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An overview of methanol as an internal combustion engine fuel

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ABSTRACT

Methanol is an alternative, renewable, environmentally and economically attractive fuel; it is considered to be one of the most favorable fuels for conventional fossil-based fuels. Methanol has been recently used as an alternative to conventional fuels for internal combustion (IC) engines in order to satisfy some environmental and economical concerns. Because of a number of relatively large research projects that have been ongoing recently, much progress has been made that is worth reporting. This paper systematically describes the methanol productions, including the productions from coal, natural gas, coke-oven gas, hydrogen, biomass etc. It introduces the potentials of methanol as a renewable resource taking into account the world supply and demand, economic benefits and the effects on human health and the environment. Thirteen methods of application such as methanol/gasoline, methanol/diesel blends which can be used on the IC engines are summarized. Finally, this paper puts forward some new suggestions on the weakness in the researches of methanol engine.

Contents

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1. Introduction

Nowadays, with reserves of these petroleum-based fuels being rapidly depleted, various alternative resources such as methanol, ethanol, or hydrogen are needed in order to replace the non-renewable resources [1]. With rising petroleum prices and global warming being a dominant environmental issue, it seems that the use of alternative fuels in the future is inevitable. Our present energy supply is based on the fossil fuels, which are non-renewable energy. Given the growing world population and atmospheric environment, increasing energy demand per capita and global warming, the need for a long-term alternative energy supply is clear. Methanol is one of the best candidates for long-term, widespread replacement of petroleum-based fuels [2]. Among renewable alternative energy sources, there are a lot of benefits to the development of alternative fuels such as alcohol fuels instead of the traditional nonrenewable oil resources, for instance, (1) it can mitigate national security and economic concerns over fuel supplies; (2) it can improve the atmospheric emissions; and (3) it can maintain the sustainable development of the resources [3]. Among gasoline and diesel replacement fuels, methanol (CH_3OH) fuel has been considered to be one of the most favorable fuels for IC engines [4,5].

Methanol is considered to be one of the most favorable fuels for engines, for instance, (1) it can be used in a high compression ratio spark ignition (SI) engine that could replace diesels in certain vocational applications; (2) it can be used in an inlet port injection SI engine; (3) it can be used in a high compression direct-injection stratified charge SI engine; (4) it can be used in a direct-injection SI engine; and (5) it can be used in a turbocharged, port-fuel-injected, high compression ratio medium duty engine [6–10].

The aim of this paper is to systematically review the methanol productions, including the productions from coal, natural gas, coke-oven gas, hydrogen and biomass etc., and to review the use of methanol as a fuel for IC engines. Finally, this paper puts forward some new suggestions in the researches of methanol engine.

2. Methanol production

Methanol synthesis has undergone continuous improvements for over nearly a century [11]. Nowadays, methanol as an alternative fuel can be produced from many ways, for instance, it can be produced from natural gas, biomass [12], or it can be produced based on coke oven gas [13], or it can be recovered through flashing vaporation in continuous production of biodiesel via supercritical methanol [14].

Among others, there are a lot of synthesis technologies, for instance, the advent of low-pressure synthesis, once-through designs, and advanced reforming technologies [11]. Nowadays, methanol is almost exclusively produced from synthesis gas [15,16], a raw material, consisting mainly of carbon monoxide (CO) and hydrogen, that is used in the large scale production of hydrogen and a wide variety of organic products in industry [17,18]. Methanol synthesis through syngas, which is a mixture of CO and hydrogen, involves the following chemical reactions [19,20]:

$$CO + 2H_2 \leftrightarrow CH_3OH \quad (1)$$

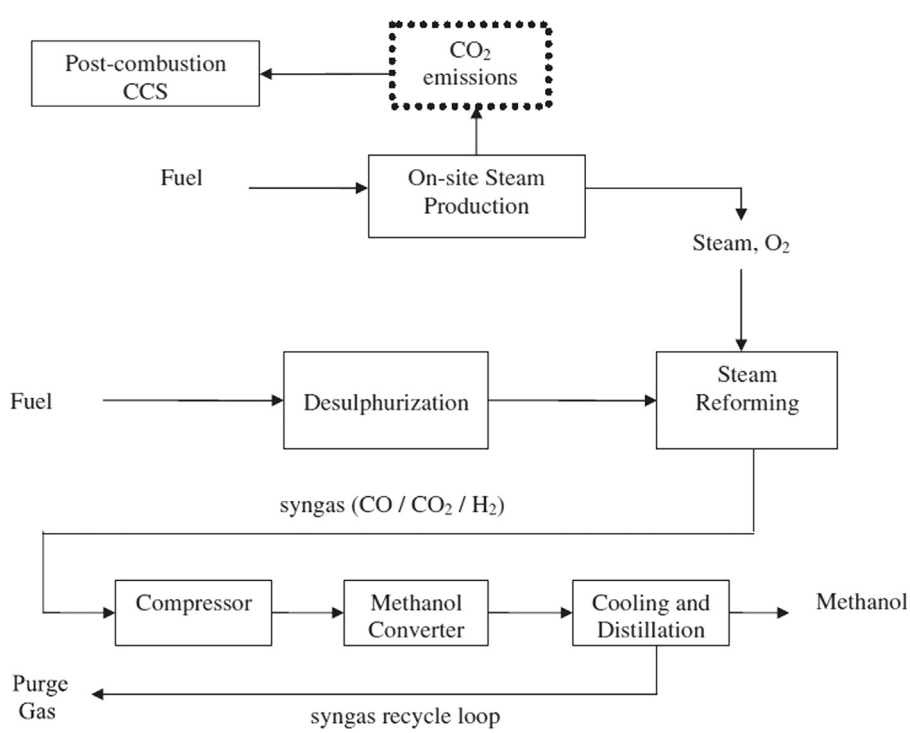

Fig. 1. The flowchart of the methanol synthesis process [19].

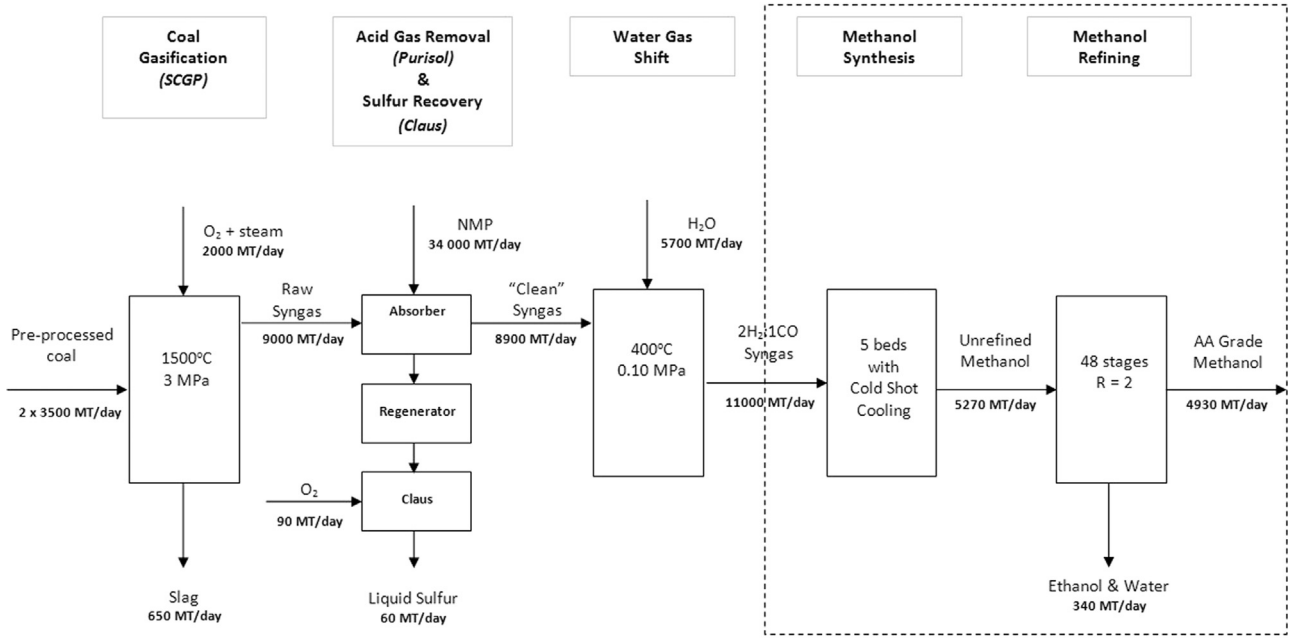

Fig. 2. The general scheme for the coal-to-methanol conversion [23].

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \quad (2)$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad (3)$$

Because reactions (1) and (2) are exothermic, it can lead to a reduction in volume. Conversely, because reaction (3) is endothermic, it can be called "reverse water gas shift reaction" (RWGSR). RWGSR can produce CO, it can be utilized to produce more methanol by reacting with hydrogen. It must be stated that the carbon dioxide (CO_2) in the flue gas can be utilized in either reaction (2) or (3) or in both reactions simultaneously. However, in either case syngas would have to be produced separately, and this can be achieved by reforming or partial oxidation of coal, coke, natural gas or petroleum [19–21]. The flowchart of the methanol synthesis process can be seen in Fig. 1 [19].

2.1. Methanol produced from coal

Methanol fuel can be produced based on coal. The comprehensive coal consumption in methanol production is about 1.42–1.59 t of standard coal equivalent per ton of methanol. Energy conversion efficiency can reach 43–48%, or even 50% in some large projects. CO_2 emissions are 2.37–3.52 t of CO_2 per ton of methanol, among which 0.079–0.117 t are discharged in the processing and 0.040–0.059 t in the public process [22].

The general scheme for the coal-to-methanol conversion is given in the block flow diagram that appears in Fig. 2 [23]. The process begins with gasification, which involves oxidation of the coal in a controlled amount of oxygen in order to produce the synthesis gas. Gasification of the Montana sub-bituminous coal was modeled after the Shell Coal Gasification Process and had been simulated on the second progress report. The product syngas was then treated in order to make it suitable for methanol synthesis. This involved removal and recovery of the acid gas (via the Purisol process with Claus sulfur recovery), as well as water gas shifting that regulated the ratio of the CO to hydrogen. Following these processes, methanol synthesis and refining were performed and simulated. The flow rates shown in the figure below were generated from the ASPEN simulation after the process scale-up [23]. Methanol syngas that can be produced based on coal is mainly from the intermittent gasification process in the fixed-bed [24–26]. The primary methanol syngas based on the fixed-bed has a lower ratio of hydrogen to carbon, so it is hard to be used to produce methanol. Thus, excessive water and CO must be transformed to sufficient hydrogen gas so as to increase the hydrogen/carbon ratio to up to an ideal level before the synthesis process [24].

Chen et al. [27] performed a simulation model for converting coal to methanol based on gasification technology with the commercial chemical process simulator. The methanol plant consisted of air separation unit, gasification unit, gas clean-up unit, and methanol synthetic unit. The results showed that gross and net efficiency in the case study was 77.7% and 63.3%, respectively, which were relatively higher than the counterparts in traditional integrated gasification combined cycle (IGCC) plants and the poly-generation plant of electricity and methanol. Zhao et al. [28] studied the application of step analysis method in coal to methanol water system; they found that the factory could save fresh water by 54 t/h and reduce waste water discharge by 54 t/h without equipment addition. If added reverse osmosis equipment to regenerate concentrate, the factory could reduce fresh water consumption and wastewater discharge by 159 t/h.

2.2. Methanol produced from natural gas

A "methanol economy" based mainly on natural gas as a feedstock has a lot of potentials, which can cope with the current and ongoing concerns for energy security and the reduction of CO_2 emissions [29].

A base plant configuration that corresponds to the standard process for methanol production from syngas was compared with the proposed one by Pellegrini et al. [12]; the proposed methanol production was coupled with a power plant fed by the un-reacted gases, and the capital and operating costs were considered. They proposed a solution based on steam methane reforming and consisted of once-through methanol synthesis followed by a power plant in which the un-reacted gases were burnt. The results proved that the modified configuration was profitable. Li et al. [30] presented a new poly-generation system for methanol production and power generation by taking biomass and natural gas as materials. The proposed new poly-generation system could achieve the optimal ratio of hydrogen to CO for methanol production by adjusting input ratio of natural gas to biomass without any energy

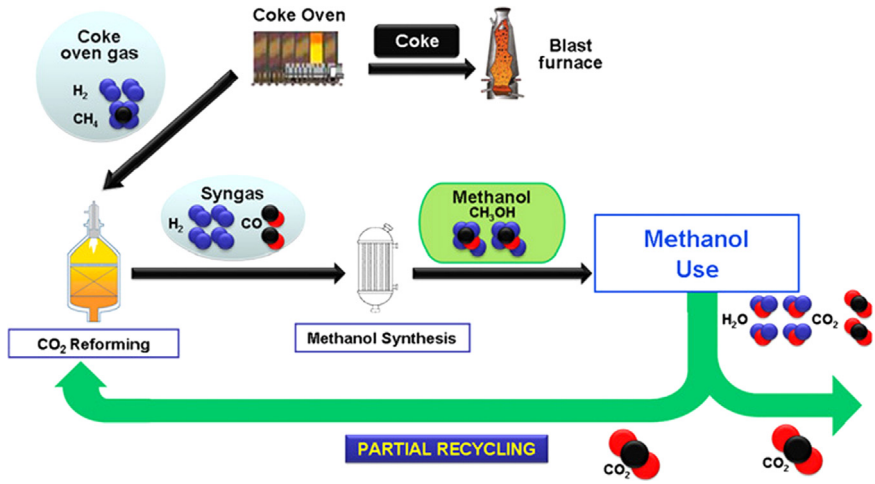

Fig. 3. The partial recycling of CO_2 by means of the CO_2 reforming of coke oven gas for methanol production [34].

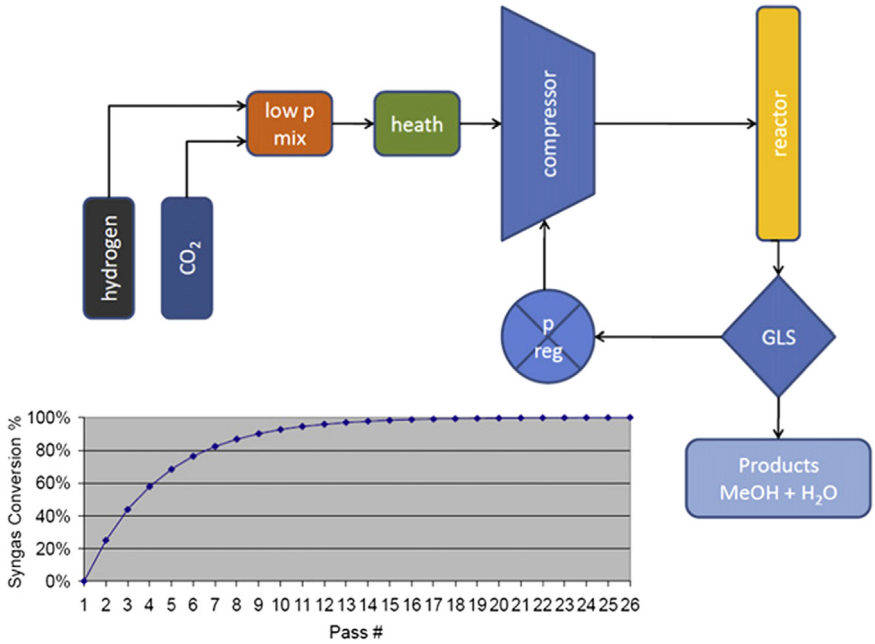

Fig. 4. Multi pass methanol production [37].

penalty. The results showed that the proposed poly-generation could get the highest energy saving ratio of 10% by adjusting the input ratio of natural gas to biomass, the output ratio of methanol to power was relatively steady between 1.5 and 2.1, and the suggested poly-generation system could reduce materials input by at least 9% compared with individual systems with same output.

Methanol direct synthesis from methane and water vapor mixtures has a high possibility to realize a high sophisticated energy recycling system with energy regeneration. Okazaki et al. [31] proposed a methanol direct synthesis system from methane and water-vapor mixture by non-equilibrium plasma chemical reactions under atmospheric pressure using a newly developed ultrashort pulsed barrier discharge in an extremely thin glass tube reactor; various effects of reaction time, water-vapor concentration and discharge parameters on the conversion efficiency and reaction selectivity had been clarified. The results showed that the methanol yield had reached the order of 1% at the water-vapor concentration of about 50%, and the value could be largely enhanced by adding rare gas such as K_r or A_r to the source gas.

Verma [32] studied the direct transformation of methane into methanol in the lower temperature range by using the methane homogeneous reaction kinetics. They analyzed the effects of operating parameters such as temperature, residence time and CH_4/O_2 input ratio on direct oxidation of CH_4 into CH_3OH in the lower temperature range suitable to catalytic conversion. They found that a higher conversion of methane into methanol could be achieved by controlling the operating parameters to their optimum values.

2.3. Methanol produced from coke-oven gas

Coke oven gases (COG), which can be considered a byproduct of coking plants, consist mainly of H_2 (about 55–60%), CH_4 (about 23–27%), CO (about 5–8%), and N_2 (about 3–5%), along with other hydrocarbons, H_2S and NH_3 in small proportions [33]. Methanol fuel can be produced based on COG. The dry reforming of COG over an activated carbon used as catalyst can be used to produce a syngas for methanol synthesis.

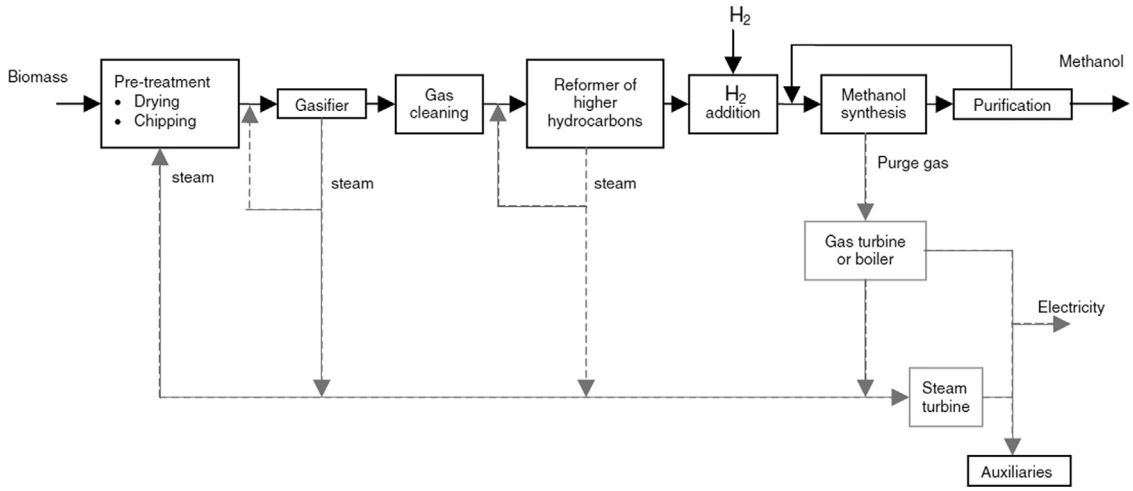

Fig. 5. Key components in biomass to methanol production facility [36].

Table 1
Methanol supply and demand balance [52].

Supply	2008	2009	2010	2011	2012	2013E	CAGA 08–13E
Namepalate capacity adjustments	59,014	67,454	76,478	86,777	95,469	101,063 (1800)	11.4
Total capacity	59,014	67,454	76,478	86,777	95,469	99,263	11.0
Macro operating rate	68.2%	62.3%	63.9%	63.1%	63.5%	65.1%	
Production	40,260	42,051	48,892	54,749	60,589	64,575	9.9
Imports	20,231	22,503	23,812	24,344	23,860	25,034	4.4
Total supply	40,260	42,051	48,892	54,749	60,589	64,575	9.9
Demand							
Formaldehyde	15,160	14,163	16,284	17,569	18,410	19,316	5.0
Acetic acid	4278	4244	4986	5189	5307	5704	5.9
Methyl tert-butyl ether (MTBE)	6985	6749	7265	7673	8169	8521	4.1
Methyl methacrylate	1328	1261	1410	1462	1507	1579	3.5
Dimethyl terephthalate (DMT)	487	467	453	457	458	468	−0.8
Methanethiol (methyl mercaptan)	432	425	420	444	461	478	2.0
Methylamines	1167	1132	1280	1360	1401	1441	4.3
Methyl chloride (chloromethane)	1713	1691	1782	1857	1916	1987	3.0
Gasoline blending & combustion	3091	4903	6158	7143	8311	9224	24.4
Biodiesel	909	832	903	1210	1314	1218	6.0
DME	1824	3338	3977	4297	4557	4734	21.0
Fuel cells	10	5	6	6	7	7	−6.4
Methanol-to-olefins	7	7	702	2479	4908	5886	289.5
Others	3038	2824	3307	3584	3872	4014	5.7
Total	40,428	42,042	48,932	54,731	60,597	64,575	9.8
Exports	20,231	22,503	23,812	24,344	23,860	25,034	4.4
Total country demand	40,428	42,042	48,932	54,731	60,597	64,575	9.8
Net	(168)	9	(39)	19	(8)	–	

Bermudez et al. [33] studied the influence of the high amount of hydrogen present in the COG on the process of drying reforming. The results showed that the reverse water gas shift reaction took place due to the hydrogen present in the COG, and that its influence on the process increased as the temperature decreased; at high temperatures (1000 °C) and with VHSVs (volumetric hourly space velocity) no higher than 1.5 L g^{-1} h^{-1}, the activated carbon FY5 was a good catalyst for the dry reforming of COG as means of producing syngas for the production of methanol. A thermodynamic study of the equilibrium of the CO_2 reforming of COG was carried by Bermudez et al. [34]. It was found that the presence of light hydrocarbons in the COG gave rise to a syngas that was more suitable for methanol production than when they were absent. The syngas from CO_2 reforming of COG is suitable for the methanol production [35]. The partial recycling of CO_2 by means of the CO_2 reforming of COG for methanol production is illustrated in Fig. 3 [34].

2.4. Methanol produced from hydrogen

Electrolytic hydrogen production is an efficient way of storing renewable energy generated electricity and securing the contribution of renewable energy in the future electricity supply. The use of this hydrogen for the methanol production results in a liquid fuel that can be utilized directly with minor changes in the existing infrastructure. Methanol fuel can be produced based on hydrogen. To utilize the renewable generated hydrogen for renewable methanol production, a sustainable carbon source is needed [36]. The recycle of CO_2 to methanol is a nice idea but with a terrible energy balance, this method supposes the availability of almost unlimited renewable energy [37].

Boretti [37] studied the opportunity to recycle the CO_2 produced by burning fossil fuels with oxy-fuel combustion using renewable hydrogen as the second feed-stock. The results showed that the demonstration project was the oxy-fuel power plant of

the Rankine type integrated with large solar ponds to collect the sun energy, the hydrogen production by steam reforming and the conversion of CO_2 to methanol through catalytic reactions within the same facility. Methanol synthesized from CO_2 can be employed directly in stead of fossil fuels without disturbing the present existing energy distribution infrastructure. The convention of CO_2 into methanol has various routes [38]; catalytic carbon dioxide hydrogenation is a mature method [39]. Fig. 4 presents a sample analysis for the multi-pass methanol production through hydrogen. The single pass efficiency is 25%. The target space velocity in the reactor is 3000 l/h/kg (cat). The high pressure is 95–125 bar and the low pressure is 20 bar. The recirculation gas is 3 times the make-up gas and the syngas conversion [37].

2.5. Methanol produced from biomass

Methanol can be produced from nearly all organic materials [40]. Biomass consists of carbon, which is already available in an enriched form, so it is advantageous for the production of synfuels containing carbon [41]. Biomass processing is the most cost-effective of the processes that have been developed for the production of methanol renewable sources [42,43].

The process for producing methanol from biomass has the same steps as that of natural gas and coal based processes: syngas production, methanol synthesis and purification [44–46]. A biomass to methanol plant consists of two main components, one is a biomass gasifier to convert the feedstock to synthesis gas, and another is a methanol synthesis plant [36]. The methanol production facility, based on the process, consists of the following basic steps: feedstock pre-treatment, biomass gasification, syngas treatment, hydrocarbon reforming, hydrogen addition, and methanol synthesis [45] (see Fig. 5 [36]).

Reno et al. [47] studied the methanol production from sugarcane bagasse through life cycle assessment, the results showed that with relation to the result of output/input ratio, the methanol production from sugarcane bagasse was a feasible alternative for the substitution of an amount of fossil methanol obtained from natural gas. A systematic analysis of interrelations between different process steps in the biomass gasification and methanol synthesis chain was made by Holmgren et al. [48]; the results could be used for making a comparison of energy efficiency, greenhouse gas emissions and economic performance for standalone and integrated biomass gasification methanol synthesis plants. Techno-economic analysis of a methanol plant based on gasification of biomass and electrolysis of water has been done by Clausen et al. [49]. They found that the lowest cost was obtained by a plant using electrolysis of water, gasification of biomass and auto-thermal reforming of natural gas for syngas production.

Shabangu et al. [50] assessed the feasibility of co-production of methanol and biochar from thermal treatment of pine in a two-stage process. They found that biochar may help in decreasing biofuel costs when local soil conditions and cropping systems justified a market and sufficiently high price for the biochar. Because biomass is rich in carbon while natural gas is rich in hydrogen, so, co-utilization of natural gas and biomass is a successful way to make efficient use of them for chemical production and power generation. Li et al. [30] proposed a new poly-generation system taking biomass and natural gas as materials for methanol production and power generation. The new poly-generation system can achieve the optimal ratio of hydrogen and CO for methanol production by adjusting input ratio of natural gas to biomass without any energy penalty. The results showed that the new poly-generation system could reduce materials input by at least 9% compared with individual systems with same output. Lundgren et al. [51] studied the methanol production from steelwork off-gas and biomass based synthesis gas. The results showed that the integration of a methanol synthesis process in steel plants increased the gas utilization efficiency and reduced the specific CO_2 emissions of the plant; methanol produced by off-gases from steelmaking combined with biomass showed competitive production costs versus petrol.

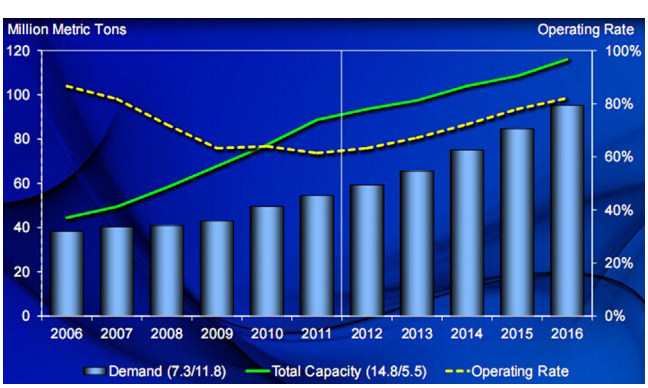

Fig. 6. The world methanol supply and demand [53].

3. World methanol supply and demand

Methanol is one of the most important raw materials in the global industry, which makes its demand increasing. Methanol also has significant commercialization effort. Methanol is a product with many useful characteristics that allow it to serve as an energy resource, a chemical feedstock, and a component or intermediate in many consumer goods. The major supply and demand for methanol are depicted in Table 1 [52]. Fig. 6 shows the world methanol supply and demand data [53]. It can be seen from Fig. 6 that the demand of methanol is increasing strongly and has been increased by approximately 2.5 times during the past 10 years, and the production capacity of methanol has been increased by approximately 3.0 times during the past 10 years. It is obviously seen that the production capacity of methanol can fully meet the demand.

Fig. 7 shows the global methanol demand growth results [53]. It can be seen from Fig. 7 that about 32% of the methanol is consumed in the production of formaldehyde. With the increase of gasoline/fuel applications, it is anticipated to fall to 25% by 2016. The use of formaldehyde is diverse; for instance, it is generally applicable in the wood industries and photographical industries. The demand from methanol to olefins (MTO) and to propylene (MTP) is anticipated to become a high growth sector, rising from 6% in 2011 to 22% by 2016, the vast majority of which is forecast to take place in China. Fig. 8 shows the China's robust demand growth data [54]. It can be seen that China represents 80% of global demand growth 2016 versus 2011, and Asia represents 70% of global demand by 2016. In China, most of the methanol produced from fossil fuels and coke-oven gas is also consumed primarily in the manufacture of formaldehyde, alternative fuels and acetic acid, all of which are important materials for the development of the modern construction, transportation, and chemical industries [55]. During the past three decades, the annual methanol consumption has increased by 71-fold from 0.33 million tons in 1983 to 23.84 million tons in 2011 [56].

4. Economic benefits of methanol

Nowadays, air pollution has become a global problem, and it limits the economic growth of industrial cities. Substitution of cleaner fuels for the current generation of fossil fuels can reduce the need for and economic cost of traditional add-on pollution controls [57]. Fig. 9 shows the prices of Brent Crude oil and Henry

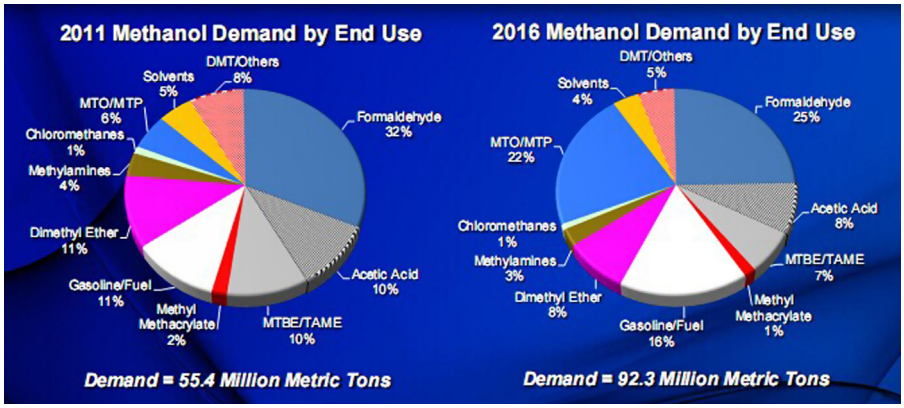

Fig. 7. The global methanol demand growth [53].

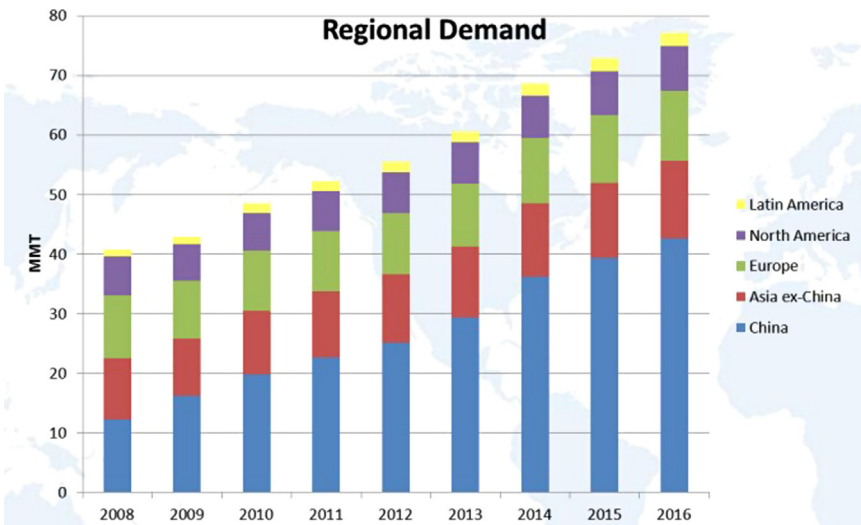

Fig. 8. The China's robust demand growth [54].

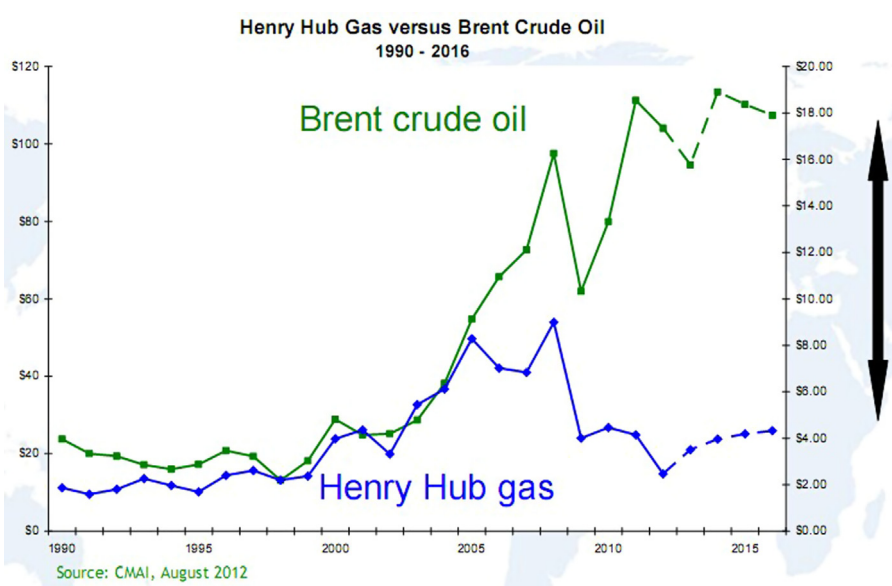

Fig. 9. The prices of Brent Crude oil and Henry Hub gas [54].

Hub gas [54]. It can be seen from the figure that compared with the natural gas and coal, high crude oil price can provide an opportunity to upgrade natural gas and coal into liquid product. Methanol is being used as an energy carrier to capture this value opportunity.

Fig. 10 illustrates the equivalent price of energy products valued as methanol for the world [53]. It can be seen from the figure that the price of methanol is almost equivalent with the price of gasoline, and even higher than the price of gasoline in the next

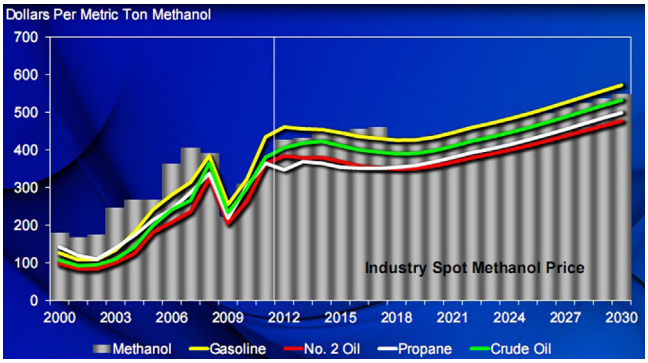

Fig. 10. The equivalent price of energy products valued as methanol for the world [53].

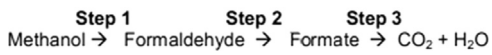

Fig. 11. Human metabolism of methanol.

Table 2
The properties of methanol, gasoline and diesel.

Fuel property	Methanol	Gasoline	Diesel
Formula	CH_3OH	C_{5-12}	C_{10-26}
Molecular weight	32	95–120	180–200
Oxygen content	50%	0	0
Stoichiometric air/fuel ratio	6.45	14.6	14.5
Low calorific value (MJ/kg)	19.66	44.5	42.5
High calorific value (MJ/kg)	22.3	46.6	45.8
Freezing point (°C)	−98	−57	−1 to −4
Boiling point (°C)	64.8	30—220	175–360
Flash point (°C)	11	−45	55
Auto-ignition temperature (°C)	465	228–470	220–260
Research octane number	108.7	80–98	
Motor octane number	88.6	81–84	
Cetane number	3	0–10	40–55
inflammability limit	6.7–36	1.47–7.6	1.85–8.2
specific heat (20 °C) (kJ/kg K)	2.55	2.3	1.9
latent heat (kJ/kg)	1109	310	270
Viscosity (20 °C) (CP)	0.6	0.29	3.9

three years (2015–2017). However, the prices of methanol, gasoline and crude oil are gradually increased after 2018 year. So, with the development of methanol production technology, it can be seen that compared with the gasoline, the price advantage of methanol is more and more obvious. In less than a decade, methanol use in China's transportation section grew from virtually zero to replacing nearly 8% of the country's gasoline requirement [58]. On the other hand, the expanded use of methanol as a clean-burning fuel source could provide tens of thousands more jobs at various skill levels and billions of dollars additionally in the clean energy economy [59].

5. Effects of methanol on human health and the environment

Methanol, also known as methyl or wood alcohol, is a colorless organic liquid at room temperature that is both flammable and toxic if ingested. Methanol not only affects the human health, but also affects the environment.

5.1. Effects of methanol on human health

Methanol is toxic to humans, and is readily absorbed by ingestion and inhalation, and more slowly by skin exposure. However, methanol is already present within the human body in small quantities

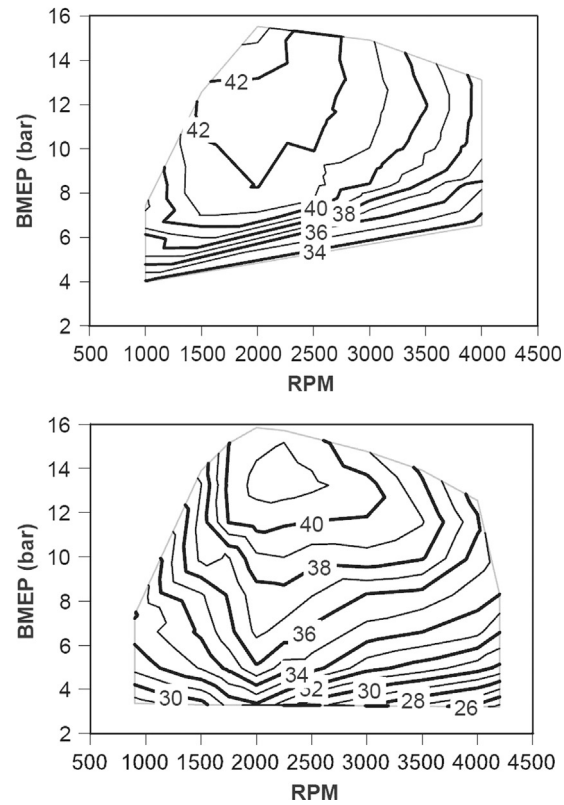

Fig. 12. The measured break thermal efficiency of the engine operating with methanol fuel and the baseline diesel engine (1) methanol: BTE (%) as a function of BMEP, RPM; (2) baseline stock 1.9 L VW TDI Diesel: BTE (%) as a function of BMEP, RPM [3].

from eating fruits and vegetables. According to the FDA, as much as 500 mg per day of methanol is safe in an adult's diet. In the body, methanol is metabolized in the liver, converted first to formaldehyde, and then to formate (see Fig. 11). As a building block for many biological molecules, formate is essential for survival. If people intake excessive methanol, the high levels of formate will buildup in the body, which can cause severe toxicity and even death. The initial symptoms of methanol poisoning (drinking one to four ounces) may be delayed for as long as 12–18 h as the body metabolizes methanol to formate, and can consist of weakness, dizziness, headache, nausea vomiting and blurred vision. In severe cases of accidental or reckless ingestion, methanol poisoning may lead to permanent blindness or death, although complete recovery is the rule in patients admitted early to a hospital [60].

So, methanol must be handled properly to ensure that it does not have negative impact. Methanol exposure can be avoided and managed safely through the proper design of fuel containers and fueling systems. No matter how much methanol you use on a daily basis, it is important for everyone to know the hazards and safety precautions involved with handling methanol.

5.2. Effects of methanol on the environment

The most important properties of methanol that define its effects on the environment are its solubility, volatility, and toxicity. The relatively high vapor pressure of pure methanol causes it to volatilize readily into the air. If released below ground, it will concentrate in soil gas within pore spaces, though it is easily

biodegradable. As a volatile organic compound, methanol can contribute to the formation of photochemical smog. Methanol can be broken down by sunlight and has a half-life of 17–18 days [61].

Methanol is a naturally occurring, biodegradable alcohol that is present in our environment and can even be found out in space. Methanol occurs naturally during the decomposition of different plants and animals life, and we come into contact with it every day in fruits, juices, and even wine. Though larger quantities of methanol can be toxic if ingested, this naturally occurring molecule has a very low impact when released into the environment because of how quickly it biodegrades [62]. The U.S Environmental Protection Agency (EPA) has determined that methanol has a limited persistence in the environment. When methanol is released into the environment, it can rapidly break down into other compounds and be completely miscible in water. Waste methanol, or water contaminated with methanol, is considered a hazardous waste and must never be discharged directly into sewers of surface waters. The recommended disposal method for methanol is incineration for heating value recovery. Concentrated liquid methanol can be used as secondary fuel in systems compatible with water-soluble waste. Waste methanol is also amenable to reclaiming by filtration and distillation [61].

6. Methanol fuel used on IC engine

The properties of methanol, gasoline and diesel fuels are shown in Table 2. Methanol is an alcohol and is a colorless, neutral, polar and flammable liquid. It is miscible with water, alcohols, esters and most other organic solvents. It is only slightly soluble in fats and oils [63]. Methanol has higher octane rating and greater heat of vaporization values as compared to gasoline, making it a suitable candidate for high compression ratio engines with larger power outputs. This is because higher octane rating allows a significant increase in the compression ratio and a higher heat vaporization value may cool down the incoming fuel-air charge, increasing the volumetric efficiency and promoting the power output [64]. Besides the auto-ignition temperatures of alcohols are higher than gasoline which makes them safer for transportation and storage [5].

Methanol is an excellent fuel in its own right or it can be blended with gasoline (85% methanol and 15% gasoline) or as pure methanol (100% methanol), although it has half the volumetric energy density of gasoline or diesel [7,15,16,65–67]. Methanol is a transportation fuel and has many significant advantages as compared to hydrogen, gasoline, and has better fuel conversion efficiencies than gasoline thanks to the larger vaporization heat, and the much better resistance to knock that make it the best option for small, turbocharged, high power density, directly injected stoichiometric engines [37,68].

6.1. Engine using pure methanol (M100) as fuel

From the engineering application perspective, methanol is an ideal alternative, renewable, environmentally and economically attractive fuel. In the 1990s, the southwest research institute proposed a high compression ratio SI methanol engine program which provides a new idea for the development of high power and high efficiency methanol engine. Fig. 12 shows the measured break thermal efficiency (BTE) of the engine operating with methanol fuel and the baseline diesel engine. In Fig. 12, it is clear that the methanol engine exhibits peak efficiency of nearly 43%, and maintains over 40% efficiency over a much wider range of speeds and loads as compared to the original diesel engine [3]. Xie et al. [69] modified a diesel engine to a methanol engine, and investigated the performance and emission characteristics. The experimental results indicated that at engine speed of 1400 rpm and full load, the methanol engine could run stably without knock when the ignition timings were 18, 15 and 12 CA before to dead center (BTDC). Dhaliwal et al. [70] studied emission effects of alternative fuels in light-duty and heavy-duty vehicles. They compared reformulated gasoline, compressed natural gas (CNG), liquified petroleum gas (LPG), methanol-85 and methanol-100 with conventional gasoline and diesel fuels; the results showed that using M100 in heavy-duty vehicles produced variable emissions trends concerning THC and CO. However, M100 offered large and consistent emissions benefits for nitrogen oxides (NO_x) and particulate matter (PM) which were the more serious problems for the baseline diesel vehicles. Gong et al. [71] studied the effects of injection and ignition timings, engine speed and load, compression ratio and injector configuration on cycle-by-cycle combustion variation in a direct-injection SI engine fueled with methanol. The results showed that these factors significantly affected the cycle-by-cycle combustion variation, the coefficient of variation reached the least at an optimal injection and ignition timings. Li et al. [8] studied the effects of injection and ignition timings on performance and emissions from a SI engine fueled with methanol. The results showed that direct-injection SI methanol engine, in which a non-uniform mixture with a stratified distribution could be formed, had optimal injection and ignition timings for obtaining a good performance and low exhaust emissions; for methanol engine, the optimization of injection timing and ignition timing could lead to an improvement of BSFC of more than 10% compared to non-optimized case in the wide load range and engine speed of 1600 rpm as compared to non-optimized case. Gong et al. [72] investigated the effects of ignition system, compression ratio, and methanol injector configuration on the BTE and combustion of a high compression ratio direct-injection SI methanol engine under light loads. The experimental results showed that the BTE of a methanol engine using a high-energy multi-spark-ignition was on average 25% higher than that using a single-spark-ignition at brake mean effective pressure (BMEPs) of 0.11–0.29 MPa and an engine speed of 1600 rpm; the BTE of a methanol engine with a compression ratio of 14:1 was 16% higher than that of an engine with a compression ratio of 16:1 at a BMEP of 0.17 MPa and an engine speed of 1600 rpm. Gong et al. [73] studied the regulated emissions from a direct-injection SI methanol engine. The results showed that the THC emission using an injector of a 10-hole × 0.30 mm nozzle was lower significantly than those of 7-hole × 0.45 mm nozzle in the overall load range and CO emission was also lower, but NO_x emission was higher at high load, they also found that the methanol engine could achieve smokeless combustion. The methanol has greater resistance to knock and it emits lower emissions than neat gasoline. The use of pure methanol as fuel at high compression ratio in a single cylinder gasoline engine was studied by Celik et al. [5]; they found that by increasing the compression ratio from 6:1 to 10:1 with methanol, the engine power and BTE increased by up to 14% and 36%, respectively. Moreover, CO, CO_2 and NO_x emissions were reduced by about 37%, 30% and 22%, respectively. Zhen et al. [4,74,75] studied the knock in a high compression ratio SI methanol engine. The results showed that the use of a high exhaust gas recirculation (EGR) rate and early spark timing had a better thermal efficiency on the knock suppression as compared to the use of a low EGR rate and late spark timing; the rich mixture effect was more apparent than lean mixture for suppressing knocking combustion; OH radicals played the predominant role during knocking combustion and the concentration of HCO radicals almost could be ignored during knocking combustion. Zhen et al. [76] also studied the ignition in a high compression ratio SI methanol engine using large eddy simulation (LES) with detailed chemical kinetics. The results showed that using smaller flame kernel could increase the demand for minimum ignition temperature, and decrease the demand for minimum ignition energy; the demands of the minimum ignition temperature

and minimum ignition energy had complementary correlation, that is, as the minimum ignition temperature decreased, the minimum ignition energy increased.

6.2. Engine using methanol/gasoline blends as fuel

Methanol fuel can be blended with gasoline in engine, it can be blended with gasoline (85% methanol and 15% gasoline) or other percentages. Zhang et al. [77] developed a detailed oxidation mechanism for the prediction of formaldehyde emission from methanol–gasoline SI engines, the influence of CH, CH_2(S), and CH_2(T) radical species and NO was considered in the mechanism. The results showed that the methanol–gasoline mechanism was validated by the jet-stirred reactor experiment data, the proposed mechanism was in agreement with the experimental data. Wei et al. [78] investigated the formaldehyde, acetaldehyde and methanol emissions characteristics as well as their conversion efficiencies on the three-way catalytic converter on a three-cylinder, SI engine when it ran on gasoline and M85 (gasoline/methanol = 15:85). The results showed that aldehydes emissions became the peak value at the critical point, and the critical temperature of HCHO was higher than that of CH_3CHO.

Gravalos et al. [79] investigated the emissions characteristics of lower-higher molecular mass alcohol blended gasoline fuels; the alcohol component of the blends consisted of methanol, ethanol, propanol, butanol and pentanol. It was found that during variable load tests, the CO and HC levels in the engine exhaust were reduced with the operation on alcohol gasoline blends, NO emissions with alcohol gasoline blends were higher than with gasoline. Canakci et al. [80] investigated the exhaust emissions of a SI engine fueled with ethanol–gasoline and methanol–gasoline fuel blends and compared to those of pure gasoline. The test results showed that the use of ethanol–gasoline and methanol–gasoline fuel blends caused to decrease in CO and unburned HC emissions significantly at the vehicle speed of 80 km/h. Siwale et al. [81] studied the effects of blends on performance, combustion and emission characteristics of a single methanol–gasoline with dual alcohol (methanol-n-butanol)–gasoline blend with regard to gasoline fuel. It was found that blend M70 (gasoline/methanol = 30:70) produced less NO_x emission than M53b17 (53% methanol, 17% n-butanol and 30% gasoline by volume), blends promoted higher NO_x emission than gasoline fuel with the increase of spark timing, and the blend M20 (gasoline/methanol = 80:20) produced the highest NO_x emission concentration in both engine variables of spark timing and BMEP.

Cay et al. [82] predicted the exhaust emissions for gasoline and methanol by using artificial neural network. It was found that the artificial neural networks models were able to predict the engine performance and exhaust emissions with correlation coefficients of 0.998621, 0.977654, 0.998382 and 0.996075 for the brake specific fuel consumption (BSFC), CO, HC and air-fuel ratio (AFR) respectively. Liu et al. [83] studied the engine power, torque, fuel economy, emissions including regulated and non-regulated pollutants and cold start performance with the fuel of low fraction methanol in gasoline in a 3-cylinder port fuel injection engine. It was found that during the cold start and warming-up process at 5 °C, with methanol addition into gasoline, HC and CO emissions decreased obviously.

6.3. Engine using methanol/diesel blends as fuel

For diesel engines, alcohols especially for methanol are receiving increasing attention because they are oxygenated and renewable fuels. Methanol fuel can be blended with diesel in engine; it can be blended with diesel (85% methanol and 15% diesel) or other percentages.

Huang et al. [84] studied the basic combustion behaviors of methanol/diesel blends based on the cylinder pressure analysis in a compression-ignition engine. The results showed that increasing methanol mass fraction in the methanol/diesel blends resulted in the increase of the heat release rate in the premixed burning phase and shortening of the combustion duration of the diffusive burning phase. Sayin et al. [85] studied the effect of injection timing on the exhaust emissions of a single cylinder, naturally aspirated, four-stroke, direct injection (DI) diesel engine using diesel–methanol blends. The results indicated that by using methanol-blended diesel fuels, smoke opacity, CO and UHC emissions reduced by 5–22%, 33–52% and 26–50%, while CO_2 and NO_x emissions increased by 14–68% and 22–69%, respectively, depending on the engine running conditions. Chao et al. [86] studied the effects of methanol-containing additive (MCA) on the emission of carbonyl compounds generated from the diesel engine. The results showed that when either 10% or 15% MCA was used, the emission factors of the carbonyl compounds (CBCs) acrolein and isovaleraldehyde increased by at least 91%.

Zhang et al. [87] investigated the regulated and unregulated gaseous emissions in a four-cylinder direct-injection diesel engine fueled with Euro V diesel fuel and fumigation methanol. The fumigation methanol was injected to top up 10%, 20% and 30% of the engine load under different engine operating conditions. It was found that the fumigation methanol resulted in significant increase in HC, CO and NO_2 emissions, but decrease in NO_x. The use of methanol in combination with diesel fuel is an effective measure to reduce PM and NO_x emissions from in-use diesel vehicles. A diesel/methanol compound combustion (DMCC) scheme was proposed and a four-cylinder naturally-aspirated direct-injection diesel engine was modified to operate on the proposed combustion scheme by Zhang et al. [88]. The results showed that the DMCC scheme could effectively reduce NO_x, particulate mass and number concentrations, ethyne, ethene and 1, 3-butadiene emissions but significantly increased the emissions of THC, CO, NO_2, benzene, toluene, xylene (BTX), unburned methanol, formaldehyde, and the proportion of soluble organic fraction (SOF) in the particles. After the diesel oxidation catalyst (DOC), the emissions of THC, CO, NO_2, as well as the unregulated gaseous emissions, could be significantly reduced when the exhaust gas temperature was sufficiently high while the particulate mass concentration was further reduced due to oxidation of the SOF.

Fumigation methanol can be applied to diesel engine for partial load displacement and thus to reduce diesel fuel consumption. Cheng et al. [89] found that the maximum amount of methanol used was 43% of the total mass of fuel consumed. At low loads, the BTE decreased with increase in fumigation methanol. At high loads, it increased with increase in fumigation methanol [89]. Li et al. [90] developed an improved multi-dimensional model coupled with detailed chemical kinetics mechanism to investigate the combustion and emission characteristics of a methanol/diesel reactivity controlled compression ignition (RCCI) engine. It was found that the methanol/diesel combustion was capable of reducing the emissions and improving the fuel efficiency. Sayin et al. [91] studied the effects of injection pressure and timing on the performance and emission characteristics of a DI diesel engine using methanol (5%, 10% and 15%) blended-diesel fuel. The results indicated that BSFC, brake specific energy consumption (BSEC), and NO_x emissions increased as BTE, smoke opacity, CO and THC decreased with increasing amount of methanol in the fuel mixture. It was also found that increasing injection pressure and timing caused to decrease the smoke opacity, CO, THC emissions while NO_x emissions increased.

Zhang et al. [92] investigated the effects of fumigation methanol on the combustion and particulate emissions of a diesel engine under different engine loads and fumigation levels. It was found that fumigation methanol increased the ignition delay but had no significant influence on the combustion duration. Fumigation

Table 3
The properties of methanol and hydrogen [98].

Fuel property	Methanol	Hydrogen
Chemical structure	CH_3OH	H_2
Oxygen content by mass (%)	50	0
Density at NTP (kg/l)	0.79	0.00008
Lower heating value (MJ/kg)	20.09	120
Volumetric energy content (MJ/l)	15.9	0.010
Stoichiometric air to fuel ratio (kg/kg)	6.5	34.2
Energy per unit mass of air (MJ/kg)	3.12	3.51
Research octane number	109	130 (λ=2.5)
Motor octane number	88.6	NA
Sensitivity (RON–MON)	20.4	NA
Boiling point at 1 bar (°C)	65	−253
Heat of vaporization (kJ kg)	1100	461
Reid vapor pressure (psi)	4.6	NA
Mole ratio of products to reactants	1.061	0.852
Flammability limits in air (λ)	0.23–1.81	0.15–10.57
Laminar flame speed at NTP, λ=1 (cm/s)	42	210
Adiabatic flame temperature (°C)	1870	2117
Specific CO_2 emissions (g/MJ)	68.44	0.00

Table 4
The properties of methanol and biodiesel [105].

Fuel property	Methanol	Biodiesel
Cetane number	< 5	51
Lower heating value (MJ/kg)	19.7	37.5
Density (kg/m^3)@20 °C	792	871
Viscosity (mPa s) 40 °C	0.59	4.6
Heat of evaporation (kJ/kg)	1178	300
Carbon content (% mass)	37.5	77.1
Hydrogen content (% mass)	12.5	12.1
Oxygen content (% mass)	50	10.8
Sulfur content (mg/kg)	0	< 10

methanol could effectively reduce particulate mass and number concentrations. Wang et al. [93] studied the operating range and combustion characteristics in a methanol fumigated diesel engine through experimental test. It was found that the methanol/diesel operating range was different in terms of load and methanol substitution percent; it was achieved over a load range from 6% to 100%. The operating range was restricted by found bounds: partial burning, misfire, roar combustion and knock. Geng et al. [94] studied the particulate matter (PM) emissions by using the same engine; it was found that the mass and number concentrations of PM significantly decreased at low and medium loads, while increased when the engine was operated at high loads.

Nagafi and Yusaf [95] examined the effect of methanol–diesel blends on diesel engine performance. In that study, the diesel engine was tested using methanol-blended diesel fuel at certain mixing ratios of 10:90, 20:80 and 30:70. Experimental results showed that the effective power and torque for diesel fuel were lower when compared to methanol-blended diesel fuel. The best mixing ratio that produced the lowest exhaust temperature was at 10% of methanol in 90% of diesel fuel. The exhaust temperature for diesel fuel was higher compared to any mixing of the blended fuel. The lowest BSFC values were obtained with 30% methanol and 70% diesel fuel. The BSFC for diesel fuel was much lower compared to any mixing ratio. In that study, it was noticed that BTE improved in almost all operation conditions with the methanol blended diesel fuels.

Zhang et al. [96] studied the effects of fumigation methanol and ethanol on the gaseous and particulate emissions in a four-cylinder DI diesel engine. The methanol or ethanol was injected to top up 10% and 20% of the engine loads under different engine operating conditions. The experimental results showed that compared with Euro V diesel fuel, fumigation methanol or ethanol could lead to reduction of both NO_x and particulate mass and number emissions of the diesel engine, with fumigation methanol being more effective than fumigation ethanol in particulate reduction. Sayin [97] studied the effects of methanol–diesel (M5, M10) and ethanol–diesel (E5, E10) blends on the performance and exhaust emissions in a single cylinder, four-stroke, direct injection, naturally aspirated diesel engine. The results showed that BSFC and emissions of NO_x increased while BTE, smoke opacity, emissions of CO and THC decreased with methanol–diesel and ethanol–diesel fuel blends.

6.4. Engine using methanol/hydrogen blends as fuel

It is effective to improve the performance of SI methanol engines through the hydrogen addition. Methanol fuel can be blended with hydrogen in engine, for instance, it can be blended with hydrogen (85% methanol and 15% hydrogen) or other percentages. Table 3 shows the physical and chemical properties of methanol and hydrogen [98].

Because hydrogen possesses high thermal and mass diffusivities, so the hydrogen enrichment can improve the formation of fuel/air mixtures in the engine intake manifolds. Meanwhile, because of the high flame speed and wide flammability limits of hydrogen, the hydrogen enrichment can also promote the turbulent combustion in conventional fuel powered engines [99–102]. Li et al. [99] proposed a laminar flame speed correlation of hydrogen–methanol blends using the computational fluid dynamics (CFD) simulation. The results demonstrated that compared with the experimental results, the proposed new correlation was suitable for the engine simulation. Ji et al. [103] investigated the effects of hydrogen addition on enhancing the performance of a methanol engine at part load and lean conditions. The test results illustrated that the engine combustion cycle variation was easily, the BTE was enhanced and the HC and CO emissions were generally reduced after the hydrogen blending.

6.5. Engine using methanol/biodiesel blends as fuel

Methanol fuel can be blended with biodiesel in engine, it can be blended with biodiesel (85% methanol and 15% biodiesel) or other percentages. Biodiesel is an alternative fuel for IC engines. It can reduce HC, CO and PM emissions, compared with diesel fuel. Biodiesel has been a lucrative commodity in the current global economic trade as there is mounting concern for issues relating to the environment and oil depletion. Biodiesel has been proven to be the next alternative renewable fuel as it is environmentally friendly, sustainable and possesses similar combustion characteristics to petroleum diesel. However, due to the higher density and viscosity of biodiesel, pure biodiesel is not widely used in diesel engines [104]. Therefore, the method of methanol/biodiesel blends was widely used. Table 4 shows the physical and chemical properties of methanol and biodiesel [105].

Cheng et al. [106] compared the effects of applying a biodiesel with either 10% blended methanol or 10% fumigation methanol. The results indicated that there was a reduction of CO_2, NO_x, and PM emissions and a reduction in mean particle diameter in both cases, compared with diesel fuel. Yilmaz [107] studied the effects of intake air preheat on performance and emissions of a compression ignition engine running on fuel concentrations of biodiesel (85%)–methanol (15%), biodiesel (90%)–methanol (10%), biodiesel (95%)–methanol (5%), neat biodiesel (B100). The results showed that preheating the intake air or lowering the methanol concentration in biodiesel–methanol blends tended to reduce the production of CO and HC while increased the production of NO emission. Anand et al. [108] investigated the combustion, performance and emissions characteristics of neat biodiesel and its methanol blend in a turbocharged,

Table 5
The properties of methanol and DME [112].

Fuel property	Methanol	DME
Chemical structure	CH_3OH	CH_3OCH_3
Density (kg/m^3)	790 (liquid)	206 (gaseity)
Boiling point (°C)	65	−25.1
Auto-ignition temperature (°C)	450	235
Lower heating value (MJ/kg)	19.9	27.6
Vaporization heat (kJ/kg)	1110	460
Research octane number	111	–
Cetane number	< 15	55–60
Stoichiometric air/fuel ratio	6.5	9.0
Oxygen content (wt%)	50	34.8
Carbon content (wt%)	37.5	52.2
Flame speed (cm/s)	45–52.3	45–52

Table 6
The properties of methanol and LPG [122].

Fuel property	Methanol	LPG
Molecular weight	32	44
Composition (% m) C	37.5	81.8
H	12.5	18.2
O	50	0
Density (kg/m^3)	790	504
Boiling point (°C)	65	−30
Stoichiometric air/fuel ratio	6.5	15.7
Auto-ignition temperature (°C)	470	466
Research octane number	111	105
Flammability limit (%v)	6.7–36.2	4–9.5
Latent heat of vaporization (kJ/kg)	1110	406
Lower heating value (MJ/kg)	19.6	46.4
Flame speed (m/s)	0.523	0.37

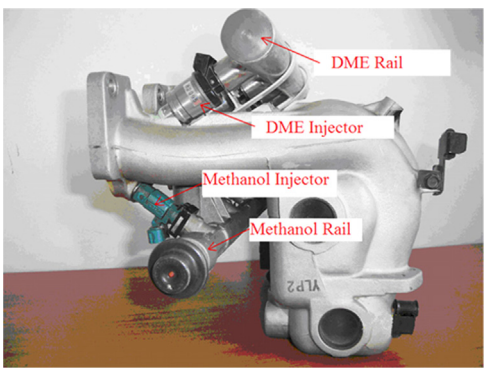

Fig. 13. Methanol and DME fuel rails and injectors installed on the intake manifolds [112].

direct injection, multi-cylinder truck diesel engine. The experimental results indicated that the ignition delay for biodiesel–methanol blend was slightly higher as compared to neat biodiesel and the maximum increase was limited to 1°. There was a significant reduction in nitricoxide and smoke emissions with the biodiesel–methanol blend. Cheung et al. [105] studied the regulated and unregulated emissions from a diesel engine fueled with biodiesel and biodiesel blended with methanol. The blended fuels contain 5%, 10% and 15% by volume of methanol. It was found that the blended fuels could lead to higher CO and HC emissions than biodiesel, higher CO emission but lower HC emission than the diesel fuel. There were simultaneous reductions of NO_x and PM to a level below those of the diesel fuel. Regarding the unregulated emissions, compared with the diesel fuel, the blended fuels generated higher formaldehyde, acetaldehyde and unburned methanol emissions, lower 1, 3-butadiene and benzene emissions, while the toluene and xylene emissions were not significantly different.

Yilmaz and Sanchez [109] studied the performance and emission characteristics in a two-cylinder, four-cycle, direct injected, water-cooled diesel engine fueled with biodiesel–ethanol (B85E15) and biodiesel–methanol (B85M15) blends. It was found that as compared to diesel, biodiesel–alcohol blends reduced NO emissions while increased CO and HC emissions at below 70% loads. It was also shown that biodiesel–ethanol blends was more effective than biodiesel–methanol for emissions reduction. Zhu et al. [110] studied Euro V diesel fuel, pure biodiesel and biodiesel blended with 5%, 10% and 15% of ethanol or methanol in a four-cylinder naturally-aspiraed direct-injection diesel engine. The results showed that compared with Euro V diesel fuel, the blended fuels could lead to the reduction of both NO_x and PM emissions of a diesel engine, with the methanol blends being more effective than the ethanol blends. The use of 5% blends could reduce the HC and CO emissions, and improved the BTE as well, but the effectiveness of NO_x and particulate reductions were more effective with increase of alcohol in the blends. With the DOC, the HC, CO and PM emissions could be further reduced. Yilmaz [111] studied the effects of intake preheat engine on performance and emissions of a compression ignition engine running on biodiesel (85)–alcohol (15%) fuels. Emissions were compared at two elevated intake air temperature and results indicated that high vaporization heat of alcohol fuels affected emissions significantly. Intake air preheat was proved to be one of the effective solutions to reduce CO and HC emissions. Reduction of alcohol concentration in biodiesel–alcohol blends also showed similar effects to preheating intake air temperature.

6.6. Engine using methanol/DME (dimethyl ether) blends as fuel

Methanol fuel can be blended with DME in engine, it can be blended with DME (85% methanol and 15% DME) or other percentages. Compared with other alternatives, DME and methanol are suitable alternative fuels for CI and SI engines, respectively. DME can be produced from a variety of feedstocks such as natural gas, coal, crude oil, residual oil, waste products and biomass. Table 5 shows the physical and chemical properties of methanol and DME [112].

The high cetane number and low boiling point of DME symbolize the short ignition delay, low auto-ignition temperature and almost instantaneous vaporization when DME is injected into the cylinder. Moreover, as DME is non-toxic and environmentally benign, whatever at low or high mole fractions (percent by volume) in air, it hardly has any odor and causes negative health effects. The DME has a low carbon-to-hydrogen ratio (C:H), a high oxygen content (around 35% by mass) and no C–C bonds in its molecular structure. DME can realize the smoke-free combustion and was also used as an ignition promoter in order to ignite a low cetane number fuel in some researches [112–117].

Liang et al. [112] studied the effects of applying the methanol/DME blended fuel in a SI engine. The engine was modified to be fueled with the mixture of methanol and DME which were injected into the engine intake ports simultaneously (see Fig. 13 [112]). The experimental results showed that the indicated thermal efficiency was increased by 25% and coefficient of cyclic variation in engine speed was decreased by 29.2% at the DME energy fraction of 85.2% in the total fuel. In addition, both flame development and propagation durations were shortened with the increase of DME enrichment level at idle condition. Meanwhile, the largest drop of HC emissions was nearly 50% compared with the original methanol engine at stoichiometric condition. However, CO and NO_x emissions increased with the addition of DME. Yao et al. [118,119] applied DME to the CNG and methanol homogeneous charge compression ignition (HCCI) combustion processes to promote ignition. The results showed that the

Table 7
The properties of methanol and ethanol [69].

Fuel property	Methanol	Ethanol
Chemical structure	CH_3OH	C_2H_5OH
Oxygen content by mass (%)	50	34.8
Density at NTP (kg/l)	0.79	0.79
Lower heating value (MJ/kg)	20.09	26.95
Volumetric energy content (MJ/l)	15.9	21.3
Stoichiometric air to fuel ratio (kg/kg)	6.5	9
Energy per unit mass of air (MJ/kg)	3.12	3.01
Research octane number	109	109
Motor octane number	88.6	89.7
Sensitivity (RON–MON)	20.4	19.3
Boiling point at 1 bar (°C)	65	79
Heat of vaporization (kJ kg)	1100	838
Reid vapor pressure (psi)	4.6	2.3
Mole ratio of products to reactants	1.061	1.065
Flammability limits in air (λ)	0.23–1.81	0.28–1.91
Laminar flame speed at NTP, $\lambda=1$ (cm/s)	42	40
Adiabatic flame temperature (°C)	1870	1920
Specific CO_2 emissions (g/MJ)	68.44	70.99

Table 8
The properties of methanol, diesel and isopropyl alcohol [132].

Fuel property	Methanol	Diesel	Isopropyl alcohol
Molecular formula	CH_3OH	C_xH_y	C_3H_8O
Molecular weight	32.042	190–220	60.09
Specific gravity	0.796	0.83	0.7851
% of oxygen by weight	50	0	26
Heat of evaporation (kJ/kg)	1100	260	666
Cetane number	<5	45–50	–
Lower heating value (kJ/kg)	11,770	42,600	24,040

DME addition could improve ignition and broaden the operating range of CNG and methanol HCCI engines.

6.7. Engine using methanol/LPG blends as fuel

Methanol fuel can be blended with LPG in engine, it can be blended with LPG (85% methanol and 15% LPG) or other percentages. LPG is by-product of natural gas production and crude oil refineries. LPG refers to the propane (C_3H_8) or butane (C_4H_{10}) or the mixtures of propane and butane in same container with specific ratio [120,121]. LPG can be used blend with methanol fuel in IC engine. Table 6 shows the physical and chemical properties of methanol and LPG [122].

Gong et al. [122] studied the effects of the ambient temperature on the firing and formaldehyde and unburned methanol emissions of an electronically controlled inlet port injection SI methanol and LPG/methanol engines. It was found that the LPG only played a part of start-aids in the LPG/methanol engine. Using additional LPG injected into the inlet port resulted in a reliable firing of the LPG/methanol engine at low ambient temperature during cold start. When the ambient temperature dropped, the mass ratio of injected LPG/methanol for the reliable firing of the LPG/methanol engine during cold start increased rapidly.

6.8. Engine using methanol/water blends as fuel

Methanol fuel can be blended with water in IC engine, it can be blended with water (85% methanol and 15% water) or other percentages. Methanol and ethanol are prone to absorb water when they are exposed to the atmosphere for a considerable amount of time, for instance, during transport or storage.

Donnelly et al. [123] concluded that, when as little as 0.1 vol% water was added to a M20 (20% methanol and 80% gasoline) blend, phase separation could occur at a temperature of 20 °C. Because of this very small water tolerance of the methanol–gasoline blend, water contamination during the methanol transport and storage had to be avoided. Besides the dependence of water content, it was also found that the tendency for phase separation was a strong function of methanol content and gasoline composition [124]. Sileghem et al. [124] studied the effects of the methanol/water blends and compared with the BTE and engine-out emissions from a production-type four-cylinder SI gasoline engine running on gasoline, pure methanol and methanol–water blends. It was shown that the BTE did not differ significantly for all fuels and was still higher than the efficiency of gasoline. NO_x emissions were reduced substantially for the fuels with higher water content because of the lower temperatures in the cylinders due to the water addition in the fuel.

6.9. Engine using methanol/ethanol/gasoline blends as fuel

Methanol fuel can be blended with ethanol/gasoline in IC engine, it can be blended with ethanol/gasoline. Using liquid alcohols, such as methanol and ethanol, in SI engines is a promising approach to transport and secure domestic energy supply. Methanol and ethanol are compatible with the existing fueling and distribution infrastructure and are easily stored in a vehicle. They can be used in IC engines with only minor adjustments and have the potential to increase the efficiency and decrease noxious emissions compared to gasoline engines [124]. Table 7 shows the physical and chemical properties of methanol and ethanol [68].

Turkcan et al. [125] studied the effects of second injection timing on the combustion and emissions characteristics of a direct injection HCCI gasoline engine by using ethanol and methanol blended gasoline fuel. The results showed that the better combustion characteristics, lower NO_x, UHC and CO emissions, and higher IMEP and indicated efficiency values were obtained by using optimal second fuel injection timings for the methanol–ethanol–gasoline fuel blends compared to the gasoline case at low equivalence ratio. Balki et al. [126] studied the effects of different alcohol (methanol and ethanol) fuels on the performance, emission and combustion characteristics of a gasoline engine. The results showed that the use of alcohol fuels increased the engine torque, BSFC, thermal efficiency and combustion efficiency. In addition, the cylinder gas pressure and heat release rate occurred earlier; CO_2 emission increased while HC, CO and NO_x emissions decreased.

6.10. Engine using methanol/ethanol/diesel blends as fuel

Alcohols, mainly methanol and ethanol, in combination with diesel fuel, have been widely investigated for reducing NO_x and the particulate emissions [127]. The solubility of ethanol in diesel fuel is affected by temperature and water content of the fuel [128]. Methanol fuel has low ability of self-ignition due to many reasons such as low cetane number, high latent heat of vaporization and high ignition temperature [129]. Methanol fuel can be blended with ethanol/diesel in engine, it can be blended with ethanol/diesel.

Karabektas et al. [130] studied the effects of blends containing various alternative fuels and diesel fuel on the performance and emission in a naturally aspirated, direct injection diesel engine. The experimental results showed that the ethanol and methanol blends yielded lower brake power, while it resulted in higher specific fuel consumption and lower CO emissions.

6.11. Engine using methanol/diesel/isopropyl alcohol blends as fuel

Among various developments to reduce emissions, the application of oxygenated fuels to diesel engines is an effective way to

Table 9
The properties of diesel, methanol and dodecanol [129].

Fuel property	Diesel	Methanol	1-Dodecanol
Molecular formula	$C_{14.342}H_{24.75}$	CH_3OH	$C_{12}H_{26}O$
Molecular weight (kg/kmol)	197.21	32.042	186.339
Stoichiometric fuel/air ratio	0.06924	0.15393	0.07462
Cetane number	45–55	3–5	–
Flash point (°C)	78	11	107
Ignition temperature (°C)	235	470	527
Viscosity at 298.15 K (mPa s)	3.35	0.59	16.136
Density (g/cm^3)	0.83	0.79	0.83
Lower heating value (MJ/kg)	42.740	20.270	39.860
Heat of vaporization (MJ/kg)	0.270	1.110	–

reduce smoke emissions. The addition of oxygen containing compounds to diesel fuel has been proposed as a method to complete the oxidation of carbonaceous particulate matter and associated hydrocarbons. In addition, many oxygenates have high cetane number and their association with diesel results in high cetane number and hence lower CO and HC emissions with little variation in NO_x emission [131]. Methanol fuel can be blended with diesel/isopropyl alcohol in engine. Table 8 shows the physical and chemical properties of methanol, diesel and isopropyl alcohol [132].

Chockalingam and Ganapathy [132] studied the performance of a CI engine fueled with diesel, methanol and isopropyl alcohol blends. Four fuel blends namely 80:10:10, 70:20:10, 60:20:20 and 50:30:20 percentages by volume of diesel, methanol and isopropyl alcohol were studied in the diesel engine. The mixing protocol consisted of first blending the additive isopropyl alcohol into the methanol and then blending this mixture into the diesel fuel. The results showed that it could improve the engine performance with blends compared to neat fuel. The 60:20:20 blends recorded a BTE of 35.92% against 30.6% for the neat diesel at maximum brake power without much change in smoke density and NO_x emissions. However, little increase in HC emissions were recorded up to 60:20:20 blends and the increase were drastic when the methanol content was above 20%.

6.12. Engine using methanol/diesel/biodiesel blends as fuel

Methanol fuel can be blended with diesel/biodiesel in IC engine. The addition of higher oxygen content and high volatility methanol can be a promising technique for using biodiesel–diesel blend efficiently in diesel engines without any modifications in the engine. Qi et al. [133] investigated the effects of using methanol as additive to biodiesel–diesel blends on the engine performance, emission and combustion characteristics of a direct injection diesel engine under variable operating conditions. The results showed that the combustion started later for BDM5 and BDM10 (methanol was added to BD50 (50% biodiesel and 50% diesel in vol.) as an additive by volume percent of 5% and 10%) than for BD50 at low engine load, but was almost identical at high engine load. The power and torque outputs of BDM5 and BDM10 were slightly lower than those of BD50. BDM5 and BDM10 showed dramatic reduction of smoke emissions. CO emissions were slightly lower, and NO_x and HC emissions were almost similar to those of BD50 at speed characteristic of full engine load.

Yasin et al. [104] studied the influences of methanol in 5% by volume (M5) in a B20 (20% biodiesel) blend on performance and combustion characteristics of a four cylinder, four stroke diesel engine. The results showed that the BSFC for B20 and B20/M5 increased, but the BSFC for mineral diesel decreased with the corresponding increased in engine speeds from 1000 rpm to 3500 rpm. The engine running on B20 and B20/M5 produced slightly higher in-cylinder pressure and peak heat release rate as compared to mineral diesel at a specific engine speed of 2500 rpm. There were significant decrease in brake specific CO (BSCO) and brake specific CO_2 (BSCO) but higher brake specific NO_x (BSNO_x) and brake specific NO (BSNO) when the diesel engine was operated with B20 and B20/M5.

Yilmaz [134] studied the performance and emission characteristics of the engine fueled with biodiesel–methanol–diesel (BMD) and biodiesel–ethanol–diesel (BED) in a CI engine. The results showed that biodiesel/alcohol/diesel blends had higher BSFC than diesel. As alcohol concentrations in blends increased, CO and HC emissions increased, while NO emissions were reduced. Also, methanol blends were more effective than ethanol blends for reducing CO and HC emissions, while NO reduction was achieved by ethanol blends.

6.13. Engine using methanol/diesel/dodecanol blends as fuel

Methanol fuel can be blended with diesel/dodecanol in IC engine. Methanol can be used in CI engines as pure or by blending with conventional diesel fuel. Problems concerning the use of methanol in diesel engines can be removed by different approaches. Using it in CI engines as diesel–methanol blends is the simplest method. The most important problem encountered in this case is the phase separation. This problem can be prevented by adding some solvent into mixture [135]. Table 9 shows the physical and chemical properties of diesel, methanol and 1-Dodecanol [129].

Bayraktar studied [129] the effects of using diesel–methanol–dodecanol blends including methanol of various proportions on a single-cylinder, water-cooled CI engine. The methanol concentration in the blend has been changed from 2.5% to 15% with the increments of 2.5%, and 1% dodecanol was added into each blend to solve the phase separation problem. The phase separation problem had been prevented by adding 1% dodecanol to each diesel–methanol blend. The results showed that among the different blends, the blend including 10% methanol was the most suited one for CI engines from the engine performance point of view. Methanol caused improvement in engine effective power. The maximum improvement of about 7% in torque was obtained with the blend of DM10.

7. Conclusions and recommendations

This paper systematically reviews the methanol fuel as an alternative in internal combustion engines, which includes the productions, supply and demand, economic befefits and the effects of methanol on human health and the environmen. Also, thirteen methods of application such as methanol/gasoline, methanol/diesel blends which can be used on the internal combustion engine are summarized in the present paper. The results showed that methanol can be produced from coal, natural gas, coke-oven gas, hydrogen and biomass etc. The production capacity of methanol can fully meet the demand. Air pollution regulation in industrial cities limits economic growth. The development and application of methanol to replace the current fossil fuels can reduce the need for and economin cost of traditional add-on pollution controls. Compared with the fossil fuels, methanol has the potential to reduce vehicle emissions, and consequently to improve the atmospheric environment and reduce regulatory pressure on economic growth and energy demand.

Despite great efforts made by researches, methanol applications is still a crucial topic concerning methanol engine design and development, and it needs further improvement: (1) from the engineering application perspective, methanol is an ideal alternative, renewable, environmentally and economically attractive fuel. The development of new methanol storage and transportation technology plays an

important role in the applications of methanol, especially in the promotion and application of vehicle engines; (2) the development of high compression ratio methanol engine to replace the high power, high efficiency vehicle engines (for instance, diesel engine) has great realistic significance; (3) the study of combustion and emission mechanisms of methanol engine is the core scientific engineering technology issure to the development of methanol engine; and (4) the development of new combustion modes such as homogeneous charge compression ignition (HCCI), premixed charge compression ignition (PCCI) and reactivity controlled compression ignition (RCCI) play an important role to the development of methanol engine. So, the authors believe that future researches should focus on these areas, which not only could help explain the combustion and emission mechanisms of methanol, but also have an important contribution to the development and application of methanol engine so as to meet the market demand.

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