Methanol: Versatile Potential Fuel
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Methanol: Versatile Potential Fuel

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IN AN EFFORT TO FIND LIQUID FUEL replacements for diminishing gasoline supplies, ethanol has so far received most of the attention and financial support. However, methanol could also be used to help solve the liquid fuel crisis. In fact, it may be easier to convert cellulosic feedstocks to methanol by **pyrolysis**[1] (destructive distillation) than to convert the same feedstock to ethanol using acid and/or **enzymatic hydrolysis**.

Characteristics of Methanol

Methanol (CH_3OH), also known as methyl alcohol, wood alcohol or methylated spirit, is a colorless, odorless and water-soluble liquid (13)[2]. At a molecular weight of 32.0 g, it is the lightest of the alcohols. Because it has one carbon atom less than ethanol (C_2H_5OH), its heat of combustion is about 22% less.

Methyl alcohol was first studied by Dumas and Peligot in 1834. Methanol, as methyl esters, is found naturally in many plants that are constituents of essential oils. Examples are salicylate, anthranilate and cinnamate (14).

Methanol will corrode lead, zinc and magnesium parts and could lead to deterioration of plastic and rubber components in automobile engines (5). It is **miscible** with water in all proportions, and also miscible with most organic liquids. It is an effective and widely used antifreeze for automobiles. Prolonged breathing of the poisonous vapors can cause blindness, so it must be used only in well-ventilated places (3). Methanol evaporates quickly. It is a good **solvent** for dyes, gums and some vegetable waxes. It contains no trace metals, sulfur or polynuclear aromatics (7).

Methanol can cause watering of the eyes if a rich air-to-fuel ratio is combusted, as in race cars (6). Using a leaner mixture will correct this problem. Lean mixtures lead to clean, odorless exhaust emissions. Methanol is less of a fire hazard than gasoline. However, the vapor-air mixture found in the storage tank is more explosive than the rich fuel and air mixture in gasoline tanks (5). Methanol, as a pure chemical, does not degrade in storage, and is easily transported in tank cars, tank trucks and tankers; it can also be moved in oil and chemical pipelines (13).

Comparison with Ethanol

Ethanol is the only nonpetroleum liquid automotive fuel commercially available, and the Department of Energy (DOE) estimates that it will be the only one available in quantity before 1985 (5).

Both methanol and ethanol are good solvents, and under certain circumstances (e.g., when ethanol contains water), require highly corrosion-resistant storage containers. While drinking ethanol may only lead to a bad hangover, methanol is toxic if drunk, and may cause death (11).

Ethanol has a higher volumetric energy content than methanol and forms a more stable gasoline blend at higher concentrations (11). Engine modifications are generally unnecessary with blends of up to about 20% ethanol, but are required to burn methanol blends higher than 10%. Also, **phase separation** due to water contamination is more severe in methanol blends than in ethanol blends.

Both pure methanol and ethanol are superior to gasoline when used in an engine specifically designed to exploit alcohol's unique properties (9). The **blending octane values** (BOV) of methanol and ethanol are 130 and 110-160, respectively (13). The following formula is used to compute the BOV:

$$BOV = (O_b = O_g (1-x))/x$$

where O_b and O_g are the octane numbers of the alco-

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[1]*See Glossary, p. 6 for definition of underscored technical terms.*

[2]*The numbers in parentheses refer to the list of references at the end of this article.*

hol-gasoline blend and the pure gasoline, respectively, and x is the volume fraction of the alcohol in the gasoline.

Versatility of Methanol

Methanol can be made from a variety of different raw materials (e.g., biomass, municipal and agricultural wastes, natural gas, petroleum, oil shale, coal, lignite) and used in a number of ways: for automotive fuel, plastics production, electricity generation, fuel cells and space heating. Figure 1 shows the various pathways to and from methanol. The basic raw ma-
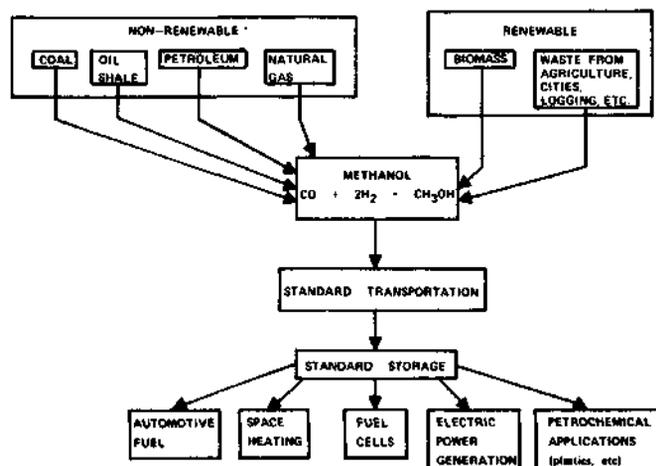
* Technically, these fossil fuels are renewable,

but it takes hundreds of thousands of years,

thus making them practically nonrenewable.

Fig. 1 — Pathways to and from methanol. Adapted from References (10) and (13).

terial is anything that contains carbon. Table 1 summarizes some properties of methanol, ethanol and gasoline.

Methanol Production

Methanol is produced from **synthesis gas**, a mixture of carbon monoxide and hydrogen (2, 8). This feedstock traditionally came from wood **pyrolysis**. More recently, it has been produced by natural gas reformation.

Crude methanol is obtained when two moles of hydrogen and one mole of carbon monoxide react in a catalyst-filled converter under pressures ranging from 1,500 to 4,000 psig (8). The crude gas is then refined. The reaction is:

$$CO + 2H_2 \longrightarrow CH_3OH$$

In practice, synthesis gas contains both carbon monoxide and carbon dioxide; therefore, both the carbon monoxide and part of the carbon dioxide are converted to methanol (2). The reaction with carbon dioxide is either:

$$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O \quad \text{(1 step)}$$
$$\text{or} \quad CO_2 + H_2 \longrightarrow CO + H_2O$$
$$CO + 2H_2 \longrightarrow CH_3OH \quad \text{(2 steps)}$$
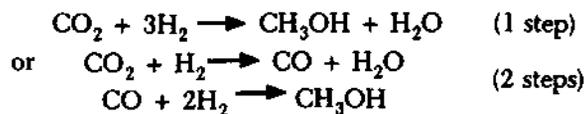
Any carbon-containing material can be used to synthesize methanol. Synthesis of methanol from coal, lignite, wood waste, agricultural residue or garbage requires more steps and gives lower yields than synthesis from natural gas.

Table 1 — Properties of Methanol, Ethanol and Gasoline.

Property	Methanol	Ethanol	Gasoline
Molecular formula	CH_3OH	C_2H_5OH	C_4C_{12}hydrocarbons
Molecular weight (g)	32.0	46.0	100 - 105
Composition, percent by wt			
Carbon	37.5	52.2	85 - 88
Hydrogen	12.6	13.1	12 - 15
Oxygen	49.9	34.7	0
Specific gravity (1)*	0.796	0.794	0.72 - 0.78
Density (lb/gal) (1)	6.63	6.61	5.8 - 6.5
Boiling point (°F) (1)	149	173	80 - 437
Flash point (°F) (1)	52	55	- 45
Latent heat of vaporation (Btu/lb) (4)	474	364	152
Heat of combustion (Btu/lb) (4)	9,612	12,780	20,260
Stoichiometric ratio (3)	6.5	9.0	14.7
Autoignition temperature (°F) (1)	867	793	495
Research octane number (4)	109	107	93
Road blending octane value (13)	130	126 (avg.)	—

*Numbers in parentheses refer to References on page 6.
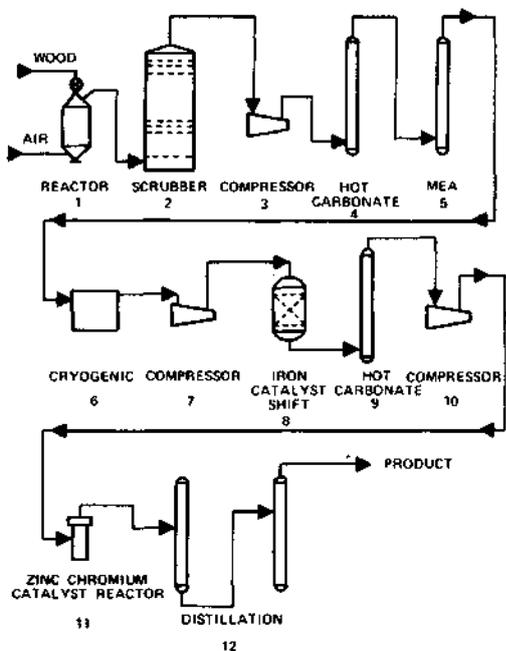
Fig. 2 — Methanol synthesis from wood waste (8).

Hokanson and Rowell (8) provide a 12-step process for converting wood waste into methanol (see Fig. 2).

1. The wood waste is partially oxidized.

2. The resulting crude gas is cleaned and cooled. After partial oxidation, the crude gas contains water vapor, tars, organics, hydrocarbons, nitrogen and carbon dioxide. After scrubbing these materials, the gas (primarily hydrogen and carbon monoxide) is cooled from about 180°F to 90°F.

3. The gas is compressed to about 100 psig.

4. Carbon dioxide is removed from the gas. During this phase, a hot potassium carbonate system is used to reduce the carbon dioxide content to about 300 parts per million (ppm).

5. Any residual carbon dioxide is removed. Here, the carbon dioxide content is further reduced to 50 ppm by scrubbing with monoethanolamine (MEA).

6. Nitrogen and hydrocarbons are removed from the gas. This is accomplished in a low temperature (cryogenic) system.

7. The gas is further compressed to 400 psig.

8. The gas is shifted to two parts hydrogen and one part carbon monoxide. This step is required because after step 6 the syngas (synthesis gas) is not yet in the ratio (2 moles of hydrogen to 1 mole of carbon monoxide) required for methanol synthesis. The shifting enables a portion of the carbon monoxide to react with water and form additional hydrogen (in the presence of an iron catalyst). This reaction is:

$$CO + H_2O \xrightarrow{\text{iron catalyst}} H_2 + CO_2$$
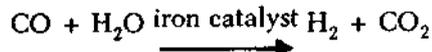
9. Carbon dioxide formed during the shift is removed. The hot potassium carbonate is again used as the removal agent.

10. The gas is compressed to 1,500 to 4,000 psig.

11. The hydrogen and carbon monoxide formed during step 8 is converted to methanol. This takes place in a zinc chromium catalyst reactor where up to 95% of the syngas is converted to methanol.

12. The crude methanol obtained in step 11 is refined. A distillation column is used to separate the methanol from higher alcohols (primarily iso-butanol, ethanol and propanol).

Gasifier Processes

Several processes (8) are available for making syngas for methanol production:

Purox — This process was developed by Union Carbide for the partial oxidation of garbage, using pure oxygen. The reactor-gasifier uses a moving bed system. Oxygen flows up through the down-flowing residue. The material passes successively through stages of drying, reduction and oxidation. Ash is removed in molten form at the bottom at a temperature of about 3000°F. A high-moisture crude gas comes out the top at a temperature of about 200°F.

According to a study by the City of Seattle, Wash., this process will produce 370 lbm of methanol from a ton of solid waste (10)

Moore-Canada — Developed by Moore-Canada of Richmond, this process employs a moving bed reactor that produces low Btu gas from wood waste. Air, rather than pure oxygen, provides the oxidizing medium. Using air leads to a high-nitrogen gas that has a heating value of 180 Btu per standard cubic foot (scf), compared to the Purox process which is 350 Btu/scf.

The Lurgi process — This reactor is designed to gasify coal with oxygen and steam at 300 to 400 psig. Only non-coking coal particles ranging from 3/8 to 2 in. can be used.

Other gasifier designs include the following:

a) — the Battelle design, which uses a moving bed reactor for partial oxidation of municipal refuse

b) — the Thermex process for gasification of wood waste to produce char and a low Btu gas

c) — the Copeland process employing fluidized reactors for the disposal of organic matter in waste liquor for the pulp industry. (It can also handle other wood waste and sludge.)

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d) — the Winkler process which uses a fluidized coal gasifier that operates close to atmospheric pressure

e) — the Koppers-Totzek process which pulverizes coal, using steam and oxygen under slagging conditions at atmospheric pressure and temperatures up to 3500°F

Utilization of Methanol

Spark-ignition and Diesel engines — Methanol, both pure and in blends, has been tested for use in automobiles. Adelman, Andrews and Devoto tested methanol extensively in a modified six-cylinder 1970 American Motors Gremlin (2, 12). The following modifications were made before the tests: the diameter of the carburetor jet was enlarged to 1.5 times what is required for operation on gasoline to accommodate methanol's lower air-to-fuel ratio (stoichiometric ratio), and the intake manifold was heated with exhaust heat to provide for methanol's higher heat of vaporization (474 Btu/lb for methanol, 153 BUT/lb for gasoline). In addition, a catalytic muffler and an air injection system were also installed to reduce hydrocarbon and carbon monoxide emissions, and the vacuum spark advance was disconnected to reduce oxides of nitrogen emissions. The vehicle then not only ran on **neat methanol**, but also passed 1975-76 federal emissions standards (Table 2).

In comparing methanol to isooctane, Ebersol and Manning obtained the following results at the same power outputs and equivalence ratios (12,13):

1. Unburned fuel in the exhaust was only 10 to 30% that of isooctane.

2. Methanol emitted lower levels of nitric oxide than isooctane.

3. Methanol emitted higher levels of aldehydes than isooctane.

The highest efficiency recorded for an automotive engine was obtained on a modified Brandt engine

Table 2 — Emissions from a 1972 Gremlin Modified for Methanol and Equipped with a Catalytic Converter.

| Fuel | Emissions (gm/mile) | | |
	Unburned hydrocarbons	CO.*	NO$_{x}$†
Gasoline	2.20	32.5	3.2
Methanol	0.32	3.9	0.35
Federal standards‡ . . .	0.41	3.4	0.40

* carbon monoxide

† oxides of nitrogen

‡ 1973 projection of 1975-76 federal standards

Source: (13).

burning methanol (9). The four-cylinder engine, tested by the National Experiment Station at Bellevue, France, was modified to burn straight alcohol. Among other modifications, the compression ratio was raised from 5.65:1 to 12:1.

Modifications for use in automobiles — The following modifications are needed to run current engines on pure methanol:

1. The stoichiometric ratio (ratio of air-to-fuel consumed) should be decreased from 14.7 (for gasoline) to 6 for methanol (13). To do this, the diameter of the carburetor jet must be enlarged by 50% to allow for methanol's low stoichiometric air-to-fuel ratio.

2. Heat from the exhaust can be recycled to the fuel intake manifold to help vaporize the fuel.

3. Some provision must be made for cold starting (10). The engine could be started on another fuel, propane, for example, until it warms up, then switched to run on methanol.

4. Plastic and other parts of the engine that could deteriorate from exposure to methanol must be replaced by corrosion-resistant materials. This includes magnesium fuel-system parts, electric fuel pumps and resin-coated paper fuel filters (5, 10). High concentrations of methanol in methanol-gasoline blends may also lead to this corrosion problem.

5. On a volume basis, a larger tank will be needed in automobiles to provide the same driving range as a tankful of gasoline.

Advantages as automotive fuel:

1. Blending gasoline with methanol improves the octane rating of the blend. When straight or neat methanol rather than gasoline is used, the engine can be operated at a higher compression ratio, thus increasing overall power output. For every increase of 1 point in the fuel octane rating, the compression ratio can be increased by about 4% (15).

2. Because it emits less pollution, methanol burns cleaner than gasoline (5). Straight methanol also reduces oxides of nitrogen emissions, compared with gasoline. In addition, exhaust emissions of carbon monoxide and hydrocarbons may be lower for methanol, compared with gasoline (7).

3. With its 50% (by weight) oxygen content, (12 g carbon, 4 g hydrogen and 16 g oxygen) and relatively low air-to-fuel ratio, methanol burns more efficiently than gasoline (7).

4. Methanol has a higher thermal efficiency (miles/Btu) than gasoline, but a lower volumetric effi-

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ciency (miles/gal) (7). Although methanol has only half the heating value of gasoline, it produces more moles of combustion products and has a higher heat of vaporation; thus, it actually provides more power in the cylinder than does gasoline (12).

Disadvantages as automotive fuel

1. Methanol blends, if water-contaminated, are susceptible to **phase separation**, which among other things, could result in engine loss of power. The engine does not break down; it simply stops running.

2. The use of methanol can lead to vapor lock problems (15). This occurs when fuel vapor is trapped in the car's fuel pump, preventing it from operating properly. Methanol-gasoline blends are more volatile than pure gasoline, thus blends could develop vapor lock problems.

3. Gasoline and methanol are not interchangeable in one carburetor (15). Therefore, a switch from the pure state of one fuel to another will require changing carburetors. Perhaps an adjustable carburetor can be designed to solve this problem.

Other Uses

Methanol can be used as a utility fuel to fire conventional boilers (2), for home heating and in power plants to generate electricity without pollution. It is also suitable for power generation by fuel cells (13).

The Department of Energy (5) lists these potential applications of methanol:

— in spark-ignition engines—10% blend, 20% blend or 100% methanol—as a near-term application (NTA)

— in diesel engines—10 to 30% methanol/90 to 70% diesel fuel or 100% methanol—as a long-term application (LTA)

— in boilers—100% methanol—(LTA)

— in gas turbines—100% methanol—(NTA)

— in utility fuel cells—100% methanol—(LTA)

— as petrochemical feedstocks—100% methanol—(NTA).

In a test of methyl-fuel (a mixture of methanol and small amounts of ethanol, propanol and isobutanol) against No. 5 fuel oil and natural gas, the following observations were made (13):

1. No release of particulates from the stack occurred.

2. NO_x emissions were less than those for either natural gas or fuel oil.

3. Carbon monoxide concentrations were less than those for oil and natural gas.

4. No sulfur compounds were emitted.

5. Methanol produced negligible amounts of acids, aldehydes and unburned hydrocarbons.

6. Previous deposits of soot (from other fuels) were burnt off with the use of methanol, permitting higher heat transfer rates.

Mobil Oil Corporation has developed a process for making gasoline from methanol. The MTG (methanol-to-gasoline) process produces a high-octane, sulfur-free and nitrogen-free gasoline fuel. According to New Zealand's Liquid Fuels Trust Board, the Mobil process has an economic advantage over the Fischer-Tropsch technology (6). Mobil is expected to build a commercial plant in New Zealand that will provide 12,500 bbl/day of sythetic gasoline from natural-gas-derived methanol.

Conclusion

Because of its versatility and potential as a liquid fuel, methanol provides a renewable source of energy that warrants attention. Its toxicity and tendency to cause corrosion need further research in an effort to make methanol a safe fuel.

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Glossary

Acid Hydrolysis — hydrolysis through the action of an acid (hydrolysis defined below).

Blending Octane Value — a measure of the octane- enhancing ability of alcohols blended with gasoline.

Cryogenic — relating to either the production or the effects of low temperatures.

Enzymatic Hydrolysis — hydrolysis through the action of enzymes (hydrolysis defined below).

Hydrolysis — a decomposition process that involves breaking a chemical bond and adding elements of hydrogen and oxygen from water.

Miscible — capable of being mixed at any ratio without separating into two phases.

Neat Methanol — straight methanol.

Phase Separation — a result of water contamination; occurs when water and part of the alcohol bleed out of the alcohol-gasoline blend and settle to the bottom of the gas tank.

Pyrolysis — a chemical change brought about by the action of heat.

Solvent — liquid substance that dissolves or disperses another substance.

Synthesis gas — a gas produced through the combination of elements or simpler compounds.

Volatility — the state of readily vaporizing at relatively low temperatures.