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Dimethyl ether as a renewable fuel for diesel engines

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Abstract: The area of automotive fuel, or fuel components, which can be produced from biomass also includes dimethyl ether, otherwise known as DME. The issue of the use of DME as a fuel is one which has been monitored until recently. Biomass can also be used as the raw material for the production of DME. DME has therefore replaced the previously-used CFCs (chlorofluorocarbons), which are now banned for their role in dangerous levels of ozone depletion. With regard to its physical properties and combustion characteristics, it is currently expected that DME will soon apply significantly as a fuel in the municipal sector and in households, and as an alternative fuel for motor vehicles with diesel engines. DME is a suitable fuel for diesel engines and can be considered as one of the most promising diesel fuel replacements. DME is a suitable fuel for diesel engines mainly due to its low self-ignition temperature and good cetane figures. It is well miscible with most organic solvents and because the polar solvent is water-immiscible. The advantage is its high levels of purity, and its being free of sulphur, nitrogen, or metals. The physical properties of DME are very similar to the physical properties of LPG. DME requires relatively complex and costly fuel accessories, but the original compression ratio of the diesel engine is maintained. A diagram of the fuel system is illustrated in the paper. The paper analyses the dependence of vapour pressure on temperature, the dependence of the density on temperature, kinematic viscosity, the flash point, the boiling point, and the solubility of water. The objective is to evaluate this interesting energy source for applications in diesel engines.

Key words: biofuel, biomass, liquefied petroleum gas, vapour pressure, density.

INTRODUCTION

There are many reasons why we should deal with alternative fuels. The main one is probably the fact that sooner or later oil reserves will exhausted and mankind will lose its ability to produce gasoline and diesel – fossil fuels without which today's traffic cannot get by. Further, using these classic carbon fuels delivers negative consequences in terms of ecology. Although there is significant emphasis on fuel quality in order to reduce emissions and fuel-efficient vehicles are being designed, these measures are not effective enough. All of this is thanks to increasing energy consumption levels in terms of oil production (which should culminate in 2020) and the related increase in emissions. Road transport continues to produce still larger quantities of substances which have a harmful effect not only on the human body, but also on the world's overall climate on a global scale (De Wit & Faai, 2010; Thamsiriroj et al., 2011; Hönig et al., 2015).

Among the most-discussed alternative fuels are:

- **Biodiesel** – a methyl ester made of vegetable or animal oil or, to put it more precisely, fat. The quality corresponds to conventional diesel which is used as biofuel.
- **Bioethanol** – an ethanol made of biomass or by using the biodegradable fraction of waste.
- **Biomethanol** – methanol made of biomass. This methanol is used as biofuel.
- **LPG** (Liquefied Petroleum Gas) – a blend of liquefied propane and butane.
- **Biogas** – a name for a fuel gas made of biomass or made by using the biodegradable fraction of waste that can be purified to natural gas quality and used as biofuel.
- **Natural gas** – a natural mixture of gaseous hydrocarbons with a majority of methane.
- **Biohydrogen** – a hydrogen made of biomass and/or from the biodegradable fraction of waste, which is used as a biofuel (Schlaub & Vetter, 2008; Küüt et al., 2011; Pointner et al., 2014).

Apart from suitable physico-chemical properties, an alternative fuel should meet a number of requirements. Material from which the fuel is obtained must be accessible, renewable if possible, and not too expensive. Actual fuel production must not be too high-tech and energy-intensive. Extracted fuel must be economically competitive and environmentally friendly. In terms of thermal cycles, the fuel should have adequate calorific value. Another criterion is the need for this fuel to be applicable for use in commonly-used cars with petrol or diesel engines, with a minimum of necessary design adaptations being required. If the fuel requires a special redesign of the entire propellant system, it would be desirable that such an equipped vehicle is affordable and is available with a large selection. In order to be able to implement a totally new fuel also requires the construction of a distribution infrastructure – the fuel must be sufficiently available. Fuel should be easy to store, should be spoilage-resistant, and handling it should be as safe as possible (Ju et al., 2014; Wang et al., 2016).

Amongst automotive fuels or fuel components which can be produced using biomass, ethers also belong to this group, whether dimethyl ether (DME) or ethyl tert-Butyl ether. DME is a colourless gas with a chloroform odour. It burns with a slightly luminescence flame and is not toxic. It mildly irritates the respiratory system and has possible narcotic effects. When mixed with air, oxygen, chlorine, and hydrogen chloride it forms an explosive mixture (Nazari et al., 2015).

It is estimated that today's worldwide annual consumption of dimethyl ether (DME) is around 150,000 tons (Šebor et al., 2006). The vast majority of dimethyl ether (90%) is used as a propellant in the manufacture of aerosols. DME has therefore replaced the previously-used freons (chlorofluorocarbons, or CFCs), which are now banned thanks to their being dangerous to the ozone layer (Laurin, 2007). DME is used in the production of methyl acetate and acetic anhydride. It is a perspective material for the production of light olefins, especially ethylene and propylene. With regard to its physical properties and combustion characteristics it is currently expected that DME will soon apply significantly as a fuel in the municipal sector and in households, and as an alternative fuel for motor vehicles with diesel engines. The issue of the use of DME as a fuel was raised pretty recently (Nazari et al., 2015).

DME can be made by using various materials, such as natural gas and biomass (biodimethyl ether). For the production of one ton of DME we need three tons of wood, which corresponds to a yield of 500 litres of DME from one ton of wood (Laurin, 2007). DME is currently produced via the catalytic dehydration of methanol (a fixed catalyst base) according to this Eq. (1):

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad (1)$$

As a catalyst for the dehydration of methanol to DME, γ-alumina alone or γ-alumina saturated with phosphoric acid is being recommended (Laurin, 2007; Liu & Chen, 2015). Methanol preheated to 300 °C is dosed into a reactor which is filled with shape-alumina or, as the case may be, diluted with inert beads (such as glass, which offers better heat conduction). The reaction mixture is conducted from the bottom of the reactor at a maximum temperature of 400 °C. It operates at a pressure of up to 1.7 MPa. Under these conditions it is possible to produce a product which contains an average of weight of 58% DME, 20% methanol, and 22% water (Šebor et al., 2006; Ju et al., 2014).

For the large-scale production of DME from natural gas it is preferred that the production of methanol and DME be integrated into a single process; this integration is also advantageous in terms of thermodynamics. The direct synthesis of DME includes, aside from the above reaction (1), both basic methanol-producing reactions (2) and (3).

$$CO + 2H_2 \rightarrow CH_3OH \qquad (2)$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad (3)$$

All three reactions must proceed simultaneously, which is something that is achieved by fitting a common catalyst for methanol synthesis and a catalyst for its dehydration (Šebor et al., 2006). In methanol factories, where methanol is produced at low pressure, DME as a by-product does not originate. There are developed processes in which methanol production is modified so that the synthesis product is a mixture of DME and methanol. In order to be able to yield the maximum levels of DME, there must be an available catalyst which is active both in the synthesis of methanol and in the subsequent dehydration to DME. Many producers work hard on the development of this technology. The production equipment is similar to that required in the manufacture of methanol. The recommended capacity of DME production is 7,000 tons per day. Expected investment costs are in advance of five hundred million USD. The investment costs were quantified as needing to be lower by 4–8% when it comes to the production of DME in comparison to the similar production of methanol. This is because energy consumption in the production of DME is about 5% lower when compared to the production of methanol (Liu & Chen, 2015).

If DME is made using biomass, then the finished product is marked as being bioDME. The USA produces DME under the trademark 'Dymel'. For its use in vehicles, DME is compressed to 0.5 MPa, which means that it is liquefied and that the liquid is refuelled into the tanks. It is processed similar to the method used for LPG, and therefore a similar infrastructure for its transportation and for providing refuelling may be used. Similar modifications may also be made in the fuel system (Šebor et al., 2006).

DME has similar physical properties to LPG. At a temperature of 20 °C it is a gas, but at a pressure of 0.5 MPa it liquefies (Kumar et al., 2011). In terms of installation, vehicle modifications consist of the addition of pressurised tanks. In order to achieve the same full-tank range, the lower specific energy is provided with compensation by installing larger tanks. Engines have a special fuel pump and injectors, an adapted control program, and common rail injection. For DME and LPG-propelled buses we need to solve the problem regarding the placement of tanks. For low-floor buses the installation of composite tanks on the roof can be considered, while in the case of medium and high-floor buses tanks can be placed under the floor (Laurin, 2007; Lee et al., 2016).

DME is injected into a cylinder in the same way as diesel fuel. Injecting DME into the combustion chamber is sufficient when compared with the injection of diesel under relatively low injection pressures, approximately 30 MPa, which ensures the required fuel dispersion. For instance, the accumulator injection system with electrically controlled injection valves, known as 'Common rail', is suitable. One of the typical arrangements for the fuel system is shown in diagram form in Fig. 1 (Laurin, 2007).

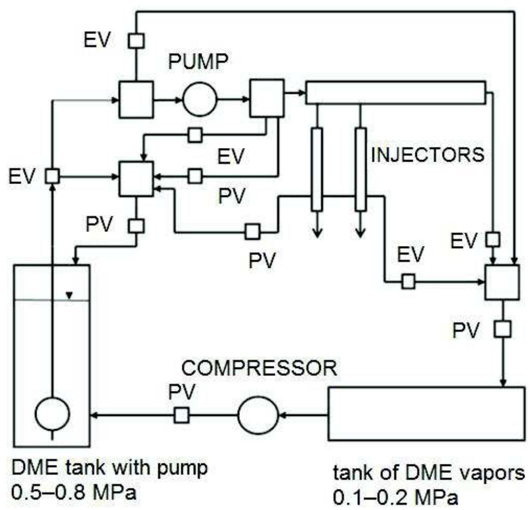

Figure 1. A diagram of the DME fuel system: EV electromagnetic valve; PCV pressure control valve; PV pressure relief valve.

Liquefied DME is propelled around the system by means of a pump which is located in the fuel tank, using a pressure of around 0.8 MPa in the high pressure pump where it is compressed to an injection pressure of 30 MPa, controlled by a regulation valve (PCV). After that, it is brought into the tank and from there to the individual injectors. Fuel injection quantity and injection timings are controlled by means of electromagnetic valves, which are controlled by the engine control unit (Laurin, 2007; Wang et al., 2016).

In order to prevent the penetration of the fuel through jets into one of the engine's cylinders after stopping the engine, the fuel must be moved from the high pressure section of the fuel system back into the tank. This option is provided up to certain pressure-relevant electromagnetic (EV) and pressurised (PV – pressure relief valve) valves. After the further reduction of the pressure levels, the DME is delivered from the fuel system into a closed tank, where it evaporates and the gaseous DME is transported via a compressor into the fuel tank. This measure will increase the safety of the entire fuel system and it also allows standard components to be used in hydraulic systems instead of perfectly gas-resistant components (Laurin, 2007; Wang et al., 2016).

In 2010 the Volvo Trucks company produced fourteen Volvo FH trucks for testing, all of which were equipped with a 13-litre engine with an output of 440 hp, which is adapted to run on DME.

This paper aims to determine the DME parameters in terms of it being a suitable energy source. Besides the parameters for applications in diesel engines, also being evaluated is the dependency of vapour pressure on temperature. The determination of this parameter is also very important when it comes to using the gaseous fuel if DME is to become an alternative for LPG fuel.

MATERIALS AND METHODS

For utilisation in diesel engines as a substitute for diesel fuel, it is necessary to determine density depending upon temperature. This is due to DME being injected into an internal combustion engine as fuel. There is a relationship between density and the calorific value of the fuel which is being analysed in this paper. For the safe storage and handling of DME it is necessary to know the flashpoint. A determination of the kinematic viscosity of DME in its liquid form is important for the prediction when it comes to mixing fuel with air in a combustion engine and the possibly of utilising a stress pump. An analysis of the solubility of water in DME is also analysed in the paper, as water is considered to be a corrosive environment.

Also, the dependence of vapour pressure on temperature was checked and compared to that of propane and butane in advance of the possibility of DME becoming an alternative to LPG (Liquefied Petroleum Gas as a blend of propane and butane in different proportions).

A sample of DME in p.a. quality was used for experimental analysis. The purity of the sample was at > 99.6% wt, with a methanol content of < 0.05% vol, and dissolved water at < 0.01% wt. Propane and butane gases were purchased from Linde Gas Company.

A diesel fuel sample was used which was compliant with the EN 590 standard without the presence of fatty acid methyl esters for laboratory tests.

Due both to the properties of the fuel and its boiling point, it was necessary to cool the fuel in the test tank by means of a cooling coil (Fig. 2). As the cooling fluid which would help to determine the boiling point, flash point, and kinematic viscosity, propyl ethylene glycol and ethanol were used.

Figure 2. Cooling coil.

The following parameters were measured:

- Volumetric and calorific value on isoperiobolic-incinerated calorimeter IKA C200 (IKA, Germany). The measurements corresponded to ISO 1928 (Fig. 4).
- The dependence of vapour pressure on temperature according to ASTM D 323 (Fig. 3).

Figure 3. An apparatus for measuring vapour pressure.

Figure 4. Isoperiobolic incinerated calorimeter IKA C200.

- The dependence of density on temperature according to the EN ISO 3675 standard.
- Kinematic viscosity according to the EN ISO 3104 standard.
- The flashpoint according to EN ISO 2719.
- The boiling point according to EN ISO 3405.
- The solubility of water in DME on Coulometer WTD (Fig. 5, Table 1).

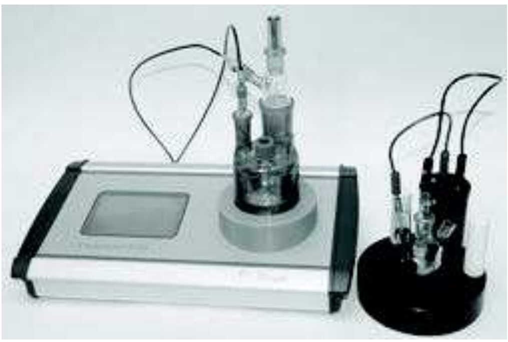

Figure 5. Coulometer WTD.

Table 1. Technical characteristics of coulometer WTD

Measuring range	1 ppm – 5% H_2O
Measurement error	0.5%
Titration flow	max. 330 mA
Indicating current	1–25 μA
Sample weight	0.002–2 g
Result display	μg, ppm, %
Power	230 V AC, 35 W
Titration container	200 mL with or without diaphragm

RESULTS AND DISCUSSION

Based on the rating of the vapour pressure by DME (Fig. 6) the practical use of DME as a substitute for commercially used LPG has been shown. For comparison, the vapour pressure of LPG at 20 °C is between 215 kPa and 770 kPa depending upon its composition (represented by propane and butane as shown in Fig. 6).

The horizontal axis *x* (Fig. 6) represents the temperature in degrees Celsius, while the vertical axis *y* represents the vapour pressure according to the Reid method (RVP) in kPa. For each sample three measurements were carried out. All of them always reached the same value on the manometer. The expected uncertainty of the result is ± 1% of the value of the result.

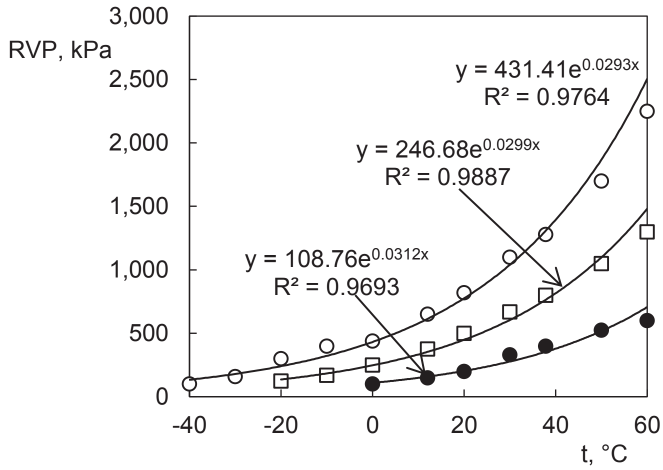

Figure 6. The dependence of vapour pressure upon the DME, plus propane and butane temperature.

An analysis of the DME vapour pressure dependant upon temperature was necessary also from the aspect of transportation, storage, distribution, and safety demands.

The horizontal axis *x* (Fig. 7) represents the temperature in degrees Celsius, while the vertical axis *y* represents the density of the fuel. For each sample three measurements were carried out. The results did not vary according to the evaluation methods, while the expanded uncertainty is ± 0.5kg m^{-3}.

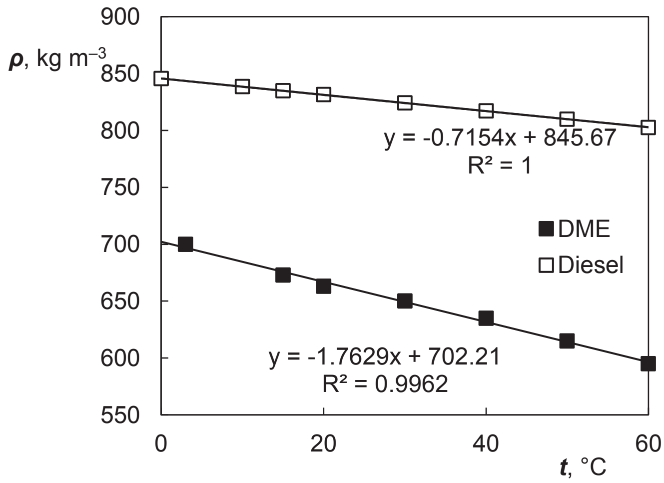

Figure 7. The dependence of the DME and diesel fuel density on temperature.

The lower density of DME when compared to diesel fuel had already signalled a lower calorific value, unlike diesel fuel. Compared with diesel fuel, the volumetric calorific value of dimethyl ether is almost half (Table 2). Engines running on DME, however, achieve a comparable performance and levels of efficiency, as in the case of the combustion of diesel (Šebor et al., 2006).

Table 2. Other measured parameters compared to the diesel fuel

	DME example	Diesel example
Kinematic viscosity at 20 °C ($mm^2\ s^{-1}$)	0.75 as a liquid (0.8 MPa)	4.09
Boiling point (°C)	-24.5	180–360
Flash point (°C)	-42	67
Water solubility (% wt.)	< 6	-
Density at 15 °C ($kg\ m^{-3}$)	673	834.37
Calorific value ($MJ\ kg^{-1}$)	28.4	36.1
Calorific value ($MJ\ l^{-1}$)	18.9	42.6
Vapour pressure at 37.8 °C (kPa)	803	-

DME has a high cetane figure, between 55 and 60 (Šebor et al., 2006; Ju et al., 2014), and is therefore suitable as a fuel for diesel engines. The compression ratio for the diesel engine also meets the DME. With the stoichiometric air-to-fuel ratio (wt) set at 9.0, the heat in vaporisation lies between 460 to 470 $kJkg^{-1}$ (Šebor et al., 2006; Wang et al., 2016).

In comparison with diesel fuel, DME contains no sulphur and has significantly different properties:

- high levels of compression;
- a low boiling point, and DME must be stored in tanks under pressure (Table 2);
- a lower density and a low energy content per unit volume of the liquid, and DME has a low calorific value (Table 2);
- a large dependence upon density levels is influenced by temperature (Fig. 7);
- a high oxygen content provides a positive influence upon the combustion process,
- low viscosity levels place a high demand on the tightness of the fuel system (Table 2);
- low water solubility levels are important in terms of limiting the corrosive environment and the efficiency of the internal combustion engine (Table 2);
- an aggressive reaction towards rubbers and plastics;
- a very low flash point (Table 2).

The boiling point of dimethyl ether is -24.5 °C (Table 2); therefore it is necessary to store it in pressurised tanks which can be filled only to 80% of their total volume due to the great dependence of the specific volume upon the temperature. Low DME viscosity places a demand on the quality of the fuel system in term of leaks. In order to avoid any damage being caused to moving parts in the fuel system, it is necessary to increase the levels of lubrication by means of suitable lubricating additives.

Compared to diesel fuel, the lower ignition temperature of dimethyl ether is an advantage. Dimethyl ether's own combustion rates also has a very positive effect on a large amount of the contained oxygen. DME has a high cetane figure between 55–60, which means that in terms of its use in diesel engines clearly provides it with an advantage (Šebor et al., 2006).

Dimethyl ether produces substantially less solid particles and nitrogen oxides (up to 90%) during the combustion process when compared to diesel fuel. On the contrary, diesel fuel combustion produces less carbon monoxide than dimethyl ether combustion. In terms of the treatment of exhaust gases only a simpler system is needed. The advantage over diesel fuel is also a lower engine noise level (Kim & Park, 2016; Lee et al., 2016).

The DME synthesis based on biomass is also currently still a subject of research. The Swedish National Energy Agency stated that influences on the price of DME which was produced from biomass included, primarily, the price of input raw materials and investment costs. The investment costs which are required for a unit with an annual capacity of 200,000 tons are estimated at around € 390 million, ie. € 2,000 per ton, € 0.27 per litre or € 14 per GJ respectively. Since DME has almost half of the calorific value of diesel fuel, the price of an equivalent amount of DME energy is around € 0.50 per litre (Laurin, 2007; Kim & Park, 2016; Lee et al., 2016).

CONCLUSIONS

Conceptual studies in this field are counting on the fact that the production and consumption of DME will increase significantly. It is expected that DME will be used as a substitute for diesel fuel and as a substitute for LPG with regard to its similar properties according to the EN 589 standard, and also as a petrochemical raw material for further synthesis.

DME is a suitable fuel for diesel engines and can be considered as being one of the prospective energy sources of the future. For use in diesel engines its liquefied form comes into consideration. In the process of switching from diesel fuel to DME no change is required in the compression ratio of the diesel engine. Switching to DME fuel however requires relatively complex and expensive fuel accessories. The DME engine output parameters engine may be the same as in the case of the diesel engine. Claims for transportation, storage, distribution, and safety are similar for DME as they are for LPG in petrol engines.

Application of the DME as a fuel for diesel engines is still in the process of development, undergoing experimental verification and the implementation of demonstration projects.

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