

Future Fossil Fuel Alternative; Di-methyl Ether (DME) A review

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Abstract-The world energy consumption is steadily growing with the industrial improvements of the developing countries and the readily available fossil fuel reserves lack in fulfilling this energy requirement. The depletion of the easily achievable reserves; gives rise to the concept of oil production from oil shale and tar sands. However, the high cost and the operational difficulties stand as the major drawback in front of these technologies. Along with these circumstances, and the environmental concerns on fossil fuel consumption which is considered as the reasoning behind 'Global warming'; world is seeking for alternative fuel technologies. In this respect, this paper aims to give an insight on the allocation of ethers, mainly di-methyl ether (DME), as fossil fuel alternatives. DME is considered as a possible candidate as LPG and diesel additive and/or substitute due to the similarity between the physical properties and its high cetane number. Moreover, DME can be produced from a variety of raw materials starting from biomass, coal and natural gas which results in production flexibility. This paper is a brief review of the possible DME production processes, and the potential DME applications especially in transportation and domestic utilizations.

Keywords-Di-methyl ether, alternative fuel, synthetic fuel, LPG, Diesel, fossil fuels.

1. Introduction

Energy is one of the principal concerns of the industrialized world. There is a continuous growth in the energy consumption with the industrial improvements of the developing countries, which results in higher amount of green house gas emissions and elevated energy prices. Moreover, natural gas and petroleum are important raw materials for industry and their consumption rate has increased more than 200 times in the last century. Among them, petroleum is the one having the fastest depletion rate because of its excessive consumption for transportation. Its overuse for transportation (about 57% of total oil consumption) causes problems in the petrochemical industry, in which petroleum is the major raw material [1-2]. According to the predicted lifetimes of precious raw materials, it is expected that there will be significant fuel shortage problems in the future. Thus, the world is looking

for new, cheaper and sustainable solutions; or by other means, alternative energy resources rather than fossil fuels. The fuel alternative of the future should have an easily available, non-petroleum feedstock that enables production and fuel versatility with reduced well to wheel green house gas emissions and enhanced fuel performance. Moreover, the infrastructure for fuel transportation and storage must be well established. Among all the alternative fuel candidates such as hydrogen, methane, methanol, bio-fuels and Fischer Tropsch fuels; ether based fuels, mainly di-methyl ether (DME) takes a profound attention [3]. DME serves as a clean, high efficiency compression ignition fuel with low NOx and SOx emissions and reduced particulate matter. It is an environmentally benign fuel and does not possess large concerns with toxicity, infrastructure, transportation and storage as the other alternative fuel options [3].

2. Di-methyl Ether (DME)

2.1. Characteristic Properties

Di-methyl ether is one of the most promising non-petroleum fuel alternatives; which enables high combustion performance with lower SO_x, NO_x and CO₂ emissions and soot free operation. It is the simplest form of all ethers with a chemical formula of CH₃OCH₃. It is a liquefied gas under 6 atm (or -24.9°C @ 1 atm) pressure and possesses similar properties with liquefied petroleum gas, LPG; thus it can be handled with an infrastructure similar to LPG [3, 4]. Upon burning DME displays a visible blue flame like natural gas which is a crucial safety indicator and it does not require an odorant since it has an ether-like scent [4].

Characteristic properties of DME and its comparison with other commonly utilized fuels are given in Table 1.

2.2. Advantages of DME as a fuel

DME is considered as a remarkable alternative for diesel and LPG with soot free operation and enhanced engine efficiency. The low auto-ignition temperature of DME and its quick vaporisation upon injection into the engine cylinder results in high cetane number (~55-60), hence improves the engine performance. Moreover, the high oxygen content (~35% wt) and the absence of carbon-carbon bonds lead to enhanced combustion kinetics, smokeless combustion, low amount of particulate matter [8, 9]. Moreover, DME is non-carcinogenic, non-teratogenic, non-mutagenic, and non-toxic [3].

By utilization of DME in light and heavy duty vehicles, well to wheel energy efficiency is expected to be 19% and 22.5% respectively, whereas the highest energy efficiency is around 26% for direct injection diesel vehicles [10]. With proper modifications on the engine injection and combustion systems, the NO_x emissions will reach the ultra low emission limits (ULEV).

Table 1. Comparison of characteristic properties of DME with some commonly used fuels [5]

	DME	Methane	Methanol	Ethanol	FTD	LPG	Gasoline	Diesel	Hydrogen
Molecular Weight (g mol⁻¹)	46.07	16.04	32.04	46.07		44.1	114	198.4	2.016
Density (g cm⁻³)	0.67 ^c	0.00072 ^b	0.792 ^b	0.785 ^b	0.76-0.79 ^e	0.54 ^e	0.71-0.77 ^e	0.80-0.86 ^b	0.00089 ^e
Normal boiling point (°C)	-24.9	-162	64	78	180-320 ^e	-30 ^e	0-210 ^e	125-400	-253 ^e
Octane Number (RON)	-	122	110	110	-	90-96	90-100	-	>125
Cetane Number	55-60	-	5	-	55-75	-	-	40-55	-
Energy content^e (MJ/kg)	28,43	50	19.5	28,4	44	46.3	42.7	43.1	119.9
Carbon Content^f (wt%)	52.2	74	37.5	52.2	85 ^e	82 ^e	85.5	87	0
Sulfur Content^f (ppm^g)	0	~7-25	0	0		10-50	~200	~250	0

a Fischer Tropsch Diesel

b Values per cm³ of vapour at standard temperature and pressure [3]

c Density at P=1 atm and T= 20°C

d Data reproduced from reference [6]

e Data reproduced from reference [6]

f Data reproduced from reference [7]

g Mass basis

In addition, well to wheel carbon dioxide emissions are comparable with direct injection diesel engines [4].

2.3. Disadvantages of DME utilization

DME has a lower combustion enthalpy compared to petroleum based fuels due to the high oxygen content. For this reason, in order to achieve the same combustion performance, a larger volume of fuel should be injected into the engine cylinder, thus a longer injection time and larger fuel storage tank is required.

The low viscosity of DME (~0.1cSt), will lead to leakage problems from the fuel supply systems; thus special attention must be given for sealing [5]. Moreover, due to its corrosive nature, DME is not compatible with most of the elastomers. In order to prevent the deterioration after long exposure times, seals can be made from polytetrafluoroethylene (PTFE) based materials [4].

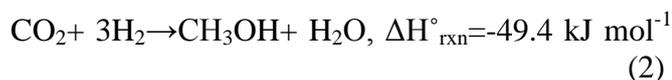
Another consequence of low viscosity reveals itself as the lower lubricity characteristics of DME [4]. Lower lubricity may cause extensive wear on the moving parts of the engine. This problem can be overcome by the introduction of some lubricants.

3. Production Processes

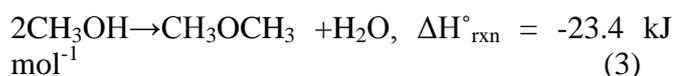
3.1. In-direct Synthesis (Conventional route)

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 [11] 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 vapor phase and the reaction is pressure insensitive [12]. Syngas provides a versatile feedstock. It can be produced either by gasification of various bio-mass sources, coal or waste material or by reformation of natural gas with steam. The latter feedstock is usually preferred since it does not contain impurities such as sulphur components and heavy metals. The reactions involved in two-step production process are as follows [3, 4, 11];

Methanol Synthesis;



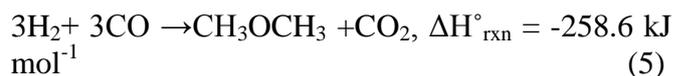
Methanol Dehydration;



Water-gas shift;



Net Reaction;



3.2. Direct Synthesis

Recently, a new system is proposed, at which, methanol synthesis and dehydration processes are combined in the same reactor for DME synthesis [13]. 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]. Additionally, the thermodynamic limitations of methanol synthesis could be withdrawn, since consumption of methanol in a consequent reaction to form DME will shift the methanol synthesis equilibrium towards higher methanol conversion [14, 15].

In direct synthesis, initially, the feedstock (biomass, coal or natural gas, etc.) is converted into syngas. Later, methanol is synthesised from syngas (given in eq.1, eq.2) and converted into DME via methanol dehydration reaction (given in eq.3) simultaneously in one step over catalysts having two active sites.

In direct synthesis of DME, a wide range of feed composition and operating conditions can be used. Feed gas composition, source of feed gas and catalyst selections are the important parameters of the process [12]. Typical reaction conditions of direct DME synthesis are tabulated in Table 2. [16].

Table 2. Reaction conditions of direct DME synthesis [16]

Reaction Conditions	Range
Temperature (°C)	240-280
Pressure (bar)	30-80
Feed (H ₂ / CO) ratio	0.5-2.0
Catalyst loading ratio (W/F) [kg-cat.*h/kg-mol]	3.0-8.0

The overall reaction is highly exothermic, thus the temperature control in the reactor is crucial to prevent run-away reactions [11]. In commercial applications, two different reactor types are utilized; fixed bed [17] and slurry phase [18]. Temperature control is difficult in fixed-bed reactor, since hot spots may occur during the process. The slurry phase reactor will overcome

this problem, thus, they will achieve better temperature control. In slurry phase reactors, the catalyst particles are suspended in an oil solvent; which ease the temperature control due to large heat capacity of the solvent [11]. These types of reactors are preferred in pilot and commercial scales. Moreover, thermally coupled heat exchanger reactor, micro-channel reactor and catalytic distillation reactors are of interest and being developed in laboratory scale.

4. Application Areas

In 1990s, the worldwide DME production was around 100,000-150,000 tonnes per annum [19] and was mainly used in aerosol industry as a propellant in the spray cans. In the recent years, DME has received a growing attention due to its potential as a fuel additive and/or alternative. Thus, DME covers a wide application area ranging from domestic and industrial utilizations to transport applications.

4.1. Domestic Utilization

DME possesses similar properties to butane and propane; which is a potential substitute for LPG [20, 21] and can be utilized for household cooking applications. DME can be blended with LPG up to 20% by weight and will be transported by the existing LPG infrastructure without any modifications. Along with these circumstances, the low greenhouse gas emissions and particulate matter emissions attracts a substantial interest on DME as a cooking fuel. Especially in China, there is a considerable potential for coal derived DME [19].

4.2. Industrial Utilization

DME was formerly used as a medical anaesthetic [19] and has found a large application area as an injection agent for sprays for paint, agricultural chemicals and cosmetics [23] in order to replace chlorofluorocarbons (CFC's) which have undesired effects on the ozone layer. Furthermore, DME can go through a phase change from liquid to gas easily, thus can be considered as a good refrigerant [18].

Moreover, DME provides an excellent potential as a feedstock in the production of several important chemicals such as olefins. DME

possesses a lower enthalpy value compared to methanol, thus, the heat of reaction required for the production of a chemical will be much lower when DME is utilized instead of methanol [5].

4.3. As a Fuel Alternative

DME is an attractive fuel alternative for compression ignition engines. Besides its high cetane number, DME can easily vaporize during injection allowing lower fuel injection pressures due to its low boiling point. The required fuel injection pressure of DME is around 220 atm at full loading, whereas the diesel engines required injection pressures higher than 1200 atm [5]. The existing diesel engines can be compatible with DME subsequent to some modifications that are required to maintain stable fuel injection to the engine [5]. Similar to the other alternative fuels, DME also has a lower energy density per unit volume compared to diesel. Thus, in order to travel the same distance, a larger storage tank must be provided on the vehicle [5, 22].

Moreover, DME is considered as a possible LPG alternative and/or substitute. It can be utilized on LPG compatible vehicles up to 20wt% blending ratio without any modifications on the engine ignition system or LPG infrastructure. For higher blending ratios or direct DME injection, modifications are required as for diesel.

4.3.1. Performance criteria

Evaluation of DME as an alternate to conventional fuels can be performed via comparison in terms of well to tank efficiencies. In Figure 1, the fuel properties of DME are compared with other fuels [3]

Considering the abundance and improvements on processing technology, petroleum based fuels owe the highest WTT efficiencies approaching up to 90% and is well above DME efficiency which is around 70%. However, it is shown that, DME fuelled compression-ignition engines has a higher thermal efficiency compared to diesel due to its structure and promising fuel properties as shown in Figure 2.

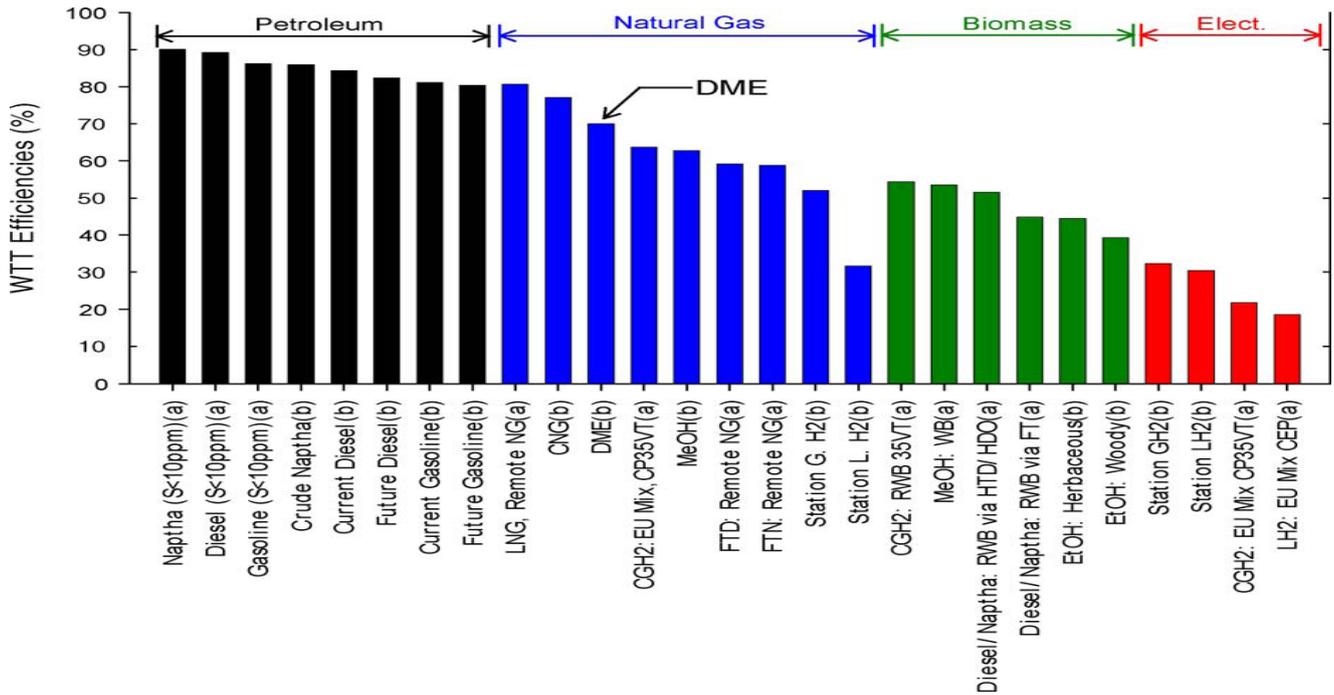


Fig.1. Well to tank (WTT) efficiencies of fuels [3]

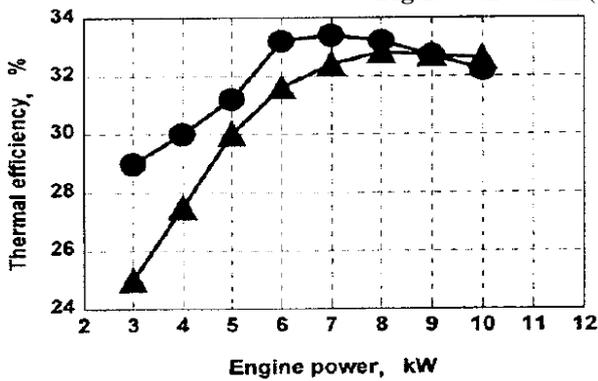


Fig.2. Thermal efficiency of DME and diesel fuelled engines [24]

4.3.2. Emissions

DME utilization in compression engine, compared with conventional diesel and other fuels, is reported as advantageous in terms of pollutant emissions as well. In relation with the improved thermal efficiency behaviour as mentioned in previous section, emitted hydrocarbon, NO_x and CO amounts are reduced in presence of DME in the engine. In Figure 3, emissions of NO_x and CO in DME fuelled engine is compared with gas-to-liquid (GTL) and diesel fuelled engines under a load of 1400 rpm [25].

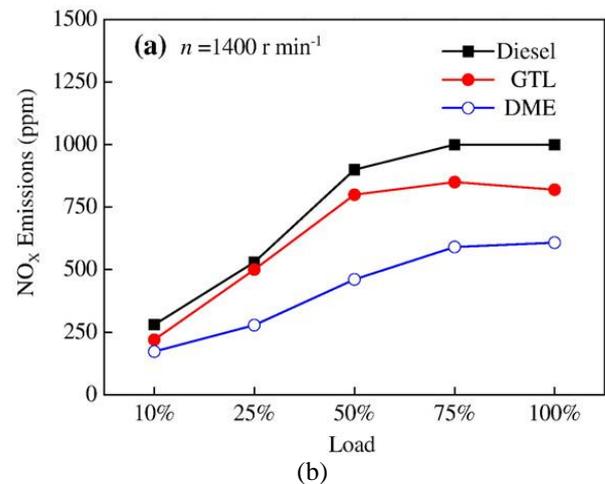
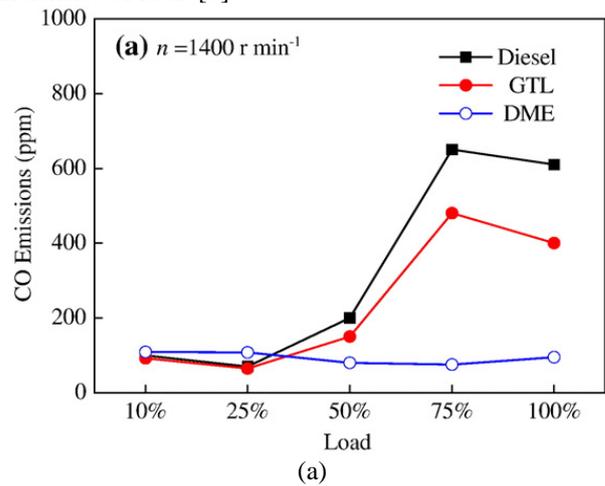


Fig. 3. (a) CO and (b) NO_x emissions with diesel, GTL and DME fuelled engines at 1400 rpm load [25]

5. Conclusion

DME is a promising new alternative fuel with its versatile feedstock and production methods. It finds a wide application area ranging from household and industrial applications to transportation. Especially, considered as a multi-purpose fuel and suggested as a LPG/diesel additive (with a maximum blend ratio of 20% for LPG) and/or substitute [26]. DME shows a good performance in conventional diesel engines with modified injection and storage systems due to its high cetane number. It provides a quiet combustion and clean burning and prevents soot formation. DME finds a primary market especially as an injection agent in aerosols and as chemical feedstock; and there is a continuously developing market for DME as an alternative fuel that is led by China, Japan and Europe. In order to use DME in daily life, as it is competitive with its promising fuel properties, the production routes should also be optimized in terms of costs to find a place in economy. Since natural gas prices are affected by several items and it is the main feedstock of DME production beside coal and biomass, DME unit costs are not stable as well.

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