Analysis on Synthesis, Storage & Combustion characteristics of DME as fuel in CI engines

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Abstract: This article reviews on various methods of production of Di-Methyl Ether (DME) avail in present scenario, its storage difficulties and the reasons for holding DME still under research as an alternative fuel. The demand for the development of alternative clean energy sources has risen with increase in the rate of depletion of oil reserves. DME, an ultraclean alternative fuel with less emission, higher cetane number has attracted the world researchers. DME is produced from a variety of raw materials starting from biomass, coal and natural gas. Despite of its greater compatibility with diesel, it has some undesirable properties that make it uncomfortable to use in present compression ignition (CI) engines. This paper presents a brief review of the possible DME production processes and its combustion characteristics.

Keywords: DME, Alternative fuel, ultraclean fuel, combustion properties.

I. INTRODUCTION

Di-methyl ether is one of the most promising non-petroleum fuel alternatives. DME is non-carcinogenic, non-corrosive, non-mutagenic, non-toxic and a sulphur free fuel [1]. The cetane number is the measure of the auto-ignition temperature of a fuel. A number of experimental studies showed that DME fuel has high cetane number (55-60), high oxygen content (35% by mass) and less noise with enhanced engine performance and emissions [2]. DME has low viscosity i.e one thirty of diesel, low lubricity and low density. Successful cold starting is available with DME down to -24°C with high vapour pressure, low heating value and low boiling point. The functional group that characterizes DME is not chemically active. So, DME is often considered to be chemically inert. The thermodynamic characteristic of DME differs much from diesel which leads to difference in DME spray characters [3]. DME is a gas at ambient temperature and pressure but it can be liquefied under low pressures (0.5 MPa at 25°C) [4]. DME in a gaseous state is invisible under standard atmospheric conditions (0.1 MPa at 298 K) [5]. When it is pressurized above 0.5 MPa, it condenses to the liquid phase. Gaseous DME is denser than air while liquid DME has a density two thirds that of water. DME is non-toxic and environmentally benign. The well-to-wheels energy efficiency of heavy and light-duty DME-fuelled vehicles are projected to be 22.5% and 19%, respectively [5]. DME is not a suitable fuel for spark-ignition (SI) engines due to its high cetane number, though the burning velocity is similar to hydrocarbon fuels. The easily-induced knock would limit the operation of SI engines. DME displays a visible blue flame when burning over a wide range of air-fuel ratios, similar to natural gas, which is an important safety characteristic. Nevertheless, the operation of DME combustion system needs the adoption of rigorous procedures for safe operation due to the wide flammability limits [5]. The SO₂ formation will be zero, because of the absence of sulphur in DME. However, with reduced well to wheel greenhouse gas emission and enhanced fuel performance DME serves to be the best alternative candidate among H₂, CH₄, CH₃OH etc.

II. DME SYNTHESIS

DME is produced from a vast variety of feedstock such as natural gas, coal, crude oil, residual oil, waste products and biomass. It has superior engine combustion and emissions characteristics, but was not considered in the past because of its high cost. Recent developments in advanced manufacturing technology of dimethyl ether showed that it could be mass-produced at an affordable cost. DME is commercially manufactured by first converting coal or natural gas to syngas (synthesis gas), which is converted to methanol in the presence of a catalyst. Methanol is then dehydrated to form DME as an end product. A significant portion of DME is also manufactured by simply dehydrating marketed methanol in order to avoid huge plant establishment cost. The global DME market has been witnessing many developments in recent years. DME is a preferred and widely accepted alternative fuel due to its clean burning properties and the focus of various regulatory bodies to reduce the dependence on oil and gas by-products for meeting the current and future energy needs [6]. However, DME production has grown from 100,000 to 150,000 tons per annum in 1990s to 200,000 in 2000’s throughout the world. A roughly worldwide usage of DME is about 150,000 tons per year and in Japan, it is about 10,000 tons per year. [8]. China has consumed more than 90% of the global DME in 2012[6]. In India, DME holds great potential especially when the country has discovered the large natural gas reserve in the Krishna Godavari basin [7]. Technologies are now available to produce DME directly from synthesis gas without passing
methanol as intermediate feedstock [6-8]. Currently, most DME is being produced by dehydration of methanol. Besides the production of DME from methanol, other production routes for DME exist. Naqvi et al (2010) studied DME production technology by using black liquor gasification, integrated with the pulp mill facility. For using biomass as feedstock, gasification is the key conversion technology to produce syngas [40]. The economical production routes that can be considered for large scale DME production is to produce synthesis gas by using coal and natural gas [8]. DME is produced either by direct synthesis from synthesis gas or by dehydration of methanol in the presence of solid-acid catalysts. Different types of solid acid catalysts, Na modified H-ZSM-5 zeolites, γ-Al₂O₃ and phosphorus modified γ-Al₂O₃, Amberlyst 35, and Nafion have been tested in DME synthesis by dehydration of methanol [9]. DME production methods are (a) De-hydrogenation of methanol and (b) Direct conversion from synthesis gas (syngas). The biomass to DME route has greater advantages. Biomass gasification/synthesis technology integrates bio-DME synthesis, fertilizer production, electricity generation, and waste heat utilization to convert waste biomass residues to DME [10].

A. Double stage synthesis
Conventionally, DME is produced via two-step process, in which synthesis gas (syngas) is first converted to methanol, followed by the dehydration of methanol over an acidic catalyst in order to form DME. Methanol dehydration reaction occurs easily over almost any dehydration catalyst at relatively low temperature ranges between 250-300°C in vapour phase and the reaction is pressure insensitive [11]. In two step synthesis of DME, natural gas or bio-gas is first converted into synthesis gas (syngas). The syngas in general, contains hydrogen(H₂) and carbon monoxide(CO) and sometimes carbon-di-oxide(CO₂). The produced syngas is converted into methanol by using various catalysts such as copper. The two step synthesis is by adopting two distinct steps, namely, synthesis of methanol by synthetic gas, methanol dehydration by the function of solid catalyst to make DME such as, ZSM-5 molecular sieve catalyst that contains γ-Al₂O₃/SiO₂. During this reaction, process conditions have great significant to methanol transformation ratio and DME selectivity. DME formation achieves maximum activity of 41.1% using HZSM-5 catalyst at low temperature of 175°C [12]. With thorough research to double stage process, mature and simple technique, and fine performance of ZSM-5 molecular sieve catalyst, high purity DME [13] can be prepared.

B. Single stage synthesis
It is a new system in which, methanol synthesis and dehydration processes are combined in the same reactor for DME synthesis. This method is referred as direct synthesis and is economically favourable since the cost of methanol separation and its preparation as a feedstock for DME synthesis reactor is avoided [11]. In the direct synthesis process, DME is synthesized directly from the synthesis gas. Research and development on technologies capable of mass-producing DME at low cost are being carried out by the JFE Group, Haldor Topsoe A/S (Denmark), Air Products and Chemicals, Inc. (United States), and others[14]. The direct conversion method is the simultaneous production of DME and methanol from syngas using appropriate catalysts. The first step of direct DME production is the conversion of the feedstock to syngas, most common by steam reforming of natural gas and for coal, oil residues and bio-mass by partial oxidation through gasification with pure oxygen. The second step for the direct route is via methanol synthesis using a copper-based catalyst while the third step is the de-hydration of methanol to DME using alumina- or zeolite-based catalysts. With the direct conversion of syngas to DME, the second and third steps can occur simultaneously in one reactor using appropriate catalysts [5]. The reaction product is a mixture of methanol and DME. After separating mixture by distillation plant, DME comes out, and unreacted methanol returns to synthesis reactor. Here, bi-functional catalyst are used, which is physical mixing outcome of two kinds of catalysts. Synthetic methanol catalyst, and methanol dehydration catalyst are the two kinds of catalysts mixed. Synthetic methanol catalyst includes: Cu-Zn-Al (O) group catalyst, such as BASF, S3-85 and IC1-512. Methanol dehydration catalyst includes: Alumina, multi porous SiO₂-Al₂O₃, Y-type molecular sieve, ZSM-5 molecular sieve, mordenite, etc. [13]. The final step is the purification of the raw product, which may also contain some methanol and water. When comparing both the synthesis process, the single stage process stands out to be better, since it involves production of DME and methanol as side products.

C. Dehydration catalysts
Usually, in dehydration of methanol into DME, solid-acid catalysts are used. Synthesis of high purity DME through Methanol can be achieved using γ-Al₂O₃ catalyst in a multistage adiabatic fixed bed reactor [15]. Mesoporous Aluminosilicate catalyst has higher activity to DME. There are different types of Al/Si catalytic ratios among them the ratio of 0.09 stands to be optimum. It is a non-crystalline solid and has a selectivity of DME equal to 0.99 at 300°C. The selectivity of DME is defined as the ratio of moles of methanol that is converted into DME to total moles of converted methanol from syngas. This is due to greater surface area of the catalyst. The yield value of DME is 0.70% at 250°C [9]. Heteropolyacids (HPA) differs much from the conventional acid catalyst. They show higher catalytic activity than solid acid catalyst. The main drawbacks of heteropolyacids are that they...
are non-porous and lower surface area values (less than 1 m²/g). By impregnated on high surface area supports, the surface area of heteropolyacid-based catalysts can be increased. Because of their solubility in polar solvents, heteropolycarids are preferred in vapour phase reactions. Among HPAs, silicotungstic acid catalyst shows higher yield at a temperature of 250°C [9]. The STA impregnated catalyst shows higher activity than pure STA catalyst. Because of improved porous and higher surface area, the activity of it increases. The maximum yield reaches to 0.84 at the temperature of 250°C [9]. The DME synthesis can also be made by dehydration of methanol using Clinoptilolite catalyst, experimental results showed that the optimum temperature is 350°C [16]. Several researches were performed in order to formulate better the use of catalyst solids such as crystalline solids, amorphous, zeolites, and quasicrystalline solids. The principal aim of these researches was not only to ensure a higher stability during the catalytic reaction but also to optimize DME production. Recently, quasicrystals are being applied in catalyst reactions due to its stable equilibrium phases even at high temperatures. The quasicrystalline materials occupy a position between crystal and amorphous materials [17]. The quasicrystal Al62,2Cu25,5Fe12,3 catalyst has been proved to be adequate for dehydrating methanol to DME due to the good reaction performance [17].

D. Production from CO₂
Methanol, as discussed, can be efficiently produced from a wide variety of sources including still available fossil fuels (coal, oil shale, tar sands, etc.) and also from varied biomass. Methanol can also be produced in a new way from chemical recycling of carbon dioxide. CO₂ which stands to a major threat to present environment, emitted enormously from flue gases of fossil fuel burning power plants or exhausts of cement, fermentation, and other industrial plants has proven to be a source of methanol production. Even the low concentrated CO₂ from our air, presently around 380 ppm, can be captured and recycled to methanol. Flue gas emitted from exhaust of automobiles is taken. It may also contain sulphur and other gases which are to be removed and only CO₂ is taken. Hydrogen (H₂) which can be obtained from the electrolysis of water is also taken. CO₂ and H₂ on catalytic regeneration with copper and zinc oxides at a constant temperature of 260°C yields methanol [18]. The most direct and studied route to methanol from CO₂ is the catalytic regenerative conversion of CO₂ with hydrogen. The methanol, which in turn can be converted into DME by dehydration process using any of the acidic catalyst. There is another way of production of DME directly from CO₂ and H₂ in which a bi-functional catalyst is used. The bi-functional catalyst is composed of a CuO-ZnO-Al₂O₃ metallic function and γ-Al₂O₃ acid function. The metallic part CuO-ZnO-Al₂O₃ is for hydrogenation of CO₂ and the acidic part γ-Al₂O₃ is for the dehydration of methanol to DME. The reaction equipment is provided with a fixed bed, and allows for operating at high temperature and pressure [30]. The optimum mixing ratio of two catalysts is 50:50 wt%. With increase in temperature, the methanol + DME yield and DME selectivity increases. However, when methanol yield reaches equilibrium, the methanol + DME yield declines with higher temperature. A two layer structure consisting of an upper layer of methanol synthesis catalyst and lower layer of mixture of methanol synthesis and methanol dehydrating catalyst stands the most effective structure for the hybrid catalyst [20]. When the amount of H₂ in the feed is increased, the conversion of CO₂ and the yield of products (DME and methanol) steadily increases. When the feed ratio of H₂/CO₂ is 4/1 the production of DME is maximum [30].

E. Improved methanol production methods
Methanol can be basically produced from carbon di-oxide and hydrogen with suitable conditions. But there exists some improved techniques for methanol production.

1) Carnol process: CO₂ emission in the atmosphere can be reduced by using fossil fuels itself using the process called the “Carnol process” in which H₂ is produced by thermal decomposition of CH₄ with carbon formed as by product. This H₂ reacts with CO₂ recovered from emission of the fossil fuel power plant to produce methanol [18]. So, the net emission of CO₂ is close to zero, because CO₂ released by the methanol used as a fuel is recycled from existing emission sources.

2) Methane decomposition & dry reforming: In this process, the environmental benefit is lower than the Carnol process, but it is better for the economic cost. This process results in the combination of CH₄ decomposition and dry reforming. The products are methanol and carbon. The dry reforming does not involved steam, CO₂ is reacted with natural gas to produce syngas (more endothermic than steam reforming). With the dry reforming, natural gas resources are used more efficiently. However, this syngas composition is not suitable for the production of methanol using existing technology in which a H₂/CO ratio close to 2 is needed [18].

3) Steam reforming & dry reforming: This way overcomes the previous disadvantage because it is possible to get a H₂/CO ratio close to 2. It uses steam reforming with a H₂/CO ratio of 3 [18]. The combination of steam and dry reforming can be used for the conversion of CO₂ emissions from fossil fuels burning power plant. It is also advantageous for reforming natural gas and geothermal sources which often are accompanied by substantial amounts of CO₂.
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4) Combining reduction and hydrogenation of CO\(_2\): The principle process is the combination of CO\(_2\) and H\(_2\) to give methanol and water as a by-product, but a third of the hydrogen and the electricity are used to produce it. So, to use hydrogen more efficiently, initial chemical or electrochemical reduction of CO\(_2\) to CO is considered. This reaction can be stated as Reverse Boudouard reaction. The direct conversion of CO\(_2\) to CO using a thermochemical cycle and solar energy is also being studied (Ga’Ivez et al. 2008), (Travnor and Jensen 2002). Then, methanol is obtained by adding hydrogen. It is also possible to produce methanol from CO\(_2\) and H\(_2\)O with an electrochemical process [18].

III. DME STORAGE

DME with low boiling point of -25\(^\circ\)C exist in vapour state under normal atmospheric condition. DME is a flammable liquid and gas under pressure. It can form explosive mixture with air so it resembles LPG to greater extend. Like LPG for gasoline engines, DME is stored in the liquid state under relatively low pressure of 0.5 MPa. Storage should be done in a tightly closed container in a cool, well-ventilated area and air should be prevented from entering into the container. Sources of ignition such as smoking, open flames are avoided while working with DME [21]. Metal containers involving the transfer of DME should be grounded and bonded. Non-sparking tools and equipment should be used for opening and closing of DME containers [21]. The department of transportation (DOT) has listed DME as a hazardous substance. The transportation of DME is similar to LPG in a sealed container truck. Leakage should be tested with soapy water and not with a flame. Storage area must meet national electric codes for class 1 hazardous areas. Storage area temperature must not exceed 52\(^\circ\)C (125\(^{\circ}\)F). Avoid long time storage of cylinders, use a first in first out inventory system [22].

A. Issues in fuel supply system

The fuel supply system consist of pressurized fuel tank, appropriate pipelines, valves, fuel feed pump and injectors which is capable of delivering fuel to the high pressure pump at a pressure of up to 1.5 MPa to prevent cavitation and vapour chock within the fuel pipeline and injection system. To keep the output of the DME engine as same as that of the diesel engine, it is necessary to increase the injection rate and quantity. The development of fuel supply system that can supply stable fuel pressure and fuel flow rate is necessary. Only the fuel system can improve, the DME engine start ability and acceleration performance which is inferior to diesel engines [23].

B. Liquid fuel tank

Although the DME tank can be designed similar to those used for LPG, a low-pressure pump and cooling system is needed between the DME fuel tank and the injection pump, this complicates the fuel supply design. To simplify this McCandless et al. developed a liquid DME fuel tank by considering the thermodynamic behaviour of DME [5]. A fuel tank, made of cast aluminium with a capacity of 40l, essentially a thermodynamic pump containing two fluids: liquid DME and a vapour-liquid mixture of driving fluid (mainly propane) with a diaphragm separating the two fluids. The propane can pressurize the DME into a sub-cooled-liquid state and functions as a driving fluid that pumps liquid DME from tank to the injection pump by means of its vapour pressure [5]. Compressed nitrogen can be used to keep DME in liquid state in the fuel tank and flow line [23].

C. Fuel line

Although DME is kept in the liquid phase under atmospheric temperature conditions, when pressurized to above 0.5 MPa the fuel-supply pressure (the feed pressure from the storage tank to the fuel pump) must be between 1.2 and 3 MPa to avoid cavitation in the fuel line [5]. Lower caloric value and lower density of DME requires higher volumetric flow rate of DME than the diesel fuel. DME has low viscosity so in order to ensure reliability and durability of the parts of the fuel system, some additive (castor) oil is added to DME [24]. DME is not compatible with most of the elastomers and can chemically attack some commonly used sealing materials and other plastic components, raising questions about the durability of injection systems handling DME. Low viscosity of DME causes the leakage from the fuel supply system which relies on small clearances for sealing [25]. So, in order to prevent deterioration after long time exposure, tolerant seals can be made from polytetrafluoroethylene (PTFE) based materials and so on. However, the peak pipeline pressure, pressure rise rate and acoustic velocity of DME are lower than diesel [26].

D. Fuel injector

DME gasifies immediately during injection, due to its low boiling point, even though it is injected as a liquid. Therefore, the high fuel injection pressures, such as 50–150 MPa, used in modern diesel injection systems are not required for DME and there is a consensus that 20–30 MPa is sufficient as long as the required amount of DME can be supplied during the corresponding
injection period even at high engine speeds [5]. DME is non-corrosive to metals and does not require special material for fuel injection equipment and component[23]. But, low lubricity of DME can cause intensified surface wear of moving parts within the fuel-injection system and hence conventional fuel delivery and fuel injection systems are not compatible with dimethyl ether[25]. DME has a high vapour pressure so the fuel needs to be pressurized to maintain DME in a liquid state. Moreover, the fuel system has to be modified considering the chemical properties of DME, such as its incompatibility with many elastomers[31]. To keep the output of the DME engine the same as that of the diesel engine, it is necessary to increase the injection rate and quantity. Therefore, the plunger diameter and its stroke along with the nozzle diameter have to be enlarged and adjustments have to be made in nozzle opening pressure [26]. Lower acoustic velocity, larger injection delay and high compression pump work is needed which are due to larger compressibility. Due to low viscosity additives are to be added. Due to lower heating value, a long injection duration or bigger nozzle hole is needed [27]. The shorter ignition delay of DME is due to higher cetane number. The start of ignition timing is also retarded which is caused by relatively larger injection delay[26]. DME has low calorific value and density, therefore larger fuel has to be supplied through the increased plunger diameter. Lower injector pressure reduces the power required for fuel pump, but this causes longer injection duration and lowers the brake thermal efficiency. Therefore, an optimum nozzle opening pressure is required i.e 15 MPa [28]. The drop in nozzle pressure for DME can lead to cavitation. The reduced viscosity of DME enhances cavitation. Cavitation affects the performance of the injector and damages the inner surface of nozzle and forms vapour bubbles [29].

IV. COMBUSTION SYSTEM

Recent work on DME has focused on its use in advanced technology, direct-injection (DI) engines as a neat fuel. Due to the presence of an oxygen atom in DME’s molecular structure, the absence of a carbon-carbon bond and its high cetane number, the DME fuelled engine appears to circumvent the traditional trade-off between oxides of nitrogen (NOx) and particulates that plagues the CI engine running on diesel fuel. The high cetane number of DME also helps in reducing combustion noise, which is another drawback of the diesel fuel fired CI engine [31].

As discussed, DME engine shows a longer fuel injection delay than that of the diesel engine at the same engine speed this is because the pressure wave propagation will take longer in the DME engine compared with the diesel engine, and consequently the DME engine shows longer fuel injection delay. DME has a greater sensitivity of ignition delay to engine speed. The higher cetane number, lower auto-ignition temperature, good atomization and ignition properties are the reasons for shorter ignition delay period and lower combustion noise that are experienced with DME [24].
Due to rapid mixing of DME with air, the rate of diffusion combustion of DME is much faster than that of the diesel and has shorter combustion duration. The heat release pattern of the DME engine stands to be the ideal pattern that is expected in a compression ignition engine [32]. The brake specific fuel consumption of DME is also lower than diesel at low and medium speed. Increased brake thermal efficiency is achieved with higher injection volume. Smokeless combustion is achieved under all operating condition of DME engine. A lower maximum pressure and rate of pressure rise for DME combustion leads to lower mechanical load and combustion noise. However, with higher oxygen content (36% weight) lower combustion enthalpy is achieved, in order to overcome this, a larger volume of fuel is usually injected into the combustion cylinder. While burning DME displays a visible blue flame like natural gas which is a crucial safety indicator. The lower heat radiation and better combustion efficiency attributed to lower incomplete combustion [7,11,28,32,33]. Thus, complete combustion is achieved with DME in most of the cases.

V. EMISSION SYSTEM

DME fuelled engine produces larger amount of mechanical work and smaller amount of wasted internal energy in exhaust gas, which is found experimentally that the exhaust gas temperature is as low as 50°C[34]. It has been demonstrated through varied experiments that emissions of particulate matter (PM), NOx, and combustion noise from compression-ignition engines are significantly lower when DME is used instead of diesel fuel as shown in fig 3. The particulate matters are found only when certain additives are added to DME [5]. NOx is not a direct fuel-combustion product but a side effect of combustion. Because nitrogen is basically chemically inert at temperatures lower than 1370 °C, NOx formation requires a high temperature (T > 1370°C), pressure and plentiful oxygen [3]. However decrease in temperature result in increase in particulate and HC emission. The cetane number will not have impact on NOx emission but increase in cetane number decreases the CO and HC emission [35]. There is no complete agreement for NOx emission from DME. Sorenson et al reported much lower NOx with DME whereas Kajitani et al reported same as NOx as diesel [36].

Fig 3. Smoke, THC and NOx emission for DME and diesel from a single cylinder DI compression-ignition engine

Whatever the amount of NOx emitted, the quantity can be further decreased by using various treatment catalysts. The conventional NOx reduction catalyst (three-way catalytic converter) technique, used in SI engine cannot be used in diesel engine because of excess oxygen in exhaust of DME engine. The conventional system works only in fuel-rich condition, with lean condition SCR(Selective Catalytic Reduction) technique, EGR(Exhaust gas recirculation) technique, etc. can be used[37]. Exhaust gas recirculation(EGR) is nothing but mixing of some exhaust gas with the intake air system. This then flows into the cylinder, where they dilute and cool the combusting gases. EGR increases PM emission on other hand. However due to increase in percentage of EGR rate, the combustion velocity increases which in turn increases the brake thermal efficiency.
With increase in intake charge temperature EGR decreases the exhaust gas temperature also [38]. The after treatment technique for NOx includes SCR, HC-SCR (lean NOx or DeNOx catalyst) catalyst, NOx absorbers etc. For a lean NOx catalyst such as zeolite or a copper substituted zeolite ZSM5 catalyst a reducing agent is usually needed to act on NOx. DME itself can act as a suitable reducing agent for this catalytic activity [39]. With these techniques NOx emission and temperature of exhaust gas can be much reduced. It is studied that HC emissions from DME are usually lower than or equal to those from the combustion of diesel fuel. DME has good mixing characteristics, so the location of the fuel rich regions in the combustion period is less, resulting in lower CO emission.

VI. SUMMARY

With huge investigations on DME-fuelled compression ignition engines, DME has proven to be an excellent alternative fuel in the automotive sector. This liquefied gas produced from various feed stocks is an environmental benign. The main features of DME such as high cetane number, high oxygen content, low boiling point helps in achieving better combustion through better mixing with air. Noiseless combustion, low emission, soot-free and sulphur free combustion stands to be its outstanding characters. However low density, low lubricity and combustion enthalpy promotes higher volume of fuel supply and need for additives whereas, optimisation of the fuel injection equipment can overcome these problems. Above all with considering the merits of DME the production of DME in large scale with suitable methodology should be promoted to achieve an eco-friendly automobile world.

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