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ASSESSMENT OF METHANOL PROPERTIES AS AN ENERGY SOURCE FOR POWERING TRANSPORT VEHICLES

Jarosław Markowski, Jacek Pielecha, Remigiusz Jasiński,
Poznan University of Technology
Institute of Internal Combustion Engines and Transport
Piotrowo Street 3, 60-965 Poznan, Poland
tel.: +48 61 665 2207, fax: +48 61 665 2204
e-mail: jaroslaw.markowski@put.poznan.pl,
jacek.pielecha@put.poznan.pl
remigiusz.w.jasinski@doctorate.put.poznan.pl

Magdalena Dudek
AGH University of Science and Technology
Faculty of Energy and Fuels
Kawiory Street 40, 30-055 Cracow
e-mail: potoczek@agh.edu.pl

Jacek Madry
SpinTechSystem Sp. z o.o., Dzialynskich 11, 63-000 Sroda Wielkopolska
e-mail: jacekmadry@wp.pl

Abstract

Legislative activity in the field of environmental protection from harmful factors resulting from the use of various types of transport functions is aimed at reducing exhaust gas emissions among other things. This activity is to stimulate the development of transport drive systems by introducing emission limits of harmful substances in exhaust gases. These restrictions are contained within the relevant legal acts dedicated to each different mode of transport. Gradual reduction of limit values for emission standards has led the industry to change the systems generating energy used to propel their vehicles. These activities are related to the wider electrification of drive systems, which use the latest electric solutions controlled with modern electronic systems. However, the difficult problem of the energy sources and storage still remains. The article describes considerations relating to the possible use of methanol as an energy source for modern vehicles.

Keywords: methanol, combustion engines, fuel cells, energy sources, operating parameters

1. Introduction

Development of drive systems for all kinds of transport means, driven by normative acts in the field of environmental protection, has reached a high technological level. Evidenced by the materials used in their construction and the technological sophistication of their processing. Despite the new technologies used in internal combustion engines it is still not possible to achieve a significant increase in energy efficiency, which is closely linked to fuel consumption. Also, the realization of the thermal processes occurring in the internal combustion engine causes the emission of nitrogen oxides, carbon monoxide, hydrocarbons, carbon dioxide and particulate matter. Therefore new ways to improve the energy characteristics of drive systems are sought after. Examples of such activities are the electrification of powertrains. Which takes the form of introduction of hybrid systems using electric motors, circuits, power generation and storage systems. The three main functions of the hybrid drive system used in passenger vehicles require the use of an internal combustion engine, electric engine, an electric energy generator and a battery. This results in a significant increase in vehicle weight. However, the combination of advantages such as high electric motor efficiency with its good driving performance, increasing the overall energy efficiency of the engine by limiting its scope of operation to the characteristic points with the greatest efficiencies and the use of electric energy storage systems along with the electricity recovery from mechanical energy, e.g.: when braking, contributes to high drive efficiency index. Good results obtained for hybrids resulting from the propulsive efficiency of the electric motor lead the trend of moving towards all-electric solutions. The main problem existing for this type of drive systems is the energy storage in the battery, as well as the efficiency of this storage process depending on the vehicle operating temperature, and the issue of the electric power sources. When it comes from low carbon sources in the form of hydroelectric power, wind power, photovoltaic cells or nuclear power plants, then the ecological character of this drive can be argued to be positive. On the other hand, when dealing with electricity used to power the vehicles, coming from coal-fueled power plants, the level of environmental performance of the vehicle turns out much lower. Such problems lead to the search for alternative sources of energy for transport means, which will not generate toxic compounds in the vehicle exhaust gases. The use of methanol as fuel for vehicle power supply systems can be considered with two energy conversion methods, either the combustion process in internal combustion engines, or by using a fuel cell [2-18].

2. Methanol as fuel for vehicle drive systems

2.1. Combustion engines

Methanol as a fuel for combustion engines is already used to a small extent, and normally to supply engines for sports use, such as: speedway motorcycles, model aircraft, or motor boats. The limited use of methanol in internal combustion engines due to its characteristics (Tab. 1). It is a fuel with a density of 798 kg/m^3, which, compared to diesel is less than about 40 kg/m^3 and higher by about 60 kg/m^3 compared to gasoline. The difference in the density of methanol in relation to diesel and gasoline of about ±10% is insignificant compared to the calorific value, which for methanol is only half that of petrol and diesel and is about 20 MJ/kg. Therefore, to produce the same mechanical energy the engine must consume two times more methanol than diesel fuel or gasoline. The octane number of methanol is 109 and indicates a high fuel resistance to knock. The problem of operating internal combustion engines fueled with methanol can also be the methanol cetane number being less than 5, which indicates a very low capacity for spontaneous combustion and spontaneous combustion temperature of 470^{o}C, which is near the upper range of temperature values for the ignition of diesel fuel and gasoline of about 250-460^{o}C. In terms of autoignition the value of the evaporation heat is also important, it is the energy that fuel takes from the environment when being sprayed in the combustion chamber in order to change from liquid to gas phase. For methanol, it is 1089 kJ/kg at a pressure of 1 bar. This is four times more than the diesel fuel vaporization heat of 250 kJ/kg, and about three times greater than the gasoline vaporization heat of 375 kJ/kg. A large amount of energy required to evaporate the fuel introduced into the combustion chamber in the form of liquid causes cooling of the mixture, in addition to a large value of the autoignition temperature of methanol makes it difficult to reliably ignite, and this translates into a low cetane number. These features, impede the fuel combustion process in a conventional reciprocating engine that is adapted for diesel fuel supply.

Methanol, in contrast to diesel fuel and gasoline, in order to achieve stoichiometric combustion for 1 kg of fuel, requires 6 kg of air. It is about 8.7 kg less than the combustion of diesel and gasoline. This indicates that it is thermodynamically possible to supply a greater mass of fuel during one engine cycle. This way it is possible to compensate the twice lower calorific value of methanol.

Despite the operational problems of internal combustion engines fueled with methanol, resulting from the physicochemical properties of the fuel, new drive systems dedicated to high-powered marine engines are being developed (Fig. 1).

Tab. 1 Fuel properties Methanol [19]

Property	Methanol	Ethanol	Diesel	Gasoline
Chemical formula	CH_3-OH	C_2H_5-OH	C_8-H_{25}	C_4-H_{12}
Fuel carbon (wt%)	38	52	85	86
Fuel hydrogen (wt%)	12	13	15	14
Fuel oxygen (wt%)	50	35	0	0
Molar mass (kg/kmol)	32	46	183	114
Liquid density (kg/m^3)	798	794	840	740
Lower heating value (MJ/kg)	20.1	27.0	42.7	43.1
Boiling temperaturę (°C at 1 bar)	65	78	180-360	27-245
Vapour pressure (bar at 20°C)	0.13	0.059	«1	0.25-0.45
Critical pressure (bar)	81	63	30	-
Critical temperaturę (°C)	239.4	241	435	-
Kinematic viscosity (cSt at 20°C)	0.74	1.2	2.5-3.0	0.6
Surface tension(N/m at 20°C)	0.023	0.022	0.027	-
Bulk modulus(N/mm^2 at 20°C)	823	902	553	1300
Cetane number	<5	8	38-53	-
Octane number	109	109	15-25	90-100
Auto ignition temperature in air (^{o}C)	470	362	250-450	250-460
Heat of vaporisation (kJ/kg at 1 bar)	1089	841	250	375
Minimum ignition Energy (mJ at Φ=1)	0.21	0.65	0.23	0.8
Stoichiometric air/fuel ratio	6.5	9.1	14.6	14.7
Peak flame temperaturę (°C at 1 bar)	1890	1920	2054	2030
Flamability limits (vol%)	6-36	3-19	0.5-7.5	1.4-7.6
Flash point (°C)	12	14	52	-45

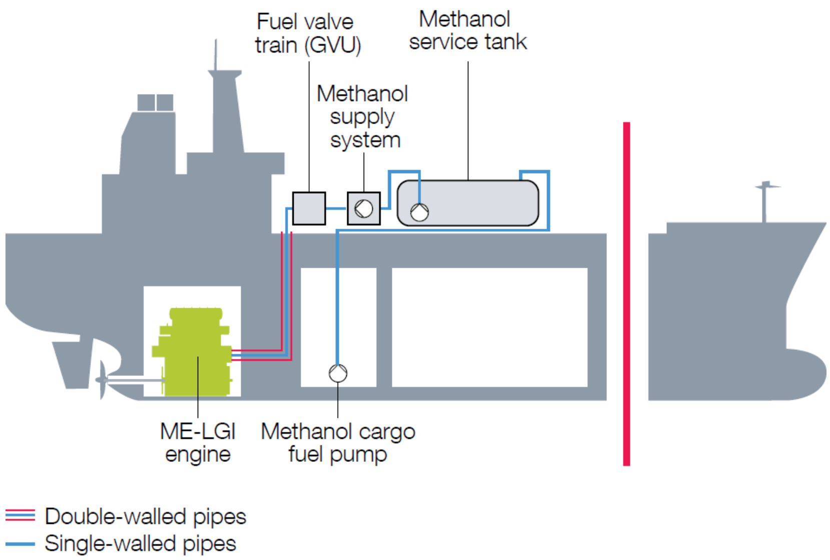

Fig. 1. General setup of a methanol drive system for marine engines [19]

The marine main engines are powered by methanol or methane in the form of liquid gas in two different solutions. The first concept implemented by the engine manufacturer MAN is to use two fuel supply systems in the engine construction. The cylinder head has four injectors installed, where two are responsible for supplying the combustion chamber with diesel fuel and two for methane or methanol in liquid form figure 2. The second concept implemented by the engine manufacturer Wärtsilä is the use of dual injectors (Fig. 3). The use of two fuel systems is due to the physicochemical properties of methanol and LNG. Problems with self-ignition and energy requirements for the evaporation of fuel spray, forcing the need for a diesel injection as an incendiary dose for the methanol fed into the combustion chamber, which is the main fuel.

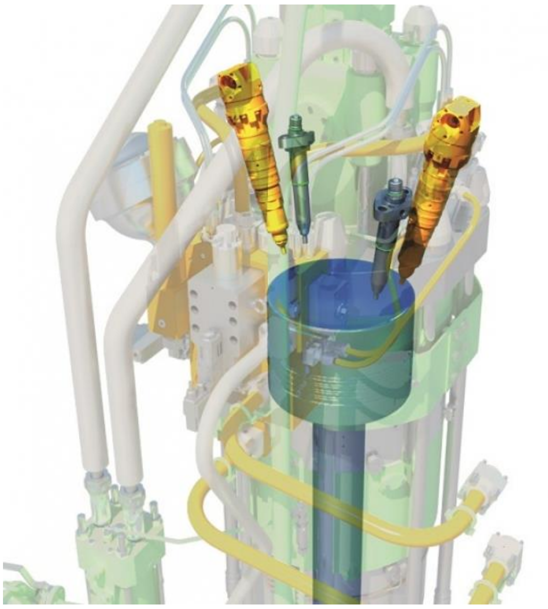

Fig. 2. Injector distribution in the head of a MAN ME-LGI engine [19]

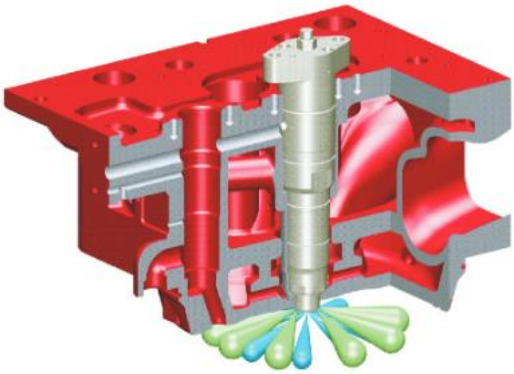

Fig. 3. The Wärtsilä 32GD fuel injection scheme [1]

Diesel injection and ignition initiates combustion in the cylinder resulting in an increased temperature and pressure of the fuel mixture in the combustion chamber. During the initial combustion process the main fuel is supplied to the combustion chamber – a gas or liquid methanol stream. The heat from the process taken to evaporate the atomized methanol fuel results in a slowdown of the combustion kinetic phase, resulting in a slower heat generation translating into slower temperature and pressure growth in the cylinder. The initial combustion process shifts to a diffusion process and is associated with the combustion of methanol, or LNG. The combustion process is characterized by a slowing kinetic phase contributing to the inhibition of nitrogen oxides formation in the combustion chamber reducing their emissions. Diffusion combustion of light fuels which are gas and methanol in the liquid phase helps reduce the formation of particulates and therefore also reduce their emissions in the exhaust. The implementation of such a combustion process had a positive effect in terms of reducing emissions of nitrogen oxides and particulate matter from the main propulsion system.

Despite the reduction of pollutant emissions in the engine exhaust gases the combustion process of methanol continues to lead to the formation of nitrogen oxides, carbon monoxide, hydrocarbons and carbon dioxide. Using the solution of engine dual fuel supply system, where the main fuel is methanol or LNG, significant improvement in reducing harmful emissions was obtained in terms of the ecology of maritime transport, but further possibilities of their limitation should still be researched. Therefore, it is necessary to use other processes to produce energy without the combustion of fuel.

2.2. Fuel cells

One of the drive system concepts using alternative fuel are the so-called hybrid systems, where fuel cells are used instead of an internal combustion engine. Fuel cells differ from each other in structure, the materials used in their construction and the efficiency of energy production depending on which fuel they use (Tab. 2) [. The classification of fuel cells is based on the electrolyte used in the cell. The used electrolyte determines the temperature of the reaction occurring in the fuel cell and fuel cell power. Each cell has advantages and disadvantages, which define the field of application for each type of cells.

PEM fuel cells (Proton Exchange Membrane or Polymer Electrolyte Membrane) are powered with pure hydrogen or reformate. PEM cell membrane is a polymeric material, such as nafion. A characteristic feature of the PEM cell is a high electricity production efficiency – up to 65% and a small amount of heat. An important advantage of PEM cells is good response time of cell systems subjected to variable loads and short start-up time. These characteristics result from the low temperature reaction occurring in the cell – at 60-100^{o}C.

AFCs (Alkaline Fuel Cell) use a KOH solution as an electrolyte. The reaction takes place at temperatures from 100 to 250°C. The reaction temperature depends on the KOH solution concentration, higher reaction temperatures can achieve higher cells electricity and heat generation efficiency. AFC cells are sensitive to any contamination and require fuel with a high degree of purity.

DMFCs (Direct Methanol Fuel Cell) have a polymer membrane, similar to PEM cells. But a different structure of the anode, which in DMF cells enables an internal reforming of methanol, and creation of hydrogen to feed the cells. DMF cells eliminate the problem of fuel storage and are attractive for portable applications due to the low reaction temperature (about 80°C). DMF cell is characterized by lower efficiency compared to the PEM cell, at only 40%.

PAFCs (Phosphoric Acid Fuel Cell) are used to build systems of cogeneration of electricity and heat. The efficiency of electricity generation is about 40%, in addition the water vapor produced by the cell can be converted to heat. The electrolyte in the PAF cells is phosphoric acid (H_3PO_4). The advantage of these cells is a high tolerance to carbon monoxide, which makes them suitable for multi-fuel use (desulfurization of fuel is important, however).

MCFCs (Molten Carbonate Fuel Cell) in which the electrolyte is a molten Li/K carbonate operate at high temperatures and are used for the production of electric and thermal power as small and medium power sources. Large temperature of the reaction occurring in the fuel cell allows it to use a variety of fuels, including natural gas, gasoline, hydrogen, and propane.

SOFCs (Solid Oxide Fuel Cell) have a membrane made of an oxide ceramic. They operate at high temperatures 650-1000^{o}C. This way they reach a high efficiency in electricity and heat cogeneration systems, as high as 85%. The disadvantage is the start and shut down time of the cell, which is reflected in their use in stationary CHP systems (Cogeneration Heat and Power). SOF cells have a high tolerance to fuel contaminants such as carbon monoxide and sulfur compounds, which allows them to use multiple fuel types.

Tab. 2 Fuel cell characteristics comparison [3-5, 8, 13]

Cell type	Fuel	Operating temp.	Eff.
PEM (Proton Exchange Membrane)	Hydrogen	60–100^{o}C	35 – 60%
AFC (Alkaline Fuel Cell)	Hydrogen	100–250^{o}C	50 – 70%
DMFC (Direct Metanol Fuel Cell)	Methanol Methanol solution	75^{o}C	35 – 40%
PAFC (Phosphoric Acid Fuel Cell)	Hydrogen	210^{o}C	35 – 50%
MCFC (Molten Carbonate Fuel Cell)	Hydrogen, methanol, methane, biogas, LPG	650^{o}C	40 – 50%
SOFC (Solid Oxide Fuel Cell)	Hydrogen, methanol, methane, biogas, LPG	650–1000^{o}C	45 – 60%

Taking into account the operating parameters of the cells in terms of their use as power supplies for vehicle propulsion systems a high efficiency in generating electricity and a short startup and shut down times of the cell should be considered the most significant characteristics. Of the presented fuel cell types the ones with properties that would make them useful as power sources in future transport are the PEM and AFC. Their efficiency in energy generation is in the range between 35 and 70%, and the operating temperature for PEM cells is 60-100^{o}C and for AFC cells 100-250^{o}C. These cells are fueled with hydrogen, therefore, if methanol is to be used as a fuel cell power supply it would be necessary to use additional external reforming systems. Such a system is used in the HDW submarine drive Type 216 manufactured by ThyssenKrupp Marine Systems (Fig. 4). The system operates on the principle of a steam reformer.

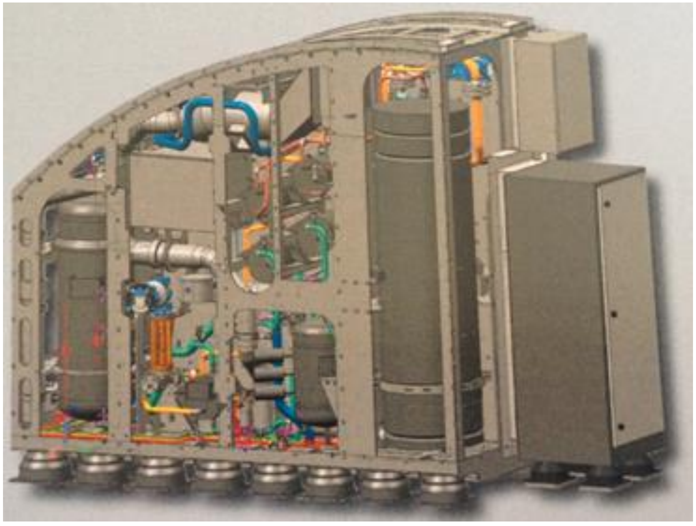

Fig. 4. Methanol reforming system installed on a HWD type 216 submarine

Primary reforming reaction occurring in the device is as follows:

$$CH_3OH + H_2O \leftrightarrow 3H_2 + CO_2$$

During the methanol reforming process a side reaction can also take place in the form of:

$$CO_2 + H_2 \leftrightarrow CO + H_2O$$

This reaction is undesirable because of reduced efficiency of the hydrogen obtaining process. The resulting carbon monoxide fed to the cell impairs its efficiency and reacts with the platinum catalyst contained in the cell and can contribute to cell damage. Therefore the process of reforming should be implemented with parameters ensuring maximum efficiency in obtaining hydrogen. Therefore the choice of catalyst and the process temperature, which may be 160-200^{o}C is pivotal. In the reforming process carried out outside the fuel cell, it is important that the reforming temperature is less than the cell operating temperature. In this situation, the heat generated in the fuel cell can be used for the reforming process.

3. Conclusions

Considering the environmental impact resulting from the combustion of fossil fuels including methanol, characterized by the emission of carbon monoxide, hydrocarbons, nitrogen oxides and particulate matter, as well as the efficiency of the processes for producing mechanical energy for vehicle drive systems, it can be concluded that the use of methanol as a fuel for fuel cells can be a good alternative to the currently used conventional fuels. The concept of adopting methanol in a function of a hydrogen carrier and storage is interesting from the perspective of ease of transporting and storing of fuel. But the key to this concept is the development of methanol reforming systems.

With a high efficiency of the realized processes, a high hydrogen production efficiency, and system miniaturization, in combination with high efficiency fuel cells, these solutions may find use in the means of mass transport such as buses, rail vehicles or various types of sea vessels. Therefore, with the currently observed rapid development of fuel cells, action should be taken to focus on the development of reforming systems.

References

[1] Christer J., Sutkowski M., Silnik Wärtsilä 32GD przeznaczony do spalania ciężkich paliw gazowych 2/2009 (137) - PTNSS-2009-206

[2] Crabtree G.W., Dresselhaus M.S., Buchanon M.V., 2004 – The Hydrogen Economy. Physics Today 57, 39–44.

[3] Avadikyan A., Cohendet P., Heraud J.A., 2003 – The Economic Dynamics of Fuel Cell Technologies. Springer-Verlag: Berlin.

[4] Tomczyk P., 2005 – Ogniwa paliwowe – czas rozwoju. Biuletyn Polskiego Stowarzyszenia Wodoru i Ogniw Paliwowych nr 1, 12–24.

[5] Hirschenhofer J.H., Stauffer D.B., Engleman R.R., 1994 – Fuel Cells. A Handbook (Revision 3), U.S. Departament of Energy, Raport DOE/METC-94/1006.

[6] Song Ch., 2002 – Fuel processing for low-temperature and high-temperature and low-temperature fuel cells. Catalysis Today 77, 17–49.

[7] Demusiak G., Dzirba D., Warowny W., 2005 – Rola gazu ziemnego w technologiach ogniw paliwowych. Przemysł Chemiczny 84, 808–814.

[8] Piela P., Czerwiński A., 2006 – Przegląd technologii ogniw paliwowych. Cz. 2. Typy ogniw paliwowych. Przemysł Chemiczny 85, 164–170.

[9] Santarelli M., Calì M., Macagno S., 2004 – Design and analysis of stand-alone hydrogen energy systems with different renewable sources. International Journal of Hydrogen Energy 29, 1571–1586.

[10] Perkins Ch., Weimer A.W., 2004 – Likely near-term solar-thermal water splitting technologies. International Journal of Hydrogen Energy 29, 1587–1599.

[11] Williams B.C., McMullan F., 1998 – Hot gas chemical Cleanup: current technological and commercial status. COAL-R092, Harwell, UK, 1998.

[12] Surygała J., 2006 – Obecne i perspektywiczne metody otrzymywania wodoru. Przemysł Chemiczny 85, 661–664.

[13] Srinivasan S., 2006 – Fuel Cells. From Fundamentals to Applications, Springer, N.Y.

[14] Tramer A., Ściążko M., Karcz A., 2005 – Techniczne aspekty wykorzystania gazu koksowniczego do pozyskiwania wodoru. Przemysł Chemiczny 84, 815–819.

[15] Jensen S.H., Larsen P.H., Mogensen M., 2004 – Hydrogen and synthetic fuel production from renewable energy sources. International Journal of Hydrogen Energy 29, 1571–1586.

[16] Radecka M., 2007 – Zastosowanie energii słonecznej do otrzymywania wodoru. Biuletyn Polskiego Stowarzyszenia Wodoru i Ogniw Paliwowych nr 2, 20–27.

[17] Machocki A., 2006 – Wodór z bio-etanolu dla ogniw paliwowych. Przemysł Chemiczny 85, 1045–1048.

[18] Zieliński J., Urbaniec K., Machowska Z., 2007 – Biomasa węglowodanowa pochodzenia naturalnego jako surowiec do produkcji wodoru. Przemysł Chemiczny 86, 1207–1214.

[19] http://www.seatrade-maritime.com/news/asia/first-methanol-powered-low-speed-diesel-engine-debuted-by-man-dt.html