

Use of Methanol as a Transportation Fuel

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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). Methanol use in non-racing vehicles has been much less successful. 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. Gasolines used in European Union countries are allowed to have 3% methanol, but it is being challenged by ethanol (allowed up to 5% now with a proposal to go up to 10%) which is valued for its low greenhouse gases. 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, fumigation, 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 (a blend of 85% methanol with 15% gasoline), 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 [2] 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 4 million E85 vehicles in the U.S., though only about 150,000 of them use E85 regularly [2]. The only role for methanol currently as a transportation fuel in the U.S. is 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 [3]. 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 rule-making 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 waiver application contained no actual data on ethanol/gasoline blends. Instead, it included data on methanol/cosolvent blends and on methyl tertiary butyl ether (MTBE), which was argued to show expected emissions impacts from ethanol as well. There was also a reference to some emissions tests conducted by the state of Nebraska on 26 vehicles, apparently with gasoline/ethanol blends, which were not identified and no data were given, but a statement said that the tests showed higher NO_x and somewhat lower CO and HC emissions [4].

Because of the lack of data, EPA was unable to grant the waiver application. But EPA also declined to deny the waiver application and, under the terms of sec. 211(f)(4), applications are deemed granted after 180 days if they have not yet been denied. On April 6, 1979, EPA issued a Federal Register notice confirming that the application had been deemed granted by expiration of the 180-day period [5].

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 [6]. 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) [7], for up to 7% MTBE [8], and for up to 5.5% of a combination of methanol with TBA in equal parts [9]. 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 [10]. (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 [11]. 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% [12].

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 [13]. This oxygen level became the effective limit thereafter. EPA granted waivers to Dupont Corporation (1985) [14] and Texas Methanol Corporation (1988) [15] 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 [16]. 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 [17]. (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.)

In workshops relating to implementation of the federal Reformulated Gasoline (RFG) program established by the Clean Air Act Amendments of 1990, EPA was informed that with the (lower density) fuels anticipated as RFG, 10% ethanol would provide approximately 4% oxygen by weight, whereas EPA’s model only extended up to 3.7% oxygen. EPA confirmed that use of 10% ethanol

would be allowed in RFG even with the oxygen at somewhat above 3.7% (no oxygen limit having been established for 10% ethanol blends).

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. EPA DENIALS/REVOCATIONS OF WAIVERS AT HIGH ALCOHOL/OXYGEN LEVELS

In March 1980, EPA denied a waiver application from Beker Industries for up to 15% methanol [18]. The denial was based largely on the absence of adequate data. (In fact, no data had been submitted on methanol without cosolvent additives.) But EPA also noted that the data submitted at high alcohol levels suggested that there could be problems, including increases in emissions and deteriorated driveability, resulting from the higher oxygen levels.

In August 1980, EPA denied a waiver application from Conservation Consultants of New England for 5% ethanol with 5% methanol (oxygen content 4.4%) [19]. The application had also requested waivers for (1) 10% methanol with 5% ethanol and (2) 8% methanol with 2% ethanol, but these requests had been withdrawn by the applicant [20]. The denial was based on absence of data, but EPA noted problems anticipated with exhaust emissions, evaporative emissions, driveability, and materials compatibility.

In October 1981, EPA granted a waiver to Anafuel Unlimited for a mixture of up to 12% methanol with 6% butanols and a proprietary inhibitor [21]. The waiver was granted under extreme duress – pressure from the White House and some senators. This would have provided around 7% oxygen in the fuel. Subsequent testing, however, showed that the test data submitted did not reflect the alcohol package in that volume and the Motor Vehicle Manufacturers' Association (MVMA) filed both a court challenge and a petition for EPA reconsideration. EPA proposed to revoke the waiver by reconsideration (1984) [22] but the D.C. Circuit Court ruled that waivers were not subject to such reconsideration beyond a 30 day period provided in sec. 211(f)(4) [23]. The D.C. Circuit Court subsequently ruled in favor of MVMA's suit, however, vacating the original granting of the waiver such that EPA's evaluation of it would resume without the tainted data [24]. EPA denied and finally revoked the waiver in 1986 [25]. In the meantime, American Methyl Corp., successor to Anafuel, had applied for another waiver with a variation of the formula at a 5% oxygen level. EPA denied that request in November 1983 [26].

In 1987, in essentially the same time period that the Texas Methanol Corporation's waiver application was pending, EPA was asked by AM Laboratories, Inc. to grant a waiver for use of up to 5% methanol with 5% ethanol, for an oxygen contribution of 4.4%, similar to that which it had denied in 1981 to Conservation Consultants. The application attached a report of a major Canadian test program that included such 5%/5% blends and in which the driveability demerits were argued not to be excessive. The automakers fiercely opposed the application, arguing that other existing data clearly showed driveability to be degraded unacceptably at levels above around 3.7%. For the first time, opposition was not limited to U.S. automakers but included opposing submissions from Toyota, as well. In January 1988, EPA issued its Federal Register notice and decision document denying the waiver [27].

3. 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 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.

While the methanol/cosolvent blends failed to catch on in the U.S., the use of MTBE provided a path for methanol to be used in gasoline. By the late 1980s, MTBE production had surpassed formaldehyde production as the greatest single use of methanol worldwide. Passage of the Clean Air Act Amendments of 1990, with the RFG program and the Oxyfuels program, gave further boosts to MTBE. The RFG program required 2.0% oxygen in RFG during warm weather months in the most serious ozone non-attainment areas, while the Oxyfuels program required 2.7% oxygen in many carbon monoxide (CO) nonattainment areas during cold months. MTBE became the oxygenate of choice in RFG and was also used to some extent in Oxyfuels regions. As these programs were being implemented, demand for methanol outstripped supply in the U.S. by so much that methanol prices reached levels of \$1.85/gallon.

The Clean Air Act Amendments of 1990 envisaged that there would be a move toward vehicles designed to run on methanol, either neat or as M85, to meet various special programs for alternative fuel vehicles (AFVs), including the Clean Fuel Fleet (CFF) Program and the California Pilot Test Program [28]. But automakers and refiners quickly showed that they could meet the emission standards with RFG and states, having determined that such programs were not cost-effective ways of reducing pollutants, convinced EPA to let them opt out of the CFF program. Frustrated with the lack of progress in use of AFVs, Congress enacted limited fleet AFV acquisition requirements in the Energy Policy Act of 1992 (EPA 92), which also contemplated methanol vehicle use. But initial implementation of this program coincided with the runaway methanol demand for MTBE use within the RFG program and associated runaway prices so methanol vehicles were largely ignored in these AFV programs that had been designed with them in mind.

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 (EPA 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 U.S. fuel supply is its use in production of methyl ester biodiesel. Although this accounts for almost all U.S. biodiesel, diesel use in the U.S. is far lower than gasoline use and only a small part of U.S. diesel fuel includes biodiesel, mostly at the 20% blend level or less. Therefore, the biodiesel use does not compensate for the loss of MTBE as a source of methanol demand.

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. A “common directive” of the European Economic Community (EEC, a predecessor to the European Union - EU) authorized alcohol blending in gasoline starting in 1988, including a low level that member countries were required to allow and a higher level that could be allowed by member countries with labeling on pumps. France authorized such higher level blends, but their use apparently did not become widespread. In Sweden, where oxygenates were allowed up to 3 wt% oxygen, methanol was also allowed up to 2% [29]. 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 [30]. 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 accordingly. 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. Figure IV.1 shows the differences in a methanol FFV from the standard gasoline version from which it was derived.

As Figure IV.1 shows, relatively few changes are needed to turn a vehicle into an FFV. 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.

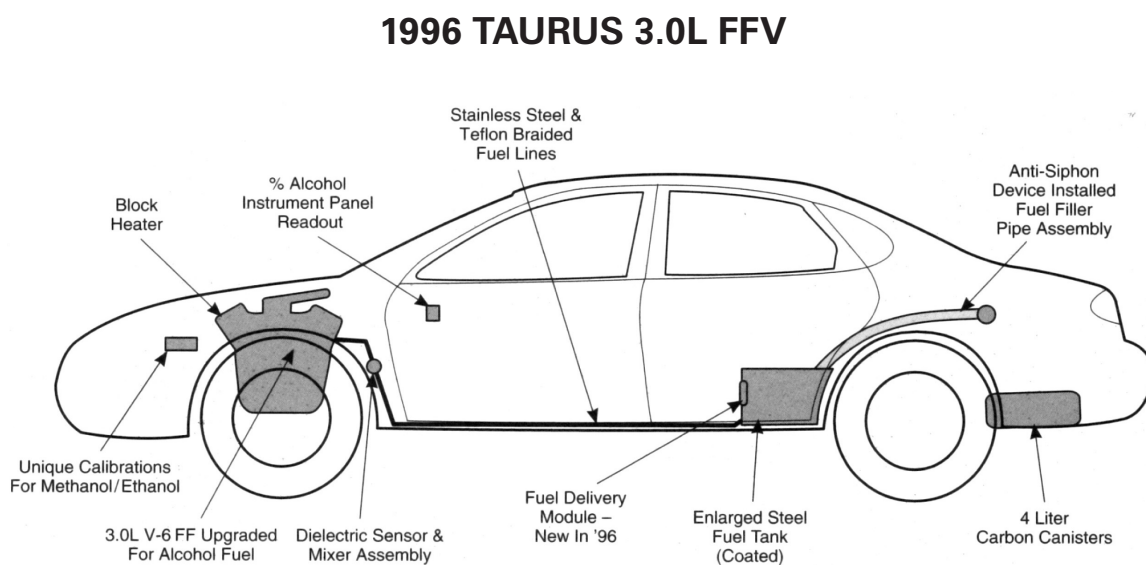


FIGURE IV.1 Changes in FFVs Compared to Straight Gasoline Models

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. While Ford showed only 10% hydrocarbons were needed, the extra 5% allowed typical specification gasoline to be used which was abundant, of course, but more importantly, inexpensive.

In 1988, the California Energy Commission established the California Fuel Methanol Reserve to increase the availability of methanol fuel across the state. The agency also entered into voluntary 10-year lease agreements with ARCO, Chevron, Exxon, Mobil, Shell and Texaco for the installation of methanol underground storage tanks and fueling pumps at 60 public retail stations. The state and local agencies would help build another 45 private fleet accessible fueling stations across the state. From the mid-1980s to the late 1990s, over 15,000 methanol FFVs were operating on California's streets and freeways, along with hundreds of methanol-fueled transit and school buses. At the height of the program in 1993, over 12 million gallons of methanol was used as a transportation fuel in the state.

While most automakers built and demonstrated FFVs, only four methanol FFV models moved from prototype demonstrations to commercial availability. They were the Ford Taurus FFV (1993-1998 model years); Chrysler Dodge Spirit/Plymouth Acclaim (1993-1994 model years); Chrysler Concorde/Intrepid (1994-1995); and the General Motors Lumina (1991-1993 model years). These mid-sized sedans were the largest selling fleet vehicles on the market, and fleets are where the vast majority of methanol FFVs were sold. By the 1996 model year, the Ford Taurus FFV was the only methanol-fueled vehicle on the market, and it too would be discontinued after the 1998 model year. By this time many of the original 10-year lease agreements with the major oil companies to operate methanol pumps at their retail stations had expired, and the methanol pumps largely turned over to pumping gasoline.

California was not the only state to demonstrate the use of methanol-fueled vehicles. Methanol fueling stations were built in 15 states between the mid-1980s and mid-1990s. The New York State Thruway Authority funded the installation of above-ground methanol stations at rest areas along the entire state-wide route of the New York Thruway, from the Tappan Zee Bridge to Niagara Falls to serve a fleet of methanol FFVs.

From these demonstration efforts, it was learned that there are no technical barriers to building methanol-fueled vehicles. It was also learned that methanol can be easily, safely and economically stored and dispensed. The cost to install a methanol fueled underground storage tank and dispenser is around \$60,000 and most installations can be completed in 60 days. Implementation of methanol FFVs and methanol infrastructure could proceed rapidly, especially considering the experience gained with ethanol FFVs and the ethanol infrastructure.

V. Methanol Blend Physical and Chemical Property Impacts

Adding methanol to gasoline causes both physical and chemical property changes, primarily an increase in vapor pressure and changed distillation and materials compatibility characteristics. These changes in physical and chemical properties can have adverse effects on vehicle operation and emissions. This section looks at these changes and identifies some ways the changes can be managed.

A. VAPOR PRESSURE

While the Reid¹ vapor pressure (RVP) of methanol is only 4.6 psi (32 kPa), compared to gasoline that is typically in the range of 7-9 psi (48-63 kPa), adding methanol to gasoline causes an increase in vapor pressure. This is because methanol combines with certain low molecular weight hydrocarbons to form azeotropes. Azeotropes have lower boiling points than the hydrocarbons from which they are made, resulting in an increase in vapor generation at lower temperatures. Figure V.1 illustrates this phenomenon which has been documented widely by several researchers [31,32]

Figure V.1 shows that the effect of methanol on gasoline vapor pressure peaks with addition of around 10% methanol by volume, and decreases with larger additions, decreasing in an almost linear fashion to 4.6 psi at 100% methanol. (However, the increase in vapor pressure varies slightly

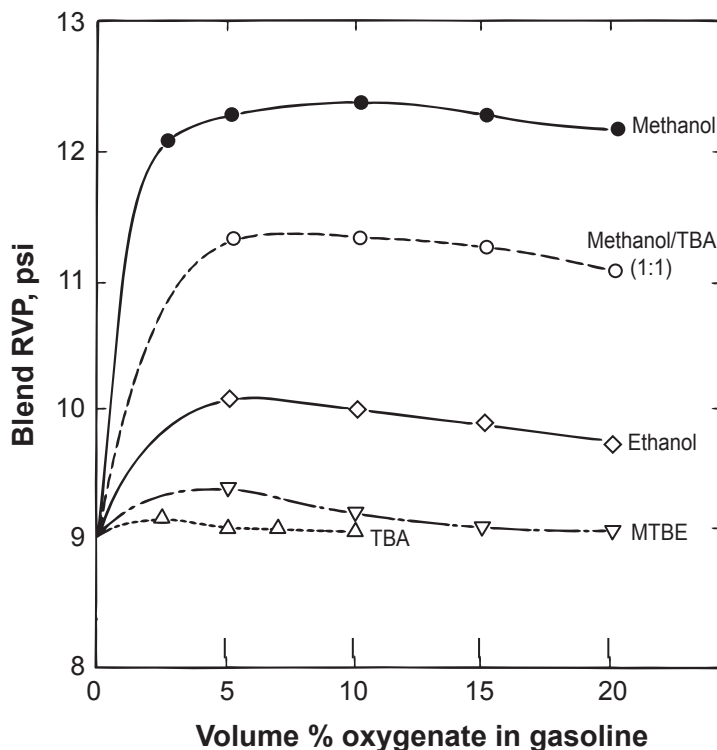


FIGURE V.1 The Effect of Alcohol Addition to Gasoline RVP (Source: Ref. 32)

¹ Reid vapor pressure refers to a specific ASTM test (D323) conducted at 100°F.

with each blend of gasoline.) What is particularly significant when adding methanol to gasoline is the very rapid rise in RVP – the vast majority of the increase occurs by the time 2-3% methanol is added. This large increase in RVP creates very large increases in vapor generated, which often overwhelm the fuel evaporative system and result in significantly increased evaporative emissions. Cosolvents can moderate the increase in vapor pressure somewhat as illustrated in Figure V.1 for a 50/50 blend of methanol and TBA, but the most effective remedy is to decrease the RVP of the base gasoline. When used with cosolvents, the RVP peak occurs at around 5% alcohol content.

Figure V.2 shows the effect methanol and other alcohols have on the distillation curve of gasoline when added at the 15 wt% level. Methanol (labeled C1 in Figure V.2) shows the largest distillation curve distortion which is caused by the methanol and its azeotropes boiling off first. After about 60% distilled, almost all the methanol is vaporized and the distillation curve reverts back to be nearly the same as for straight gasoline.

B. WATER TOLERANCE

While methanol is soluble in gasoline, the presence of water may cause phase separation (water and methanol separate out of solution). Whether phase separation occurs depends on the amount of water and the temperature – high water content and low temperatures favor phase separation. Methanol is the worst alcohol in regard to phase separation, which is one of the reasons that higher molecular weight alcohols have been frequently recommended as cosolvents for methanol/gasoline blends. Cosolvents ameliorate phase separation, vapor pressure increase, and materials compability problems. The EPA has required cosolvents for all methanol blend waivers for these three reasons. For high methanol content fuels such as M85, phase separation is not a problem because of the large capacity of methanol to absorb water.

Figure V.3 shows the water tolerance of a gasoline with various concentrations of methanol. This figure vividly illustrates how methanol addition quickly causes the temperature at which phase separation occurs to rise. For example, 10 wt% methanol will separate when the blend is cooled to a temperature of only 15°F (-9°C). At 15 wt% methanol the phase separation temperature rises to just below freezing.

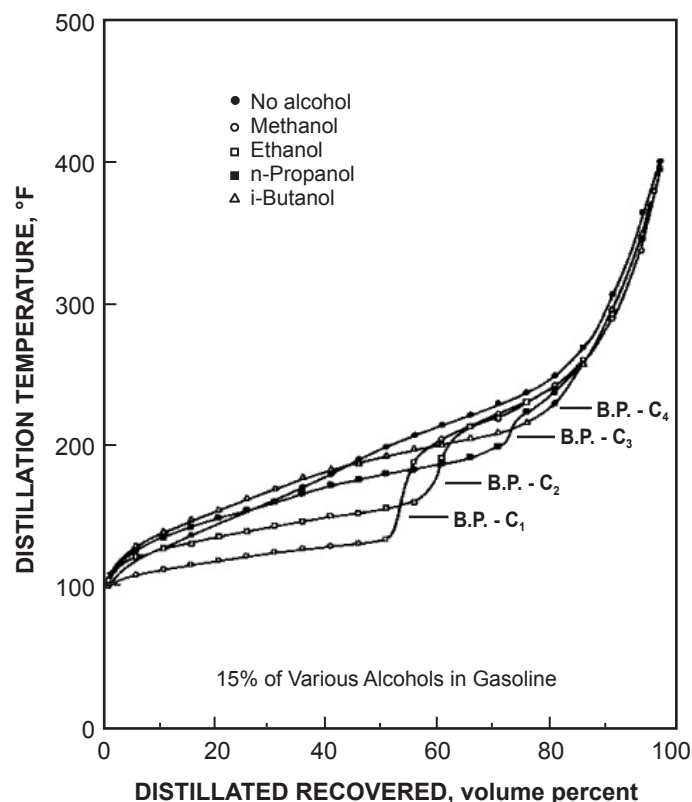


FIGURE V.2 The Effect of Alcohol Addition to Gasoline Distillation
(Source: Ref. 31)

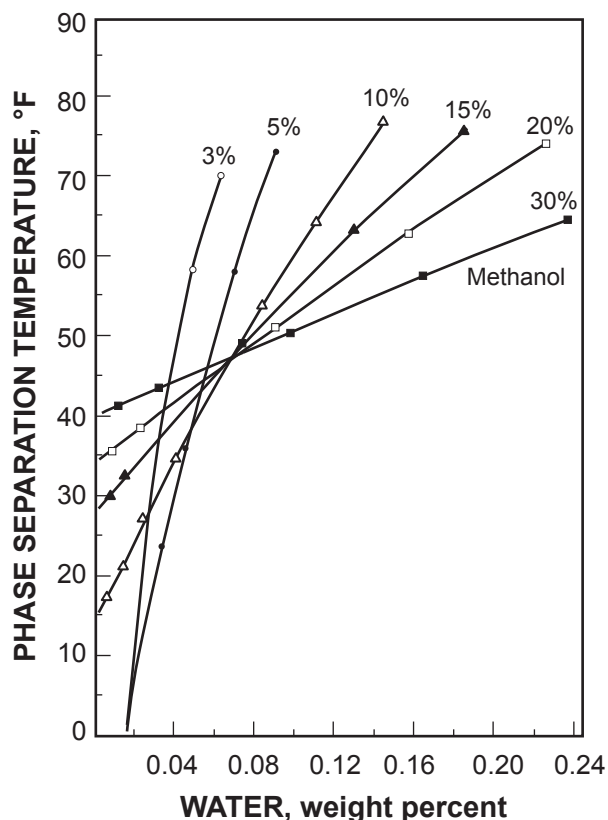


FIGURE V.3 The Water Tolerance of Methanol Added to Gasoline (Source: Ref. 31)

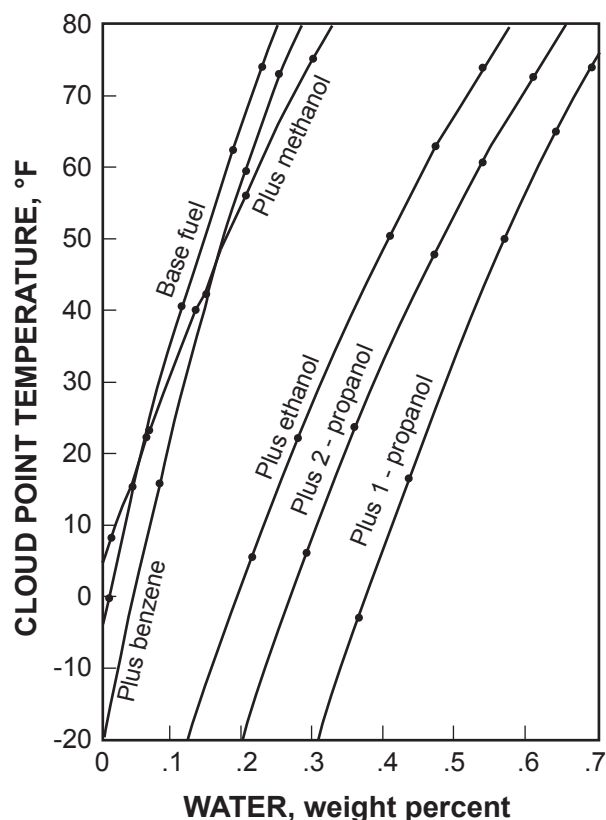


FIGURE V.4 The Impact of Cosolvents on the Water Tolerance of a 10 wt% Blend of Methanol in Gasoline (Source: Ref. 31)

Cosolvents can have a dramatic effect on the water tolerance of gasoline blended with methanol. Figure V.4 shows the impact that adding 5 wt% alcohol cosolvents can have on the water tolerance of a 10 wt% blend of methanol in gasoline. The higher alcohols of Figure V.4 significantly improve the water tolerance of methanol blends.

The composition of the gasoline can also have a large impact on methanol solubility. Gasolines with high aromatic content will dissolve more methanol than gasolines with high paraffinic content. Table V.1 shows the large impact gasoline composition can have on methanol solubility.

C. MATERIALS COMPATIBILITY

Automotive fuel systems contain a wide range of elastomeric² and metallic components. The elastomers are used primarily as seals and fuel lines but vehicle manufacturers have recently been moving to fuel lines that are non-metallic all the way from the fuel tank to the engine fuel system, which greatly increases the amount of wetted area between the elastomers and the fuel. Many fuel tanks are now non-metallic as well for reasons of cost and ability to be molded into complex shapes that maximize volume in tight vehicle confines.

²Elastomer is a generic term that includes all soft parts in a fuel system including rubbers, plastics, nylons, fluorosilicones, urethanes, etc.

TABLE V.1 Methanol Solubility Based on Gasoline Composition (Source: Ref. 32)

Aromatics in Gasoline, Volume Percent		Methanol Solubility, Volume Percent	
		-10° to 0°F	32° to 37°F
16		2-3	5-10
28		5-10	15-20
31		5-10	>50
42		>50	>50
Gasoline Composition			Minimum Temperature at which 10% Methanol will Dissolve, °F
Saturates	Aromatics	Olefins	
100	-	-	80
65	21	14	44
43	2	55	20
20	78	2	4

Elastomers must not crack, leak, or become permeable to fuel; if they do, vehicle safety is impaired and/or evaporative emissions increases will occur. No elastomer is completely unaffected by exposure to fuel, with changes occurring in volume (swell), tensile strength, and elongation. The addition of methanol to gasoline causes changes in elastomers that are difficult to predict. Figure V.5 illustrates testing done on various generic elastomers used in fuel systems (measuring swell) using two gasolines, neat ethanol, and a blend of the base gasoline and 10% methanol [32]. In general, neat methanol caused less swelling of the elastomers than the blend of 10% methanol in gasoline, and in most cases, the 50% aromatic gasoline caused more swelling than 10% methanol. Only the fluorocarbon showed more swelling in methanol and the 10% blend than in either of the gasolines tested.

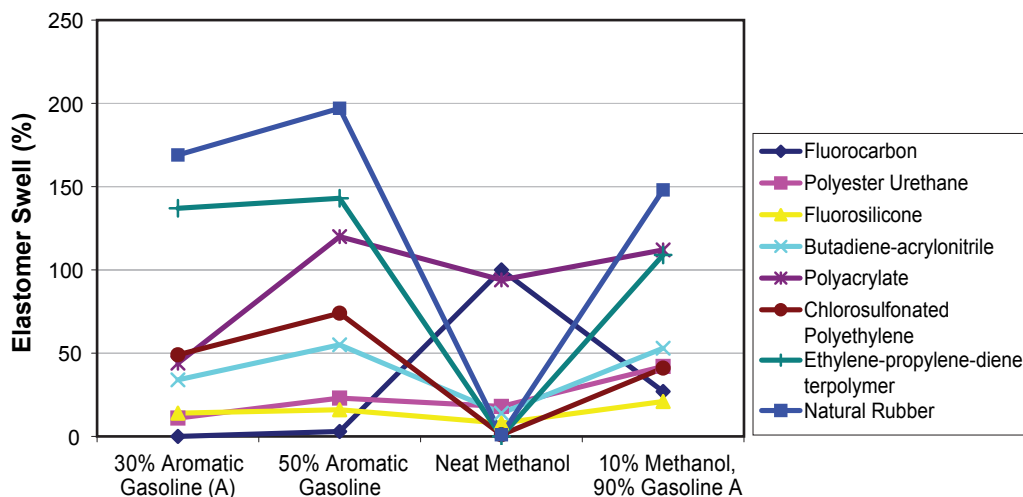


FIGURE V.5 Elastomer Swell from Exposure to Gasoline, Methanol, and a 10% Methanol Blend (Source: Ref. 32)

Figures V.6 and V.7 show additional test data complementary to the results in Figure V.5 for polyester urethane and fluorocarbon over the entire range of methanol blends from 0 to 100% [33]. These data show that elastomers change continuously with percent methanol content, with the greatest change often occurring with an intermediate blend. A field trial of 4% and 15% methanol in gasoline in Norway reported swelling of some fuel lines, though the amount was not quantified [34]. In a similar field trial of M15 in New Zealand, problems with fuel lines were observed along with other fuel system elastomers including carburetor needle valve seats, fuel tank level floats, and fuel pump diaphragms [35]. The problems reported in the New Zealand fleet test were judged to be relatively minor and were easily corrected by replacement with new parts. Without a control fleet, it is not known whether these problems represented a significant change or not.

These data suggest that the impact of methanol on elastomer materials is relatively benign compared to high aromatic gasolines. However, these tests were done using new elastomers and relatively pure fuels. As elastomers age in service, they are less amenable to change. There are several instances of field problems caused by changes in fuel properties. For example, the change to ultra-low sulfur diesel fuel caused numerous fuel system leaks because the elastomers were adversely affected by a relatively small change in fuel properties. New versions of the same elastomers worked, illustrating the impact aging can have on fuel system elastomers. Other confounding factors include

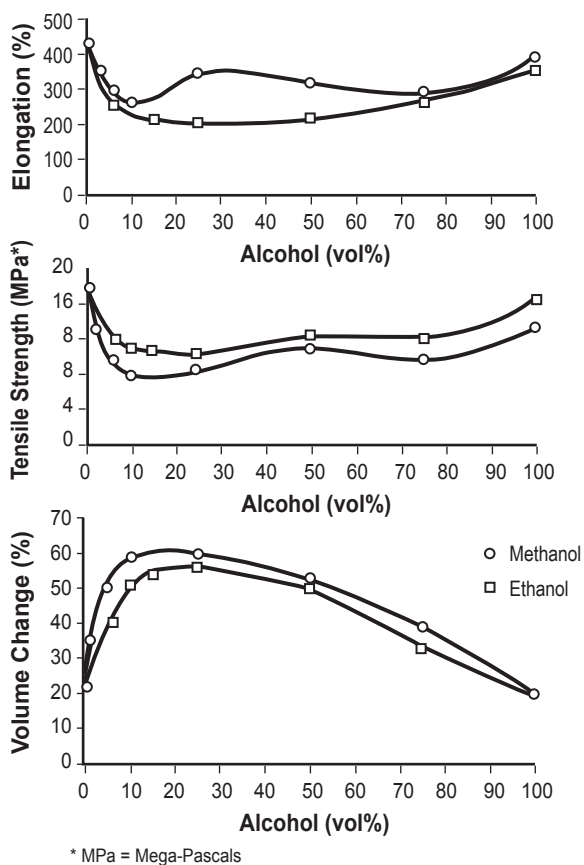


FIGURE V.6 Polyester Urethane Compatibility with Ethanol and Methanol Blends (Gasoline A from Figure V.5; Source: Ref. 33)

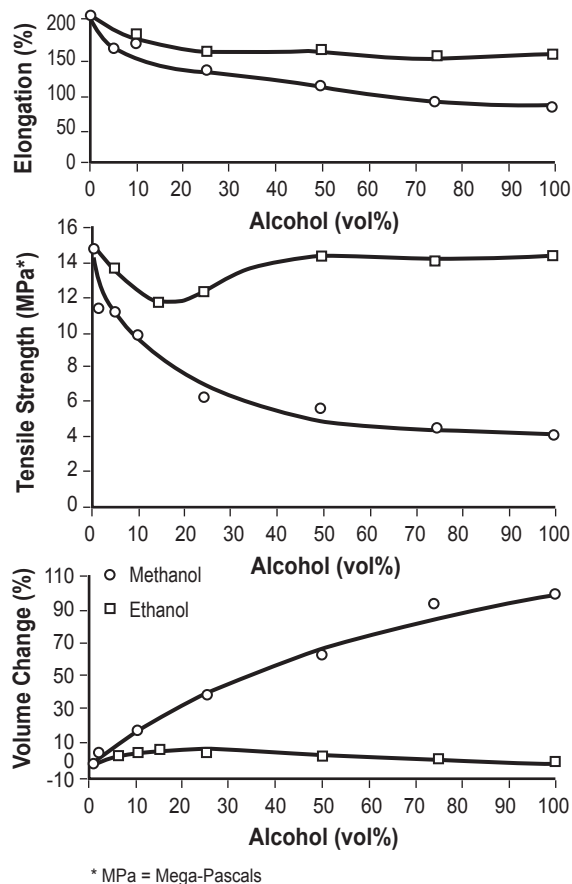


FIGURE V.7 Fluorocarbon Compatibility with Ethanol and Methanol Blends (Gasoline A from Figure V.5; Source: Ref. 33)

the shape of the elastomer and whether it is attached to a metal that might be attacked by methanol. Complex-shaped elastomers may react differently than the uniform elastomer shapes used for testing.

Methanol fuels of all types can be extremely aggressive toward magnesium and, if they contain dissolved or separated water, toward aluminum, also [36]. Steel and other ferrous metals are usually only slightly affected unless the blend has a separated water phase, in which case some pitting may occur. Additives have been found to be effective in reducing the corrosive effects of methanol in gasoline (blends of up to 10%) on copper, cast iron, steel, and aluminum [37]. Corrosion inside 4-stroke engines can be controlled through the use of properly formulated engine oils [38].

Methanol blend fuels often cause material deterioration problems with nonmetals usually in proportion to the amount of methanol in the blend. Methanol-rich fuels have been shown to cause shrinkage, hardening, swelling or softening of cork gasket material, leather, Viton, and polyurethane [36]. Buna-N, Delrin acetal, high-density polyethylene, polypropylene, and Nylon 6/6 showed good resistance to these effects in the same study. A potentially serious problem may occur in the reaction to methanol fuels displayed by polyester-bonded fiberglass laminate at somewhat elevated temperatures (approximately 118°F [47.8°C]). Softening, swelling, blistering, and signs of delamination were observed in this popular fuel storage tank and tank lining material [36]. Reactions at room temperatures (approximately 73°F [22.8°C]) were less severe, but still noticeable. Note that these issues only refer to vehicles designed for gasoline fuel only. Vehicles designed for M85 have elastomers compatible with methanol.

D. OXYGEN CONTENT

Gasolines and diesel fuel produced from crude oil are composed entirely of compounds that are composed almost entirely of carbon and hydrogen with very small amounts of nitrogen and sulfur. In contrast, methanol is 50% oxygen with the remainder being carbon and hydrogen. As a result, methanol needs less air for complete combustion since the oxygen in its composition displaces the need for oxygen in the air. The stoichiometric air/fuel ratio for methanol (weight basis) is 6.45 (mass air to mass methanol) compared to about 14.7 for gasoline. Figure V.8 shows the impact this has on blends of gasoline and methanol. As methanol is added to gasoline, the oxygen content of the blend goes up, but, since the oxygen does not contribute to heating value, the volume of fuel needed to generate the same power increases. (This discussion assumes that the efficiency of the engine does not change with the amount of methanol, which is reasonable for fixed compression ratio engines.) Thus, a blend of 10% methanol in gasoline requires approximately 105% of the volume of straight gasoline to make the same amount of power. If an engine were capable of operating on 100% methanol, it would require twice as much fuel volume compared to an engine running on straight gasoline.

The preceding discussion assumes the engine is designed for gasoline but is using methanol blends with gasoline. Engines optimized for use of methanol blends where methanol is the predominate component, such as 85% methanol (M85), can be made more efficient through use of higher compression ratios and other engine adjustments optimized to methanol. In addition, an engine optimized for high methanol blends can have higher specific power output, creating the opportunity to reduce engine displacement for a given application. With both an engine optimized for methanol and reduced engine displacement, significant increases in energy efficiency are possible relative to gasoline engines.

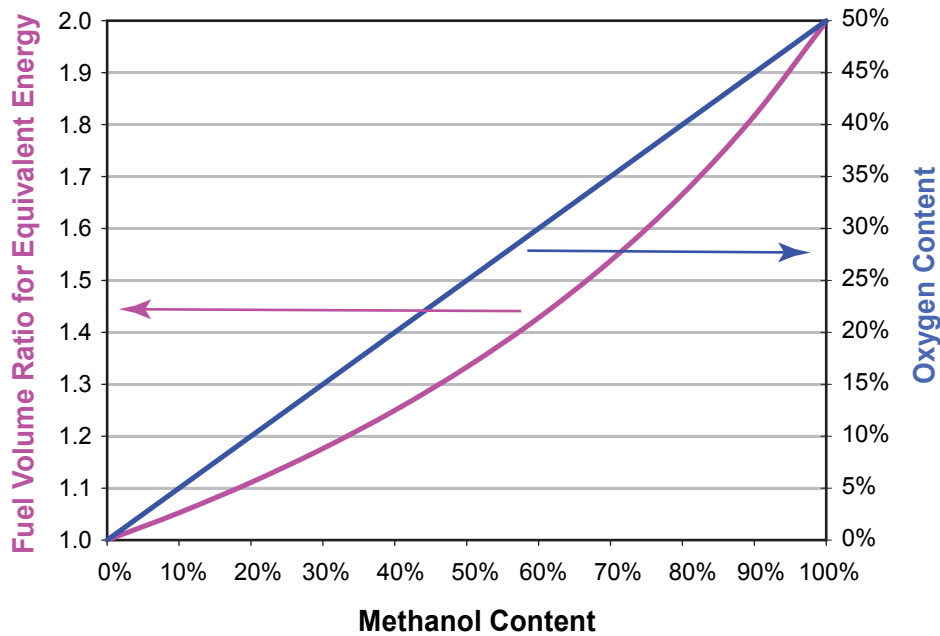


FIGURE V.8 Oxygen Content and Fuel Volume Ratio for Gasoline/Methanol Blends

E. OCTANE VALUE

Methanol has good octane properties compared to gasoline. With a research octane value of 108.6 and a modified motor octane value³ of 88.6, methanol has sufficient octane to allow engines optimized for methanol to have high compression ratios with the attendant benefits of improved power and efficiency. When used in blends, the high octane value of methanol can be used to reduce the refining severity of the associated gasoline blendstock, allowing increases in refinery output and efficiency.

³The standard motor octane test must be modified to include fuel heaters to enable methanol to be tested.

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, driveability⁴, and cold-start performance. The amount of increase depends on the amount of methanol in the blend, as illustrated in Figure V.8. Vehicles with feedback fuel systems that use an oxygen sensor in the exhaust stream will be able to compensate up to the excess flowrate built into the fuel system by design. However, the amount of excess flowrate built into a vehicle fuel system varies with each vehicle powertrain family and may also change with time, as fuel pump performance degrades and deposits build up that constrict fuel flow.

Most current technology fuel systems have the capability to adjust fuel flow in response to environmental factors such as altitude, temperature, humidity, and changes in fuel properties that affect stoichiometry, such as hydrocarbon composition and oxygen content. This capability is called adaptive learning and takes place after the vehicle is warmed up⁵ and the feedback control system is operating. The objective of adaptive learning is to fine-tune the system to dither the air/fuel ratio around the stoichiometric value as determined by the oxygen sensor so that the three-way exhaust catalyst will operate efficiently. As methanol is added to gasoline, the stoichiometric air/fuel ratio changes, and the feedback control system must adjust accordingly.

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. During these modes, changes in fuel stoichiometric air/fuel ratio will be reflected directly in vehicle operation since the engine control system has no way of detecting that a different fuel is being used.

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 compared to gasoline. Methanol's flash point is 52°F (11°C) compared to gasoline, which has a typical flash point of -43°F (-45°C). Thus an engine configured to use methanol instead of gasoline will not start below 52°F without external starting aids.

Another large 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. The fact that methanol is a homogeneous liquid with a single boiling point combined with the need for much more energy to vaporize it results in much less vapor generation at typical starting temperatures than gasoline, which has some hydrocarbons that vaporize at low temperatures.

⁴ Driveability is a measure of vehicle operational problems such as stalling or surging during warm-up, unstable idle, uneven acceleration, non-linear throttle response, occurrence of vapor lock, etc. Good driveability is an absence of operational problems.

⁵ Being "warmed-up" generally means three criteria have been met for vehicles with catalyst emission control systems: 1) the oxygen sensor temperature is around 600°F, 2) the coolant temperature is around 150°F, and 3) a predetermined amount of time has elapsed from the time the engine has started (from a few seconds to 1-2 minutes).

When methanol is blended in gasoline, it adversely affects cold-start capability in a number of similar ways. While methanol depresses the lower end distillation of the gasoline into which it is blended, the vapor that is generated has disproportionately more methanol in it making the vapor leaner than that from straight gasoline. The higher latent heat of vaporization of methanol makes the vapor generated more difficult to heat up, resulting in lower temperatures during starting events. A blend of 5% methanol in gasoline needs 14% more energy to vaporize completely [32], with most of that difference accounted for before 50% distilled, as illustrated in Figure V.2. Moreover, if the gasoline has had its front end volatility adjusted to compensate for the azeotroping effect when methanol is added, the low boiling hydrocarbons that provide much of the vapor for cold-weather starting, such as butane, will have been reduced, causing further detriment to cold-starting capability.

In Otto-cycle spark ignition engines, more fuel is introduced during cold-start than is necessary for complete combustion so that sufficient fuel vapor is generated to get into the flammable range. In testing conducted with gasoline at -22°F (-30°C), it was found that the amount of gasoline needed to achieve cold-start was eight times the stoichiometric value. With a blend of 10% methanol having the same RVP as the gasoline, it was found that fuel needed to be added at the rate of 14 times the

stoichiometric value [32]. Despite the adverse impacts adding methanol can have to cold-start performance, fleet tests of low-level methanol blends did not report statistically significant changes in cold-start performance.

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. As explained previously, adding methanol to gasoline causes the engine to operate leaner, especially during cold-start and warm-up, when driveability defects are most likely. 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 Figure VI.1). 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.

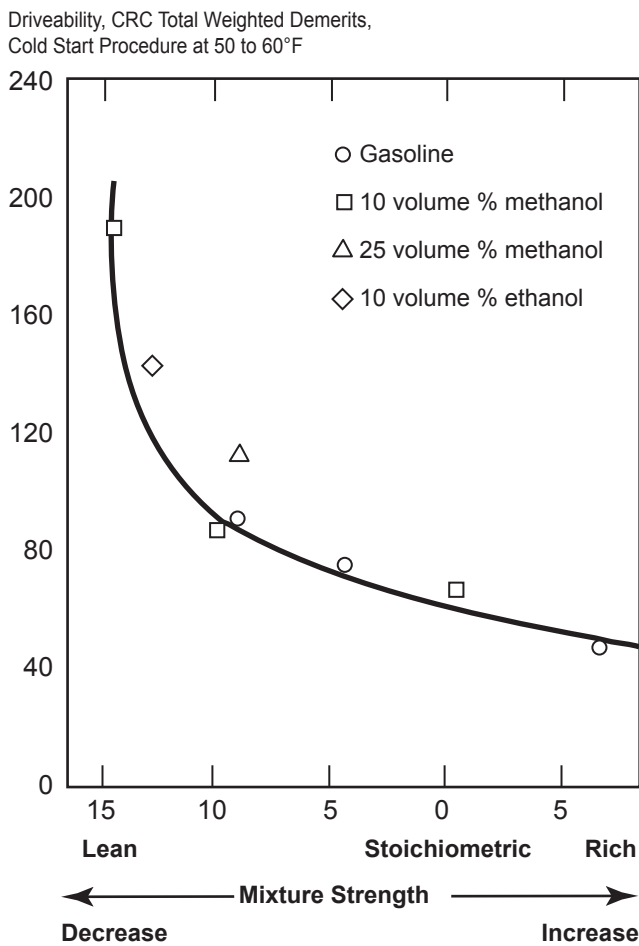


FIGURE VI.1 Adding Methanol to Gasoline is Equivalent to Leaner Gasoline Calibration in Terms of Driveability (Source: Ref. 32)

C. ACCELERATION

When a driver evaluates acceleration, it is often not just how quickly the vehicle will accelerate, but the quality of that acceleration (i.e., linear throttle response, no surges or stumbles, etc.). If the vehicle is not fully warmed up, methanol blends can cause the vehicle to exhibit slower acceleration and the driveability problems just identified. 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. However, if the vehicle spends a significant amount of time at full-throttle, acceleration may be impacted depending on the full-throttle calibration using gasoline. For example, tests of early carbureted vehicles in Brazil calibrated to use 20% ethanol found that acceleration was better using 20% ethanol than straight gasoline [39]. 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. All things equal, use of methanol results in faster acceleration because its higher octane and latent heat of vaporization allow for more spark advance than gasoline. Engines optimized for methanol can easily be more powerful than similar displacement gasoline engines, with the result being faster acceleration.

D. FUEL ECONOMY

As shown in Figure V.8, 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 (see Figure VI.2) [40]. However, when the change in energy content was taken into account, there was no change, indicating that the engine efficiency was not affected. (Note that 30% methanol was the maximum blend this vehicle could accommodate without driveability problems. Cold-starting using 30% methanol was not tested.) Vehicle users experience a wide range of fuel economies depending on weather and on how the vehicle is used, and may not be able to distinguish the impacts of low-level methanol blends.

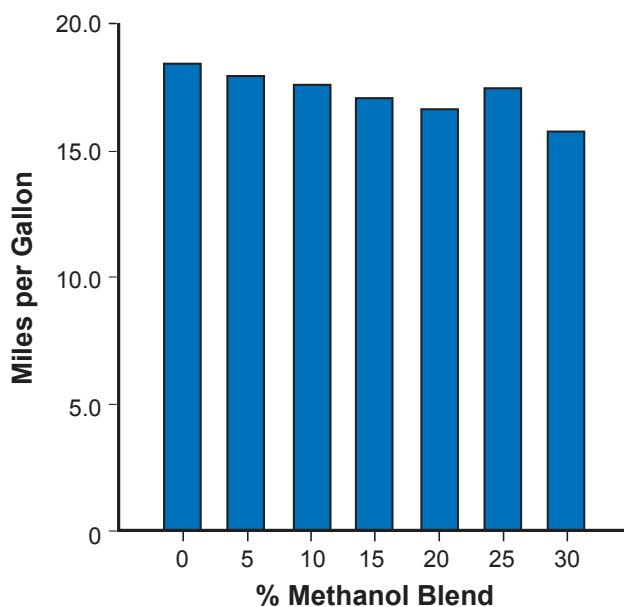


FIGURE VI.2 Impact of Methanol Blends on Fuel Economy
(Source: Ref. 40)

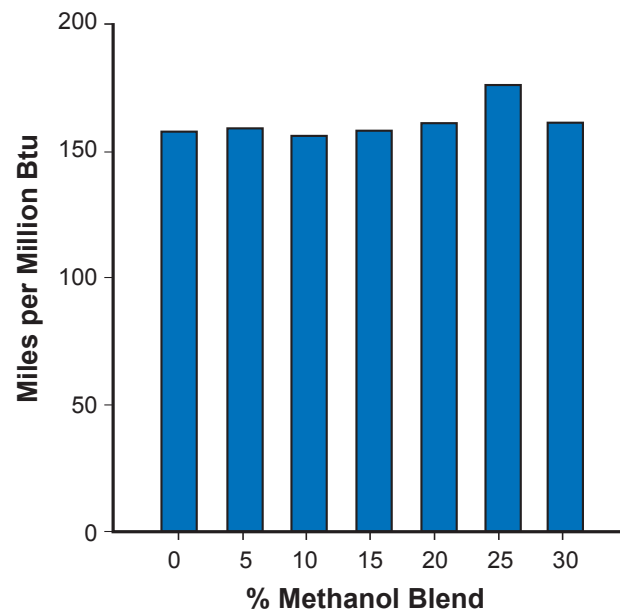


FIGURE VI.3 Impact of Methanol Blends on Energy Economy
(Source: Ref. 40)

VII. Emissions Impacts

A. PRIMARY REGULATED EXHAUST EMISSIONS

Methanol has some inherent emission advantages over gasoline when combusted in internal combustion engines. Emissions of CO are a function of combustion stoichiometry and will not be significantly different from gasoline combustion as the same stoichiometry [33]. Likewise, HC emissions will be similar in magnitude compared to gasoline, but unburned methanol has significantly lower reactivity as an ozone precursor in the atmosphere compared with most gasoline HCs. This advantage is offset somewhat by increased formaldehyde emissions from methanol combustion, but modern catalyst systems are very effective at reducing formaldehyde emissions, resulting in a net benefit for methanol over gasoline. Figure VII.1 shows general engine-out emission trends for CO and HCs with stoichiometry for methanol combustion.

Emissions of NO_x are typically lower than those from gasoline when methanol is combusted under similar engine conditions (see Figure VII.2). 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 NO_x emissions by 30% [40,41]. This advantage is significantly negated if the engine compression ratio is increased and/or other engine changes are made to maximize the specific power potential of methanol. Research by Volkswagen showed that increasing the compression ratio to 13:1 to take advantage of methanol's higher octane increased engine-out NO_x emissions to the same level as for gasoline at a compression ratio of 8:1 [42]. However, with modern three-way catalyst systems, the inherent advantage of lower engine-out NO_x emissions is not a significant advantage.

Recent development of the homogeneous charge compression ignition (HCCI) combustion system holds promise for internal combustion engines using neat methanol as fuel. When methanol is used in HCCI

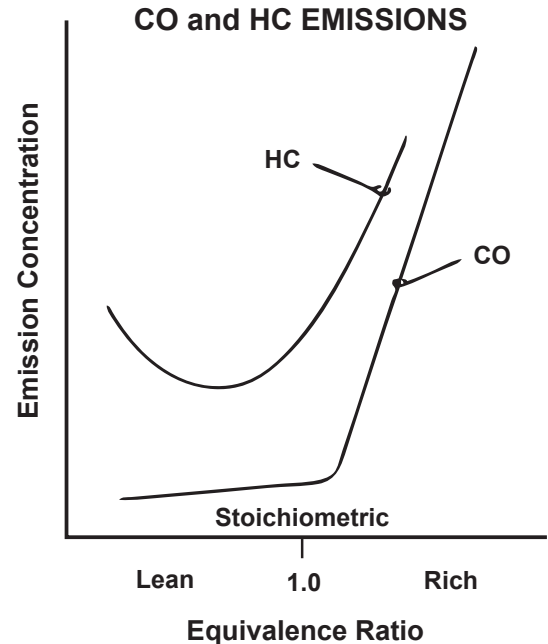


FIGURE VII.1 Engine-Out CO and HC Emission Trends (Source: Ref. 33)

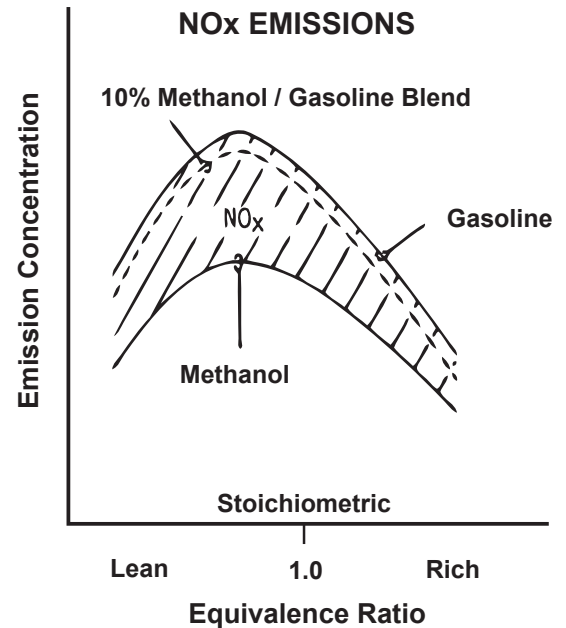


FIGURE VII.2 Engine-Out NO_x Emission Trends Compared to Gasoline at Constant Compression Ratio (Source: Ref. 33)

engines, emissions of NO_x can decrease to near-zero [43]. HCCI engines have the potential to replace both gasoline and diesel engines.

Blends of methanol and gasoline affect vehicle emissions according to the amount of oxygen introduced into the blend from the methanol. Figure VII.3 shows general trends and confidence intervals for tests of many vehicles using a range of methanol blends (including co-solvents) [44]. These are tailpipe emissions from typical emission control systems for vehicles of that era (early 1980s), which included an oxidation catalyst. The addition of oxygen through methanol and its co-solvents causes the fuel stoichiometry to move leaner with the result that CO and HCs are reduced with NO_x increasing slightly. These results were corroborated by the Coordinating Research Council in tests performed for the U.S. Department of Energy [45].

The U.S. Environmental Protection Agency (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 [46]. The vehicles were 1990 and 1992 models, all equipped with fuel injection and three-way catalyst feedback emission control systems. The gasoline used was representative of a summer-time gasoline and the ethanol was splash-blended (i.e., the hydrocarbon portion was not tailored for ethanol blending). 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. (There was no indication whether these vehicles would have acceptable driveability at the higher blend levels tested.)

While the magnitude of the emission changes varied among the six vehicles EPA tested, they all showed the trends illustrated in Figure VII.3. 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 (the equivalent of 40% ethanol or 28% methanol). For HCs, the reduction was 32% while NO_x increased 64%. Thus, while these vehicles were at least ten years newer than the ones tested to develop the data of Figure VII.3, the same trends persisted, no doubt due to the fact that most emissions from vehicles with modern catalytic emission control systems occur during open-loop operation, e.g., cold-start, warm-up, and wide-open-throttle acceleration. It should be noted, however, that these vehicles had diminished response to fuel oxygen content compared with the data of Figure VII.3, though still significant.

A more recent study using late-model vehicles fueled with 20% ethanol (7% oxygen) was conducted by Orbital Engine Company

Regression Lines and 95% Confidence Intervals

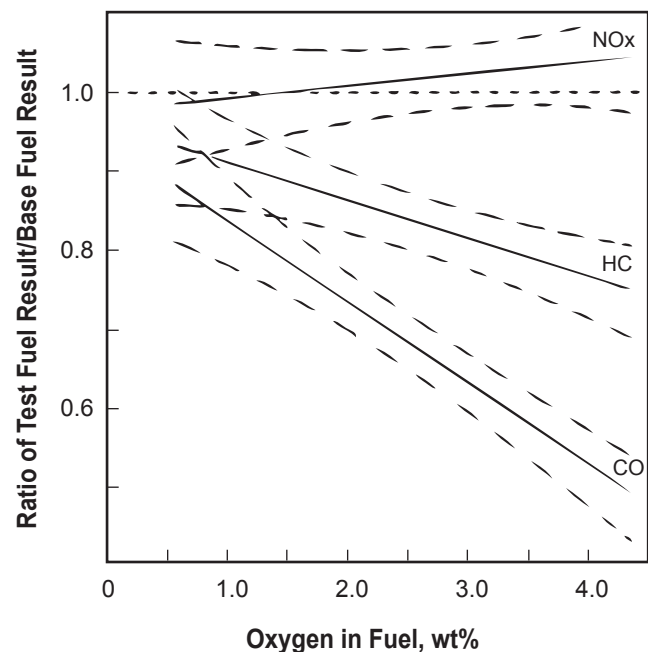


FIGURE VII.3 Emission Trends for Blends of Methanol in Gasoline (Source: Ref. 44)

for Environment Australia [47]. They tested five 2001 model year vehicles, with all of them having electronic fuel injection and three-way catalyst emission control systems. These vehicles were chosen to be representative of the fleet in Australia, but they have the same fuel and emission control systems as their counterparts in other parts of the world, except for perhaps different calibrations.

The emissions of these vehicles were tested using the U.S. Federal Test Procedure, the same as EPA used in its test program. Orbital found that on average, HC emissions decreased by 30%, CO emissions decreased by 29%, and NO_x increased by 48% when using 20% ethanol. These results are similar in direction but larger than what EPA had found (i.e., 16% decrease in total HCs, 22% decrease in CO, and 32% increase in NO_x at 7% oxygen). One difference between these two groups of vehicles is that the Orbital vehicles were purchased new and were operated 4,000 miles before emissions testing was conducted, while the vehicles tested by EPA were in-use vehicles (their individual mileage accumulations were not listed). It should also be noted that percent change in emissions is being compared among these three groups of vehicles, not absolute emissions levels, which were different for all the vehicles tested.

These changes in emissions are indicative of the inability of the fuel systems to compensate completely under all circumstances for the oxygen addition from the ethanol. One potential long-term impact of the oxygen addition is more rapid deterioration of the catalyst. Orbital measured catalyst temperatures that were higher during wide-open-throttle using 20% ethanol compared to straight gasoline in every vehicle due to the inability of the fuel system to maintain the desired stoichiometry. Elevated catalyst temperatures during wide-open-throttle cause more rapid catalyst deterioration and increases in all emissions as the catalyst degrades. This is in fact what Orbital found after driving its vehicles for 80,000 km (50,000 miles) and retesting emissions [48]. Only two of the five vehicles showed decreased HC and CO emissions at 50,000 miles, while all the vehicles showed decreases in HCs using 20% ethanol during testing at 4,000 miles. Four out of five vehicles showed an increase in NO_x at 50,000 miles using 20% ethanol, which is the same result as was obtained during the 4,000 mile testing except that the vehicles showing the decrease were not the same at 4,000 and 50,000 miles. Orbital investigated the vehicle with the most emissions deterioration and found that the catalyst had a large decrease in conversion efficiency, with higher catalyst operating temperatures being the most likely reason. This vehicle had a low power-to-weight ratio and therefore operated at high engine loads for a greater percentage of the time, which accelerated its catalyst deterioration due to higher exhaust temperatures. The effect on the other vehicles was similar but more gradual.

These test programs suggest that using intermediate to high level methanol blends in vehicles not designed for them can reduce CO and HC emissions in the short term, but cause increases in all emissions over the long term if the catalyst is more rapidly degraded.

B. CARBON DIOXIDE EMISSIONS

The predominate compound from the combustion of methanol is carbon dioxide, as from gasoline. 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) maintained by Argonne National Laboratory shows carbon dioxide emissions for flexible-fuel vehicles using 85% methanol (M85) to have carbon dioxide emissions that

are 96% those of a similar vehicle using gasoline [49]. 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% 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. Methanol vehicles with engines optimized for methanol could achieve even greater fuel savings with corresponding decreases in carbon dioxide emissions.

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 [50] (see Figure VII.4 for general trends in aldehyde emissions from both methanol and gasoline). Tests of neat methanol vehicles have shown that formaldehyde is the predominant toxic emission from methanol combustion [51]. 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

Neat methanol produces lower levels of vapor compared to gasoline because of its higher boiling point compared to the initial boiling point of gasoline. Early work by Union Oil Company found that methanol vapor degraded the ability of automotive charcoal canisters to adsorb vapors compared to gasoline [36]. However, the M85 vehicles produced and used in the U.S. met the same evaporative emission standards as comparable gasoline vehicles and long-term deterioration of the charcoal was not reported as a problem.

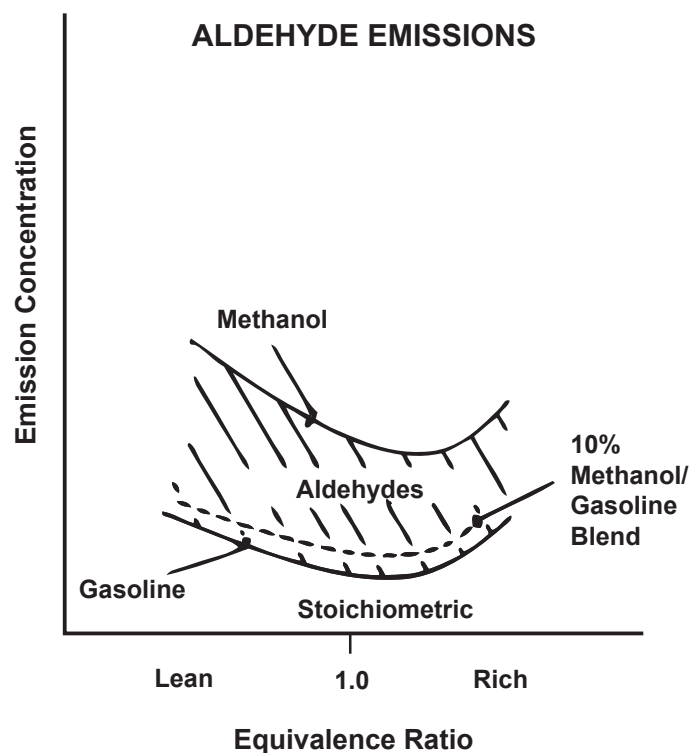


Figure VII.4 Aldehyde Emission Trends for Methanol and Gasoline
(Source: Ref. 33)

As explained in Section V, adding methanol to gasoline will greatly increase the amount of vapor generated along the lower half of the gasoline distillation curve. Since vehicle evaporative systems are sized for gasoline, adding methanol to gasoline that has not been modified to reduce its front end volatility (0 to 50% distilled) will almost certainly result in saturation of the canister and, consequently, very high 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 [52]. For evaporative emissions certification of M85 vehicles, EPA requires tests using M85, straight gasoline, and the blend of the two with the highest vapor pressure [53].

As fuel systems have moved away from steel tanks and lines to plastic, permeation emissions from methanol and methanol blends is likely. (Permeation is the evaporation of fuel through elastomeric materials used in the fuel system, but primarily from the lines and tanks.) In the U.S., testing has been done to measure the permeation emissions of ethanol blends in gasoline. It was 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 [54]. 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. For example, treatments for plastic tanks have been developed (fluorination and sulfonation) to reduce permeation losses. Multi-layer fuel tanks that contain a continuous layer of a reduced permeation component in the middle have also been developed. While the techniques to reduce permeation undoubtedly cost more than plain plastic tanks, they are the same techniques used to reduce permeation emissions from gasoline vehicles designed to meet the most stringent evaporative emissions standards, i.e., the PZEV (partial zero-emission vehicle) standard in California. As more stringent evaporative emission standards become more prevalent, the cost differential for methanol vehicles with such fuel systems will become insignificant.

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. This type of assessment of the GHGs from transportation vehicles is known as "well-to-wheels". In this case, it is assumed that the methanol is used in internal combustion engine vehicles specifically designed for methanol, which take advantage of methanol's properties to increase efficiency.

The GREET model was used predominately for this analysis [49]. GREET only includes preliminary numbers for methanol from coal and methanol from biomass. An independent estimate of the well-to-wheels GHGs of methanol from coal was made for this analysis.

The following methanol production resources were included:

- Natural gas
- Coal

- Coal with sequestration of carbon dioxide
- Biomass

The natural gas case is included as a benchmark for comparison since natural gas is the predominate resource currently used to produce methanol. However, it should be understood that this natural gas case is specific to North America – methanol made from natural gas elsewhere or under specific circumstances could have higher or lower GHGs. The coal cases are also specific to North America and assume use of bituminous coal (properties taken from GREET). 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 [55]. Methanol from biomass is assumed to use wood as the resource with gasification technology.

The methanol internal combustion engine vehicles are assumed to be 7% more efficient than their gasoline counterparts [49]. The reasons include higher octane value, lower combustion temperature, and more efficient combustion.

Figure VII.5 shows the results. Methanol (MeOH) from natural gas is projected to produce just slightly less GHGs than gasoline – this is due primarily to the assumption that methanol vehicles are 7% more efficient. With the range of GHG emissions possible from both gasoline production and methanol production from natural gas, it is most likely that this difference is not significant. 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. 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 because all the

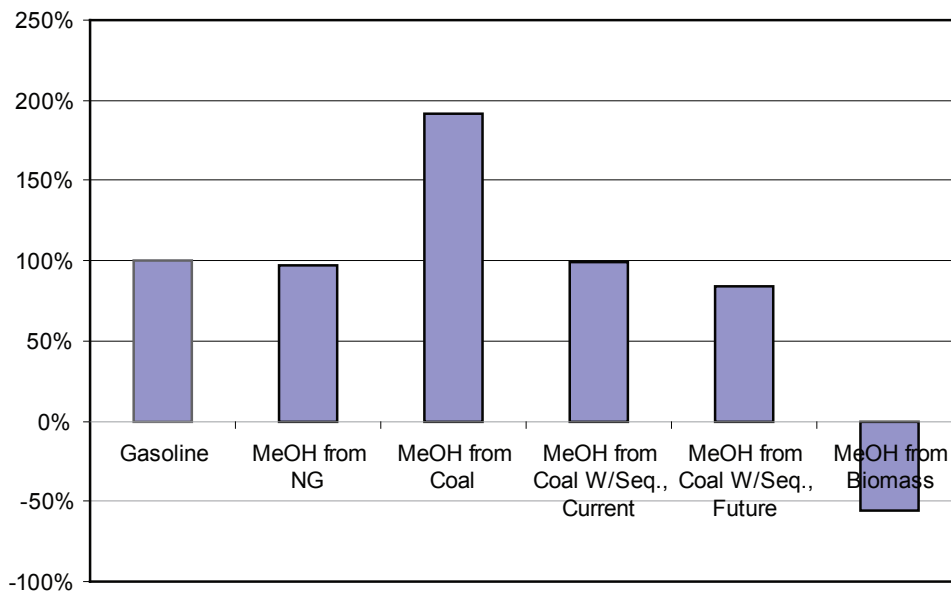


FIGURE VII.5 Methanol “Well-to-Wheel” GHGs from Various Resources

carbon used to make it is renewable (i.e., the carbon emitted is sequestered back into the ground by regeneration of the feedstock)

The coal cases here assume plants that only make methanol. Plants that combine methanol production with electricity generation have the potential to produce methanol more efficiently than stand-alone plants. The efficiency of producing methanol using the Air Products LPMEOH™ methanol production technology has been estimated to be 71%, compared with the 55% assumed here for stand-alone plants [56]. Methanol produced in these facilities would have correspondingly lower GHGs.

VIII. Infrastructure Impacts

Methanol is made in numerous places around the world and is often transported via ocean tanker to various countries that consume it. This section focuses on the distribution, storage and retail dispensing of methanol within countries for use in transportation vehicles.

A. DISTRIBUTION

Methanol is typically shipped via railroad tank car, barge, and truck tanker, depending on volume and distance [57]. In the U.S., only a very small amount of methanol is sent through pipelines, and only over very short distances [58]. 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. During the introduction of methanol, methanol movement would initially represent a small minority of all the liquid fuel being transported via pipeline. Intermittent transport of methanol in petroleum pipelines faces the problems of potential interface mingling and the need for additional storage suited for methanol. Where petroleum products are taken out of the pipeline, the cut-point is designed to protect the product that would be most unacceptably degraded, while leaving as much of the interface in a product that would not be degraded, if possible. For example, methanol could possibly be shipped neat, wrapped with different classes of gasoline at each end. The interface could stay with the methanol, thus providing some of the gasoline that would otherwise be blended to produce, for example, M85. The proliferation of different products for pipelines to wrap, however, makes such arrangements increasingly complicated. If methanol had to be wrapped with products other than gasoline, such cutting would be unacceptable. In those cases, much of the interface – the “transmix” – would have to be removed and reprocessed, possibly by a small regional transmix separator but in some cases it would have to be shipped back to a refinery. Such separations will be much more difficult with interfaces composed of methanol and petroleum fuel.

In addition, the methanol will remove any existing water and petroleum residues in the pipeline, further degrading the quality of the interface volume.

One technique to minimize interface volume is through the use of a device that physically separates batches within a pipeline, commonly called a “pig.” The use of pigs may not solve the water uptake and deposit removal problem, however, and it is unknown how frequently it is practical to send pigs through the line (pipelines generally only go in one direction – the pigs would have to be transported back to the place of their insertion). These issues and others will need to be explored before it will be known whether shipment of methanol through existing petroleum pipelines will be practical.

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 arrestor 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 methanol-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 [59]. 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 [60]. Most underground storage tanks use submersible pumps, which must have materials compatible with methanol. As the methanol is pumped from the underground tank, it travels through piping to the dispenser (see Figure VIII.1). 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.

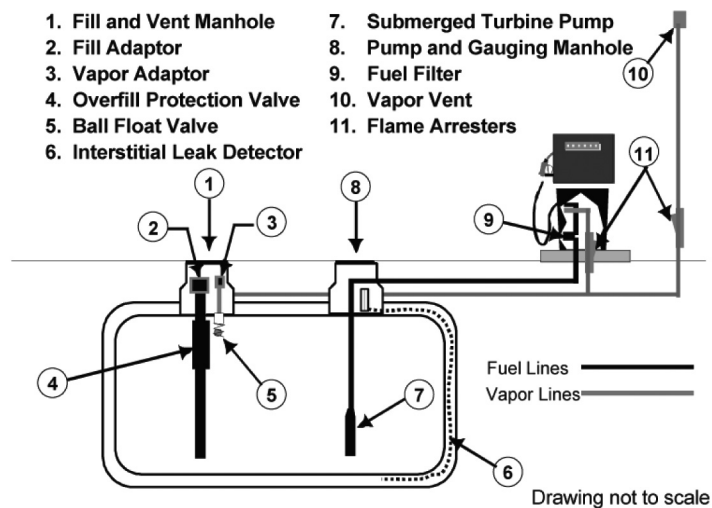


FIGURE VIII.1 Methanol Refueling Station Schematic (Source: Ref. 60)

For threaded pipe connections, Teflon[®] tape or paste is preferred for use with methanol. Pipe dope intended for use with gasoline will be dissolved by methanol, creating leaks. Bolted connections must use gaskets compatible with methanol.

Dispensers designed for petroleum fuels typically use steel, cast iron, aluminum, brass, bronze, and stainless steel. Of these, only the steels and cast iron are compatible with methanol. In addition, dispensers use several gaskets and elastomers which are unlikely to be methanol-compatible. Dispenser manufacturers have developed units compatible with methanol; these must be used to prevent malfunction and fire hazards from leaks.

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 [59].

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 [59]. 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 Figures VIII.2 and VIII.3) was developed

by the Methanol Fuel Cell Alliance, an industry consortium led by BASF, BP, DaimlerChrysler, Methanex, Statoil, and Ballard [61]. 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 [62].



FIGURE VIII.2 The Identic Spill-Free Methanol Refueling Nozzle In Use (Source: Ref. 61)

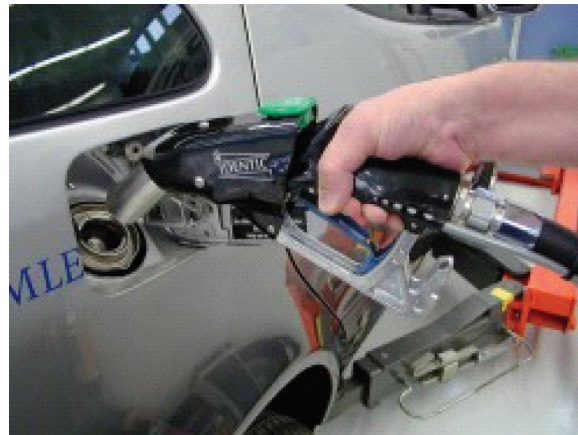


FIGURE VIII.3 The Identic Spill-Free Methanol Refueling Nozzle In Use (Source: Ref. 62)

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 [63]. 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 [64,65,66,67].

A. USE OF METHANOL IN BLENDS WITH DIESEL FUEL

Methanol has very limited solubility in diesel fuel (only a few percent) and was not considered seriously as a means of using it in diesel engines. Other oxygenates have been seriously considered for blending into diesel fuel [68].

B. USE OF METHANOL IN EMULSIONS WITH DIESEL FUEL

The very limited solubility of methanol in diesel fuel led to extensive research to find ways of using methanol through emulsions [63,69]. Through the use of emulsions, it was found possible to add large amounts of methanol to diesel fuel (tests using 10-30% were common). The disadvantages found to methanol emulsions included the following:

- Roughly an equal amount of emulsifier was needed as methanol, making the fuel expensive.
- The addition of methanol quickly degraded the cetane number of the emulsion, necessitating engine injection timing changes or addition of an ignition improver additive.
- Emulsions become quite viscous at low temperatures and tend to separate in the presence of water.
- Emulsions tend to corrode fuel injection system components and cause elastomer compatibility problems.
- Since the volumetric heating value of emulsions is reduced relative to diesel fuel, adjustments to increase fuel flow may be necessary to maintain full power.

For these reasons, no emulsions of methanol and diesel fuel have been commercialized to date.

C. USE OF METHANOL THROUGH FUMIGATION

Fumigation is a method to introduce alcohol into a diesel engine by carburetion or vaporization in the intake manifold with subsequent ignition by diesel fuel injection. This requires addition of a carburetor, fuel injection system, or vaporizer along with a separate fuel tank, lines, and controls for the methanol. Methanol delivery must be limited at all loads to prevent misfire and at intermediate and high loads to prevent engine knock. In the midload range, up to 50% of the fuel energy can be derived from methanol, while at lower engine loads, up to 80% diesel fuel energy substitution has been demonstrated [63]. The typical overall replacement value has been much lower, however. The control requirement of an engine to achieve its maximum diesel fuel displacement value increases the complexity of the engine control system. An advantage of a fumigation system is that switching from fumigation to straight diesel fuel operation may be possible – clearly a desirable option if methanol supplies are intermittent.

Turbocharged engines present difficulties for methanol fumigation. In general, it is easier to introduce the methanol before the turbocharger, but methanol is difficult to vaporize totally because of its high latent heat, and liquid impingement on the compressor wheel will cause damage rapidly. Introduction of the methanol downstream of the compressor alleviates this problem but makes installation more difficult.

Overall, fumigation is best suited to retrofit applications where it can have beneficial effects on emissions [70].

D. USE OF METHANOL IN DUAL INJECTION ENGINES

In dual injection engines, a second injection system is added just for methanol. The original injection system injects just enough diesel fuel to ignite the methanol. Dual injection engines are very effective at using large amounts of methanol – displacements of 90% at full-load and 50% at idle and low-load have been achieved by numerous researchers [63]. Engines configured this way have shown essentially the same efficiency as their diesel fuel counterparts, with the emissions advantages of methanol (i.e., lower NO_x and particulates). Dual injection engines never achieved commercialization, no doubt due to their increased cost (a second fuel system) and the inconvenience of having two fuel systems onboard.

E. 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). Also, it could allow the same engine to use methanol and diesel fuel alternatively as the operator sees fit.

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. (Conversion kits for existing trucks were also made

available.) As of 1986, about 1,700 trucks using ignition-improved ethanol (new and converted) were in operation in Brazil [63].

Since most ignition-improvers have nitrogen in their composition, concern was expressed that this nitrogen would contribute to NO_x emissions. Extensive testing showed that only a small fraction of this nitrogen ended up as NO_x and overall, NO_x emissions decreased based primarily on the emission characteristics of methanol [63].

Overall, ignition-improved methanol represents a way to use methanol in existing and new diesel engines albeit with suitable modifications to address materials compatibility issues. 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 [71].

F. 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 [72]. 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 NO_x 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 [73] and Navistar developed a methanol version of its DT-466 4-stroke diesel engine also using glow plugs [74].

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 [43].

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.

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 [75]. 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. NO_x 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.

The Engine Manufacturers Association (EMA) represents the interests of small engine manufacturers. While most do not address use of methanol, individual manufacturer guidelines for using ethanol blends provide some insight. While some small engine manufacturers accept use of ethanol blends, they recommend that the fuel not be allowed to stay in the fuel system while the engine is not being used. This is presumably because their fuel systems are not compatible with ethanol under conditions of constant exposure. Deterioration of plastic parts such as lines and tanks are probable, as is corrosion of the fuel system and even of internal engine parts—the crankcase of two-stroke engines, for example. 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 [76].

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 reduced 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 NO_x. 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 elastomeric and plastic parts that will be degraded by methanol. Fuel lines are likely to swell and soften, 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.

Appendix A. Properties and Characteristics of Importance for Fuel Specifications

Most or all methanol plants in the world today have been designed to produce methanol to exacting chemical grade standards. A less stringent “Commercial Grade Methanol” specification has also been used where a high level of chemical purity has not been required. Methanol below chemical grade can result from running a chemical methanol plant below design standards for purity, from contamination in storage and transport, or from other processes, such as recycling methanol used in a chemical process, such as in the production of dimethyl terephthalate.

With renewed interest in using methanol as a fuel for internal combustion engine and fuel cell vehicles and/or as a blending component for gasoline, there could be a need to consider the adoption of standards for such use based on the properties of methanol and its effect on the properties of the blended fuels. Such standards could take a number of forms, including standards for the methanol itself, standards for methanol/cosolvent mixtures, and/or standards for the final blended fuels. Some of the parameters that should be considered for inclusion in such standards would apply to both neat methanol fuel use (e.g. M100 and/or M85) and low level methanol blends (e.g. 5-10%, including cosolvents), while other parameters would probably be different for high level vs. low level blends. Some of the fuel methanol parameters could involve less purity than chemical grade standards, but concerns related to fuel use could suggest the need for additional parameters not relevant with the ultra-pure chemical standards.

The ASTM in the U.S. has developed and maintained a specification for M85 for use in FFVs [77]. California developed an M85 specification guideline [78] though it has been superseded by the ASTM specification. California also developed a neat methanol specification guideline for methanol used in heavy-duty vehicles or for blending of other near-neat methanol fuels [79]. These specifications and guidelines represent the accumulated experience of using methanol as a vehicle fuel in the U.S. The following narrative provides insight into the importance of the components of various fuel properties and characteristics that are addressed by the specifications.

A. PROPERTIES OF CONCERN FOR LOW LEVEL METHANOL BLENDS

Water Tolerance

Methanol has a very high miscibility with water, while both methanol and water have a fairly low solubility with many of the hydrocarbons constituting gasoline. The solubility of both methanol and water in gasoline depends on the composition of the gasoline, with aromatics having the highest mutual solubility, followed by olefins. Therefore, methanol is susceptible to carry water contamination into gasoline and to attract additional water once in a vehicle’s tank. With accumulation of water or significant temperature drops, the fuel blend is prone to separate into distinct phases with distinct water/methanol and gasoline phases. If this occurs in the tank, the aqueous phase will fall to the bottom, but the separation could occur at other points in the fuel system and could potentially cause a variety of problems including failure to start because the engine is starved of the volatile hydrocarbons, knocking because the gasoline has lost the octane of the methanol (and possibly of aromatics partially separating), filter plugging, and corrosion, among others.

Avoidance of phase separation and water-associated problems involves numerous precautions in marketing and distribution of methanol blends. With regard to fuel composition, water tolerance can be addressed (beyond limits on the methanol content) through a combination of use of cosolvents (usually higher alcohols), formulation of the gasoline blendstock, and limits on water content of the methanol and/or blended fuel, such as at point of sale. Unfortunately, formulating the blendstock for high water tolerance generally works against formulating for emissions control.

ASTM D 4814, the U.S. Standard Specification for Automotive Spark Ignition Fuel, includes a specification for water tolerance, with maximum phase separation temperature provided for specific regions month-by-month. Unfortunately, the test procedure for the standard, D 6422, has apparently shown poor repeatability, and the phase separation standard of D 4814 may be eliminated in the absence of a reliable test method. In the absence of such a standard, a limit on the water content of the methanol and blended fuel, along with possible cosolvent requirements, may be the only available control parameters. Specific gravity might also be used as a proxy for water content of the methanol but will not indicate the water tolerance of the blended fuel.

Volatility/Distillation

Volatility properties of gasolines, including gasoline/alcohol blends, are important to avoid both problems in cold-starting (inadequate volatility) and drivability problems such as vapor lock, as well as excess evaporative emissions (excess volatility). Volatility parameters typically include vapor/liquid ratio, vapor pressure, and distillation measures such as relationships between temperatures and percents evaporated. Blending methanol with gasoline at low levels typically boosts the vapor pressure and creates a bulge or “knee” in the distillation curve, which can be reduced with use of cosolvents, but blendstocks may need to be specially designed to provide acceptable volatility characteristics. Merely reducing light ends to compensate for the front end volatility boost may result in starting problems and other drivability degradation.

Carbonyls

Carbonyls are often present as by-products of methanol/higher alcohol production and represent toxicity concerns in high concentrations.

Acetone

Concerns have been expressed regarding acetone, including concerns over uncontrolled combustion and possible damage to vehicles. The “Commercial Grade” methanol specifications used in EPA waivers also included an acetone limit, though that may not have derived directly from fuel concerns or experience.

Acidity

Low molecular weight acids can be very corrosive to metals, particularly in aqueous solutions, which could result from methanol’s high water miscibility. One way of controlling them would be a limit on weight percent of acetic acid.

Alkalinity

Excess alkalinity could reflect an excess of ammonia, which could also be corrosive or have undesirable combustion properties, possibly controlled through weight percent.

pHe

Levels of pHe below 6.5 in fuel methanol can result in formation of film or excessive wear of certain engine parts, while pHe levels above 9.0 can adversely impact plastic pump parts.

Nonvolatiles

Nonvolatiles could be present from various sources and could result in clogging of fuel and engine components or could cause increases in exhaust emissions through incomplete combustion.

Copper

Copper is known to be a catalyst of low temperature oxidation of hydrocarbons and to contribute to formation of gums and polymers.

Corrosion/Conductivity

Corrosion is a concern generally for alcohol/gasoline blends, including possible corrosion from the alcohols, from water carried by the alcohols, or from excess acidity or ammonia. While test methods do not exist for all metals used in vehicle systems, a few do exist and should be considered, among them copper strip corrosion and the NACE Rust Test adopted by the National Association of Corrosion Engineers. Conductivity can also be used as an indicator of total ions, which will serve as a control on ionic corrosivity.

Ash

Ash is more likely to be present from cosolvent alcohols than from the methanol itself but could also be a concern and should be considered.

Gum

Presence of gums in fuel can cause formation of deposits that could impede the functioning of moving parts within engines and fuel systems, as well as plug filters, etc. Alcohols have been known to dissolve gums in storage and transport vessels, carrying them into vehicle fuel systems. Although the alcohols are not themselves likely to form gums, impurities in the alcohols, such as copper, can contribute to gum formation. Test procedures exist for presence of gums, both as “existent gums” and as “solvent washed gum,” i.e., gum present after a heptane wash of the fuel.

Sulfur

Sulfur reduces the effectiveness of emissions control systems and causes them to degrade more rapidly. In addition, it can cause engine oil to degrade more rapidly and corrode engine parts. The U.S. and Europe have adopted strict limits on the sulfur content of gasoline, and methanol addition should not be allowed to cause the standard to be exceeded.

Sulfates

Sulfates, particularly inorganic sulfates, have been believed to cause deposits both in fuel dispensing pumps and in vehicle fuel injectors, with the latter resulting in engine misfiring and poor driveability. Sulfate ions are also of concern in regard to electrolytic corrosion. Consideration should be given to including either a total sulfate specification, inorganic sulfate specification, or both.

Chlorides/Chlorine

Low concentrations of chloride ions can be corrosive to metals. A test procedure exists for chloride ion. Chlorides and chlorine generally are also of concern relating to corrosion, formation of dioxins in combustion, and other possible toxic combustion products, so that a total chloride or an inorganic chlorine test might also be considered.

Purity and Appearance

Standards can specify purity and appearance characteristics as general precautions against other concerns not specifically identified.

B. PROPERTIES OF CONCERN FOR HIGH LEVEL METHANOL FUELS (E.G., M85)

Most of the parameters of concern and possible types of specifications indicated above will also be applicable to neat methanol and M85, some to a greater degree and some to a lesser degree. There are some differences, however, as described below.

Volatility/Distillation

Unlike with low level methanol blends, the primary volatility concern with high level methanol fuels is inadequate vapor pressure for cold-starting, particularly in low ambient temperatures. RVP has traditionally been used to assure starting with hydrocarbon fuels but has sometimes been found inadequate for M85. Although there is no generally accepted specification, General Motors Corporation has proposed a “Cold Starting Performance Index” that correlates better with starting than RVP does. Volatility and distillation parameters for M85 fuels, as with lower level blends, are determined primarily by the composition of the hydrocarbon fraction of the fuel. For driveability generally (beyond starting concerns), the same distillation specifications that apply to other spark engine fuels can be used for M85.

Flame Luminosity

Methanol burns with a flame that is nearly invisible in direct sunlight, which raises safety concerns if fires were to occur and go unnoticed. Flame luminosity can be provided by design of the hydrocarbon portion of the fuel, with higher concentrations of aromatics, particularly certain aromatics, providing greater luminosity. Consideration should be given for including a flame luminosity specification.

Lubricity

Methanol provides less lubricity than hydrocarbon fuels, which can result in increased wear on various engine fuel system components with very high level blends. Lubricity additives are one means of addressing this. Either a fuel lubricity standard or a requirement for additives meeting an additive standard could be used.

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