USE OF METHANOL AS A TRANSPORTATION FUEL

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The capability of methanol to replace petroleum fuels has been known for a long time. Now that the future availability of crude oil is in question, methanol is receiving renewed interest since it can be readily made from remote natural gas and from the world’s extensive coal and biomass resources. Methanol has a long history of use in racing vehicles where it is valued both for its power producing properties and its safety aspects (primarily the fact that it burns without producing black smoke). There was high interest in using methanol as a gasoline blending component for its octane value and emissions characteristics in the U.S. when lead was phased out of gasoline and more stringent emission standards were passed. Several methanol/cosolvent blends were approved for use but the oxygenate methyl tertiary butyl ether (which uses methanol in its manufacture) quickly became more popular and displaced any methanol/cosolvent blends. During the 1980s and through much of the 1990s, most gasoline in Western Europe contained a small percent of methanol, usually 2-3%, along with a cosolvent alcohol. This paper recounts the U.S. experience and lessons learned with methanol fuels both in blends with gasoline and as a near-near fuel (i.e., M85, 85% methanol and 15% gasoline). Topics covered include significant blend regulatory rulings, the impact of blending methanol on the physical and chemical properties of gasoline, vehicle operational and emissions impacts, “well-to-wheel” greenhouse gas emissions, flexible-fuel vehicle characteristics and experience, use in heavy-duty vehicles and non-road engines, and infrastructure (storage, distribution, and dispensing) impacts.

I. Executive Summary

The capability of methanol to replace petroleum fuels has been known for a long time. Now as the future availability of crude oil is increasingly called into question, methanol is receiving renewed interest since it can be readily made from remote natural gas and from the world’s extensive coal and biomass resources. Much work was done previously around the world to identify the proper ways to design and modify vehicles to use methanol either as a neat fuel or in blends with gasoline. Extensive fleet tests were also conducted, with the majority occurring in the U.S. where methanol vehicles were sold commercially in the early 1990s. This report presents several significant findings from that work and experience.

Methanol has a long history of use in racing vehicles where it is valued both for its power producing properties and its safety aspects (methanol is harder to ignite, creates less radiant heat, and burns without producing black smoke). There was significant interest in using methanol as a gasoline blending component for its octane value and emissions characteristics in the U.S. when lead was phased out of gasoline and more stringent emission standards were established. Several methanol/cosolvent blends were approved for use but the oxygenate methyl tertiary butyl ether (which used methanol in its manufacture) was preferred. During the 1980s and through much of the 1990s, most gasoline in Western Europe contained a small percent of methanol, usually 2-3%,
along with a cosolvent alcohol. Today, China is the leader in using methanol as a transportation fuel where between 3 and 5 million tons were used last year.

Using methanol as a gasoline blending component represents the most expeditious way to use large amounts of methanol as a transportation fuel. Methanol addition increases octane value and will cause decreases in hydrocarbon, toxic, and carbon monoxide emissions. Most modern fuel systems with feedback control should be able to accommodate low-level methanol blends (up to 10%) without difficulty, though exceptions are possible. Using low-level methanol blends does require good house-keeping practices in transport, storage, and dispensing, to assure that water addition is minimized to prevent phase separation. Adding methanol to gasoline increases vapor pressure which could lead to increases in evaporative emissions during warm weather. Addition of a cosolvent (typically higher alcohols) ameliorates both these issues and adjustment of the gasoline specifications can eliminate the increase in vapor pressure. Careful tailoring of the gasoline used to make methanol blends can maximize the benefits of methanol addition and increase gasoline refining efficiency.

In the early 1980s, there was considerable interest in using methanol as a fuel for both petroleum displacement and air quality reasons. To achieve the quickest displacement and largest impact on air quality, it was desired to use methanol neat or near-neat as a transportation fuel. In the U.S., fleet demonstrations of methanol vehicles were very successful given the vehicles’ low emissions, 20% increase in power, and 15% increase in energy efficiency. However, the decrease in vehicle range (the fuel tank could not be expanded sufficiently to counteract the decrease in methanol heating value) and the sparse number of methanol refueling facilities caused methanol vehicle drivers great anxiety. This directly led to the development of methanol flexible fuel vehicles (FFVs) which could use methanol or gasoline in the same tank through the use of an alcohol fuel sensor that measured the methanol content of the fuel going to the engine. This freed drivers from worrying about running out of fuel while the development of methanol infrastructure caught up with demand. The objective was to introduce large numbers of methanol FFVs, build a broad fueling infrastructure network, then transition back to dedicated methanol vehicles. FFVs performed the same or better than their gasoline counterparts with the same mass emissions, though this was also a plus since methanol emissions were shown to be less reactive. Fleet tests of FFVs occurred around the world with the most in the U.S. FFVs peaked in 1997 in the U.S. at just over 21,000 with approximately 15,000 of these in California which also had over 100 refueling stations.

Relatively few changes are needed to turn a vehicle into a methanol FFV, and the incremental cost is less than the cost of most optional equipment on cars today. There is a drawback to methanol FFVs – in order to accommodate gasoline, the engine cannot be modified to achieve the power gains and efficiency improvements possible when only using methanol as a fuel except through the addition of a major change such as variable compression ratio. Tuning methanol FFVs to favor methanol over gasoline will allow some of these benefits to be realized.

In parallel with FFV development in the U.S., was the development of a methanol fuel specification what would allow vehicles to achieve cold-start and improve the visibility of methanol flames. The end result was a blend of 85% methanol with 15% gasoline known as M85. The ASTM in the U.S. maintains the specification for M85 which has been recently updated (2007).

The physical and chemical properties of methanol make it very well-suited for use as a spark-ignition engine fuel, but its ability to combust without forming soot (due to the lack of carbon-to-carbon bonds) has attracted diesel engine designers to find ways of using it as well. Many ways of using methanol in diesel engines have been researched including use in blends, emulsions, fogging, with the addition of ignition improvers, in dual injection engines, and in engines modified to achieve direct compression ignition of methanol. Note that of these methods, only use of ignition
improvers and compression ignition resulted in engines that displaced all diesel fuel use, though complete displacement was not viewed as a requirement since the emissions benefits of methanol were typically greater than the percent diesel fuel it replaced. Diesel engines could also be converted to spark ignition, but this change essentially makes them Otto Cycle engines. Looking forward, homogeneous charge compression ignition (HCCI) systems offer the opportunity to design both heavy-duty and light-duty engines for compression ignition of methanol and methanol/dimethyl ether blends with very low emissions and high efficiency.

The technology for bulk storage of methanol is well-established. Methanol fuels can be accommodated at retail service stations assuming the proper tank, piping, and dispenser is used. New dry-break, spill-free dispensing nozzles alleviate safety and human contact concerns about refilling methanol vehicles.

Greenhouse gases (GHGs) from methanol made from coal will increase relative to using gasoline unless carbon dioxide sequestration is implemented. Methanol made from natural gas will have similar GHGs as gasoline. Methanol made from biomass should have significantly lower GHGs.

II. Introduction

The capability of methanol to replace petroleum fuels has been known for a long time. The ease with which crude oil can be extracted and made into fuel has long made petroleum-based gasoline and diesel fuel the preferred choices for transportation vehicles. Now that the future availability of crude oil is in question, methanol is receiving renewed interest since it can be readily made from remote natural gas, numerous biomass resources, and from the world’s extensive coal resources. Methanol is an excellent fuel for internal combustion vehicles, and fuel cell vehicles using either proton exchange membrane fuel cells that operate on hydrogen or direct methanol fuel cells.

Like hydrogen, methanol can also be used as an energy carrier with the advantage of being a liquid fuel with high energy density and proven safety. As envisioned in the Methanol Economy®, methanol is made from carbon dioxide via catalytic reduction with hydrogen or by electrochemical reduction with water [1]. The carbon dioxide would initially come directly from fossil-fuel power plants and chemical plants and eventually from the atmosphere itself. Methanol produced efficiently from atmospheric carbon dioxide and hydrogen from water can provide energy for fuel use and could be the raw material from which synthetic hydrocarbons and chemicals are made.

Methanol has a long history of use in racing vehicles where it is valued both for its power producing properties and its safety aspects relative to gasoline: it is harder to ignite, it burns more slowly, it emits no black smoke and emits lower radiant energy, which makes surrounding materials less likely to catch fire. Interest in using methanol as a blending component in the U.S. was intense when the octane enhancer lead was legislated out of existence. It received additional interest with passage of the Clean Air Act Amendments of 1990, which envisaged vehicles designed to run on methanol, either neat or as M85, to meet various special programs for alternative fuel vehicles. The automakers were very successful at engineering vehicles to use M85. These vehicles performed the same or better than their gasoline counterparts with the same mass emissions, though this was also a plus since methanol emissions were shown to be less reactive. Fleet tests of M85 vehicles occurred around the world with the most in the U.S. M85 vehicles peaked in 1997 in the U.S. at just over 21,000 with approximately 15,000 of these in California which also had over 100 refueling stations. But automakers and refiners quickly showed that they could meet these emission standards with reformulated gasoline and states convinced the U.S. Environmental
Protection Agency (EPA) to let them opt-out of the alternative fuel vehicle programs. In addition, by the mid-1990s, competition from other alternative fuels, notably ethanol and natural gas, dampened some of the impetus to implement methanol. Ethanol represented the greatest competitor since the same technology to make M85 vehicles worked equally well to make vehicles using 85% ethanol (E85). Ethanol's tax credit, long history of use in blends, and strong lobbying support from agricultural interests eventually displaced M85 in the U.S. Today, there are over 7 million E85 vehicles in the U.S. [2], though only about 150,000 of them use E85 regularly [3]. Methanol is currently used as a component to make biodiesel, where it is reacted to form methyl esters. China is currently the largest user of methanol for transportation vehicles in the world.

Interest is again high to use methanol as a transportation fuel, particularly in regions of the world where there is an abundance of readily available feedstocks (coal, natural gas, biomass) from which methanol can be produced. Much work was done in many countries previously to identify the proper ways to modify vehicles to use methanol either as a neat fuel or in blends with gasoline. This report presents many of the most significant findings from that work.

III. Methanol Blend Regulation

While it has long been known by engine designers that methanol could be used as an internal combustion engine fuel, it was not until emissions and oil dependency concerns were raised in the United States that methanol was recognized more widely as a potential transportation vehicle fuel. In 1970, Roberta Nichols and co-workers at the Aerospace Corporation published a report identifying the emissions benefits of methanol as a transportation fuel [4]. Later in 1970, a methanol-fueled vehicle was entered by Henry Adelman of Stanford in the Clean Air Car Race. His vehicle (an AMC Gremlin) placed first in the liquid fuel class for overall performance while meeting the 1975 emission standards, despite very few engine modifications. This demonstration of the capabilities of methanol piqued interest in its use. Then, in 1971, the EPA announced a proposed rulemaking to phase out use of lead in gasoline. This gave interest in methanol another boost because of methanol's high octane rating. The EPA followed the interest in methanol closely and in 1973 commissioned both Exxon (now ExxonMobil) and the Institute of Gas Technology (now the Gas Technology Institute) to conduct resource-through-end-use studies of alternative fuels to petroleum for highway transportation. Both of these studies rated methanol very highly for its ability to use existing infrastructure, for its non-petroleum resource base, for its low emissions, and because it could be used in internal combustion engines without drastic modifications. Then in the fall of 1973, the Arab oil embargo of crude oil sales to the U.S. greatly escalated the interest in alternative fuels, of which methanol was prominent. Following is the history and status of methanol regulation as a fuel in the U.S. and Europe.

A. United States

The Clean Air Act amendments of 1977 included the creation of section 211(f), which prohibits the introduction into commerce of any fuel or fuel additive that is not substantially similar to fuels used in vehicle certification. The EPA may issue a waiver of the prohibition if a party demonstrates that the fuel/additive will not cause or contribute to the failure of any emissions control device or system.

1. EPA Waivers Granted and Oxygenate Allowances as “Substantially Similar”

The first waiver request for an oxygenated compound received by EPA was submitted by Gas Plus and the Illinois Department of Agriculture in June 1978 for “Gasohol”, a blend of 90% gasoline and 10% ethanol. The Gasohol waiver application included no specifications defining use of
the waiver. Because EPA issued no notice granting the waiver, it also failed to impose any specifications. This led to a need to subsequently issue interpretation of the waiver in April 1982 clarifying that blends of less than 10% could also be used [5]. Although it is not specified anywhere, EPA has also interpreted these percentage limits to apply by volume rather than by weight or mole. The 10% limit on ethanol was generally believed to translate to approximately 3.5-3.7% oxygen in the gasoline by weight based on sample analysis.

In 1979, EPA issued waivers for up to 7% tertiary butyl alcohol (TBA) [6], for up to 7% MTBE [7], and for up to 5.5% of a combination of methanol with TBA in equal parts [8]. These waivers allowed about 2% oxygen by weight in the fuel blend. In October 1980 EPA promulgated its first real Interpretive Rule defining what fuels and additives were considered substantially similar to certification fuels [9]. (Prior to this, it considered only those identical to fuels and additives used in certification to be “substantially similar” or “sub-sim.”) It treated aliphatic ethers and alcohols other than methanol as sub-sim in volumes contributing 2% or less oxygen by weight.

In July 1981, EPA issued a revised Interpretive Rule further defining “sub-sim.” It allowed for use of up to 2.75% methanol with an equal volume of TBA (or higher alcohols), as previously provided by waiver, essentially confirming that allowances made in waivers are applicable to all marketers, not merely the applicant [10]. EPA was asked in this rulemaking to increase the oxygen limit to 3.7%, equivalent to that of Gasohol, but EPA declined to do so based on observed NOx increases, keeping the sub-sim oxygen limit at 2% [11].

In November 1981, EPA granted a waiver for use of ARCO’s “Oxinol,” allowing up to 4.75% methanol with an equal amount of TBA, which provides approximately 3.5 - 3.7% oxygen [12]. This oxygen level became the effective limit thereafter. EPA granted waivers to DuPont Corporation (1985) [13] and Texas Methanol Corporation (1988) [14] allowing methanol/cosolvent combinations up to 3.7% oxygen and including ethanol as a cosolvent alcohol, in addition to higher alcohols already allowed.

EPA also granted a waiver for up to 15% MTBE in 1988, which provides approximately 2.7% oxygen [15]. This waiver was requested and granted at less than the oxygen limit allowed for alcohols because of the high volume of the oxygenate itself. Because oxygenates have various properties, distillation impacts, etc. that are significantly different from gasoline hydrocarbons, 15% was seen as the acceptable limit for oxygenates, independent of the oxygen contribution.

In 1991, on a petition from the Oxygenated Fuels Association, EPA revised the Interpretive Rule on sub-sim to allow for mixtures of MTBE (or ETBE) and aliphatic alcohols other than methanol up to the 2.7% oxygen limit in gasoline [16]. (This corresponds to the 15% MTBE limit. The 2.7% oxygen from ETBE would allow about 19% ETBE but it was not expected that this high cost oxygenate would be used at such a level.)

It should be noted that the methanol blend waivers approved remain in effect today, though the promulgation of additional regulatory requirements for gasoline additives means that some additional testing would be needed before they could be marketed by large companies.

2. Use of Methanol in U.S. Fuels

In the mid-1980s ARCO undertook the only serious effort at marketing methanol blends in the U.S., using its Oxinol mixture of methanol and TBA. It used the Oxinol in some of its own gasoline and also marketed it to independent refiners and blenders. Many of those independent customers subsequently discontinued purchase of the Oxinol, however, citing reports from customers of phase separation and/or damage to elastomers and other real or perceived problems. ARCO discontinued its marketing of Oxinol sometime around 1986. EPA’s final regulation on fuel volatility in March of 1989, which allowed a one psi differential for ethanol blends but not for methanol/cosolvent blends, put the methanol blends at an additional major disadvantage and
probably represented their death-knell in the U.S. EPA’s reformulated gasoline (RFG) and conventional gasoline anti-dumping program, based on models which favored even lower volatility, made this barrier even greater. In addition, EPA’s Complex Model for RFG, use of which became mandatory as of January 1, 1998, did not include parameters representing blending of methanol either for volatile organic compound reduction credit or for calculation of aldehyde emissions to meet the toxics emissions standards. In order for methanol/cosolvent blends to be used in RFG, the model would have to be “augmented,” which would require substantial and expensive emissions testing with a wide variety of fuel blends and vehicles.

By early in this decade, detection of MTBE in groundwater in various locations raised concerns that led a number of states to ban use of MTBE, and its use fell off sharply as a result, largely through substitution of ethanol. Then, the Energy Policy Act of 2005 (EPAct 05) eliminated the oxygen requirement for RFG while imposing a “Renewable Fuel Standard,” essentially a requirement for use of increasing volumes of ethanol by refiners. Absent the RFG oxygen requirement, refiners’ concerns about liability for leaks of MTBE have prompted all major U.S. refiners to cease blending of MTBE and it has virtually disappeared from U.S. gasoline supply since May 2006.

With the elimination of MTBE, the only significant use of methanol in the U.S. fuel supply is its use in production of methyl ester biodiesel.

B. Use of Methanol Blends in the European Union

Methanol fuel blends were introduced in the Federal Republic of Germany in 1968 with use of 2% methanol/2% TBA blends, reaching general use around 1977. The German government set a limit of 3% methanol. During the 1980s and through much of the 1990s, most gasoline in Europe contained a small percent of methanol, usually 2-3%, along with a cosolvent alcohol. The current EU standard, EN 228, as last revised in 2004, allows up to 3% methanol to be used, with a requirement for a cosolvent (“stabilizing agent”). In January of 2007, the European Commission proposed a new fuel standard that would require all fuels marketed in Europe to meet a standard for greenhouse gas emissions, which would include a reduction in greenhouse gas (GHG) emissions by 1% per year from 2011 through 2020, with the intent that these reductions be met largely through increasing the biofuels content of the fuel. The proposal states that a new gasoline standard will be promulgated that will allow up to 10% ethanol to accommodate the GHG emissions reductions, compared to the current standard that allows only 5% ethanol.

IV. Methanol Use in Flexible Fuel Vehicles

In the early 1980s, there was considerable interest in using methanol as a fuel for both petroleum displacement and air quality reasons. To achieve the quickest displacement and largest impact on air quality, it was desired to use methanol neat or near-neat as a transportation fuel. Ford developed a version of their Escort in 1981 that ran on 90% methanol and a 10% hydrocarbon blend specifically tailored to give reliable cold starts [17]. Forty of these methanol Escorts were put into fleet use in Los Angeles and their 20% increase in power and 15% increase in energy efficiency made them very popular in comparison to the gasoline versions. These initial vehicles were so successful that Los Angeles asked for more and in 1983 Ford delivered an additional 501. However, the refueling infrastructure was not expanded sufficiently and the decreased driving range (approximately 230 miles versus 300 for gasoline) became an issue. This experience directly led to the development of methanol flexible fuel vehicles (FFVs) which could use methanol or gasoline in the same tank through the use of an alcohol fuel sensor that measured the methanol content of the fuel going to the engine and adjusted the fuel flow rate and spark advance accord-
ingly. This freed drivers from worrying about running out of fuel while the development of methanol infrastructure caught up with demand. The objective was to introduce large numbers of methanol FFVs, build a broad fueling infrastructure network, then transition back to dedicated methanol vehicles.

Relatively few changes are needed to turn a vehicle into an FFV (see Fig. 1). An alcohol fuel sensor is used to monitor the fuel mixture and signal the on-board computer to adjust fuel flow and spark timing (current model ethanol FFVs have eliminated the sensor – performing that task with software). Larger fuel injectors are used to compensate for the methanol’s lower energy content to assure that the same amount of maximum engine power is produced. Because methanol is corrosive and will attack certain metals (such as aluminum and magnesium) and elastomers (including rubber and polyurethane), electroless nickel plated or stainless steel fuel tanks and stainless steel or Teflon™-lined fuel lines are employed, and methanol-compatible elastomers are used in all fuel-wetted parts. An anti-siphon device is installed in the filler neck and an enlarged carbon canister is installed to contain evaporative emissions when co-mingling occurs in the fuel tank, i.e., when the fuel in the tank contains 5-20% methanol with the remainder gasoline.

There was a compromise, however, in the methanol FFVs – in order to accommodate gasoline, the engine was not modified to achieve the power gains and efficiency improvements demonstrated by Ford in their first methanol Escorts. Nonetheless, FFVs were perceived as the “missing link” in the transition to methanol.

When FFVs were first sold, the incremental retail price was around $350. The manufacturers never revealed the incremental cost of making FFVs nor fully defined what changes they made. Today, after millions of ethanol FFVs have been sold, the situation has not changed, but estimates of the incremental cost are now between $50-100. Methanol FFVs built in large volume would be expected to have a similar incremental cost, though perhaps slightly higher if more expensive fuel system materials are required relative to ethanol, and whether methanol FFVs can do without a fuel sensor as ethanol FFVs have learned to do.

In parallel with FFV development, was development of a methanol fuel specification what would allow vehicles to achieve cold-start and improve the visibility of methanol flames. The end result was a blend of 85% methanol with 15% gasoline known as M85.
VI. Methanol Blend Vehicle Operational Impacts

Because methanol blends have a lower heating value than straight gasoline, the vehicle’s fuel system must be capable of supplying an increase in total fuel volume at all operating conditions to maintain vehicle power, driveability, and cold-start performance. Vehicles with feedback fuel systems have the capability to adjust fuel flow in response to environmental factors and changes in fuel properties that affect stoichiometry. This capability is called adaptive learning and takes place after the vehicle is warmed up and the feedback control system is operating. The objective of adaptive learning is to dither the air/fuel ratio around the stoichiometric value so that the catalyst will operate efficiently. Engine operating modes where adaptive learning is not in effect include cold-start, warm-up before the feedback control system is active, prolonged idle, wide-open-throttle acceleration, and closed throttle deceleration.

A. Cold-Start

Methanol has several characteristics that increase the difficulty of cold-start in internal combustion engines. The most important of these is the high flash point of methanol, 52°F, compared to gasoline, -43°F. Another difference is that methanol requires about 3.5 times more energy per unit mass to vaporize it compared with gasoline. Factoring in the need for twice as much methanol as gasoline to produce the same power, the difference is a factor of 7. Blending methanol in gasoline also adversely affects cold-start capability. A blend of 5% methanol in gasoline needs 14% more energy to vaporize completely [18], with most of that difference accounted for before 50% distilled.

B. Driveability

Owners of modern vehicles expect nearly flawless operation in terms of driveability, which includes no stalling or surging during warm-up, idle at a constant speed, smooth acceleration without stumbles or sags, linear throttle response, and absence of vapor lock. Testing by General Motors has shown that adding methanol to gasoline is equivalent to operating with a leaner calibration using gasoline in terms of causing driveability demerits (see Fig. 2) [18]. Recent tests of existing gasoline vehicles using up to 30% ethanol without driveability problems suggests that current vehicles that have feedback emission control systems have the capability to compensate for low-level methanol blends and should not have degraded driveability.

C. Acceleration

When a driver evaluates acceleration, it is often not just how quickly the vehicle will accelerate, but the quality of that acceleration. If the vehicle is not fully warmed up, methanol blends can cause the vehicle to exhibit slower acceleration and the driveability problems. When the vehicle is fully warmed up, the driver may not notice any change if the fuel system compensates for the methanol addition through the feedback control system. Tests of early carbureted vehicles in Brazil calibrated to use 20% ethanol found that acceleration was better using 20% ethanol than straight gasoline [19]. The reason was that the
calibration was too rich for maximum acceleration when using straight gasoline, while using 20% ethanol made the stoichiometry closer to the best value for maximum power. Whether methanol blends result in faster or slower acceleration depends on the base stoichiometry of the vehicle.

D. Fuel Economy

Adding methanol to gasoline reduces the heating content per unit volume of fuel. Controlled dynamometer tests have shown that adding methanol to gasoline reduces fuel economy [20]. However, when the change in energy content was taken into account, there was no change, indicating that the engine efficiency was not affected.

VII. Emissions Impacts

A. Primary Regulated Exhaust Emissions

Emissions of CO are a function of combustion stoichiometry and will not be significantly different from gasoline combustion for methanol at the same stoichiometry [21]. Likewise, HC emissions will be similar in magnitude compared to gasoline. Emissions of NOx are typically lower than those from gasoline when methanol is combusted under similar engine conditions. This is due primarily to the lower peak flame temperature of methanol, and secondarily, to the high latent heat of methanol, which reduces pre-ignition temperatures. When operating an engine at constant compression ratio, substituting 100% methanol for gasoline has been shown to reduce NOx emissions by 30% [20,22]. However, research by Volkswagen showed that increasing the compression ratio to 13:1 to take advantage of methanol’s higher octane increased engine-out NOx emissions to the same level as for gasoline at a compression ratio of 8:1 [23]. Recent development of the HCCI combustion system holds promise for internal combustion engines using neat methanol as fuel. When methanol is used in HCCI engines, emissions of NOx can decrease to near-zero [24].

Blends of methanol and gasoline affect vehicle emissions according to the amount of oxygen introduced into the blend from the methanol [25]. The addition of oxygen through methanol and its cosolvents causes the fuel stoichiometry to move leaner with the result that CO and HCs are reduced with NOx increasing slightly. These results were corroborated by the Coordinating Research Council in tests performed for the U.S. Department of Energy [26].

EPA tested six in-use passenger cars chosen to have fuel and emission systems representative of popular ones in use in 1995, using blends of up to 40% ethanol in gasoline [27]. All the emissions tests were conducted on a chassis dynamometer using the Federal Test Procedure. While these tests were conducted using ethanol, they are representative of methanol blends up to 28% based on the same oxygen content, which is the primary driver in criteria emissions changes. Based on a linear regression of the results, EPA found that these vehicles on average showed a 45% reduction in CO emissions at 14% oxygen in the blend. For HCs, the reduction was 32% while NOx increased 64%.

A more recent study using 2001 model year vehicles, fueled with 20% ethanol (7% oxygen) was conducted by Orbital Engine Company for Environment Australia [28]. The emissions of these vehicles were tested using the U.S. Federal Test Procedure. Orbital found that on average, HC emissions decreased by 30%, CO emissions decreased by 29%, and NOx increased by 48% when using 20% ethanol. Orbital also measured catalyst temperatures in every vehicle. Elevated catalyst temperatures during wide-open-throttle causing more rapid catalyst deterioration and increases in all emissions was found after driving 50,000 miles and retesting emissions [29]. Only two of the five vehicles showed decreased HC and CO emissions at 50,000 miles, while all the
vehicles showed decreases in HCs during testing at 4,000 miles. Four out of five vehicles showed an increase in NOx at 50,000 miles.

B. Carbon Dioxide Emissions

The predominant compound from the combustion of methanol is carbon dioxide. For the same amount of energy, methanol will produce 94% as much carbon dioxide as gasoline. Engines that have been optimized for methanol with increased efficiency will have lower carbon dioxide emissions. The Greenhouse gases, Regulated Emissions, and Energy use in Transportation model (GREET) shows carbon dioxide emissions for flexible-fuel vehicles using M85 to be 96% those of a similar vehicle using gasoline [30]. This increase relative to neat methanol is due primarily to the 15% gasoline in M85. GREET also includes a “neat” methanol vehicle that has been optimized for M90. This “neat” methanol vehicle has carbon dioxide emissions which are 89% of those of a similar gasoline vehicle. The decrease relative to the M85 vehicle is due primarily to the built-in assumption in GREET that the “neat” methanol vehicle is 7% more fuel efficient than the similar gasoline vehicle.

C. Toxics

When methanol is combusted, the HC emissions are composed primarily of unburned methanol and aldehydes, with formaldehyde being dominant. Testing has shown that neat methanol will produce about twice the level of aldehydes as gasoline [31]. Tests of neat methanol vehicles have shown that formaldehyde is the predominant toxic emission from methanol combustion [32]. Aldehyde emissions are effectively controlled by use of a catalytic converter. Gasoline produces additional toxics such as 1,3-butadiene, benzene, hexane, toluene, and xylene, which arise from various hydrocarbons. When methanol is added to gasoline, production of these toxics is correspondingly reduced. In addition, if the methanol addition causes a lean shift in stoichiometry, the overall decrease in HC emissions associated with that shift decreases toxic emissions in proportion.

D. Evaporative Emissions

In response to requests for use of methanol/gasoline blends in the U.S., the EPA developed a modified evaporative index to capture the change methanol causes to gasoline front end volatility. Methanol/gasoline blends that meet the modified evaporative index should not cause increases in evaporative emissions. In one of EPA’s rulings on a methanol/gasoline waiver request, they commented that properly formulated blends will not decrease the ability of the carbon canisters to adsorb vapors [33]. As fuel systems have moved away from steel tanks and lines to plastic, permeation emissions from methanol and methanol blends is likely. In the U.S., testing found that the ethanol in ethanol blends tended to be preferentially absorbed into the plastic fuel lines and tanks, and then evaporated away from the surface [34]. Since the impact of methanol on elastomers is similar to that of ethanol, and in some cases worse, it is likely that methanol blends will cause permeation emissions as well. Permeation emissions can be prevented by proper material selection and design changes.

E. “Well-To-Wheel” Greenhouse Gases

While methanol combustion does not result in significantly different emissions of carbon dioxide compared with gasoline, the situation changes when the entire resource-extraction-through-end-use path is considered. The GREET model was used predominately for this analysis [30]. The natural gas case, as well as the bituminous coal case are specific to North America. Two levels of sequestration are included: 75% efficiency reflective of current technology and 90% efficiency which is the U.S. Department of Energy goal for 2012 [35]. Methanol from biomass is assumed
to use wood as the resource with gasification technology. Methanol from natural gas is projected to produce just slightly less GHGs than gasoline due primarily to the assumption that methanol vehicles are 7% more efficient [30]. Methanol from coal without sequestration produces almost twice the GHGs of gasoline—a result that is not unexpected given the high carbon content and low hydrogen content of coal (see Fig. 3). Methanol made from coal with today’s level of carbon sequestration efficiency shows very similar GHG emissions compared to gasoline—improvement in carbon sequestration could lower GHGs about 15% further. Finally, methanol from biomass has a net GHG credit of just over 50% because all the carbon used to make it is renewable.

VIII. Infrastructure Impacts

A. Distribution

Methanol is typically shipped via railroad tank car, barge, and truck tanker, depending on volume and distance [36]. In the U.S., only a very small amount of methanol is sent through pipelines, and only over very short distances [37]. Pipeline transport is the most cost-effective long-term method for transporting fuels because of the volumes and distances involved. Many countries have pipelines for the transport of petroleum products, but using these pipelines to transport methanol faces several hurdles. Some existing pipelines may be diverted to dedicated methanol use. Once these pipelines are cleaned, they will not have the problems associated with intermittent use in petroleum pipelines just discussed, and water pick-up and residue removal should not be problems. Even so, potential material compatibility issues with existing pipelines require research, and the availability of storage tanks suitable to store methanol remains a question when using existing petroleum pipelines for dedicated methanol transport.

B. Storage

Bulk storage of methanol should be done in appropriately designed horizontal or vertical storage tanks. To limit moisture infiltration, a conservation vent with a flame arrester is recommended, or nitrogen blanketing. Proper grounding is essential, given methanol’s low conductivity.

For storage at retail service stations, the underground tank is preferred. Underground storage has several advantages: the fuel stays at a relatively constant cool temperature; the above-ground space is maximized for vehicle refueling; and refilling from tanker trucks can be done using gravity rather than a pump. Tanks for methanol can be made from stainless steel, carbon steel, or metha-
nol-compatible fiberglass. In the U.S., methanol tanks placed underground must have secondary containment because methanol is classified as a hazardous chemical. Secondary containment includes:

- Double-walled tanks
- Placing the tank in a concrete vault
- Lining the excavation area surrounding the tank with natural or synthetic liners that cannot be penetrated by methanol

For underground methanol tanks at service stations, conservation vents with flame arrestors are typical to prevent water absorption rather than nitrogen blanketing. Conservation vents are usually configured to allow venting to occur only when the pressure in the tank exceeds 7-21 kPa (1-3 psi), and when the vacuum in the tank exceeds 5-10 cm (2-4 inches) of water [38]. This is especially important when storing neat methanol since the vapor space in the tank will be flammable, unlike storage of gasoline or M85 where the vapor space will be too rich to be flammable. Existing underground petroleum tanks must be thoroughly cleaned before storing methanol to remove all water and sediment. Some underground storage tanks use liners which must be methanol-compatible. In addition to moisture infiltration from the air, water often gets into underground storage tanks from inadequate seals on the refilling manholes. Efforts should be made to prevent water infiltration from the surface above since this water often includes impurities such as sodium and chloride ions that greatly increase the corrosiveness of methanol.

C. Service Stations

Service stations must be capable of moving methanol from the underground storage tank to the dispenser and into the vehicle. As the methanol is pumped from the underground tank, it travels through piping to the dispenser. Like tanks, piping for methanol can be made from stainless steel, carbon steel or methanol-compatible fiberglass. In the U.S., piping comes under the same rules as underground tanks, i.e., double-walled piping or secondary containment is required. For threaded pipe connections, Teflon® tape or paste is preferred for use with methanol. Dispenser manufacturers have developed units compatible with methanol; these must be used to prevent malfunction and fire hazards from leaks [39].

Most dispensers include filters, both spin-on and those with replaceable elements. The most durable filters include nylon filter elements and methanol-compatible adhesives. Because methanol is very aggressive to many metals and because the products of corrosion can cause problems in methanol vehicle fuel systems, it is recommended that methanol filter element pores be 3 µm mean diameter, instead of the 10 µm mean diameter typical of those for gasoline [38]. Filter elements with small mean diameter pores are more susceptible to build-up of static electricity. This is particularly a problem for methanol because of its low conductivity. In severe cases, the discharge of static electricity from the filter element to the housing can cause rapid erosion of the housing from the inside, eventually causing a hole to appear. Changing the filter before back-pressure builds significantly will minimize build-up of static electricity.

When used for methanol, dispensing hoses designed for gasoline will rapidly degrade and put debris into the vehicle, which will, in turn, clog its fuel filter. Even methanol-compatible dispensing hoses have been found to release plasticizers and should be soaked for 24 hours in methanol to remove them before installation [38]. Break-away fittings are recommended for most dispenser applications and need to be methanol-compatible.

Conventional nozzles designed for methanol are available, but a better solution is the “dry-break” or “spill-free” nozzle. The spill-free nozzle (see Fig. 4) was developed by the Methanol
Fuel Cell Alliance, an industry consortium led by BASF, BP, DaimlerChrysler, Methanex, Statoil, and Ballard [40]. Fiber optic communications are built into the nozzle and the vehicle fuel receptacle to ensure proper fueling without an electronic interface. Use of such a nozzle eliminates spills and concern about fire safety and human contact with methanol [41].

IX. Methanol Use in Diesel Heavy-Duty Vehicles

The physical and chemical properties of methanol make it very well-suited for use as a spark-ignition engine fuel, but its ability to combust without forming soot (due to the lack of carbon-to-carbon bonds) has attracted diesel engine designers to find ways of using it as well. Many ways of using methanol in diesel engines have been researched including use in blends, emulsions, fumigation, with the addition of ignition improvers, in dual injection engines, and in engines modified to achieve direct compression ignition of methanol [42]. Note that of these methods, only use of ignition improvers and compression ignition resulted in engines that displaced all diesel fuel use, though complete displacement was not viewed as a requirement since the emissions benefits of methanol were typically greater than the percent diesel fuel it replaced. Diesel engines could also be converted to spark ignition, but this change essentially changes them to be Otto Cycle engines. Numerous fleet tests of heavy-duty vehicles with methanol engines have been conducted [43,44,45,46].

A. Use of Methanol with Ignition Improvers

Ignition improvers (also referred to as cetane improvers) promise an attractive means to allow the use of methanol in diesel engines. The addition of ignition improvers to methanol can give it the same ignitability characteristics as diesel fuel. This allows the use of methanol in unmodified diesel engines, avoiding complicated and costly engine modifications (though the fuel injection system will have to be modified for increased flow capacity and for compatibility with methanol).

While no ignition-improved methanol has been used other than in fleet demonstrations, ignition-improved ethanol has been used as a fuel in diesel engines in Brazil since Mercedes-Benz do Brasil initiated a test project using buses in 1979. The initial experience was favorable and in 1983 22-ton and 32-ton class trucks with engines converted to use ignition-improved ethanol were introduced for sale by Mercedes-Benz do Brasil. As of 1986, about 1,700 trucks using ignition-improved ethanol (new and converted) were in operation in Brazil [42].

Since most ignition-improvers have nitrogen in their composition, concern was expressed that this nitrogen would contribute to NOx emissions. Extensive testing showed that only a small fraction of this nitrogen ended up as NOx and overall, NOx emissions decreased based primarily on the emission characteristics of methanol [42]. The cost of the ignition improver is also a factor in whether ignition-improved methanol represents a viable fuel. In this regard, dimethyl ether has shown promise [47].
B. Use of Methanol in Diesel Engines Using Compression Ignition

Several researchers demonstrated that diesel engines could achieve compression ignition of methanol with the assistance of glow plugs or “hot spots” in the combustion chamber. The Detroit Diesel Corporation used this concept to build a compression ignition version of their popular 2-stroke diesel engine that was used in hundreds of transit buses in the U.S. and in other heavy-duty vehicle applications [48]. This engine achieved compression ignition of methanol at low loads by glow plug heating, and at high loads by retaining large amounts of burned gases which heated the incoming methanol so it would reach ignition under compression. These engines had very low NOx emissions and the only particulate emissions they emitted were from consumed lubricating oil. While these engines are no longer in use and have been replaced by newer-design 4-stroke engines (no methanol versions), they illustrate the capability to design engines for compression ignition of methanol. Caterpillar developed a methanol version of their 3306 4-stroke diesel engine using glow plugs to achieve ignition [49] and Navistar developed a methanol version of its DT-466 4-stroke diesel engine also using glow plugs [50].

Looking forward, homogeneous charge compression ignition offers the opportunity to design heavy-duty engines for compression ignition of methanol with very low emissions and high efficiency [24].

X. Non-Road Engines and Vehicles

A. Small Engines

Millions of small engines are utilized daily in lawn mowers, chain saws, leaf blowers, etc. Most at the smallest end of the market are two-stroke design, while some of the larger engines in this category are four-stroke. The vast majority are single-cylinder with simple fuel systems consisting of a tank, shut-off valve and very simple carburetor. Because this category of engines is very price competitive, materials are chosen on the basis of cost and are not engineered to withstand the same level of misuse that automotive fuel system components are engineered for. Corrosion inhibitors have been found to be successful in reducing the corrosion of 2-stroke engine materials and would have to be introduced as a component of the fuel [51].

These small engines are typically calibrated to operate on the “rich” side of stoichiometric for reasons of stable operation, easy starting, and durability. As such, these engines can typically accommodate fairly large percentages of methanol in gasoline without adverse impacts on operation. In tests of a single-cylinder (123 cc displacement) genset engine, it was found to operate without any adverse impacts using 30% methanol in gasoline [52]. This was due primarily to the fact that this engine was still operating rich of stoichiometric using 30% methanol in gasoline at zero engine load. At full-load, 30% methanol in gasoline reduced the CO emissions from 8.7% down to 4.8%. Similarly, HC emissions were reduced from 730 to 495 ppm. NOx emissions were not measured, but at these rich stoichiometries, it is likely that they were very low in all cases. Aldehyde emissions were not measured, but it would be expected that formaldehyde emissions would increase significantly from the combustion of methanol.

B. Large Engines

Large non-road engines are typically derived from transportation engines, though some are purpose-built. A characteristic they all have in common is a simple fuel system and no emission control system (though this is changing in the U.S., which is implementing emission standards for non-road engines.) Large non-road engines typically are not set-up to operate as richly as their smaller counterparts. Consequently, adding methanol to their fuel will be noticed more readily in
terms of more difficult cold-starts, degraded transient response to rapid throttle changes and re-
duced maximum power output. Clogged fuel filters are likely soon after introduction of methanol
blends since the methanol will remove any residue that has built up in the fuel system over time.

Changes in emissions for these engines using methanol blends should be similar to those for
small engines: significantly reduced CO and HCs, and slight increases in NOx. Since these engines
rarely have catalysts, methanol blends would be expected to increase emissions of formaldehyde,
while hydrocarbon toxics would be expected to decrease, as explained in Section VII.

Using methanol blends in large non-road engines is likely to cause corrosion of the fuel system
components and increased wear of the engine unless oil changes are made more frequently. Many
of these engines use carburetors, which are made of metals that will corrode, and have many elas-
tomeric and plastic parts that will be degraded by methanol. Fuel lines are likely to swell and so-ten, leading to leaks as they deteriorate. Filter elements tend to separate since the glue used in
manufacture has been shown to dissolve when exposed to methanol.

Addendum

An expanded version of this report is available at the Methanol Institute web site [53].
References

11. Ibid. at 38584.