Methanol as an Alternative Transportation Fuel

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ABSTRACT:

This paper is General review of methanol as an alternative transportation fuel, Analysis of conversion pathways from technical, economical and environmental point of view. Concerns with petroleum oil supplies and greenhouse gas emissions have stimulated research into new alternative fuels, including natural gas, ethanol, methanol, bio diesel, electricity and hydrogen. Methanol has been promoted as an alternative transportation fuel from time to time over the past forty years. In spite of significant efforts to realize the vision of methanol as a practical transportation fuel in the US, such as the California methanol fuelling corridor of the 1990s, it did not succeed on a large scale. This white paper covers all important aspects of methanol as a transportation fuel.

Keywords: methanol, transportation, use, production.

1. INTRODUCTION

In the aftermath of the first oil crisis in 1973, the potential of methanol as a liquid fuel to satisfy world transportation demand was highlighted by Reed and Lerner [Reed, W1]. Although methanol was being manufactured from hydrocarbon feedstock (natural gas and coal) through a gasification process at production levels small compared to diesel or gasoline, the process was well established and could be scaled. Any feedstock that could be gasified into synthesis gas could potentially be used in the manufacture of methanol. Soon afterwards, the potential of using renewable resources (biomass) were described. [Hagen] The ultimate approach, the recovery of CO2 from the atmosphere for methanol manufacturing, was discussed in 2005 by Prof. George A. Olah and his colleagues at the University of Southern California. They have coined the phrase "methanol economy," with methanol as a CO2 neutral energy carrier [Olah].

Initial interest in methanol was not in its role as a sustainable fuel, but as an octane booster when lead in gasoline was banned in 1976. The Clean Air Act Amendment in 1990 envisioned the potential of methanol blends as means of reducing reactivity of vehicle exhaust, although in the end, refiners were able to meet the goals with the use of reformulated gasoline and after treatment catalysts [EPA-1]. Interest in alternative fuels, including methanol, was also raised after the first and second oil crisis.

The only role for methanol currently as a transportation fuel in the world is as a component to make bio diesel, where it is used as a reagent to form methyl esters.

2. PRODUCTION PROCESSES AND FEEDSTOCKS

The typical feedstock used in the West in the production of methanol is natural gas, although a substantial fraction of the world's methanol is made from coal. Methanol also can be made from renewable resources such as wood, forest waste, peat, municipal solid wastes, sewage and even from CO_2 in the atmosphere. The production of methanol also offers an important market for the use of otherwise flared natural gas.

3. PRODUCTION PROCESSES

The methanol production is carried out in two steps. The first step is to convert the feedstock into a synthesis gas stream consisting of CO, CO_2, H_2O and hydrogen. For natural gas, this is usually accomplished by the catalytic reforming of feed gas and steam (steam reforming). Partial oxidation is another possible route. The second step is the catalytic synthesis of methanol from the synthesis gas. Each of these steps can be carried out in a number of ways and multiple technologies offer a spectrum of possibilities which may be most suitable for any desired application.

The steam reforming reaction for methane (the principal constituent of natural gas) is:

$$2\ CH_4 + 3\ H_2O \rightarrow CO + CO_2 + 7\ H_2 \text{ (Synthesis Gas)}$$

This process is endothermic and requires externally provided energy of reaction.
In the case of coal, the synthesis gas is manufactured through gasification using both oxygen and steam (including water-shift reaction):

$$C + \tfrac{1}{2}O_2 \leftrightarrow CO \text{ (Partial oxidation)}$$

$$C + H_2O \leftrightarrow CO + H_2 \text{ (Water-gas reaction)}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \text{ (Water-gas shift reaction)}$$

$$CO_2 + C \leftrightarrow 2\ CO$$

Biomass is converted into synthesis gas by a process similar to that of coal. In the case of biomass, the synthesis gas needs to be upgraded (through reforming or water-gas shifting) and cleansed to produce a synthesis gas with low methane content and proper H_2- to-CO ratio. There are tars (heavy hydrocarbons) as well as ash (that can be removed dry or as a slag) that are produced in the gasification, and they need to be removed upstream from the catalytic reactor Once the synthesis gas of the correct composition is manufactured, methanol is generated over a catalyst; in the case of natural gas,

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$$CO + CO_2 + 7 H_2 \rightarrow 2$$
$$CH_3OH + 2 H_2 + H_2$$

There are excellent catalysts that have been developed for the catalytic production of methanol, operating at relatively mild conditions (10's of atmospheres, a few hundred degrees C), with very high conversion and selectivity.

The natural gas process results in a considerable hydrogen surplus. If an external source of CO_2 is available, the excess hydrogen can be consumed and converted to additional methanol. The most favorable gasification processes are those in which the surplus hydrogen reacts with CO_2 according to the following reaction:

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

Unlike the reforming process with steam, the synthesis of methanol is highly exothermic, taking place over a catalyst bed at moderate temperatures. Most plant designs make use of this extra energy to generate electricity needed in the process. Control/removal of the excess energy can be challenging, and thus several processes use liquid-phase processes for manufacturing of methanol. In particular, Air Products developed the Liquid Phase Methanol Process (LPMEOH) in which a powdered catalyst is suspended in an inert oil. This process also increases the conversion, allowing single pas

TABLE NO. 1: PHYSICAL AND CHEMICAL PROPERTIES OF METHANOL FUEL:

Fuel type		Gasoline	Ethanol E100	Methanol M100	Methanol with cosolvent 50%methanol
Chemical formula					
RON					
MON					
(R+M)/2					
Specific gravity	Kg/l	0.75	.794	.796	.789
Stoic air/fuel ratio		14.6	9	6.4	8.8
Net heat of Combustion (LHV)	MJ/l	32	21	16	21
Net heat of Combustion (LHV)	MJ/kg	43	27	20	21

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Energy density	MJ/L	32	21	16	21
Lower flammability limit	%VOL	1.4	3	6	
Upper flammability limit	%VOL	7.6	19	36	
Autoignition temperature	K	514	638	738	
Flash temperature	K	230	285	280	
Laminar flame speed	MJ/kg	33	41	50	
Vapour pressure	psi	9	2.3	4.6	
Latent heat of vaporization	MJ/kg	.27	.85	1.1	.80
Vaporization energy/LHV	MJ/kg	0.006	0.031	0.058	0.03

Methanol has lower energy density than gasoline, ethanol or diesel (not shown). The engine fuel system needs to deliver larger flow rates of methanol than gasoline, and also the fuel range (miles driven on a tank-full) decrease. These effects depend on the blending level of methanol in the gasoline. For comparable vehicle efficiencies, the range is decreased by 50% when using M100. However the efficiency of operation of the engines in the vehicle demonstrations described in Section I is comparable or slightly better to that when using gasoline, when compensating for the lower heating value of the fuel [Pefley] With a dedicated methanol engine, the vehicle can be as efficient as a diesel, or about 25-30% more efficient than conventional vehicles operating on gasoline. [Brusstar] The range of dedicated high-efficiency methanol vehicles is about 30% lower than conventional gasoline vehicles.

The flame speed of stoichiometric air mixtures with ethanol and methanol at 1 bar, 300K are comparable to that of n-heptane, which is in small amounts present in Primary-Reference-Fuel (PRF) gasoline simulants. The flame speed of iso-octane, which is in high concentration in PRF gasoline, is substantially slower than the flame speed of either alcohol or n-heptane. Faster flame speed is useful for maximizing the performance of spark ignited engines.

Methanol has been used as a diesel fuel, and the heavy-duty engines described in Section I were compression ignited. Various approaches have been used to achieve ignition in methanol engines: electrical ignition (spark plug) or glow plug; ignition-improving additives; very high compression ratios (> 22:1); dehydrating some of the methanol into DME before injection; and pilot ignition with diesel fuel. Although any of these approached work, successful diesel engines used one or more combinations of the first three. [Short, Mueller] Modern interest in use of methanol as a fuel in compression engines has been displaced by DME, a methanol-derivative and an excellent compression ignited fuel. Trucks, refueling stations and DME plants have been completed in

Sweden, in the BioDME project, a combination of Chemrec, Volvo, the paper industry and government, generating the methanol/DME from black liquor [Landaly].

4. RELATIVE PROMISE AS A WIDELY USED TRANSPORTATION FUEL:

VEHICLES PERFORMANCE:

When methanol is used in FFV, the requirement of operation in conventional gasoline prevents substantial modification of the engine characteristics. Performance of methanol FFV's has been comparable or slightly better than conventional gasoline. [Nichols] However, options exist for better performance/efficiency using the excellent combustion properties of methanol. These options are discussed below.

- ***Light Duty Applications with dedicated vehicles***

Work done at EPA's National Vehicle and Fuel Emissions Laboratory with small- displacement, stoichiometric light-duty engines [Brusstar1] demonstrated improved brake thermal efficiencies over the baseline diesel engine and low steady state NOx, HC and CO, along with inherently low PM emissions. The engine is also expected to have significant system cost advantages compared with a diesel engine of comparable torque/power, mainly by virtue of its low-pressure port fuel injection (PFI) system and simpler aftertreatment. While recognizing the considerable challenge associated with cold start, the alcohol-fueled engine nonetheless offers the advantages of being a more efficient, cleaner alternative to gasoline and diesel engines.

An interesting alternative to dedicated methanol vehicles, which are needed to achieve the efficiency advantages described above, is to use two tanks, the main tank filled with gasoline and the second tank filled with methanol. This concept, Direct Injection Alcohol Boosted (DIAB), uses direct injection (DI) of methanol when the engine is prone to knock (usually at conditions of high torque). [Cohn] The charge cooling, which derives from the high latent heat of vaporization of methanol, is primarily responsible for the knock suppression. Due to the charge cooling from the DI process, the effective octane rating [Bromberg1] greatly exceeds the chemical octane rating that these fuels would exhibit using conventional induction methods such as port fuel injection (PFI). In the DIAB concept, DI of the knock suppressing fuel is used only in the amount required to prevent knock and gasoline is supplied to the cylinder by conventional PFI. Since the engine operates at stoichiometry (using a typical oxygen feedback), a very high specific torque output can be produced while emissions can be maintained at low levels through the well-proven and relatively simple three-way catalyst system without the use of EGR as a major diluent. The technology opens the possibility of a spark-ignited gasoline engine operating at high compression ratio (12 - 14) and high boost ratios of 2.0- 2.5 times ambient pressure, which is sufficient to produce a torque output equivalent to or greater than more highly turbocharged heavy duty diesel engines operating lean with significant EGR. The methanol-boosted DIAB engine can be almost as efficient (as measured by BTE, brake thermal efficiency) as a diesel and have comparable specific CO2 emissions as well. The concept has been demonstrated and proven in systematic dynamometer tests at Ford [Stein]. In addition, Honda has independently investigated the concept [Kamio].

- ***Medium/Heavy Duty Applications with dedicated vehicles***

Following tests with light duty SI methanol engine, the EPA's National Vehicle and Fuel Emissions Laboratory conducted engine tests for medium duty applications in a dedicated alcohol (methanol and ethanol) engine, using high level blends of alcohols. [Brusstar] A 4.5-liter V6 diesel engine was modified for spark ignition (SI) operation and port fuel injection (PFI), for use with M85. The high octane number of alcohol fuel, together with its latent heat of vaporization, makes it well suited to high compression ratio and boosted applications [Bromberg2, Kapus]. Moreover, alcohol's high laminar flame speed relative to gasoline [Marinov] enables greater charge dilution with EGR, reducing the need for throttling at light to moderate loads, while still allowing for stoichiometric operation. Stoichiometric operation eliminates the need for a lean NOx catalyst and instead lower-cost, proven three-way catalysts can be used. This technology approach was developed as part of EPA's Clean Automotive Technology Program. [Brusstar1] Brusstar and Gray concluded that "the engine developed … shows promise with either E85 or M85 fuel, as a clean and efficient alternative to other heavy duty engines." They concluded that the M85 and E85 engines could provide efficiencies comparable or higher than the diesel, in dedicated fuel, high compression ratio turbo charged/downsized engines (allowed because of the high antiknock properties of methanol or ethanol).

5. METHANOL AS TRANSPORTATION FUEL IN THE WORLD:

Methanol has attractive features of use in transportation:

- It is a liquid fuel which can be blended with gasoline and ethanol and can be used with today's vehicle technology at minimal incremental cost. THERE ARE NO TECHNICAL HURDLES.
- It is a high octane and safe fuel, and has combustion characteristics that allow engines to match the best efficiencies of diesels while meeting current pollutant emission regulations, although it has the drawback of reduced energy density.
- There is a very large potential supply of methanol since it can be made from natural gas, coal and biomass feedstocks

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- It is currently produced from natural gas and coal at costs that are comparable to or less than gasoline and diesel fuel on an energy basis
- It is an attractive green house gas reduction option in the longer term, if produced from renewables/biomass. A bridging option is to use methanol derived from natural gas, with a CO2 intensity that is no worse than conventional fuels. There is also the possibility of achieving greenhouse gas reduction by CO2 sequestration in the methanol generation process.
- Multiple ways exist for introduction of methanol into the infrastructure (light blends or heavy blends) and into the vehicles (light duty or heavy duty applications). The optimal approaches are different in different countries and in different markets.

6. CONCLUSION

- Methanol is a safe and viable transportation fuel, although it is not as good a fuel as ethanol in terms of energy density and ease of handling. While significant investment needs to be made for large-scale methanol deployment in the transportation sector, there is no technical hurdle both in terms of vehicle application and of distribution infrastructure.
- As a long term strategy to substantially replace petroleum fuel by renewable, methanol offers the following advantage
    - Thermo-chemical production of methanol from biomass is energetically efficient and the technology has been well developed.
    - In comparison, large-scale bio-chemical production of ethanol from cellulose biomass is promising, but currently the technology is not sufficiently developed.
- Methanol from non-renewable could be used as a bridging option towards transition towards renewable methanol. Methanol can readily be made from natural gas or coal (there is plentiful supply of both feedstock's) so that large-scale production, infrastructure, and vehicle use could be developed. The system that is developed can then be applied to renewable methanol. It should be further noted that such system is also amenable to the use of renewable ethanol, should large scale bio-production of cellulose ethanol be realized in the future.
- Non-crop based biomass derived fuels have the potential to supply a major part of the US transportation liquid fuel; this is especially so if substantial decrease of energy use in transportation is achieved. Renewable methanol from thermo-chemical biomass conversion is an attractive and viable future fuel option.

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