, resulting in improved engine efficiency. However, In certain instances, DISI engines may emit high concentrations of soot. Seko et al. (1986) reported that mixing the charge downstream of spark plug along the swirl flame propagation and setting of spark plug nearer to combustion chamber wall both raise engine performance and help to improve exhaust emissions for methanol fuel in a diesel engine with spark. Behringer et al. (2014) compared spark formation and droplet size from a spark eroded and laser drilled injector with fuels (gasoline (RON95), ethanol and 1-butanol) in a DISI engine. Increased fuel flow rates, better fuel dispersion and secondary injection effects, laser drilled injectors became easy replacements for spark eroded injectors and beneficial to alcohols utilization in the DI engines (Behringer et al. 2014).

When using alcohol blends in a GDI engine, Dageförde et al. (2013) observed that strong fuel accumulation and improved particle oxidation circumstances were found, but that turbulence formation during the short injection pulse (SIP) was similar. This results in a less severe rise in particle number emissions for larger SIP intervals with multi-hole injectors (Dageförde et al. 2013). The DICI operates by drawing only air via the intake manifold in combustion chamber. After compressing air, fuels are injected straight into the cylinder just before reaching TDC and combusted by the elevated temperature of the compressed air. DICI has many advantages over SI, in terms of reduced air pumping loss, absence of pre-ignition or knock, higher combustion efficiency, limited unburned HC and CO emissions. Comparatively DICI also has some disadvantages i.e., complicated high-pressure fuel injection system, high level of NO_x and soot generated during CI combustion. To achieve minimal NO_x and PM emissions from ordinary diesel engines, McCandless and Li (1997) devised and developed a unique, electromechanical common rail direct injection system for liquid dimethyl ether. On the other hand, the basic characteristics of this new tech drives the demand for primary alcohols DI in CI engines. For alcohol based dual fuel operation, Saxena and Maurya (2020) installed a solenoid-based PFI with a controller on the CI engine for uniform energy intake at varying rp for varying engine load and speed. In CIs, the stratification of ratio of actual and stoichiometric air fuel ratio has to be modified to bring down the level unburned HC and CO emissions to an acceptable position (Aziz et al. 2020). Operating the dual-fuel (methanol-biodiesel) DI engine led to ITE of 53.5% and Emission of NO_x that almost meet the Euro VI criteria (Huang et al. 2020). Injecting methanol towards the onset of the intake stroke helps fuel–air mixing and slightly increasing the methanol flowrate minimises CO emissions, while elevating ITE (Huang et al. 2020). Simulations performed by Giramondi et al. (2021) indicated that ethanol is greatly influenced by the initial temperature inside the cylinder on a dual fuel DICI engine. The swirl number has only a little influence on ethanol's combustion behavior. Using DI instead of PFI, the EGR dilution tolerance was enhanced by 2–3% and the lean burn tolerance (higher equivalence ratio) was enhanced by 0.1 lambda (Kolodziej et al. 2017). In order to enhance the mixture of oxygenate (mostly alcohols) and fuel, PPC employs a gap between fuel injection and the fuel combustion, also known as the ignition dwell. EGR, a lower intake temperature, or the use of a high RON fuel can all be employed to stretch the

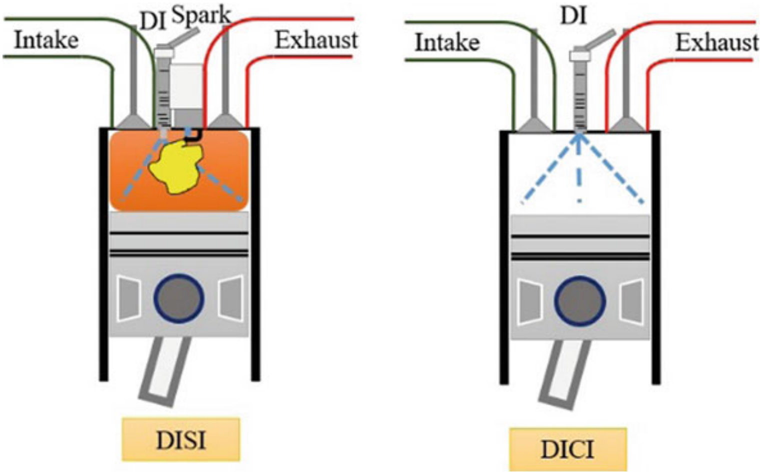


Fig. 4.7 DISI and DICI combustion techniques (reproduced and adapted from Tunér (2015))

ignition dwell even more. These ways were applied to avoid completely premixed or completely heterogeneous situations inside the combustion chamber. PPC resulted in negligible soot, NO_x, HC, and CO emissions while meeting the expectations of efficiency. PPC is very fuel flexible by adapting the injection parameters according to the self-ignition attributes of fuel, PPC can be made feasible for many liquid alternative fuels. Pictorial view of DISI and DICI combustion methods for alcohols in ICEs have shown in Fig. 4.7.

Shamun et al. (2016) employed ethanol, methanol, and naphtha gasoline in a engine with heavy duty applications operating in PPC mode. In PPC mode, gasoline achieved the highest concentration of soot mass, followed by methanol and ethanol. Methanol emitted a higher particle number than ethanol owing to the fuel's corrosive nature. Both examined alcohols emitted particles in the nucleation mode only, whilst gasoline also emitted particles in the accumulation mode (Shamun et al. 2016). The combustion phasing in PPC mode for SOI 160 °ca bTDC and SOI 40°ca bTDC at the higher loads revealed to be highly sensitive to intake temperature and pressure (Svensson et al. 2019). In a SI methanol-gas engine, neat methanol maybe utilized, provided that the engine has been customized in accordance with the fuel characteristics or additive mixed methanol may be used as a fuel for a DICI engine that has been slightly adjusted (Heinrich et al. 1986). These two methodologies were assessed to be acceptable for specific heavy-duty engine applications based on vehicle convertibility, safety, durability, fuel processing and transportation, renewability and environmental considerations (Heinrich et al. 1986).

4.3 Summary

In order to pursue a sustainable transportation energy for future, renewable oxygenated drop in fuels like alcohols (mostly methanol, ethanol and butanol) can be blended with today's petroleum fuels. A considerably improved performance and emissions characteristics were found in RCCI combustion compared to CI combustion. Due to their promising higher BTE and lower NO_x and PM emissions, HCCI engines are gaining traction as the future modes of ICEs. For SI engines, medium–high load efficiencies are decreased because of knocking. The varying octane available on demand dual fuel technique with alcohols as an octane promoter allows for the preservation of the engine's optimum efficiency. An integration of thermal insulation, minimal turbocharger after cooling, and EGR may allow a high-temperature combustion in the diesel engine, to combust low-cetane "soot less" alcohols such as ethanol and methanol in a mixing-limited diffusive combustion. PPC conceptual engines has been able to achieve both the efficiency and emission goals. Even though alcohols have been extensively studied for usage in automotive applications to until now, the diverse propulsion systems and operating situations of non-automotive applications highlight the need for further study in this area. Apart from utilizing advanced engine technologies such as EGR, diesel particulate filter, and others to maximize the efficiency and emissions of alcohol, key engine parameters such as pressure and timing of injection, CR, intake air pressure and temperature must be optimized for engine specifics. The comparatively smaller variations in engine operation, operating costs and environmental performance reflect that in the end, manufacturing and distribution of various alternative fuels are more relevant and vary country to country, region to region as per the availability. The fuel of the future will be a fuel that meets the fuel property requirements and has promising manufacturing processes, renewability, scalability, longevity, and affordability.

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Chapter 5
Methanol Fuel in Compression Ignition Engines

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Abstract Degradation of air quality, rising overall temperature of the earth, dependency on fossil fuels, and energy security are among the primary reasons driving the alternative fuel initiatives worldwide. Methanol is considered by many researchers as one of the relatively cleaner, carbon neutrally producible alternatives to traditional internal combustion (IC) engine fuels. Methanol being liquid at standard conditions can allow the pre-existing infrastructure for storage and transportation of traditional fuel to be used with minimal modifications. However, there are challenges with methanol when used as IC engine fuel compared to conventional fuels such as diesel or gasoline. This chapter begins with a summary of methanol utilization in the market and IC engines, followed by methanol characteristics, and then the comparison of methanol with traditional fuels is presented. The challenges in the design of fuel injection systems for methanol are discussed in detail. Methanol and diesel have a substantial difference in their properties, therefore, modifications in fuel injection systems are required in the diesel engines to use methanol fuel. A summary of injection strategies for methanol in CI engines, including recent studies and their engine performance along with engine modifications is presented. The challenges in the design of fuel injection systems for methanol are discussed in detail. An overview of methanol injection strategies in compression ignition engines, including recent research and its engine performance and engine improvements. Low temperature combustion has been known to reduce soot and nitrogen oxide emissions. The studies related to performance of methanol or methanol-diesel in LTC mode are also reviewed. Finally, an overall perspective is provided, emphasizing the performance of methanol in IC engines. The study concluded that methanol has better LTC characteristics. It is very promising in limiting engine soot and nitrogen oxide to an ultra-low level.

Keywords Methanol · CI engine · Dual fuel · RCCI · DDFS

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Abbreviations

AFR	Air Fuel Ratio
BDMx	X fraction of Methanol in BD blend
BSFC	Brake Specific Fuel Consumption
BSNO	Brake specific Nitrogen Oxide
CA50	Crank Angle for 50% Fuel Mass Burned
CNG	Compressed Natural Gas
CO_2	Carbon Dioxide
CRDI	Common Rail Direct Injection
D/M	Injection of Diesel before Methanol
DDFS	Direct Dual Fuel Stratification
DI	Direct Injection
DOC	Diesel Oxidation Catalyst
EGR	Exhaust Gas Recirculation
EURO6	European Emission Standard
FuelMEP	Fuel Mean Effective Pressure
HCCI	Homogeneous Charge Compression Ignition
IC	Internal Combustion
IEA	International Energy Agency
ITE	Indicated Thermal Efficiency
M/D	Injection of Methanol before Diesel
NOx	Nitrogen Oxide
PM	Particulate Matter
PPC	Partially Premixed Combustion
RoHR	Rate of Heat Release
SOC	Start of Combustion
STRTGx	Strategy Number x.
TPC	Total Particle Concentration
BD	Biodiesel (B) and Diesel blend
BSCM	Brake Specific carbon monoxide
BS-IV	British Standards- IV
CA	Crank angle
CI	Compression Ignition
CO	Carbon Monoxide
COV_{IMEP}	Coefficient of Variation of IMEP
CVI	Close vale injection
D-C	Direct injection of Diesel
DDI	Dual Direct Injection
DMDF	Diesel Methanol Dual Fuel
ECU	Engine Control Unit
EOI	End of Injection
EVs	Electric Vehicles
HC	Hydrocarbon

HRR	Heat Release Rate
ICCI	Intelligent Charge Compression Ignition
IMEP	Indicated Mean Effective Pressure
LTC	Low Temperature Combustion
MX	Methanol with X volume fraction
PFI	Port Fuel Injection
PODE	Poly-Oxymethylene Dimethyl Ethers
RCCI	Reactivity Controlled Compression Ignition
SI	Spark Ignition
SOx	Sulphur Oxide
TDC	Top Dead Center
ULSD	Ultra-Low Sulphur Diesel

5.1 Introduction

Since the 1970s, pollution caused by exhaust from vehicles has been a prime concern at both local and global levels (Miller 2021). From being a reason for health issues on an individual level to gradually leading to significant phenomena like global warming, one of the major reasons for the degradation of the environment, engine exhaust needs to be eliminated or reduced to acceptable levels. Currently, fossil fuels provide more than 80% of global energy demand, with the utilization in the transportation sector accounting for more than 95% of this energy (Energy Statistics 2020). The two prominent types of engines are gasoline and diesel based. It is accounted that around 77.6 million motor vehicles were produced globally in the year 2020 (2020 Statistics 2020). Over the previous two decades, worldwide transportation energy consumption has gradually climbed at a pace of 2–2.5% a year. The International Energy Agency (IEA) anticipated a significant increase in global transport energy consumption of roughly 50% by 2030, which might be doubled by 2050 (Weidmann and Menrad 1984). It has resulted in two major problems: rapid depletion of fossil fuels and pollution from its use in the IC engines.

Emission standards are the emission regulatory frameworks that have been evolved over the years to regulate the emission levels from different sectors, including the transportation sector. The rising number of IC engine vehicles and their implications on air pollution and related issues have resulted in stringent emission criteria. For example, the NOx emission limit in BS-VI is reduced by ~70% from BS-IV; in some cases, the reduction is about ~88%. Similarly, the limits in light vehicles have been reduced even up to ~90% (IICT Policy Update 2016). Such rigid regulations have resulted in huge pressure on automobile manufacturers and has resulted in a shift towards electric vehicles (EVs).

Major contaminants from gasoline engines are carbon monoxide (CO), hydrocarbons (HCs), aromatic hydrocarbons, and carbon dioxide (CO_2). On the other hand, diesel engines release harmful species like particulate matter (PM), sulphur (SOx) and nitrogen oxides (NOx) etc. NOx leads to smog formation, also toxic in nature and causes lung disease. Hydrocarbon emissions can cause cancer and contribute to formation of ground-level ozone. Particulate Matter (PM) can penetrate deeper into the lungs and cause vascular diseases (Balakrishnan et al. 2019; Little Flower 2006).

Traditional combustion in diesel engines has NOx-soot trade off problems. Advanced combustion techniques such as low temperature combustion (LTC) has been mainly developed to reduce the NOx and soot emission simultaneously (Kimura et al. 1999; Assanis et al. 2003). Diesel engines operating on LTCs have shown lower NOx and soot emissions (Kimura et al. 2001; Lewander et al. 2009; Okude et al. 2004; Saxena and Maurya 2017). Still, the need to control the emissions is exponentially increasing, adhering to drastic environmental changes experienced such as global warming and ozone depletion.

The growing utilization of fossil fuels presents serious concerns about human health and the environment. Also, the rapidly rising usage of fossil fuels leads to a significant increase in oil prices. A substantial amount of the budget of the non-oil producing countries goes in purchasing crude oil, and for some countries, it may be a concern for energy security. These global needs also drive the community of researchers to look for alternative fuels, specifically for transportation worldwide.

Use of alternative fuels can give an upper hand in terms of fuel efficiency, emission control, NOx—soot trade off, and reduction in the fossil fuel consumption rate. For instance, using sulphur-free fuels (Mohankumar and Senthilkumar 2017) such as natural gas would also significantly reduce particulate matter and sulphur oxides. Other fuel alternatives (Bro and Pedersen 1977) like biofuels, CNGs, hydrogen, and synthetic combustibles, including methanol (Chikahisa et al. 1981), ethanol, and butanol, can potentially control harmful emissions and their adverse effects. The growth in usage of hydrocarbon fuels like petrol and diesel has been one of the major contributors to the emission of greenhouse gases such as CO_2 (Tuner 2016). Compared to diesel and gasoline, methanol has a lower CO_2/MJ ratio (Tsang et al. 2010), resulting in lower CO_2 emission for given power output of the engine. Further, it can be prepared in a carbon neutral manner, and has potential to pave the path for carbon neutral IC engine technology.

Many studies have concluded that the performance of a diesel engine can be improved significantly using an innovative fuel injection system with addition of alternative fuels such as methanol (Cheng et al. 2008; Li et al. 2020b; Popa et al. 2001; Zhang and Wu 2016). Techniques like methanol fumigation (Geng et al. 2014; Liu et al. 2015; Saxena and Maurya 2017; Xie et al. 2006), blending (Guo et al. 2011; Huang et al. 2004; Qi et al. 2010; United States Environmental Protection Agency 2018; Zhang and Wu 2016) have shown considerable improvement in NOx and soot emissions of a diesel engine. Further, challenges of higher HC and CO emissions have been reduced using catalytic converters (Svensson et al. 2016; Zhang and Wu 2016). Over the years, several combustion techniques have been evolved including low temperature combustion (Colban et al. 2007; Jia and Denbratt 2018; Li et al. 2013; Valera and Agarwal 2019) capable of improving performance and emission characteristics of the IC engine. These combined with alternative fuels has shown immense potential to reduce NOx and soot emissions to ultra-low levels and improve the overall engine efficiency (Li et al. 2013; Maurya and Agarwal 2009, 2014; Wissink and Reitz 2015). Advances in injection technology (Minato et al. 2005), after exhaust treatment such as EGR (Adelman et al. 1972; Huestis et al. 2007; Li et al. 2006) have further aided in combustion control and have shown potential to improve overall performance of diesel engines.

Therefore, with an attempt to design fuel injection strategies for methanol fuel injection in existing SI and CI engines, this chapter delineates the required changes in traditional SI and CI engine combustion systems. Furthermore, a comprehensive review is presented for recent developments of methanol fuel applications in CI engines as these are the main contributors to mentioned issues due to their widespread use in heavy-duty vehicular applications. Finally, the problems and challenges which demand further research are illustrated.

5.2 Properties of Methanol

CH_3OH is one of the promising and reliable alternatives as a fuel for the transportation sector. It has many excellent fuel properties, which makes it one of the promising alternatives for traditional fuels. Methanol is an oxygenated fuel containing about 50% by weight of oxygen and has a low stoichiometric air–fuel ratio. It has a high latent heat of vaporization, leading to lower overall engine temperature and NOx formation. Its high-octane rating results in high resistance to engine knocking therefore, higher compression ratios can be used leading to higher engine efficiency. The flammability limit of methanol is wider as compared to diesel and gasoline. Therefore, it can operate at leaner mixtures and provide a better fuel economy and lower NOx, CO, and HC emissions. Methanol is a simple molecule and does not have a long chain of hydrocarbons. So, it is easily available in pure form and has clean combustion characteristics, therefore lower CO and HC formation. Methanol has a high flame velocity and faster combustion, hence it has a shorter combustion duration. A comparison of methanol properties with diesel and gasoline is presented in Table 5.1. It is also one of the most traded chemicals globally for its utility in producing silicones, adhesives, paints, pharmaceuticals, and extensively used in the automotive and wood industry. However, it can be toxic when indigested, inhaled or absorbed through skin. It metabolises to formic acid and formaldehyde with indigestion which can accumulate and causes a toxic effect referred as methanol toxicity. A higher concentration of about 1.5–2 g/L can lead to death if left untreated. It may even cause permanent damage to vision. However, it can be cured if medical care is provided on time. It has a wide range of industrial and household uses (World Energy Outlook 2021). The popular methods for methanol production are shown in Table 5.2. Methanol can be prepared from a wide range of raw materials such as synthesis gas and biomass, including wood, agricultural by-products, and municipal waste, using well-established thermal chemical technology. Methanol production is also possible by the direct oxidative conversion of methane, natural gas, or any other source, avoiding the initial preparation of syngas. Most importantly, it can also be

Table 5.1 Properties of methanol as compared to diesel and gasoline (Awad et al. 2018; Tuner 2016; Umebayashi et al. 2002)

Property	Methanol	Diesel	Gasoline
Chemical formula	CH_3OH	$C_{8\text{-}25}$	$C_{5\text{-}10}$
Carbon content (wt.%)	37.48	~85	~86
Hydrogen content (wt.%)	12.5	15	14
Oxygen content (wt.%)	49.93	0	0
Molar mass (kg/kmol)	32.04	~183	~106
Density (kg/m^3)	792	840	737
Vapor pressure (bar at 20 °C)	0.13	<<1	0.25–0.45
Viscosity (mPa-s at 20 °C)	0.596	3.3	0.5–0.6
Auto-ignition temperature (°C)	423	250–450	257
Lower heating value (MJ/kg)	20.1	42.7	44.0
Volumetric Energy Content (MJ/m^3)	15,871	35,869	31,746
Heat of vaporisation (kJ/kg)	1089	250	180–350
Cetane number	<5	38–53	8–14
Octane number	108.7	15–25	82–92
Stoichiometric AFR (kg/kg)	6.5	14.6	14.7
Adiabatic flame temperature (K)	2143	~2327	~2275
Flammability limits (volume %)	6.7–36	0.5–7.5	1.3–7.6

Table 5.2 Production processes for methanol (Zhang et al. 2011a)

Sources	Process	Energy conversion efficiency
Coal	Coal → Syngas → synthesis of crude methanol → Refining	Typically, 43–48%
Natural gas	Natural gas → Syngas → synthesis of crude methanol → Refining	60–65%
Biomass/municipal solid waste	Biomass/Waste → Syngas → synthesis of crude methanol → Refining	42–52%
Catalytic Hydrogenation of CO_2	$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$	–

prepared by reductive hydrogenative recycling of CO_2 from natural or industrial sources, including fossil-fuel-burning power plants, cement plants, etc., and eventually from the atmosphere itself. Therefore, it can be a significant player in reducing carbon footprint.

5.3 Challenges to Methanol as an IC Engine Fuel

Methanol has many excellent properties as an IC engine fuel. Its production can also be scaled up to levels of gasoline and diesel. However, there are certain key challenges with methanol when used as a fuel in IC engines. It has almost half the lower calorific value compared to gasoline and diesel. For the same amount of fuel, the refuelling distance is much lower for methanol. The fuel tank size should be almost doubled to have a similar refuelling distance, which will result in an extra carrying load to the vehicle. Methanol is inherently a good SI engine fuel, but it is challenging to use it in CI engines because of its poor self-ignition characteristics. It is essential to use ignition/cetane improvers or separate ignition sources to facilitate the ignition of the fuel without the requirement of major engine modifications (Egebäck et al. 1997). The lubricity of methanol is lower as compared to diesel due to the lower viscosity. Therefore, the wearing of the engine component such as cylinder bore and the rings will be higher (Ryan et al. 1986). Also moving elements of fuel injector such as injector needle will be subjected to higher wear. The combustion of methanol may result in the formation of acidic compounds such as formic acid as a reaction product (Otto et al. 1985; Ryan et al. 1986). The products formed after rusting could act as abrasive, leading to the higher wear of the engine. Some of the specific issues are described as follows:

Material Compatibility: Methanol is a dipolar and protic solvent and poses challenges to many plastics and metals. Many polymers are susceptible to swelling and changes in their physical properties, while the metals can corrode in methanol. Many studies have focused on corrosion characteristics and its prevention for methanol (Marbach et al. 1981; Ryan et al. 1986). The corrosion inhibitors such as Octel-Starreon DCI-11, morpholine, piperazine, and hexamethylenediamine can be added to methanol in very minute quantities to reduce its corrosivity. In a methanol environment, stainless steel or nickel-plated components may function better (Jahnke and Schoenborn 1985; LoRusso and Cikanek 1988a). Al-10% Si alloy-coated steel does not suffer from corrosion in deaerated methanol containing 0.1–30% H_2O and no other contaminants (Tuner 2016). Fluoroethylene, propylene-perfluoroalkoxy, among other polymers, has strong chemical resistance and can be used for manufacturing of injector rubber and plastic components, which can assist in preventing methanol leaking in a diesel engine (Methanol Institute 2016).

Wearing and Lubrication Characteristics: Abnormal wearing may lead to premature failure of the system. Methanol, due to its lower viscosity and corrosive nature, may increase engine wear. Also, the products formed after rusting could act as an abrasive, leading to the higher wearing of the engine (Ernst et al. 1983; Ryan et al. 1986). In the injector, the motion of the injector needle is liable to wear. The main regions in the injector subjected to wear are needle lower and upper seats, nozzle-needle sliding area, and needle-stem contact surface (Miller and Savonen 1990). The design of the injector is very crucial, and abnormal wear in the injector may result in leakage, change in flow rate, or even lead to needle wobble. It is critical that the injector performs its intended function, i.e., supply fuel at the precisely controlled quantity and desired conditions. Any divergence from it may adversely affect the fuel atomization characteristics. The atomization process is at the heart of the combustion process; proper fuel distribution and better atomization are required to achieve higher efficiency of the combustion. Also, the emissions due to poor or abnormal combustion will largely depend upon the injector performance. Other challenges involve blowby of formic acid formed during combustion of methanol, wall washing involving removing lubricating film at the cylinder wall due to unburnt methanol.

Cold Starting, Aldehyde Emissions and Vapor Locking: It is challenging to prepare homogeneous methanol mixtures with traditional fuels like gasoline and diesel. When compared to gasoline, forming a homogenous mix of diesel with methanol is more difficult. To improve the stability and miscibility of methanol-diesel fuel blend, fuel additives like oleic-iso butanol, 1,2-epoxypropane and epoxyethane are added to the mixture (Hasimoglu et al. 2008). Also, methanol has a high latent heat of vaporization that helps lower overall engine temperature and NOx emission, however, it will lead to cold starting problem, especially in countries with colder climates (Gong et al. 2017; Liu et al. 2017). Two commonly used techniques to improve cold starting performance are the use of an ignition improver or a glow plug involving an electric fuel heating system (Havenith et al. 1987; LoRusso and Cikanek 1988b; Mueller and Musculus 2001).

In some cases, methanol evaporation in fuel lines may cause vapour locking, which can be prevented by employing a pressurized fuel supply system for methanol. Apart from the above, the formaldehyde emissions are quite high for methanol engines. Aldehyde emissions can cause inflammation in eyes and skin of humans and are carcinogenic in nature. Inhalation of aldehyde can cause nausea, headaches or respiratory irritations. Certain flora and fauna, particularly aquatic plants, are extremely susceptible to diseases from aldehyde exposure (Health 2002).

5.4 Methanol in IC Engines

Historically, methanol has been used as a knock suppressor in racing cars. Cars like Alfa Romeo and Bugatti used methanol blends in their Grand Prix cars (Valera and Agarwal 2019). It was also used during world wars due to gasoline shortages in Germany and France (Huestis et al. 2007). The initial usage of methanol in the transport sector was started due to the oil crisis, and by the mid-1970s, small vehicles based on methanol were tested (Ernst et al. 1983). Later, countries like China, Sweden also started their larger fleet trials. Currently, China is the top country at employing methanol (M15, M30, M85, and M100) in their road transport sector (Zhang et al. 2011b). In the aviation sector, methanol is used for its high-octane number and latent heat. However, researchers suggested that methanol with very low calorific value is unsuitable for aircraft as a main fuel (Price n.d.). Apart from lower calorific value, methanol is a polar molecule and therefore soluble in water. The water present in methanol can result in higher wear in the engine (Shukla et al. 1992).

As described earlier, there are certain difficulties with methanol. So, to utilize methanol in gasoline and diesel engines, certain changes in the engine's fuel system are required as described in Sect. 5.1. Despite the challenges, methanol, because of its excellent properties, has been employed in IC engines. It is either used in pure M100 form or in combination with other fuels. In dual fuel mode, operation can be realized using fumigation or blending of methanol with other fuels such as diesel or gasoline. Some advanced engine concepts allow the CI operation of methanol engines without the need for auxiliary ignition systems. These strategies employ Port Fuel Injection (PFI), Direct Injection (DI) and a combination of the PFI and DI systems. Some recent development also involves the use of Dual Direct Injection (DDI) systems in which both the fuels are directly injected into the combustion chamber. The injection methods, along with ignition methodology, have resulted in advanced engine concepts such as Homogeneous Charge Compression Ignition (HCCI), Reactivity Controlled Compression Ignition (RCCI) and Direct Dual Fuel Stratification (DDFS). These techniques have been extensively studied for gasoline and diesel and have also shown promising results for methanol (Colban et al. 2007; Jia and Denbratt 2018; Li et al. 2014; Maurya and Agarwal 2009, 2011; World Health Organization 2014).

In the port fuel injection system, methanol is injected at relatively low pressures into the inlet port during suction stroke in the upcoming stream of air. The resulting fuel mixture is then supplied to the combustion chamber, where it ignites through various means. The main key feature of the injection system is the requirement of low-pressure fuel lines and pumps. Historically, it has been used in conventional gasoline engines, however, nowadays it is being widely used in the dual fuelling of methanol engines.

In the direct injection system, the methanol is directly injected into the combustion chamber during the compression stroke. The auto ignition of the methanol is difficult and usually some ignition assistance is required in conventional CI engines (Havenith et al. 1987; Mueller and Musculus 2001). However, techniques like HCCI, RCCI rely on the formation of auto-ignitable air–fuel mixtures and usually do not rely on ignition systems (Shim et al. 2020). RCCI is a dual injection technique involving the PFI and DI injections of two fuels with different reactivity. Methanol in traditional SI engines requires fewer modifications to the engine than in CI engines. In an SI engine, mainly the number of injector nozzles and/or a larger diameter nozzle is anticipated. Moreover, the addition of an ignition improver to the fuel may be required. The amount of methanol in the mixture largely governs the modification requirement. Studies have shown that no fuel additives or modification in the fuel system is required for 2–3% methanol by volume in gasoline engines. However, as the methanol quantity increases by more than 5%, it is necessary to change materials in some parts of the fuelling system. When the mixture contains up to 15% methanol, the fuel injector nozzle should have a larger diameter (Kowalewicz 1993). Apart from the above changes, modification to the cylinder head and addition of fuel heating systems may be required in traditional CI engines.

5.5 Injection Strategies for Methanol in CI Engines

Fuel injection system and injection strategies have significant effects on combustion and emission characteristics of an engine. Fuel injection system can be considered as the heart of an IC engine. Its main role is to supply a metered quantity of fuel at desired state at any instant. Fuel injectors are one of the key components of a fuel supply system. Advancement in the manufacturing sector has allowed intricate injector design resulting in precisely drilled fine orifice injectors, capable of providing better control over fuel swirl, coupled with modern electronics results in lower Sauter mean diameter of the fuel droplets, improved air–fuel distribution, lower wall wetting. It can result in better combustion characteristics, improved engine performance and lower emission caused by non-homogeneity in air–fuel mixture (Colban et al. 2007). It can allow better application of multi-fuel approaches by exploiting their properties. For example, fumigation of methanol in SI or CI engines results in lower overall temperature and NOx emissions at similar efficiencies (Houser et al. 1980; Shukla et al. 1992; Yusaf et al. 2013). In this section, several methanol injection methodologies including recently developed, along with their performance and required changes to fuel injection systems are discussed.

5.6 Pure Methanol Fuelled CI Engines

In compression ignition engines, the air–fuel mixture is compressed to high pressure and temperatures until it auto ignites. The method has been widely used to employ diesel in IC engines and has fundamentally higher efficiency. Methanol requires assistance with its ignition in traditional CI engines, and spark and glow plugs have been widely tested for such purpose (Pischinger 1983). The surface ignition temperature of methanol is lower than diesel fuel and hence hot surface ignition may be an appropriate igniting method for methanol. Apart from the fuel injector, the engine cylinder head will need modification to accommodate an auxiliary ignition system such as a glow plug. Methanol-based modified diesel engines with glow plug have been tested and shown promising results (Baranescu et al. 1989; Havenith et al. 1987; Mueller and Musculus 2001; Suresh et al. 2010). The studies indicated significantly lower soot, NOx emissions and have quieter operation at similar efficiencies. This is possibly due to molecular oxygen in the methanol, allowing better combustion hence lower soot formation than diesel. Also, methanol shows a significant charge cooling effect, lowering the cylinder temperature and pressure. Hence lower NOx and smoother engine operations. However, the glow plug-assisted ignition strongly depends on glow plug temperature and proximity to a fuel jet. Major challenges with the technique are the erosion rates of glow plugs due to high ignition power, high unburned HC emission and complexity with the design of the head to accommodate the ignition system for mass production (LoRusso and Cikanek 1988b). Another method to incorporate methanol in diesel engines at higher volumes involves the pilot injection of diesel fuel. In this approach, fuel mixture ignites due to self-ignition of pilot fuel such as diesel rather than using external source. The procedure requires an additional fuel system for diesel pilot injection. It consists of injecting a smaller quantity of diesel into the combustion chamber to facilitate the fuel ignition process. A single-hole injector and small distributor type injection pump can be used in each cylinder for pilot injection. The cylinder head requires modification to incorporate two injectors for main and pilot fuel injections. The method can reduce hydrocarbon emissions and unburned methanol to the same order as conventional diesel operation. A study suggested that the optimum proportion of pilot fuel was about 4–10% of the total energy supplied (Chikahisa et al. 1981). Minor adjustments in the amount of pilot fuel or methanol can result in substantial variations in power output. Compared to diesel fuel, the emission of smoke is significantly reduced due to relatively complete combustion with methanol (Chikahisa et al. 1981; Li et al. 2020b). Further, Diesel Oxidation Catalyst (DOC) can help in reducing the NO_2 proportion substantially in NOx emissions (Geng et al. 2015).

Li et al. (2020b) numerically studied the effect of injection strategy on a diesel/methanol dual-fuel direct-injection engine. Methanol/Diesel (M/D), Diesel/Methanol (D/M) and Methanol/Diesel/Methanol (M/D/M) injection approaches were tested. The in-cylinder pressure curve for D/M approach showed that for a given diesel injection timing, with increase in dwell period, peak pressure shifted away from TDC, also as the in-cylinder pressure found to decrease with delayed injection and cooling effect was more profound. While for methanol before diesel (M/D) injection has shown a large possibility of knock and leads to higher emissions and lower combustion efficiency. They suggested that the methanol injection should not be too delayed, and dwell should not be very small to reduce knocking and misfire. At optimal conditions, D/M showed about 4 mg/kgf of soot while M/D and M/D/M showed only 1 mg/kgf of soot. NOx emission was at around 22 g/kgf with D/M and M/D/M while about 19 g/kgf with M/D. High CO emissions were observed with M/D and M/D/M approach of around 19 g/kgf while D/M showed very low CO emission of only 1 g/kgf. The D/M mode showed better combustion and fuel economy and prevented knocking. However, at both low and high loads, M/D/M mode was found to be the most effective injection approach.

5.7 Methanol Fumigation

It is one of the oldest techniques to employ methanol in IC engines. When fuel is introduced into the engine by injecting, vaporizing, or carburetting into the intake air, it is called fumigation (Houser et al. 1980). The fuel is supplied separately from a dedicated fuel tank and fuel lines to an injector, vaporizer or carburettor unit. The fumigation system requires minimum modification to the engine in terms of the fundamental design and includes the addition of a methanol injector in the air intake manifold, flow control, and managing systems. A schematic port fuel direct injection engine is shown in Fig. 5.1. The independent fuel supply allows better

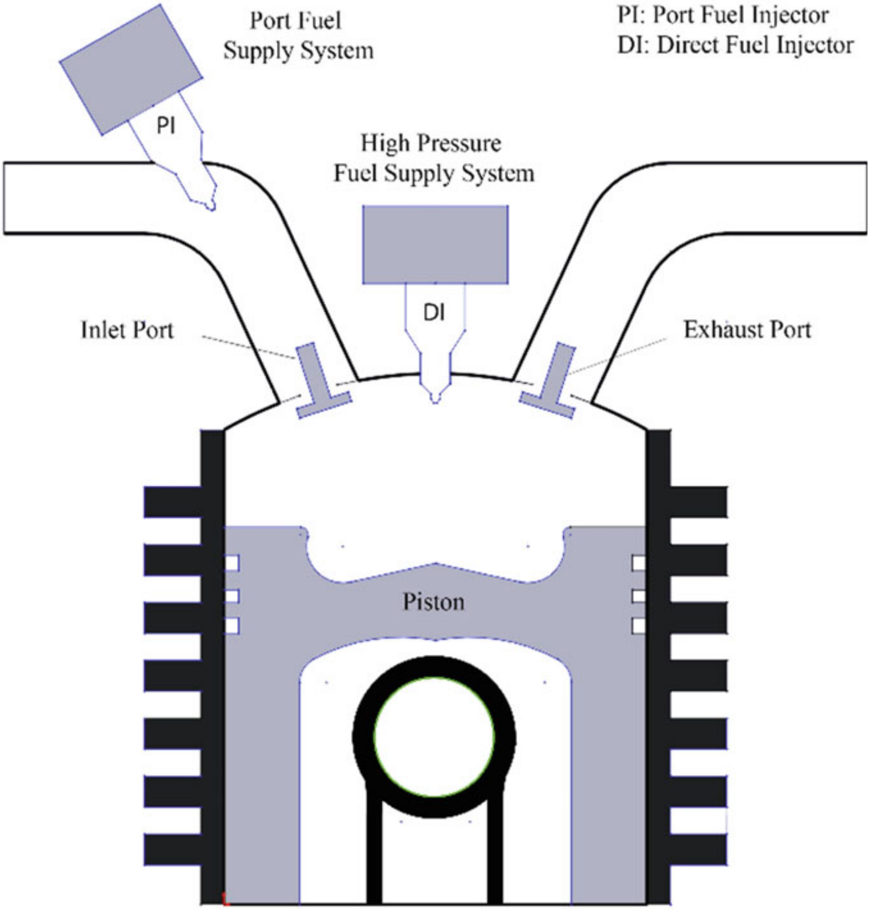


Fig. 5.1 Port and direct injection engine concept

control over the methanol supply. The system can also operate on pure diesel by disconnecting the methanol source. For similar smoke emission levels, the power output from a fumigated system is higher. Fumigation can replace diesel fuel with alcohol. Fumigation may displace up to 50% of the demand for diesel fuel (Ecklund et al. 1984). A particulate emission study for a methanol-fumigated diesel engine reported that particle mass and number concentrations dropped as the amount of fumigation methanol increased (Zhang and Wu 2016).

Popa et al. (2001) investigated the emission of NOx and smoke with two different injection systems: one that used premixed methanol injected through a carburettor with direct injection of diesel (D-C) and another that used a single injector to inject both methanol and diesel directly. For the same engine power, lower NOx and NO were observed with carburetted methanol dual fuel diesel engine operation. Also, at higher engine power, smoke from D-C injection was lower compared to dual direct injection. It was concluded that the D-C method is efficient while dual direct injection allows higher substitution rates while maintaining smooth engine operation. Cheng et al. (2008) investigated the effect of engine load on methanol fumigation with biodiesel fuel. 10% methanol fumigation at constant properties showed that NOx, particulate matter and CO_2 emission were reduced compared to ultra-low sulphur diesel fuel. However, it was found that with methanol fumigation, CO, HC were higher significantly while BSNOx were decreased by 8.2%. Houser et al. (1980) investigated the effects of alcohol fumigation on a four-stroke diesel engine. The study showed that with 40% methanol fumigation, the NOx emissions were reduced for all operating conditions. They concluded that methanol fumigation has a limited substitution rate. The result suggested that higher methanol levels are limited by lower thermal efficiency, while the lower limit is dependent on engine knocking. Verhelst et al. (2019) investigated the performance of a methanol-diesel dual fuel diesel engine. High premixed methanol ratio of 70% was used in a 6-cylinder turbocharged diesel engine. A higher ignition delay and shortened combustion duration were observed due to higher physical delay and faster laminar burning flame velocity associated with methanol. Emissions of HC, CO, formaldehyde and NO_2 were increased with higher premixing ratios. However, NOx and soot emissions were significantly reduced. Further, a Diesel Oxidation Catalyst (DOC) reduced the NO_2 proportion which was found to be lower than conventional diesel engines. It was suggested that maximum methanol premixing ratios depend upon load, in-cylinder pressure at high speeds. Also, the emission characteristics of the engine were poor at low engine load and speed. A high HC, CO and formaldehyde emissions were observed even with DOC.

Zhang et al. (2011a) studied the emission characteristics of methanol fumigation in a DI diesel engine. The study found that the PM mass and number concentration of a methanol fumigated engine depends upon the engine load and engine speed. NO_X and particulate matter emissions were reduced with an increasing fumigation ratio. However, HC and CO emissions were found to increase with the level of fumigation. At all engine loads, the premixed methanol injection method dramatically decreases NOx levels. Whereas, the smoke levels were low only at high engine loads. It was due to soot burnout at higher temperature at high engine loads.

Geng et al. (2014) studied the PM emission characteristics of a diesel-methanol dual-fuel engine. A heavy-duty diesel engine with turbocharging and intercooling was employed in the study. They reported that at low and medium engine loads, the diesel/methanol dual fuel (DMDF) approach efficiently reduces the quantity and mass concentrations of particles, however at high engine loads, particulate matter emissions rise. They also reported that diesel oxidation catalyst (DOC) in the pure diesel and DMDF modes could efficiently decrease particle mass and number concentrations. Liu et al. (2015) studied the performance of a port premixed methanol in a naturally aspirated diesel engine and a turbocharged engine. The experimental result showed that the premixed methanol significantly reduces fuel consumption, NOx and soot emissions. In addition, World Energy Outlook (2021) found a decrease in NOx and PM emissions, but an increase in HC and CO emissions for port-injected methanol. The addition of an oxidation catalyst to a dual fuel system can reduce NOx, soot, HC and CO emissions. Saxena and Maurya (2017) found out that total particle number concentration is higher at full engine load and increases with fuel premixing ratio, particularly in the case of methanol-diesel dual-fuel operation. Additionally, when the engine's compression ratio increases, the peak particle number and mass concentration decrease.

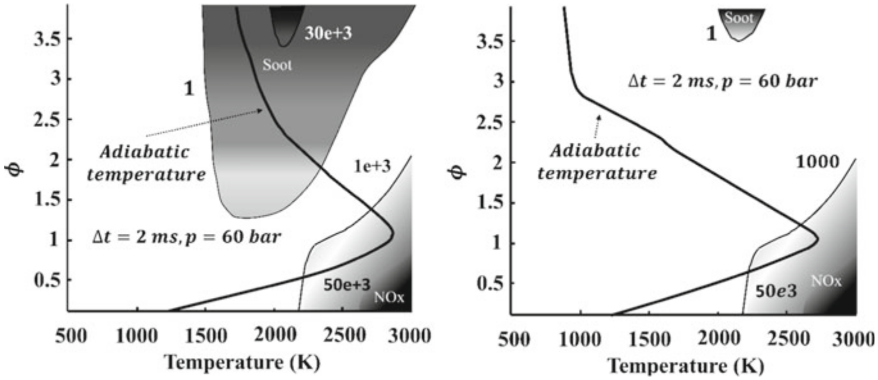
5.8 Blending with Diesel Fuel

In the fumigation system, the fuels have their separate fuel supply system. Fuel blending is another widely used approach involving dual fuel injection. It can be effectively used without the requirement of any major engine modifications (Chu 2008; Huang et al. 2004; Qi et al. 2010; Yao et al. 2008). In this method, a blend of two or more fuels is directly injected through a single injector into the combustion chamber. The fuel injection system requires adding a fuel mixing and control system to the pre-existing DI system. The addition of high oxygen content and high volatility components to diesel or biodiesel, such as methanol, can be a promising strategy in diesel engines. Diesel combined with up to 15% methanol by volume requires only minimal engine adjustments (Wei et al. 2015). Huang et al. (2004) examined the combustion behaviour of CI engines fuelled with the methanol-diesel blend. It was reported that increasing the methanol mass fraction in diesel/methanol blends increases the heat release rate in the premixed burning phase and reduces the diffusive burning phase combustion duration. A solvent consisting of oleic and iso-butanol was added into the diesel/methanol blends to develop the stabilized diesel/methanol blends (Qi et al. 2010). Guo et al. (2011) employed considerably high methanol ratios (20–30% by volume) by using 1,2-epoxypropane and epoxyethane to reduce the particulate emission in the methanol-diesel engine. At lower speed, the emission levels of CO, PM were considerably low and brake specific fuel consumption was higher compared to diesel fuel. However, it was noted that these emissions were increasing with engine speed. It was concluded that 20–30% methanol in diesel is economical and clean.

Qi et al. (2010) studied the performance of ternary blends (biodiesel-diesel-methanol) in the diesel engine. The ratios taken were such that biodiesel (B) and diesel (D) were mixed in equal proportion; BDM0 (50% BD each), BDM5 (~5% methanol, 95% BD) and BDM10 (~10% methanol, 90% BD). The methanol-to-diesel ratio has a considerable influence on the performance of diesel engines that operate on methanol-diesel blends. The peak in-cylinder pressure varied slightly and showed higher peak pressure with BD as it does not have low energy density fuel. The result showed lower smoke emission as methanol percentage was increased as it has clear burning characteristics. However, it resulted in a higher fuel consumption rate due to lower energy density of methanol as compared to diesel. Also, alcohol-diesel fuel blends generated more aldehyde emissions as compared to conventional diesel engines. HC and CO emissions were increased, and NOx emissions were decreased. Yao et al. (2008) investigated the effect of methanol ratio in diesel blend on the performance of CI engine. In the investigation, methanol ratios of 10, 20, and 30% by volume were utilized, with pure diesel serving as a reference for performance evaluation. It was reported that the mixed fuel usually resulted in better performance than the conventional single fuel approach. Ciniviz et al. (2011) investigated the effects of methanol and diesel fuel blends on performance and exhaust emissions, finding that as the amount of methanol in the fuel mixture increases, brake specific fuel consumption and nitrogen oxide emissions increase, while brake thermal efficiency, carbon monoxide, and hydrocarbons decreases, compared to single diesel fuel operation. However, some investigation on methanol-diesel blends employing M5, and M15 blending ratios concluded that methanol-diesel blend fuelled engines develop higher torque and output power with both the ratios (Jikar et al. 2011; Najafi and Yusaf 2009). It can be said that methanol-to-diesel blending is an excellent way to incorporate methanol without significant modification in the engine while reducing diesel consumption. In addition, when compared to diesel operation, the engine performance for blended fuel is higher. However, the methodology has a restriction of the miscibility limit of methanol in diesel. NOx emissions are usually reduced with methanol blending due to the cooling effect. Moreover, CO and HC emissions increase as compared to diesel engines. Certain advanced injection strategies are developed to improve the methanol substitution rates in diesel fuel engines and reduce NOx emissions from the engine. These techniques involve the combination of SI and CI approaches and have been found to be useful with methanol.

5.9 Advanced Injection Concepts for Methanol

In recent years, several revolutionary engine designs, including Homogeneous Charge Compression Ignition (HCCI), Partially Premixed Compression Ignition (PPCI), and Reactivity Controlled Compression Ignition (RCCI), have been employed with many fuels, including methanol. Recently the Direct Dual Fuel Stratification (DDFS) approach was also used and showed an expanded operating load limit compared to RCCI mode. All these techniques are grouped under low-temperature combustion techniques. The main motive behind the development of such methods is low to ultra-low emission profiles of NOx and soot compared to conventional approaches. Equivalence ratio (ϕ)-temperature (T) maps are widely used to study the effects of charge quality and in-cylinder temperature on emission characteristics of an engine. The ϕ-T curve map along with in-cylinder pressure and heat release rate curve allows identification of combustion processes inside the combustion chamber and aid in the assessment of NOx and soot emissions. Svensson et al. (2016) constructed maps to understand the effect of equivalence ratio and temperature on different emission species with methanol and diesel fuels. Figure 5.2 shows a ϕ-T map for NOx and soot emissions with diesel and methanol fuel. It also shows a calculated adiabatic flame temperature for an initial temperature of 1000 K and an initial pressure of 75 bar. It can be observed that the methanol combustion will show very low soot emissions and has a wide range of operation at a given emission level from the engine. It is one of the motivations for investigating the performance of methanol in diesel engines.



(a) ***Diesel fuel (mixture of n-heptane and toluene)***

(b) ***Methanol***

Fig. 5.2 ϕ-T map for **a** diesel and **b** methanol fuel (Shukla et al. 1992)

Homogeneous Charge Compression Ignition (HCCI) engines: HCCI mode combines the air–fuel mixture preparation feature of SI engine with compression ignition strategy of CI engine. A PFI system is preferred in the HCCI mode to prepare a premixed charge, which auto-ignites due to premixed charge compression. The engine operates at considerable low pressure and temperature and results in drastic NOx emission reduction.

Xie et al. (2006) studied the effect of EGR on the performance of HCCI mode with three high octane number fuels, namely methanol, ethanol and gasoline. A modified single-cylinder PFI engine with an injection pressure of 2.9 bar was used in the study. M100 fuel showed ignition advancing behaviour and the peak pressure was attained before reaching top dead centre. It will result in more compressive work and is unfavourable. Methanol was found to have better auto-ignition characteristics as compared to rest of the tested fuels. Air–fuel ratio and engine temperature affect the CO and HC emission characteristics of an HCCI engine. At a lower air–fuel ratio and high engine temperature, more elevated CO and HC emissions were observed. CO emissions with M100 fuel were found to be lowest from the rest of the fuels and were found to increase with leaner combustion. It may be due to lower average combustion chamber temperature as a result, more unburned fuel. The HC emissions were found to be increased as compared to the SI engine. NOx in the HCCI engine decreases with an increase in air–fuel ratio due to lower average cylinder temperature.

Maurya and Agarwal (2009) investigated the effect of mixture quality and intake air temperature on the performance of methanol and gasoline fuelled HCCI engines. A 2-cylinder 4-stroke engine with a PFI system was employed in the study. For intake air temperatures of around 100–150 °C, methanol showed a wider range of relative air–fuel ratios of roughly 3.5–6.5 compared to 2.6–4.4 for gasoline. The start of combustion (SOC) was observed to be sensitive to the temperature history of intake air. It was found to be more sensitive for gasoline than methanol for considered operating range. In comparison to gasoline, which had a maximum combustion efficiency of 91.7% and showed more fluctuations, methanol had a higher combustion efficiency ranging from 90 to 96.6% and showed less variation with quantity and temperature of intake air. Methanol had a much higher indicated thermal of 49%, compared to 37.95% for gasoline. It is related to more pressure variations observed in the in-cylinder pressure curve. It was concluded that intake air temperature and air–fuel ratio are key parameters in HCCI combustion. Methanol showed better HCCI characteristics than gasoline. The authors have also investigated the effect of injection timing on PM emission (Maurya and Agarwal 2011) of a methanol-based HCCI engine and have compared the performance of methanol with ethanol (Maurya and Agarwal 2014). In the PM emission study, a DI diesel engine was modified to include a PFI system for premixing of fuel with air and the effect of injection timing was studied. Effect of injection timing on HC emissions was dependent on the injection strategy. Closed fuel injection showed nearly constant HC emission with increasing injection timing, whereas open valve injection showed an increase in HC emission. Nevertheless, NOx emissions were limited to 22 ppm, which is far lower than those of a conventional diesel engine. Total particle concentration (TPC) was found to increase with richer mixtures. TPC with leaner mixtures were found comparable to gasoline. Open valve injection showed more TPC compared to close valve injection (CVI) as fuel mixture was more homogenous in CVI. It was concluded that the mixture homogeneity and injection timing affect the PM and HC emissions of an HCCI engine. Lower homogeneity of the air–fuel mixture in the combustion chamber promotes higher PM emissions. For the comparative study (Maurya and Agarwal 2014) a modified 4-cylinder diesel engine was used with a PFI system. The performance of methanol, ethanol, and gasoline in HCCI mode was compared. In comparison to methanol, the maximum gross indicated thermal efficiency of ethanol and gasoline was higher. The indicated efficiency was affected by relative air fuel ratio. The efficiency was found to decrease at leaner operation for all the tested fuels. However, the effect of the leaner mixture was more on ethanol compared to methanol. This could be due to combustion stability at leaner operation for methanol as it has a low stoichiometric ratio and a high laminar burning velocity. Gasoline showed very poor performance with leaner mixture. It was reported that the maximum indicative thermal efficiency of ~45% and combustion efficiency of 99% for a fairly rich mixture was achieved with methanol. NOx emission was found to be more sensitive to relative air fuel ratio than intake air temperature. Richer mixture emitted more NOx due to higher cylinder temperature. The emission of NOx was found to be considerably reduced as compared to the conventional combustion approach. CO emissions were found to be dependent on and intake air temperature. Rich mixtures emitted lower CO and HC compared to lean mixtures. Its reason being high combustion temperature and more available time for its oxidation due to advancing combustion phasing. The emissions of HC and CO were higher in HCCI mode as compared to traditional combustion. Author suggested that main sources of HC were due to wall quenching, crevice volume. It was concluded that methanol has good HCCI characteristics.

Zhang and Wu (2016) investigated the performance and combustion characteristics of a methanol fuelled HCCI engine. The in-cylinder pressure and combustion phasing were found to be sensitive to intake air temperature. This is because HCCI combustion ignition is due to a compression-initiated chemical reaction and higher intake temperature promotes HCCI combustion. It was found that the maximum cylinder pressure and heat release rate were increased with an increase in the fuel–air ratio, engine speed and intake temperature. HCCI combustion was found to be very sensitive to engine boundary conditions. It was reported that even little cyclic variation in charge condition during compression stroke altered HCCI combustion and engine performance. For a given equivalence ratio, higher engine speed reduced the indicated thermal efficiency mainly due to variation of combustion phasing.

Gharehghani (2019) investigated the optimal operating range of natural gas, methanol and ethanol fuels. A single-cylinder E6 engine was used in the study. It was reported that natural gas performed better at high loading conditions, while ethanol and methanol were a good choice for lower loads. An equivalence ratio of more than 0.3 resulted in higher NOx and HC emissions the Euro 6 emission limits. However, it was suggested that a 3-way catalytic converter and dual-mode operation could help achieve lower emission levels with HCCI mode.

Although the HCCI engines have high thermal efficiency and lower NOx emission than traditional engines (Assanis et al. 2003). HCCI combustion has several main challenges, such as regulating ignition timing especially at high loads, limited power output, and weak cold-start capability.

Partially Premixed Compression Ignition (PPCI) Engines: When fuel is injected into the combustion cylinder near TDC, it premixes with air before ignition. Premixing reduces the local fuel concentration, resulting in lower fuel rich zones and better combustion. This approach is referred to as the partially premixed compression ignition approach. The injection timing falls somewhere between traditional and HCCI combustion. Lower fuel-rich zones result in better combustion and lower soot formation compared to conventional diesel combustion. To reduce NOx emissions, a large amount of EGR is used, thereby lowering NOx and soot emissions simultaneously. Prolonged ignition delay for PPCI combustion is practically realised by controlling combustion phasing using reactive fuel, EGR, or early direct injection. The HC and CO emissions are high as combustion is highly diluted. Another reason is fuel impingement on the cylinder walls due to direct and port fuel injection. Recent developments in PPCI mode involve split injection using fuel injectors with narrow holes and EGR. Initial injections are for better premixing, while later injections are used to start ignition. It results in more homogeneous mixture formation, lowering NOx and soot emissions with EGR.

Shamun et al. (2016) studied the PM emission of an alcohol fuelled HD engine operating in PPC mode. A six-cylinder Scania D13 engine along with methanol, ethanol and gasoline as fuel are used in the study. Reducing the intake O_2 concentration, usually increases emission of soot (Huestis et al. 2007). However, methanol showed a different trend. At ambient and lower O_2 concentrations, emission of soot was found to be slightly more and it was minimum at a span of 15% and 16% for ethanol and methanol respectively. Also, compared to ethanol, methanol showed almost double the amount of soot emission. However, compared to diffusion combustion of methanol, soot emission was roughly half with PPC mode. Among all the three fuels, gasoline showed highest soot emission with largest particle size with count mean diameter up to 93 nm. More EGR resulted in increase in soot particle size. PM emissions were found to be independent of inlet temperature for methanol PPC combustion. The study reported that common rail pressure showed negligible effect on tail pipe PM emissions with methanol PPC combustion. In PPCI mode, NOx-soot trade-offs were absent in alcohols while for gasoline, it was found to depend on intake O_2 concentrations. Only ethanol and gasoline showed an exponential increase in CO and HC emissions with lower intake O_2 levels. Also, at a given intake O_2 concentration, methanol diffusion combustion showed a lower specific HC and NOx emission compared to methanol PPC. Author concluded that alcohol fuels were better than gasoline in PPC mode and were able to meet Euro VI emission standards. However, the author showed concern regarding products of internal corrosion of the fuel system and volatile PM emission which could be dangerous to organisms and the environment.

Shamun et al. (2018) studied the charge cooling effect of methanol in PPC strategy using a six-cylinder Scania HD engine. An air preheater was employed to heat incoming air. In-cylinder pressure analysis showed that at lower fuel mean effective pressure (FuelMEP), motoring curve and combustion curve showed complete separation between the end of injection (EOI) and start of combustion (SOC). Before SOC, pressure dip was observed in the rate of heat release (RoHR) curve indicating combustion was mainly in premixed mode. At higher fuelMEP, motoring and combustion in-cylinder pressure curve separation was reduced. From the RoHR curve, it was concluded that fuel ignition took place during the injection period resulting in-cylinder pressure overlap. First phase of combustion occurred mainly with premixed flame while second phase with mixing controlled diffusion flame. Start of injection (SOI) was found to have a significant effect on pressure and temperature of the cylinder prior to combustion. Author suggested that combustion should occur near TDC, delayed SOC can result in loss of displacement work during expansion phase as combustion products will have to fill more volume. Higher work potential was found with lower temperature methanol combustion as it lowered the heat transfer rate from the combustion system and compression work. High intake air temperature showed higher combustion efficiency and, therefore lower CO and HC emissions. Energy analysis showed very small combustion losses of 0.3% while losses due to heat transfer was highest. Methanol showed lower heat transfer loss compared to iso-octane fuel due to retarded SOI and longer combustion duration. NOx emissions were lower in methanol as compared to iso-octane mainly due to charge cooling effect and more quantity of methanol for given FuelMEP. Generally lower λ reduces NOx emissions, however in present study NOx emission was found to increase with lower λ. Also, common rail injection pressure at higher FuelMEp showed an increase in NOx formation due to better fuel spray characteristics and fuel mixing. Resulting in better fuel mixing and faster combustion leading to higher in- cylinder temperature which promotes NOx formation.

Zincir et al. (2019) investigated the effect of intake temperature on a methanol PPC engine at low loads. A modified six-cylinder Scania HD engine was used and the experiments were conducted at low load and idle conditions. Two different injection strategies were tested for idle conditions; single and split injection. Ignition delay and combustion duration at low load, were found to decrease with increasing intake temperature. Split injection showed a longer combustion duration and shorter ignition delay. Maximum combustion efficiency was found to be 99% and it was increasing with increase in intake temperature. Thermodynamic efficiency was found to decrease slightly with increase in intake temperature. It was reported that the thermodynamic efficiency was 26% and 30% with split and single injection strategy. The reduction in efficiencies were related to more heat loss with exhaust due to increase in CA50 from 5° to 9° CA. CO emissions were found to be almost constant at different loads. Author reported that CO emissions were mainly dependent upon the equivalence ratio, which was constant in the study. Poor combustion with CA50 sweeps resulted in poor combustion and therefore higher CO and HC emissions. Author concluded that methanol PPC can show stable operation at low and even at idle conditions.

In comparison to HCCI, PPCI provides a wider range of operating load due to additional combustion control of ignition timing. Its combustion has a higher proportion of premixed flame than conventional mode, but it is less efficient than HCCI combustion. As a result, when compared to traditional combustion, it produces less soot (Shim et al. 2020). However, when compared to conventional diesel, it emits more CO and HC. PCCI engine performance can be improved by employing multiple fuel injection and/or a fuel injector that has a narrow spray distribution. PCCI combustion is typically less efficient than HCCI combustion. RCCI provides even more control by combining fuel reactivity regulation with ignition timing and has a wider range of operating range.

Reactivity Controlled Compression Ignition (RCCI) Engines: The RCCI is a dual fuel approach that involves injecting two fuels with different reactivity through the port and direct injection. In this approach, a low reactivity fuel is injected into the intake port using a PFI system. It premixes the fuel with the incoming air, which is then sucked into the combustion chamber. A high reactivity fuel is injected directly into the combustion chamber using a DI system with single or multiple injection strategies. Methanol is a low reactivity fuel, while diesel is highly reactive. The combination of both fuels is suitable for the application of methanol-diesel RCCI engines. The high reactivity fuel is responsible for the ignition of the fuel mixture. Apart from the equivalence ratio stratification, the fuel reactivity gradient in the combustion chamber adds a control parameter in RCCI mode.

Li et al. (2013, 2014) numerically investigated the combustion and emission characteristics of methanol-diesel RCCI engine and compared it with PCCI diesel combustion engine. Increase in the methanol mass fraction resulted in retarded ignition timing and lower HRR peak. Methanol, being premixed, shortens the combustion duration significantly over mixing controlled combustion of diesel. Below 60% methanol, addition of methanol was found to reduce emission especially CO and

HC. Authors believed that this was due to more homogeneous fuel distribution with methanol premixing. As a result, the combustion temperature was high in more region which promoted oxidation of CO and HC. CO was found to decrease monotonically while HC emissions increased at a methanol contribution more than 60%. It was interesting to note that, Initially NOx and soot emission were decreased with increase in methanol contribution suggesting eliminated NOx-soot trade off. Reduction in NOx formation at elevated temperature was due to the fact that in addition to high temperature, reaction time plays a role in NOx formation. Higher methanol fraction retarded the ignition timing resulting in reduced available time for the NOx formation reaction. Soot emissions usually increase with lower cylinder temperature. However, premixed methanol improves the fuel distribution and reduces the local fuel rich zones within the combustion chamber. It reduced the soot formation in the engine. The most critical operational factors for overall engine performance and emissions were found to be the initial temperature and EGR rate (Li et al. 2014). Author suggested that optimized RCCI combustion with methanol-diesel fuel can meet the stringent emission regulation with improved performance than conventional diesel engines.

Jia and Denbratt (2018) examined the effect of methanol configuration in a methanol-diesel dual-fuel engine. The methanol injection was tested in two configurations: port injection into the intake manifold and direct injection in the combustion chamber. Three injection strategies were tested with dual diesel injection in the RCCI engine. Two direct injection conditions were tested with methanol; injection in compression stroke (STRTG1) and another slightly after TDC (STRTG2). The effect of injection pressures on methanol-air mixing and combustion were found to be negligible with STRTG1. It showed lower combustion efficiency and therefore higher CO, methanol and HC emissions. Soot emissions with port injection were found to be less than 0.01 g/kWh which is lower than Euro 6 limits. However, STRTG2 exceeded the limit. The port injection configuration was able to achieve ultra-low NOx and soot emissions. The ratio of split injection duration for dual diesel showed considerable effect on the performance of the engine. Port fuel injection and injection during compression stroke strategies showed insignificant difference in net indicated efficiency or HC and CO emissions. RCCI engines have shown better performance at higher loads, but at lower loads, these have low thermal efficiencies.

Duraisamy et al. (2020) studied the methanol-diesel and methanol- Polyoxymethylene Dimethyl Ethers (PODE) RCCI combustion mode. A modified 3-cylinder, turbocharged diesel engine with a CRDI system was used. In terms of modification to the engine, a port fuel injection system with an open ECU was added to a diesel engine. Both the dual fuels showed a longer ignition delay and reduced the combustion duration compared to conventional diesel engines. The reason being, high octane number and high heat of vaporization of methanol resist the auto-ignition and extend the ignition delay. While, high laminar burning flame velocity of methanol and more uniform fuel distribution reduced chemical delay resulting in faster combustion. A higher COV_{IMEP} was observed in RCCI mode as compared to conventional combustion. Author suggested that it was due to variation of pressure, mixture composition, temperature due to local cooling effect of methanol port injection. COV_{IMEP}

was found to increase with increase in premixed methanol. Conventional combustion showed higher combustion efficiency compared to RCCI mode. The indicated brake thermal efficiency with RCCI mode was found to be higher as compared to conventional combustion at high premixed methanol, showing a peak at 80% of premixing. Brake specific carbon monoxide (BSCM) was found to increase with methanol premixing with both the fuels in RCCI mode. BSCM emission varied from 0.5 to 5.5 g/kWh for methanol/diesel when premixing was increased to 80%. On the other hand, brake specific nitrogen oxide (BSNO) was found to decrease with increase in premixed methanol. Compared to conventional diesel operation, with premixing ratio of 85%, methanol-diesel RCCI more resulted in 95% reduction of BSNO. Soot emissions were found to decrease with increase in premixed methanol due to more premixed combustion and more homogeneous fuel reactivity gradient. Also, methanol being a simple molecule with lower carbon to hydrogen ratio results in lower soot formation. Dual fuel RCCI was able to reduce 90% soot emission compared to conventional mode of operation. The study concluded that the higher methanol mass fraction results in prolonged ignition delay and a decrease in in-cylinder pressure for both methanol-diesel and methanol-PODE operations. The brake specific NOx and soot emissions were significantly lower as compared to conventional diesel combustion.

Direct Dual Fuel Stratification (DDFS): The Direct Dual Fuel Stratification (DDFS) technique employs two direct injectors in the combustion chamber (Fig. 5.3). DDFS offers a thermal efficiency equivalent to RCCI and HCCI and exceptionally low NOx and soot emissions (Li et al. 2020a; Shirvani et al. 2021; Wissink and Reitz 2015). It can fulfil the EURO6 emission requirements without the need for after treatment. It can result in a very high methanol substitution rate, displacing up to 90% of diesel fuel demand and very low emissions. The optimized DDFS case has higher thermal efficiency, lower emissions, reduced need for the in-cylinder starting temperature, and a larger possibility for energy recovery than the RCCI mode (Shirvani et al. 2021). Intelligent Charge Compression Ignition (ICCI) is a fairly new concept in combustion. Two CRDI systems were used separately on a modified single-cylinder engine, each controlled by its ECU which regulates fuel injection, injection timing and number of injections in real-time.

Two complementary fuels are alternately injected into the cylinder during the intake and compression strokes to create arbitrary stratified conditions. The ignition timing and combustion rate are adjustable, allowing for higher thermal efficiency and minimal NOx emissions. With changes in engine operating conditions, the injection timing, fuel split ratio, and fuel split number may be adjusted in real-time, regulating in-cylinder stratification. If flexible injection techniques are paired with other engine boundary conditions, such as EGR rate, intake pressure, and intake temperature, engine operating ranges can be expanded to lower or greater loads while retaining high efficiency and clean combustion (Li et al. 2020a). ICCI differs from RCCI in terms of the location of fuel injection. In ICCI mode, the location of the injectors is such that they directly inject the fuel into the combustion chamber. However, in RCCI mode, one injector was placed at the intake port and other at the cylinder

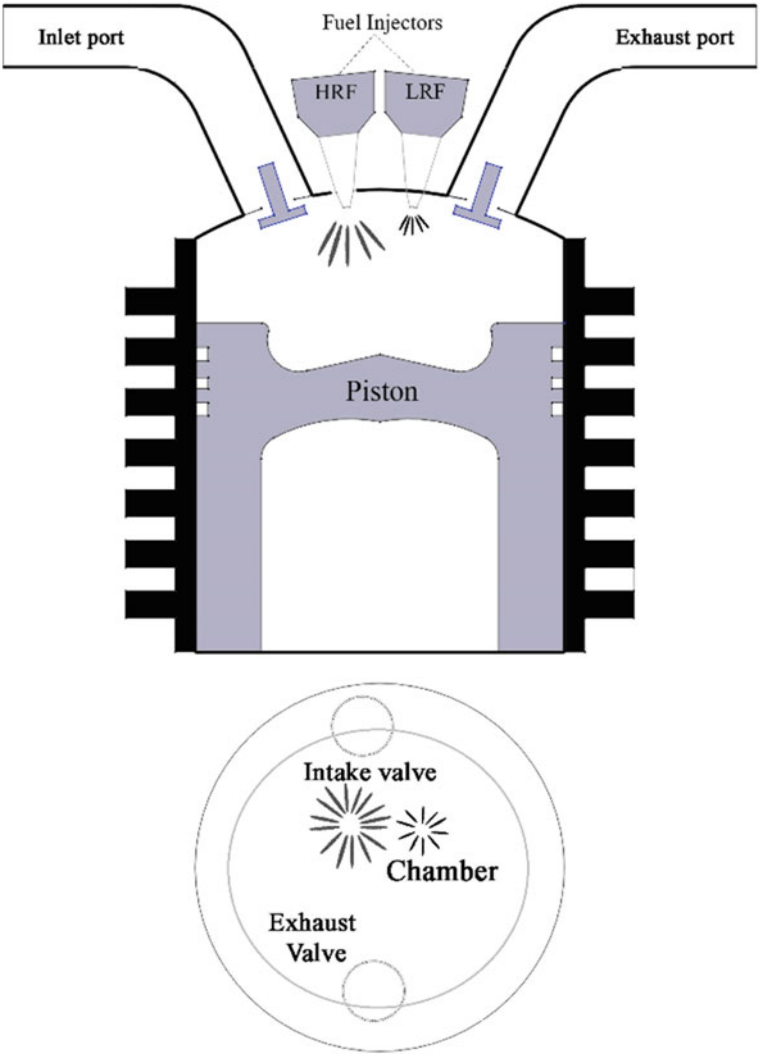


Fig. 5.3 Two injector configuration: HRF (high reactivity fuel) and LRF (low reactivity fuel) (Li et al. 2020a)

head. Hu et al. (2018) investigated the combustion characteristics of methanol with pilot injection of diesel in a constant volume combustion chamber. A six orifice GDI injector was employed for direct injection of methanol into the combustion chamber. The study found that with pilot injection, ignition delay in diesel-methanol dual fuel mode increases.

Huang et al. (2020) employed ICCI combustion mode to explore the effects of injection strategy on the performance of methanol- biodiesel dual-fuel engine. The study focused on investigating the combustion and emission characteristics of ICCI mode fuelled with methanol and biodiesel. They reported that the CO and HC emissions were under acceptable levels for medium to high loads. Indicative thermal efficiency (ITE) of 53.5% was achieved with NOx emissions of less than 0.6 g/kWh. For methanol, a two-stage split-injection method reduced HC and CO emissions while producing exceptionally low NOx. At the same time, biodiesel helped to achieve the specified thermal efficiency while lowering nucleation particles. A summary of injection strategies and their performance and emission characteristics is presented in Table 5.3.

5.10 Conclusions

The chapter has reviewed application of methanol in IC engines. A comprehensive review of studies involving methanol fuel in conventional CI engines, followed by the challenges and modifications in the fuel injection system has been presented. A review of performance of methanol in Low Temperature Combustion (LTCs) mode is presented. Key takeaways of the study are:

- It is difficult to use pure methanol in conventional diesel engines, and appropriate fuel additives and/or fuel injection system modifications such as addition of glow or spark plug are required.
- Methods like pilot injection, dual-fuel engine concept can lower the diesel fuel consumption while reducing the soot and NOx emissions of the conventional diesel engine. The pilot injection has low noise and NOx emission levels with higher economy. Blending is also an excellent way to incorporate methanol without significant modification in the engine while reducing diesel consumption. Usually a larger orifice injector or multiple injector with mixing system (when fuel used is not premixed) is required. However, the miscibility of methanol-diesel at higher methanol fraction is a challenge and requires blend stabilizers. Exhaust after treatment can further reduce the limitation of high CO and HC emission
- Low-temperature combustion (LTC) modes have shown to be effective at reducing NOx and soot emissions without the use of an after treatment system. These techniques allow for a high methanol substitution rate. Methanol has shown the potential to reduce NOx and soot emissions even further, to ultra-low levels with extended operating load limits in low temperature combustion modes.
- Homogeneous Charge combustion ignition has shown high combustion and thermal efficiency with methanol in comparison to gasoline. It has shown ultra-low soot and NOx emissions. However, carbon monoxide and unburned hydrocarbon emission is high compared to conventional SI engine. The performance of the engine was sensitive to history of intake air temperature, relative air–fuel ratio, injection temperature, engine speed especially wall boundary condition.

Table 5.3 Methanol injection strategies and their performance and emission characteristics

Technique	Modification in Fuel injection system	Performance/application	Advantages	Challenges
Pure methanol CI	Mixing of ignition improver, modification in cylinder head for glow or spark plug	Quieter operation, similar efficiencies as compared to conventional diesel engine	NOx and Soot ↓	HC and CO ↑
Fuel blending	Larger diameter nozzle or/and with more number of nozzle. A fuel mixing system is required. Addition of blend stabilizers	Higher torque and output power	NOx ↓ with increase in methanol mass fraction	HC and CO ↑ with increase in methanol mass fraction, problematic with lower miscibility fuels
Methanol fumigation	Additional fuel supply system is required	Higher efficiencies at high loads	NOx and PM ↓	HC and CO ↑
Methanol HCCI engine	Design of piston and combustion chamber is critical	Efficiency depends upon equivalence ratio. EGR improves the HCCI engine performance	NOx and PM ↓ ↓	HC and CO ↑ ↑, higher misfires, difficult to control ignition timing. Lower operating range at higher engine loads
Methanol PPCI engine	Fuel injector with narrow spray, preferably capable of multiple injection characteristics, Air preheater is preferable and a HC and CO catalytic converter, EGR system	Efficiency depends upon temperature of intake air, O_2 intake, injection strategy (single and multiple injection)	NOx ↓ and PM ↓. Better combustion control and extended high operating load over HCCI	Higher chances of wall wetting, more HC and CO emissions. lower thermal efficiency compared to HCCI
Methanol RCCI engine	Addition of PFI system to pre-existing CI engine. Addition fuel control system	Better combustion control than HCCI,	NOx and smoke ↓ ↓	Low thermal efficiency at lower loads

(continued)

Table 5.3 (continued)

Technique	Modification in Fuel injection system	Performance/application	Advantages	Challenges
Methanol DDFS	Modified cylinder head to incorporate dual direct injectors	High indicated thermal efficiency	High substitution rates of Methanol, CO, HC and soot ↓	Complex engine design, NOx emissions are more compared to RCCI, need further investigation to understand the effect of injector design and its orientations on performance of DDFS engines

Effects like wall quenching can increase the HC emission to unacceptable levels. Although, these can be reduced using catalytic converters. Applicability of this mode need better management and system control and it is suitable for lower load application.

- Partially premixed combustion ignition has added ignition control over homogeneous charge combustion ignition. It has shown an extended operating range. Methanol has shown a stable carbon monoxide and hydrocarbon emissions compared to ethanol and gasoline with variation in intake oxygen concentration. However, soot emission showed an increase with decrease in oxygen concentration.
- Reactivity controlled compression ignition and direct duel fuel stratification are dual fuel approaches with added combustion control using fuel stratification. Reactivity control CI engine running on methanol-diesel fuel has shown better performance at higher loads. A port fuel system has shown better performance in terms of lower NOx and soot emission for reactivity-controlled CI compared to direct fuel injection. Its performance depends upon methanol premixing ratio, exhaust gas recirculation levels, single or multiple fuel injections. Very high substitution rates of up to 90% methanol has been reported using recently developed direct dual fuel stratification technique. It employs dual direct injector to create arbitrary stratified conditions. It has demonstrated the potential for the development of an efficient engine for medium to high load applications while emitting acceptable levels of carbon monoxide and hydrocarbons.
- Low temperature combustion engines are in the development phase. The combustion performance has shown strong dependency on many parameters such as incoming charge conditions, exhaust recirculation levels, intake air temperature, engine boundary conditions. The applicability and reliability of low temperature

combustion engines will require better system monitoring and control systems. Further research should focus more on development of such systems to improve the dynamic response of the engine.

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Chapter 6
Butanol Fuel in Internal Combustion Engines

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Abstract Butanol is actively being researched by scientists for its suitability as a renewable fuel for internal combustion engines. Physical and chemical properties of butanol motivate researchers to use it as a fuel in internal combustion engine. Butanol is a four-carbon alcohol and has five isomeric structures. Butanol has a comparatively higher energy density and lesser vapor pressure compared to other alcohol such as ethanol, which makes it more attractive as fuel or blending agent. The objective of this chapter is to examine the potential of bio-butanol as a replacement for conventional fuels such as diesel/gasoline in internal combustion engine. To fulfill this objective, a literature review was performed and some important results were highlighted. In addition to literature review, experiments were performed in a single cylinder diesel engine to investigate the impact of diesel fuel blended in small proportion with butanol. In this regard, DB15 (15% v/v blend of butanol with diesel) was selected as a test fuel and results were compared with baseline diesel. Results pertaining to performance characteristics such as brake specific fuel consumption, brake thermal efficiency and brake specific energy consumption are discussed. The novelty in the current study is that numerous current and upcoming research directions are outlined in chapter. Research in ethanol/methanol fuel has increased since past few decades, but research on butanol is still limited.

Keywords Butanol · Engine · Performance characteristics · Renewable fuel

6.1 Introduction

With the increase in population throughout the world, the demand for vehicles for transportation has also increased, both in rural and metro cities. Due to this, the demand of conventional fossil fuel has scaled up. Conventional fuels are also known to produce relatively high emission. To decrease the engine emission, legislations

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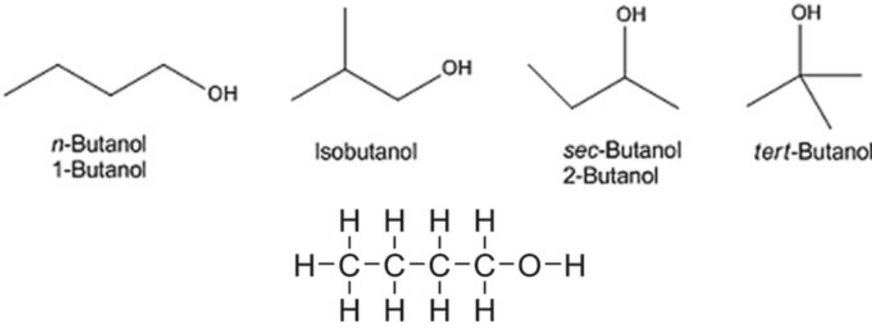


Fig. 6.1 Chemical structure of butanol

are becoming stringent with introduction of every successive emission norm. Among many alternative fuels available, alcohols are considered (due to its advantages over other renewable fuels such as biodiesel) as a solution to meet high fuel demand and reduce emission. Among alcohols, n-butanol fuel is actively being researched for use in internal combustion (IC) engines (Karagöz 2020; Saraswat 2020; Zhen et al. 2020).

For consumers, cost of renewable fuel should be comparable with conventional fuel. Cost factor lets the consumer decide on buying a type of fuel. Raw material for making renewable fuel should be natural resource and sometimes, the availability of this raw material is an issue. As discussed by author (Jiang et al. 2015), in the process of n-butanol fermentation industry, the cost of feedstock consists of approximately 3/4th of the total cost of production of butanol. If cost of raw material is reduced, final cost of fuel may be reduced. Due to higher production cost of butanol, other alcohols (Ethanol and methanol) are more likely used in IC engine.

Figure 6.1 shows chemical structure of butanol. n-butanol (C4H9OH) is a four-carbon, straight-chained, saturated compound also known as butyl alcohol. n-butanol can replace methanol and ethanol because it has a unique advantage for example it is weak hydrophilic, it has lower corrosion potential, it is suitable to transport through the pipeline. Furthermore, n-butanol has superior thermophysical properties as compared with methanol and ethanol such as high energy concentration, lower ignition temperature, lower volatility and higher viscosity than methanol and ethanol. Also, n-butanol has good blend properties, so it doesn't require any additional additives to prepare the blend (Zhen et al. 2020; Sharma and Agarwal 2020). The lower cetane fuels have longer ignition delay period than higher cetane fuels. Naturally, alkyl nitrate additives have a potential to increase cetane number about 3–7. The most important additives existing are nitro ethane, 1-tetradecane, 1-octadecanol, isobutyl stearate and Dioctyl adipate (DOA) etc. These additives are available and are cost effective which can be used as the cetane number booster. Although ethanol is used as blend with gasoline by majority of countries, its production capacity is rather limited and not every country can produce it from corn and sugarcane or similar feed-stocks. There is a need to diversify feed-stokes to produce primary alcohols across the globe. Hence, there is a need to explore alcohols other than ethanol to meet the energy demand in near future. Keeping these factors in mind, some higher alcohols such as butanol are being actively investigated by researchers for use as transport fuels. It is shown in the literature that higher blends of butanol causes also cold start problems. However, its lower blend with gasoline several advantageous. Different isomers of butanol exist, depending on the location of hydroxyl group-OH in the molecular structure. Amongst these isomers, physical properties of iso-butanol are quite similar to gasoline therefore it's considered as a suitable alternative bio-fuel candidate. Its relatively longer carbon chain vanquishes the hydrogen bonding effect because of the polarity caused by the -OH group. Important properties of butanol adapted from literature are shown in Table 6.1.

Considering the above advantages, the prime objective of this research article is to review use of n-butanol and diesel blend in IC engine. Experiments were performed in a single cylinder diesel engine to investigate the impact of diesel fuel blended in small proportion with butanol. DB15 (15% v/v blend of butanol with diesel) was selected as a test fuel and results were compared with baseline diesel. Results pertaining to performance characteristics such as brake specific fuel consumption (BSFC), brake specific energy consumption (BSEC) and brake thermal efficiency (BTE) along with its emission characteristics are discussed. The novelty in the current study is that numerous current and upcoming research directions are outlined in chapter. Current investigates was performed on engine performance on lower butanol blend. This

Table 6.1 Important test fuel properties[a]

Properties	Butanol
Molecular formula	C4H10O
Density @ 20 °C (g/cm^3)	0.811
Molecular weight (Kg/Kmol)	74.12
Viscosity (mm^2/s) @40 °C	2.544
Cetane number	25
Lower heating value (MJ/Kg)	32.7
Flash point (°C)	36
Auto-ignition temperature (°C)	343
Boiling point (°C)	118
Oxygen content (% w/w)	21.6
Motor octane number	84
Stoichiometric air/fuel ratio	11.2
Carbon content (wt.%)	64.8
Hydrogen content (% w/w)	13.6
Latent heat of vaporization (KJ/Kg)	716
Research octane number	96
Surface tension @ 27 °C (N/m)	24.7

[a] Adapted from literature

article aims to comprehend the effect of blending butanol with diesel fuel in diesel engine's performance characteristics. Number of publications in alcohol fuel diesel engines has increased since past few decades, but number of publication on butanol is still limited.

6.2 Use of Butanol as a Fuel in IC Engine

Karagöz et al. (2020) investigated performance as well as emission characteristics with diesel-waste tire oil-butanol blends in a compression ignition (CI) engine with varying engine load. Authors observed that the BTE increased while BSFC decreased with increase in engine load. Additionally, carbon monooxide (CO) and oxides of nitrogen (NOx) emissions increased while hydrocarbon (HC) emission decreases with use of diesel-waste tire oil-butanol blends. Saraswat et al. (2020) investigated performance, combustion and emission characteristics using n- butanol fuel blend with acetylene fuel in a CI engine. Authors observed that the BSEC reduced with increase in engine load. In addition to this, authors reported reduced CO and NOx emissions. Similarly, Zhen et al. (2020) investigated the impact of bio-butanol in spark ignition (SI) and CI engine. Authors observed that the BTE increased along with BSFC, however gaseous emissions marginally reduced. Sharma and Agarwal (2020) carried performance as well as emissions characteristics using gasohol fuel in direct injection spark ignition engine. Authors found that the BSFC decreased with increase in engine speed. However, HC and NOx were reported relatively higher. Sharma et al. (2020b) investigated energy and exergy for the hydroxyl fuel in CI engine. Authors found that the BTE improves with increase in hydrogen–hydrogen oxygen (HHO) concentration and load on engine. Authors also reported that fuel provides higher rate of oxidation improving temperature and pressure. Similarly, Sharma et al. 2020a) investigated the performance as well as emission characteristics using hydroxy-diesel blend in CI engine under dual fuel mode. Authors discovered that the BTE and BSEC was increased with hydroxyl-diesel blend. Likewise, Mamat et al. (2019) investigated performance, combustion and emission characteristics with higher alcohol and authors observed that the alcohol fuels have oxygen concentration and high latent heat of vaporization which enhance anti-knock qualities and combustion efficiency.

Li et al. (2017) investigated the effect of exhaust gas recirculation (EGR) on blend ratio of diesel butanol blend. Authors reported the performance characteristics of natural gas with diesel/butanol blends. Authors observed that BTE and NOx decreased with addition of EGR while CO emissions increased with addition of EGR fraction. Similarly, Nabi et al. (2017) investigated indicated torque (IT), indicated power (IP), Indicated specific fuel consumption (ISFC) and emission with neat diesel and butanol-diesel blends. In this investigation authors reported higher BSFC, less power, boosted pressure as a result of using n-butanol blends as it has low energy content. They also reported reductions in particulate mass (PM) when using n-butanol blends.

Zoldy et al. (2010) investigated viscosity, cetane number and flash point with butanol blended diesel fuel in IC engine. They suggested blending lower butanol content with diesel due to chemical properties of butanol. Nayyar et al. (2017) investigated the performance and emission characteristics experimentally and analytically with diesel n-butanol blends in VCR engine. Authors observed that BTE improved with butanol-diesel blend while smoke and NOx reduced. Yanai et al. (2014) examined combustion characteristics, emission characteristics and BTE of DICI engine. Authors observed stable ignition, nearly zero soot and relatively lesser NOx emission. Tankai et al. (Zhang et al. 2017) investigated emission characteristics and BTE in a single cylinder research engine using renewable fuel. Authors found that the indicated thermal efficiency (ITE) was improved while HC and CO emission reduced. Liu et al. (2015) investigated the effect of the air dilution, effective compression ratio (ECR) and emission characteristics by using n-butanol fuel in homogeneous charged compression ignition (HCCI) engine. Authors observed that the ITE enhanced whereas BSFC slightly increased. Huang et al. (2018) investigated effects of BMEP on the performance, combustion and emission characteristics using n-butanol/diesel/PODE blend in diesel engines. Authors found that the use of the PODE in n-butanol diesel blend improved the BTE and combustion efficiency. With increase in BMEP, soot, CO and HC resulted in reduction in concentration while NOx emissions increased.

Fushimi et al. (2013) investigated the effect of butanol isomers with butanol/gas/diesel blend in CI engine. Authors observed that the smoke emission reduced with increase in 1-butanol content. Similarly BTE of butanol isomers blend with gas oil blend decreased. Saxena and Maurya (2018) investigated the effect of butanol-diesel blend in CI engine for performance, combustion, gaseous and nanoparticles emission characteristics. Authors reported that increment of butanol increases the ignition delay, BTE and heat release rate. Xie et al. (2016) investigated the performance and emission characteristics of Homogeneous Charge Compression Ignition (HCCI) engine with butanol fuel. Authors reported that the EGR and combustion phasing can be postponed to moderate peak pressure and pressure rise rate. With this, thermal efficiency BSFC and NOx emission improved while HC emission decreased. In this context, Yadav and Ramesh (2018) has investigated the performance and smoke characteristics in a dual fuel engine with butanol-diesel blend. Authors reported decrease in smoke, NOx and CO_2 emission while HC and CO emission increased. Likewise, Ibrahim (2016) investigated the performance and combustion characteristics in diesel engine with butanol-biodiesel-diesel blends. Authors reported that the thermal efficiency and specific heat ratio decreased whereas BSFC increased. Cheng et al. (2016) investigated the emission characteristics and thermal efficiency of PPCI diesel engine with iso-butanol/diesel blend. Authors observed that the PPCI was helpful to form superior homogenous mixture that helped in 70% reduction in smoke and marginally increase in NOx emission. Liu et al. (2018) investigated the effect of early injection partially premixed combustion (PPC) strategy on the performance of IC engine with butanol-diesel blend. Authors observed that the peak value of heat release rate (HRR) improved and the heat release duration reduced with addition of n-butanol.

Fig. 6.2 Indicated specific fuel consumption under different injection modes at spark timing ranging from 12 to 28 °C BTDC. (Feng et al. 2018)

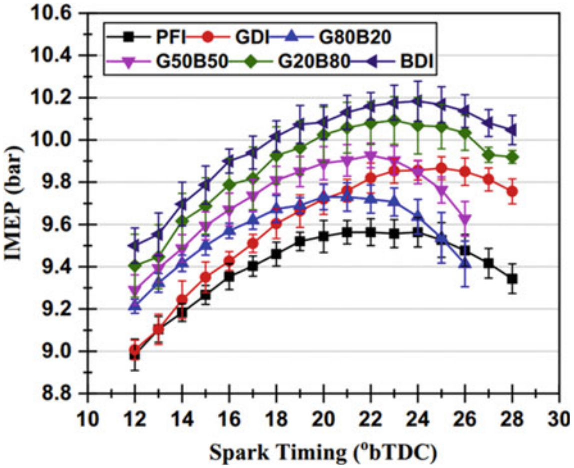


Figure 6.2 exhibits the variation of ISFC in different gasoline/butanol fuel blends at various spark timing. ISFC increases with an increase in the butanol fraction in bend. A raise in the mass fraction of butanol injection resulted in a decline in fuel economy due to the high ISFC requirement for the engine to maintain output power. ISFC was minimum at about 22° crank angle before TDC. Probable reason of this could be lesser heating value of butanol as compared to gasoline, which causes a higher ISFC of gasoline/butanol fuel blend.

Figures 6.3 show torque variations with engine speed for various gasoline/butanol blends. As seen in the Fig. 6.3, engine torque decreased with increase in butanol content in fuel. Since butanol has a lower heating value as compared to gasoline fuel, this resulted in reduction in engine torque and brake power. Similarly, authors also found that brake torque increases with increase in engine load. Also, volumetric efficiency variation for different gasoline/fuel blends was discussed by author. It was reported that gasoline has the highest volumetric efficiency as compare to butanol blend fuel probably because of relatively lower saturation pressure on gasoline fuel. Consequently, the heavy fuel vaporizes before inflowing the cylinder when using gasoline/butane blends. Butanol has a higher LHV as compare to gasoline and this reduces the butanol intake temperature and in turn increases the volumetric efficiency of the mixed fuel. In another graph by same author in same manuscript, variation of exhaust gas temperature for the different gasoline/fuel blends for various engine speeds was discussed. Exhaust gas temperature decreased with an increase in the butanol concentration in the fuel blend as compared to the gasoline fuel at all engine speed. Butanol fuel absorbs higher heat from the cylinder to evaporate and reduces the in-cylinder temperature. Probable reason for this could be high latent heat of vaporization of butanol fuel. Unburned hydrocarbon is main source of rise in EGT. Therefore, a rise in the EGT of the blends is desirable because of superior conversion efficiency in catalytic converter.

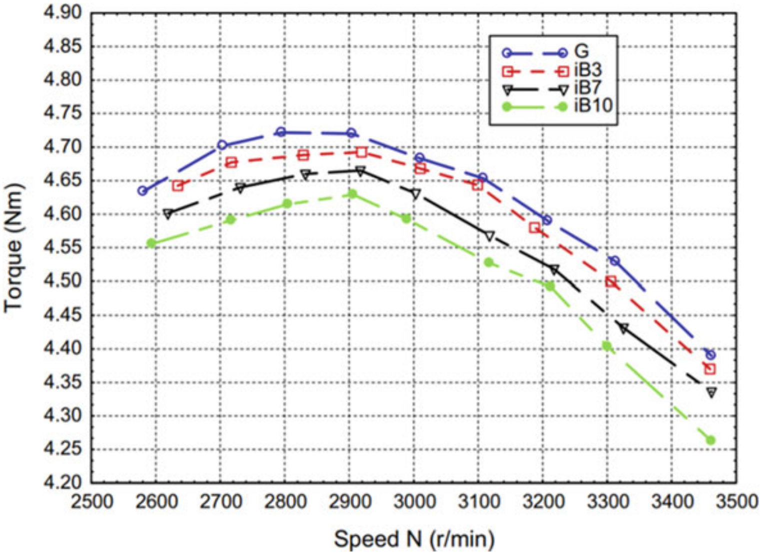


Fig. 6.3 Performance characteristics of butanol fuel (Elfasakhany 2015)

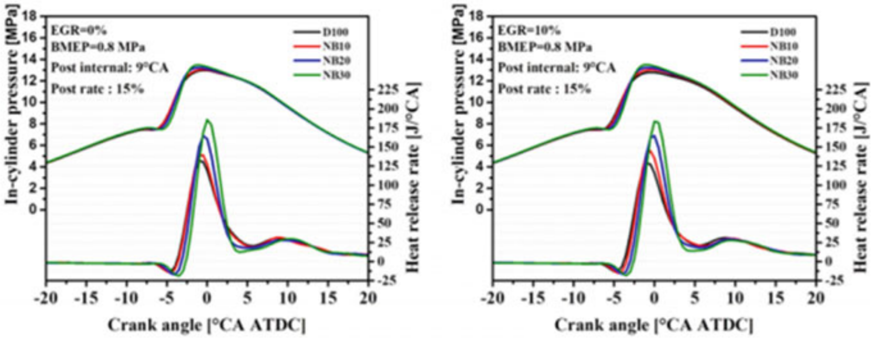
Figure 6.4 depicts the contribution of variable EGR rate on the in-cylinder pressure and HRR, during a post injection of fuel. It is found that with growth in EGR rate, the value of maximum cylinder pressure drops and the peak of HRR increased. Probable reason for this trend could be, the exhaust gases include components of higher specific heat capacity such as CO_2 and vapor. Therefore, the maximum in-cylinder temperature reduces, leading to a decreased in-cylinder pressure. Authors concluded that the change in cylinder pressure and HRR is primarily due to property of fuels with the EGR rate of 0–10%.

6.3 Experimental Setup

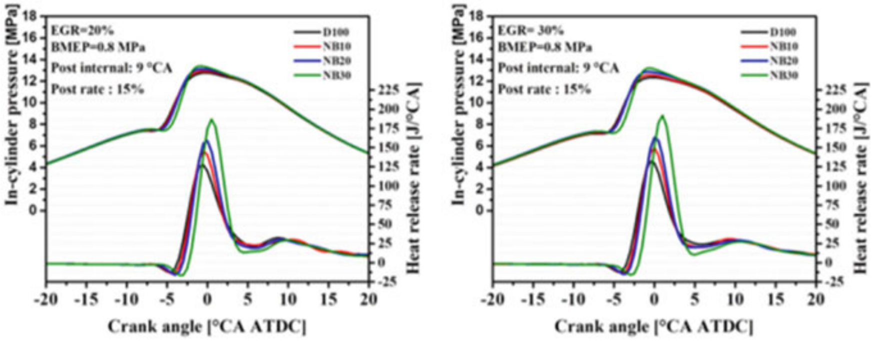
In this experimental study single cylinder, water cooled diesel engine equipped with eddy current dynamometer was used to test butanol fuel. Specification of the engine is shown in Table 6.2 and schematic of the experimental setup is shown in Fig. 6.5.

The engine was coupled with ECU (PE3 Series ECU, Model PE-3-8400P) and a load cell of strain gauge type (range 0–50 kg). Experimental setup had two fuel tanks, one for diesel and other for DB15. Engine oil control unit and coolant control unit was part of the test cell. During the experiments, performance characteristics were measured (BTE, BSFE, BSEC).

Test Fuel: Feasibility for lower blend of butanol with diesel was explored. Two test fuels baseline diesel and DB15 (15% v/v blend of butanol with diesel) was selected as a test fuel. Volume of the fuel flow was adjusted to account for lower calorific



(a) EGR = 0 (b) EGR = 10%



(c) EGR = 20% (d) EGR = 30%

Fig. 6.4 Variation of in-cylinder pressure with crank angle degree (Zhou et al. 2020)

Table 6.2 Engine specifications used in this experiment

Engine specifications	
MFG and model of the engine	Kirloskar engine oil Ltd. model TV1
Number of cylinders	Single
Mode of the fuel	Dual
Bore × length	8.75 cm × 11 cm
Connecting Rod's length	23.4 cm
Maximum rating of power	3.5 kW
Number of strokes	Four
Revolution per minute	1500
Injection point	0° BTDC to 25° BTDC
Compression ratio	12:1–22:1

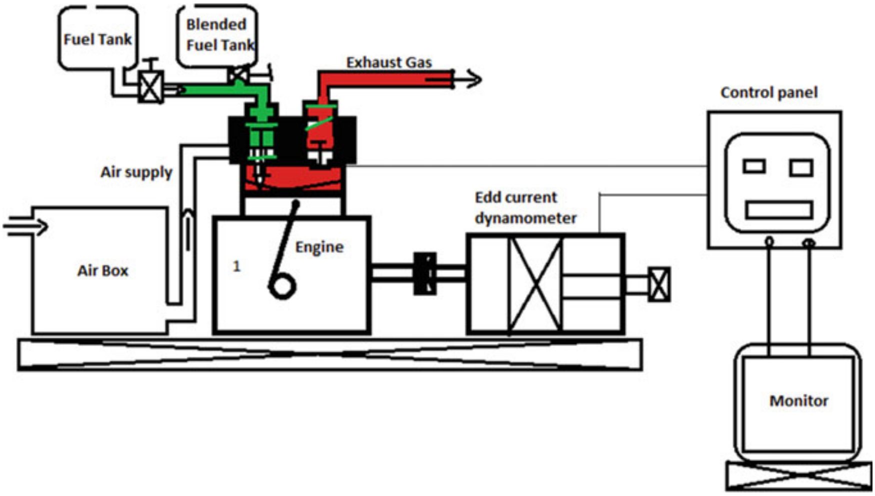
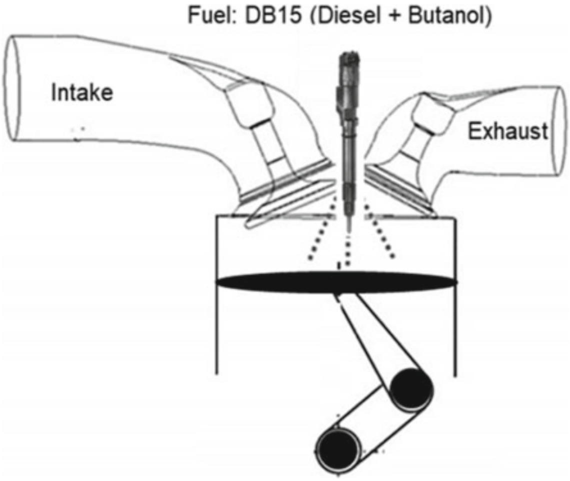


Fig. 6.5 Line diagram of engine setup

value of butanol. Figure 6.6 shows the schematic of fuel injector injecting fuel in combustion chamber. Dual fuel injection was not part of the present experiments. The injection point of the selected engine can vary from 0° BTDC to 25° BTDC. However, for the present experimental setup, it was fixed at 23° BTDC.

Fig. 6.6 Schematic of diesel butanol blend injection system. The fuel was blended externally, and used in existing diesel injector



6.4 Results and Discussion

Figure 6.7 shows the variation of BTE with engine torque for diesel and DB15 (15% v/v blend of butanol with diesel) at varying load on engine. With higher engine load BTE increased to a maximum value and became constant for all the test fuels. The baseline diesel fuel resulted in minimum BTE for the entire engine operating condition.

The possible reason could be higher flame speed, shorter combustion durartion for oxygenated fuel. The oxygenated fuel absorbs heat from combustion chamber during the vaporization which could raise the thermal efficiency of engine.

Figure 6.8 observed the effect of BSFC with engine torque for diesel and DB15 test fuels at varying engine load. With increased engine load, BSFC decreased, reached a minimum value and becomes constant for all the test fuels. DB15 fuel resulted in maximum BSFC at no load but as the engine load was increased, diesel fuel resulted in relatively higher BSFC.

Figure 6.9 observed the effect of BSEC with engine torque for diesel and DB15 test fuels at varying engine load. With increase in engine load, BSEC decreased, reached a minimum value and becomes constant for all the test fuels. DB15 fuel resulted in maximum BSEC at no load but as the engine load was increased, diesel fuel resulted in relatively higher BSFC. Table 6.3 shows the summary of BSEC, BSFC, and BTE for comparison.

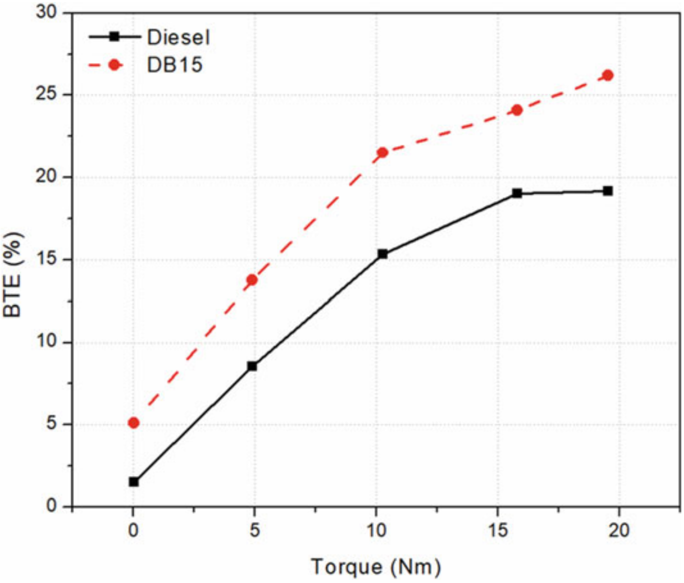


Fig. 6.7 Variation of BTE with engine torque

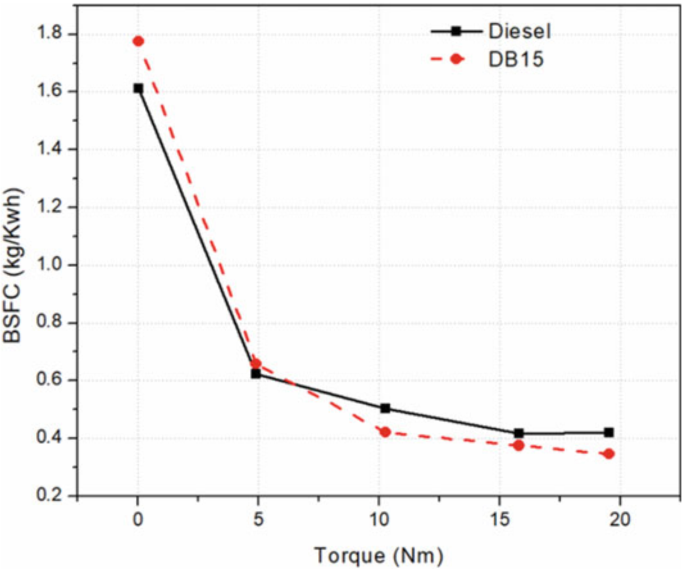


Fig. 6.8 Variation of BSFC with engine torque

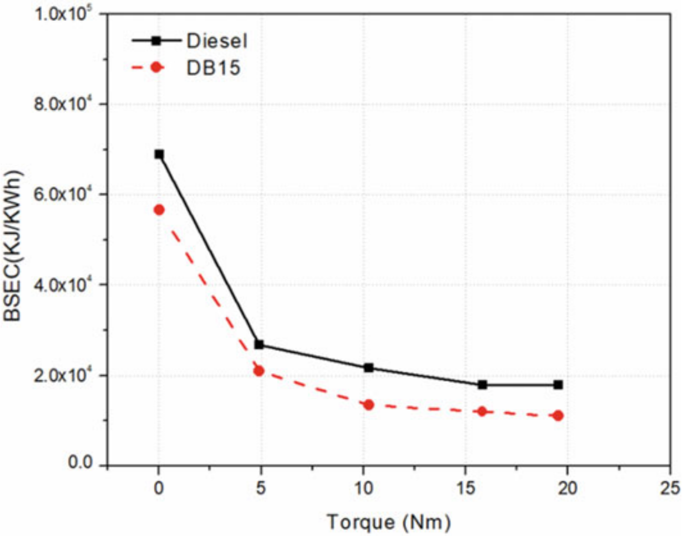


Fig. 6.9 Variation of BSEC with engine torque

Table 6.3 Summary table (BSEC, BSFC, and BTE) for comparison at different test fuel (diesel)

	BSEC	BSFC	BTE
Diesel	↑	↑	↓
DB15	↓	↓	↑

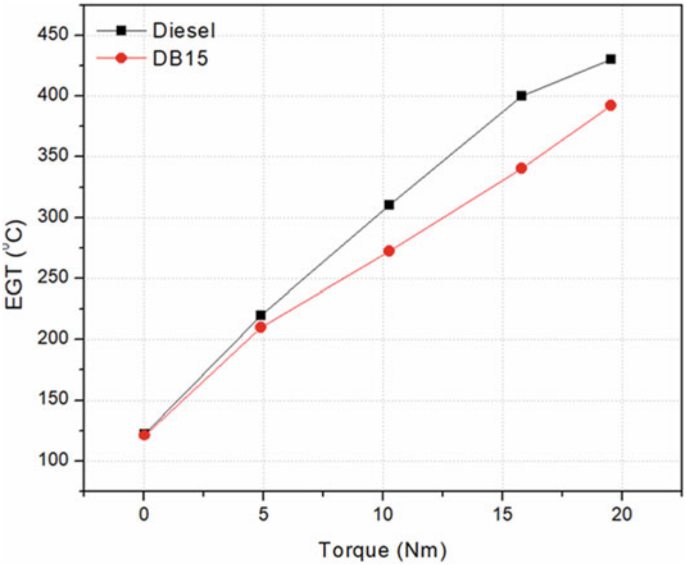


Fig. 6.10 Effect of EGT with load

Figure 6.10 shows that EGT increased when load increase for both test fuel and it is observed that maximum temperature of exhaust gas is at maximum load. EGT was found to be relatively lower for oxygenated fuel. The difference among the load increased as the load was increased.

6.5 Challenges of Butanol/Alcohol as Fuel in IC Engine

Based on the above discussion it appears the butanol is a promising fuel for use in IC engine. However, there are a few challenges associated with it. Some of them are listed in below table.

Factor	Challenges
Corrosive	Fuel pumps, fuel lines, storage tanks and dispensing equipment may get corroded. Alcohols are hygroscopic in nature; therefore engines may require upgraded fuel pumps
Natural habitats	*Natural habitats* may be destroyed including rainforests to grow crops for producing bio-alcohols
Energy content	Lower energy content and increased BSFC
Cold weather	It is difficult to use 100% alcohol in cold weather due to lower energy content and flash point than gasoline. It may cause poor low temperature starting and operation

(continued)

(continued)

Factor	Challenges
NOx emission	Increased NOx emissions due to increase in peak cylinder temperature
Oxidation stability	Poor oxidation stability compared to baseline gasoline
Lubrication Property	Rapid lubricating oil degradation
Vapor lock	Lower boiling point of alcohols may create vapor lock on a hot day

6.6 Outlook and Conclusions

Renewable and cleaner fuels for IC engines are necessary. This study critically reviewed the use of lower blend of butanol in IC engine. In addition to review, experiments were performed to assess the performance characteristics of DB15 (15% v/v blend of butanol with diesel). Some of the key outcome are as follows:

- It was reported in literature that volumetric efficiency, break power, torque and EGT was lower for butanol blend fuel.
- Because of butanol's sustainable and clean nature, this may be highly beneficial for environmental management, fulfilling global energy demand, and achieving sustainability objectives for generations to come.
- From present experiments, the baseline diesel fuel resulted in minimum BTE for the entire engine operating condition.
- Also, DB15 fuel resulted in maximum BSFC at no load but as the engine load was increased, diesel fuel resulted in relatively higher BSFC.
- DB15 fuel resulted in maximum BSEC at no load but as the engine load was increased, diesel fuel resulted in relatively higher BSFC.

Overall, replacement of fossil fuels with butanol may reduce the import of fossil fuels. In addition to this, government across the world is applying and encouraging the use of new and renewable fuel related policies. Further investigations are needed to examine the addition of butanol on engine combustion and emission characteristics.

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Chapter 7
Biofuel Combustion Generated Particles Analysis

Farzad Jaliliantabar, Abdul Adam Abdullah, Paolo Carlucci,
and Sudhakar Kumarasamy

Abstract Soot emission or carbon black is considered as a major challenge recently. Generally, internal combustion engines have been introduced as the main source of these materials specially in urban areas. Different methods are proposed to control soot emission of diesel engine such as DPF (Diesel Particulate Filter) which is attached to the engine exhaust line and the microstructure and size of NPs were introduced as important parameters on its efficiency. In addition, biodiesel has become widely accepted as an appropriate substitution for diesel fuel, however, the using of biodiesel fuel may change the structural characteristics of soot emission. It is observed that biofuel has higher soot oxidative reactivity, and it is more reactive than diesel fuel, which is an advantage for DPF regeneration. Smaller size of particles in biodiesel fuel soot compared to diesel fuel is mentioned as a reason for this phenomenon. For instance, it is reported that the fractal dimension of micro algae, cotton seed, waste cooking oil, eucalyptus oil, tea tree oil and diesel fuel is 2.02, 1.97, 1.85, 1.75, 1.80, 1.73, 1.69 (nm) respectively. Filtration efficiency which is a crucial characteristic of the DPFs for biodiesel fuel and diesel fuel was found to be much different. These differences are attributed to the morphology of the produced soot of the fuel burning. The source of the biodiesel fuel is introduced as an impactful parameter on engine NPs morphology and size. For example, the primary diameter of the soot emission from the above fuels is 20.1, 14.8, 14.8, 15.5, 14.5, 15, 17.5 and 20.75 nm, respectively. The result of these study reveals that structure and morphology of soot emission come from biofuel combustion is different from diesel

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fuel and these properties should be investigated for any unique biofuel resource individually. However, the smaller size of the biofuel combustion generated soot is an advantage of these fuels to enhance their oxidation reactivity.

Keywords Biofuel · Engine · Soot microstructure · Particulate matter

7.1 Introduction

Soot has been one of the environmental challenges in recent years. This is due to the negative effect of soot on environment and human health. These undesired particles that are released into the atmosphere will cause acid rain, odors, global warming, smog, and even health issues. These particles are toxic for human health, causes diseases such as asthma and even stroke. Soot is an undesired particle because of incomplete combustion of hydrocarbon (Chen et al. 2016). Soot is generated at almost all combustion processes, especially when biomass and fossil-based fuel is involved (Baldelli et al. 2020). Soot primarily comes from the diesel engine combustion. Other sources of soot include burning of coal, and charred wood, which comes from factories and oil refining industries (Niranjan and Thakur 2017). It usually formed in the fuel rich zones inside the engine cylinder (Savic et al. 2016).

Furthermore, the performance of the engine is reduced by these particles due to damaging the metal surface, decreasing the mean surface temperature, and causing wear to engine (Bassiony et al. 2016). Hence, since last decade, stringent regulation on soot and particulate matter have been implemented by many governments body such as EPA (United States Environmental Protection Agency) to control pollution (Zhao et al. 2020).

Research on soot morphology now is a popular subject, especially since decade ago after more emphatically regulation introduced in a few countries. Many control methods of soot emission have been introduced, either on the internal combustion engine characteristics itself, combustion technology or type of fuel used. Soot formation of internal combustion engine strongly depends on the type of combustion system, control process and temperature of the system (Distaso et al. 2019). In other words, different diesel engine specification, different operational practices and fuel type will change the soot characteristics (Huang et al. 2017). In this chapter, the topic is narrow to the soot morphology and microstructure recorded by microscopy techniques for different type of biofuels.

7.2 Soot Formation

Generally, soot formation comprises a few steps. The steps are pyrolysis, nucleation, surface growth or coagulation, and aggregation (Li et al. 2018) (Fig. 7.1). Pyrolysis is the thermal decomposition of materials in an inert atmosphere at high temperature conditions. This is an irreversible process and involves a change of chemical

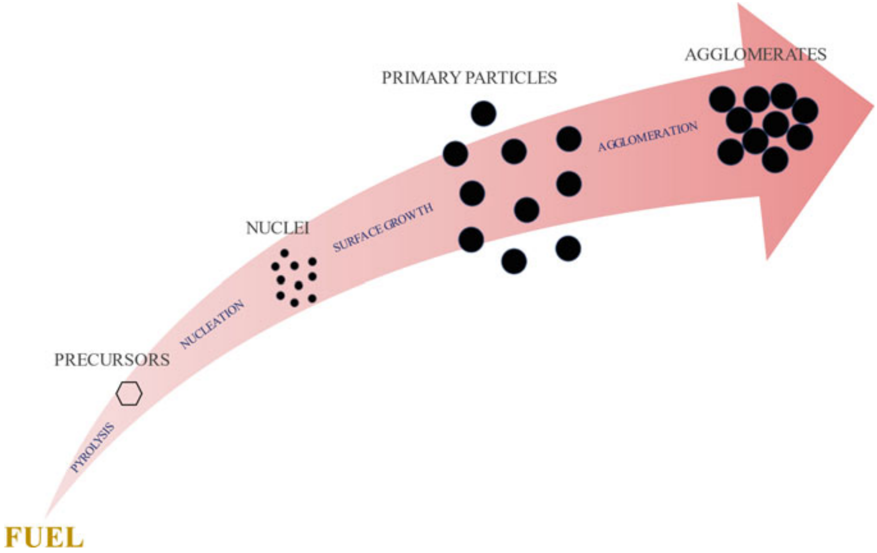

Fig. 7.1 Soot formation process

composition. The free radical mechanism plays a significant role in pyrolysis process and formation of these radicals is heavily affected by presence of O, O_2 or OH. Next process is the growth of poly-aromatic hydrocarbon (PAH). PAH molecule bond with other PAH molecule to form larger PAH molecules and becomes precursors for soot nucleation. Nucleation is the first step in formation of an embryonic species. Therefore, in this context, nucleation is the condensation of gas phase soot which form bigger three-dimensional soot particles. Next, surface growth process will occurred which means the mass of the soot particles increases due to addition of molecules from gas phase. After that, these big particles will attach to each other in a chain structure. Finally, the particles combine to form bigger clusters of primary particles. This step is called aggregation (Bassiony et al. 2016).

7.3 Soot Emission Microstructure and Morphology

Soot emitted form diesel engine can be controlled by two methods, either by limiting the soot formation during combustion or before the exhaust gas release to the atmosphere. The first method involves modification, and advancement of the diesel engine structure, or the synthesize of the new type of fuel. The second method includes using DPF (Diesel particulate filter) filter to trap soot (Niranjan and Thakur 2017). The microstructure and morphology of the soot emission are effective on the efficiency of these methods in controlling the soot emission. To understand more about soot morphology, different techniques can be utilized. According to Baldelli et al., soot

Table 7.1 Examples of microscopy and spectroscopy

#	Method
1	Scanning Probe Microscopy (SPM)
2	High Resolution Transmission Electron Microscopy (HRTEM)
3	Transmission Electron Microscope (TEM)
4	Scanning Electron Microscope (SEM)
5	Helium Ion Microscope (HIM)

morphology and maturity can be investigated by method of microscopy (Baldelli et al. 2020). Microscopy in this study refer to examination of soot in microscale from the captured images (Orhan et al. 2016). However, for diesel engine, it is recommended by Ibrahim et al., to apply the five methods which are listed in the Table 7.1 (Bassiony et al. 2016). Generally, the results of studies which utilized the TEM and HRTEM methods for characterization of soot emission have been selected for this chapter.

The most common morphological and microstructural properties of the soot particles are primary particle number (N_p) (Verma et al. 2021), radius of gyration (R_g), agglomerates mass (M_g), pre-factor (k_f), fractal dimension (D_f) (Soriano et al. 2017), primary particle diameter (d_p), aggregate size distribution, nano structure, projected area-equivalent diameter (d_a) and fringe length. Figure 7.2 shows some of the structural properties of the soot emission which is usually studied in the microstructural and morphological analysis by TEM.

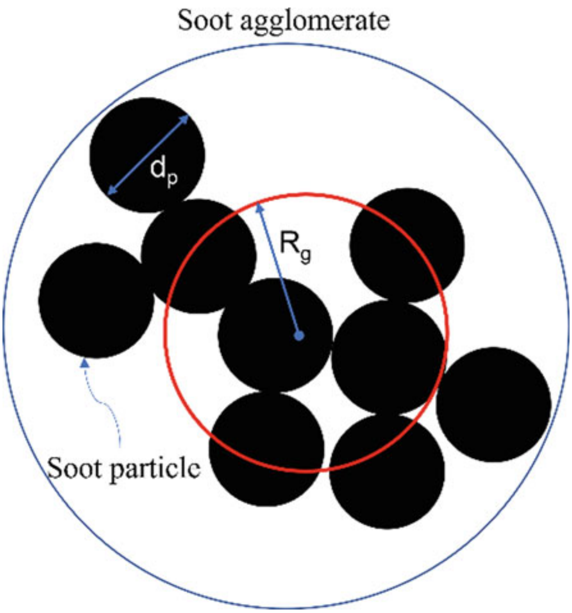

Fig. 7.2 Some of the structural properties of soot aggregates

The growth process of the soot particles can be analyzed by the structural properties of soot aggregates such as primary particle diameter, fractal dimension and gyration radius. Generally, the simple properties of the soot aggregates can be determined using processing of soot TEM images. These properties are primary particle diameter (d_p) (Verma et al. 2019), projected area (A_a) and radius of gyration of soot aggregates (R_g) (Verma et al. 2021). Some of other structural properties of soot particles and aggregates can be calculated using these three properties. The first characteristic is the primary particle number (N_p) which is calculated by Morán et al. (2018):

$$N_p = \left(\frac{A_a}{A_p}\right)^{\alpha} \tag{7.1}$$

where A_p is the projected area of the projected primary particle which is $\pi {d_p}^2/4$, α is the empirical coefficient which is used to deal with the particle overlapping effect which is set to 1.09. The other property is the fractal dimension od particles (D_f) which can be calculated by Si et al. (2017):

$$N_p = k_f\left(\frac{R_g}{d_p}\right)^{D_f} \tag{7.2}$$

The gyration radius of aggregates can be calculated using the pixel-based analysis of the TEM images and following equation (Guan et al. 2016):

$$R_g^2 = \frac{1}{m_{pixel}}\sum_{i=1}^{m_{pixel}} r_i^2 \tag{7.3}$$

where m_{pixel} is the number of pixels of the analyzed aggregates and r_i distance between each pixel of the analyzed aggregate and its center of gravity.

The agglomerates mass (M_g) of soot particles is calculated using the primary particle diameter and primary particle number in the aggregate. The density of the soot particle is assumed to be 2.0 g/cm^3.

7.4 Soot Morphology and Microstructure of Biofuels

Different fuels or additives have been studied as substitution for diesel fuel. These fuels were made from various resources and have different chemical composition compared to base diesel fuel (Jaliliantabar et al. 2020). Some examples of these fuels are biodiesel fuels, oxygenated fuel. Biodiesels is derived from animal fats or vegetable oils, and labelled as renewable sources (Zhang and Boehman 2013). It has been reported that biodiesel fuel decreases the soot emission of diesel engine (Kannan et al. 2011). Hence, it is introduced as a substitution for diesel fuel (Chandran 2020). Oxygenated fuel is any fuel with increasing of oxygen contain when oxygenates ingredients is blend (Zhang and Balasubramanian 2018). Nanofuel is defined as liquid fuel with energetic nanomaterials that behaved as potential energy carrier. Studies revealed that the use of nano additives can slightly increases engine performance and reduces emission of exhaust gases. Nano additives can enhance the ignition performance by reduction of oxidation temperature and increase of cetane number of fuels. There are few experiments which combined two or more of these additives, like (Chacko and Jeyaseelan 2020) which studied the combination of graphene oxide and biodiesel to diesel fuel.

Aside from these three categories, there are also other fuels which are not categorized by the researcher in their publication. Examples are ethylene and propene, also known as unsaturated hydrocarbon chain. This category may not increase the oxygen content, but at some point, combustion characteristic of diesel engine is improved. Bhardwaj et al. stated that fuel formulation generally effect soot morphology by three mechanism (Bhardwaj et al. 2017). Firstly, to some extended, new fuel formulation may inhibit soot precursor. Secondly by blocking PAHs building, hence stagnating the particle growth and particle agglomeration. Thirdly, fuels containing high molecular oxygen compare to commercial diesel improves oxidation of larger soot particles.

Wei et al., studied the soot morphology of oxygenated fuels (Wei et al. 2020). The fuels in their study were a commercial diesel fuel as a base and 11.5, 8.3 and 13% methanol (M11.5), dimethyl carbonate (DMM13) and dimethyl methane (DMM13) respectively as oxygenated additives. They had studied the morphology and microstructure of these fuels and stated that soot particles from all test fuels have an almost spherical shape and agglomerates in chain like shape. M11.5 fuel blend recorded the lowest and diesel fuel recorded the highest primary particle diameter. The other results for primary particle number (N_p), radius of gyration (R_g) and agglomerates mass (M_g) were in and ascending order as M11.5 < DMM13 < DMC8.3 < Diesel. These results are in accordance with the oxygen content value and cetane number of fuels (Wei et al. 2020). In other words, more oxygen during combustion improves the combustion quality by providing more oxygen to react with carbon molecules and reduces the chance of soot formation (Zhang and Boehman 2013). Same results have been reported for biodiesel fuel (Savic et al. 2016). Cotton seed, microalgae and waste cooking oil which have oxygen in their molecular structure showed similar changes in soot morphology and microstructure. Moreover, it is revealed that, the level of unistructural of soot increased by increase in the biodiesel blend percentage. The fringes of the soot are shorter and has more curved while the distance between these fringes is far more apart. Furthermore, the soot particles of biodiesel fuel become more compact, hence reduces the primary particle sized. It seems this lower size of the soot particles is not only for biodiesel fuels from plant base biodiesel fuel. The biodiesel animal fat resources (Lapuerta et al. 2012) also showed smaller primary particles size compare to diesel fuel which means more active surface. Moreover, similar to plant base biodiesel, fringe images captured to be more curvature, increasing the probability to become smaller due to exfoliation.

Table 7.2 Some of the microstructural properties of soot emission for oxygenated fuels (DMC 8.3, DMM 13 and M11.5) (Wei et al. 2020)

Fuel	D_f		D_p (nm)	R_g (nm)	N_p	M_a (g) ($\times 10^{-15}$)
	D_{fm}	D_{fp}				
D100	20.7	1.9	9.5–50	167.95	296	4.4
M11.5	1.74	1.78	7.5–42.5	125.69	144	1.4
DMC8.3	1.95	1.9	12.5–43.5	152.94	189	2.7
DMM13	1.87	1.82	6.5–41	143.58	156	1.6

Wei et al. (2020) found that all three test fuels have smaller R_g, N_p and M_a than diesel fuel. These properties suppress the soot precursors, resulting the particles collision to be less frequent. Fractal dimension for oxygenated fuel were lower value than diesel fuel. Fractal dimension measure and characterized the complexity level of the soot structure. The lower value of D_f for oxygenated fuel is maybe due to the weakened of the growth rate and relinquish p_f particle precursor concentration (Table 7.2).

The natural gas (NG) is another biobased fuel which is getting more attention by researchers as NG has potential of emitting lower harmful emission compared to fossil fuel. Moreover, NG is customarily less expensive than diesel fuel. The soot is a complex matter and posed bad effect to marine surroundings. For instance, it will increase the temperature in the artic which will rises and may melt the sea ice (Trivanovic et al. 2019). Trivanovic et al., investigated the uses of NG as fuel for marine engine. The model experiment focused on primary particle sizes (D_p), aggregate size distribution and nano structure of the soot. However, for NG to be ignited, diesel pilot was used at small quantity. The sample for diesel and NG was collected during combustion at >350 °C using thermophoresis principle. Microscopy results in this work was categorized into two category namely projected area-equivalent diameter (d_a) and primary particle diameter (d_p). d_p was calculated using pair correlation method (PCM), which instead of measuring the individual primary particle size, this method evaluates the overall average within the soot aggregates. NG in this experiment reported by Trivanovic et al. to be prone to produces slightly larger primary particles (d_p) but has smaller aggregates (d_a) compared to diesel fuel only. Generally, diesel da recorded value of 215 ± 17 nm while NG recorded value of 191 ± 12 nm. The d_p for diesel was 31 ± 1.6 nm which is lower than that for NG which has value of 34 ± 1.1 nm. Trivanovic et al. (2019) recorded clear different trend compare to normal log for NG distribution. The size distribution was in the range of 10–100 nm, while diesel distribution occurred with bell curves. Author here specified that soot oxidation of lean to slightly rich fuel–air mixture, mass concentrations and particles size of soot will be decreased as particle number concentration increased. Meaning that under oxidation, larger aggregates were disintegrated to form smaller aggregates. Authors noted that NG combustion is premixed that does not advocate soot formation during combustion. Compared to diesel, overall soot concentration was seen to be reduced in a large scale. However, since NG required small quantity of diesel to initiated, authors claimed that diesel fuel that works as a pilot also provided fuel rich zone, which induced the soot formation. The reason why NG produce lower soot mainly because of lack of nucleation site available for soot precursor. Therefore, soot particles of NG can grow bigger and have high d_p but have low tendency to agglomerate (low d_a).

However, soot particles from the petrol diesel combustion usually are nearly spherical or sometimes called as spherules. These spherules then agglomerate with other soot particles and form large aggregates. But for biodiesel, it seems to be a different story. It may have almost similar outer core and inner core, but it seems to be more reactive. Savic et al., investigated the biodiesel fuel soot morphology (Savic et al. 2016). The biodiesel fuel which was used in their study came from microalgae (MA), cotton seed oil (CSO) and waste cooking oil (WCO). MA biodiesel were tested at blend of 5%, 20% and 50% volume. The authors used microscopy analysis method in determining soot formation. Microscopy involves images investigation by transmission electron microscopy at 15,000–40,000 magnification and CCD camera to infer soot internal structure. Expected result for this method was primary particle diameter (D), fractal dimension (D_f), number of spherules/primary particles and fringe length. Their results indicated that biodiesels have smaller aggregate size of soot compared to petrodiesel. All test fuels show similar trend which the higher the engine load (%), the lower the aggregate sizes. As for D_f, no clear trend or distinction could be seen either for petrodiesel or biodiesels. Highest value obtained was MA at 50% volume with engine load at 50% while the lowest value obtained by combustion of petrodiesel at 50% load. Primary particle size (d_p) at load of 50% was 21 ± 2 nm, which aligned with published result from other researchers. For the biodiesels, all three biodiesel fuels presented lower dp compared to diesel. Microalgae (MA) showed a slightly larger d_p, compared to the CSO and WCO. But a clear trend could be seen as the more the value of MA volume %, the lower the d_p.

Bhardwaj et al. (2017) investigates the relationship between biofuels and combustion emission. The biofuels involve were paraffinic oil (PF), and blend of Di-n-butylether (DBE)/2-methyltetrahydrofuran (2-MTHF). They focused on few parameters to distinguish the differences of soot emission from biofuels combustion and diesel fuel combustion. The parameters were primary particle size, PM number emission concentration, size distributions and elemental composition of soot particles. PM mass and number of PM and size distribution were measured. At medium load, a reduction of 80% and 95% of PM mass was seen for non-oxygenated biofuel PF and 2-MTHF/DBE respectively. However, at high load, mass of PM of PF fuel only shows a reduction of 45% while 2-MTHF/DBE maintain a reduction at 95%. Primary particle size for each fuel was measured using TEM microscope. Diesel fuel recorded the highest number of mean primary particle dimeter with value of 27 nm, followed by 2-MTHF/DBE with value of 25 nm. The lowest recorded was PF fuel with value of 22 nm. These results aligned with the results of PM mass that surface activity of smaller value of particle is higher, which increase the soot oxidation rate. Hence, directly decrease the soot formation.

The palm biodiesel fuel is one of the popular types of biodiesel fuel specially in southeast of Asia. The soot for this biodiesel fuel has a typical shape, which is chain-like structure with spherical shape. This fuel produces more particles with primary particle diameter less than 20 nm. This is due to the free aromatic and unsaturated components of palm biodiesel fuel (Salamanca et al. 2012). For Kranja biodiesel fuel the size of primary particles is smaller than diesel fuel and it is reported that the internal oxidation rate of soot emission for this fuel is improved due to the more disorder structure of the generated soot compared to diesel fuel. The primary particle diameter of Kranja biodiesl fuel was 0.3 nm lower than diesel fuel (Morajkar et al. 2020). The smaller diameter of the soybean methyl ester (SME) and canola methyl ester (CME) biodiesel fuels is also reported however the primary particle diameter for CME had been smaller than SME (Merchan-Merchan et al. 2012).

However, the smaller size of soot emission for biodiesel fuel is reported in most of the studies but there are also some studies which stated the different results. Hwang et al., studied the microstructure of soot emission for a diesel engine fueled by three different biodiesel fuels. Their results showed that the primary particle size of Kranja (22.41 nm) and Jatropha (22.39 nm) biodiesel fuels is bigger than the diesel fuel (22.27 nm) while for waste cooking oil biodiesel fuel (20.70 nm) is smaller than diesel fuel (Hwang et al. 2019). They stated the oxygen content and higher surface oxidation reactivity of biodiesel fuels as the reason for smaller primary particle diameter of waste cooking biodiesel fuel. Then, the oxidation is not only started at the surface of the particle, but it occurs in the inner layer and core of the particles due to this oxygen content of biodiesel fuel. The reason for slightly bigger size of the Kranja and Jatropha biodiesel fuels soot particles was the higher value of unburned hydrocarbons emissions.

A comparison between the biodiesel fuel from soy and palm oil sources with the conventional diesel fuel, gas to liquid fuel from natural gas shoed the higher oxidation rate of the biodiesel soot. One reason for this higher oxidation reactivity rate for biodiesel fuel as it was mentioned earlier is the smaller size of the soot emission for biodiesel fuel (Soriano et al. 2017). It was also approved that even diesel fuel and natural gas derived liquid fuels with similar physiochemical properties have different microstructural and morphological characteristics (Soriano et al. 2017).

The higher soot oxidation rate of biodiesel fuel due to its inherent oxygen content prevent the surface growth of the soot particle and formation of big soot particles (Verma et al. 2019). Furthermore, the higher oxygen content of biofuel will cause the formation of smaller soot particles. For instance, the reduction of the primary particle diameter for biodiesel with 2.2 and 14% of oxygen content were 2.4 and 21%, respectively (Verma et al. 2019). Moreover, the particle mass in the aggregates were reduced due to smaller size of the particles for biodiesel fuel. The amount of oxygen content of the biodiesel is an effective parameter on most of the microstructural properties of soot emission (Verma et al. 2021).

Some of the microstructural properties of different biodiesel fuel are shown in the Table 7.3. As it can be seen in the Table 7.3, almost the D_f of the biodiesel fuels from different resources is higher than diesel fuel. On the other hand, the average of d_p for these biodiesels fuel is lower than diesel fuel. However, the D_f, R_g and d_p for

Table 7.3 The microstructural properties of soot emission for different type of biofuels

References	Fuel	D_f	R_g (nm)	d_p (nm)
Savic et al. (2016)	Diesel	1.72–1.85	NA	18.3–23.2
	Micro algae	1.81–2.22		12.4–27.8
	Cotton seed	1.91–2.02		13.4–16.2
	Waste cooking oil	1.82–1.92		14.1–15.5
Zhang et al. (2017)	Diesel	NA	NA	14.26–20.28
	Coconut (B100)			13.46–17.26
	B20			13.96–19.36
	B50			13.85–17.73
	B96T4			13.6–16.45
	B90T10			12.59–15.96
Rohani and Bae (2017)	Diesel	1.689	48–55	17–21
	Orange oil	1.649	33–40	15–16
	Eucalyptus oil	1.75	36–42	14–15
	Tea tree oil	1.798	33–39	14–16
	Coconut	1.702	49–54	16–19

biodieel fuel are different for various biodiesel fuel. One effective parameter which is highlighted in the literature for different structural properties of soot emission for biodiesel fuel is the difference in their oxygen content value (Verma et al. 2020).

Alcohol base biofuels are the other oxygenated biofuels which can be added to diesel fuel (Xu et al. 2020). Similar to the findings for the biodiesel fuel, the smaller size of the soot particle for alcohol based fuels is reported (Luo et al. 2018). It is reported that the mean diameter, mean fractal dimension and radius of gyration for soot particle from combustion of bioethanol fuel were reduced approximately by 21.4, 4.1 and 7.6%, respectively compared to diesel fuel (Fayad et al. 2020). The primary particle diameter of diesel fuel blended with n-octanol were reduced by 1.3 and 5.4% for diesel fuel blended with 15 and 30% n-octanol, respectively (Zhou et al. 2022). The fractal dimension for these n-octanol/diesel blend fuel were reduced by 1.6 and 7.8% for same fuels. The primary particle diameter and fractal dimension were decreased with increase in the percentage of the n-octanol blended diesel fuel which was due to the increase in the oxygen content of the fuel blends.

7.5 Conclusions

In this chapter the effect of the different biofuel on soot emission microstructure and morphology in diesel engine have been introduced. Based on the outcome of this chapter following conclusions can be stated:

- The morphology and microstructure of the soot emission for biofuel is different from diesel fuel. Generally, the soot emission of the biofuel is smaller than that for diesel fuel.
- The smaller size of the soot emission for biofuel increases its oxidation reactivity due to providing higher surface area for oxidation. This improves the performance of the DPF for biofuel compared to the diesel fuel. Moreover, the inherent oxygen content of the biofuel causes the higher oxidation rate of biofuel compared to diesel fuel. This inherent oxygen content of biofuel makes a significant difference between oxidation of diesel fuel and biofuel which is the oxidation occurred not only from the surface of the particle but in the inner layers of the particle.
- Although the effect of biofuel on soot microstructure and morphology for biofuel is similar, different results of these properties is reported for different biofuel.
- The oxygen content of biofuels is the main contributor of their higher soot particle oxidation rate. The oxidation rate of soot particle increases with increase of the biofuel oxygen content percentage.

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Chapter 8
Engine Performance and Emissions of Fuels from Waste Products for Sustainable Environment

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Abstract Recycling waste products is necessary to sustain the environment without being polluted. This chapter includes the recycling of vegetable waste, fruit waste, plastic waste and engine oil waste to produce alcohol, pyrolysis plastic oil and treated waste engine oil. Various proportions of these fuels are blended with diesel and tested for solubility. The properties of the fuel blends are found as per the guidelines of ASTM standards. By comparing the properties such as cetane number, energy content and kinematic viscosity considering diesel fuel as base, competent blends are chosen. Performance, combustion and emissions of fully instrumented CI engine is performed by fueling the chosen blends under various brake powers. Results of the properties test indicates that the blends containing 15% bioethanol, 85% of diesel along with pyrolised plastic oil of 20% (BE15RPO20); pyrolised plastic oil of 75% along with 25% of biobutanol (RPO75BB25); treated waste engine oil 20% along with 15% of bioethanol and 85% of diesel (BE15PWEO20); treated waste engine oil 75 and 25% biobutanol (PWEO75BB25) are found to be competent. Out of the four, the two blends containing 15% bioethanol are found to be producing 5.6% higher thermal efficiency. Other two blends are producing 0.7 and 1.7% higher thermal efficiencies. All the four blends produce 6–10% low emissions of oxides of nitrogen at higher brake power higher than 70%. However, the emissions at lowest brake power are found to be marginally higher. This replaces around 80% of diesel fuel for fueling CI engines, thereby decreases pollution to environment.

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8.1 Introduction

Renewable liquid fuels are to be found out to replace the dependency of fossil fuel. To meet out the liquid fuel requirement, India is importing crude oil and to reduce the dependence as well as to reduce the pollution caused by the emission from the automotive, alternate (Nouni et al. 2021) solution is necessary. Alcohols are one among the liquid fuels which are renewable and can also be manufactured at a competent cost from biomass. Researchers attempted the blends of diesel along with ethanol and butanol leaving the methanol as methanol is not allowed to use commercial India. Most studies utilized use of alcohol along in Compression Ignition Engines (CI). Out of these diesel-ethanol blends and diesel butanol blends are most attractive. Significance in utilizing ethanol (Prathipati et al. 2021) and butanol is that manufacturability from biomass and renewable. The limitations of using these blends are very marginal when the percentage of ethanol in diesel-ethanol blends is 15% and of butanol is 20%. Higher than this volume are reported as the additional usage of additives for lubricity, solubility (Sakthivel et al. 2018) and energy content. One among the less utilized waste products are the pyrolised plastic oil and biofuel manufactured from waste products. Treatment of waste engine oil was performed (Prabakaran 2021a) along with desulphurization to obtain a fuel as diesel-like. This fuel was fueled in diesel engine and tested. The report showed that the yield from the treatment was about 60% of the volume of the input. Also, the performance engine fueled with the diesel-like fuel was found competent to diesel performance. Microwave pyrolsis method was adopted to treat the used automotive lubricating oil to obtain fuel for CI engines. The author reported that the temperature of the process and the yield are interdependent. The report listed the safe disposal, treatment and the further analysis of the process. The author extended the study in analyzing the parameters involved in the microwave assisted pyrolsis of the waste automotive oil. The author attained (Arpa et al. 2010) a yield of 88% by weight of the input oil by altering the process parameters. This study tested the composition of the treated oil and reported that the oil contained lighter aliphatic and as well as aromatic hydrocarbons, low sulfur and contaminants free. The report included the continuous treatment of the oil with electrical power. A study was (Effendy et al. 2021) performed the thermal analysis for the treatment of waste engine oil and the yield reported in this study was 77% and the temperature used for this yield was reported as 550 °C. Utilization of this treated oil was performed by blending with diesel fuel. Various compositions of the blends of the treated oil and diesel were prepared and the properties were tested. It was reported that the highest energy content was obtained by blending 20% of the treated oil into diesel fuel. This study tested the FTTR test for the lubricity and reported that fuel blend possessed competent viscosity with respect to diesel engine fuel. Another unutilized waste product is plastic wastes. The annual report about plastic waste (Bhattacharya et al. 2018) indicated that 33, 60,348 tons/annum is generated and are to be recycled for various utilizable purposes. To decrease this impact a policy has been made to use only higher thickness plastic bags (greater than 50 microns) for carrying light materials. These wastes are accumulated in the land and preventing the percolation of rain water into the ground. Recycling of waste plastic bags, the best suited process is pyrolysis. A study was performed by the utilization of pyrolised (Vanapalli et al. 2019) plastic oil and diesel as fuel for engine on performance and emissions. Author used the plastic oil up to 20% along with diesel and tested in three speeds 1200, 1500 and 1800 rpm in three load conditions with constant compression ratio. The report showed that the blend containing 20% plastic oil produced low smoke, brake specific fuel consumption, high cylinder pressure and low NO_X. However, the author stated that the increase in engine speed resulted in higher oxides of nitrogen from the engine. An assessment was performed by using the plastic pyrolytic oil (Melikoglu and Turkmen 2019) and diesel up to proportions or 50% to fuel CI engine. The author formulated the blends of plastic oil and diesel, tested the compound analysis in gas chromatograph. The test engine results depicted that the increase in the proportions of plastic oil increased the thermal efficiency, decreased the fuel consumption at higher load conditions. Also, it was reported the plastic oil in the blend increased the heat release, ignition delay and cylinder pressure. However, a marginal increase in carbon monoxide from the engine was observed. Four types of plastics were taken as (Boopathi and Gopinath 2021) input such as: High-density polyethylene, low-density polyethylene, polypropylene and styrene for the recycling into plastic oil by the pyrolysis method. The author studied the properties of the plastic oil from the four sources and tested in CI engine for the performance and emissions. The report depicted that polypropylene pyrolysis oil was found superior to other three resources with respect to the properties. Hence, the author continued the research work for testing the blends of plastic oil and diesel in various proportions for performance. It was reported that there was increase in the cylinder pressure and heat release rate by the increase in the proportions of plastic oil in the blend. Also, it was reported that there was an increase in CO, HC & NO_X. This was attributed to the presence of unsaturated HC and higher carbon atoms present in the plastic oil. The author continued the experiments by hydrogenating using various catalysts to reduce unsaturated carbon in PPO. Zeolite A was utilized for the treatment of waste plastic into oil and used as fuel for (Miandad et al. 2017) CI engine with diesel waste plastic oil in the proportions of up to 30%. The engine produced low oxides of nitrogen and hydrocarbon when fueled with fuel blend containing 20% of plastic oil. This also produced higher thermal efficiency and higher fuel consumption. The author concluded that the fuel blend of 20% plastic oil along with diesel. Bioethanol can be manufactured from various resources such as waste straw of wheat, sorghum distillery, potato peel off, waste fruits and waste vegetables other than from corn. This study treated the input material by wet torrefaction (Huang et al. 2015) and this includes the acid treatment of 0.01–0.02 M sulfuric acid. The author reported that this method improved calorific value. The yield of bioethanol by this method was stated as 19.21 g/L. Bioethanol production from food wastages was attempted by a researcher. The author had considered one country as a model and projected the food wastages and the conversion of these food wastages into bioethanol. Approximately 1 million liters will be wasted without conversion of the food wastages up to 2030. These wastages are also added to the cereals wastages projected in 2023 for the wastages that will be produced from wheat, maize, rice and potatoes, hence, conversion is necessary to utilize the diesel bioethanol blend containing 10% of bioethanol. Bioethanol was produced using sweet potato by diluting 1:1 by enzymatic hydrolysis with alpha-amylase at a temperature of 90 °C and at a (Prabakaran 2020) temperature of 60 °C glucoamylase enzymes, fermentation at 30 °C along with 3.3 kg/l of cerevisiae. The yield of bioethanol from this process was reported as 10,598 L per hectare. Blending of bioethanol into diesel is one among the alternate fuel to replace diesel from 1980 onwards. The increase in the bioethanol content decreases the cetane number, energy content, and kinematic viscosity and increases the heat of vaporization. Also, higher than 20% by volume of ethanol (Prabakaran 2021b) usage in the diesel-bioethanol blend suffers the separation of bioethanol from diesel into two liquid phases. To prevent this, the additives (Prabakaran and Vijayabalan 2016) and co-solvents are necessary. Many researchers attempted to fuel diesel-bioethanol blends with various additives and co-solvents for the improvement of the decrease in the properties of the final blend. This study considers the base fuel as 15% of bioethanol and 85% of diesel to blend with plastic pyrolysis oil and treated waste engine oil. This is to prevent the phase separation, lubricity problems and loss of power due to higher bioethanol content. Biobutanol is another alcohol which is possessing superior properties compared to bioethanol. A study was (Zheng et al. 2015) conducted for the manufacturing of biobutanol from the waste resources, to maintain sustainability and to prevent land filling by the wastes. The major limitations stated are the low yield rate of the available process and this can be ratified by the utilization of the segregated wastes as input. This is enabling the proper solvent utilization to convert the accumulated biomass into biobutanol for obtaining higher yield rate. This study also includes the utilization of diesel-biobutanol blend and the performance of CI when fueled with these blends. The author concluded that the usage of diesel-biobutanol fuel blend can approach to flexi fuel applications in the forthcoming future. A detailed review was performed in a study (Balasubramanian 2019) of producing biobutanol from biomass feed stocks and their challenges to improve the yield. The author followed various methods to produce biobutanol such as fed batch fermentation, fermentation on continuous basis and fermentation with two stages. The study included the various recovery methods of biobutanol such as adsorption, stripping by gas, pervaporation with their respective challenges. The effects of sporulation and solventogenesis were also depicted. This study (Qin et al. 2018) stated that the significance of this work was to eliminate the challenges involved in the usage of Clostridia. This study concluded with the economic analysis of these processes for the further study. A research was performed to analyze the major challenges involved in the production of acetone butanol through (Abedini et al. 2020) fermentation. This study stated the recent advancement with the technoecomonical and considering the environmental impacts along with commercial feasibility. The raw material utilized for this study was lignocellulosic biomass for the production of biobutanol. Most researchers studied diesel-bioethanol and diesel-biobutanol blends to replace diesel fuel for fueling compression ignition engines. Ethanol was initiated to fuel CI engines along with diesel had taken progress from 1985 onwards.

Researchers attempted various proportions of ethanol along with diesel using additives and co-solvent for improving the properties of the final blend to suit diesel fuel properties. A novel attempt (Vivek et al. 2019) was made by using butanol as co-solvent for utilization of diesel-ethanol blends. Diesel-bioethanol was utilized as fuel containing up to 45% of volume with n-butanol as co-solvent (Huang et al. 2009). The author studied the solubility and properties analysis of the various proportions of the diesel-bioethanol blends and tested the solubility under three different temperatures (5, 15 & 25 °C). The author compared the properties of these blends and concluded that blend containing 45% bioethanol can be used as fuel along with 10% n-butanol as co-solvent to prevent the phase separation of ethanol from diesel under low temperatures. Similar study (Prabakaran 2019) was performed by using the pyrolised waste engine oil as additive to diesel-bioethanol blends containing 15% bioethanol and 10% pyrolised waste engine oil possessed closer properties with respect to diesel fuel. Also, it was reported that this blend produced competent performance and emissions in comparison to that of diesel at higher brake power conditions. One more study was performed by adding biobutanol into.

The novelty in this study is that the ethanol and butanol used is prepared from residues of vegetable cut wastes, fruits and food. This study eliminates 50% use of diesel for fueling compression ignition engine as ethanol cannot be blended directly to recycled waste engine oil and pyrolised plastic oil. This study decreases the impact of waste products on environment. Also, the recycling of plastics increases the opportunity of ground water level improvement by rain water percolation. Hence, a base blend of diesohol containing 15% of ethanol has been considered for blending with the recycled waste engine oil and pyrolised plastic oil.

The objective of this study is to replace diesel by recycled plastic oil (RPO) and pyrolised waste engine oil (PWEO) along with biobutanol (BB), bioethanol (BE) for various proportions. The prepared blends are tested for essential properties and the suitable blends are chosen comparing diesel. The suitable blends are then tested in a compression ignition engine for performance under various brake power conditions and the results are compared for further suggestions. The test has been performed without modifying the engine operating parameters.

8.2 Materials and Methods

This section includes the fuels used, preparation of blends, testing the properties, Experimental Set up and Uncertainty analysis. Diesel used in this study is Bharat Stage VI diesel of low sulfur procured from the commercial stockiest. The fuels used in this study are Bioethanol (Prabakaran 2020), Biobutanol (Vivek et al. 2019) manufactured from the waste vegetables, waste fruits and waste food. This has been procured from the bulk manufacturing bio recycling facility with the properties tested as per the American Society of Testing and Materials (ASTM). This section includes: Base fuel preparation such as diesel-bioethanol blends (BE) and diesel-biobutanol blends (BB); Blending of diesel-bioethanol blends with Pyrolised Waste

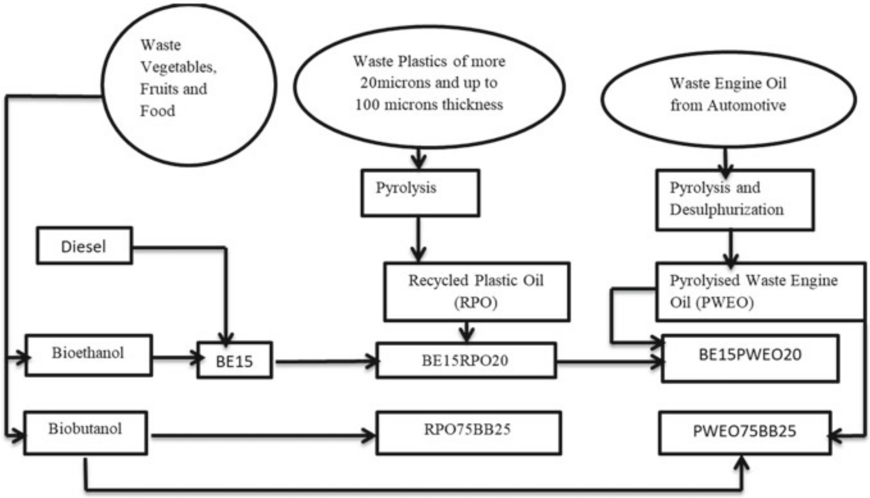


Fig. 8.1 Flow chart of the fuel blend preparation

(Prabakaran 2019) Plastic Oil (RPO) and Pyrolised Waste (Melikoglu and Turkmen 2019) Engine Oil (PWEO), Blending of diesel-biobutanol blends with RPO and PWEO in various proportions in increments of 5%. The prepared fuel blends are then tested for the essential properties such as Kinematic viscosity, Energy Content, Cetane Number and Flash Point. Before the property test, the fuels are tested for stability in controlled environment of 25 °C for 20 days to ensure single liquid phase of the blends without suffering from separation into two or more layers of liquid phase. Figure 8.1 depicts the schematic representation of the work as a layout. Figure 8.2 indicates five representative samples of the fuel blends prepared in this study.

8.2.1 Base Fuel Preparation

Bioethanol has been blended with diesel using burette filled with bioethanol and diesel in a closed container supported with magnetic stirrer. This process has been performed with full attention such that bioethanol dispersed is being prevented from vaporizing to the atmosphere. The stirring of the fuel blends are continued for 5 min @1500 by magnetic stirrer (Vivek et al. 2019) for three to four times with a time interval of 10 min. This is performed to improve the homogeneity of the blends prepared. Bioethanol from 0–20% in increments of 5% are prepared and kept undisturbed for solubility. Similarly, biobutanol has been blended with diesel and stirred well with magnetic stirrer and kept for solubility test in 25 °C for (Abedini et al. 2020) 20 days.

Fig. 8.2 Representative samples of fuel blends kept at 25 °C for a period of 20 days

Table 8.1 Various proportions of blends

FUEL	Proportions in percentage by volume					FUEL	Proportions in percentage by volume					FUEL	Proportions in percentage by volume				
D	95	90	85	80	–	**BE15**	95	90	85	80	75	**BB25**	5	10	15	20	25
BE	5	10	15	20	–	**RPO**	5	10	15	20	25	**RPO**	95	90	85	80	75
D	95	90	85	80	75	**BE15**	95	90	85	80	75	**BB25**	95	90	85	80	75
BB	5	10	15	20	25	**PWEO**	5	10	15	20	25	**PWEO**	5	10	15	20	25

8.2.2 Testing the Properties of Fuel Blends

Fuel blends are tested for essential properties after the test for solubility. Kinematic viscosity of the fuel blends are tested by Red wood viscometer, Energy Content by Bomb Calorimeter, Ignition delay method is used for arriving Cetane Number and Flash point by closed cup apparatus. The list of instruments (Vivek et al. 2019) with the uncertainty is listed in Table 8.2.

For each blend five samples are being tested and the average of the five has been considered for analysis and comparison. Properties of various proportions of diesel-bioethanol, diesel-biobutanol, diesel-bioethanol-RPO, RPO-biobutanol, diesel-bioethanol-PWEO, PWEO-biobutanol blends are presented in the Tables 8.3, 8.4, 8.5 and 8.6.

Table 8.2 List of instruments used for testing of properties of fuel blends

Property	Instrument used	Accuracy	Percentage of Uncertainty (%)	ASTM standard
Flash point, ºC	Pensky-Martens closed cup apparatus	±0.1 ºC	±0.05	ASTM D975
Calorific value	Bomb calorimeter	1 J/g	±0.1	ASTM D240-19
Cetane number	Ignition delay principle	±0.1	±0.07	ASTMD976/ ASTMD4737

8.2.3 Experimental Set up

The compression ignition engine used for the testing of fuel blends and diesel as base fuel is a fully instrumented four stroke water cooled (Fig. 8.3) and controlled with eddy current dynamometer for varying the load conditions. Air preheater is installed in the suction side of the engine to maintain the temperature in the range of 80–85 °C. This is to improve the pre combustion temperature of the blends containing alcohol-which is generally possessing higher heat of vaporization. The temperature of the intake air and the out coming air in the air preheater are indicated with digital output. Mass flow rate of air in the intake manifold has been measured and monitored by orifice plate and U tube manometer. The pressure in the cylinder during the engine operation is measured by Kistler water cooled pressure transducer and the crank position at any instant is measured by encoder. AVL data acquisition system has been installed in the lines which captures the signals of pressure in combustion chamber, thermocouples, orifice place, and processes the data input into required

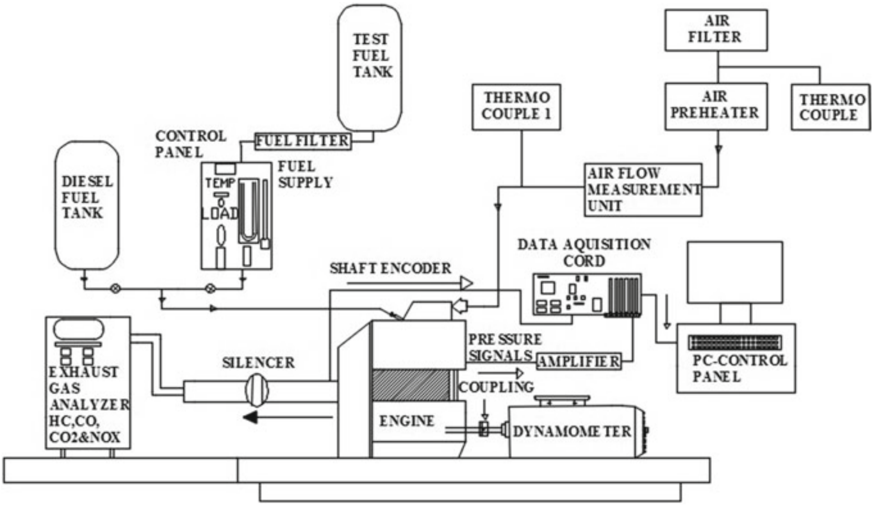


Fig. 8.3 Schematic layout of experimental set up

data such as thermal efficiency, pressure with respect °CA, HRR. The exhaust gases from the engine are captured and analyzed using AVL Di Gas analyzer. Smoke levels of the engine are captured and analyzed by the AVL smoke meter. Specifications of the engine, gas analyzer, pressure transducer (Table 8.1 Appendix), eddy current dynamometer (Table 8.2 Appendix), crank angle encoder (Table 8.3 Appendix) and gas analyzer are listed in the Tables 8.5, and 8.6.

8.2.4 Uncertainty and Error Analysis

The total uncertainty of the experiment (Huang et al. 2009) has been obtained by root mean square method and the individual uncertainties are ±0.12% for engine speed; ±0.49% for the load conditions; ±0.62% for mass flow rate of air into the cylinder; ±0.82% for mass flow rate of the fuels; ±0.27% for thermal efficiencies; ±1.1% for emissions of oxides of nitrogen and ±0.8% for emissions of carbon monoxide.

$$\text{Total uncertainty} = \sqrt{0.12^2 + 0.49^2 + 0.62^2 + 0.82^2 + 0.27^2 + 1.1^2 + 0.8^2 + 0.25^2 = 2.1\%}$$

Before utilization of each fuel blend the engine is run for 15 min as warm up cycle and after the steady state conditions, each set of experiments are performed. The coolant temperature is maintained in the range of 80–90 °C with humidity of 70–73%. The digital monitors are verified for constant values of the specific parameters. The ambient temperature in the test room is in the range of 30–35 °C and atmospheric pressure.

8.3 Results and Discussion

This section includes the subsections viz: Results of the solubility and Properties, Results of the Performance parameters, Results of the combustion parameters and Results of Emissions.

8.3.1 Results of the Solubility and Properties

Blends of recycled waste engine oil-alcohol (Balasubramanian 2019) and pyrolised plastic oil-alcohol are tested in the range of 5–40 °C for a period of 20 days in the

Table 8.3 Properties of the base fuels

Property/Fuel	Diesel	Bioethanol	Biobutanol	RPO	RPO95 BB5	RPO90	RPO85	RPO80	PWEO
	D	BE	BB			BB10	BB15	BB20	
Kinematic viscosity	4.0	1.6	2.6	5.2	5.09	5.065	4.95	4.75	7.8
Energy content	42,500	28,590	34,000	44,800	44,270	43,780	42,960	42,570	34,000
Cetane number	50	8	25	54	52.4	50.6	48.8	46.4	64
Flash point	71	13	35	82	79.2	76.8	74.6	72.7	210

Table 8.4 Properties of diesel bioethanol & diesel biobutanol blends

Property/Fuel	Diesel	Bioethanol	BE 5	BE10	BE15	Biobutanol	BB5	BB10	BB15	BB20	BB25
Kinematic viscosity	4.0	1.6	3.92	3.85	3.8	2.6	3.9	3.85	3.78	3.72	3.69
Energy content	42,500	28,590	41,100	40,380	39,940	34,000	42,300	41,840	41,430	41,050	40,820
Cetane number	50	8	47.8	46	44.4	25	49	48.4	47.8	47.2	46.5
Flash point	71	13	70.1	69.5	67.8	35	69.5	68.6	67.9	66.8	66.2

Table 8.5 Properties of BE15 with RPO & PWEO in various proportions

Property/Fuel	BE15	RPO	RPO—volume in percentage					PWEO	PWEO—volume in percentage				
			5	10	15	20	25		5	10	15	20	25
Kinematic viscosity	3.8	5.2	3.9	3.95	4.1	4.15	4.34	7.8	4.5	4.7	4.95	5.1	5.2
Energy content	39,940	44,800	41,050	42,980	44,100	44,800	46,200	34,000	39,100	38,900	37,700	37,100	36,810
Cetane number	44.4	54	46.1	47.4	49.2	50.1	50.4	64	45.6	46.2	47.1	47.9	48.3
Flash point	67.8	82	68	69.7	70.2	71.1	72.1	210	72.1	76.4	80.5	83.4	86.8

Table 8.6 Properties of Blends of RPO, PWEO and BB for chosen proportions

Property/Fuel	BB25	RPO	PWEO	RPO75BB25	PWEO25BB75
Kinematic viscosity	3.69	5.2	7.8	4.5	4.55
Energy content	40,820	44,800	34,000	43,600	39,800
Cetane number	46.5	54	64	47.5	51.5
Flash point	66.2	82	210	79.2	92.4

temperature controlled atmosphere. The results show that the blends kept in this range of temperature are found in a single liquid phase and not suffering a phase separation. Figure 8.1 show the representative sample of the blends after 20 days.

The essential properties of the prepared blends are tested as per the ASTM standards and listed in the table. From the Tables 8.3, 8.4, 8.5 and 8.6 it is seen that the blends containing 15% of bioethanol and 20% of recycled plastic oil; 25% of biobutanol and recycled plastic oil of 75%; 15% of bioethanol and 20% pyrolised waste engine oil; 25% of biobutanol and 75% of pyrolised waste engine oil are competent when compared with diesel properties. The essential properties considered for the comparison are cetane number, energy content, kinematic viscosity and density. The addition of recycled plastic oil into diesel-bioethanol blends containing 15% ethanol increases the energy content, cetane number and density. However, the volume increase above 20% increases the density and kinematic viscosity higher than the limit compared to diesel engine fuel. These properties are considered as important for the fuel atomization and fuel consumption for any compression ignition engine. Similarly, the addition of biobutanol decreases the kinematic viscosity and density of recycled plastic oil and up to 25% volume the properties are found competent with respect to diesel. Further increase in the addition of biobutanol into recycled plastic oil decreases the energy content and cetane number which is not attractive for a fuel. Hence, this limit has been considered as the maximum possible limit for this fuel blend. Similar results are found by the addition of pyrolitically treated waste engine oil into blend containing 15% of bioethanol and the addition of biobutanol into pyrolitically treated waste engine oil. Tables 8.3, 8.4, 8.5 and 8.6 presents the properties of base fuels and fuel blends used. Kinematic viscosity in mm^2/s, Energy Content in kJ/kg, Flash Point in °C and cetane number no units.

The base blends considered are BE15RPO20, RPOBB25, BE15PWEO020 and PWEO75BB25.The novelty in these blends is that two blends are containing the diesel fuel up to 85% volume in the base of 15% bioethanol as bioethanol is not blending with the recycled plastic oil and pyrolitically treated waste engine oil and the other two blends are containing only waste treated fuel and bio manufactured fuel. This replaces the diesel fuel 100% to fuel compression ignition engine. The listed four blends are tested for performance, combustion and emission characteristics in the standard compression ratio of 17.5:1 and two steps higher as 19:1 and 20.5:1 for suiting the parameter compression ratio of the engine to fuel these four chosen blends.

8.3.2 Performance Parameters

This section includes the analysis of thermal efficiency, exhaust gas temperature and the specific fuel consumption of the test engine operated under five brake power conditions. The base fuel considered is diesel fuel. Initially for the four blends the brake thermal efficiency are compared with diesel for various proportions of bioethanol, biobutanol. The chosen four blends are confirmed with respect to the produced brake thermal efficiency also other than the comparison of properties. The chosen four blends are found producing higher thermal efficiencies compared to that of those produced by other fuel blends with different proportions. Seven set of thermal efficiency graphs are generated and analyzed to authenticate the chosen the four blends with respect to diesel by fueling in compression ignition engine. The addition of bioethanol into diesel increases the rate of atomization of fuel which is due to decrease in the kinematic viscosity, density and the combustion efficiency. The trend of the brake thermal efficiency are found increasing up to 15% volume of bioethanol addition into diesel, beyond this limit i.e., for the blend containing 20% bioethanol and 80% of diesel show a decrease in the brake thermal efficiency. This is due to t dominance created by the presence of bioethanol which results in higher heat of vaporization. This decreases the temperature of the combustion chamber and thus decreases the rate of oxidation, although the fuel contains higher content of oxygen and possess other properties competent compared to diesel fuel. The addition of biobutanol into diesel fuel also increases the thermal efficiency, up to a volume of 25% of biobutanol in the blend. This is due to the increase in the rate of atomization of the fuel blend resulted from the decrease in the kinematic viscosity, density and oxygen content. Biobutanol also possesses higher heat of vaporization compared to diesel fuel. This leads to low temperature of the combustion chamber after the injection of fuel during the injection of fuel blend, this resulted in low rate of oxidation and hence, low thermal energy release compared to other proportions of fuel blends. Hence, the limit of 25% volume of biobutanol has been considered as maximum limit along with diesel. However, biobutanol is blend able with recycled plastic oil and pyrolitically treated waste engine oil and hence, biobutanol has been blended with these two waste treated fuels and tested for thermal efficiency under five brake power conditions. Instead of bioethanol direct blending with the two waste treated oils the blend of diesel bioethanol containing 15% of bioethanol is considered as base blend and the proportions of treated waste engine oil and recycled plastic oil are increased in the increments of 5%. Biobutanol has been considered as direct blending and the proportions of two waste treated oils are increased in increments of 5%. The brake thermal efficiency results are analyzed and considered as base for choosing the fuel blends.

It is seen from the Fig. 8.4 that the addition of PWEO increases BTE uniformly for higher BP. The BTE produced by BE15PWEO20 are similar compared to diesel at tested load conditions. This may be by the bioethanol in the fuel blend which increases the rate of combustion and the presence of PWEO improves the essential properties. The increase in the essential properties increases the BTE significantly.

Fig. 8.4 Variation of BTE of 15% bioethanol and 20% treated waste engine oil blends

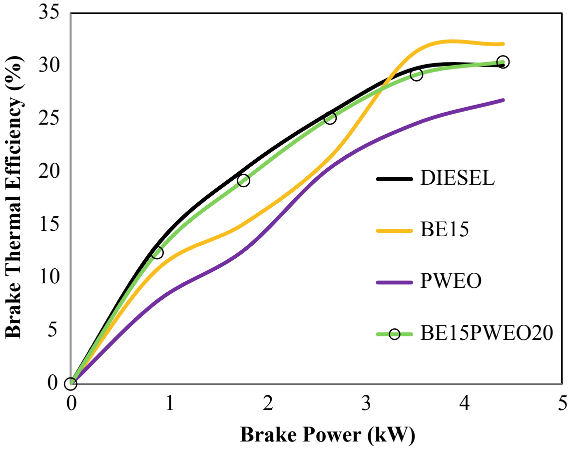


Table 8.6 depicts the properties of the blends of BE15 and PWEO. This makes the fuel blend BE15PWEO20. The improved properties are able to overcome the dominance of heat of vaporization of bioethanol present. From the properties Tables 8.3, 8.4, 8.5 and 8.6 it can be observed that the properties of BE15PWEO20 are competent to diesel. This blend possesses the higher cetane number out of the three blends, an increase in the viscosity of 16.5% compared to diesel and higher oxygen content due to the presence of ethanol cum higher octane rating results in higher combustion rate. This in turn improves the rate of thermal energy release and results in higher thermal efficiency. The increases in the thermal efficiencies of the fuel blends are found to be BE15PWEO – 5.6%; BE15RPO20 -4.8%; RPO75BB25 – 0.7%; PWEO75BB25 – 1.7% in comparison to diesel at rated power conditions. These increases in thermal efficiencies are attributed to the closer kinematic viscosity, cetane number and flash point. The kinematic viscosity provides the atomization of fuel blend and prepares the pre-combustion phase homogeneity; cetane number provides the start of combustion and the flash point the trigger in the rate of combustion. The cumulative impact is found to be the reason for the increase in thermal efficiency (Fig. 8.5).

It is observed BE15 addition into RPO20 increases the thermal efficiency. This is due to the increase in the necessary properties for a diesel engine fuel. This results in suppression of heat of vaporization. This leads to the higher rate of oxidation and combustion. These results in increased rate of heat energy release and thus increase BTE. The BTE of BE15RPO20 is found similar to that of base fuel at tested conditions indicating that this fuel blend can replace diesel. This decreases the volume of diesel consumption by 85% from fueling full diesel operation for compression ignition engines.

From Fig. 8.6 it is seen, the lowest thermal efficiency has been produced by PWEO which is due to the higher kinematics viscosity, leads to poor atomization and low rate of heat energy. The increase in biobutanol up to 25% decreases the kinematic viscosity and increases rate of combustion in the combustion chamber. This increases the BTE and this eliminates considerable consumption of diesel by RPO and the bio

Fig. 8.5 Variation of BTE of 15% bioethanol and 20% Recycled Plastic Oil

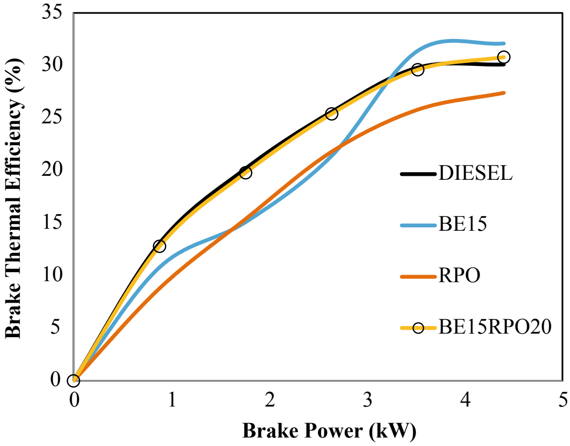
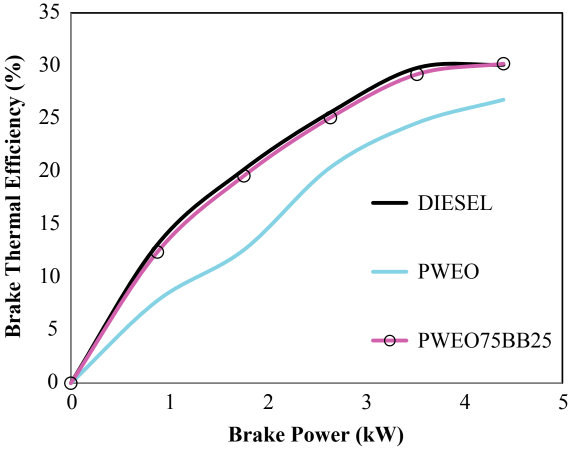


Fig. 8.6 Variation of BTE of 25% biobutanol and 75% of treated waste engine oil



manufactured biobutanol manufactured using vegetables and fruits wastes. The BTE of PWEO75BB25 is found to be closer to diesel. These fuel blends are progressed for combustion and emission characteristics.

Figure 8.7 depicts the change in BTE versus change in BP for the fuels RPO75BB25, RPO. Lowest BTE are observed by fueling RPO, which can be attributed to higher kinematic viscosity and density possessed. The addition of biobutanol into RPO decreases the kinematic viscosity and density. This decrease in these properties improves combustion rate of the fuel injected during the injection time. This may be by the presence of higher amount of oxygen availability in the incylinder and the better atomization of the fuel. The BTE of RPO75BB25 observed at all load conditions is similar to diesel. This is result of improved properties of the fuel blend. Fueling this fuel blend eliminates100% of diesel to fuel compression ignition engine

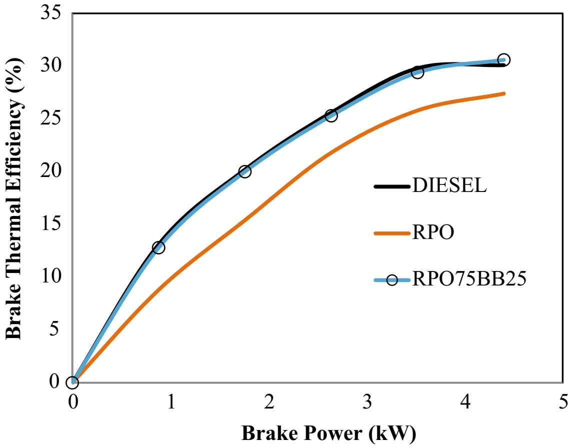


Fig. 8.7 Variation of BTE of 25% biobutanol and 75% of recycled plastic oil

by the waste plastic oil and biobutanol manufactured from waste products. This leads to environmental protection and as well as utilization of waste products (Fig. 8.8).

It is observed from figure that diesel is producing higher amount of oxides of nitrogen under tested conditions. BE15RPO20 is produces lower oxides of nitrogen. The reason for these low oxides of nitrogen is due to the presence of bioethanol and

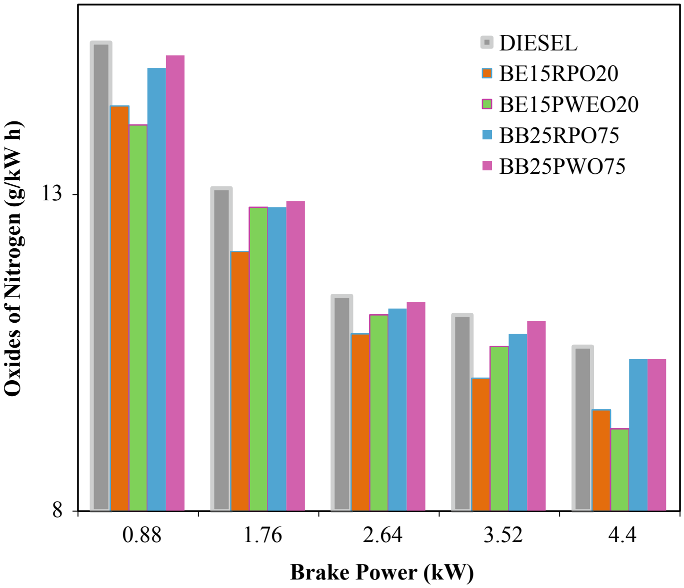


Fig. 8.8 Variations of Oxides of Nitrogen of the fuel blends of alcohol and recycled fuels

possessing lowest energy content among the fuel blends. Also, the cetane numbers of the chosen blends are competent to diesel fuel. Out of the four blends the blend containing PWEO are producing higher NO_X which is due to higher amount of fuel delivered and leading to higher heat energy release, rising the incylinder temperature. However, NO_X emissions are found to be lower in comparison to diesel at all brake power conditions.

Smoke emissions are other significant emissions to indicate the performance of compression ignition engine. It is observed from Fig. 8.9 that the four chosen blends are producing slightly higher smoke emissions at all load conditions. This is due to improved properties of the fuel blend which is leading to the higher smoke emissions. However, the difference is very marginal and can be ignored compared to that of diesel.

EGT of fuel blends are measured and analyzed with respect to five load conditions. From Fig. 8.10 it is seen that the results of EGT of the chosen blends are found to be low with respect to diesel. This may be by the presence of alcohol in the blends suppressed the maximum temperature of the incylinder by the cooling effect, although the conversion rate of the released heat energy into work is found to be higher which leads to higher brake thermal efficiency. It can also be observed that at higher brake powers, the EGT of blends are increasing by the increase in the cylinder temperature by the improved combustion that ratifies cooling. Similar results by fueling diesel-ethanol, diesel-ethanol-n-butanol, diesel-ethanol-pyrolised waste

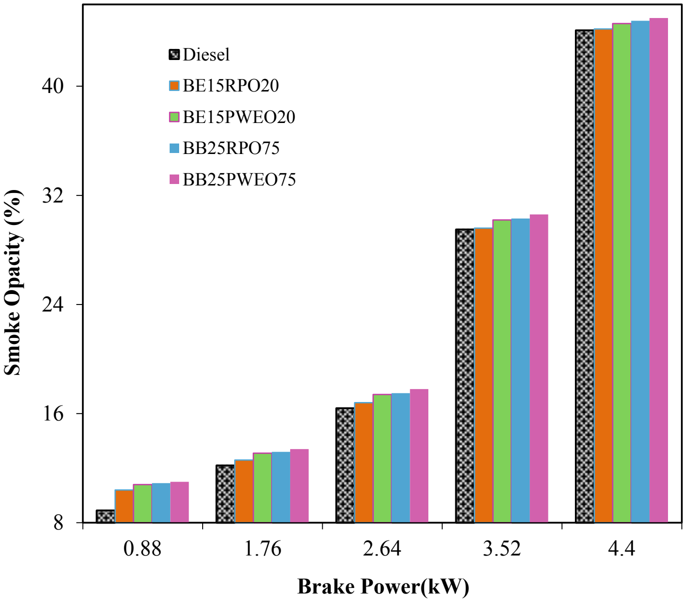


Fig. 8.9 Emissions of Smoke produced from the Engine by fueling fuel blends

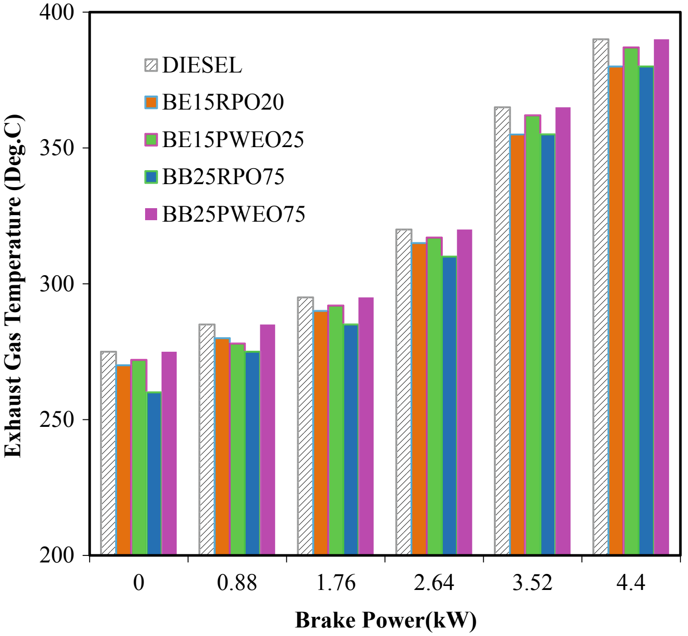


Fig. 8.10 Variations of Exhaust Gas Temperature of the fuel blends under various brake powers

plastic oil, treated waste engine oil-butanol are presented by previous researchers (Abedini et al. 2020).

CO emissions are one of the indicates the less efficiency of combustion in a CI engine. It is observed from Fig. 8.11 that the CO emissions of the fuel blends produced from the engine under five brake power conditions and diesel for comparison. From the results it is seen that higher brake power lowers the emissions of smoke, which in turn shows the improvement in percentage of combustion in the combustion chamber when fueled with the chosen blends. Similar results are (Prabakaran 2019) presented by previous researchers such that higher the brake power lowers the emissions of CO by fueling plastic oil along with diesel-ethanol, butanol, treated waste engine oil with butanol, diesel-butanol in CI engine.

Peak cylinder pressure indicates higher heat energy release during combustion of CI engine. From Fig. 8.12 it is seen that cylinder pressure of the engine increases with increase in brake power when fueled with selected fuel blends. Peak pressures at 55% of rated power condition and below are marginally low compared to diesel, which is due to the low heat energy released in the incylinder by the presence of alcohol in the chosen blends. Also, the increase in the load on the engine increases the cylinder peak pressure which is due to higher incylinder temperature leading to the higher rate of combustion cum oxidation of the fuel blends injected. Previous researches also, showed the similar results in fueling the alcohol blends (Huang et al. 2009) with diesel, plastic oil and treated waste engine oil.

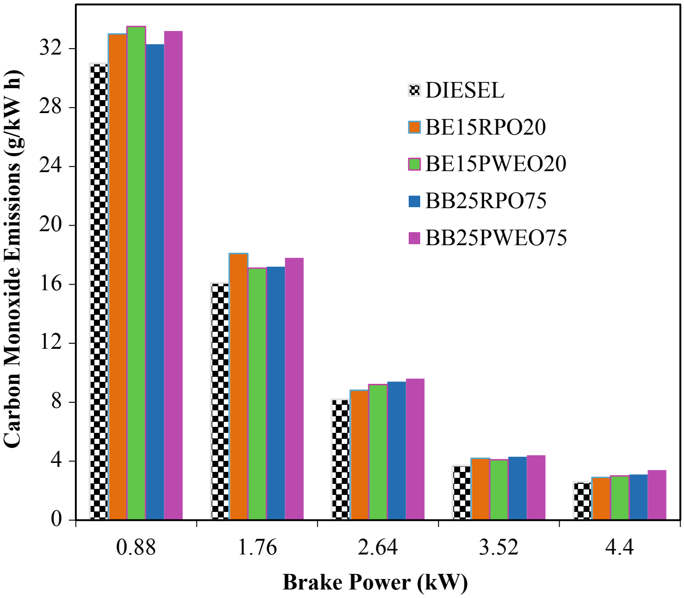


Fig. 8.11 Variations of Carbon Monoxide (CO) Emissions versus Brake Power

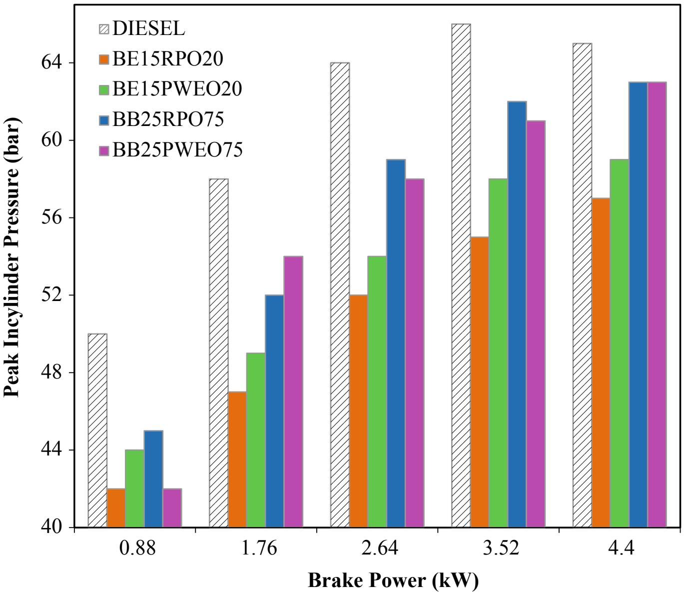


Fig. 8.12 Variation of incylinder pressure of CI engine with respect to BP

8.4 Conclusion

An assessment has been performed to replace diesel fuel for fueling the compression ignition engines by the blends of biofuels and recycled waste plastic oil cum pyrolised waste engine oil without any modifications in the existing operating parameters of the engine. The experimentation has been conducted in stages: Choosing the blends in the base of properties and analyzing the brake thermal efficiencies followed by testing the performance cum emissions characteristics when fueled in CI engine under five brake power conditions. The salient conclusions are drawn from the experimentation and presented as:

- Solubility results leads to a conclusion that the prepared blends of various proportions of alcohols, recycled plastic oil and pyrolised waste engine oil are found to be stable up to 20 days under temperature of 25 °C without suffering from any phase separation in the liquid phase. Hence, these blends are found to be suitable for fueling the engine.
- It can be concluded from the results of the properties that the fuel blends BE15RPO20, BE15PWEO20, RPO75BB25 and PWEO75BB25 are found to be closer in comparison to diesel fuel properties.
- It can be concluded from the results of the brake thermal efficiencies of the fuel blend that these are found to be suitable for replacing diesel to fuel CI engine. Maximum of 5.6% higher thermal efficiency is produced by fueling these blends.
- 10% low emissions of oxides of nitrogen is produced by fueling these blends and the emissions of smoke are found to be competent.
- Peak pressure of cylinder and peak heat release rate produced by the engine are found to be competent to that of diesel.
- Emissions of carbon monoxide from the engine by fueling the chosen blends are found to be closer to diesel fuel and marginally higher at low brake power conditions.

As a sum up, without any modifications in the existing CI engine the chosen fuel blends BE15RPO20, BE15PWEO20, RPO75BB25 and PWEO75BB25 are found to be suitable to replace diesel fuel. This study reduces approximately 85% of diesel fuel consumption and decreases the volume of import of crude oil from other countries. The sustainability of the land and water quality can be maintained by the recycling of the waste products in a useful and utilizable activity. Future work can be performed by studying the influence of engine operating parameters by fueling these blends.

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Part III
Biogas for Internal Combustion Engines

Chapter 9
The Role of Renewable Gas in the Mobility Emission Mitigation Strategies

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Abstract The European Union (EU) ambitious targets planned for 2050, are demanding for zero greenhouse gas (GHG) emissions. In this context, member countries governments, large companies and SMEs are working to meet their products, services and goods to these new requirements. EU has emphasized measures to mitigate emissions in the transport sector, which represents a quarter of GHG emissions. Therefore, the development of vehicles powered by alternative fuels such as natural gas, liquefied petroleum gas and electricity, has been spectacular in recent years. However, alternative second-generation fuels are being developed. They are called renewable gases such as biomethane, hydrogen and syngas which further reduce GHG emissions. The aim of renewable gases is to remove CO_2 from the feedstock and/or the production processes, which presents a wide range of R&D opportunities. There are still many barriers such as the high price of vehicles, the availability of refuelling points in large cities and transport corridors, the confidence of all stakeholders in these technologies, the development of low emissions policies and the Administration's support for fleet renew. Therefore, it is essential to develop R&D projects to minimize emissions and try to reduce the overall costs (production, transport and supply) of renewable gases. Currently, the price of natural gas for vehicles is 60% lower than gasoline 95 and 40% lower than diesel per 100 km. These trade margin are a firm argument for the development of renewable gases for sustainable mobility and for their injection into the grid. This Chapter analyses the state of the art and the necessary lines of research in order to efficiently apply renewable gases to sustainable mobility.

Keywords Renewable gas · Biomethane · Hydrogen · Syngas · Sustainable mobility · Biogas · CO_2 emissions

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Acronyms

SME	Small and Medium Enterprises
EU	EU
CO_2	Carbon dioxide
R&D	Research and development
GHG	Greenhouse Gas
CNG	Compressed Natural Gas
LNG	Liquefied Natural Gas

9.1 Introduction

For several years, EU has been highlighting the need to combat against climate change. Mitigating the risks of climate change is one of the highest priorities of governments and therefore they are focusing their policies on this objective. All member countries are committed to reduce their GHG emissions and, at the same time, to promoting, developing, and encouraging direct action plans to minimize GHG emissions.

As part of the Energy and Climate package, the EU sets targets for 2020:

- 20% reduction in greenhouse gas emissions compared to 1990
- 20% of total energy consumption from renewables
- 20% increase in energy efficiency

The same targets will be more ambitious by 2030:

- Reduction of at least 40% of greenhouse gas emissions compared to 1990
- At least 32% of total energy consumption from renewables
- At least 32.5% increase in energy efficiency

EU member countries have also taken on binding national targets for raising the share of renewable energy in their energy consumption by 2020 and subsequent years accordingly to the Renewable Energy Directive (European Union 2018). The commitment of the EU is firm and the roadmap foreseen for the achievement of these objectives by increasing energy efficiency as well as plans (European Commision 2017, 2016) to support innovation and finance the development of low-carbon technologies is very clear.

Both the key targets for 2020 and 2030 are focused on achieving the long-term goal: By 2050 the EU wants to substantially reduce its emissions by 80–95% compared to 1990 levels. Moreover, the EU strongly believes that an energy-efficient, low-carbon economy will boost the economy, create jobs, and improve Europe's competitiveness by reducing its dependence on foreign energy sources.

At the same time, another of the problems derived from pollution that directly affects citizens is air quality in urban areas. Several city councils in large European cities are already taking drastic measures to reduce pollution, mostly produced by the combustion of traditional hydrocarbons such as diesel and petrol, both in the vehicles that drive through them and by the generation of heat in boilers, which directly affect the health of their citizens, as well as the atmosphere.

Several scientific studies (Dominici et al. 2006; Fiordelisi et al. 2017; Peng et al. 2009) in the field of health care have counted and demonstrated the relationship between air quality in cities and pneumological diseases and increased cardiovascular risks. Urban air pollution is associated with acute (short-term) and chronic (long-term) stroke and other cardiovascular and respiratory effects. In large cities, there is an increase in the number of patients admitted to hospitals on the same days of high pollution levels. NOx, SOx and fine particulate concentrations directly affect lung alveoli and cause respiratory diseases (Rob et al. 2013).

9.1.1 Sustainable Mobility as a New Essential Energy Vector

According to the EU's official body, the European Environment Agency, CO_2 emissions from transport accounted for 27% of the total in 2017. In 2018, GHG produced by this sector increased by 0.9%. An upward trend in this sector is confirmed as in 2019, the latest year for which data is available, emissions had increased by 0.8% (excluding the maritime sector), compared to the previous year.

Likewise, the increase in the number of vehicles of all types in large cities has led to an increase in the concentration of substances that are harmful to human health.

As a result, the concept of mobility is evolving towards more environmentally and economically efficient vehicles and the term sustainable mobility has been adopted.

All the stakeholders involved, as detailed below, have found in the implementation of sustainable mobility an opportunity to reduce emissions, improve air quality, create jobs and reduce associated costs, as the main strengths to support the development of this new concept.

Although several lines of research have already existed for several years, renewable gases have taken on a leading role as a fundamental vector for achieving the objectives proposed for sustainable mobility. Renewable gases can be considered as second-generation alternative fuels as they are artificially manufactured in order to reduce CO_2 emissions in the feedstock and production processes.

It is important to highlight those renewable gases are not an enemy of electric vehicles. They are fully compatible for two reasons: the first is that the full cycle of emissions from well to wheel and subsequent scrapping must be considered. The second reason is that in order to achieve sustainable mobility in all sub-sectors—road, maritime, railways and aviation—it is necessary for some fuels to complement the shortcomings of others, such as power supply, autonomy and fuel availability.

9.2 Renewable Gases in Mobility

9.2.1 *Biomethane in Mobility*

All cities in Europe have abundant raw materials to produce fuels. These are assets that are daily disposed of in sewers, dumped in landfills and stored on farms. If all of this waste produced in an average city were stored in one place and the gases produced during decomposition were captured, it could generate enough GWh in the form of fuel to power all of the public buses in that city (Sanitary Landfills 2010).

Biomethane is produced by the removal of impurities from the biogas and the subsequent separation of CO_2 and CH_4 molecules.

Biomethane is also called "methane 2.0", i.e. it is the same methane molecule with the same physic-chemical characteristics, artificially produced from waste, fully compatible with methane molecules of fossil origin. This is the first advantage of producing biomethane, as it is fully compatible with fossil methane and can therefore be mixed in transport networks or in the tanks of natural gas vehicles.

Another fundamental advantage is that the biomethane production process removes the emissions that would have been produced with the decomposition of raw materials: landfills, sewage or slurry, being fully aligned with European Directives (European Union 2018; European Commision 2016; European Union 2009) which demands GHG emission reductions.

By using biomethane in mobility, the emission cycle can be lower than 0, i.e. if the efficiency of the biomethane production processes is optimized, the transport distances of biomethane for its application are reduced and the power of the engines is maximized, it is possible to remove more emissions than those produced in the complete cycle of biomethane from the well to the wheel.

As we said previously, the biomethane is exactly the same molecule than methane, this means that they can be blended without any physic-chemical change or alteration in the mixture itself, opening up a huge range of possibilities for injecting biomethane into existing pipelines.

Also, another of the uses on which we will focus in this paper is the propulsion of combustion engine vehicles such as natural gas vehicles (NGVs). This is one of the great advantages of biomethane, as natural gas vehicles are a mature technology in Europe, with many vehicle manufacturers offering vehicles with natural gas combustion engines in their catalogue (NGVA 2019; GASNAM 2020), such as spark ignition engines. In other words, the molecule that produces the movement of the vehicle is methane, which could be replaced or mixed in any percentage with biomethane.

The number and type of vehicles is growing steadily, during 2019, 87.410 NGVs were registered and during 2020, 65.019 vehicles. The year 2020 was the first year in which the number of NGV registrations has fallen since the commercialization of NGVs began in the 1980s. Undoubtedly, this has been caused by the global covid-19 pandemic, in which the automotive sector in general has been strongly affected. The first records for 2021 already predict an improvement in sales for this year. More and more private municipal fleets are replacing their buses and trucks with NGV-powered

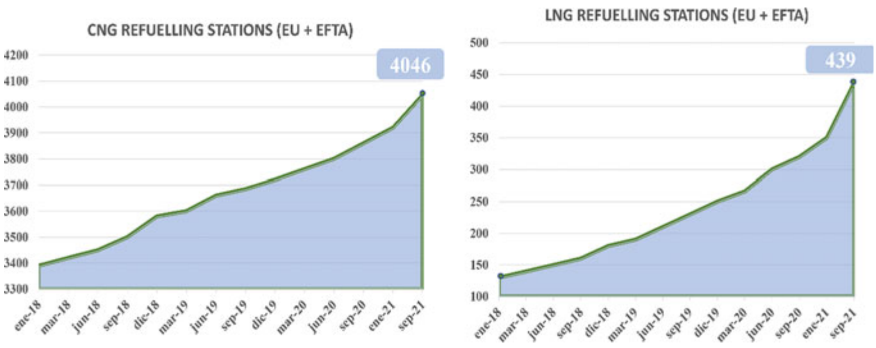

Fig. 9.1 CNG & LNG stations in Europe (NGVA 2020)

ones in line with their demanding emission reduction and air quality improvement plans. Likewise, private fleets of trucks and vans are also growing in the number of vehicles powered by NGVs. Finally, private NGV passenger cars are also growing as there is no difference in driving compared to traditional petrol or diesel vehicles.

On the other hand, natural gas vehicles could not be marketed without a network of refueling points throughout their area of operation. This network of gas refueling stations is also growing year by year in Europe. During 2020, 400 LNG filling stations and 4,000 CNG filling stations were reached (NGVA 2020). In 2021, continues to grow and forecasts are very optimistic for the coming years as shown in Fig. 9.1.

In addition to this growth in numbers, the quality, energy efficiency and economic performance of gas plants is also growing, e.g. through improvements in CNG compressors or BOG management in LNG plants. The refueling infrastructure of gas stations is fully compatible with biomethane and is therefore a vector of entry to the decarbonization of the sector and the reduction of emissions in mobility. Also, as this is a mature yet growing sector, new infrastructure in the coming years could be located close to biogas upgrading points for biomethane production, which could further reduce the balance of emissions by reducing the transport of molecules.

We would like to highlight that one of the advantages of the use of biomethane in mobility is the biomethane production process itself, since during the biogas upgrading phase CO_2 is captured and can be used as a by-product, either to produce syngas or for other multiple uses in other sectors. This is a great strength of biomethane, which should be thoroughly analyzed in future research, from an environmental and economic point of view, as it revalues its process and adds value to the production chain.

9.2.2 Hydrogen in Mobility

Another renewable gas technology is the hydrogen. The hydrogen economy is a developing model, in which hydrogen appears as an energy vector to replace fossil fuels (IEA 2019). This chemical element cannot be considered an energy source, but it can be considered an energy vector which can be stored, transported, and produce zero emissions energy. Hydrogen is a key sustainable solution for decarbonizing the economy and achieving climate neutrality by 2050.

In the transport market, hydrogen represents an alternative as a source of zero GHG emissions compared to conventional vehicles. The main challenge is to improve the autonomy. At present, we can find several hydrogen vehicles on the market (GASNAM 2020), although this technology is not yet ready for large-scale production.

The world is moving towards decarbonization. In large European cities, traffic causes 40% of nitrogen oxide emissions (De Energía 2019). Many cities are vetoing part of their territory to the most polluting vehicles.

The role of hydrogen in transportation is the transition to a clean, low-carbon energy system that is becoming more recognized around the world. Its massive deployment is still many years away, as its costs are high and the limited number of hydrogen stations affect its large-scale production.

The studies (DOE 2021; Liu et al. 2020; Paster et al. 2011), usually called "*well to wheels reports*", conclude that GHG emissions could be reduced by hydrogen in three different ways:

- If hydrogen is obtained from renewable sources and is used in fuel cells, a 50% reduction in CO_2 emissions is achieved, compared to those produced with the same hydrogen in alternative engines.
- If hydrogen is obtained from renewable sources and burned in reciprocating engines, the reduction in emissions is very drastic.
- If hydrogen is obtained from fossil fuels (by reforming natural gas) and used in fuel cells, CO_2 emissions are reduced because the efficiency of the fuel cell is greater than that of alternative engines.

The hydrogen powered vehicle is an alternative fuel vehicle that uses hydrogen as its primary source of energy to propel itself.

This vehicle generally uses hydrogen as one of two methods:

- Combustion: Hydrogen is burned in an internal combustion engine, in the same way as gasoline.
- Fuel cell: Hydrogen oxidizes and the electrons it loses is the current that will circulate through fuel cells that drive electric motors, in this way the fuel cell works as a kind of battery. However, batteries have a limited energy storage capacity, while the fuel cell is designed to allow a continuous supply of reagents.

The main difference between fuel cells and internal combustion engines is that the internal combustion engine presents their optimum operating point (offering less specific fuel consumption) or near their maximum power point (González 2017). While fuel cells have higher energy conversion efficiencies than internal combustion engines, therefore their importance in the transportation sector.

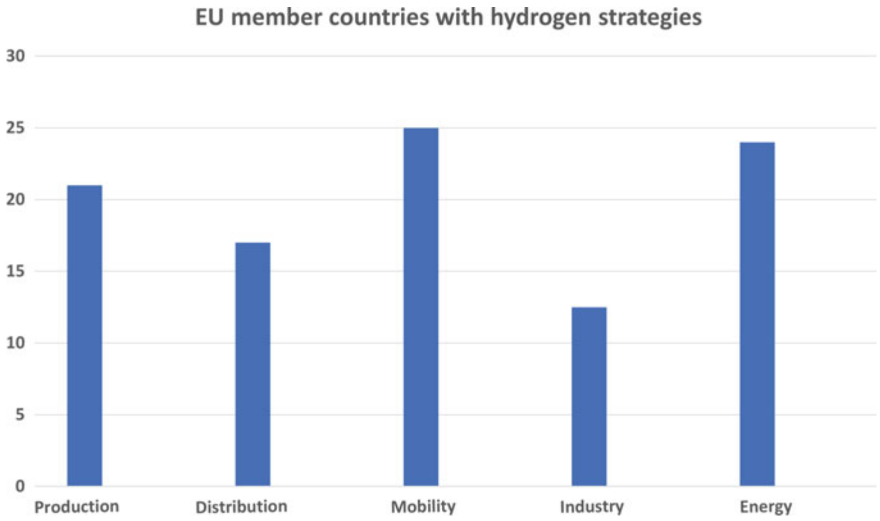

Fig. 9.2 Member countries EU with hydrogen strategies

Hydrogen is emerging as a research target and important future technology in sectors such as mobility, industry and energy to achieve climate and energy targets. Mobility is the sector where countries foresee the greatest potential for hydrogen.

In the following Fig. 9.2 (Brahy et al. 2020) are summarized the number of EU member countries that mention hydrogen in their national strategies in relation to a specific application.

9.2.3 *Synthetic Natural Gas or SYNGAS*

Synthetic natural gas, abbreviated SYNGAS, are methene molecules produced artificially from other raw materials such as carbon dioxide, hydrogen, coal, biomass, through thermal or reforming processes (Rostrup-Nielsen and Christiansen 2011).

If the energy sources needed in these processes are of renewable origin, we are talking about a renewable natural gas with a total balance of zero or even negative emissions.

Many energy sources and processes can be used to produce these methane molecules.

One of the most interesting, is the methanation process using CO_2 obtained from the biogas upgrading process and green hydrogen obtained by electrolysis of water from renewable electrical energy sources. With this process it is possible to reach a level of emissions per kilogram of syngas very close to zero or even lower than this. There are several references in the literature about this production process (Bi et al. 2006; Ren et al. 2020; Hernández et al. 2017; Zhan et al. 2009) which could be summarized in the following Fig. 9.3.

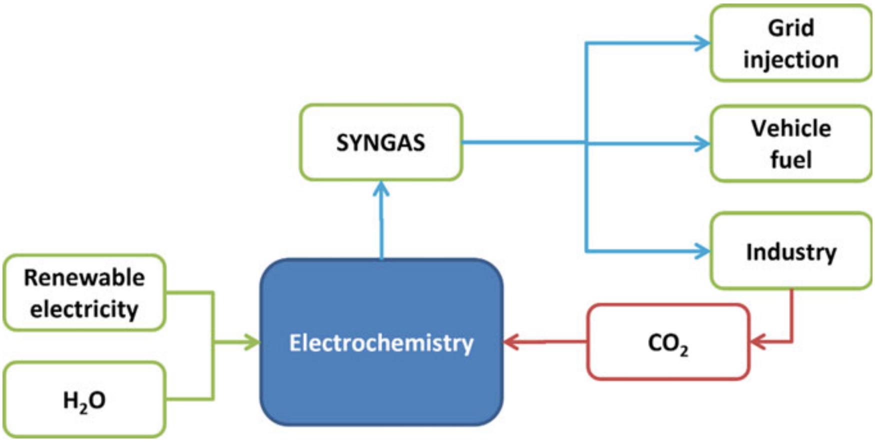

Fig. 9.3 SYNGAS production

The syngas production process can be summarized in the following equation:

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

This equation shows different challenges and points for improvement in research, production and GHG emissions reduction in each of its four elements:

- H_2: it must be green hydrogen obtained from renewable sources. There are still many technological and commercial challenges to reduce their production, storage and transportation costs.
- CO_2: Any quantity of CO_2 produced in any industrial process as waste, can be revalued as a by-product to obtain syngas. The main challenge is to reduce emissions in the transport of this molecule from its point of origin to the syngas production plant. The best solution would be for them to be adjacent, i.e. there would be no need to transport the molecule and so no emissions due to transport.
- CH_4: Is the desired product which could be used for grid injection or for mobility use
- H_2O: the vapors obtained must also be treated appropriately from a technological point of view so that they do not present a risk to people or to the industrial process.

Syngas is an alternative that is fully aligned with the EU's objectives of reducing greenhouse gas emissions and sustainable mobility (Ribullen et al. 2020).

Moreover, the range of opportunities that syngas opens up is very large. It can lead to CO_2 storage in multiple formats (geological storage or carbonation), for subsequent methanation from renewable energy sources (PTCO$_2$ 2012). On the other hand, the green hydrogen produced can also be stored in different thermodynamical state (compressed or cryogenic) and then transported to produce syngas.

Excess feedstock production (biomethane and CO_2 from upgrading, as well as hydrogen) would no longer be a handicap in the development of these feedstocks, as they can be stored for further processing in syngas production technologies.

Biomethane upgrading plants and hydrogen production plants have very high costs (CAPEX and OPEX), so large amount shall be produced to minimize the cost per Nm^3/h to guarantee a return on investment. This barrier, i.e. the fear of investors, whether public or private, of risking their funds in a very incipient market, can be considerably reduced if secondary processes are developed which could increase the value of the products obtained.

Syngas is clearly a real alternative to justify investments as it can produce economic value and greenhouse gas emission savings. It can be a fully effective alternative to take advantage of peaks in electricity generation that, otherwise, might be lost, adding economic and environmental value to all these energy generation processes.

9.3 Biomethane

The biomethane production process is initiated through the production of biogas from municipal solid waste, sewage and/or animal waste. All chemical elements other than CH_4 must then be removed from this biogas to produce biomethane, which can be injected into the natural gas grid or used with natural gas vehicles, with a total balance of emissions very close to zero or even less than zero.

9.3.1 Biogas Potential

In view of the forthcoming environmental and energy policies planned in EU countries under the three Mobility Packages published in 2017 and 2018 by the European Commission, biogas is presented as a key player in achieving the objectives of reducing greenhouse gases, such as CO_2, and improving air quality in cities.

According to the EU (European Union 2016), biogas is currently mainly used for electricity production (62%), followed by heat production (27%) and direct use in transport as fuel or injected into the gas distribution network (11%) after an upgrading process (Fig. 9.4).

The EU forecasts biogas and biomethane production in 2030 to account for 2.7% and 3.7% respectively of the energy consumed in 2030 in the EU.

New European policies have laid the groundwork for all member countries to align with this through the development of local regulations that are currently being drafted or updated. European policy frameworks promote the development of biogas as a key player in waste management, the circular economy and renewable energy.

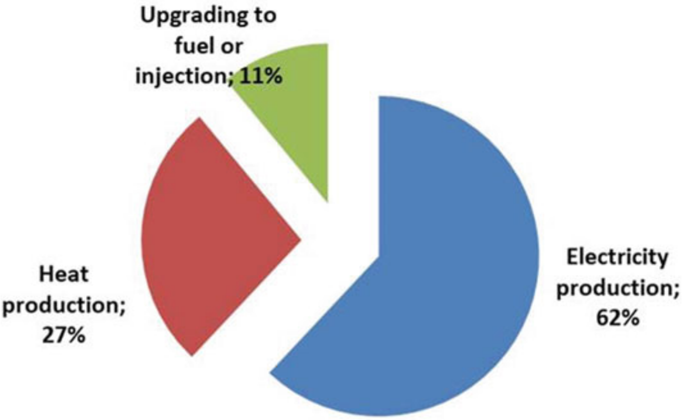

Fig. 9.4 *Biogas uses in EU*

9.3.2 Biogas Production

Anaerobic decomposition (in the absence of oxygen) of organic matter produces a gas with a CH_4 (methane gas) composition of more than 60%, called biogas. It can be used as a renewable fuel as its lower calorific value is 13.89 KWh/kg (IDEA 2014), helping to reduce emissions of so-called greenhouse gases.

Biogas can be produced from a wide range of feedstocks and used in all energy sectors, contributing to the EU's decarbonisation, renewable energy and energy security objectives.

In 2014, the level of biogas production (Eurostat 2014) in the EU was 1,73 GWh, representing approximately 7.6% of all primary renewable energy production in the EU. As of today, the European Biogas Association (European Biogas Association 2020) indicates that 167 TWh of biogas and 26 TWh of biomethane have been produced and that by the end of 2019 there were 18.943 biogas plants and 725 biomethane plants in Europe.

Almost 10% of this biogas is produced by wastewater treatment plants, approximately 21% originates from municipal waste landfills and the remaining 69% is biogas produced by anaerobic digestion of feedstock such as agricultural, industrial or household waste and energy crops.

An overview of the different ways of producing biomethane and syngas from biogas can be found in the figure of the *thinkstep* report (Thinkstep 2017) as shown in Fig. 9.5.

There are several industrial processes to produce biomethane. The main parameters to define the type of biomethane produced are:

- Origin of feedstock.
- Upgrading process: To inject the biomethane into the natural gas pipeline or to use it as a vehicle fuel, the carbon dioxide and impurities shall be removed.

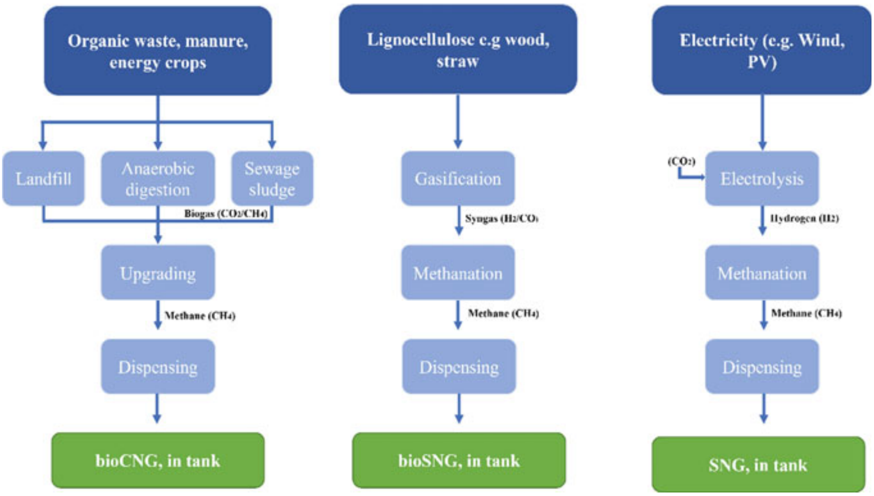

Fig. 9.5 Biomethane and syngas from biogas

The different raw materials define the quality of the biogas, i.e. the chemical composition in methane, carbon dioxide and other elements, which we will call impurities.

Biogas production is a fully consolidated technology. Generally, the chemical composition of biogas is made up of methane (50–80%), carbon dioxide (20–50%) and other elements (up to 15%) such as nitrogen, oxygen, ethane, propane and siloxane. This biogas is mainly used for heat production as an energy source for various industrial processes. Biogas can also be used as a source of renewable fuels either for injection into the natural gas grid or for use as a vehicle fuel. However, in order to be used as a renewable gas, the biogas shall be upgraded to obtain high quality methane, also called biomethane because of its renewable origin.

9.3.3 Biogas to Biomethane. Why is the Upgrading Needed?

The technical justification for this improvement process shall be found in the Wobbe Index and in the Methane Number (Partho et al. 2018), which are used to compare the energy efficiency of combustion with different gas compositions.

Wobbe Index is a critical parameter for the interchangeability of gaseous fuels. Two fuels with identical Wobbe Index will have the same energy output under the same operating conditions. The higher Wobbe Index, the higher energy density of the gas (Burrie and Florisson 1989; Liu and Dumitrescu 2019).

Gases with a higher concentration of methane (up to 95%) reach a Wobbe Index of roughly 55Mj/Nm^3, while gases with a lower concentration (around 70%), such as biogas, have a Wobbe Index of roughly 30Mj/Nm^3.

On the other hand, Methane Number measures the ratio between the volume composition of CH_4 and Hydrogen. For a gas with a pure methane composition, it is assigned a Methane Number equal to 100. This parameter is vital in internal combustion engines, as they are designed to operate in certain ranges and will also define the performance of the engine.

Unlike Wobbe Index, Methane Number is inversely proportional to methane concentration in the gas. For concentrations up to 95%, Methane Number will be around 84, while for concentrations of 70% (such as biogas), the Methane Number will be about 130.

9.3.4 Biogas to Biomethane. Upgrading Process

Upgrading is the process which carbon dioxide and impurities are removed from the biogas, obtaining biomethane, which can be applied to vehicle propulsion or to pipeline injection. Upgrading is an industrial process that is divided into two clearly differentiated stages as shown in Fig. 9.6.

The first stage involves the particles and impurities removal. Through physical and chemical filters, all the particles are removed. Then, drying is applied by a knockout pot and a blower, so moisture is removed. A second drying phase may be necessary, depending on the origin of the biogas, in which aftercoolers are generally used to condense and remove the moisture.

It is very important to define the origin of the biogas (Bragança et al. 2020; Kazimierz 2017; Arnold n.d.; Ryckebosch et al. 2011; Sun et al. 2015), since depending on the raw material, a series of auxiliary stages will be necessary to remove impurities that may be present, such as volatile organic compounds, sulphur compounds, oxygen, nitrogen and siloxanes.

The economic and environmental feasibility of the project may be conditioned on these ancillary processes. Therefore, it is essential to define the origin of the biogas in order to obtain renewable gas with low or zero emissions into the atmosphere according to the objectives established by the EU.

Currently, there are research lines for the development of by-products obtained in the complete process of biogas upgrading. It is very important to emphasize, and

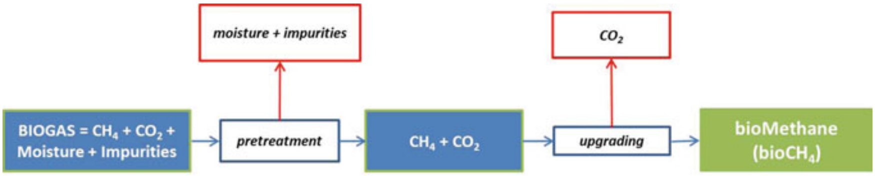

Fig. 9.6 Biomethane process

they must also be supported technically, financially and politically by official organizations, because the greater viability of these by-products, the higher development of renewable gases.

Once all impurities are removed, the biogas could be compressed if necessary, as pre-treatment for the second stage: CO_2 removal.

9.3.5 CO_2 Removal Technologies

To define the upgrading process, several factors come into play, such as the origin of the raw material, the efficiency of the process, the cost effectiveness analysis of the facilities and the future application of the biomethane as well as the possible by-products obtained, mainly CO_2.

There are several technologies applied to obtain biomethane from biogas. Once the biogas impurities and moisture are removed, it is possible to remove the CO_2 and it is possible to separate the two molecules (CH_4 and CO_2) and get energy, economic and environmental efficiency from both. These technologies are:

- Water scrubbing (Petronela et al. 2015; Budzianowski et al. 2017; Bauer et al. 2013; Muñoz et al. 2015; Niesner et al. 2013)
- Cryogenic separation (Muñoz et al. 2015; Baena-Moreno et al. 2019; Baccioli et al. 2017)
- Physical absorption (Muñoz et al. 2015; Niesner et al. 2013; Chunyan et al. 2018)
- Chemical absorption (Muñoz et al. 2015; Niesner et al. 2013)
- Pressure swing adsorption (Muñoz et al. 2015; Niesner et al. 2013; Hoyer et al. 2016)
- Membrane separation (Muñoz et al. 2015; Niesner et al. 2013; Baena-Moreno et al. 2019; Hoyer et al. 2016)
- Methane enrichment (Seman et al. 2019)
- Hydrate formation (Castellani et al. 2017; Filarsky et al. 2018)
- Organic solvent scrubbing (Bauer et al. 2013; Muñoz et al. 2015)
- Methanogenesis (Muñoz et al. 2015; Bassani et al. 2015)

To define the upgrading process, several factors come into play, such as the origin of the raw material, the efficiency of the process, the cost effectiveness analysis of the facilities and the future application of the biomethane obtained as well as the possible by-products obtained, mainly CO_2.

In addition, two or more CO_2 removal technologies could be applied and the pre-treatment of the biogas could be improved because a few of these technologies are applied to clean some impurities as H_2S, N_2 or O_2, as described in the literature.

9.3.6 Well to Wheel Cycle

From the emissions point of view, whatever the future application of the biomethane obtained, not only the emissions captured, and the emissions emitted in the upgrading process that must be assessed.

There are also other factors that must be evaluated to have the complete emissions cycle and to be able to compare the different types of fuels, both renewable and fossil fuels. These factors are:

- Transportation of raw material: The transport of raw materials to the treatment industries for obtaining biogas and subsequent upgrading to obtain biomethane should be kept to a minimum to reduce emissions from this transport as much as possible.[1] For this reason, upgrading facilities are currently being built at the raw material collection centres themselves, such as farms, landfills or water treatment plants.
- Transportation to market: The transportation of fuel to the point of supply can play a crucial role in the total CO_2 emissions. Therefore, to minimize the emission values, biomethane industries are installed in locations close to the supply points. The environmental cost of transporting energy sources is a very high cost regardless of the fuel to be transported. That is why appropriate locations must be requested so that the total balance of emissions is in an acceptable range.
- Conditioning: Methane for vehicle use, whether of fossil or renewable origin, cannot be introduced directly into combustion engines. There are two fully mature supply technologies on the market around the globe: Liquid Natural Gas (LNG) and Compressed Natural Gas (CNG). LNG are cryogenic methane molecules, i.e. in temperature ranges between $-150\,°C$ and $-120\,°C$ and pressure ranges between 2 and 10 bar. CNG are methane molecules at room temperature and pressures of 250 bar. In order to supply natural gas under these thermodynamic characteristics, conditioning by cryogenic and/or compression processes is necessary. Both processes produce emissions that must be evaluated over the complete emissions cycle. In addition, there is another methane thermodynamic composition to be supplied to vehicles, the Adsorbed Natural Gas (ANG). This an alternative to supply methane with less emission due the less pressure needed (35 bar)
- Distribution: LNG and CNG storage and final distribution to vehicles also requires electric engines whose emissions must be added to the total balance.

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[1] It would be pointless in obtaining renewable energy sources if all these emissions savings are spent on transportation or in other auxiliary tasks inherent to the production and consumption of this renewable energy.

9.3.7 Adsorbed Biomethane

There are other ways of natural gas vehicle supply with mature technology, although not widely distributed in the market. The most important is adsorbed natural gas (ANG).

It is a great advantage that the same calorific value or energy could be obtained to generate mechanical traction for vehicles through combustion engines at lower pressures than those of CNG, about 30–40 bar pressure instead 250 needed with CNG.

These pressures can be achieved by methane adsorption in nanoporous materials. This pressure reduction implies a lower cost of compression and a lower cost of storage of the methane molecules. The application of this technology for mobility, combined with biomethane, has the potential to reduce emissions and total operating costs.

At moderate pressures (30–40 bar), an ANG tank stores more methane or biomethane than a CNG tank at the same pressures. However, at high pressures (200–250 bar), a CNG tank stores slightly more natural gas than an ANG tank at the same pressures.

The use of moderate pressures instead of high pressures has several implications in favour of ANG. On the one hand, the price of lower pressure compressors is about six times less than a high-pressure compressor. According to our estimations, based on the power, flow rate, etc. of 50 bar and 250 bar compressors, a 50 bar compressor consumes about half of electrical energy compared with a 250 bar compressor.

This is important because, the lack of filling stations in large cities and transport corridors, ANG could be the solution. In fact, ANG tanks could be refilled using the secondary gas transport networks at 60 bar.

If the decision is focused towards the establishment of a dense filling stations network, operating at moderate or low pressures represents a significant investment reduction compared to facilities operating at pressures of 200–250 bar.

We can find in the literature (Pfeifer 2011; Prosniewski et al. 2019), one of the main targets is storage tanks for adsorbed natural gas, which are made of lighter materials than CNG tanks, as they have to withstand lower pressures. Furthermore, ANG tanks have a high degree of conformability, i.e. is not mandatory a cylindrical geometry, so 20% more space could be used if we compared to CNG vehicles.

9.4 Hydrogen

Hydrogen is the most abundant element in the universe, on Earth rarely appears alone, it is found as part of chemical compounds such as water or hydrocarbons.

Hydrogen cannot be considered as a primary source of energy as fossil fuels, but as a means of transporting energy (Coria Rodil 2021), which is why it is called an energy vector (González 2017). It can be considered an energy vector which can be stored, transported, and produced zero emissions energy. Hydrogen is a key sustainable solution for decarbonizing the economy and achieving climate neutrality by 2050.

Transport, one of the areas that most depends on fossil fuels, the hydrogen represents an alternative fuel as a source of zero emissions to conventional vehicles. The main problem is the low autonomy compared to gasoline or diesel vehicles. Nowadays, we can find several hydrogen vehicles on the market (NGVA 2019; GASNAM 2020), although this technology is not ready for large-scale production.

9.4.1 Hydrogen Production

Currently, the production of hydrogen in the world is approximately 70 million Tons. Most hydrogen comes from fossil sources (coal, oil and natural gas), about 96% of total production, from steam reforming of natural gas (≈50%), reforming of petroleum (≈30%) and coal gasification (≈20%). The only process that is not based on these compounds is the electrolysis of water, which accounts 3.9% of total production and 0.1% of other processes.

Table 9.1 represents the different energy sources from which hydrogen is produced, obtaining most of the reforming of natural gas (6% of the global use of natural gas). Furthermore, 95% of the production is consumed on site (González 2017).

Hydrogen is classified according to the use of renewable sources during generation process:

- "*Grey hydrogen*", the most used in the chemical industry or in large oil refineries, is not a completely zero GHG emissions, because the production requires fossil fuels.

Table 9.1 Hydrogen origin (González 2017)

Method	Process	Raw material
Thermal	Steam reformed	Natural Gas
Thermal	Thermolysis	Water
Thermal	Pyrolysis	Biomass/Natural Gas
Thermal	Gasification	Biomass/Coal
Electrochemical	Electrolysis	Water
Electrochemical	Photoelectrochemical	Water
Biological	Photobiological	Water and Seaweed
Biological	Fermentation	Bacteria
Biological	Anaerobic digestion	Biomass

- As an alternative, "*blue or low carbon hydrogen*" also requires fossil fuels in the production process, but send out less carbon than grey hydrogen, because it is removed with carbon capture and storage (CCS technology).
- The low GHG emissions option is "*green hydrogen*", produced from renewable energies. Green hydrogen is not very frequent in the market, although it is the final objective of all environmental policies in the UE.

Hydrogen production methods that do not produce carbon dioxide are: Electrolysis (with electricity provided by renewable energies such as solar and wind), thermochemical cycles of water and photolysis of water (Table 9.2).

According to the report regarding hydrogen economy developed by IHS Markit (Markit 2020), the costs to produce green hydrogen have fallen by 50% since 2015 and could be reduced by an additional 30% by 2025, due to the benefits of greater scale and more standardized manufacturing.

Green hydrogen produced by electrolysis, powered by renewable energy is the preferred hydrogen fuel technology. The International Energy Agency (IEA) states (IEA 2019) that 1 kg of green hydrogen contains approximately 33.3 kWh and is priced at 3.50 EUR to 5.00 EUR, which is between € 0.10–0.15/kWh.

Table 9.2 Hydrogen production (Markit 2020; IEA 2015)

Process	Efficiency (%)	Centralized/decentralized	Emissions (g CO_2/kWh H2)	Price (€/kWh H2)
Natural Gas (SMR without CCS)	70–75	Both	288–292	0,07–0,15
Natural Gas (SMR with CCS)	60	Centralized	42,7	0,09–0,15
Coal Gasification (without CCS)	50–60	Centralized	659	0,07
Coal Gasification (with CCS)	40–50	Centralized	20,3	0,08
Biomass Gasification	56	Decentralized (close to source)	0	0,07–0,08
Electrolysis (with wind)	65–70	Both	0	0,11–0,15
Electrolysis (with Electrical Grid)	30	Decentralized	440	0,2
Thermochemical (Solar energy)	30	Centralized	0	0,18
Thermochemical (Nuclear energy)	30	Centralized	0	0,06

9.4.2 Hydrogen Storage

Currently, the storage presents a technical difficulty that limits the use of hydrogen as a large-scale energy source. To achieve the general use of hydrogen as an energy vector, the cost for its transport and storage must be reduced. The main barriers for storage are:

- Hydrogen stores a lot of energy per unit of mass, but very low energy per unit of volume,
- Hydrogen energy density (8 MJ /L) is lower than gasoline energy density (32 MJ /L) and requires between 5–13 kg of hydrogen to achieve an appropriate autonomy in a fuel cell vehicle.

In addition, to being such a volatile gas under ambient conditions, for use in vehicles it must be compressed at high pressures or stored cryogenically, which increases the weight of the vehicle and costs energy.

The cost is 4–8% of the hydrogen energy, in case of being compressed and if it is liquefied, the cost is around 40% of its energy.

In the case of huge hydrogen producing facilities, high storage tanks would be needed to conserve what is produced during the day. The technology of this tanks is very complex so it has been proposed to store the hydrogen in underground caves (geological storage) as an alternative which should be analyzed from a R&D point of view.

There are different hydrogen storage systems, based on its final application, whether in a gaseous state by compressing it, in a liquid state at cryogenic temperatures or fixing it in advanced materials.

Compressed Hydrogen

For transport sector, it is stored in tanks for compressed hydrogen that are classified into four types I to IV, depending on the proportion of metal and composite materials used in its manufacture. It is one of the most developed techniques, due to its simplicity and cost. Light tanks at 70 MPa, type IV, are installed in vehicles like the Toyota Mirai, and they are composed of three layers:

- A layer made of a nylon-based plastic polymer with low hydrogen permeability
- A carbon fiber epoxy resin interlayer that provides rigidity to the structure
- A fiberglass-based composite outer shell to protect the reservoir possible abrasions.

Therefore, the use of composite materials in this type of tanks reduces the weight of these devices, more suitable for use in the automotive industry. Currently, research is focused on finding lightweight materials, capable of withstanding high pressures (100 MPa) and of moderate cost to build new tanks.

Liquid hydrogen

Liquid hydrogen requires cryogenic technologies (−253 ºC). In this thermodynamic state, the volumetric capacity (Orcajo et al. 2012) is double that obtained at high pressure (74 kgH_2 / m^3). It is a technology with a high level of maturity, and it is very attractive for applications such as air and space transport since it has a higher volumetric energy density compared to compressed hydrogen.

But the liquefaction process demands 40% of the chemical energy contained in hydrogen and tanks are required to preserve the temperature (−253 ºC), which implies a higher cost.

Solid storage

Currently, solid state (DOE 2021) materials are attractive due to improved safety, high energy density (volumetric), and better energy efficiency. Current research (Panella et al. 2005; Gómez-Gualdrón et al. 2017; Allendorf et al. 2018; Boateng and Chen 2020) on hydrogen storage is focused on finding materials that allow more accumulation in less volume. Solid storage materials can be divided into two classes:

- Chemical adsorption or chemisorption: The case of metal hydrides, in which it is intended that the hydrogen molecule dissociates into two atoms and can bond by entering the atomic network of a hydride and forming a new compound. The wide variety of hydrides allows use in different applications, although it is an expensive technology.
- Physical adsorption or physisorption: Hydrogen is adsorbed on materials due to its large surface area and microporosity, through the formation of weak molecule-surface bonds. For example, carbon nanotubes, zeolites, MOFs (Metal–Organic Frameworks), a cheaper technology than hydrides, but still under development.

9.4.3 Hydrogen Applications

Most of the hydrogen is used for industrial purposes, in chemical applications, such as ammonia syntheses (50%), followed by oil refineries (37%) and ethanol production plants (8%). The rest is distributed in the pharmaceutical, food, electronics, aerospace industries. However, the fact that hydrogen can be an energy carrier has given rise to new applications:

- Transportation: Fuel cell electric vehicles (FCEV) provide a low-carbon mobility option. The competitiveness of FCEV depends on the costs of fuel cells and service stations. Aviation and shipping have limited low-carbon fuel options available and represent an opportunity for hydrogen-based fuels.
- Stationary: Stationary fuel cells allow high efficiency, low emissions and stationary electricity generation both in large plants and in domestic use, combining the generation of heat and electricity in buildings.
- Energy storage: Hydrogen is one of the main options for storing renewable energy.

The reasons for treating hydrogen as a fuel in transport are mainly environmental and of a foresight nature due to the depletion of fossil fuels. Hydrogen fuel is considered a good candidate to contribute to the decarbonization of the transport sector if it is produced by renewable energy sources.

9.4.4 Fuel Cells Electric Vehicle (FCEV)

The role of fuel cells in transport is the transition to a clean, low-carbon energy system that is becoming more recognized around the world. Its massive deployment is still a few years away, as its costs are high, and the limited number of hydrogen stations affect its large-scale production.

FCEV's offer several significant advantages over other vehicles:

- They can drive distances without refueling (more than 500 km), which is why they pose the autonomy problems of electric vehicles.
- They can refuel quickly (3–5 min), like gasoline or diesel vehicles, which increases comfort for the consumer.
- The chemical hydrogen storage medium has a higher energy density than the batteries used to store electricity in electric vehicles, so the amount of stored energy (kWh) is low. This increases its attractiveness for vehicles that require large energy storage (heavy vehicles or long term).
- You can take advantage of the existing distribution and sales infrastructure for gasoline.

Table 9.3 summarizes some of the typical values of power, distance without refueling and efficiency of the batteries most used in the automotive industry.

FCEVs will be especially important for the decarbonization of passenger cars (taxis) and heavy vehicles (heavy transport service buses and trains). To do this, the prices of the FCEVs will have to tend to the prices of the vehicles in use today

Table 9.3 Comparison between different types of vehicles (Coria Rodil et al. 2021)

Method	Power (kW)	Driving Range (km)	Efficiency (%)
PEMFC	10–200	500	44–45
MCFC	20–30	500	30
PAFC	20–200	300	40
Petrol	10–100	600	25–30
Diesel	10–200	800	30–35
Natural Gas	10–200	600	35–40
Electric accumulator	10–100	100–300	65
Hybrid vehicle	10–100	500	40–50

(gasoline and diesel). This requires a cost reduction in fuel cell systems and in the hydrogen storage tank.

There are currently a limited number of manufacturers offering fuel cell vehicles. Toyota and Hyundai dominate the market and new models produced by Audi and BMW are expected by 2021.

More 500 fuel cell vehicles are in operation across Europe, many of them funded by European programs. The largest Hydrogen Europe (Hydrogen Mobility Europe 2021) is deploying more than 1,4000 FCEVs by 2020 and demonstrating the feasibility of hydrogen mobility in different applications (IEA 2015).

European automakers are behind large leading companies in Japan and Asia. Europe is expected to have a 30% market share of global FCEV sales by 2030 (Hydrogen Council 2020).

The major Western and Asian countries plan to deploy a significant hydrogen infrastructure in the next decade. The total goal is for more than 3,000 stations by 2025 to provide hydrogen to approximately 2 million FCEVs.

The FCEVs are like conventional vehicles, but they have more advanced components:

- Fuel Cell Stack: Converts hydrogen and oxygen gas into electricity to drive the electric motor.
- Electric motor: It powers the vehicle in a much more fluid, calm and efficient way than an internal combustion engine and requires less maintenance.
- Battery: Saves the energy generated from the regenerative brake and provides additional energy for the electric motor.
- Hydrogen storage tank: Stores hydrogen gas at very high pressure to increase conduction range.
- Power control unit: Controls the flow of electricity.

Currently 11.000 hydrogen cars circulate around the world, half of them in California. Nowadays, fuel cell electric vehicles are priced significantly higher than any gasoline, diesel, hybrid or electric vehicle. The components of the FCEVs such as the fuel cell system, the hydrogen tank and the battery, represent half of the total cost of the vehicle, while the fuel is approximately 25% of the total cost. By 2030, these components are expected to represent 30% of the TCO (Hydrogen Council 2020).

9.4.5 Fuel Cells in Other Vehicles

Trucks

Fuel cell trucks represent the most economical technology for decarbonizing medium and heavy-duty transportation. The BEV alternative is less attractive for heavy vehicles. Fuel cell trucks would be a direct replacement for diesel trucks as they can be refueled in a few minutes and reach a range of hundreds of kilometers.

Hyundai has sent to Switzerland 10 units of what will be the first active fuel cell-powered heavy transport truck. Equipped with a 190 kW fuel cell that is fed by seven tanks, which offer a total storage capacity of 32.09 kg of hydrogen that allows a range of approximately 400 km on a single charge. Its goal is to launch 1,600 units by 2025 (García 2020).

The Californian company Nikola has started to manufacture its Nikola hydrogen truck by 2023, Nikola Tre promises between more than 1,000 km of autonomy and an estimated recharge time between 10 and 15 min. It has also started to create a hydrogen supply network for its trucks. With the purchase of five electrolyzers capable of generating eight Tons of hydrogen per day that will feed its electric trucks powered by fuel cells.

Mercedes-Benz has announced a fuel cell electric truck, Mercedes-Benz GenH2 Truck for 2023, although it is still a prototype. Mercedes-Benz has revealed an autonomy of more than 1000 km. This truck will have a double fuel cell system capable of providing 300 kW of power (2X150 kW) (García 2020).

Several projects are currently developing including REVIVE from FCH JU that will test 15 fuel cell garbage trucks at 7 locations (Berger 2018).

Buses

Zero emission fuel cell buses with a range of more than 600 km and rapid refueling methods have become a good alternative to diesel buses.

The technical performance of fuel cell buses and associated refueling infrastructure has been validated through various projects and tests. Hydrogen fuel cells have been shown to meet their needs in city buses. However, fuel cell buses are not yet a fully commercial proposition due to the relatively high costs of these vehicles, but improvements are expected.

The latest demonstration projects (European Commision n.d.) are designed for this sector to begin to scale and achieve more profitable fuel cell buses.

The public bus company of Barcelona, *Transportes Metropolitanos de Barcelona* (TMB), has bought for 6.4 million euros from the Portuguese manufacturer Caetano Bus, 8 hydrogen buses for an urban service in Spain. These buses will be an H_2 City Gold LHD model, 12 m in length and a 60 kW fuel cell of Japanese origin. Motorization and the electronics will be provided by Siemens (García 2020). Is estimated a consumption of 20 kg of hydrogen and an autonomy of 330 km. This acquisition is supported by the JIVE program (European Commision n.d.).

Germany gives another boost to hydrogen for its long-distance bus application. FlixBus, one of the long-distance bus travel operators, together with the German technology Freundenberg have launched a project, with the aim that they have an autonomy between km charges and the hydrogeneration refueling is less than 20 min.

9.4.6 Research Lines in Hydrogen

The main research lines of hydrogen are related to: production, transportation and storage.

Regarding the production, it is important to develop advanced and efficient processes aimed to produce hydrogen economically from sustainable resources. Also, in the context of fuel cells technologies, is very interesting the research in lowering the cost and enhancing the performance and durability of technologies applied to fuel cells.

In the context of hydrogen storage, the configuration of storage systems are active fields of research, also the study of the properties of the materials involved.

Regarding vehicles, most major companies are involved in research on hydrogen as fuel.

EU is involved in promoting research and innovation projects on hydrogen under Horizon 2020 research program, which are managed through the Fuel Cells and Hydrogen Joint Undertaking (FCH JU), a joint public–private partnership supported by the Commission.

The Commission and FCH JU are association partners in Hydrogen Europe, the European Hydrogen and Fuel Cell Association. Hydrogen Europe promotes hydrogen as the enabler of a zero-emission society (European Union n.d.).

Several documents related to the action of EU in the context of research on hydrogen are:

- Role of hydrogen in National Energy and Climate Plans (Hydrogen, Fuell Cells n.d.).
- Hydrogen generation in Europe—Overview of costs and key benefits (European Union n.d.).
- EU strategy on hydrogen COM (2020) 301 final (July 2020).
- Factsheet—EU hydrogen strategy (European Union 2020).
- Hydrogen from renewable power—Technology outlook for the energy transition (Irena 2018)
- Sector Forum Energy Management / Working Group Hydrogen (JRC 2016).

9.4.7 Hydrogen Potential

Although nowadays green hydrogen (produced using renewable energy) is 2–3 times more expensive than blue hydrogen (that produced using fossil fuels), according to Hydrogen generation in Europe (Irena 2018) the hydrogen produced using renewable electricity, the well-known green hydrogen, could be competitive with fossil fuel alternatives by 2030. This is due to falling costs for solar and wind energy, better performance and economies of scale for electrolyzes. Therefore, investment costs for electrolysis facilities must also decrease significantly. Also the taxes applied to CO_2 emission can also help green hydrogen to be more competitive.

Table 9.4 Hydrogen companies

Company/organization	Website	Company/organization	Website
Air liquide	airliquide.com	Ford	ford.com
Alstom	alstom.com	Fuel Cell & Hydrogen Energy Association	fchea.org
American hydrogen association	clean-air.org	General Motors	gm.com
Areva	areva.com	Helion	helion-fuelcells.com
Asociación española del hidrógeno	aeh2.org	IEA The International Energy Agency	iea.org
The French hydrogen Association	afh2.org	International Association for Hydrogen Energy	iahe.org
Axane	axane.com	MTU	mtu-online.com
Ballard	ballard.com	NREL National Renewable Energy Laboratory	nrel.gov

The main stakeholders in the development of hydrogen technologies in the world are those related to the automotive industry. However, the development of technologies and the aim for the introduction of new energy sources in the global energy matrix have increasingly involved companies and organizations that carry out studies on the production and use of hydrogen. Table 9.4 shows a list of some organizations and companies committed with the use of hydrogen.

9.5 Renewable Gas Valorisation

Renewable natural gas is a fuel that is obtained by different processes of degradation of organic matter (animal, vegetable and wastewater waste) which, after being cleaned, produces biomethane, which is a renewable fuel neutral in CO_2 emissions. Furthermore, renewable gas is fully interchangeable with natural gas, so it can be distributed by means of current networks.

Biomethane is a clean fuel which is obtained from biogas, which in turn is produced due to anaerobic decomposition of organic matter, which is present in urban waste, sewage, and agricultural, livestock and forestry waste. Biomethane is a biogas subjected to an upgrading process, which consists of the removal of different components such as CO_2, which can also be used to obtain syngas. The biomethane obtained can be injected into the gas pipeline network or for the use in vehicles.

Regarding hydrogen, it can be obtained from surplus electrical energy from renewable sources. There are many applications of this hydrogen, among which we can mention the generation of synthetic natural gas using surplus CO_2 produced in industrial processes. It can also be injected straight forward into the gas pipeline network.

It can also be used as fuel for vehicles. Also, hydrogen is miscible with natural gas so that the same distribution networks can be used.

Hydrogen can be used to generate electricity and heat. It can consider that, when using hydrogen to produce electricity, heat is also obtained simultaneously. It can be considered as the fuel of the future. The process to obtain electricity from hydrogen is the inverse process to that used in its production. When hydrogen reacts with oxygen, water and electricity are produced. This process is performed in the so-called hydrogen fuel-cell.

We remark that classical renewable energy sources, such as wind or photovoltaic energy, have a strong dependence with climatological and meteorological factors. Clearly, these sources of energy have periods of high electricity generation. This excess of electricity can be used to produce hydrogen, which can be sold directly, or even be used to generate electricity in periods in which there is a deficit in the production from renewables.

In the next figure it is shown a schematic plot of a hydrogen fuel-cell with both electricity and heat is produced. It can be observed that there is residual hydrogen that can be reused (Fig. 9.7).

From the environmental point of view, the use of hydrogen is more efficient than other sources of energy, such as those based on oil, coal or natural gas, since it does not emit CO_2 to the atmosphere so air pollution and hence greenhouse effect is avoided. The EU is highly concerned on this topic, as reported in many official documents (European Union 2020) and also European projects.

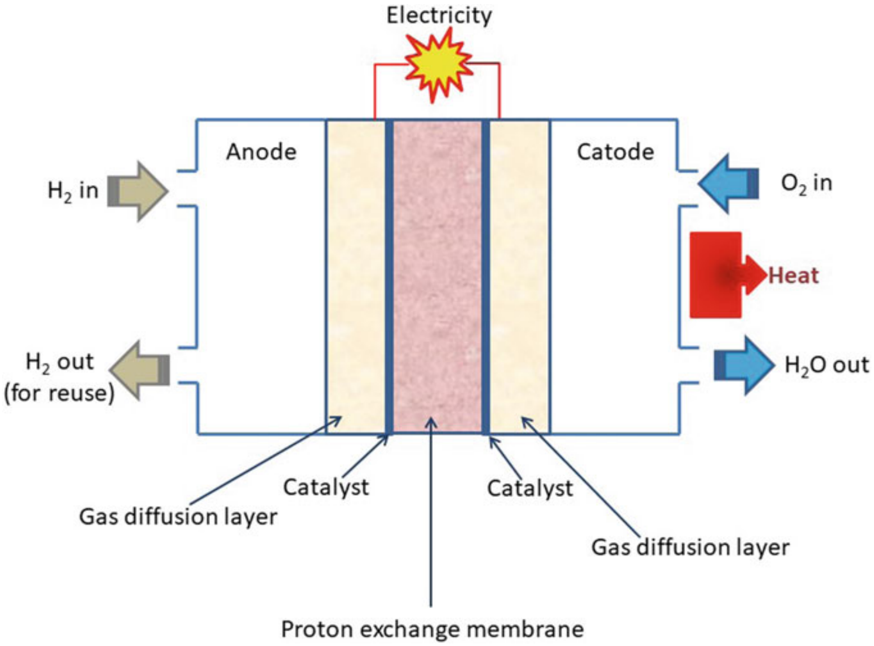

Fig. 9.7 Hydrogen fuel cell

Hydrogen is getting an increasing importance in mobility, mainly in Europe and Japan. In the case of Japan, the accident of the nuclear plant of Fukushima gave rise to a change of tendency in the sources of energy. Currently, we can note that Japan was the first country in planning to generate a hydrogen society, by adopting a Basic Hydrogen Strategy. As reported by the Switzerland Global Enterprise (Switzerland Global Enterprise 2020) the hydrogen market in Japan is expected to grow to JPY 408.5 billion by 2030, which produce very good business opportunities.

Also in Europe and USA, hydrogen has gotten an increasing importance regarding mobility. The interest of using hydrogen in transportation is the introduction of zero-emission vehicles which, at the same time are more efficient than internal combustion engines. Most of the vehicles based on hydrogen are vehicles and transit buses.

Currently there are not many vehicles with fuel based on hydrogen due to the cost of fuel cells and the limited number of fuelling stations. However, in several countries in Europe, such as Germany or France there is a quite huge network of hydrogen-fuel stations which is currently increasing.

9.5.1 Power to Gas Technology

A very interesting technology that is being more important each day is the so-called power-to-gas technology. Essentially, this process aims to generate hydrogen, using electrolysis of water making use of surplus renewable energy. The hydrogen generated in such a way is then injected into the natural gas network. As mentioned above, fluctuations in the renewable energies demand, especially during the night, are solved with this possibility of using the excess of energy to produce hydrogen.

In addition, it shall be mentioned that as the use of hydrogen increases, the use of natural gas is reduced with positive consequences regarding air pollution and greenhouse effect. However, it is important to mention that the presence of hydrogen in gas networks may produce safety problems due for instance to a phenomenon in which a flame moves upstream. This process is called flashback and may limit the quantity of hydrogen that can be injected in the natural gas pipeline system.

See for instance (Zhao et al. 2019) for details on flashback phenomenon and the effect on users burners. It is usually accepted that natural gas pipelines can safely operate with a 5–10% hydrogen content, although current technology allows to analyse more in detail the specifications of the amount of hydrogen that can be injected in the natural gas system.

In this sense SoCalGas Rule No. 30 regulates the specifications of gas to be injected into the utility pipeline. SoCalGas refers to Southern California Gas Company and is a relevant project related to power-to-gas technology is SoCalGas, which is leader in the USA. There are also many research projects in Europe related to hydrogen applications. Just to name some of the most recent ones. See (Hydrogen, Fuell Cells n.d.) for details on these and other projects (Table 9.5).

Table 9.5 Research projects

Acronym	Title	Year	Project pillar
BEST4Hy	SustainaBlE SoluTions FOR recycling of end of life Hydrogen technologies	2020	Cross-Cutting
CoacHyfied	Coaches with hydrogen fuel cell powertrains for regional and long-distance passenger transport with energy optimized powertrains and cost optimized design	2020	Transport
COSMHYC DEMO	COmbined Solution of Metal HYdride and mechanical Compressors: DEmonstration in the Hysoparc green H2 MObility project	2020	Transport
eGHOST	Establishing Eco-design Guidelines for Hydrogen Systems and Technologies	2020	Cross-Cutting
FCH2RAIL	Fuel Cell Hybrid PowerPack for Rail Applications	2020	Transport
GREEN HYSLAND	GREEN HYSLAND—Deployment of a H2 Ecosystem on the Island of Mallorca	2020	Overarching
HYPSTER	Hydrogen pilot storage for large ecosystem replication	2020	Energy
HyStorIES	Hydrogen Storage In European Subsurface	2020	Energy
MultHyFuel	MULTI-FUEL HYDROGEN REFUELLING STATIONS (HRS): A CO-CREATION STUDY AND EXPERIMENTATION TO OVERCOME TECHNICAL AND ADMINISTRATIVE BARRIERS	2020	Cross-Cutting
PROMETEO	Hydrogen PROduction by MEans of solar heat and power in high Temperature Solid Oxide Electrolysers	2020	Energy
SH2APED	STORAGE OF HYDROGEN: ALTERNATIVE PRESSURE ENCLOSURE DEVELOPMENT	2020	Transport
SH2E	Sustainability Assessment of Harmonised Hydrogen Energy Systems: Guidelines for Life Cycle Sustainability Assessment and Prospective Benchmarking	2020	Cross-Cutting
StaSHH	SUSTAINABLE AND COST-EFFICIENT CATALYST FOR HYDROGEN AND ENERGY STORAGE APPLICATIONS BASED ON LIQUID ORGANIC HYDROGEN CARRIERS: ECONOMIC VIABILITY FOR MARKET UPTAKE	2020	Energy
StaSHH	Standard-Sized Heavy-duty Hydrogen	2020	Transport
BEST4Hy	SustainaBlE SoluTions FOR recycling of end of life Hydrogen technologies	2020	Cross-Cutting
CoacHyfied	Coaches with hydrogen fuel cell powertrains for regional and long-distance passenger transport with energy optimized powertrains and cost optimized design	2020	Transport

(continued)

Table 9.5 (continued)

Acronym	Title	Year	Project pillar
COSMHYC DEMO	COmbined Solution of Metal HYdride and mechanical Compressors: DEmonstration in the Hysoparc green H2 MObility project	2020	Transport

9.5.2 Hydrogen and Methane Blending

Hydrogen blending with natural gas is quite interesting. As indicated in Kong et al. (2021) 15% of hydrogen blending in natural gas produces safe combustion without changing the properties of gas and without decreasing the efficiency of fuel and gas, both in domestic and commercial applications. The same authors propose a relation of 4:1 relation, that is 80% methane versus 20% hydrogen. This mixture is mathematically represented by a k-ε model, typical in turbulent flows applications, which is numerically solved.

According to De SAntoli (2017), it is useful to blend hydrogen into the gas pipeline network in order to improve the output of renewable energy systems. The authors propose to incorporate relatively low concentrations of hydrogen, namely in the range 5%-30% in volume, claiming that this is a viable situation without increasing risks in end-user devices.

Blended processes have particular interest in the contexts of reducing CO_2 emissions, according to several sources, such as the Natural & bioGas Vehicle Association (NGVA Europe), which is the European association promoting the use of natural and renewable gas as a transport fuel, this reduction can be up to 95%. Biomethane and synthetic gas can be used as fuels and they allow to reduce very significantly carbon emissions.

We would like to highlight that biomethane is produced in an artificial way from organic material coming from agriculture, plants or food waste. It's composition is the same as that of natural gas and hence it can be used injected in the natural gas distribution network or as fuel in natural gas vehicles.

9.5.3 Renewable Gas Potential in Transport

As we have indicated in this chapter, the potential for renewable gases is very large in Europe and globally and it is worth continuing to invest in them as their ceiling is still far away.

Table 9.6 summarized the number of vehicles on the road in Europe according to the European Vehicle Association (ACEA). As its shows, there are over 35 million vehicles.

Not only is the number very high, but the average age of the fleet is around 11–12 years, i.e. there is a large number of vehicles on the road that could be replaced.

Table 9.6 Vehicles in Europe (ACEA 2021)

Vehicles in use	2015	2016	2017	2018	2019
Passenger cars	224.338.696	229.041.465	234.122.014	238.533.039	242.727.108
Light commercial	25.510.684	26.137.417	26.982.519	27.676.122	28.110.951
Medium and high commercial	5.765.018	5.881.445	6.020.307	6.143.333	6.229.282
Buses	641.040	651.552	664.694	680.836	692.207
Total commercial vehicles and buses	31.916.742	32.670.414	33.667.520	34.500.291	35.032.440

In addition, the propulsion technologies of older vehicles are more polluting as they do not comply with the latest (and more restrictive) EURO requirements that have been implemented in the last 10 years. The GHG emissions of an older vehicle fleet will be much higher than those of a new vehicle fleet with more environmentally efficient propulsion technologies.

A summary of the average age of the vehicle fleet can be found in Table 9.7.

In addition to the above, in Table 9.8 are listed the number of vehicles powered by so-called clean technologies is insufficient to meet the EU targets.

Biomethane, in its compressed form, is a very interesting fuel for buses and, in its liquefied form, for large heavy trucks.

As can be seen in Table 9.8, natural gas is mainly used as a fuel for buses. This is very good news for biomethane, as methane-powered buses could be powered by biomethane without any risk or possible damage to the engine. Likewise, these urban buses are concentrated in large European cities such as Madrid, where more than 90% of its fleet of around 2000 buses is powered by natural gas. In other words, natural gas vehicles are a proven and mature technology and, therefore, there is a large scope for replacing most urban buses powered by diesel with new units powered by biomethane.

Central and local governments should promote the use of alternative vehicles and incentivise their use, i.e. through tax benefits and support for fleet renewal.

Table 9.7 Average age of fleets (ACEA 2021)

Vehicles in use	2015 (≤5 years)	2010 (≤10 years)	> 10 years	Total	Average age (in years)
Passenger cars	10.934.070	10.995.014	133.930.738	242.727.242	12,2
Light commercial	1.191.114	1.018.158	15.734.071	28.675.882	11,4
Medium and high commercial	223.049	136.671	3.486.093	5.666.451	12,1
Buses	32.761	30.938	391.081	689.620	11,3

Table 9.8 Vehicles classification by fuel (ACEA 2021)

Vehicles in use	Petrol (%)	Diesel (%)	Battery electric (%)	Plug-in hybrid (%)	Hybrid electric (%)	Natural gas (%)	LPG (%)	Other (%)	Unknown (%)
Passenger cars	52.90	42.30	0.20	0.20	0.80	0.50	2.70	0.10	0.20
Light commercial	7.80	89.50	0.30	0.00	0.00	0.50	1.00	0.10	0.80
Medium and high commercial	1.30	97.80	0.00	0.00	0.00	0.40	0.20	0.00	0.20
Buses	0.80	94.50	0.60	0.00	0.70	2.70	0.20	0.10	0.30

It would be very interesting to start with a strong strategy for the renewal of the last mile delivery vehicles or municipal fleets such as refuse trucks, ambulances, official cars, police cars, etc. as these are the vehicles that drive the most kilometres and therefore the vehicle groups that emit the most greenhouse gases into the atmosphere.

9.6 Guarantees of Origin

Guarantees of Origin is a certification and quality seal that ensures the renewable origin of the energy consumed (in whole or in part).

It is the only existing way to promote the development of renewable energies of all types of renewable gases. There are different ways of certifying the origin of raw materials as well as the industrial processes which are still developing in the production.

Guarantees of Origin is a fundamental tool for public Administrations to promote the development of renewable gases in form of tax advantages, Gross Domestic Product development and job creation.

Likewise, companies can compete among themselves and improve their corporate social image. From the environmental point of view, the improvement of their products has necessarily led to the discovery of new sources of raw materials and processes of better quality and lower cost for the end consumer.

Particularly in the area of mobility, the development of new alternative fuels such as renewable gases have also led to the development of better combustion engines: more efficient, sturdy and low noise. Furthermore, the savings for the end consumer, whether a particular or a company with a fleet of vehicles.

There are still challenges to be overcome in the development of guarantees of origin for renewable gas:

- Remove double-counting of registered green gas
- Incentive to gas producers to inject renewable gas into the grid
- Development of Authorized Third Parties to submit the Guarantees of Origin
- Development of the market for guarantees of origin as an economic vector
- Labelling regulation boost for each Nm3/h of renewable gas produced: where, when and how it was produced
- Flow of Guarantees of Origin throughout the production chain of renewable gases: origin of raw materials, origin of electrical energy, manufacturing process

Nowadays, regulations are being developed by all EU member countries. However, there is still a long way to go and it is an important research target to be explored. There are projects launched by the EU such as REGATRACE, and for independent bodies as ERGaR, to develop and enhance a system of emissions, trading and control of renewable guarantees of origin and regulation. Anyway, they are still the first steps to be developed for a full implementation of renewable gases in mobility and grid injection.

For example, in Spain, the standard *UNE 0062: Guarantees of origin of biomethane* (AENOR 2020) was recently developed, and a few years ago, the UNE EN 16,325:2013 + A1 standard about electricity guarantees of origin. The last standard is very interesting because it could be useful as a starting point for the implementation of guarantee of origin standards for renewable gases. In other words, it is not an unknown concept and it is already applied in other fields such as renewable electricity.

On the other hand, the European regulations about hydrogen and syngas are still in a very incipient stage, so the approval process shall be speed up.

The Commission Delegated Regulation EU 2019/1745 of August 13, 2019, which completes and modifies Directive 2014/94 / EU of the European Parliament and of the Council regarding recharging points for motor vehicles category L, the supply of electricity in port to inland waterway vessels, the supply of hydrogen for road transport and the supply of natural gas for road and inland waterway transport and the Delegated Regulation EU is repealed 2018/674 of the Commission.

In Europe, regarding stationary applications, there are regulations related to the protection of workers (directive 89/391 / CE); protection of workers exposed to risks of explosive atmospheres (directive 99/92 / CE); equipment protection (directives 98/37 / CE, 99/9 / CE and 97/23 / CE); and protection of the environment and the population (SEVESO II directives 96/82 / CE and 2000/33 / CE).

Other international and regional standards are summarized in the Table 9.9.

Finally, the area of guarantees of origin should be developed through legislation that provides a legal framework for investors, engineers, builders and end-users. It is essential to promote these projects that will provide support to the renewable gases market and possible investment strategies.

9.7 Conclusions

In later years, EU has strongly promoted GHG emission reduction policies, especially aimed to make a cleaner transport.

Renewable gases are a totally valid and proven reality solution to achieve these objectives:

- Biomethane and syngas are the same methane molecules that are already used in vehicles. The only difference is that they are produced by industrial processes instead of being created by natural processes over many thousands of years. Artificial methane and natural methane are fully compatible and could be mixed in tanks or pipelines.
- Hydrogen is a valid and clean source of energy to produce electricity for the transport and other sectors. Electricity is a valid fuel for vehicle mobility, so the lower GHG emissions in the production process, the lower emissions in transport sector.

Table 9.9 International regulations

Standard	Country	Type
US Department of Labor, OSHA: 29 CFR 1910.103 Hydrogen	USA	Safety
ISO TR 15,916 Basic Considerations for the Safety of Hydrogen Systems	USA	Safety
GB 4962–2008 Technical safety regulation for gaseous hydrogen use	International	Safety
KS B ISO 15916 Basic consideration for the safety of hydrogen system	Korea	Safety
GB 4962–2008 Technical safety regulation for gaseous hydrogen use	China	Safety
ISO 14687–2 Hydrogen Fuel—Product Specification, Part 2: PEM fuel cell applications for road vehicles	International	Fuel specification
GB/T 7445–1995 Pure hydrogen, high purity hydrogen and ultra-pure hydrogen	China	Fuel specification
ASTM D7634-10 Microscopic Measurement of Particulates in Hydrogen Fuel	USA	Tests of contaminants
ISO TC197 Working Group 9 (ISO 16110–2) Hydrogen Generators Using Fuel Processing Technologies Part 2: Test Method for Performance	International	Performance of generators
US Department of Labor, OSHA: 29 CFR 1910.103 Hydrogen	USA	Installation of generators
NFPA 55 Storage, Use and Handling of Compressed Gases and Cryogenic Fluids in Portable and Stationary Containers, Cylinders and Tanks: Chap. 10 Gaseous Hydrogen Systems	USA	Storage and transport
IEC 60,079–29-2 Explosive atmospheres—Part 29–2: Gas detectors—Selection, installation, use and maintenance of detectors for flammable gases and oxygen	International	Hydrogen detectors
US Department of Labor, OSHA: 29 CFR 1910.103 Hydrogen	USA	Safety

The average age of buses and light commercial vehicles in Europe is over 11 years. Likewise, the average age of heavy commercial vehicles and passenger cars in Europe is over 12 years. More than 95% are powered by petrol and diesel. In other words, there are a large number of vehicles in Europe that could be replaced by vehicles powered by renewable gases and therefore reduce overall GHG emissions. There is also a slight tendency to replace these vehicles with alternative fuels, although their number is still practically negligible.

This is an opportunity for the development of renewable gases as a key vector in the reduction of GHG emissions required by the new European guidelines.

The smooth and reliable development of R&D projects about renewable gases could bring to Europe not only a reduction of GHG emissions but also opportunities to generate employment, reduce costs for public and private companies, reduce household expenditure and improve the vehicle fleet.

In scientific research, renewable gases offer a multitude of alternatives for the identification of raw materials and their transformation into energy sources, as well as for storage and transport. In our opinion, it would be necessary to promote research in at least the following areas in order to encourage the use of renewable gases as a real alternative in mobility:

- sources of methane, hydrogen and syngas feedstocks
- methane, hydrogen and syngas storage: compressed, liquefied, geological, adsorbed
- capture, transport and storage of CO_2 as a source of renewable gases

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Chapter 10
Hydrogen in Spark Ignition Engines

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Abstract In the present world, there is a huge demand for spark ignition (SI) engines in transportation sector as there is an increase in population of light commercial vehicles such as motorcycles and cars. Petrol powered SI engine produces less noise and vibration with high thermal efficiency as compared with diesel engines. Utilization of hydrogen as fuel in SI engines has found to improve the combustion and performance characteristics of engines. The primary fuel petrol and secondary fuel hydrogen are induced in the inlet manifold. The various percentage of hydrogen used in the SI engines include 5, 10, 15, 20 and 25%, together with different ratios of petrol fuel. Whenever hydrogen induced in the SI or compression ignition (CI) engines for safety purpose a flame arrester is used. This current was assessed to calculate the combustion, performance and emission characteristics of a high-speed single cylinder SI engine operating with different hydrogen–petrol blends. The various percentage of hydrogen was inducted along with petrol fuel to reduce the tailpipe emissions. The hydrogen was mixed with base fuels such as P95H5 (95% petrol, 5% of hydrogen),

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P90H10 (90% petrol, 10% of hydrogen), P85H15 (85% petrol, 15% of hydrogen), P80H20 (80% petrol, 20% of hydrogen) and P75H25 (75% petrol, 25% of hydrogen). About 20% of hydrogen blend showed greater brake thermal efficiency of 26.8% when compared with base fuel. Furthermore, 25% of hydrogen mixed with petrol drastically reduced the hydrocarbon content, carbon monoxide content and exhaust gas temperature petrol by 22.8%, 40.26% and 15.61%, respectively, when compared with base fuel at full load condition.

Keywords Hydrogen · Petrol · Hydrocarbon · Brake thermal efficiency · Carbonmonoxide

10.1 Introduction

The fossil fuel powered industries are under immense pressure to meet the required strict emission targets. Fossil fuel shortages and environmental pollution demand some cleaner and sustainable fuel that can dominate both the power and internal combustion engine industry (Brayek et al. 2019). Hydrogen and fuel cells have the potential to minimise greenhouse gas emissions in a variety of applications due to their high efficiency and near-zero emission operations. According to a study financed by the Energy Department, hydrogen has the potential to reduce emissions in the following ways: (a) in light-duty highway vehicles, emission reduction is more than 50% to 90%, compared with today's petrol vehicles; and (b) in specialty vehicles, emissions are reduced by more than 35%, compared with contemporary diesel and battery-powered lift trucks; and (c) transit buses have shown to be 1.5 times more fuel efficient than diesel fuelled internal combustion engine buses and 2 times more efficient than natural gas powered buses. Auxiliary power units (APUs) reduce pollutants by more than 60% when compared with idling truck engines. Combined heat and power (CHP) systems reduce emissions by 35–50% when compared with traditional heat and power sources (Changwei and Wang 2009). The most difficult aspect of producing hydrogen, especially from renewable sources mainly depends on the investment. On a per-mile basis, hydrogen must be cost-competitive with conventional fuels and technology for use as transportation fuel cells. Another challenge is the storage of hydrogen as it is highly flammable. Apart from being a clean burning fuel having superior physico-chemical properties, hydrogen has already established its space in energy sector (Changwei et al. 2010). Hydrogen can be produced from a range of local sources, including natural gas, nuclear power, biomass, and renewable energy sources such as solar and wind power. These characteristics make it a desirable fuel for transportation and electricity generation. It can be readily utilized in automobiles, homes, portable powers, and a variety of other applications. Natural gas is now the most common source of hydrogen generation, accounting for roughly three-quarters of the total dedicated hydrogen production of around 70 million tons per year. This accounts for around 6% of global natural gas consumption (Das 2007). In comparison to typical fossil fuels like petrol, diesel, and natural gas, hydrogen has a wider range of combustion parameters like faster diffusion rate and flame propagation (Dash et al. 2020). Hydrogen also possesses quite low ignition energy. Because of a variety of factors, hydrogen has recently gained momentum as a viable energy resource for upcoming generation of automotive. In addition to hydrogen atoms, all common fossil fuels contain carbon atoms and moreover carbon dioxide (CO_2) is a major product generated during the conversion of the fuel to energy. The hydrogen releases just water as a by-product but not CO_2 which is a major greenhouse gas. However, pure hydrogen suffers storing issues which can be addressed by blending with other liquid fuels. Production, storage, portability, transport, and purity are the main drawbacks that prevent hydrogen from becoming a widely used engine fuel (Edmondson and Heap 1971). Over a wide spectrum of air–fuel ratio, hydrogen can be utilized in IC engines. Over many decades, several researchers have attempted to use hydrogen as an engine fuel with varying levels of success. Several successful projects have proved that hydrogen is far superior to present automotive fuels in many ways. Elkelawy and Bastawissi 2013 studied the inclusion of hydrogen to a petrol powered spark ignition engine at various operating regime. They observed that the engine's idle speed is roughly maintained around its initial objective as hydrogen enrichment levels rise, while spark timing varies somewhat with and without hydrogen addition. With hydrogen, however, the intake air flow reduces. The SI engine with hydrogen enrichment has a higher indicated thermal efficiency. The periods of flame generation and propagation, as well as COVimep, decrease as the proportion of hydrogen infusion is increased. They also reasoned that with the decreased in-cylinder temperature and increased residual gas percentage, NOx emission reduces as hydrogen enrichment increases. CO and HC emissions initially fall with the addition of hydrogen but when the hydrogen energy share hits 14.44% the emission begin to rise again. Shivaprasad et al. (2014) experimentally studied the performance of a high speed Lombardini make 9 kW@4400 rpm petrol engine with the inclusion of hydrogen share from 0–25 vol.%. Hydrogen addition resulted in improved brake mean effective pressure. Furthermore, 20% hydrogen inclusion results in maximum BMEP at engine speed of 3000 rpm. They also witnessed a rise in BTE up to 20% hydrogen share. By hydrogen enrichment, reduction in CO and HC emission is seen, whereas, rise in NOx emission is also seen. Elumalai et al. 2021 observed that for direct injection hydrogen powered SI engine the performance is improved at partial loads. Technically, no CO_2 emission is reported and minor HC and CO forms as a result of engine oil burning inside the cylinder, however, NOx emission increased considerably for λ value of 1 to 2 (9). Studied the performance of a four cylinder water cooled engine powered by mixture of petrol and hydrogen, where hydrogen is added by direct injection. They employed unique lean burn technology for the engine trial. The oxygen content in the combustion system is increased due to the lean burn. Additionally, hydrogen has a faster flame propagation rate, which may aid in CO oxidation. After infusing 10% share of hydrogen, the mean effective pressure and thermal efficiency are enhanced by 10% and 4–4.5%, respectively. Although lean burn can enhance thermal efficiency and reduce throttling loss, it increases COV and HC emissions. With an acceptable injection technique and lean burn circumstances, the COV can be lowered to below 1% and HC emission can be identical to the standard objective level. The inclusion of hydrogen raises the peak cylinder warmth, resulting in a considerable rise in NOx emissions; however, using lean-burn technology, NOx can be dramatically reduced while power and fuel efficiency can be significantly improved. Ji and Wang 2009 studied the hydrogen powered SI engine characteristics with ECU operated time-based manifold injection system. All experiments are conducted at speeds ranging from 1100 to 1800 rpm. For comparison purposes, baseline observations are made with petrol. In the event of hydrogen operation, maximum braking power is reduced by 19.06%, while peak brake thermal efficiency is raised by 3.16%. They reasoned that due to lower volumetric efficiency of hydrogen, the brake power is lowered. Karim 2003 have made numerical investigation to optimize the various injection strategies, such as port fuel injection (PFI), direct injection (DI) and combination of PFI + DI, on the hydrogen fuelled SI engine characteristics. At wide-open throttle, the suggested hybrid technique can satisfy low and high load situations without anomalous combustion. At low and high load areas, the hybrid approach of PFI + DI has higher suggested thermal efficiency and engine operation consistency than port fuel injection and in-cylinder direct injection, respectively. From the literatures, it was observed that limited works have been reported on hydrogen powered SI engine. Moreover, some results are also contradictory with respect to NOx and HC emissions. In this backdrop, much quality based work needed to be done on hydrogen powered SI engines in order to draw some strong conclusions and plan future prospects.

In Table 10.1 two symbols are used the upward triangle shows an increase and downward triangle shows a decrease. NC means no change.

Table 10.1 Performance and emissions characteristics of SI engines fuelled by hydrogen

H_2 Supply	Load (%)	Performance		Emission Characteristics				References
		BSFC	BTE	CO	NOx	HC	PM/Smoke	
9.4–37%	25–100	NC	▲	▼	▼	▲	▼	Li and Karim (2006)
9.4–37%	50–75	NC	▲	▼	▲	▲	▼	
2–9.5 lpm	25	NC	▲	NC	▼	▼	▼	Masood et al. (2007)
2–9.5 lpm	50–75	NC	▲	▲	▲	▲	▼	
2–9.5 lpm	100	NC	▲	▲	▼	▼	▼	
10–40%	10	▲	▼	▼	▼	▼	▼	Murugesan P et al. (2017)
10–40%	30	▲	▼	▼	▼	▼	▼	
10–40%	50	▼	▲	▼	▼	NC	▼	
10–40%	70–90	▼	▲	▼	▼	▼	▼	
0–46%	100	▲	▲	▼	▲	▲	▼	Navale et al. (2017)
10–100%	20–100	▼	▲	▼	▲	▼	▼	Negurescu et al. (2012)
0–38.6%	100	▲	▲	▲	▼	NC	–	Perumal Venkatesan et al. (2021)

Table 10.2 Comparison of properties of various gases versus hydrogen

Properties	Methane	Propane	Octane	Methanol	Hydrogen
Density (kg/m^3)	0.656	2.009	780	793	0.083
LHV (MJ/kg)	50	45.6	47.9	22.4	120
Viscosity (10–5 Pas)	1.03	0.43	0.53	0.61	0.84
Stoichiometric ratio	17.2	15.6	14.7	6.5	34.3
Combustible range (%)	5–15	2.1–9.5	0.95–6	6.7–36	4–75
Adiabatic flame temperature (°C)	1949	1980	1927	1963	2254
Ignition energy (mJ)	0.30	0.30	0.26	0.14	0.017
Ignition temp (°C)	540–630	450	415	460	585

10.2 Materials and Methods

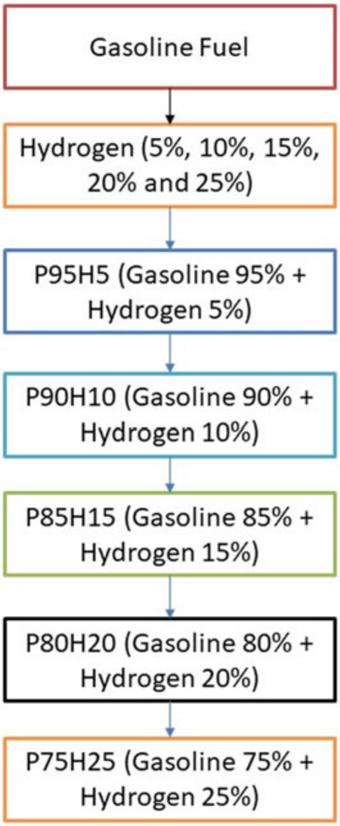
10.2.1 Hydrogen

Hydrogen is a clean-burning fuel when compared with other types of alternative fuels like biofuel, CNG, LPG, and biodiesel. There are various methods to produce hydrogen gas such as steam reforming and electrolysis of water. Now-a-days, many application sectors use hydrogen as an energy source (Rahaman et al. 2009). The use of hydrogen in IC engines is a very lesser quantity because of safety and handling issues. There are many benefits when hydrogen is used as a fuel in an IC engine, the results were obtained have more advantages than conventional fuels inclusive of lesser noise, lower vibration, greater efficiency, and cut down the emission. Hydrogen is the only gas having greater octane (>130) when compared with other types of gases. Hydrogen has the only demerit of storage and handling when used in an IC engine. And also, a very much less quantity of hydrogen can only be used in the combustion process of an IC engine (Sandalcı and Karagoz 2017). Table 10.2 shows the comparison of properties of various gases versus hydrogen.

10.2.2 Fuel Preparation

The present investigation was analyzed in SI engine powered by hydrogen blend petrol. From the study, primary fuel is used as petrol and secondary fuel is hydrogen. The hydrogen mixed with base fuel was prepared the fuel blend of P95H5 (95% g Petrol, 5% hydrogen), P90H10 (90% petrol, 10% hydrogen), P85H15 (85% g Petrol, 15% hydrogen), P80H20 (80% g Petrol, 20% hydrogen), and P75H25 (75% g Petrol, 25% hydrogen) as shown in Fig. 10.1.

Fig. 10.1 Flowchart depicting concentration of fuel used in analysis



10.3 Experimental Setup

The experiment was carried on single cylinder PRODIT petrol engine. Table 10.1 provides details of engine. The research lab consisted of test rig including an eddy current-type dynamometer, exhaust gas analyzer, petrol metering device as well as other auxiliary equipment (Saravanan and Nagarajan 2009a). A diagrammatic representation of the test rig is given in Fig. 10.2. A 50 kg hydrogen cylinder was used to supply hydrogen in the intake manifold. Cylinder contains compressed hydrogen at 200 bar. The hydrogen stream regulate framework had been fitted at the upper corner of the hydrogen cylinder that consisted of hydrogen controller as well as the hydrogen flow pointer. The hydrogen control process controls the hydrogen stream supplied to the engine as well as the quantity of hydrogen stream could be defined by hydrogen stream pointer (Changwei and Wang 2009). The petrol engine was modified for utilizing hydrogen along with gasoline. The flame trap placed was placed in the middle of the hydrogen cylinder and engine which is used to suppress the back fire in Fig. 10.3. The prepared electronic controller was connected with the data processor to

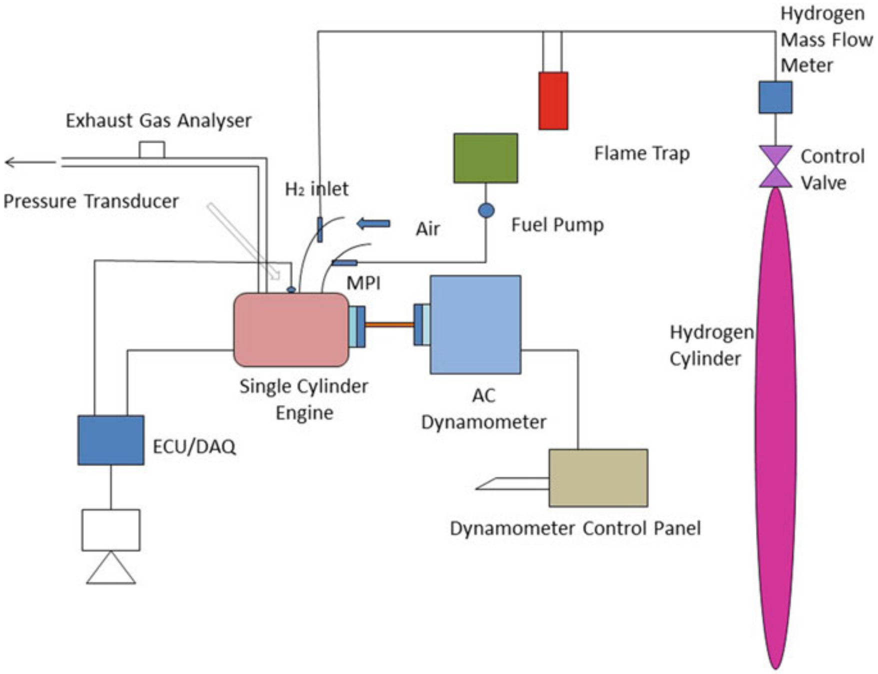


Fig. 10.2 Experimental setup

the RS-232 port. The exhaust release from the test engine had been assessed utilizing exhaust gas analysis apparatus that was located at exhaust system. An assessment of sensor performance, including ranges, cross sensitivity, reliability, durability, and expense are made. As hydrogen leakage are probable, hydrogen sensors are installed at hydrogen connectors that are regularly isolated, where hydrogen may concentrate in buildings air inlet and outflow pipes. While developing a hydrogen detection technique, aspects such as sensor reaction times, detection limit, sensor serviceability, sensor maintenance and calibration needed, issues arising due to sensitivity, and field of view should be considered. Special attention must be paid to the identification of hydrogen leaks and hydrogen flame in hydrogen test cells. Apart from detecting gaseous hydrogen to ensure a safe test cell atmosphere, hydrogen leakage should also be monitored as leakage could easily produce flames without warning. Especially, a hydrogen leakage would not be easily detected using a gaseous hydrogen monitoring device until it leads to ignition. The experiment assessed at engine speeds of 2000–4000 rpm by incrementing the speed around 500 rpm. Using a controller, the various mass fraction of hydrogen (5, 10, 15, 20, and 25%) was inducted along with base fuel. The present study intended to analyze the operation as well as release of toxic gas attributes in a high velocity SI engine that had utilized hydrogen enhanced besides ECU regulated MPI system. Table 10.3 shows that specification of engine.

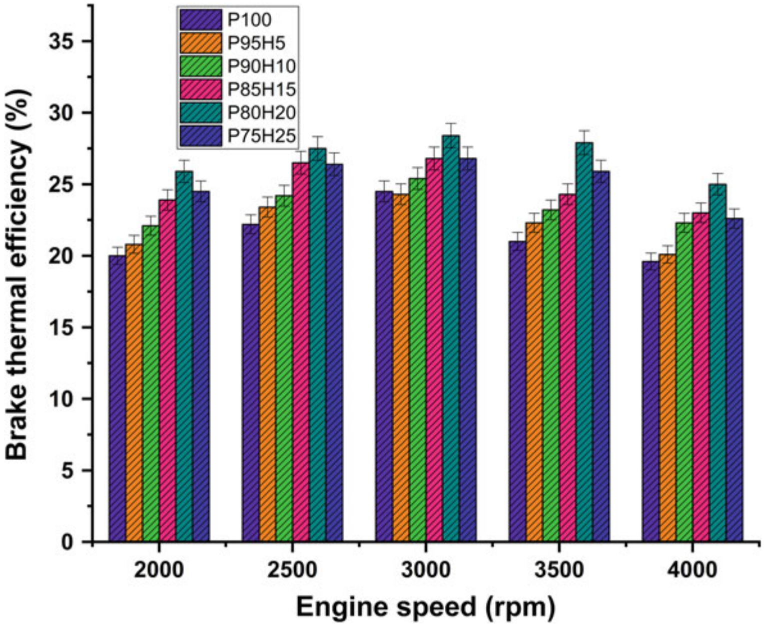


Fig. 10.3 Graph depicting speed versus BTE

Table 10.3 Engine specification

Engine model	PRODIT Gpetrol engine
Bore (mm)	90
Stroke (mm)	85
Compression ratio	9.6
Maximum torque	23 Nm
Maximum power	11 kW
Ignition timing	9.1^0 CA before TDC
Fuel	Petrol fuel + hydrogen

10.3.1 Uncertainty Analysis

The results of the analyses performed using various apparatus largely depend on the standard of the manufacturers. To overcome the drawbacks and to assure standard results using the instruments, uncertainty analyses of various systematic parameters are performed. Errors and uncertainty while using instruments largely depend on various natural conditions, perceptions, assembling of the instruments, working conditions, and also on the accuracy of the instruments. The evaluation tests were performed fourtimes and the average values were taken for the assurance of vulnerability in this work as shown in Table 10.4.

Table 10.4 Uncertainty analysis

S. no	Parameters	Systematic errors (±)
1	Load indicator	0.2
2	Speed sensor	1.0
3	Temperature sensor	0.1
4	Pressure sensor	0.5
5	Crank angle encoder	0.2
6	Smoke meter	1.0
8	Fuel burette	1.0
9	Manometer	1.0

$$\sqrt{\begin{array}{c}[uncertaintyofload]^2 + [uncertaintyofspeed]^2 + [uncertaintyofTemp]^2 + \\ [uncertaintyofunburntPressure]^2 + [uncertaintyofCA]^2 + \\ [uncertaintyofsmoke]^2 + [uncertaintyoffuel]^2 + \\ [uncertaintyofmanometer]^2\end{array}}$$

$$= \sqrt{[0.2]^2 + [1]^2 + [0.1]^2 + [0.5]^2 + [0.2]^2 + [1.0]^2 + [1.0]^2 + [1.0]^2 + [1.1]^2 + [0.1]^2}$$

$$= 2.21\%$$

10.4 Results and Discussion

The two fuels used in the SI engine include the primary fuel petrol and the secondary fuel hydrogen. The hydrogen mixed with base fuels were P95H5 (95% petrol, 5% hydrogen), P90H10 (90% petrol, 10% hydrogen), P85H15 (85% petrol, 15% hydrogen), P80H20 (80% petrol, 20% hydrogen), and P75H25 (75% petrol, 25% hydrogen). The various concentrations of hydrogen and petrol fuels filled with SI engine were found performance and emission characteristics.

10.4.1 Brake Thermal Efficiency

Figure 10.3 expose the variations of brake thermal efficiency (BTE) and different speed conditions of SI engine. The BTE evaluates the performance of the engine. The induction rate of hydrogen was increased with increase in the BTE of engine for all load conditions. petrolIt was clearly observed that the highest BTE was 26.05% for P80H20 at speed 3500 rpm. It might be due to premixed charge of hydrogen and petrol and high energy density of hydrogen which exhibits better oxidation process (Saravanan and Nagarajan 2009b). The BTE of P95H5, P90H10, P85H15, P80H20, and P7525 is 20.1%%, 22.3%, 23.0%, 25.0%, and 22 0.06%, respectively, when compared with 17.6% for without hydrogen induced P100. It could be attributed that the flame speed of hydrogen is three times greater than the petrol and wide range of flammability of hydrogen which scattered throughout the chamber can be achieved by complete combustion petrol. The petrol mixture blended with hydrogen showed faster combustion and enriched energy value thus resulting in better combustion efficiency. The results also showed that BTE of 0% hydrogen induction showed lower BTE than other test fuel condition due to energy value of petrol premixed charge was lower than hydrogen premixed charge. Moreover, 20% hydrogen enrichment was exhibited 14.4, 10.5, 5.6 and 5.4% higher BTE P95H5, P90H10, P85H15 and P75H25 at rated speed condition. Addition of hydrogen above 20% to the petrol fuel showed decrease in BTE, due to the irregular flame propagation and start of combustion which leads to notice the unstable engine operation. Saravanan et al. 2007 as the fraction of hydrogen added increases accumulation of hydrogen increases in the cylinder which results in a decrease in the amount of air required for complete combustion. For these reason, the 25% hydrogen enrichment fuel was found to have low thermal efficiency (Satyapal 2017).

10.4.2 Brake Mean Effective Pressure

Figure 10.4 exhibits the difference of brake mean effective pressure (BMEP) for the hydrogen enrichment petrol in SI engine. In Fig. 10.4, it was clearly seen that gradual increase in hydrogen concentration in the fuel mixture gradually increases the BMEP all speed condition. Due to greater value of octane number and wider range of flammable limits found in the hydrogen fuel, the combustion pressure also increases the BMEP. In addition, the hydrogen has faster flame propagation and greater adiabatic temperature when compared with the petrol fuel that are helpful for uniform combustion throughout the chamber. By increasing the hydrogen concentration by 25%, the BMEP was decreased by 4.5% when compared with P80H20. Combination of multi-directional flame propagation and less entry of air into the manifold leads to inferior combustion rate. The P80H20 showed higher value of BMEP when compared with the other test fuels. It might be due to unidirectional flame propagation and less flame quenching zones leading to better combustion rate thereby enhanced BMEP (Shivaprasad et al. 2014).

10.4.3 Carbon Monoxide

Figure 10.5 displays graph depicting the difference in carbon monoxide (CO) with various engine speed condition for petrol enriched hydrogen. Normally, petrol operated SI engine emits more CO at higher speed condition due to poor air utilization and fuel rich zone in chamber petrol. The test results showed that a reasonable reduction of CO emission was found in the hydrogen enriched SI engine. It was mainly due to

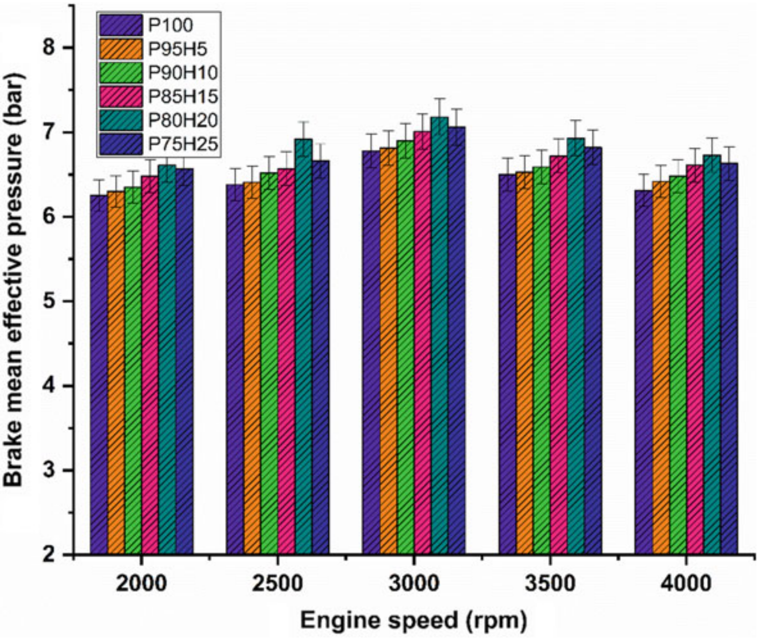


Fig. 10.4 Graph depicting speed versus BMEP

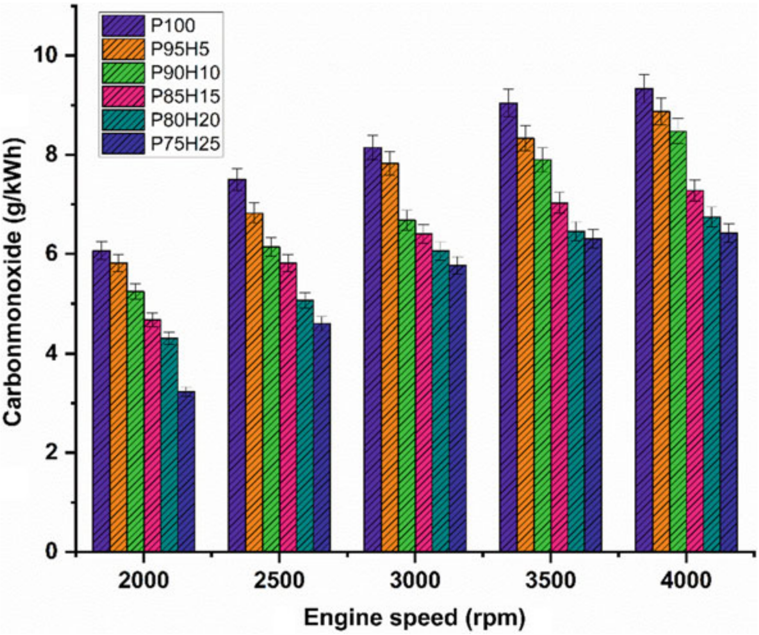


Fig. 10.5 Graph depicting speed versus CO

the absence of carbon atoms in the hydrogen fuel leading to restriction of CO formation (Shivaprasad et al. 2014). When increasing the hydrogen concentration with the petrol, the drastic reduction of CO emission was observed whereas beyond 25% hydrogen enrichment the CO emissions start to increase. This result increases the wall impingement and enhances the ignition lag that results in incomplete combustion. The magnitude of CO emission for the fuels P95H5, P90H10, P85H15, P80H20, and P75H25 were reduced by 8.8%, 14%, 31.3%, 33.5%, and 41.2%, respectively, when compared with P100. It can be inferred that more chances for formation of OH radical by hydrogen enrichment can results in better combustion efficiency. Utilization of hydrogen along with petrol leads to positive impact on greater flame velocity, faster combustion rate, and higher stoichiometric air–fuel ratio that results in improve the CO oxidation. The 25% of hydrogen induction showed 26.2%, 13.5%, 9.8% and 4.7% lower CO emission than hydrogen induction of 5, 10, 15, and 20% respectively. The hydrogen produces higher combustion temperature when compared with the petrol which aids to enhance the carbon oxidation. The maximum CO reduction was achieved by 25% of hydrogen induction because of high adiabatic flame temperature and wide flammability which enhance the CO conversion rate into CO_2. While increase in the hydrogen induction beyond 25% leads to replacement of air quantity that results in poor air utilization and lower volumetric efficiency therefore reduced CO_2 formation.

10.4.4 Hydrocarbon

Figure 10.6 exhibits the difference in hydrocarbon (HC) emission with respect to variable engine speed for hydrogen enrichment with P100. From the results, it can be seen that petrol powered SI engine produced higher HC emission than hydrogen assisted combustion of petrol. When increasing the hydrogen concentration, the HC emission was drastically reduced at all speed condition. It could be ascribed that addition of hydrogen and formation of OH radial in to the combustion process enhances the oxidation of fuel. The test results also revealed that the premixed charge of hydrogen and petrol were found to minimize HC emission because of high post-combustion temperature and enhanced oxidation reaction which promoted faster combustion rate. The other possibility to reduce the HC emission for hydrogen induction was by lowering the quenching distance and high flame velocity those results in shortening the combustion duration (Shivaprasad 2018).

The shortening of quenching distance and combustion duration helps to burns the fuel completely during combustion which in turn reduces HC formation. The HC emission for P95H5, P90H10, P85H15, P80H20, and P8025 was reduced by 6.7%, 9.8%, 11.6%, 19.7%, and 22.8%, respectively, when compared with the P100. The P100 found highest HC emission of about 224 ppm. It was mainly due to the lesser chemically correct mixture of petrol which enabled more amount of fuel to enter

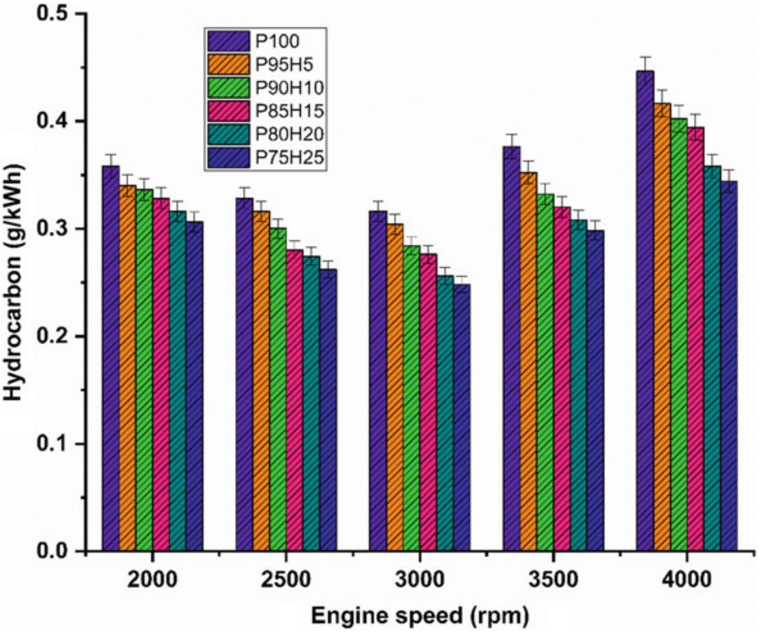


Fig. 10.6 Graph depicting speed versus HC

into the chamber and inferior air utilization also results in HC formation. The 25% of hydrogen induction drastically reduced the HC emission as related to P100. It might be due to high stoichiometric air–fuel mixture of hydrogen (34:1) and high diffusivity with air that results in more air utilization and promote the initial oxidation of hydrocarbon.

10.4.5 Oxides of Nitrogen (NOx)

The effect of hydrogen enrichment with P100 on formation of NOx emission in SI engine is portrayed in Fig. 10.7. Evolution of higher temperature during combustion results in NOx formation in the engine. While increasing the concentration of hydrogen gradually increase the NOx emission in SI engine. It could be attributed to higher heat value of hydrogen dissipate more amount of heat during combustion that aids to promote the nitrogen oxidation (Soberanis and Fernandez 2010). In addition, higher hydrogen induced in to the inlet manifold raises the combustion rate which enhances the post-combustion temperature. The NOx emission for P95H5, P90H10, P85H15, P80H20, and P8025 was increased by 11.3%, 21%, 40.6%, 55%, and 62.3%, respectively, when compared with P100. The 25% of hydrogen induced in to the base fuel showed the maximum rate of formation of oxides of nitrogen at rated speed

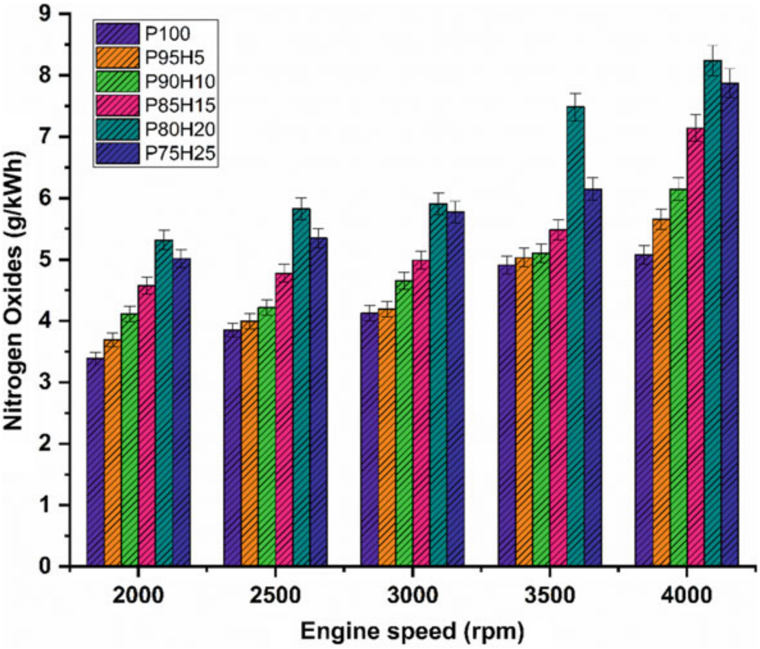


Fig. 10.7 Graph depicting speed versus NOx

condition. This was mainly due to the wide flammability and high cylinder temperature produced during combustion which exhibited more NOx formation (Verhelst and Wallner 2009). The lowest oxides of nitrogen are observed for blend P100 which was 18.2% lower when compared with 25% of hydrogen induced fuel. This result was responsible for lower heating value and less air–fuel ratio of P100 which results in fuel rich zone in cylinder therefore lower combustion temperature (Verhelst et al. 2006).

10.4.6 *Exhaust Gas Temperature*

The impact of hydrogen enrichment with P100 on exhaust gas temperature (EGT) in SI engine was represented in Fig. 10.8. The shorter combustion rate and high cylinder temperature leads to production of higher EGT. It was evident that hydrogen enriched fuel observed higher EGT than normal fuel because of high adiabatic flame temperature of hydrogen which resulted in enhanced post-combustion temperature. EGT for all test fuels was lower under low speed condition. At full speed condition, high rate hydrogen induction with base fuel produced superior EGT than lower rate of hydrogen induction. It was mainly due to more air utilization and better combustion leading to rise in cylinder temperature (White et al. 2006). When increasing the hydrogen concentration linearly the EGT increases for all speed condition. The

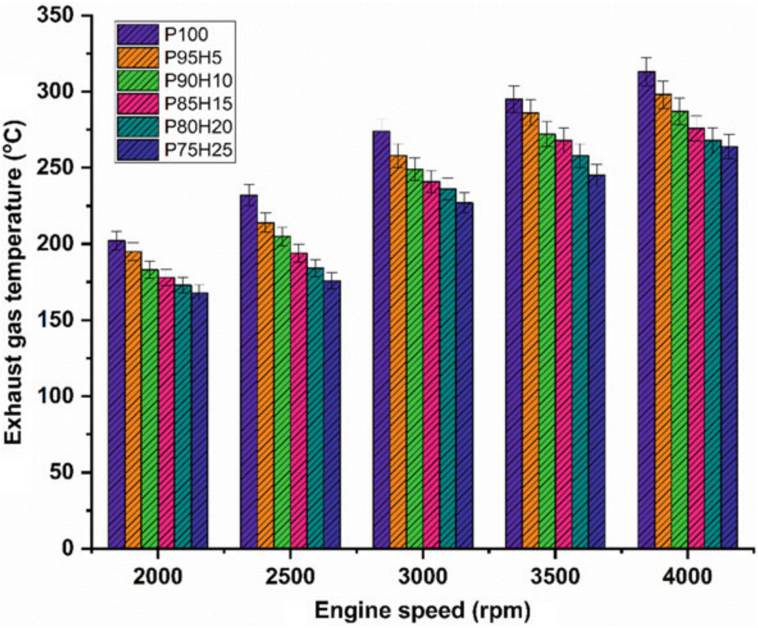


Fig. 10.8 Graph depicting speed versus EGT

highest EGT was observed for 25% of hydrogen induction owing to a higher diffusivity of hydrogen which leads to easily mix the fuel with air thereby increasing the homogenous charge preparation. The EGT of P95H5, P90H10, P85H15, P80H20, and P75H25 was increased by 4.7%, 8.3%, 13.4%, 14.3%, and 15.6%, respectively, when compared with the 0% of hydrogen induction with base fuel. This result showed that the dual effect of higher flame propagation of hydrogen and low quenching distance together improved the combustion rate of the test fuels (Yu et al. 2017).

10.5 Conclusions

In the present study, the P100 inducted along with various percentage of hydrogen through intake manifold to assess the SI engine characteristics. The ultimate aim of this study was to find the optimum percentage of hydrogen induction with P100 for use in SI engines. Based on the experimental results, it was clearly identified that hydrogen enriched P100 showed better performance and lower emission value. The effect of hydrogen enrichment with P100 on SI engine performance and emission parameter was exposed in Fig. 10.9.

(a) The highest BTE noticed for the fuel P80H20 was about 26.05% at rated speed condition owing to superior heating value and flame velocity of hydrogen which exhibits better combustion rate.

(b) While increase the hydrogen enrichment beyond 25%, unstable engine operation and knocking also was observed due to partial replacement of oxygen and poor air utilization rate that resulted in fuel zone in chamber thereby inferior combustion rate.

(c) The HC and CO emission of P75H25 was reduced by 22.8% and 41.28%, respectively, when compared with base fuel. Due to wider flammability, high flame velocity, and absence of carbon particle in hydrogen fuel which reduce the quenching distance thereby increase the cylinder temperature and oxidation rate of CO and HC.

(d) In contrast, when increasing the hydrogen concentration with P100, NOx emission was linearly increased due to high adiabatic flame temperature of hydrogen and high stoichiometric air–fuel ratio (34:1) leads to consumption of more quantity of air during the combustion thus resulting in high peak cycle temperature.

Scope of Future

The various future scope of the study includes:

(a) Instead of petrol different fuels like biodiesel, biofuel and so on can be used.

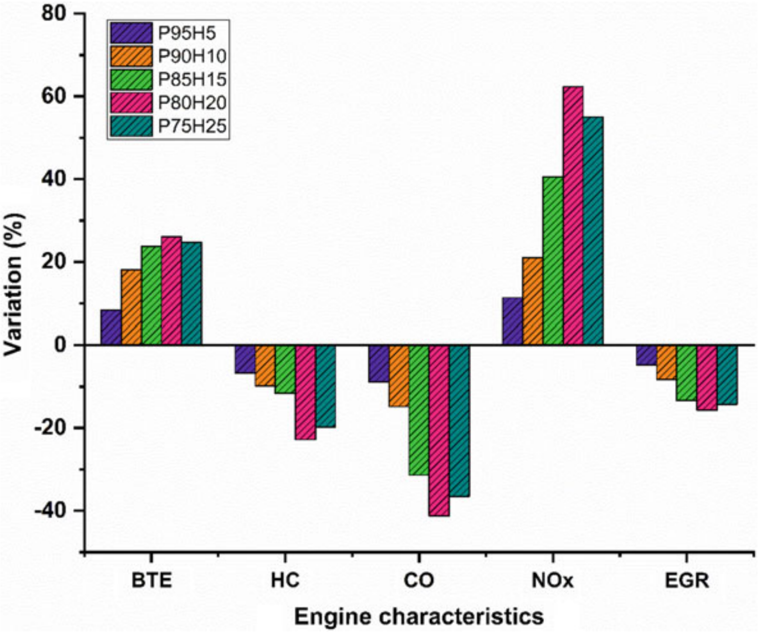


Fig. 10.9 Bar graph depicting overall results and discussions

(b) Instead of hydrogen different gases like LNG and CNG can be used.

Abbreviations

P100	Pure petrol fuel
P95H5	95% petrol fuel + 5% of hydrogen
P90H10	90% petrol fuel + 10% of hydrogen
P85H15	85% petrol fuel + 15% of hydrogen
P80H20	80% petrol fuel + 20% of hydrogen
P75H25	75% petrol fuel + 25% of hydrogen
EGT	Exhaust Gas Recirculation
BTE	Brake Thermal Efficiency
HC	Hydrocarbon
CO	Carbon monoxide
NOx	Oxides of Nitrogen
ID	Ignition Delay
BMEP	Brake Mean Effective Pressure
LHV	Lower Heating Value
NC	No Change
PFI	Port Fuel Injection
H_2	Hydrogen
DI	Direct Igntion
SI	Spark Ignition

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Chapter 11
Advances in the Utilization of Biogas in Diesel Engines: An Exergy Based Approach

Saket Verma, L. M. Das, and S. C. Kaushik

Abstract In order to reduce the use of fossil fuels in the transportation sector, various alternatives have been explored in the past. Biogas is an interesting candidate in this context with its large potential in countries like India, which can be utilized for vehicular as well as decentralized power generation applications. Biogas is a renewable fuel that is produced from organic waste materials through anaerobic digestion process. The produced raw biogas contains methane as the fuel; however, carbon dioxide is also present in considerable amount. This inert gas reduces the flame speed and heating value of biogas and eventually deteriorates engine performances. The auto-ignition temperature of biogas is high enough that it cannot be directly utilized in the diesel engines. One of the easiest and flexible ways to utilize biogas in diesel engines is through 'Dual Fuel (DF)' technique. In this technique biogas is used as the main gaseous fuel and another liquid fuel (commonly diesel) is used as the pilot fuel. In this way, existing diesel engines can use biogas as the fuel with minimum engine modifications. Nevertheless, the performance of biogas DF engine has been found to be much poor than the standard diesel engine, especially at the low loads. It has been shown that there are many engine parameters, e.g. engine load, type and quantity of biogas, injection timing of the pilot fuel etc., which can affect the performance and emission characteristics of a DF engine. This article presents an overview of these effects on a biogas operated DF engine and suggests various techniques to enhance the performance of the engine.

Keywords Biogas · Diesel · Dual fuel · Emissions · Exergy · Irreversibility · Second-law analysis

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11.1 Introduction

The world energy demand is continuously increasing driven by industrial growth, fast developing economies and evolving technologies. Ever since the industrial revolution, we are relying on fossil fuels to fulfil energy demands that still constitute up to 80% of the world's total energy supply (Key World Energy Statistics 2020). Consequently, extensive use of carbon based fuels has released huge amount of noxious pollutants in the atmosphere disturbing the ecological stability. In the present times, world is facing twin challenges of continuously increasing energy demand and dire need to curtail the environmental pollution. The Intergovernmental Panel on Climate Change (IPCC) says that major decarbonization actions are required to restrict the global warming to 1.5 °C (IPCC 2018). Therefore, various countries have pledged to reduce their fossil fuel usage to achieve the target of net zero emission using renewable technologies. Although several steps have been taken in this direction, such as enhancing the use of solar and wind energies, use of biomass and nuclear energies etc., they are still insufficient (Fig. 11.1). Yet, the major part of the world's total energy consumption is satisfied by fossil based energy sources and this scenario is likely to remain until 2050 (EIA 2019). Therefore, it will be required to continuously explore the new technologies and improve the existing ones to maximize the utilization of alternative and renewable fuels as a replacement to fossil fuels.

In this context, biogas is an important renewable fuel with vast potential in the agrarian states. Biogas is a renewable fuel that is produced from organic waste materials through anaerobic digestion process. It is composed of methane (CH_4), carbon dioxide (CO_2) and traces of minority gases such as nitrogen, hydrogen, sulfur dioxide and water vapor (Rafiee et al. 2021). It can be seen that only methane is the major combustible gas component in biogas, hence it sometime refers to as biomethane.

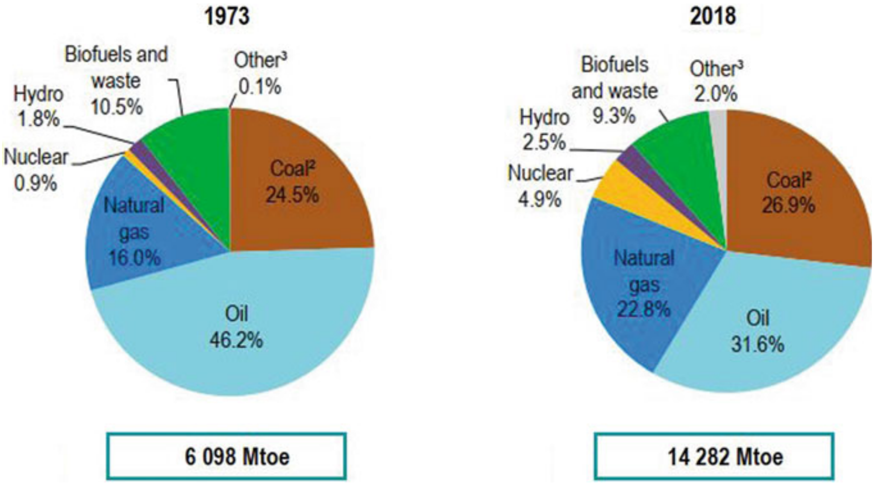


Fig. 11.1 Share of world total energy supply by sources (Key World Energy Statistics 2020)

Biogas has been promoted as an alternative cooking fuel in the developing countries for many decades. As a case in point, India has a huge potential of biogas production; there have been nearly five million biogas plants installed in India as on 2017 (Energy Statistics 2018). Similarly, China has developed many domestic biogas plants in the recent decades. Nevertheless, a policy shift has been observed, where governments are focusing on small to medium size biogas based energy generation plants (Jiang et al. 2011). Many counties have launched schemes to develop integrated urbane waste management and biogas plants, where generated biogas can be utilized as vehicular fuel (CEN/TC 408 2016; SATAT 2018). Therefore, there is a shift in policies to graduate from domestic to industrial level utilization of biogas, which could be a significant push for future biogas technologies.

11.1.1 Dual Fuel Technology

The liquid petroleum fuels provide significant part of world energy supply, which are majorly used in automotive and industrial sectors (EIA 2019). Diesel engines are extensively used in heavy duty as well as passenger vehicles. Furthermore, decentralized power generation units employ diesel engines throughout the world. However, diesel engines are very polluting in nature and therefore the emission limits are increasingly tightened to reduce their utilization. One of the ways to reduce the pollution from diesel engines is to replace diesel fuel with some renewable fuels such as biogas. Biogas has fuel properties so that it can be utilized in the combustion engines. Biogas is a high Octane fuel, therefore it can be easily utilized in a spark ignition (SI) engine. On the other hand, it has very low Cetane number, low flame speed and low calorific value. These properties make it difficult to directly utilize biogas in a diesel engine (Henham and Makkar 1998). It is not possible to simply replace biogas with diesel in the existing diesel engines due to high auto-ignition temperature (600–650 °C) of biogas. Instead, if small amount of diesel fuel (or any other liquid fuel with high Cetane number) is used along with biogas, then it is possible to achieve the ignition of the gas-air mixture. This simultaneous utilization of a liquid fuel (called pilot fuel) and gaseous fuel (called main fuel) in a diesel engine is called Dual Fuel (DF) technique (Karim 1980). The DF technique has many advantages, e.g. ease of operation, low maintenance, low initial cost and reduced smoke emission. Fuel flexibility is another major advantage of a DF engine, as it can be easily switched between DF and conventional single fuel (i.e. using liquid fuel only) mode (Verma et al. 2019). It provides operational control in the event of insufficient availability of biogas. This is very important because production of biogas depends on multiple factors ranging from availability of organic waste, production techniques and even seasonal variations. The literature shows that utilization of biogas in DF engine is not only advantageous from the environmental viewpoint but also cost-effective by replacing diesel fuel. Barik and Murugan (Barik and Murugan 2014) studied the cost implication of biogas production and cost saving by its utilization in DF engines. They reported the biogas cost of ₹96.00/m^3 as the operational cost. Similarly, (Das et al. 2021) reported that for a small size diesel engine (3.5 kW), the levelized unit cost of electricity was 0.36 USD/kWh with the payback period of 7.5 years. However, it was also showed that scale-up and use of biodiesel are possible methods to reduce both the levelized unit cost of electricity and payback period. On the environmental benefits, such a decentralized power unit would render 9.54 tonnes (82%) of CO_2 reduction per year compared to diesel only system.

11.1.2 Challenges with Biogas Dual Fuel Technology

A DF engine operating on biogas has its own challenges, such as low thermal efficiency, and high hydrocarbon (HC) and carbon monoxide (CO) emissions as compared to standard diesel engine operations (Verma et al. 2017a, b). The performance of a DF engine depends on many engine operating parameters, such as engine load (Verma et al. 2017a, b; Tippayawong et al. 2007), quantity and quality of gaseous fuel (Verma et al. 2017a, 7b) and injection timing (IT) and type of the pilot fuel (Verma et al. 2017a, b, 2018). The effect of these parameters on the performance and emission characteristic of a biogas DF engine are systematically presented in this article. These studies have helped the performance enhancement of a DF engine over the time, however there is significant scope still left for the improvement. In addition to that performance of the DF engine can also be improved by modifying the design parameters such piston bowl optimization, compression ratio optimization and fuel injection system development (Belgiorno et al. 2019; Verma et al. 2019). These techniques combined with alternative fuels such as biogas and alcohol can improve the engine performance and reduce CO_2 emissions. Furthermore, there are some novel combustion approached being investigated recently that could bring radical changes and improvements in the biogas utilization in IC engines. Therefore, other advancements in the combustion techniques are also presented in brief for the interested readers.

11.2 Energy and Exergy Analysis Applied to Engine Processes

11.2.1 Energy Analysis

Energy analysis is based on the first-law of thermodynamics, which stipulates that energy is a conserved quantity. Therefore, energy flow is always balanced across any energy system, which can be mathematically represented as sum of input energies is equal to sum of output energies. In the engine system, input energy $\left(\dot{E}_{in}\right)$ is associated with chemical energies of the fuels (pilot and main fuels in case of DF operation), which is given by:

$$\dot{E}_{in} = (\dot{m}_L \times LHV_L) + (\dot{m}_G \times LHV_G) \tag{11.1}$$

where, $\dot{m}$ and *LHV* represent mass flow rate and lower heating value of the fuels respectively. The suffix '*L*' stands for liquid pilot fuel and suffix '*G*' stands for gaseous main fuel. Output energies from the system are related to the engine work output ($\dot{E}_W$), exhaust heat loss ($\dot{E}_{exh}$), wall heat loss ($\dot{E}_Q$) and unaccounted energies ($\dot{E}_{un}$). The rate of engine work output ($\dot{E}_W$) is measured using a dynamometer in terms of brake power output. The wall heat loss ($\dot{E}_Q$) is calculated from Annand's correlation and the procedure given by (Heywood 1988). The rate of energy transfer with exhaust ($\dot{E}_{exh}$) is calculated by the following expression (Cengel and Boles 2015):

$$\dot{E}_{exh} = [(\dot{m}_L + \dot{m}_G) \times (1 + \Psi) \times C_{p,exh} \times (T_{exh} - T^0)] \tag{11.2}$$

where, Ψ represents ratio of mass flow rates of air to fuels. $C_{p,exh}$ shows average specific heat of exhaust gases at temperature of T_{exh}. T^0 shows reference/atmospheric temperature. There are various other process in an ICE operation, such as auxiliary devices, radiation heat transfer etc., where energy is dissipated. The sum of these energies are denoted by unaccounted energy ($\dot{E}_{un}$), which is given by the net difference in input and output energies.

The ratio of engine work output to input energy for engine system is called energy efficiency:

$$\eta_E = (\dot{E}_W / \dot{E}_{in}) \times 100 \tag{11.3}$$

11.2.2 Exergy Analysis

Exergy analysis is based on the second-law of thermodynamics, which analyses the system in terms of quality of the energy, also called availability. The second-law of thermodynamics says that exergy is non-conserved quantity that continuously decreases due to irreversibilities in the processes. The decrease in exergy or availability of the system is knows as exergy destruction. In the present system, total exergy destruction ($\dot{E}x_D$) will be given by the difference in in-flow and out-flow exergies as follows:

$$\dot{E}x_D = \dot{E}x_{in} - \underbrace{(\dot{E}x_W + \dot{E}x_Q + \dot{E}x_{exh})}_{total\ outflow\ exergy} \tag{11.4}$$

The rate of in-flow (input) exergy ($\dot{E}x_{in}$) to the system is given by the sum of rate of liquid fuel and gaseous fuel exergies:

$$\dot{E}x_{in} = (\dot{m}_L ex_{ch,L} + \dot{m}_G ex_{ch,G}) \tag{11.5}$$

where, $ex_{ch,L}$ shows specific chemical exergy accompanied with the pilot liquid fuel, which is calculated using empirical correlation given by (Kotas 1995). On the other hand, specific chemical exergy of gaseous fuel ($ex_{ch,G}$) is calculated using the following relation (Kotas 1995):

$$ex_{ch,G} = \sum_i x_i ex^o_{ch,i} + T^0 \sum_i x_i R \ln x_i \tag{11.6}$$

where, biogas is considered an ideal gas mixture with its 'i' number of constituents. x_i is the mole fraction of any species in the gas mixture of biogas. T^0 is the reference temperature.

The exergy output ($\dot{E}x_W$) from work transfer is same as that of energy work output ($\dot{E}_W$). The rate of exergy transfer associated with heat losses from cylinder walls ($\dot{E}x_Q$) is calculated by the following equation (Cengel and Boles 2015):

$$\dot{E}x_Q = \sum \left(1 - \frac{T^0}{T_g}\right) \dot{E}_Q \tag{11.7}$$

where, T_g is the instantaneous gas temperature. The hot exhaust gases carry physical exergy, which is given by Cengel and Boles (2015):

$$\begin{aligned}\dot{E}x_{ex} = &\left[\dot{m}_{exh} \times C_{P,exh} \times \left(T_{exh} - T^0\right)\right] \\ &- \left[\dot{m}_{exh} \times T^0 \times \left\{C_{P,exh} \times \ln\left(\frac{T_{exh}}{T^0}\right) - R \times \ln\left(\frac{P_{exh}}{P^0}\right)\right\}\right]\end{aligned} \tag{11.8}$$

here, P_{exh} and $\dot{m}_{exh}$ are pressure and mass flow rate of exhaust gases respectively.

The exergy efficiency is an important parameter to measure the overall performance of the engines. The exergy efficiency of the engine is given by the ratio of work exergy output to input exergy:

$$\eta_{Ex} = (\dot{E}x_W / \dot{E}x_{in}) \times 100 \tag{11.9}$$

The total exergy destruction ($\dot{E}x_D$) can be evaluated using Eq. (11.4) that is using exergy balance across the system. The total exergy destruction consists of various sources of irreversibilities corresponding to different processes in an IC engine. The highest source of irreversibility is the combustion process that is accompanied by highly irreversible chemical reactions between the fuels and oxidant (Caton 2000). Therefore, it becomes significant to accurately evaluate the combustion irreversibility and look for suitable remedial measures. The rate of combustion irreversibility ($\dot{I}_{comb}$) can be calculated by Eq. (11.10).

$$\dot{I}_{comb} = T^0 \times \dot{S}_{gen} \tag{11.10}$$

In the above equation, the rate of combustion irreversibility is calculated using the rate of entropy generation ($\dot{S}_{gen}$) in the combustion process and reference temperature (T^0). Furthermore, the rate of entropy generation is calculated by Eq. (11.11) (Alkidas 1988).

$$\dot{S}_{gen} = \sum \dot{m}_{i,p} s_{i,p} - \sum \dot{m}_{j,r} s_{j,r} - \sum (\dot{E}_Q / T_g) \tag{11.11}$$

where subscripts '*p*' represents product and '*r*' represents reactant mixtures respectively. $\dot{m}$ and s are mass flow rate and specific entropy of the various species in the product and reactant mixtures.

Mechanical friction in the operation of IC engines is another source of irreversibility ($\dot{I}_{fri}$). It can be calculated using mechanical efficiency of the engine. Moreover, mixing of air, fuel and residual charge inside the engine cylinder also contribute to irreversibility. Mixing irreversibility ($\dot{I}_{mix}$) is calculated from the following equation (Kotas 1995):

$$\dot{I}_{mix} = -T^0 \sum_i^n n_i \overline{R} \ln y_i \tag{11.12}$$

where is n is the number of components in the mixture. n_i and y_i are number of moles and mole fraction of the ith species in the ideal gas mixture. Finally, the unaccounted in-cylinder irreversibility ($\dot{I}_{un}$) can be obtained by Eq. (11.13).

$$\dot{I}_{un} = \dot{E}x_D - (\dot{I}_{comb} + \dot{I}_{mix} + \dot{I}_{fri}) \tag{11.13}$$

11.3 Impact of Engine Operating Parameters

The performance and emission features of a diesel-biogas DF engine depend on various operating and design parameters of the engine. The effects of some of the important operating parameters are explained in the subsequent sections from the perspectives of exergy analysis. The results are based the experimental study conducted on a single cylinder, four-stroke diesel engine (Kirloskar TAF1) for which important engine parameters are shown in Table 11.1.

11.3.1 Engine Load and Pilot Fuel Substitution Ratio

The engine load is an important operating parameter, which significantly impacts the performance of a DF engine. The effect of engine load on the fuel demand by a diesel-biogas DF engine is shown in Fig. 11.2. The variation of diesel flow rate is plotted against the engine load for both conventional single fuel (diesel only) and DF modes. It can be seen that fuel demand continuously increases with the engine load, as the power output of the engine is also increased. The diesel flow rates increase for both single and DF modes, however the quantity is lower in case of DF mode (in DF mode, diesel serves as the pilot fuel). It is because some diesel fuel is substituted by the main fuel (biogas), hence diesel consumption is reduced; however it does not represent reduction in total fuel/energy consumption (refer to Fig. 11.3). The effect of engine load on the energy consumption (total energy = pilot + main fuel) is shown in Fig. 11.3. The brake specific energy consumption (BSEC) decreases with the engine load for both single and DF modes of the engine operation. It can also be seen that DF mode has much higher BSEC at the low loads as compared to single fuel operations. It shows that DF engines have poor conversion efficiency at the low load operations, which improves significantly at the higher loads. Similarly, it is shown in the subsequent sections that low load emission features of a DF engine is also poor, which requires especial attention.

Another important parameter is the pilot fuel substitution in the operation of a DF engine. Pilot fuel substitution represents, how much liquid pilot fuel is substituted by

Table 11.1 Engine design and operating parameters

Engine parameters	Values
Swept volume	661 cm^3
Bore and stroke	87.5 mm × 110 mm
Rated brake power	6 bhp/4.4 kW
Compression ratio	17.5:1
Rated speed	1500 rpm
Nozzle injection pressure	200 bar
Standard injection timing	23.0° BTDC

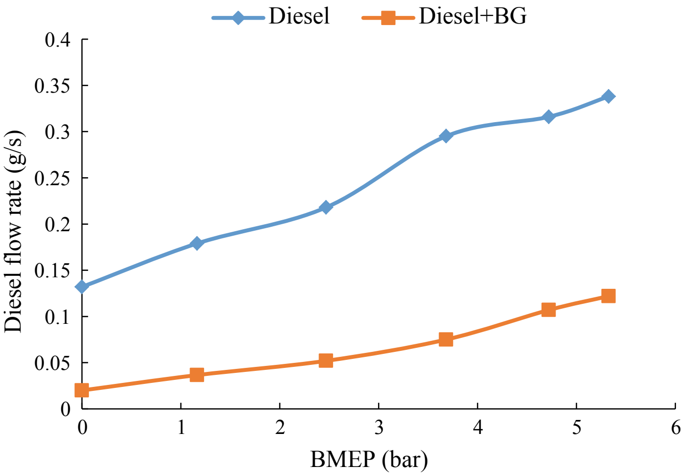


Fig. 11.2 Variation of diesel flow rate with engine loads in a single fuel and DF (diesel-biogas) engine

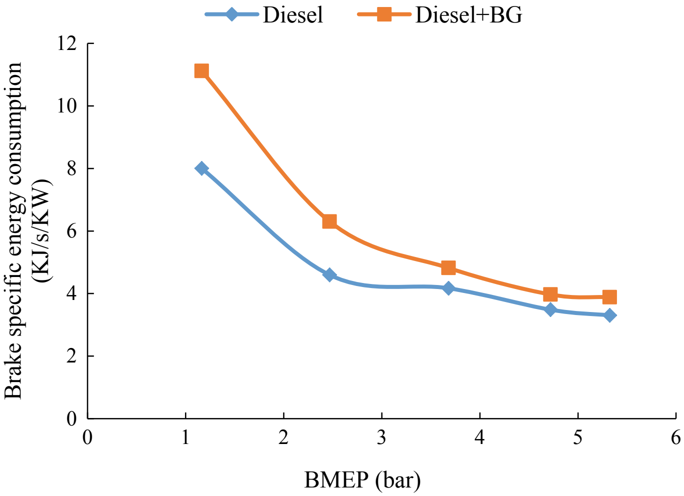


Fig. 11.3 Variation of brake specific energy consumption with engine loads in a single fuel and DF (diesel-biogas) engine

the gaseous main fuel during the DF mode as compared to the single fuel mode under the similar operating conditions. Theoretically, any ratio of pilot and main fuels can be used in a DF engine, however there are practical limitations depending on various factors such as type of fuels and engine load. It has been observed that a biogas DF engine shows higher pilot fuel substitution at the lower loads than at the higher loads. Barik and Murugan (2014) studied the biogas energy share with the engine load for

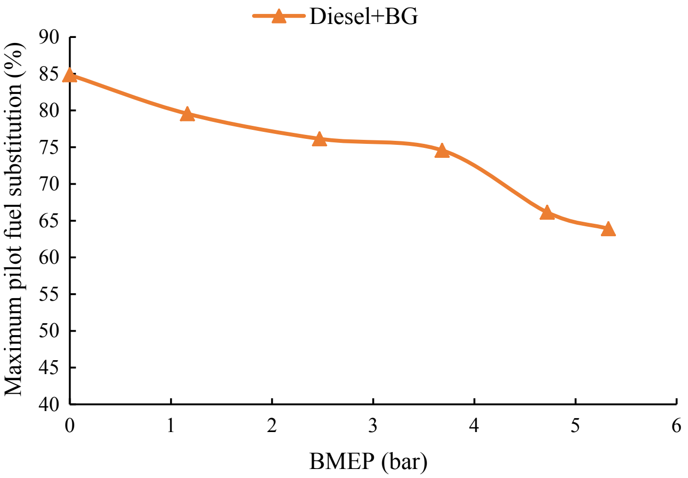


Fig. 11.4 Variation of brake specific energy consumption with engine loads in a single fuel and DF (diesel-biogas) engine

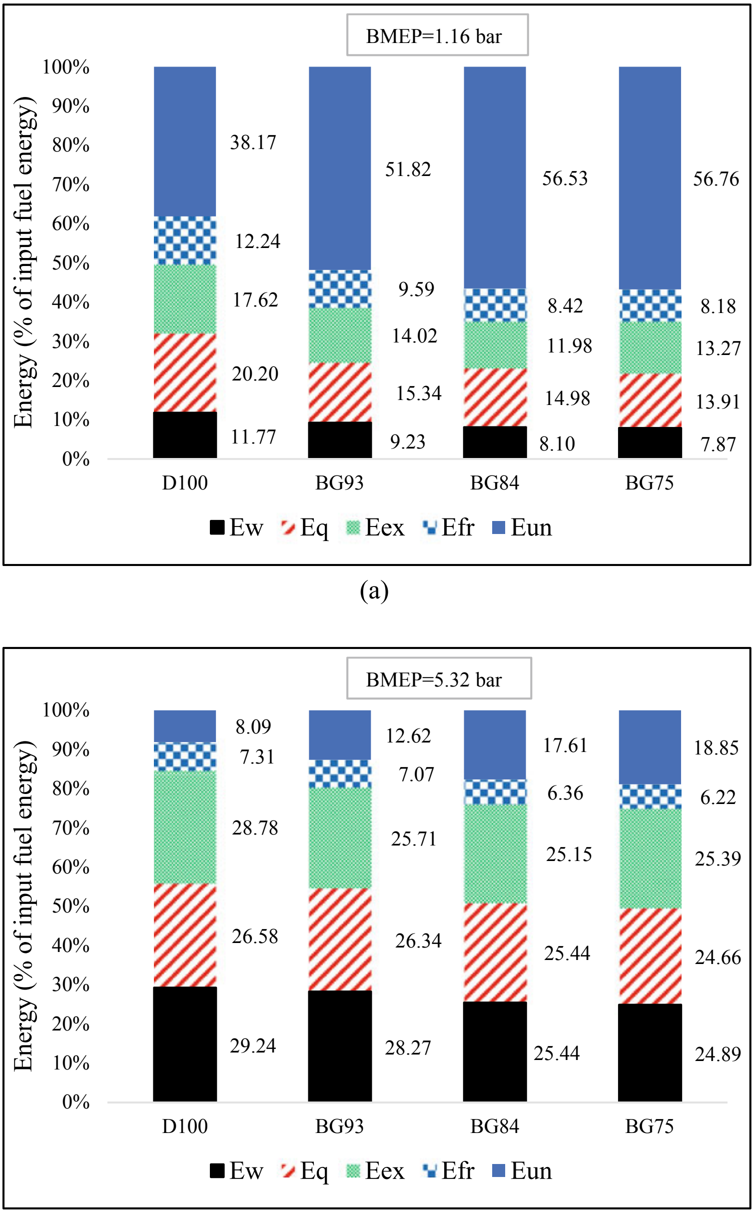
various biogas flow rates. It was found that energy share decreases with the lower biogas flow rates and higher engine loads. There is a maximum limit up to which a gaseous fuel can be used in DF engine; in other words, there are maximum pilot fuel substitutions corresponding to the operating conditions of a DF engine. The variation of maximum pilot fuel (diesel) substitution is shown in Fig. 11.4 with the engine load for a diesel-biogas DF engine. It can be seen that maximum pilot fuel substitution decreases as more engine load is applied on the engine. It has been found that in the DF operation of a diesel engine, the ignition delay period is elongated as compared to single fuel operation (Liu and Karim 1995). In addition to that biogas as the main fuel further affects the ignition delay in a DF engine due to its poor combustion characteristics as a fuel. Longer ignition delay causes many combustion anomalies such as misfire and knocking leading to reduced engine performance and emission characteristics. Ignition delay is longer at low load operation due to low power demand in a diesel-biogas DF engine. However, at higher engine loads, longer ignition delay tend to cause frequent engine knock due to high rate of pressure rise. Hence, stable engine operation requires more amount of pilot fuel, which causes reduced pilot fuel substitution.

11.3.2 Methane Enrichment in Biogas

As explained in the introduction, biogas could be approximated as the mixture of methane (CH_4) and carbon dioxide (CO_2). Though biogas is mainly composed of CH_4 and CO_2, their content in a raw biogas vary depending on the feedstock, method of production, type of processing and even with the seasonal variations. The CH_4 content in a raw biogas could vary from 40 to 80% depending of the above mentioned factors. It is CH_4 that carries the heating value in biogas, whereas CO_2 is an inert gas. Therefore, higher methane content in biogas improves its heating value and other fuel characteristics suitable for combustion engines. Furthermore, high CO_2 in biogas decreases its energy density. Hence, raw biogas are not suitable for mobile application due to storage constraints. Therefore, raw biogas is processed to improve its CH_4 content for various applications such automobile fuel. On the other hand, CH_4 enrichment in biogas is energy and resource extensive process. For stationary applications, such as decentralized power generation, it could be beneficial to use the raw biogas. Therefore, it becomes important to characterize the diesel-biogas DF engine with different biogas content.

In Figs. 11.5 and 11.6, three compositions of the biogas with 75%, 84% and 93% CH_4 contents have been compared using energy and exergy analyses. The energy and exergy distribution are shown for two engine load conditions corresponding to brake mean effective pressure (BMEP) of 1.16 bar and 5.32 bar respectively. Note that these conditions represent typical low and high engine load conditions respectively in the presented engine setup. All the components of the energy and exergy distribution (as shown in Sect. 11.2) are shown in the normalized terms, i.e. % of total input fuel energy/exergy. The notations, BG75, BG84 and BG93 represent biogas with 75, 84 and 93% CH_4 contents respectively. D100 represents the conventional single fuel operation with diesel fuel. It can be seen that energy transfer with work increases as the CH_4 content in biogas is increased, which is true for both low and high loads. At the low load, work transfer with DF engines are lower than single fuel operation. However, at the high load, BG93 shows much closer work transfer as that with the D100. The energy transfer with heat transfer and exhaust are higher with the D100 case than DF cases. This is because of better combustion characteristics of single fuel operation as compared to biogas DF operations. It can also be seen that there is not significant variations in the energy distribution of BG75 and BG84 both at low and high loads. Whereas, the energy distribution of BG93 is similar to D100, especially at high load.

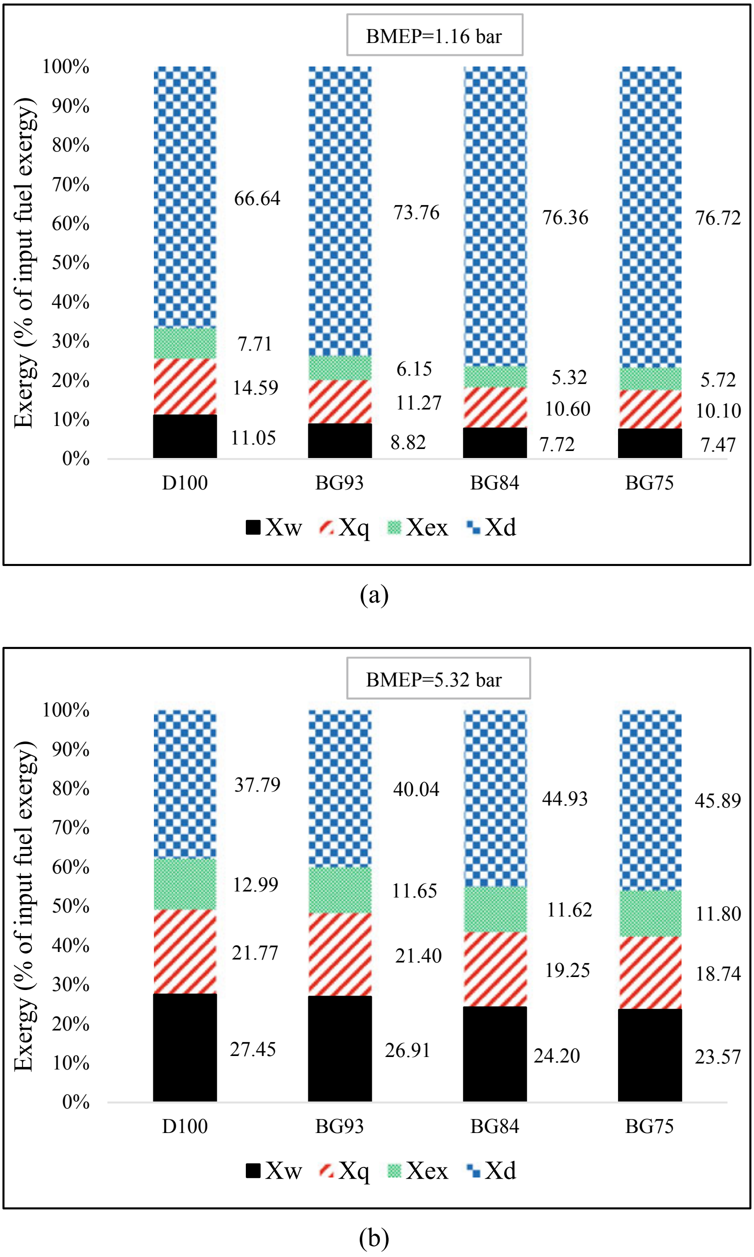
The exergy distribution for all the four mentioned cases are shown in Fig. 11.6. Again, the exergy distribution is normalized as % of total input fuel exergy. It can be seen that exergy destruction is considerably higher at the low load condition for all the cases. It shows poor utilization of the available exergy under low pressure and temperature conditions during low load of the engine. It is important to note the exergy destruction for DF cases, which are significantly higher than the single fuel (D100) case. The exergy destruction is considerably reduced at the high load, however biogas DF operations show higher exergy destruction. It can be noted that in combustion engines, highest exergy destruction takes place due to combustion process. It has been found that combustion irreversibility decreases at the high load conditions, and hence the exergy destruction. Furthermore, improved combustion efficiency at the high load helps in reduction of total exergy destruction. Similar to energy distribution, the exergy distribution for BG75 and BG84 are found comparable, whereas BG93



(a)

(b)

Fig. 11.5 Energy distribution of various biogas compositions for **a** low load and **b** high load conditions for DF engine



(a)

(b)

Fig. 11.6 Exergy distribution of various biogas compositions for **a** low load and **b** high load conditions for DF engine case shows better improvements. The exergy transfer with heat transfer and exhaust are found lower with the DF cases as compared to single fuel case.

Another important aspect of any engine design is emission. The impact of CH_4 content in biogas on the emission characteristics of the biogas DF engine is shown in Figs. 11.7, 11.8, 11.9 and 11.10. A clear contrast can be seen in the variation of NO_x emission with the engine load between single and DF cases in Fig. 11.7. The diesel engine produces higher specific NO_x emission at low load due to poor engine efficiency and hence lower power output. As the power output increases with the

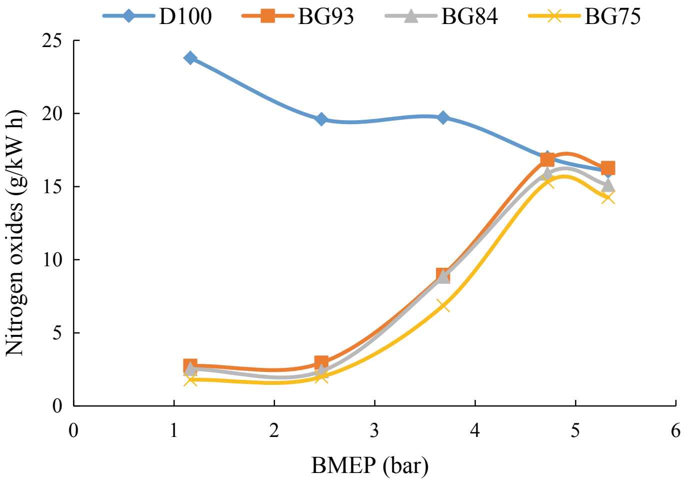


Fig. 11.7 Variation of NO_x emission with the engine load for various methane contents in biogas

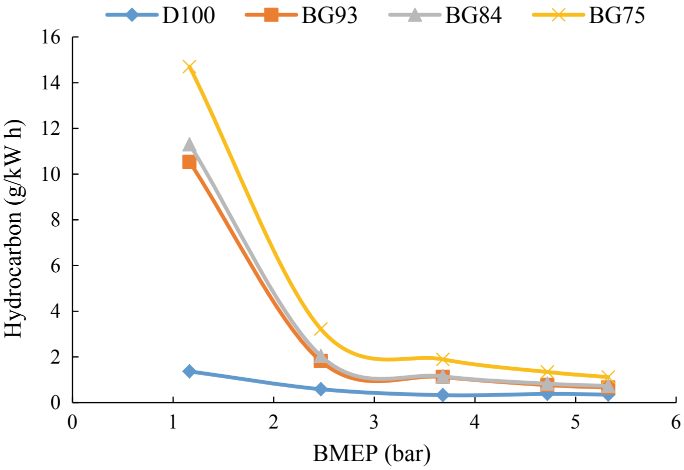


Fig. 11.8 Variation of HC emission with the engine load for various methane contents in biogas

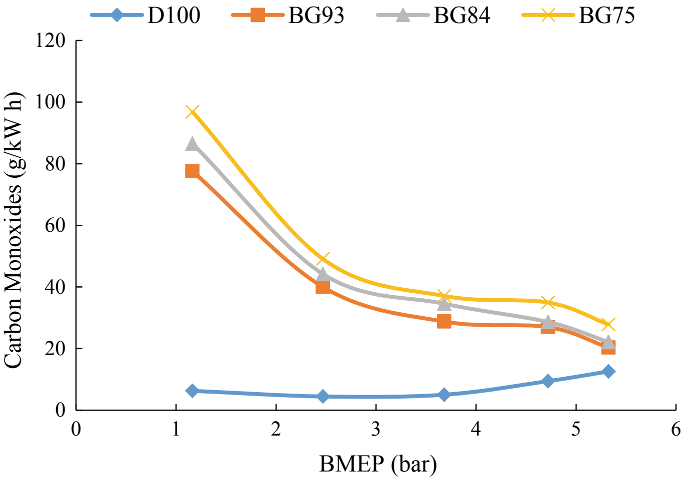


Fig. 11.9 Variation of CO emission with the engine load for various methane contents in biogas

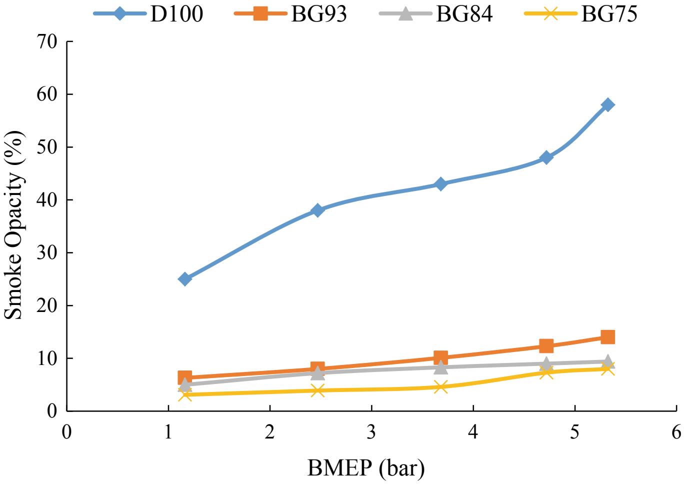


Fig. 11.10 Variation of smoke emission with the engine load for various methane contents in biogas

engine load, the specific NO_x emission shows a decreasing trend. For a biogas fueled DF engine, the NO_x emission remain very low at the low loads, which increases at the high load. This is because very small NO_x generation is found with biogas as the fuel at the low loads. Furthermore, NO_x emission is found higher with the higher CH_4 contents in the biogas. Even at the full load, BG93 DF case shows slightly higher NO_x emission as compared to single fuel case. Whereas, BG75 and BG84 DF cases show slightly lower emissions than single fuel case.

Figure 11.8 shows the variation of HC emission with the engine load for all the single and DF cases. It can be seen that HC emission decreases with the engine load for all the cases. However, the rate of reduction is drastic of DF cases, especially from low to mid load conditions. This is because biogas fueled DF engine generates excessive unburned HC emission at the low loads. A low calorific value biogas combined with lean condition at the low load creates poor combustion condition. Furthermore, as mentioned earlier, biogas contains considerably amount of CO_2. It has high specific heat, which works as heat sink during combustion process causing decrease in the combustion temperature. A low temperature combustion generates partial combustion products and hence high HC emission. At the high load, fuel–air ratio is improved and high fuel flow rates cause rapid heat release leading to improved combustion temperature. HC emissions are higher with the DF cases compared to single fuel case. Among the DF cases, HC emission is highest with BG75, however differences are lowered at higher loads.

Carbon monoxides (CO) are another major pollutant from IC engines. In addition to that it also contributes to poor engine efficiency as it carries significant fuel chemical energy. It is produced near the rich fuel–air regions in the combustion chamber due to insufficient availability of oxygen. Most of the global CO emissions come from vehicular emissions. CO is a colourless, tasteless but poisonous gas. Figure 11.9 shows variation of CO emission with the engine load for various methane contents in biogas. It can be seen that variation of CO emission is similar to the HC emission between single and DF cases. CO emissions are higher with all the DF cases throughout the engine load spectrum. However, one noticeable difference between single and DF is that for a single fuel operation, CO emission increases with the engine load, which is opposite for the DF cases. It is because of very lean mixture formation between biogas and air at the low load. This lean mixture has low heat release rate and flame speed that tend to be quenched easily. Under this condition, the pilot fuel injected during DF operation could not burn completely, leading to the generation of high CO emissions. As the engine load is increased, the mixture strength is improved and high combustion temperature helps in complete combustion of the fuel. Among DF cases, BG75 shows highest and BG93 shows the lowest CO emissions with the engine load.

Smoke or particulate emission is generated due to agglomeration of carbonaceous materials and organic compounds during late phase of combustion process in a diesel engine. Smoke emission from the diesel engines is one of the most hazardous and challenging problems. Variation in the smoke emission with the engine loads for various methane contents in biogas is shown in the Fig. 11.10. As it is evident from the figure, biogas DF engine shows significant reduction in smoke emission over diesel engines. All the biogas DF cases show very small smoke emissions throughout the engine load range. It is because of the dominant pre-mixed combustion in the DF operation compared to diffusion combustion in the single fuel diesel operation. As a major portion of fuel–air mixture is provided in the form of homogeneous biogas-air mixture, smoke formation is reduced. Furthermore, a gaseous fuel tends to produce much lower smoke emission compared to a liquid fuel due to better mixing and oxidation characteristics. The CO_2 concentration in biogas also contribute to reduction in smoke emissions. According to the study conducted by Zhao et al. (2000) on diesel engine, addition of CO_2 suppressed both NO_x and smoke emissions. It was further explained by Liu et al. (2001) that the presence of CO_2 enhanced concentration of O and OH atoms in the combustion process. These free radicals increased oxidation of the soot particles and helped in reduced smoke and particulate emissions. It can be seen that smoke emission increases with the CH_4 content in the biogas, hence BG75 shows the lowest smoke emissions. Though smoke emission shows increasing trend for DF cases with the engine load, it still remains significantly low compared to the single fuel operation.

11.3.3 Pilot Fuel Injection Timing

In this section, the importance of pilot fuel injection timing on the characteristics of a diesel-biogas DF engine has been highlighted. In order to do so, a comparative evaluation between single and DF modes are presented. Single fuel mode (Diesel only) represents the base line condition, whereas DF mode employs biogas as the main fuel and diesel as the pilot fuel. The results are shown for two fixed engine loading conditions, one corresponds to a low load (BMEP = 1.16 bar) and other corresponds to a high load (BMEP = 5.32 bar) for both single and DF operations. Moreover, the effect of pilot fuel injection timings (ITs) have been shown at five ITs of 20, 23, 26, 29 and 32° BTDC (before top dead centre). The standard injection timing is 23° BTDC for single fuel conventional diesel engine operation.

The in-cylinder pressure variation reveals important information in the engine processes. Figure 11.11 shows the peak cylinder pressure values with variation in

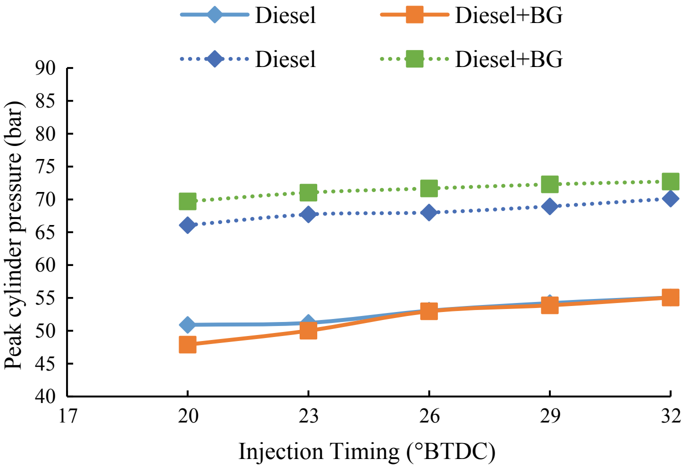


Fig. 11.11 Variation in peak cylinder pressure with the injection timing at low load (solid lines) and high load (dotted lines) for single and DF operations

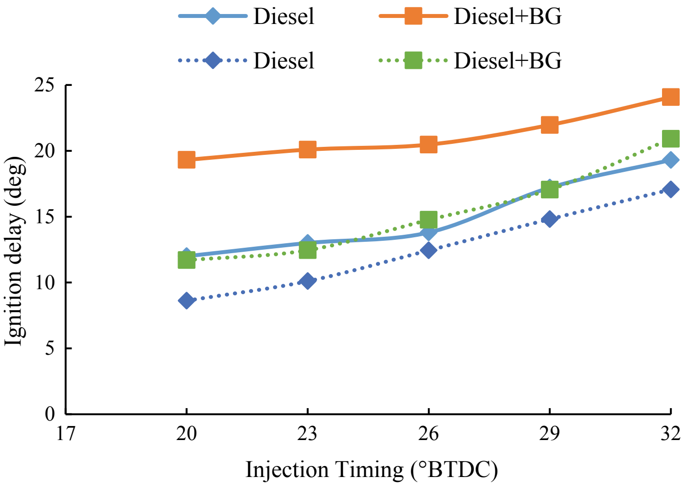


Fig. 11.12 Variation in ignition delay with the injection timing at low load (solid lines) and high load (dotted lines) for single and DF operations

the injection timings (ITs) for single and DF modes at low and high load conditions. It can be seen that both single and DF modes show similar peak pressures at the low load. However, the peak pressures are higher with DF operations at the high load. Furthermore, peak pressure increases with the advancement in the IT both at low and high loads. As the IT is advanced from 20° to 32° BTDC, the peak pressure rises by 4.04 bar for the single fuel and 3.04 bar for the DF operations respectively at the high load. The main reason for rise in the peak pressure is due to the changes in the ignition delay with the variation of ITs. For the similar conditions as that for peak pressure, variations in the ignition delay with ITs are presented in Fig. 11.12. It can be seen that advancing the IT results in higher ignition delay for single as well as DF operations. With longer ignition delay, more amount of injected fuel accumulates and mixes with the air before combustion. At the point of ignition, the accumulated fuel burns rapidly releasing large amount of energy in short period of time. This high rate of heat release suddenly increases the in-cylinder pressure and temperature, which could be hazardous for structural integrity of the components. Another observation is that ignition delay is higher with the DF mode as compared to single fuel mode. In DF modes, premixed gaseous fuel–air mixture has found to undergo pre-ignition reactions affecting the ignition delay period (Lata et al. 2011; Selim 2001). The highest ignition delay was observed with low load DF case at the IT of 32° BTDC, which also caused highest heat release rates. Another important factor with biogas-diesel DF is the presence of CO_2 in the biogas. It reduces the in-cylinder temperature at the point of fuel injection, which could also increase the ignition delay.

Variations in the maximum pilot fuel substitution with ITs for biogas-diesel DF mode are depicted in Fig. 11.13. Higher substitution is found for the low load condi-

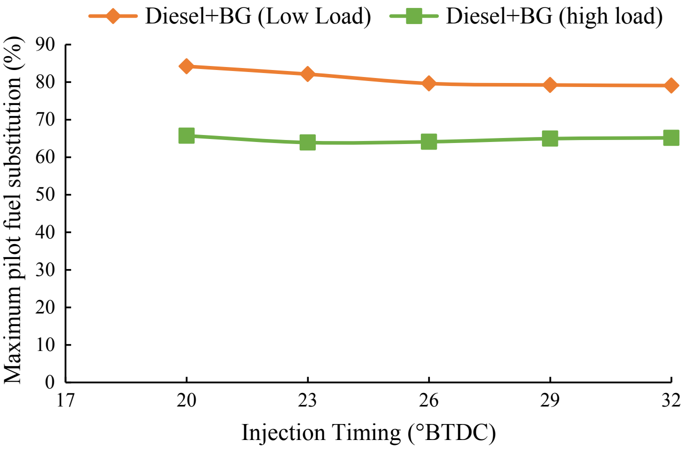


Fig. 11.13 Maximum pilot fuel substitution with the injection timing for DF engine

tion than at the high load condition. Whereas with the IT, the maximum substitution decreases moderately. The maximum substitution was found as 84.2% for IT of 20° BTDC that reduced to 79.1% for IT of 32° BTDC at the low load condition. At the advance ITs, large amount of pilot fuel is required to reduce the ignition delay and successful operation of the DF engines. At the high load, longer ignition delay produces sever engine knocks. To counter this situation, maximum substitution is limited at the high load condition, which is lower than the corresponding values at the low load conditions. Variation in the exergy efficiency with IT are shown for single and DF operations in Fig. 11.14. The exergy efficiency increases and then decreases as the IT is advanced. It can also be seen that DF modes have lower exergy efficiencies both at low and high loads as compared to single fuel modes. Therefore, there are optimal ITs, at which the exergy efficiencies are highest. The maximum exergy efficiencies of 24.4% (high load) and 8.5% (low load) were obtained at the ITs of 26° BTDC and 32°BTDC respectively for the DF mode.

Nevertheless, exergy efficiency of DF modes are lower than the single fuel mode. The poor efficiency of the DF mode could be better understood by identifying the source of exergy destructions. The major source of exergy destruction, i.e. combustion, mixing, friction and unaccounted irreversibilities are presented in Fig. 11.15 for single and DF modes at their optimized conditions. It can be seen that combustion process causes high irreversibility for both single and DF modes. It has been shown that combustion of simpler molecule and at elevated temperature cause lower irreversibility (Caton 2000). Due to higher flow rates and rich fuel–air ratio, the combustion temperature increases with the engine load. Therefore, the combustion irreversibility is lower at the high load for the single fuel mode. However, a careful look at DF mode shows opposite feature, where combustion irreversibility is increased with the engine load. We need to consider the total exergy destruction to better understand this phenomenon. It shows that the sum of combustion

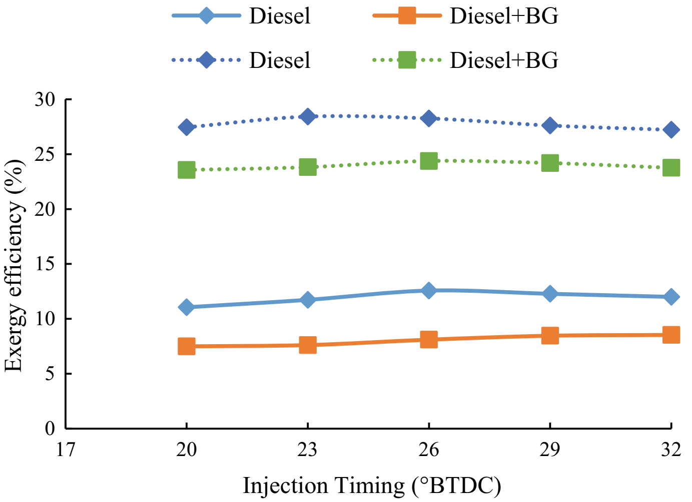
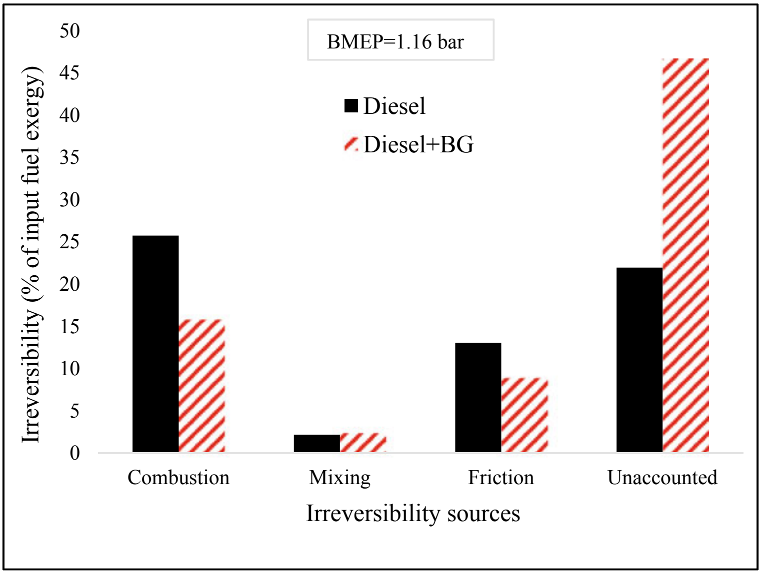
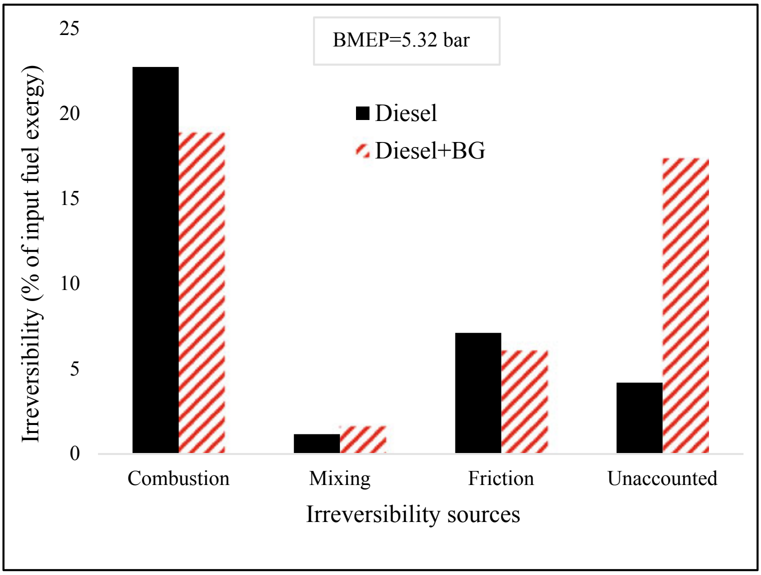


Fig. 11.14 Exergy efficiencies of the single and DF cases with the injection timing at low load (solid lines) and high load (dotted lines)

and unaccounted irreversibility is still higher for the DF mode, though it decreases with the engine load. This is because at low load, incomplete combustion results in lower combustion irreversibility, however high amount of chemical exergy is transferred to the unburned gases. As chemical exergy of unburned gases are difficult to utilize (Alkidas 1988), and in the present case it has shown under unaccounted irreversibility. As the engine load is increased, the combustion process is improved and lower amount of partial products of combustion are produced. In this process, the combustion irreversibility is increased and unaccounted irreversibility is decreased as shown in the results. Consequently at the full load condition, the combustion irreversibilities are 22.74% for single fuel and 18.89% for DF modes respectively. However, the total irreversibility is still higher for the DF mode as compared to the single fuel mode. Instead, mixing irreversibility is smaller compared to the combustion irreversibility for both single and DF modes. It possible that premixing of biogas and air leads to higher irreversibility, however their relative magnitudes are smaller. In contrast, irreversibility due to mechanical friction is sizable amount of the total input fuel exergy. The frictional loss is proportional to the engine speed. As the presented results are shown for the constant engine speed, the frictional irreversibility is same for all the cases. The variation in the numerical values shown in the graph is due to its normalization with the input fuel exergy. However, higher rate of pressure rise with DF modes cases minor increase in friction irreversibility.



(a)



(b)

Fig. 11.15 Irreversibility of single and DF engines at the **a** Low load **b** High load

11.3.4 Type of Pilot Fuel

In this section, the effects of pilot fuels properties on the performance and emission characteristics of a biogas DF engine have been presented. In this regard, two renewable pilot fuels have been selected, namely Jatropha biodiesel and Gas-to-liquid (GTL). The comparison has been made with diesel as the standard pilot fuel. It can be seen that a completely renewable fuel based DF technology is possible with biodiesel-biogas and GTL-biogas combinations. The results are shown based on energy and exergy analyses, and important emissions are also discussed. In the presented results, there are three cases of DF operations with the mentioned pilot fuels (see Table 11.2 for fuel properties). Biogas is the main fuel in all the cases. The engine operation is studied by the varying engine loads from BMEP of 1.16–5.32 bar, while all other operating parameters are kept constant.

Variation in energy and exergy efficiencies with engine load is shown in Figs. 11.16 and 11.17 for different pilot fuels in a biogas DF engine. First observation is that for any operating conditions, the energy efficiencies are higher than corresponding exergy efficiencies. This is because lower calorific values of all the fuels are smaller than their specific chemical exergies. Therefore, in terms of total input energy, the exergy input is higher resulting into lower exergy efficiencies. Second observation is that all DF cases show poor efficiencies at the low load as compared to diesel engine. When comparison is made between DF cases, biodiesel as the pilot fuel showed comparable results as that with the diesel pilot fuel. This is noticeable as biodiesel has lower calorific value than diesel. Perhaps, improved combustion with biodiesel in DF operation compensates for low energy density and hence the performance loss. However, this effect is visible at the higher loads, where biodiesel-biogas DF engine shows some loss in performance that is exergy efficiency decreases up to 1.1% as compared to diesel-biogas DF operation. It is also possible to utilize suitable combustion enhancer to further improve the performance of biodiesel-biogas DF engine (Verma et al. 2021). Nevertheless, DF engine performance is considerably improved for all the cases at the higher loads. GTL as the pilot fuel shows very much comparable results to diesel in DF operations with biogas. It should be noted that GTL fuel has lower bulk modulus than diesel. Hence, the compressibility effect on GTL lead to slower pressure build-up in the fuel injector causing actual injection

Table 11.2 Properties of the liquid fuels: diesel, biodiesel and GTL

Properties	Diesel	Biodiesel (Jatropha curcas)	GTL
Specific gravity	0.84	0.92	0.77
Viscosity (cSt) at 40 °C	2.44–2.7	4.32	1.94
Calorific value (MJ/kg)	43	38.5	44.37
Flash point (°C)	35	174	104
Cetane number	51	51–58.2	79

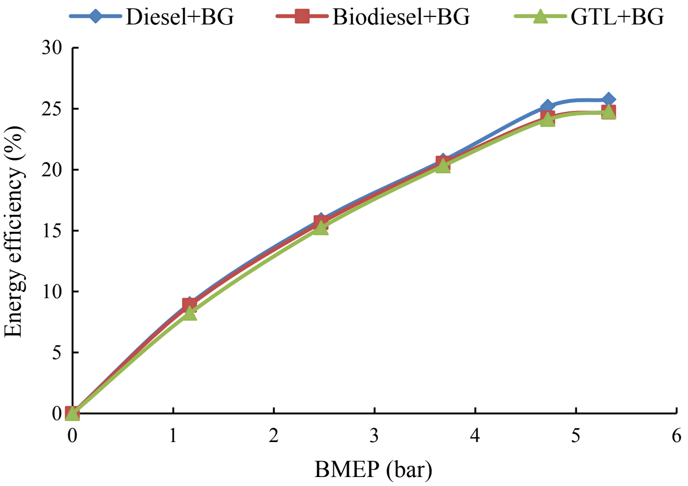


Fig. 11.16 Variation of energy efficiency with engine load for diesel, biodiesel and GTL as the pilot fuels

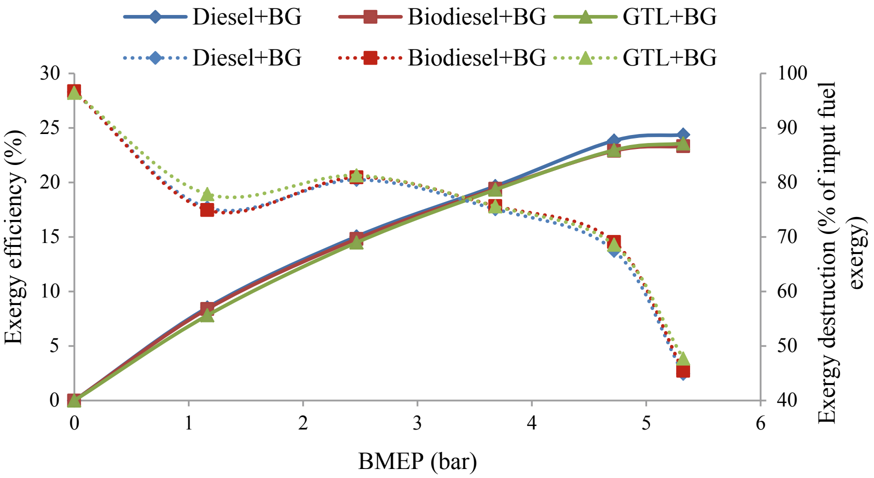


Fig. 11.17 Variation of exergy efficiency (sold lines–left axis) and exergy destruction (dotted lines–right axis) with engine load for different pilot fuels

timings to be retarded. It appears that better fuel properties of GTL compensate for change in the injection timings. It appears that with properly optimized injection parameters, GTL could give better results than diesel.

Exergy destruction is also shown in Fig. 11.17 for different engine loads. Very high exergy destruction of 73.28 and 76.34% (of total incoming fuel exergy) are observed with biodiesel-biogas and GTL-biogas DF cases at the low load. This is due to poor

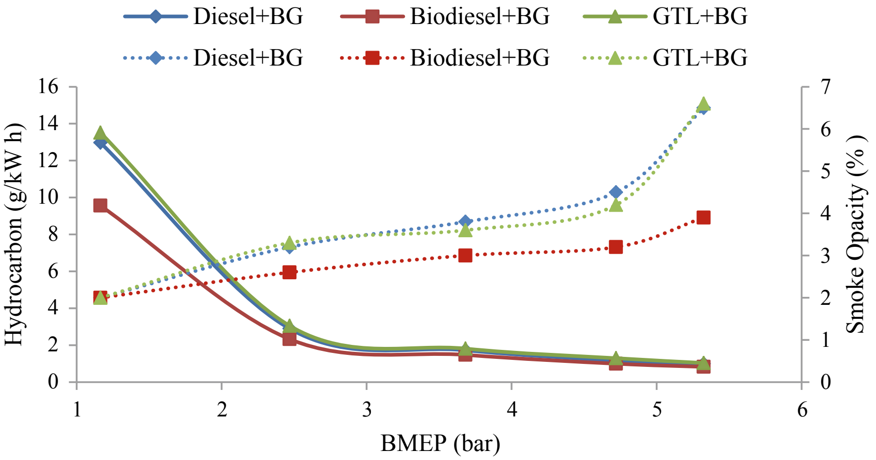


Fig. 11.18 Variation of hydrocarbon (solid lines–left axis) and smoke (dotted lines–right axis) emission with engine load for diesel, biodiesel and GTL as the pilot fuels

combustion and lower conversion efficiency at the low load. However, it is reduced to 44.69 and 46.79% at the full load due to improved combustion. At this condition, diesel-biogas DF case shows 44.01% exergy destruction. Therefore, biodiesel case shows comparable, whereas GTL shows slightly higher exergy destruction than diesel in DF operations.

Hydrocarbon (HC) emissions from biogas DF engine with different pilot fuels are shown in Fig. 11.18 As discussed previously, HC emissions from a biogas DF engine is significantly higher, especially at the low engine loads. However, as compared to diesel-biogas DF operations, improvements are shown by biodiesel-biogas DF operations. It can be seen from Fig. 11.18 that as high as 26% reduction in HC emission is possible with biodiesel as the pilot fuel at the low load conditions. Oxygenated fuels such as biodiesel improves the combustion efficiency, which reduces the incomplete combustion in DF engines. The GTL-biogas DF case shows HC emissions much similar to that with the diesel-biogas case throughout the engine load spectrum. Significantly high amount of HC emissions are found at the low load. However, as the load is increased, great improvement in the HC emissions are recorded. At full load, HC emissions of 0.97, 0.79 and 1.01 g/kW h were recorded with diesel-biogas, biodiesel–biogas and GTL–biogas DF cases respectively.

It can also be seen in Fig. 11.18 that biodiesel as a pilot fuel reduces the smoke emission as compared to diesel in the DF mode. The reduction is found higher at the high loads. At full load, 2.6% reduction in smoke emissions is recorded with biodiesel as the pilot fuel over diesel. The structure of the fuel has great influence on smoke generation in IC engines. Higher carbon containing fuels with high molecular weight produce higher smoke emissions. The higher hydrogen to carbon ratio of biodiesel produces lower smoke emissions. Moreover, improved flame speed helps in increasing the soot oxidation reaction rate, which causes reduced smoke emissions.

On the other hand, GTL shows similar smoke emissions as that with diesel as the pilot fuel.

11.4 Advances in the Combustion Methods for Biogas

11.4.1 Optimization of Engine Design Parameters

One of the biggest challenges of combustion engine is their polluting nature, which has though reduced significantly with the engine advancements, it is still higher than the permissible limits. In addition to that the emission regulations are continuously tightened by the various governments. Therefore, current engine research is extensively focused on advanced combustion methods along with less polluting alternative fuels. As discussed in the previous sections, DF engine offers potential solution in this regard, and hence various academic and industrial researches are being conducted on optimization of design and operating parameters of the DF engine. Belgiorno et al. (2018) showed that significant improvement in performance and emission characteristics can be achieved by optimizing the main DF engine parameters. In this work, they analyzed the effects of important parameters such as compression ratio, fuel injection pressure, combustion phasing and the air–fuel ratio. It was found that compression ratio has significant effect on hydrocarbon emission; further improvement was suggested by optimizing the piston bowl geometry. Similar results were reported by Di Blasio et al. (2015), who found that DF offered remarkable reduction CO_2 emission, however with the penalty of methane hydrocarbon emission. It was also reported that higher bowl/crevices volume ratio considerably reduced the methane hydrocarbon emission. In further support of this study, Königsson et al. (2013) reported that crevice volume is responsible for 70% of hydrocarbon emissions from DF engine. The importance of piston bowl geometry and combustion chamber design are supported by tudied the impact of diesel in other researchers in the literature (Lee and Park 2017; García et al. 2021; Hariharan et al. 2021).

Injection system design is another important parameter that impacts DF engine. In addition to the effect of injection timing explained previously in this article, there are other injection parameters such as injection pressure, injected fuel distribution, multiple injection, direct injection etc. which could significantly impact the DF engine characteristics. Valladolid et al. (2017) found that with the help of local pilot fuel distribution, DF engine combustion instability and emissions can be controlled. The results showed that appropriate control over diesel fuel distribution could achieve the lower emission levels than the regulation limits without an after-treatment device in a marine engine. Liu et al. (2015) studied the impact of diesel injection pressure on a 6-cylinder diesel-methanol DF engine. It was found that combustion duration and brake specific fuel consumption decreased with the increase in diesel injection pressure. On the emission side, CO, HC and smoke emission decreased, whereas NOx emission increased with the increase in diesel injection pressure. Split injection strategy was studied by Yousefi et al. (2018) on a natural gas-diesel heavy-duty DF engine. It was found that split injection significantly increased the heat release rate and hence peak cylinder pressure compared to single injection. It was possible to achieve a compromise between HC/CO and NO_x emission using split injection strategy. Similarly, multiple injection strategy was suggested by Huang et al. (2019) on a natural gas–diesel DF engine, which was found to improve the performance.

11.4.2 Blends of Pilot Fuels

It has been shown that use of biodiesel in a biogas DF engine has specific advantages. Biodiesel is an oxygenated fuel, which can be produced from vegetable or animal based fatty acids (Shahid and Jamal 2011). Therefore, biodiesel is a non-toxic, biodegradable and renewable alternative fuel. The properties of biodiesel is close to diesel, consequently it is a suitable alternative to diesel fuel. However, biodiesel has higher viscosity than diesel, which requires adequate modification in the fuel injector for efficient and long term operations. Also, stability of biodiesel during long term storage is a big concern, which creates difficulties in the planning and operation. Therefore, blends of diesel and biodiesel are more commonly used in the various applications (Ali et al. 2016). Furthermore, a ternary blend of diesel–biodiesel-ethanol has reported to offer improved characteristics over single fuels (Hulwan and Joshi 2011; Zhu et al. 2013). Ethanol is also a renewable fuel but with low density, therefore a good additive for diesel–biodiesel blends. However, it has low Cetane number, high heat of vaporization and poor heating value. These properties of ethanol may adversely affect the overall fuel property of the ternary blend, hence adequate proportions are to be maintained to achieve the potential benefits. Kwanchareon et al. (2007) studied the properties of diesel–biodiesel–ethanol blend and found that higher Centane number of biodiesel compensates for the ethanol if ethanol is below 10% in the blend. The heating value of the blend is also not much different than the diesel, however both HC and CO emissions are lowered significantly at the high load. Nevertheless, Ghobadian et al. (2009) have shown that engine power and torque output decreased as the proportion of biodiesel/ethanol increased in the blend. Sarkar and Saha (2018) investigated on the effect of ternary blend of diesel–biodiesel-ethanol on a biogas DF engine with intake charge heating. Their results show that a ternary blend could give improvement or deterioration of the engine characteristics depending on the blending proportions. It was reported that a blend of 72% diesel 20% biodiesel and 8% ethanol gave overall superior performance compared to diesel-biogas DF engine. Especially, HC and CO emissions are significantly reduced, whereas engine efficiency remains nearly unaffected. Paul et al. (2015) studied the effect of higher percentage ternary blend of diesel–biodiesel-ethanol on a CNG fueled DF engine. Their results showed that a blend of 30% diesel, 50% biodiesel and 20% ethanol could not only reduce the emission but also enhances the engine efficiency. At the same time, it was also possible to utilize higher amount of CNG in the DF operation of the engine. In a similar study, Senthilraja et al. (2016) found that increasing the ethanol proportion in the ternary blend reduced the NO_x emission, whereas HC and CO emission were increased. Nevertheless, it is possible that biofuel blends could enhance the performance limit of the biogas DF engine, and therefore this area should be further explored in detail.

11.4.3 Homogeneous Charge Compression Ignition (HCCI)

Another method for utilization of biogas in the diesel engine is homogeneous charge compression ignition (HCCI). The HCCI is a combination of techniques employed in SI and CI engines. In HCCI, a premixed fuel and air mixture is supplied to the engine and the combustion starts with auto-ignite of the mixture as a result of the temperature increase in the compression stroke. Therefore, it takes features of premixed fuel from the SI engine and auto-ignition of the mixture from the CI engine (Stanglmaier and Roberts 1999; Yao et al. 2009). Therefore, HCCI offers engine efficiency close to conventional diesel engines, whereas NO_x and smoke emissions could be suppressed simultaneously. On the other hand, there are some associated challenges on successful and wide range operation of HCCI engines. One of the major challenges is control of the combustion phasing, because there is no direct control parameter unlike conventional combustion methods. Consequently, the start of combustion and the combustion rate are influenced by parameters such as fuel–air chemistry, residual rate, compression ratio, intake temperature and so on, making is difficult to realize the combustion phasing and control. Hence, HCCI engines are constrained by short operation range, high HC and CO emission, high engine noise and cold start.

As discussed before, biogas is a high octane fuel, hence its compression ignition is not feasible. Hence, a high Cetane value fuel (e.g. diesel) is used in combination with biogas to achieve the homogeneous compression ignition. It should be noted that HCCI technique is different from DF technique from the perspectives of delivering the high Cetane value fuel. In HCCI combustion, the fuels are premixed and no fuel is injected during compression. Nathan et al. (2010) studied the HCCI operation using biogas as the main fuel, and diesel as the high Cetane value fuel for combustion control. It was reported that though biogas showed poor engine efficiency (both with SI and DF engines), its HCCI operation showed the efficiency close to conventional diesel engine. NO and smoke emissions were lowered for all the test conditions, however, very high HC emissions were recorded. Gasoline injection oxygen enrichment, and delayed heat release are some strategies explored by Bedoya et al. (2012) to expand operating range of a biogas-fueled HCCI engine. Exhaust gas recirculation has been suggested as an effective strategy by Kozarac et al. (2014), to control the biogas fueled HCCI engine. In one of the studies, HCCI combustion of biogas was studied by Sudheesh et al. (2010) using diethyl ether as the Cetane additive. It was found that diethyl ether could provide stable HCCI operation using biogas. Furthermore, biogas HCCI combustion resulted in reduced HC, smoke and NO_x emissions, however CO emissions were increased. Feroskhan et al. (2021) presented a comprehensive investigation on the effect of various operation parameters on diethyl ether-biogas HCCI engine. Hence, utilization of biogas using HCCI method has the potential to achieve high efficiency along with minimized emissions. At present, biogas fueled HCCI combustion seems more attractive towards stationary power generation applications.

11.5 Summary

Biogas is a renewable fuel, which will have an important contribution in the future renewable energy mix. It could be utilized as an alternative fuel for automotive as well as different power applications. The diesel engine is a widely used and well established technology in the world, which can be slightly modified to utilize biogas in Dual Fuel (DF) technology. The performance and emission features of a biogas DF engine depends on various operating parameters; some of the important parameters are discussed in this chapter. Another important addition in the perspectives of the readers is to employ exergy analysis for performance characterization and comparison of the DF engines. A brief methodology of energy and exergy analyses is presented and important concepts are explained. The effect of important operating parameters on the performance and emission characteristics of the biogas DF engine can be summarized as following:

(i) The engine load is a crucial parameter that significantly affects the biogas DF engine. It is found that low load performance of the DF engine is very poor. In addition to that at the low load, excessive HC and CO emission are major issues. Pilot fuel substitution is another important parameters, which decreases with the engine load. The low load performance of biogas DF engine can be improve by reducing the pilot fuel substitution, though it is limited.

(ii) The composition of biogas is also found to significantly affect the features of DF engine. It is found that higher CH_4 content (above 90%) in biogas improves the engine performance, which is closer to the performance of the conventional diesel engine. On the other hand, lower CH_4 content could be utilized in a stationary application, where reduced performance may be compensated by the reduced requirement for CH_4 enrichment in biogas.

(iii) Injection timing of pilot fuel considerably influence the performance and emission features of the biogas DF engine. It is found that there are optimized IT advances, where best performance and emission can be achieved, however achieving both the conditions at same time could be difficult. Most importantly, IT advance is found capable of enhancing the low load performance of the biogas DF engine.

(iv) Pilot fuel properties are important to improve the DF engine performance, and renewable fuels such as biodiesel and GTL can be effectively used as replacements for diesel. Especially, oxygenated fuels like biodiesel is found to offer enhancement in the emission characteristics from biogas DF engine. Pilot fuel properties can be curated to get enhanced performance from the biogas DF engine.

It can be seen that biogas DF engine can have a large potential in the coming years. However, it still has a lot of scope for improvements in the area of performance and emissions. A biogas DF engine need particular attention to improve its low load features. It will require fundamental research for combustion of biogas as well as applied techniques. Improvising the pilot fuel injection characteristics, use of combustion enhancers and design modifications could be crucial ideas to tackle these issues.

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