Methanol as an alternative transportation fuel in the US:

Options for sustainable and/or energy-secure transportation

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Abstract

Methanol has been promoted as an alternative transportation fuel from time to time over the past forty years. In spite of significant efforts to realize the vision of methanol as a practical transportation fuel in the US, such as the California methanol fueling corridor of the 1990s, it did not succeed on a large scale. This white paper covers all important aspects of methanol as a transportation fuel.

Keywords: methanol; transportation;use; production

EXECUTIVE SUMMARY

- Methanol has been used as a transportation fuel in US and in China. Flexible fuel vehicles and filling stations for blends of methanol from M3 to M85 have been deployed. It has not become a substantial fuel in the US because of its introduction in a period of rapidly falling petroleum price which eliminates the economic incentive, and of the absence of a strong methanol advocacy. Methanol has been displaced by ethanol as oxygenate of choice in gasoline blends. Nevertheless, these programs have demonstrated that methanol is a viable transportation fuel.

- Large scale production of methanol from natural gas and coal is a well developed technology. Methanol prices today are competitive with hydrocarbon fuels (on an energy basis). There is progress on the economic conversion of biomass to methanol using thermo-chemical processes. Sufficient feedstock of natural gas and coal exists to enable the use of non-renewable methanol as a transition fuel to renewable methanol from biomass. A variety of renewable feedstock is available in the US for sustainable transportation with bio-methanol.

- Analysis of the life cycle biomass-to-fuel tank energy utilization efficiency shows that methanol is better than Fischer-Tropsch diesel and methanol-to-gasoline fuels; it is significantly better than ethanol if a thermo-chemical process is used for both fuels.

- The thermo-chemical plants for generation of methanol are expensive — they are approximately 1.8 times that of an equivalent (in terms of same annual fuel energy output) bio-chemical ethanol plant.

- Methanol has attractive features for use in transportation:
  - ➢ It is a liquid fuel which can be blended with gasoline and ethanol and can be used with today's vehicle technology at minimal incremental costs.
  - ➢ It is a high octane fuel with combustion characteristics that allow engines specifically designed for methanol fuel to match the best efficiencies of diesels while meeting current pollutant emission regulations.
  - ➢ It is a safe fuel. The toxicity (mortality) is comparable to or better than gasoline. It also biodegrades quickly (compared to petroleum fuels) in case of a spill.
  - ➢ Produced from renewable biomass, methanol is an attractive green house gas reduction transportation fuel option in the longer term.

> ➢ Multiple ways exist for introduction of methanol into the fuel infrastructure (light
>   blends or heavy blends) and into vehicles (light duty or heavy duty applications).
>   The optimal approaches are different in different countries and in different
>   markets.

- To introduce methanol significantly into the market place, both methanol vehicles and fuel infra structure have to be deployed simultaneously.

While significant investment needs to be made for large scale methanol deployment in the transportation sector, there are no technical hurdles either in terms of vehicle application or of distribution infrastructure. In comparison, the technology for bio-chemical ethanol production from cellulosic biomass is not sufficiently developed yet.

Methanol from non-renewable coal or natural gas could be used as a bridging option towards transition to renewable methanol for sustainable transportation. Methanol can readily be made from natural gas or coal (there is plentiful supply in the US of both) so that large scale domestic production, infrastructure, and vehicle use could be developed. The resulting transportation system could then be transitioned to the renewable methanol. It should be further noted that such system is also amenable to the use of renewable ethanol, should large scale bio-production of cellulosic ethanol be realized in the future.

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I.   HISTORY OF METHANOL AS A TRANSPORTATION FUEL IN THE U.S.

In the aftermath of the first oil crisis in 1973, the potential of methanol as a liquid fuel to satisfy US transportation demand was highlighted by Reed and Lerner [Reed, W1]. Although methanol was being manufactured from hydrocarbon feedstock (natural gas and coal) through a gasification process at production levels small compared to diesel or gasoline, the process was well established and could be scaled. Any feedstock that could be gasified into synthesis gas could potentially be used in the manufacture of methanol. Soon afterwards, the potential of using renewable resources (biomass) were described. [Hagen] The ultimate approach, the recovery of CO_2 from the atmosphere for methanol manufacturing, was discussed in 2005 by Prof. George A. Olah and his colleagues at the University of Southern California. They have coined the phrase "methanol economy," with methanol as a CO_2 neutral energy carrier [Olah].

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

The early interest in methanol resulted in several programs, mainly based in California. An experimental program ran during 1980 to 1990 for conversion of gasoline vehicle to 85% methanol with 15% additives of choice (M85). Gasoline vehicles were converted to dedicated methanol vehicles, for use of high methanol blends. These dedicated methanol vehicles could not be operated on gasoline, and limitations of the distribution system (small number of refueling stations; maintenance of these stations; poor locations) resulted in operator dissatisfaction. While the vehicle operation was either comparable or superior to the gasoline counterpart, the implications of the limited distribution resulted in the decision to implement flex-fuel vehicles in subsequent programs [Acurex]. Evaluation report for California's Methanol Program concluded that "the result [was] a technically sound system that … frustrated drivers trying to get fuel, generating an understandably negative response to the operator" [Ward].

The vehicles used in the initial program were provided by US automakers, which, in 1982 were subsidized to produce a fleet of vehicles for use mainly in the California fleets. The automakers provided spark-ignited engines and vehicles that were well engineered, which addressed issues with methanol compatibility. Ten automakers participated, producing 16 different models, from light duty vehicles to van, and even heavy duty vehicles (buses), with over 900 vehicles. One of the fleets, with about 40 gasoline based and methanol-based vehicles (for direct comparison), was operated by DOE laboratories from 1986-1991. Both the baseline gasoline and retrofitted M85 vehicles were rigorously maintained, with records to determine their performance. The operators were satisfied with the performance of the retrofitted M85 vehicles. The fuel efficiency of the vehicles was comparable to that of the baseline gasoline vehicles, even though some of them had increased compression ratio, a surprising result. The fuel economy of the M85 vehicles was lower than for the gasoline vehicles, because of the lower energy density of methanol. The methanol vehicles may have required increased maintenance, but it is not clear whether it is due to M85 operation, as the report mentioned that the operators were more sensitive to potential failures in the retrofitted vehicles, and they may have driven those vehicles harder because of the improved performance. There was increased aging of the performance of the emission catalyst in those vehicles operating in M85, but the report notes that this could have been due to the lubricating oils. [West] These vehicles performed the same or better than their gasoline counterparts with comparable mass emissions, which was a plus since methanol emissions were shown to be less reactive in terms of ozone formation potential. [Nichols] Acceleration from 0 to 100 km/hr was 1 s faster than the original vehicle. [Moffatt].

Following the dedicated vehicle program, fleets with FFV were tested, mostly in California. Ford build 705 of these FFV. The vehicle models included the 1.6L Escort, the 3.0L Taurus, and the 5.0L Crown Victoria LTD. There were even a few 5.0L Econoline vans. The broad spectrum of vehicles showed that the technology was applicable to any size engine/vehicle in the light duty market. [Nichols]

The successful experience with these vehicles resulted in automakers selling production FFV vehicles starting in 1992. The production vehicles are described in next section.

M85 FFV vehicles in the U.S. peaked in 1997 at just over 21,000 [DOE1] with approximately 15,000 of these in California, which had over 100 public and private refueling stations. At the

same time there were hundreds of methanol-fueled transit and school buses. [Bechtold] Ethanol eventually displaced methanol in the U.S. In 2005 California stopped the use of methanol after 25 years and 200,000,000 miles of operation. In 1993, at the peak of the program, over 12 million gallons of methanol were used as a transportation fuel.

In addition to California, New York State also demonstrated a fleet of vehicles, with refueling stations located along the New York Thruway.

High performance experience with the use of methanol for vehicles has been obtained in racing. Methanol use was widespread in USAC Indy car competition starting in 1965. Methanol was used by the CART circuit during its entire campaign (1979–2007). It is also used by many short track organizations, especially midget, sprint cars and speedway bikes. Pure methanol was used by the IRL from 1996-2006, and blended with ethanol in 2007. [W1] Methanol fuel is also used extensively in drag racing, primarily in the Top Alcohol category, as well as in Monster Truck racing. Methanol is a high performance, safe fuel, as will be described in Sections VIII and X.

The failure of methanol in becoming a substantial transportation fuel component in US may be attributed to the following factors:

> i. Methanol has been introduced in a period of rapid falling petroleum fuel prices, as shown in Figure 1. Therefore, there has been no economic incentive for continuing the methanol program.

> ii. There is no strong advocacy for methanol (unlike ethanol) as a transportation fuel. Therefore, it has been displaced by ethanol as oxygenate of choice in gasoline blends. Furthermore, while generating methanol from biomass thermo-chemically is a well developed technology (see later section), there is little advocacy for that as a pathway towards replacing petroleum fuel with renewables. Instead, crop-based ethanol has been promoted by the federal government (through tax incentives) as the transition fuel towards cellulosic bio-fuel production.

While methanol has not become a substantial transportation fuel in US, its present large industrial scale use and the former availability of production methanol FFV have demonstrated that it is a viable fuel and technology exists for both vehicle application and fuel distribution.
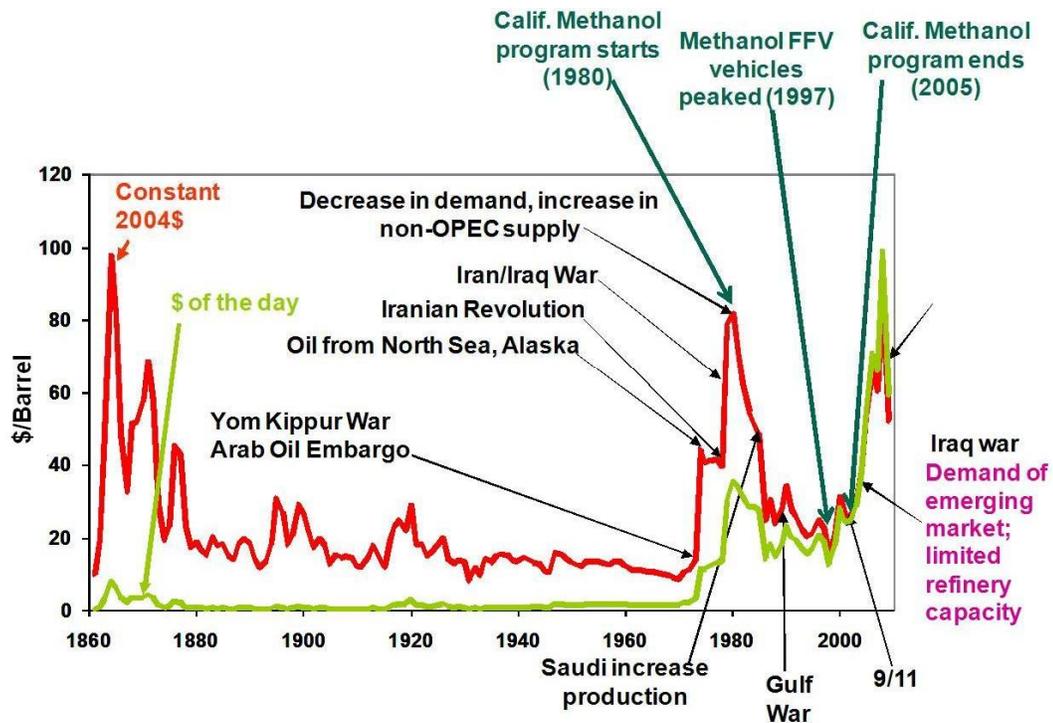
Figure 1. Methanol transportation program history relative to petroleum price. (Source: EIA; event labels partially from WRTRG Economics.)

A. **VEHICLES**

The US automakers manufactured four methanol FFV production models: [Bechtold]

- Ford: Taurus FFV (1993-1998);

- Chrysler: Dodge Spirit/Plymouth Acclaim (1993-1994);

- Chrysler: Concorde/Intrepid (1994-1995);

- GM: Lumina (1991-1993).

All these vehicles were mid-sized sedans. The vehicles were mainly acquired by governmental and rental fleets, although there were also a small number of private owners.

The 1993 Taurus was the first vehicle to be certified as a Transitional Low Emission Vehicle (TLEV) by the California Air Resource Board. The Chrysler 1995 model was also certified as a TLEV. Lack of interest by vehicle purchasers in alternative fuels, driven in part by falling oil prices, resulted in all automakers to stop production, with Ford being the last

manufacturer offering methanol FFV. These vehicles were offered at the same prices as their gasoline counterparts. [Aldrich]

The vehicles had good performance, even though they were modification of conventional gasoline vehicles and did not use the full potential of the methanol octane.

Although combustion of methanol in diesel engines is difficult, there were some heavy duty vehicles tested during this period. Neat unassisted methanol ignites poorly or not all in diesel engines; adequate operation can be achieved by the use of ignition improvers (high cetane improvers), by the use of a glow plug, and/or by the use of heavy EGR (Exhaust Gas Recirculation). Several methanol vehicles were produced. For use in transit buses, Detroit Diesel Corporation built vehicles with a 2-stroke engine that had very low emissions (very low soot and low NOx) [Miller]. Caterpillar developed a methanol version of their 3306 4-stroke diesel engine using glow plugs to achieve ignition [Richards]; Navistar developed a methanol version of its DT-466 4-stroke diesel engine also using glow plugs [Koors].

Presently there are no production methanol-capable vehicles in the US.

B. **FUELS**

There have been several applications to the EPA for the use of methanol for blending with gasoline. There was a waiver allowed by the EPA for light blends of methanol in gasoline, and in the mid-1980s ARCO marketed methanol blends in the US (see section on blending, Section XI.B). [EPA2] The additive Oxinol (a mixture of methanol and TBA as a co-solvent) was marketed by ARCO to other independent refiners and blenders, and used it in its own distribution system. It was discontinued in the mid-80's due in part to low gasoline prices and complaints about phase separation in cold weather and potential damage to fuel system parts (because of the methanol corrosive properties). EPA's final regulation on fuel volatility in March of 1989 put the methanol blends at a major disadvantage by providing a waiver on vapor emissions for ethanol blends but not for methanol blends

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

An "Open Fuel Standard" (OFS) Act has been introduced in Congress by bipartisan teams of members of the House and Senate, although not acted upon in the 111th Congress. The bill's

requirement calls for automakers to provide a minimum fraction of ethanol/methanol/gasoline FFVS, 50% of all vehicles by 2012 and 80% by 2015. The bill has been introduced in both the House and Senate. In July 2009, the House passed a comprehensive energy bill that included modified provisions of the OFS giving the Secretary of Transportation the authority to require alcohol flexible fuel capability. Congress is expecting to address major energy legislation in the 112th Congress, and many groups will be pushing in support of the OFS. [OFS].

II.   RELEVANT EXPERIENCES OF OTHER COUNTRIES

Much work is and has been done in many countries to identify the proper ways to modify vehicles to use methanol either as a neat fuel or in blends with gasoline.

A.   CHINA

China is currently the largest user of methanol for transportation vehicles in the world. Interest in China on the use of methanol as a transportation fuel is high (but local) as there is an abundance of readily available feedstocks (coal, natural gas, biomass) from which methanol can be produced. [Li] While in 2007 natural gas contributed about 15% of the methanol production in China, the development plan for coal chemical in China projects that in 2010 coal would be the feedstock of choice for methanol production, with an estimated 80% market share, expected to grow to 90% by 2015. In Shanxi, a major coal producing province, only a very small fraction of the methanol produced in 2007 was used for transportation, with 130,000 tons (40 million gallons) of methanol used officially as fuels, mostly as M15 blends (see comments below about illicit blending with methanol) [Li]

The adoption of methanol as a transportation fuel in China has lagged the use of methanol in some of its provinces, mainly because of the attitude of the Central Government. In ths Shaanxi Province, M15 introduction in 2003 was limited to four cities, but by 2007 it had spread to all 11 cities across the province. Several other Provinces in China (with coal producing facilities) have been promoting use of methanol-gasoline blends since the 1980's [C1Energy]

Presently, M5, M10, M15, M85 and M100 methanol gasoline are sold on the market, mainly by private fuel stations and by Sinopec in Shanxi and Shaanxi provinces. M15 is the most commonly used grade. China's state-run oil majors have been unwilling to popularize any methanol gasoline blends.

The extent to which methanol is being considered by local governments is exemplified by the fact that one of the Provinces (Shaanxi) intends to blend methanol into all gasoline used in the province by the end of 2010. Several companies have set up methanol gasoline blending centers, with a total capacity of 600,000 tons/yr (200 million gallons). Retail price of the M15 blend in May 2010 was 10% lower than conventional gasoline by volume (5% cheaper than conventional gasoline by energy). Price advantage is one of the reasons private gas stations choose to supply

the methanol gasoline. With retail pricing controlled by the central government, there is a significant incentive for private retailers to identify lower costs wholesale fuel additives. The methanol gasoline is very popular among taxi drivers, as the drivers can save about Yuan 600 per month on the price differential between M15 and gasoline.

Although methanol use should help with air quality issues in China, the main reason why it is being pursued is economic, with low production costs and potential for local production. The methanol gasoline can reduce emissions of carbon monoxide, hydrocarbon and nitrogen oxides, with comparable or better performance, especially at high loads. Coal is abundant in Shanxi and Shaanxi provinces, and methanol fuel is an outlet for their surplus methanol production capacity at present.

In 2007 there were 40 regional standards in 5 provinces, with 17 of these in practice, including low methanol blends. Additional 4 Regional Standards were published in Shanxi province alone in 2008. The Central Government finally acted in late 2009, publishing a National Standard for the use high blends (M85) of methanol. However, the National Standard has little relation with the most commonly seen low blend methanol gasoline (M15) [Peng]. China is in the final stages of reviewing a national standard for M15 (October 2010). This work included a 70,000 kilometer road test on M15 blends.

China's two top oil companies have shown little interest in promotion of methanol gasoline. Sinopec has only several gas stations in Shanxi supplying the methanol gasoline, and PetroChina has no such business in the whole country. The two oil majors have been reluctant to announce whether they would supply methanol gasoline in Zhejiang and Shaanxi. In spite of this, by the end of 2007 there were more that 770 methanol refill stations, 17 with M85, mostly not associated with the two top oil companies. The medium-term trend for China is an oversupply of refinery capacity [Yingmin]. Under those conditions, Sinopec and PetroChina would not proactively sell methanol-mixed gasoline in their network, but distributors and independent gas stations are blending methanol into gasoline.

In 2007, official consumption rate of M15 was 530,000 tons (180 million gallons), with over 40 million refueling operations. In addition, there were over 2000 taxis in Shanxi operating on M100 from a limited number of private refueling stations. In addition to light duty vehicles, by 2007 there were 260 buses, with 100 running on M100. The use of methanol in transportation in

China is likely to be substantially higher than the official numbers, as there have been no national standard for blending. Part of the problem with estimating the methanol use in China is the nature of methanol fuel blending in China. The official methanol use is done in provinces with methanol demonstration programs/specifications that have some level of approval from the central government. However, most of the methanol used in China is illegal blended with gasoline based simply on methanol's favorable economics. The illegal blending occurs between the refinery and the vehicle tank. The 2010 estimated amounts of methanol consumption in China transportation sector are very large, between 4.5 and 7 million tons of methanol (about 1.5-2 billion gallons). [McCaskill1, Sutton] Thus, China is carrying out a larger uncontrolled study of methanol use in transportation that the corresponding well controlled tests in the US.

In addition to coal-to-methanol in China, there are efforts in methanol from renewable resources. American Jianye Greentech Holdings, Ltd., a China-based developer, manufacturer and distributor of alcohol-based automobile fuels including methanol, ethanol, and blended fuels, has a waste conversion facility and to build a second one in Harbin, China, that converts municipal waste, construction waste, plant waste and sewage sludge into alcohol-based fuel. The new facility will be capable of treating 500,000 tons of waste per year and 450,000 tons of sewage sludge per year, while generating 100,000 tons (30 million gallons) of alcohol-based fuel and an electrical output of 20MW annually. [AJG]

Vehicles

China is leading the effort in the developing of methanol dedicated and FFV:

- Chery Automobile completed demonstration of 20 methanol FFV models, for full-scale production. Shanghai Maple Automotive: 50,000 methanol cars in 2008.

- Shanghai Maple Automotive completed demonstration of fleet methanol M100 cars.

- Chang'an Auto Group introduced FFV: Ben-Ben car.

Recently announced production levels of methanol vehicles suggest a fast ramp-up: for 2011, the FAW Group estimates a production of 30,000 vehicles, and Geely Group (Shanghai Maple) announced 100,000 vehicle capacities. [FAW] The annual production rates are much higher than those of the American automakers during the 1993-1998 production years of methanol FFV's.

B. **EUROPEAN UNION METHANOL EXPERIENCE**

In Europe, implementation of methanol fuels has been limited to light blends. The were first introduced in the Federal Republic of Germany in the late 60's, with composition slightly lower than those allowed in the US by the EPA (4% methanol and cosolvent, vs. 5.5% in the US), but reaching general use by the late 70's. The use of light methanol blends spread through Europe during the 1980s and through much of the 1990s. An agreement was reached to set minimum allowable methanol concentration in gasoline in 1988 through member countries of the European Economic Community (which eventually became the European Union), along with a maximum level of methanol blends, when identified as such with appropriate labeling on the pumps. One of the countries that allowed the use of the higher methanol blends was France, although it was implemented in only a few refueling stations. In Sweden there was an oxygenate requirement that specified a maximum blending of methanol of 2 %. [SMFT].

The European interest in Alternative Fuels is driven mostly by desire to curtail CO_2 emissions. In 2004 a European standard increases the amount of methanol in gasoline to comparable levels of those by the US EPA, 3% methanol, to be mixed with a cosolvent. Further desires to decrease emission of green house gases drove additional standards. In 2007, a proposal was introduced for the increased use of biofuels to decrease the green house emissions of tranportation fuels by 1% per year from 2011 to 2020. The biofuel of choice was ethanol from biomass, with ethanol blends comparable to those in the US (10% ethanol). The ethanol allowable had been 5% until then. The amendment approved in 2008 replaces the BioFuel Directive with a Directive on the promotion of Renewable Energy Sources. The new Directive requires that the emissions of green house gases decrease by 10% by 2020. Presently, there are discussions in European Community about issues of Indirect Land Use Change (ILUC), and its contribution to green house gases, as the reduction in green-house gases is determined by life-cycle analysis.

There are substantial efforts in Scandinavia for the production of biofuels. Their vast forest and paper industry has easily accessible feedstock for the production of biomethanol. In Sweden, VärmlandsMetanol AB is building a biomass-to-methanol plant, with an annual production of 100,000 tons (30 million gallons) of fuel-grade methanol from forest-residue biomass. Investment for the plant will be about $416 million, and it is expected to be operational in 2013. The VärmlandsMetanol plant will be the first full-scale commercial biomass-to-methanol plant. The

plant will gasify about 1,000 tons of wood biomass per day and convert the resulting syngas into methanol 400,000 liters/day (100,000 gallons/day) of methanol, in addition to providing heating in a Combined Heating and Fuels (CHF) plant [Gillberg]. The biomethanol is expected to be used in engines with no modification or in mid-blends (up to 25%) in flex-fuel vehicles. They are considering the possibility to produce gasoline through the Methanol-to-Gasoline (MTG) process, although the gasoline produced by this process has substantially higher costs than the methanol (on an energy basis), as will be described in Section V.F., the thermochemical process allows high energy efficiency and enables very pure synthesis gas to be produced from a wide range of feedstocks with low energy consumption. Although there are few details, the capital cost from the methanol plant alone will result in a levelized cost of methanol of over $3/gallon.

III.   U.S. PRODUCTION VOLUMES AND PRIMARY CURRENT USES

Worldwide, at the end of 2009, there were over 245 methanol plants with an annual capacity of over 22 billion gallons, up from 215 methanol plants in 2008 and a capacity of 19 billion gallons (60 million tons). Presently (2010) there is substantial overcapacity because of the economic slowdown, with production about level in 2008-2009 of 13.6 billion gallons (42 million tons). [McCaskill]. The global methanol industry generates $12 billion in economic activity each year, while directly creating nearly 100,000 jobs. [Dolan]

Because of economies of scale, the industry is shifting towards large plants (megaplants). From 2004-2007, 7 megaplants started up with a combined capacity of 10 million metric tones (3 billion gallons) of methanol, about a quarter of current global demand.
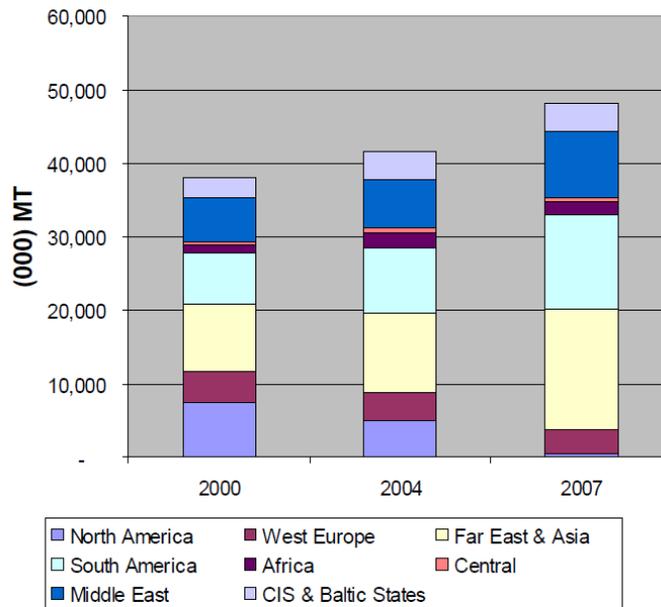
Figure 2. Shifting worldwide global methanol production

Historically, the US was a world-class methanol manufacturer. As shown in Figure 2, with changing economic conditions, and with plenty of "stranded" natural gas in Trinidad, the US industry moved there for less expensive production [MHTL]. While in 2000 the US produced about 20% of the world supply of methanol, by 2009 the US production is down to about 2%. At its peak, there were 18 methanol production plants in the United States with a total annual capacity of over 2.6 billion gallons per year. Most of these plants have been dismantled and sold

overseas, with little idle capacity in the US/Canada. However, with low natural gas prices in North America, some of the idling plants are being re-opened. [CNRP]

The annual demand and supply for methanol in the US for 2008-2010 (2010 is an estimate) are shown in Table 1 [McCaskill]. It is likely that the numbers for 2010 will exceed the estimated values in Table 1. There was a large drop in production and demand in 2009, because of the recession. The demand and supply are leveling off in the recovery, but will take some time to return to the values in 2008.

Table 1. Supply/demand in the US (1000 metric tons) (note: 1 metric ton ~ 330 gallons)

	Supply/demand			Average Annual Growth Rate		
	2008	2009	2010 est	2008	2009	2010 est
Capacity	980	980	980	0	0	0
Production	852	790	790	6.5	-7.3	0
Operating Rate, %	87	81	81			
Imports	5,492	4,817	4,600	-4.5	-12.3	-4.5
Total Supply	6,344	5,607	5,390	-3.1	-11.6	-3.9
Formaldehyde	1,778	1,436	1,611	-15	-19.2	12.2
MTBE & TAME	744	757	682	71.7	1.9	-9.9
Acetic Acid (HAc)	1,180	1,100	1,100	12.3	-6.8	0
Dimethylterepthalate (DMT)	376	228	101	-61.7	-39.4	-55.8
Methyl Methacrylate	265	202	207	-13.1	-23.8	2.8
Fuel Applications	340	269	320	54.8	-21	18.9
Dimethyl Ether	25	28	28	0	11.1	0
All Other	1,275	1,210	1,208	275.7	-5.1	-0.2
Domestic Demand	5,982	5,230	5,257	9.9	-12.6	0.5
Exports	216	373	120	41.2	72.9	-67.8
Total Demand	6,198	5,603	5,377	10.7	-9.6	-4
Inventory Build/(Pull)	146	4	13			

Table 2. Main US plants, production (2009) and feedstock (1000 metric tons)

	Production	Feedstock
Eastman Chemical, Kingsport, TN	215	coal
LaPorte Methanol/Lyondell, Deer Park, TX	615	NG
CF Industries, Woodward. OK	120	NG
Praxair, Geismar, LA	45	NG

The methanol uses in the US are also shown in Table 1. Most of the methanol is for chemical production of formaldehyde and acetic acid. While MTBE and TAME were dominant in the past, production is decreasing as MTBE has been banned in the US and is being replaced by ethanol. The largest US producers and their feedstocks are listed in Table 2 [Dolan.].

The historical US cost of methanol, gasoline and E85 are compared in Figure 3. The costs of E85 and gasoline in Figure 3 are average prices at the refueling stations. The cost of methanol represents the addition of the wholesale price, plus distribution (20 cents per gallon gasoline equivalent [Stark, Short]) and taxes, assumed to be 40 cents per gallon gasoline equivalent (18 cents/gallon federal tax and about 22 cents/gallon state tax [gastax]). The costs have been referenced to equal energy content, and are shown in dollars per gallon gasoline equivalent.
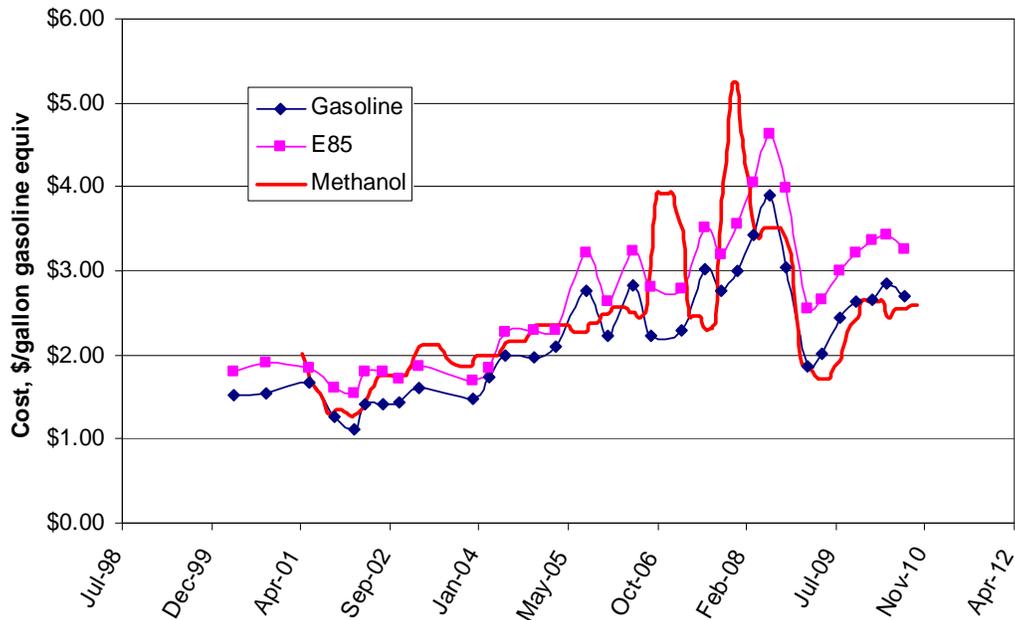
Figure 3. Normalized costs of liquid fuels, E85, gasoline at the gas station, and estimated costs of methanol at the station [AFDC, Methanex]

It is clear that the costs of methanol and the other liquids show a long-term correlation. However, the prices can be decorrelated during periods of ~ 1 year. With distribution and taxes, methanol costs are comparable to those of gasoline. The price spikes in 2006 and again in early 2008 represent temporary price increase of the natural gas feedstock. The methanol price is affected substantially by the price of natural gas, which has been volatile in the past 5 years.

However, it is possible to design vehicle that take advantage of the improved combustion characteristics of alcohol fuels. As described in Section IX-A, vehicle efficiency of dedicated or two-tank (Direction Injection Alcohol Boosting) vehicles can be increased by ~25-30% over that of conventional gasoline vehicles (port-fuel injected, naturally aspirated engine) or 10-15% over

that of high performance gasoline vehicles (Gasoline Direct Injection, GDI, with aggressive turbocharging and downsizing). With that improvement in performance, both E85 and methanol are attractive options compared with gasoline for the consumer. These options are not possible if the vehicles are designed to also operate on conventional gasoline (*i.e.,* FFV).

PRODUCTION PROCESSES AND FEEDSTOCKS

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

A. **PRODUCTION PROCESSES**

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

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

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

This process is endothermic and requires externally provided energy of reaction.

In the case of coal, the synthesis gas is manufactured through gasification using both oxygen and steam (including water-shift reaction):

$$C + \tfrac{1}{2}O_2 <-> CO \qquad \text{(Partial oxidation)}$$

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

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

$$CO_2 + C <-> 2\ CO$$

Biomass is converted into synthesis gas by a process similar to that of coal. In the case of biomass, the synthesis gas needs to be upgraded (through reforming or water-gas shifting) and cleansed to produce a synthesis gas with low methane content and proper H_2-to-CO ratio. There

are tars (heavy hydrocarbons) as well as ash (that can be removed dry or as a slag) that are produced in the gasification, and they need to be removed upstream from the catalytic reactor

Once the synthesis gas of the correct composition is manufactured, methanol is generated over a catalyst; in the case of natural gas,

$$CO + CO_2 + 7\ H_2 \rightarrow 2\ CH_3OH + 2\ H_2 + H_2O$$

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

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

$$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O$$
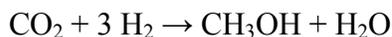
Unlike the reforming process with steam, the synthesis of methanol is highly exothermic, taking place over a catalyst bed at moderate temperatures. Most plant designs make use of this extra energy to generate electricity needed in the process. Control/removal of the excess energy can be challenging, and thus several processes use liquid-phase processes for manufacturing of methanol. In particular, Air Products developed the Liquid Phase Methanol Process (LPMEOH) in which a powdered catalyst is suspended in an inert oil. This process also increases the conversion, allowing single pass. [ARCADIS]

B. RESOURCES

1) Natural gas

Globally, there are abundant supplies of natural gas, much of which can be developed at relatively low cost. The current mean projection of global remaining recoverable resource of natural gas is 16,200 Trillion cubic feet (Tcf), 150 times current annual global gas consumption, with low and high projections of 12,400 Tcf and 20, 800 Tcf, respectively. Of the mean projection, approximately 9,000 Tcf could be economically developed with a gas price at or below $4/Million British thermal units (MMBtu) at the export point. [MITNG]

Table 3 shows the proved US reserves of natural gas (NG), for different years [BPSR]. The proved reserves in the US of NG gas has steadily grown. At the end of 2009, conventional NG had a R/P (Reserves-to-Production ratio) of 12, not including shale-gas. Also shown in Table 3 are the corresponding US share of world-wide NG reserves.

Table 3. Proved resources of NG and coal in the US, and annualized prices

		at end 1989	at end 1999	at end 2008	at end 2009	Share of world total	US Resource/ Production
NG proved reserves (not including shale-gas)	Trillion m^3	4.73	4.74	6.93	6.93	3.7%	12
NG prices (yearly average)	($/MMBTU)	1.70	2.27	8.85	3.89		
Coal proved reserves							
Anthracite and bituminus	Billion tons				110		
Sub-bituminous and lignite	Billion tons				130		
Total	Billion tons				240	28.9%	245
Coal prices (Central Appalachian Spot Price)	($/ton)	31.59	31.29	118.79	68.08		
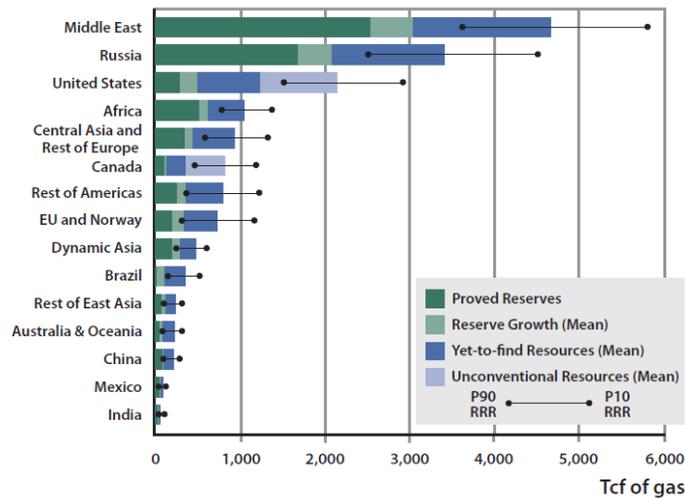
Figure 4. Proved reserves of NG, reserved growth, estimated undiscovered resources, and unconventional resources in the US and elsewhere in the world [MITNG]

The US has considerable amounts of NG, especially if unconventional sources (*i.e.*, shale-gas) are included. Only Russia and the Middle East have larger reserves. It is interesting to note that China has small reserves of natural gas, which is one of the reasons why methanol is preferentially made from coal there.

Unconventional gas, and particularly shale gas, will make an important contribution to future U.S. energy supply and carbon dioxide (CO_2) emission reduction efforts. Assessments of the recoverable volumes of shale gas in the U.S. have increased dramatically over the last five years. The current mean projection of the recoverable shale gas resource is approximately 650 Tcf (18 trillion m^3), with low and high projections of 420 Tcf and 870 Tcf, respectively, as shown in Figure 4. Of the mean projection, approximately 400 Tcf (11 trillion m^3) could be economically developed with a gas price at or below \$6/MMBtu at the well-head. [MITNG] Shale gas triples the amount of natural gas proved reserves.

The environmental impacts of shale development are manageable but challenging. The largest challenges lie in the area of water management, particularly the effective disposal of fracture fluids. Concerns with this issue are particularly acute in those regions that have not previously experienced large-scale oil and gas development.

2) Coal

About 1/4 of the limited US methanol production comes from coal. The US has very large resources of coal, as shown in Table 3. At the present rate of consumption, there are over 200 years of proved coal reserves. The US has also a large share of the worldwide proved reserves of coal.

Table 4. Time-to-exhausting of reserves if entirely committed to methanol production for 10% displacement ofgasoline (2009); R/P refers to reserve to production ratio.

	R/P methanol ratio (years)
NG to methanol	121
including shale gas	429
Coal to methanol	> 1000

C. RESERVE/PRODUCTION METHANOL POTENTIAL OF US FOSSIL RESOURCES

It is interesting to determine the potential for methanol to satisfy a substantial fraction of the liquid fuel required in the US using conventional feedstocks, such as natural gas and coal, as a bridge to sustainable transportation fuels from biomass. Assuming that 10% of the gasoline consumed in the US is replaced by methanol (approximately 28 billion gallons of methanol per year), the time to exhaust the proven reserves of coal and natural gas is shown in Table 4. It is

assumed that the entire reserves are committed to methanol production. The purpose of Table 4 is to give an estimate of the time-to-exhaustion of the reserves, before other resources (such as biomass-to-methanol) can be developed.

Although proved reserves of NG probably can not be shifted entirely to methanol manufacturing, in principle it is possible to use for methanol production a large fraction of the shale-gas reserves recently made economically recoverable through improvements in drilling technology.

Finally, there is plenty of coal to satisfy even a larger substitution of liquid fuels by methanol.

Alternatively, 10 billion gallons of methanol per year can be produced if 10% of the domestic production of natural gas and coal is used to produce methanol. [Dolan]

D. **OTHER REQUIREMENTS (CATALYSTS).**

Methanol is produced in industrial low-pressure synthesis over a copper oxide-zinc oxide-alumina ($Cu/Zn/Al_2O_3$) catalyst in a process developed by ICI of England. This catalyst is extremely active and highly selective. The catalytic reactor operates from 5-10 MPa and 200-280C, with modern applications on the lower end of these operating conditions. Generally these catalysts are prepared in tablet form. They are shipped in their fully oxidized form and must be activated/reduced in-situ by passing H_2/N_2 (1 mol% H_2) over the catalyst bed. This must be carefully controlled at low temperature to preserve crystalline structure and physical integrity to ensure optimal performance.

The copper based catalyst system is a much less robust system than previous catalysts and is more susceptible to poisoning and deactivation. The catalyst is particularly sensitive to chlorine and sulfur. With sulfur levels below 0.025 ppmv and chlorine levels below 0.0125 ppmv a catalyst life of two to four years can be expected. Cleanup of the synthesis gas to this level is not uncommon or difficult. Methanol yields of 99.5% (relative to other organic byproducts when water production is not accounted for) of converted $CO + CO_2$ can be expected.

Large amounts of catalysts would be required for a "methanol economy". To make 6 billion gallons (20 million tons) of methanol per year (that is, China), about 3000 tons of catalysts are required. For the 28 billion gallons of methanol for replacement of 10% of the gasoline

consumption in the US, approximately 15,000 tons of catalyst would be required, a large but feasible number. [Albemarle]

IV.   FEASIBILITY OF PRODUCTION FROM RENEWABLE SOURCES

The main driving force for biofuels in the US, Energy Independence and Security Act (EISA), mandates that non-food based biofuels ramp up starting in 2010 to about half of the mandated 36 billion gallons by 2022. [EISA] In order to meet this production goal, cellulosic biofuel production must begin in the near term and ramp up to the 2022 goal.

Methanol can potentially added to the mandated non-food biofuels. As opposed to bioethanol, that has feedstock limitations, methanol can be produced by thermochemical process (gasification) from a wide range of products, including wood, agricultural wastes, municipal wastes and other biomass resources. Although mature gasification technologies exist, from bubbling fluid bed, indirectly heated fluid beds, and entrained bed, the technology needs improvement for cost reduction and scale-up. These processes have yields that are typically 170 gallons of methanol per ton of biomass (wood). The US generates 240 million tons of waste wood per year. Thus the waste wood could potentially produce 41 billion gallons of methanol, a quantity that would have satisfied the EISA mandate for 2022.

Modern natural gas-to-methanol facilities are characterized by methanol selectivities above 99% and first law process efficiencies above 70% [Olah]. The use of biomass and coal as the feedstock decreases the overall efficiency to the range of 50-60%, in part due to the lower hydrogen to carbon ratio of biomass and coal, along with the added gasification complications due to char and ash content of these feedstocks (see Sections V.B. and V.C. below).

A.   BIOMASS RESOURCES IN THE US

The Billion Ton Vision study addressed viability issues for sustainable biomass feedstocks for both near term (without energy crops) and longer term (with energy crops). [Perlack] The amounts of the potentially available sustainable feedstocks are shown in Figure 5. The upper sets of numbers (labeled "High Yield Growth with Energy Crops" and "High Yield Growth without Energy Crops") are projections of availability that will depend upon changes to agricultural practices and the creation of a new energy crop industry. For biomass-to-fuels production in the near term, only the "Existing & Unexploited Resources" amounts are relevant. Notice that the

expected availability of forest resources is comparable to that of agricultural resources. However, with forest resources, harvesting and transportation results in increased biomass cost.
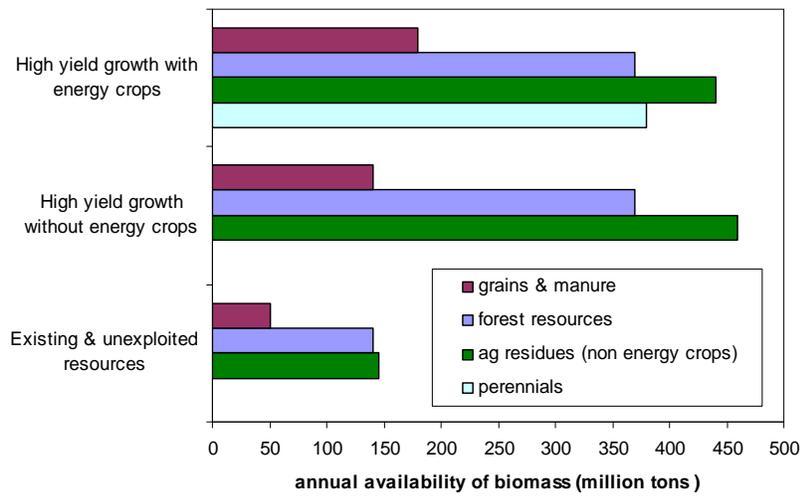
Figure 5. Estimated annual availability of biomass in the US [Perlack]

Prior studies of biofuel production from agricultural resources have been largely based on bio-chemical processes. The biochemical processes (producing ethanol), however, are not sufficiently developed at the present time for large scale economic conversion of forest and non-food based biomass. There are technical barriers, although if successful, biochemical processing is likely to be economically attractive.
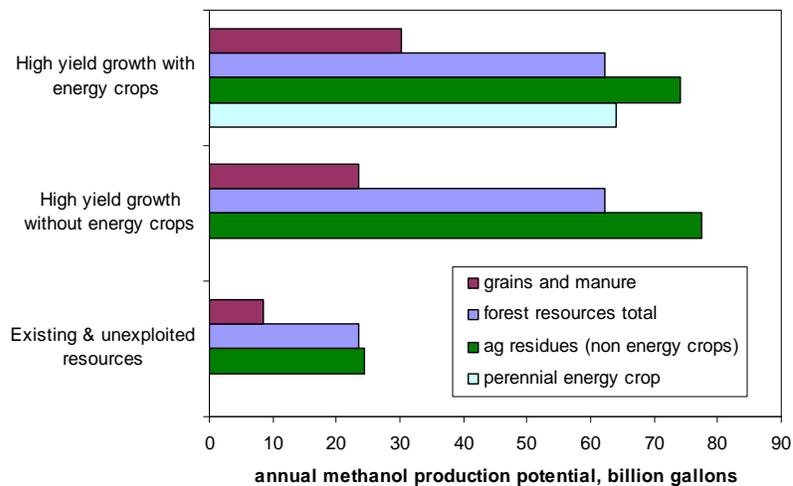
Figure 6. Potential annual production of methanol if all the corresponding biomass availabilities are used for methanol manufacturing. [adjusted from Perlack]

On the other hand, thermochemical processing of biomass is better suited to the production of biofuels from a large variety of feedstocks, and can be adjusted to match a variety of feedstocks, simplifying the handling/storage issue that arise from crop based biomass, which is abundant during harvesting but needs storage for year-around fuel production. Thermochemical process technology is the only currently viable means to provide a technology for processing this major portion of the expected biomass feedstock. However, thermochemical plants are more complex and will result in increased costs.

The potential of biomass-to-biomethanol in the US can be estimated from the amounts of available biomass in Figure 5, assuming a conversion efficiency of 55% (biomass to methanol). The resulting potential annual methanol production is shown in Figure 6. To replace all the gasoline used in the US, approximately 300 billions gallons of methanol are required annually. Alternatively, to replace the entire diesel consumed in the US would require 100 billion gallons annually of methanol. Thus the displacement of a substantial fraction of the US consumption of liquid fuels requires the use of non-crop based biomass. Non-crop based biomass derived fuels have a potential to replace a major part of the US transportation liquid fuel; this is especially so if substantial decrease of energy use in transportation is achieved.
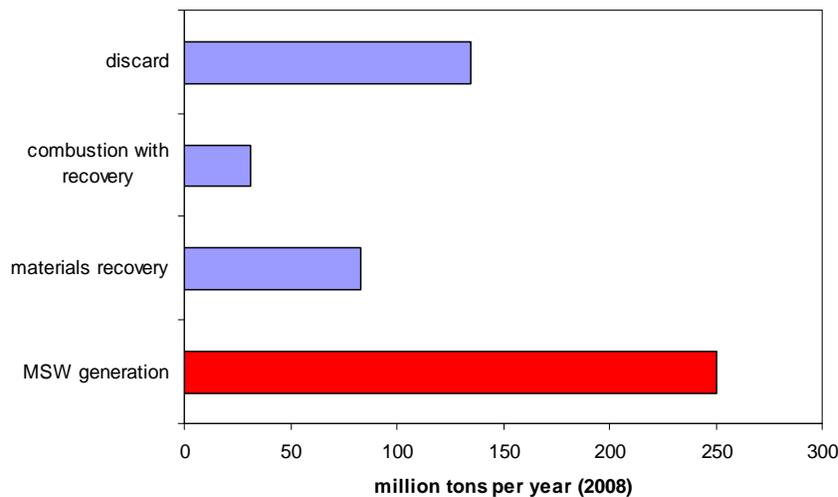

Figure 7. Generation, Materials Recovery, Combustion With Energy Recovery, and Discards of MSW, 2008 (in million of tons)

A separate type of biomass is Municipal Solid Wastes (MSW). Although not directly from biomass, a large fraction of the material in this waste stream was originally biomass. The use of

waste to liquids could be attractive in that a substantial cost of the biomass cost (collection and transport) is being borne by a separate party, and indeed the cost of the feedstock can be negative.

The fate of MSW in 2008 in the US is shown in Figure 7. About 1/3 of the waste is recycled or composted, about 10% used for waste-to-energy (electricity or heat), and the rest is discarded or combusted.

Refuse Derived Fuels (RDF) can be produced from the discarded MSW. Refuse-derived fuel (RDF) or solid recovered fuel (SRF) is a fuel produced by shredding and dehydrating solid waste. RDF consists largely of organic components of municipal waste such as plastics and biodegradable waste. The heating value of the RDF is variable, depending among other things on the level of recycling and recovery, and is particularly sensitive to the removal of plastics. [Higman]. The heating value is about half that of coal, or about 15 MJ/kg, and slightly lower than wood feedstocks. If all the "discarded" wastes are converted to methanol, about 10 billion gallons of methanol can be generated per year.

It should be noted that conversion of wood, agricultural and municipal wastes to methanol can be an effective green-house mitigation. A substantial amount of these wastes generate methane (under anaerobic conditions), which is released to the atmosphere. Methane is a much stronger green-house gas than CO_2. Thus, direct conversion of these wastes to fuels and eventually to CO_2 through combustion can result in a decreased impact on climate change.

B. METHANOL PRODUCTION EFFICIENCY

Methanol is not an energy source, it is an energy carrier. Energy from other sources is converted into methanol, which can then be used in internal combustion engines. The efficiency of the energy conversion process (energy in the methanol divided by the energy in the feedstock and the energy consumed in the process) is important in that it impacts the costs and the climate change benefits of the methanol.

In this section we summarize several studies on the efficiency of conversion of biomass to methanol. In order to determine the biomass-to-methanol conversion efficiency, it is necessary to determine the efficiencies of the two steps in the methanol manufacturing process: biomass-to-syngas and syngas-to-methanol.

The production efficiency from syngas to methanol can only be estimated from published data as methanol producers keep their efficiency numbers close to their chests. The production of methanol from natural gas experiences higher production efficiencies on average compared to conversion from biomass. Syngas to methanol conversion efficiencies of 71.2%, 80.1% [Allard] and 77.1% [Berggren] are estimated. The overall efficiency of natural gas-to-methanol assumed in determining the above syn-gas to methanol efficiencies were a low of 64% to a high of 72% [Allard] and 69% [Berggren].

One of the first studies to report the conversion efficiency of woody biomass to methanol was produced for the Organization for Economic Cooperation and Development (OECD). In this report, conversion efficiency to methanol is 56.5% [OECD] with an estimated overall biomass-to-tank efficiency of 52%. [Ofner] The biomass conversion efficiency was lower than for natural gas but higher than coal, reported in the same study as 65% and 55% respectively. [OECD]

More recently (2003) Azar and colleagues estimated a conversion efficiency of woody biomass to methanol of 60% [Azar]. These estimates are based largely on the work of Williams *et al*. [Williams] where an in-depth techno-economic study of methanol and hydrogen from biomass was performed. In the study, the group calculated thermal efficiencies of 53.9%, 56.8%, 57.6% and 61.0% with IGT, MTCI, BCL and Shell biomass gasifiers respectively, for further details see Table 5.

Table 5. Properties of feedstock and process parameters for biomass to methanol technologies. Adapted from Williams and Stark [adapted from Williams, Stark]

	Bubbling Fluidized Bed (IGT)	Indirectly heating fluid bed (MTCI)	Indirectly heated fast fluidized bed (BCL)	Entrained Bed (Shell)	Entrained bed (Shell Coal)
Dry ash-free composition	$CH_{1.52}O_{0.68}$	$CH_{1.63}O_{0.66}$	$CH_{1.54}O_{0.65}$	$CH_{1.52}O_{0.68}$	$CH_{0.91}O_{0.11}$
HHV (GJ/dry ton)	19.28	19.40	19.46	19.28	29.69
Initial moisture (%)	45	45	45	45	5
Moisture after drying	15	20	10	11	5
Biomass to syn-gas	82%	90%	80%	85%	80%
Syn-gas to fuel efficiency	66%	63%	72%	72%	76%
Overall Thermal efficiency	54%	57%	58%	61%	61%

The effect of process innovation and technology development with time, as well as due to large-scale implements of the technology (nth-of-a-kind plants), has been evaluated recently. It has been determined that the gasification efficiency can increase by about 5-10% in the future. [Faaij, Hamerlink]. Although the investigation was for a given technology, it is expected that the same gasification efficiency improvement will carry out throughout all the gasification technologies described in Table 5. The sys-gas to methanol process, on the other hand, is well mature, and it is not expected to show further mass-scale improvement.

From these studies it can be concluded that the overall efficiency of conversion of biomass to methanol is 50-60%, assuming a gasification efficiency of 80%. For natural gas conversion to methanol (the baseline case), the overall efficiency is 64-72%. [Allard, Stark]

It is interesting to note that using a 55% efficiency of conversion of biomass to methanol, since the heating values of dry biomass is around 18 MJ/kg and that of methanol is about 20 MJ/kg, the output methanol from a plant is about half that of the input biomass. That is, a 1000 ton/day biomass (dry) will generate 500 tons of methanol per day (160,000 gallons/day).

C. **LIFE CYCLE ENERGY EFFICIENCY ANALYSIS**

A recent investigation by A. Stark at MIT, evaluated the relative energetic efficiencies of potential fuels using a thermodynamic life cycle analysis. On the bases of first law of thermodynamics, (using boundaries around the different steps of the system for energy and mass conservation) energy/mass flows and efficiency of energy conversion were analyzed for the several energy conversion steps to obtain the overall system efficiency. The first law efficiency of an energy conversion step is defined as the ratio of power in the desired product over the power inputs (including all sources, including electricity, steam and the power associated with the flow rate of the feedstocks into the given step). The life cycle analysis is performed by treating each of the major steps (fuel production, fuel distribution, automotive end use) as individual energy conversion steps and integrating the first law efficiencies of each.

An uncertainty analysis is perform by associating different probability distribution functions to the first law efficiency for each of the processes and to the uncertainties in the associated heating values. Outputs from a given step that are not directly related to the desired product (such as thermal energy from exothermic processes that is not used in that given step or byproducts that

not associated with the fuels) are ignored. A MonteCarlo simulation is used to evaluate the resulting efficiency of many potential processes, each process with characteristics given by the assumed probability distribution function. Other energetic inputs, such as the energy required to build the plant, harvest and transport the initial feedstock, are not included in the analysis, since all the processes to be investigated incur the same costs. Also, the end use step (that is, the use of the fuel in an engine) is not included in the analysis, although it has been discussed by Stark [Stark]
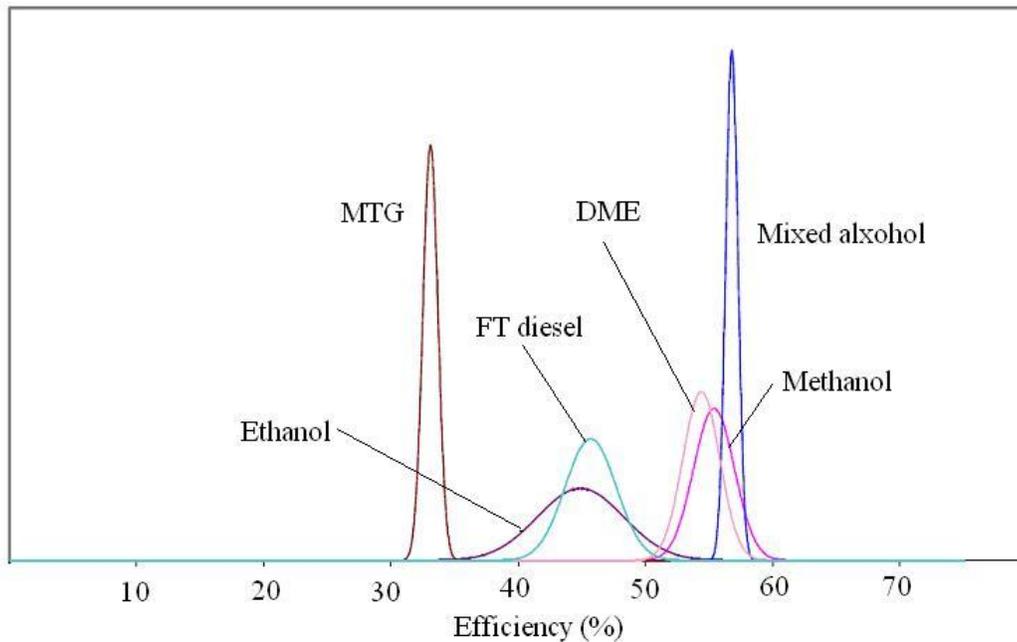
Figure 8. Probability distribution function of biomass to tank utilization efficiency from the MonteCarlo analysis [Stark]

Figure 8 shows results for the MonteCarlo life-cycle analysis (biomass-to-tank) for a multitude of alternative fuels. [Stark] It includes the best fuel distribution method, specific to each fuel and to distance between fuel production plant and refueling stations. The spread of the curves represented the uncertainty in the overall efficiency due to uncertainty in the efficiency of the different steps in the process. Not all the uncertainties in the efficiencies are the same as, for example, the process for syngas-to-methanol, for example, is very mature, but that for syngas-to-mixed alcohols is not. It should be noted that Stark used efficiency values for the syngas-to-mixed alcohol are research goals, rather than achieved values. The spreads are smallest for methanol and DME and mixed alcohol, and widest for FT diesel. Note that the efficiencies of

methanol and DME conversion are about the same; that of mixed alcohols is a little higher (although with less confidence, not well represented in the calculations used to obtain Figure 8); that of Fischer Tropsch diesel and Methanol-to-Gasoline (MTG) are lower.

D. **METHANOL FROM BIOMASS: CAPITAL COST OF METHANOL PLANTS**

The capital costs of biomass to methanol depends on the route taken for gasification, but typically runs between 2-3 $/gallon for indirectly heated gasifiers, and 3-5 $/annual gallon of methanol for directly heated gasifiers. [Phillips, Dutta] It is important to realize that these are costs of a 10^{th} of a kind plant, excluding development costs which many commercial biomass gasification plants are incurring today (discussed later in this report). The 2000 dry ton per day plant analyzed in these reports generate about 300,000 tons of methanol per year (~ 100 million gallons per year), a relatively small methanol plant by today's standards [Olah]. A world-class plant generating 1 million tons of methanol per year (a Mega-plant), would cost around ~ 650 M$ if indirectly heated and about twice as much for directly heated. In this report we quote 2010 dollars.

A megaplant (> 1,000,000 tons per year) would produce about 330 million gallons of methanol per year, or about 160 million gallons gasoline-equivalent. These units are feasible with natural gas or coal as the feedstock, but may be too large for using biomass due to the cost of collection, storage and transportation of the biomass. If the goal is to make a substantial fraction of the US gasoline consumption through methanol (say, 10% displacement of the gasoline used in the US in 2009), a production of 28 billion gallons of methanol would be required, requiring about 90 megaplants. The investment cost associated with these megaplants is about $56 billion dollars. This investment is large, especially when considering that it addresses only 10% of the US appetite for liquid fuels in transportation. For comparison, it is estimated that the US investment in ethanol through the end of 2007 has been $22 billion dollars, for a total (planned and current as of Dec 2007) annual capacity of about 14 billion gallons. [NEFL] Thus comparing based on the same annual output fuel energy, the capital cost of the thermo-chemical methanol plant would be about 1.8 times that of the bio-chemical ethanol plant (from corn).

If the size of the methanol plants is limited to 2000 tons/day dry biomass [Williams, Phillips], the number of plants required would increase to about 300 plants.

Probably the largest commercialization hurdle for the companies pursing the thermochemical route is the high capital costs associated with these technologies. In addition to the gasification and catalytic reactors required for today's mature methanol plants from hydrocarbon fuels (natural gas and coal), the syngas from biomass gasification must be cleaned to protect the catalysts used in the downstream syngas to fuel reactor which requires additional capital costs. The need for a cleaning step allows flexibility of the plant, being able to operate in a wide range of fuel, including MSW. When considering the cost savings for not having to pay the tipping fees at municipal dumping grounds, MSW feedstocks may avoid almost all the purchase costs of other biomass feedstocks, significantly offsetting the high capital cost of the plants. [RFS2]

Table 6. Gate feedstock methanol cost (2010$, adapted from BiomassPP and BPSR)

Year	2007	2009	2012	2017
Wet Herbaceous				
Total Feedstock Logistics, $/Dry Ton	$92.61	$69.41	$47.36	$43.79
Total Feedstock Logistics, $/gal methanol	$0.95	$0.66	$0.39	$0.35
Gallons methanol/dry ton	98	106	122	125
Dry herbacious				
Total Feedstock Logistics, $/Dry Ton	$56.39	$43.68	$36.75	$31.50
Total Feedstock Logistics, $/gal methanol	$0.58	$0.42	$0.30	$0.25
Gallons methanol/dry ton	98	106	122	125
Dry woody feedstock				
Total Feedstock Logistics, $/Dry Ton	$54.44	$44.63	$36.75	
Total Feedstock Logistics, $/gal methanol	$0.93	$0.53	$0.38	
NG				
$/MMBtu	$6.95	$3.89		
$/gallon methanol	$0.61	$0.34		

E. **METHANOL FROM BIOMASS: FEEDSTOCK COSTS**

In the production of biofuel from biomass, the costs of the biomass, as delivered to the gate of the plant, is a substantial fraction of the biofuel cost. In the US DOE Biomass Program Plan, system analysis of biofuels from a range of feedtocks (wet herbaceous, dry herbaceous and woody) are being investigated. Costs of the different feedstocks have been estimated. Table 6 shows the estimated costs (2010$) of the different feedstocks delivered to the plant gate. They have also estimated the decreased costs as the technology is implemented (*e.g.*, as it becomes mature) with time, as a result of focused R&D and improved methods. [BiomassPP, BPSR] Also

shown in Table 6 are historical yearly-averaged costs of natural gas for a NG-to-methanol plant during 2007 and 2009, for comparison.

The cost of the feedstock is a substantial fraction of the cost of methanol, even in the case of natural gas (the price of methanol has hovered around ~ $1/gallon). It is expected that by 2012 the biomass feedstock methanol costs of the biomass feedstocks will be comparable to 2009-2010 costs of NG feedstock.

Table 7 shows the breakdown of the costs for wet herbaceous feedstock. The costs are about evenly split between harvesting/collection, storage/queuing, preprocessing and transportation/handling. Large decreases in costs are expected from economies-of-scale and experience through the entire process, about 1/2 for transportation and preprocessing, and about 2/3 for collection and storage.

In the case of some wastes, the costs of the feedstock can actually be negative. This is the case for municipal solid waste (garbage), with a tipping fee ~ $50/ton, or just about the negative of the biomass cost ($30- $90/ton in Table 7). This cost differential results in a difference of gate feedstock methanol cost of about $0.8/gallon methanol. The potential for much lower production costs is the reason why there is substantial R&D activity in biofuel production from MSW.

Table 7. Breakdown of logistics gate wet herbaceous feedstock methanol costs, (2010$ per gallon methanol); adapted from [BiomassPP]

Year	2007	2009	2012	2017
Total Feedstock Logistics, $/gal methanol	$0.95	$0.66	$0.39	$0.35
Harvest and collection	$0.32	$0.21	$0.09	$0.09
Storage and queuing	$0.24	$0.18	$0.09	$0.07
Preprocessing	$0.18	$0.12	$0.08	$0.06
Transportation and handling	$0.22	$0.16	$0.12	$0.12

F. **METHANOL FROM BIOMASS: PRODUCTION COSTS**

Methanol synthesis is the most energy efficient conversion from syngas to a liquid fuel. Furthermore, the synthesis of methanol from natural gas or coal through the syngas process is one of the most well established industrial chemical processes, with production costs that are relatively well known. The production of methanol from biomass is more cost intensive due to complications with biomass gasification. The need for further gas cleanup and slag control

increases the capital intensity of a biomass to methanol plant and lead to lower energy conversion efficiency. These problems are shared by all biomass-to-fuel plants which employ gasification.

Because different alternative fuels are investigated in this section, costs per unit energy is a good measure for comparison. The cost of alternative fuels is difficult to estimate, as some of the processes are better understood than others, but none is mature. Thus the costs need to be taken with a degree of skepticism, specially when comparing costs from different authors with different models. However, these studies provide some indication about the relative potential of the different fuels.

In one of the first detailed techno-economic assessments of biomethanol production, the breakeven gate price (the price that meets the operating and capital costs of the plant, including feedstocks, power, personnel and amortization of the plant) was ~ $19-23 /GJ [Williams, Stark]. Williams assumed a delivered price of dry biomass of $75/ton, or about $4.1 /GJ [Williams]. The cost of the feedstocks are a significant fraction of the gate price of the methanol)

Table 8. Production costs of alternative fuels from biomass, in 2010 dollars; $/gallon and $/GJ; MTG is methanol-to-gasoline fuel; FTD is Fisher Tropsch diesel; DME is dimethyl ether.

fuel		$/gallon	$/GJ	Year of study	Ref
		1.18-1.42	18.95-22.90	1991	Katofsky
		0.93-1.02	15.36-16.55	2003	Spath
Methanol		0.65-1.02	10.79-16.91	2006	Kumabe
	Near term	0.69-1.01	11.50-16.80	2006	Faaij
	Long term	0.41-0.53	6.82-8.92	2006	Faaij
		1.54	17.60	1996	Lynd
Ethanol		1.46	16.55	2003	Kumabe
		1.06	12.13	2005	Phillips
MTG		>5.00	31.50	1990	Sugiyama
FTD		3.05	22.45-29.54	2003	Spath
		1.75	12.96-18.73	2006	Hamelinck
DME		1.14	15.36	2003	Spath

In 2003 further assessment of this system was performed by the National Renewable Energy Laboratory (NREL). A production price of $15.4-16.5 /GJ methanol was estimated for a delivered biomass cost of ~ $4.1/ton [Spath].

Most recently, an estimate of the breakeven gate price for methanol from biomass in Europe was estimated to be $11-16 /GJ in the short term evolving to $6.5-8.5 /GJ in the long term due to improved technology as more production facilities employing biomass gasification are built and operated [Faaij].

Table 8 summarizes the estimates of costs of production for alternative fuels given in 2010$/gallon (uncorrected by energy value) and $/GJ [Katofsky, Kumabe, Lynd, Sugiyama]. It should be noted that the costs indicated in Table 8 come from different studies by different investigators with different assumptions. This is the case of the production of ethanol from biomass, which requires mixed-alcohol catalyst that are in the process of being developed, with no catalyst yet providing the selectivity and productivity assumed in the calculations [Phillips, Duffa]. The estimated cost number for ethanol from mixed alcohols is a research goal, rather than demonstrated. [Stevens] On the other hand, highly optimized methanol catalyst with high productivity and selectivity exist, and are used commercially. [Albemarle]

The costs in Table 8 reflect the breakeven gate price of the methanol rather than the prices that will be charged to the vehicle operator at the fueling station (which would include distribution, state and federal taxes, and retail station profit).

The estimated prices of future bio-methanol and the present price of methanol from natural gas are comparable, while the cost of future ethanol is substantially lower than today's price.

G. **METHANOL FROM BIOMASS: WATER REQUIREMENTS**

The thermochemical process for biomass conversion to fuels requires substantial amounts of water. As a reactant, water is needed for the steam reforming process and for the water gas shift reaction. In the BCL gasifier, it also acts as the fluidizing agent in the form of steam. Water is required for thermal management. [Phillips]

The water consumption in the production of ethanol is a raising concern. In order to minimize fresh water intake as well as to minimize discharges to the environment, today's ethanol plants recycle most of its water, using centrifuges and evaporators. The boiler system used for steam generation requires high quality water, provided from wells that draw from the local aquifer. Water usage by today's corn ethanol plants range from 3-7 gallons per gallon of ethanol

produced. This ratio however has decreased over time from an average of 5.8 gal/gal in 1998 to 4.2 gal/gal in 2005. [Phillips, Dutta]

A primary design consideration for any thermochemical process is the minimization of fresh water requirements, which therefore means both minimization of the cooling tower and utility systems water demands and a high degree of water recycle. Air-cooling was used in several areas of the process in place of cooling water in recent plant designs [Phillips]. For thermochemical indirectly heated gasifiers, cooling tower water makeup uses 70% of the fresh water demand. Water for the boiler is about 20% and 50% for the indirectly and directly heated gasifiers, respectively. The indirect and direct design require 1.4 gallons and 0.9 gallons of fresh water for each gallon of methanol produced, respectively (numbers scaled from Phillips and Dutta). The water consumption in methanol plants designs is considerably lower than today's ethanol plants, even after accounting for the lower energy density of the methanol. However, it needs to be determined whether the high levels of water economy can be reached in commercial thermochemical plants.

H. R&D IN THE US AND WORLDWIDE

In the US the R&D effort is mainly focusing on biological process of cellulosic fuels. The biological processes attempt to develop specialized microbes that would break down cellulose in the feedstock. Presently, there are no biological means of processing the lignin into useable products. Another route is thermochemical processing, where the biomass is gasified in oxygen-poor environment, creating a mixture of hydrogen and carbon monoxide. Depending on the biomass and processing conditions, the ratio of hydrogen to carbon monoxide can vary, and can be adjusted by either water-shifting the products, or by hydrogen injection [Bure]. Although the work is focusing in ethanol and bio-diesel (through Fisher-Tropsch), methanol is much easier to produce, and in some of the cases (as for Range Fuels and FischerTropsch) it is a step in the manufacturing of the heavier alcohols.

In the US, Range Fuels is commercializing a thermochemical process to the manufacturing of methanol from non-food biomass, to be used to eventually make ethanol, using mixed alcohol catalysts. [Range] Range has operated a pilot plant for over 7 years using over 20 different nonfood feedstocks. Range Fuels broke ground in building its first commercial plant late in late 2008 and is expected to be operational in 2010. During the first phase, the Soperton plant will

gasify non-food biomass such as woody biomass and grasses the production of methanol. In later phases the methanol reactor will be modified for the production of ethanol by a mixed-alcohol catalyst. The Soperton Plant will initially use woody biomass from nearby timber operations, but plans to experiment with other types of renewable biomass as feedstock for the conversion process, including herbaceous feedstocks like miscanthus and switchgrass. Range Fuels plans to eventually expand the annual capacity of the plant to 60 million gallons of cellulosic biofuels, with a permit to produce 100 million gallons of ethanol and methanol. It is expected that in 2011 Range Fuels will generate about 4 million gallons of methanol [RFS3] Range investment has been over $200 million. For a first-of-a-kind plant, the cost of the methanol produced is expected to be over a factor of 3 higher than from conventional sources, such as natural gas or coal.

In Germany, Choren is attempting to produce Fischer-Tröpsch Diesel from various biomass feedstocks. The three-stage gasification reactor includes low temperature gasification, high temperature gasification and endothermic entrained bed gasification. Choren will be building a commercial Plant in Freiberg/ Saxony Germany that is expected to be operational in 2011 or 2012. Initially, the plant will use biomass from nearby forests, the wood-processing industry and straw from farmland. [Choren, Bure].

In Sweden, a pilot scale plant is producing methanol from black liquor (a hazardous sludge byproduct of paper puling). [Varmlands] If every paper mill in the US used this process, it could generate 28 million tons of methanol per year (9.3 billion gallons). The Swedish company, Chemrec, has collaborated with Weyuerhaueser in the US, and built a plant in New Bern, NC. The plant started operation in 1996, with a capacity of 330 t/day dry solids, with air as the oxidant, at atmospheric pressure. The plant became idle in 2008, after about 50,000 hours of operation, due to high operating costs. In August 2007, Chemrec, in collaboration with NewPage, started a design process for a plant in Escanab, MI. The plant would produce methanol and dimethyl ether from the gasification of kraft pulp black liquor. However, in 2009 NewPage discontinued work due to escalating costs. Rick Willett, president and CEO of New Phage, said that "unlike Europe, the demand for methanol … as transportation fuel has not developed in North America. The lack of demand for these products in our country doesn't support the feasibility of the project. To be a viable project, the costs for the installation would need to be much lower and the current market prices for methanol and dimethyl ether would need to improve as well." [NewPage]

Chemrec has opened the first commercial plant for production of DME in September 2010 in Pitea, Sweden, using Chemrec's gasification process and Haldor-Topsoe providing the gas clean-up and fuel synthesis processes. [Pitea]

All the thermochemical gasification technologies generate synthesis gas which is then converted to methanol, mixed alcohols, or higher components (including FT diesel, jet fuel). In addition, the methanol can be further upgraded to gasoline through the MTG process. There are a large number of demonstration/commercial units that are being constructed in the US and elsewhere that include a biomass gasification unit. Table 9 provides information on a few of them. Where possible, the cost of the unit, and the annual production rate are listed. The end product expected is also listed, as well as a reference. Table 9 is not meant to be a comprehensive listing of all biomass gasification plants. It is important to note that these are development units, mostly, and that the cost include a substantial development charges and are not representative of 10th-of-a-kind plant costs.

Olah and the Lotus group have advanced the potential of using CO_2 directly from the atmosphere as a carbon-neutral fuel. [Olah, Lotus] Techniques for the production of synthetic methanol through the extraction of atmospheric CO_2 are well developed and understood but are not being employed on an industrial scale. The methanol production process requires hydrogen, which can be manufactured by electrolysis using non-carbon emitting power plant, such as nuclear, hydroelectric or even renewable (wind or photovoltaic). An early solution would be the co-location of the hydrogen producing facility with a conventional power station which would simplify the collection of the CO_2.

In Canada, using renewable electricity from wind and waste carbon dioxide, Blue Fuel Energy plans to produce low-carbon methanol (Blue Fuel methanol) and low-carbon DME (Blue Fuel DME)—at a cost expected to be equal to or lower than that of the above-mentioned fuels. They claim that their Blue Fuel methanol has much lower carbon intensity than wheat and corn-based ethanol. Two immediate markets have been identified: a gasoline blendstock to help fuel suppliers meet the new low carbon fuel requirements regulation; and as a biodiesel feedstock to help biodiesel producers in western North America further reduce the carbon intensity of their fuels. [BFE]

In Iceland, CRI (Carbon Recycling International) is finishing (2010) a plant which will produce around 2 million liters of Renewable Methanol (RM) fuel per annum, expandable to more than 5 million liters a year by 2011, removing 4.5 thousand tons per year of CO_2 from the atmosphere. The production process is clean and the byproduct is oxygen. RM will be blended with gasoline and sold at gasoline stations throughout the greater Reykjavik area by the end of 2010. [CRI]

Table 9. Selected biomass gasification projects under construction/consideration

		costs ($M)	annual production (M g)	Proposed product	
<mark>Precommercial, methanol</mark>					
Range Fuels	Soperton, GA	256	40	MeOH/EtOH	http://www.greencarcongress.com/2010/08/rangemeoh-20100818.html
Chemrec	Ornskoldsvik	350	34	MeOH/DME	http://www.greencarcongress.com/2009/06/chemrec-20090626.html
Varmlands	Hagfors, Sweden	416	36	MeOH/DME	http://www.greencarcongress.com/2010/07/varmlands-20100731.html
<mark>Commercial, NG</mark>	MegaPlant	800	323	methanol	
<mark>Biomass Gasification</mark>					
Enerkem	Alberta, CA	80	10	EtOH	http://www.renewableenergyworld.com/rea/news/article/2010/09/enerkem-building-trash-to-fuels-plant
	Pontotoc MS	250	20	EtOH	http://www.enerkem.com/en/our-locations/plants/pontotoc-mississippi.html
	Quebec, CA	?	1	EtOH	http://www.enerkem.com/en/our-locations/plants/westbury-quebec-canada.html
					http://www.bizjournals.com/memphis/stories/2009/03/30/newscolumn1.html
Coskata	Melbourne, Austr	394	66	EtOH	http://www.greencarcongress.com/2010/10/coskata-20101010.html
	Madison, PA		0.04	EtOH	
			59	EtOH	http://www.greencarcongress.com/2009/10/coskata-unveils-semicommercial-feedstockflexible-ethanol-facility-springboard-for-fullscale-commerci.html
Choren	Greiswald	660	69	diesel	http://www.greencarcongress.com/2007/03/choren_close_to.html
	Freitag		5	BTL	
Neste Oil	Porvoo/Imatra, Fi	697	61	FT	http://www.greencarcongress.com/2010/10/nse-20101011.html
Clear Fuel/Rentech	Collinwood, TN	(DOE 23)	16	jet fuel	http://www.greencarcongress.com/2010/02/clearfuels-20100227.html
CEA/Uhde	France	151		FT/jet fuel	http://www.greencarcongress.com/2010/03/uhde-20100328.html
Solena/BA	East London		16	Jet fuel	http://www.greencarcongress.com/2010/02/ba-solena-20100215.html
SilvaGas/Rentech	LAX		2	Jet fuel	http://www.greencarcongress.com/2009/08/rentech-20090818.html

V. PHYSICAL AND CHEMICAL PROPERTIES OF METHANOL FUEL

The combustion relevant properties of several fuels for spark-ignited vehicles are shown in Table 10.

Table 10. Properties of the alcohol fuels and gasoline

Fuel type		Gasoline	Ethanol E100	Methanol M100	Methanol with cosolvent
Chemical formula			C_2H_5OH	CH_3OH	50% methanol /TBA
RON			129	133	114
MON			102	105	96
(R+M)/2			115	119	105
Specific gravity	kg/l	0.75	0.794	0.796	0.789
Stoic air/fuel ratio		14.6	9	6.4	8.8
Net heat of Combustion (LHV)	MJ/l	32	21	16	21
Net heat of Combustion (LHV)	MJ/kg	43	27	20	27
Energy density	MJ/liter	32	21	16	21
Lower flammability limit	% vol	1.4	3	6	
Upper flammability limit	% vol	7.6	19	36	
Autoignition temperature	K	519	638	738	
Flash temperature	K	230	285	280	
Laminar flame speed (1 bar, 300K)	cm/s	33	41	50	
Vapor pressure	psi	9	2.3	4.6	
Latent heat of vaporization	MJ/kg	0.27	0.85	1.1	0.80
Vaporization energy/LHV		0.006	0.031	0.058	0.03

Table 10 shows the properties of gasoline, ethanol, methanol and methanol with cosolvents. [J1297, Bromberg, Hara, Liao] It also shows the flame speed of gasoline, ethanol and methanol. The cosolvent in the last column is TBA, tert-butanol.

Methanol has lower energy density than gasoline, ethanol or diesel (not shown). The engine fuel system needs to deliver larger flow rates of methanol than gasoline, and also the fuel range (miles driven on a tank-full) decrease. These effects depend on the blending level of methanol in

the gasoline. For comparable vehicle efficiencies, the range is decreased by 50% when using M100. However the efficiency of operation of the engines in the vehicle demonstrations described in Section I is comparable or slightly better to that when using gasoline, when compensating for the lower heating value of the fuel [Pefley] With a dedicated methanol engine, the vehicle can be as efficient as a diesel, or about 25-30% more efficient than conventional vehicles operating on gasoline. [Brusstar] The range of dedicated high-efficiency methanol vehicles is about 30% lower than conventional gasoline vehicles.

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

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

Methanol has other physical properties relevant when used as a transportation fuel. Unless used neat, the vapor pressure of the fuel is increased, affecting evaporative emissions (discussed in Section VII). It has toxic characteristics which are compared to those of gasoline and ethanol in the Environmental and Health Impact section. It has also open air combustion characteristics that make it safer than other transportation fuels, discussed in Section IX. Finally, it has corrosion properties that require modification of some components in contact with the methanol, discussed in Section X.

VI.   REGULATED AND UNREGULATED EMISSIONS IMPACTS

The California pilot program for methanol in the 1980's and 1990's was driven in part by air quality standards, with the goal of reducing ground-level ozone in urban center. The use of high blends of methanol decreases ozone precursors CO, hydrocarbon and NOx emissions. [Jeffries] With the development of the three-way catalyst for spark ignition engines, the advantage of lower emissions and lower reactivity from methanol fuels has been eliminated. [Sheehy]

HC emissions from methanol combustion mainly consist of unburned methanol and aldehydes. Testing has shown that neat methanol combustion will produce about twice the level of aldehydes as gasoline [Bechtold1], with formaldehyde being the predominant toxic emission from methanol combustion [CRCAO]. Aldehyde emissions are effectively controlled by use of a catalytic converter. [Fan]

Blending small amounts of methanol with gasoline greatly increases the vapor pressure. High evaporative emissions issues occur for light methanol blends, and for high blends when used in FFV's, when gasoline is introduced in a tank that contains small amounts of methanol. Canisters to control evaporative emissions of FFV's need to be able to handle operation with gasoline (9 psi RVP), M85 (around 7.5 psi RVP) and M5 (12.5 psi RVP). The issue is further complicated since most gasoline today is already blended with ethanol. Further research would be needed to investigate the possible effects of blending methanol with ethanol gasoline blends.

Although methanol vapor degraded the ability of conventional automotive charcoal canisters to adsorb vapors compared to gasoline [Keller], vehicles produced and used in the US programs met the same evaporative emission standards as comparable gasoline vehicles. Long-term deterioration of the charcoal was not reported as a problem. For the FFV Taurus, 4 canisters (as opposed to a single canister for gasoline) were required for certification for evaporative emissions across the full spectrum of fuel combinations. [Nichols]

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, high evaporative emissions.

A. Cᴏʟᴅ sᴛᴀʀᴛ ᴇᴍɪssɪᴏɴ

Cold start emissions with methanol blends, as with ethanol blends, require seasonal adjustment of the fuel formulation. Because of the alcohols high flash temperature (temperature at which fuel vapors form an ignitable mixture in air) (see Table 10), cold start during cold weather is challenging compared with gasoline. In spite of this, fleet tests of low-level methanol blends did not report statistically significant changes in cold-start performance. [Bechtold] In the case of methanol, cold weather start is further problematic because of the larger evaporative cooling of the methanol.

Recently unregulated emissions and combustion characteristics of low-content methanol-gasoline blends were investigated for low-blends of methanol. [Fan] The study concluded that while engine-out methanol and formaldehyde (unregulated emissions) increased almost linearly with the methanol content in the fuel, the conventional three-way catalyst (TWC) has a high conversion efficiency for those unregulated emissions. At the tailpipe, the TWC reduced the regulated and unregulated emissions from the methanol-gasoline engine to the same levels as those generated by a conventional gasoline engine

In engine startup tests in a medium duty dedicated M85 engine, the EPA [Brusstar] used a few design approaches to avoid the considerable spike in raw fuel emissions at cold startup found in previous investigations. [Dodge] The high compression ratio, combined with a relatively high engine cranking speed of about 800 rpm, provided a higher peak compression temperature, and hence improved low-temperature ignition behavior. A port deactivation device was also employed to enhance the spray breakup over the intake valve in the helical port during startup, which was found to give substantial improvement in startability. Taken together with conventional startup fueling and spark advance strategies, the engine was able to achieve startup on the first cycle. More work needs to be done on start emissions in cold weather conditions. [Brusstar]

B. Gʀᴇᴇɴ Hᴏᴜsᴇ Gᴀs Eᴍɪssɪᴏɴs

The implication of methanol as a transportation fuel has been analyzed by several authors in the past. In order to provide comparison between options, multiple steps need to be investigated: production, transportation, and use in vehicles. Methanol can be manufactured from a wide range of feedstocks, such as renewables (biomass, including municipal wastes), coal (as in China), CO_2

and natural gas. In the US, the use of natural gas is the preferred method for the manufacturing of methanol, as it is also abundant [MITNG]

The impact of the use of methanol on Green House Gas emissions is dependent on the source of the methanol, as indicated in Table 11 (adapted from Sheehy). CA RBOB (California Reformulated gasoline Blendstock for Oxygen Blending) represents today's conventional gasoline vehicles. Methanol from natural gas can slightly decrease the carbon intensity compared to the baseline gasoline case because of the increased hydrogen content of the natural gas (lower carbon intensity of methane), while in the case of coal (as is the case in China), the carbon intensity nearly doubles. The carbon intensity is small in the case of biomethanol, if the Indirect Land Use Change Effect (ILUC) is small.

Table 11. Life cycle Carbon intensity, including Indirect Land-Use Change (ILUC); adapted from Sheehy, MethInst; RBOB is reformulated gasoline for oxygen blending; ULSD is ultra low sulfur diesel; CCS is carbon capture and sequestration.

Source	[Sheehy] WTW (g/MJfuel)	[Sheehy] ILUC (g/MJfuel)	[MethInst]
Fuel			
CA RBOB	96	n/a	96
Ethanol (corn)	68	30	
California (CNG)	68	n/a	
Electricity (CA average)	124	n/a	
ULSD	95	n/a	
Biodiesel (soy)	21	62	
LNG	73-93	n/a	
Methanol (NG)	88	n/a	90
Methanol (NG) in dedicated vehicles	67		
Methanol (coal)	190	n/a	182
Methanol (coal with CCS)	89	n/a	90
Methanol (coal with CCS, future)			77
Biomethanol (renewable)	5	unknown	?

Gasoline has comparable GHG emissions than methanol from natural gas, while methanol from coal has approximately twice the GHG generation. The best results are provided by the use of biomass for methanol generation.

The coal-to-methanol carbon intensity value in Table 11 assumes that the plants only make dedicated 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 [ARCADIS] methanol production technology has been estimated to be 71%, compared with the 55% assumed here for stand-alone plants [Fletcher]. Methanol produced in these facilities or in PolyGeneration units in China would have correspondingly lower GHGs.

Use of methanol to satisfy the Low-Carbon Fuel Standard introduced in CA is unlikely, unless the methanol is generated from renewables. [Sheehy] In the Methanol Institute Study [MethInst], the methanol engine was assumed to be 7% more efficient than conventional gasoline engines, due the characteristics of methanol as a fuel. It should be noted that with high methanol blends, dedicated vehicles could decrease carbon intensity by 30%, as the engines can be more efficient.

A detailed investigation of the overall efficiency and Green House Gas emissions of fossil and alternative fuels was performed by Volvo. [Volvo] Figure 9 summarizes their conclusions. They have assumed that the methanol engine has the same efficiency as the gasoline engine. If the potential improvement of efficiency of methanol (or ethanol) engines, the efficiency of methanol engines will be larger than those for DME, with lower GHG emissions.
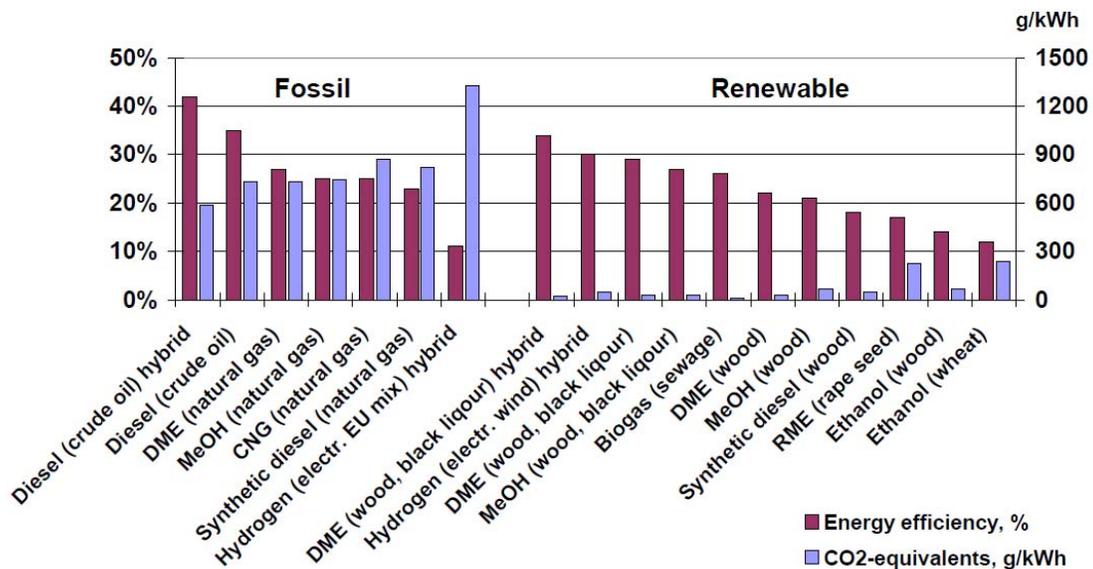

Figure 9 Well-to-wheel analysis for different fossil and alternative fuels [Volvo]

VII.   ENVIRONMENTAL AND HEALTH IMPACTS

A.   HEALTH IMPACT

Methanol is produced in small amounts in the human body as part of the metabolic process, and occurs naturally in some fruits. At high enough concentrations it is poisonous. Ingestion of 10 ml can cause blindness and 60-100 ml can be fatal if the condition is untreated. [Toxicity]

US OSHA permissible exposure limit for general industry in air (40 h/week) is 1900 mg/m³ for ethanol, 900 mg/m³ for gasoline, and 260 mg/m³ for methanol. When methanol is blended in gasoline, although the overall vapor pressure increases (see section VI), the partial vapor pressures of some gasoline compounds with high toxicity, such as benzene and 1,3 butadiene, decreases. It is difficult to smell methanol in air at methanol concentrations less than 2,000 ppm (1500 mg/m³).
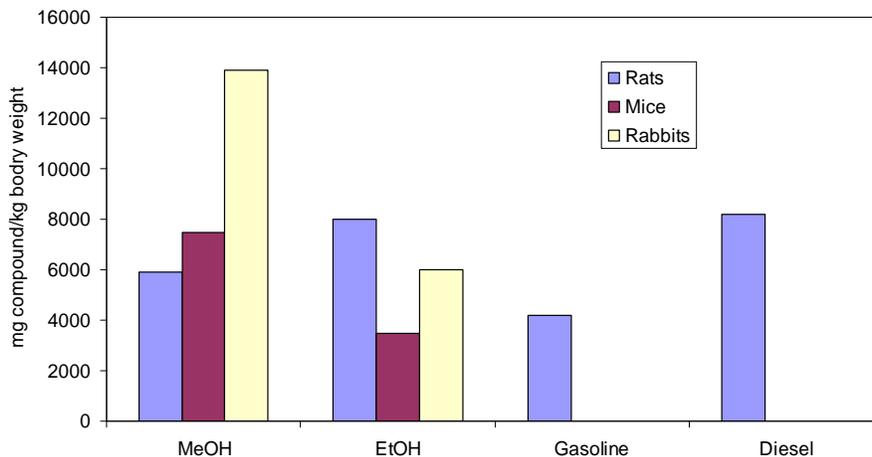

Figure 10. Oral LD50 values for common fuels [Short Stark]

For exposure to toxic chemicals, the most common measurement of prompt toxicity is the median lethal dose, LD50, defined as the dose at which 50% of the test population is killed. For methanol there are three primary methods of exposure: ingestion, inhalation and dermal contact. [Stark] The toxicity of chemicals is determined by observing following exposure the response of a population of test animals (commonly mice and rats, but in some cases, rabbits and dogs), compared with a similar population that is not exposed. The duration of exposure and the time of

observation are not uniform across investigators, but there are well known rules to adjust for variations.
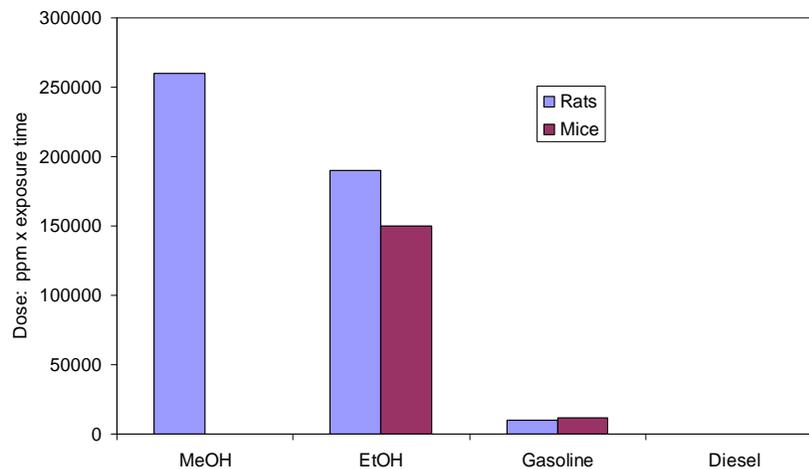

Figure 11.   Inhalation LD50 values of common fuels [Short, Stark]

The LD50 health effects of conventional fuels as well as alcohol fuels are shown in Figures 10. 11 and 12 for oral, inhalation and dermal contact, respectively. These figures show that methanol toxicity resulting in death as a result of ingestion, is comparable in terms of LD50 to the other fuels. In the case of inhalation of the vapors, methanol is actually less toxic than either gasoline or ethanol. (adapted from Stark, Short)
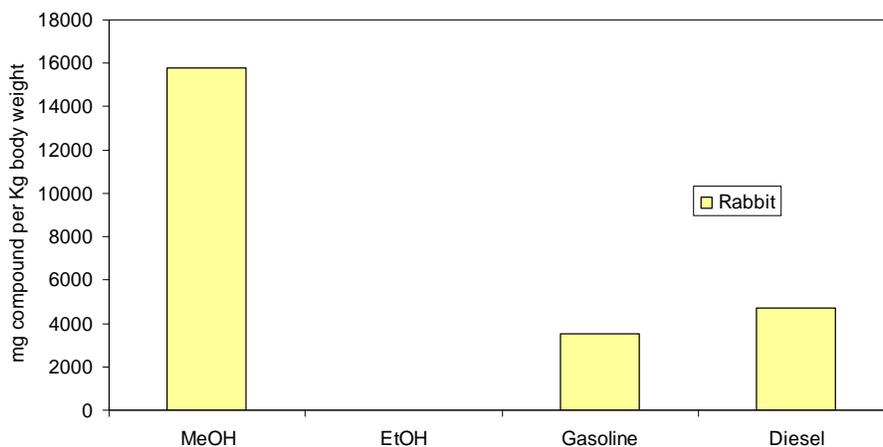

Figure 12. Dermal LD50 for common fuels and alcohols

Dermal absorption during accidental exposure during refueling is a concern. Methanol and ethanol are either even or less toxic than gasoline or diesel. Comparison of risks of alcohol fuels to those of fossil fuels is shown in Figure 12.

The use of methanol as a fuel has met resistance, more than most fuels, due to claims that it is unsafe for public utilization due to toxicological concerns. As discussed above, the issue of toxicity is often overstated as methanol's toxicity (death) is on the same order as other fuels being considered as gasoline and diesel substitutes. Further, methanol is being used and has been widely used as windshield washer fluid without any major concern, and in this case the fluid is literally spread across the road. In the California test, with over 200 million miles of methanol driving, there was not a single case of accidental methanol poisoning.

The discussion above related to mortality from acute exposure. Morbidity of a compound is the non-lethal negative health effects caused by exposure, inhalation or injection of the compound. Morbidity is harder to quantify in a standardized way since morbidity is not an absolute like mortality. Methanol can cause blindness and other neurological effects when a relatively small amount is ingested, while much more is needed to cause death.

There are also high morbidity risks associated with gasoline and its components due to the carcinogenic nature of aromatic hydrocarbons. Methanol has not been determined to be a carcinogen. However, at the present time (November 2010) the EPA is carrying a toxicological review of methanol.

In 2007, methanol was the primary substance in 2,059 exposures and 11 deaths in the United States [Bronstein]. The primary route of exposure is oral consumption, with common reasons being intended suicide, substitution when ethanol is not available, or unintentional exposure. Close to 90% of cases in 2007 were unintentional exposures, and 510 of these were patients younger than 6 years. [Bronstein] The quantity of methanol necessary to cause physiological effects is dependent on the concentration of the solution and the metabolic process involved, and the levels causing physiological effects in adults are between15 and 500 ml of a 40% solution. [McMahon] According to McMahon, it is imperative for healthcare personnel, especially in emergency rooms, to become knowledgeable about the signs and symptoms of methanol ingestion, as well as the various monitoring parameters essential for accurate diagnosis and

treatment. The availability of ethanol and fomepizole as antidotes has dramatically enhanced the ability to treat these overdoses and subsequently reduce related toxicities. [McMahon]

B. **ENVIRONMENTAL IMPACT**

Methanol, like ethanol but unlike hydrocarbon fuels, is water soluble. As a consequence, it is transported through diffusion and convection through the environment at much faster rate than hydrocarbons. A ground spill migrates substantially through the subsurface water, while hydrocarbon's mobility is much lower (gasoline agglomerates above the water table, forming Non-Aqueous Liquid Phase pockets). In addition to fast migration, methanol bio-degrades much faster than hydrocarbons. Fast transport and degradation result in short lifetimes. Hydrocarbons, on the other hand, comprise many stable compounds, which include some, such as aromatics, that are highly toxic to bio-organisms and degrade slowly.

Table 12. Half-lives (in days) of common fuel components, adapted from Howard.

	Soil	Air	Surface Water	Ground Water
MeOH	1-7	3-30	1-7	1-7
EtOH	0.1-1	.5-5.1	0.25-1	0.5-2.2
Benzene	5-16	2-21	5-16	10-720
Toluene	4-22	0.4-4.3	4-22	7-28
Tri-methyl-benzene	7-28	0.1-.6	7-28	14-56

Table 12 shows the half-life of common fuels in soil, air and water. Compared to hydrocarbon based fuels, methanol lifetime is substantially shorter. Ethanol degrades even faster than methanol and has comparable transport properties to methanol. In the case of a large methanol spill, the environment is likely to recover quickly.

A catastrophic failure is the case of methanol dispersion in surface water. While most hydrocarbon components would float on the surface, methanol would dissolve in the water. In the case of a river with limited water throughput, the methanol would form a "plug" that would flow down river and may prevent human consumption of the water until the methanol flows downstream or degrades. The concentration of the methanol "plug" decreases fast due to dilution/mixing by diffusion and turbulent mixing with upstream/downstream waters while

degrading [Jamali], and the environment recovers quickly. One of the consequences of this scenario is that barge transport of methanol in rivers should be carefully monitored and precautions taken. On the other hand, releases in open waters results in very quick decrease of methanol from the source of the spill [Katsumata]

According to the International Programme on Chemical Safety of the World Health Organization (WHO) the LC50 values (contamination where half the population dies) in aquatic organisms range from 1300 to 15900 mg/liter for invertebrates (over 48 and 96 hr exposures), and 13000 to 29000 mg/liter for fish (over 96 hour exposure) [WHO]. Even in the event of a large scale spill these times of exposure are unlikely to occur due to the rate at which methanol dissipates.

VIII.   FUEL HANDLING AND SAFETY ISSUES

A.   FUEL HANDLING: VAPOR PRESSURE AND PHASE STABILITY

Blends of methanol and gasoline result in two issues that need to be addressed, especially for low methanol blends: increased vapor pressure, and phase separation in the presence of water.

Adding a small amount of methanol to gasoline results in a significant rise in vapor pressure; the evaporative emissions could increase by up to 50% [Cox, API]. The use of cosolvents with the methanol moderates the increase in vapor pressure (RVP of 11 psi versus 12.5 psi without the cosolvent). The increase in vapor pressure requires the use of larger canisters for accumulating the evaporating emissions (see section VI above)

The second issue is phase separation in the presence of water. Methanol addition increases substantially the temperature at which phase separation occurs. This problem is exacerbated because the aqueous phase is denser than gasoline, and thus sinks to the bottom of the tank where it then is introduced into the fueling system. The use of cosolvents is needed in colder weather.

B.   SAFETY

As mentioned above, methanol has been used for racing in the US. The main reason for this choice was its safety (methanol is harder to ignite, creates less radiant heat, can be controlled/extinguished with water, and burns without producing black smoke, facilitating rescue). 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. Gasoline additive, such as in M85, is sufficient to provide adequate luminosity.

For the regular driving, methanol offers a substantial decrease in the risks of fuel fire deaths compared to gasoline for the same reasons as in racing. For M100 a 90% reduction in fuel related automotive fires is projected, while a smaller reduction of 40% is projected for M85 [Machieli].

Since methanol vapor is heavier than air, it will linger close to the ground or in a pit unless there is good ventilation, and if the concentration of methanol is above 6.7% in air it can be lit by a spark, and will explode above 12 C.

IX. OTHER END USE ISSUES FOR TRANSPORTATION

A. FEDERAL INCENTIVES FOR METHANOL VEHICLES

Although there are many federal financial incentives for the introduction of alternative fuels, only three incentives apply to methanol, and of these, two have lapsed. The qualified alternative fuel motor vehicle tax credit, (< $4,000 for a light duty vehicle or < $32,000 for a Heavy duty vehicle) still applies through the end of 2010, but there are no qualified methanol vehicles. [AFVDOE]

B. MATERIAL COMPATIBILITY

Methanol is more corrosive than ethanol; material compatibility issues of methanol fuels require modifications of engine fuel systems. Both elastometers (soft components used for seals and fuel lines) as well as metals, if not chosen properly, can be attacked by methanol. However, work done in California and elsewhere has demonstrated that methanol compatible vehicles can be effectively designed. There are no technical hurdles.

Methanol fuels at any concentration can be extremely aggressive toward magnesium and, if they contain dissolved or separated water, and towards aluminum [Ingamells]. 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 gasoline blends (blends of up to 10%) on copper, cast iron, steel, and aluminum [Liu]. Properly formulated engine oils have also shown to be able to control corrosion inside 4-cycle engines [Schwartz].

The compatibility issues of methanol with fuel system components increase with methanol content. Methanol-rich fuels have been shown to cause shrinkage, hardening, swelling or softening of soft fuel system components [Schwartz]. Alternative materials, however, exist that are do not show sensitivity to methanol exposure. It is not clear whether conventional fiber-reinforced tanks are compatible with methanol fuels when exposed high ambient temperatures. Softening, swelling, blistering, and signs of delamination were observed in this popular fuel storage tank and tank lining material at 50 C [Keller]. Reactions at room temperatures (23°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.

The refueling system at the service stations has to be designed with care. Tanks, pumps, lines and spigots need to be methanol compatible. The California Energy Commission identified the design elements for a methanol compatible fueling system. [Rawson]

X. RELATIVE PROMISE AS A WIDELY USED TRANSPORTATION FUEL

A. VEHICLES PERFORMANCE

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

Light Duty Applications with dedicated vehicles

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

An interesting alternative to dedicated methanol vehicles, which are needed to achieve the efficiency advantages described above, is to use two tanks, the main tank filled with gasoline and the second tank filled with methanol. This concept, Direct Injection Alcohol Boosted (DIAB), uses direct injection (DI) of methanol when the engine is prone to knock (usually at conditions of high torque). [Cohn] The charge cooling, which derives from the high latent heat of vaporization of methanol, is primarily responsible for the knock suppression. Due to the charge cooling from the DI process, the effective octane rating [Bromberg1] greatly exceeds the chemical octane rating that these fuels would exhibit using conventional induction methods such as port fuel injection (PFI). In the DIAB concept, DI of the knock suppressing fuel is used only in the amount required to prevent knock and gasoline is supplied to the cylinder by conventional PFI. Since the engine operates at stoichiometry (using a typical oxygen feedback), a very high specific torque output can be produced while emissions can be maintained at low levels through the well-proven and relatively simple three-way catalyst system without the use of EGR as a major diluent. The

technology opens the possibility of a spark-ignited gasoline engine operating at high compression ratio (12 - 14) and high boost ratios of 2.0- 2.5 times ambient pressure, which is sufficient to produce a torque output equivalent to or greater than more highly turbocharged heavy duty diesel engines operating lean with significant EGR. The methanol-boosted DIAB engine can be almost as efficient (as measured by BTE, brake thermal efficiency) as a diesel and have comparable specific CO_2 emissions as well. The concept has been demonstrated and proven in systematic dynamometer tests at Ford [Stein]. In addition, Honda has independently investigated the concept [Kamio].

Medium/Heavy Duty Applications with dedicated vehicles

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

The potential of directly injected spark ignited heavy-duty vehicles has been explored. [Blumberg, Bromberg3]. The high octane of methanol, as well as the large evaporative cooling of methanol, have been shown to strongly suppress and, for all practical purposes, eliminate the knock in spark ignited direct-injection engines [HEDGE, Stein1, Cristie] High compression ratio and/or aggressive turbocharging/downsizing can be achieved when this fuel is used in conjunction with direct injection. Small, very high power density, spark ignition engines which are fueled with ethanol, methanol or mixed alcohols can be used as a substitute of heavy duty diesel engines, with higher engine thermal efficiency and much reduced size and weight. In this manner a 4 liter engine could potentially be used to replace a diesel engine with a displacement as high as 11 liters. The extreme downsizing indicates the potential of a SI, knock-free engine, operating at the same peak pressure as the diesel engine and higher engine speeds. However this aggressive downsizing may not be practical because other constraints (durability, exhaust temperatures). More modest downsizing up to 5 liters could offer a practical solution. [Bromberg3]

A direct injection alcohol engine downsized by around a factor of two relative to a diesel engine could have an efficiency advantage over the diesel of about 4% for prolonged high torque operation in long haul trucks. In addition, it has been shown that reforming about half the methanol or ethanol would result in capture of about 5% of the energy in the exhaust, as a bottoming cycle. [Bromberg3] The lean operation allowed with reformate could result in an additional 5% improvement in efficiency but would require more expensive aftertreatment. There could also be a small increase in efficiency with up-speeding and further downsizing.

The efficiency estimates do not include the fuel penalty for diesel engine aftertreatment regeneration, which when included will further increase the comparative advantage of the spark ignited engine by a few percentage points. Use of a smaller displacement spark ignition engine with a three-way catalyst exhaust treatment system in place of a diesel engine could reduce engine system (engine plus exhaust treatment) cost by $10,000 - $15,000, if the volumes are significant and the cost of developing/modifying the engine is spread over a large number of engines.

B. **BLENDING STRATEGIES**

Methanol can be used either in dedicated methanol vehicles, in flex fuel vehicles (where various RFS gasolines can be introduced into the vehicles), or in vehicles with multiple tanks. Blending strategies vary depending on the application.

For flex fuel vehicles, methanol in the US can be used either as a low methanol blend, or high methanol blend. For low level blends, the main issue is commingling of multiple fuels in the tank, while for high methanol blends, the main issue is material compatibility [Sheehy].

There are regulatory issues that presently determine the near-time potential of methanol in the US. For low level blends, there is a waiver on record for methanol as an additive to gasoline at the federal level. [EPA] There are no significant regulatory issues that limit the potential of high level blends.

However, in a low level blend scenario, methanol faces two significant challenges. Most states will require an ASTM standard and test procedure for low level blends of methanol with gasoline. California also explicitly prohibits the use of methanol as an oxygenate in gasoline without a full multimedia evaluation impact analysis. [Sheehy]

Although various blends of up to 15 percent methanol have been requested to date, current EPA waivers limit methanol and cosolvents concentration in fuel blends to 5.5%. Higher methanol blends will require EPA certification. The EPA methanol waivers require the use of cosolvents to address the increased volatility of the fuel, the phase separation at low temperatures, and the material compatibility issues. ASTM D4814 (Standard Specification of Automotive Spark Ignition Fuel) stipulates that methanol/gasoline blends are similar to gasoline if the methanol concentration less or equal to 2.75% (by vol) with an equal amount of cosolvent. There is not federal requirement for the adoption of ASTM standards for gasoline blends, but states have opted to incorporate these standards.

An interesting option is higher blends, around 70% methanol. This blend raises fuel economy of methanol in par with E85 fuel economy (heating value volumetric density), still lower than gasoline [ASTM D5797]

Another interesting option is the replacement of ethanol in E85 blends, by a blend of methanol/gasoline. Turner suggests that mixing E85 and a M57 gasoline/methanol blends at arbitrary ratios, the stoichiometry ratio (air/fuel ratio) of the fuel remains constant, as well as the volumetric energy content. Thus, there needs to be no modification of the fuel injection rate or the air/fuel ratio, over a wide range of gasoline/ethanol/methanol blends. [Turner]

Methanol is registered by the EPA as a fuel additive by five companies. [EPA1]

C. **CHANGES REQUIRED IN LDV**

Alcohol sensor monitors to determine fuel mixture, adjust fuel flow rate and spark timing may be required in FFV with ethanol/methanol/gasoline. The cost of the sensor is unclear, and it depends on volume (to spread the development costs). Sensors from $20-$100 have been proposed. The use of microwaves sensing has potential, but has yet to be commercialized [Sappok] Additional costs in a methanol vehicle are due to stainless steel fuel system, larger fuel tank, wear-resistant piston rings, exhaust valve seat insert, with an incremental cost of $50-150. The costs increments for a light duty vehicle are shown in Table 13. It is assumed that large scale production of sensors will drop the price of the sensor. It is also assumed that present or near present catalysts are adequate, as they have determined to be adequate for emission control. [Brusstar, Fan]

Table 13. Cost increment to OEM for methanol-compatible vehicles (adapted from Sheehy)

Component	Total
Fuel sensor	$20
Fuel System Materials	$50
Fuel Pump/larger tank	$120
Catalyst	--
Evaporative System	$20
Total Estimated costs	**$210**

It is estimated that the cost increment for an ethanol FFV is about $100. Part of the reduced incremental costs for ethanol FFV's is that the industry has selected materials that are compatible with ethanol that are no more expensive than previous gasoline-only compatible materials. It seems that in the case of methanol, methanol-compatible materials may be more expensive, resulting in the small incremental cost described in Table 13.

D. **DISTRIBUTION**

Most of the methanol consumed in the US is produced overseas. It is brought to the US in ocean faring vessels. Once on land, it is transported by barge, railroad or truck tanker, depending on the distance and volume [Stark]. The cost of shipping is the same for all liquid fuels (on a volumetric basis) [Short]

The most economical method for delivery of methanol over land is through pipeline. Various petroleum refined products can be subject to co-mingling with methanol during shipment in a multi-product pipeline. Transmix occurs at the beginning and end of a product shipment since it is shipped in sequence with other products in order to keep the pipeline full and flowing. Handling the transmix that contains methanols presents difficult logistics. If the commingling is with gasoline, it is possible to use the transmix for blending with methanol at the distribution sites, after the methanol has been removed from the pipeline. If the methanol is wrapped with diesel, home heating oil, biodiesel or aviation fuel, it is necessary to process the mixture and restore it to methanol and other specific products. In the U.S., only a very small amount of methanol is presently sent through pipelines, and only over very short distances [Pipeline, Bechtold] In addition, the methanol will mobilize any existing water accumulated at the low points of the pipeline and petroleum residues in the pipeline, further degrading the quality of the interface volume.

One technique to minimize the transmix volume is by the use of a "pig," which could be used to make a physical barrier separating the methanol and the hydrocarbons in the pipeline. Pigs are not used frequently in pipelines, as they travel in the pipeline only in one direction and have to be sent back. The use of pigs does not solve the water uptake and deposit removal problem. 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 and storage tanks require further R&D.

Pipeline operators are reluctant to ship methanol in the established petro-fuel infrastructure. However, after taking necessary precautions Celanese Canada successfully moved 4000 tons of methanol (1.3 million gallons) 750 miles from Edmonton to Vancouver the mid 1980s [Mills]. This shipment was deemed to be very successful with only minor changes in the shipments composition.

E. **INFRASTRUCTURE**

Storage of liquid fuels (including methanol) at service stations is preferably done with underground tanks. As an underground tank costs ~ $50,000, in the California program undergrounds tanks were subsidized. The small traffic from the limited number of methanol vehicles does not generate sufficient revenue to pay for the pump installation costs without the subsidy.

Underground methanol tanks need to be properly grounded (because of the low electrical conductivity of methanol), and should provide moisture barriers, including flame arresters. A variety of methanol-compatible tank materials exist (stainless steel, carbon steel or methanol-compatible fiberglass). In the US, underground methanol tanks need secondary containment because methanol is classified as a hazardous chemical. Secondary containment can include double-walled tanks, tanks in a concrete vault (CONVAULT) or synthetic liners impermeable to methanol).

Conversion of gasoline or diesel tanks to methanol requires thorough cleansing, maybe with the addition of a liner that is methanol compatible. The submerged pump, the hose and the nozzle need to be made from materials that are methanol compatible. Aggressive filtering is recommended in order to prevent introduction of foreign matter into the vehicles, 3 μm filtration for methanol gasoline blends, as opposed to conventional gasoline for which 10 μm filtration is adequate. [Bechtold2]

Nozzles designed for methanol are available, but a better solution is the "drybreak" or "spill-free" nozzle. The spill-free nozzle have been developed [EAE] by the Methanol Fuel Cell Alliance, an industry consortium led by BASF, BP, DaimlerChrysler, Methanex, Statoil, and Ballard [CFCP]. 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.

Market segments opportunities

The cost of providing high blends of methanol in a 1/4 of the US gas stations (~ 180,000) at $50,000 per station, would be about 2.5 billion dollars. Even if the process is subsidized, the station operators may be unwilling to install them, as the traffic would be small, especially during

the introduction phase. Fuel retailers get ~ 2 cents per gallon margins for conventional hydrocarbon fuels. With methanol, higher margins per gallon would be required to provide an incentive to invest in the infrastructure, or the tanks need to be subsidized (as has been the case with some E85 stations). The Open Fuel Standard Act, if passed, would create a fast-growing fleet of alcohol compatible vehicles.
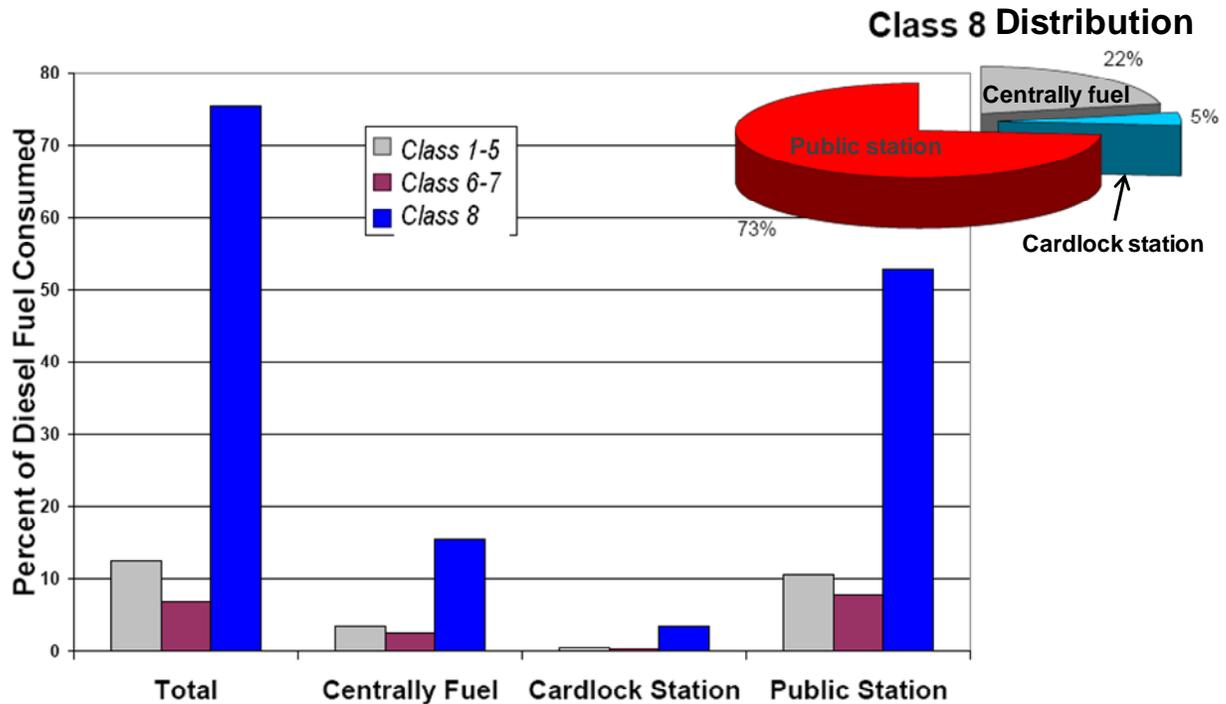

Figure 13. Percentage of diesel consumed by class and by refilling method

A very attractive alternative market for methanol has been identified: the heavy duty long haul and the centrally refueled HD vehicles [Bromberg3]. The fuel consumption breakdown for different class of heavy duty vehicles in the US is shown in Figure 13. [Jackson] Class 8 vehicles, which are used mainly for long haul, consume about 75% of diesel fuel in the US, and are mainly refueled in public stations (truck stops).

There are other markets where diesel replacement can have substantial effect, such as in centrally fuelled fleets, such as buses and vocational trucks that operate on urban environments. The fraction of the diesel fuel consumed by these vehicles is about 15%.

The US diesel fuel consumption in 2005 by long-haul class-8 trucks was about 25 billion gallons. For buses, the consumption was slightly over 1 billion gallons. Other trucks, with 6-liter

engines and larger, consumed about 9 billion gallons. The total diesel fuel consumption for US heavy duty vehicles in 2005 was around 35 billion gallons [AER06]

For heavy duty vehicles in 2005, centrally fueled vehicles consumed about 20% of the diesel fuel, cardlock station about 5% and public stations (mostly truck stops) about 75%.

In contrast, about 55% of the diesel fuel is consumed by heavy duty vehicles that refill at more than 5000 truck stops in the US. Although this is a large number, it is only about 2.5 times the number of present (2010) E85 stations in the US. The average diesel provided by these stations is about 200,000 gallons per month although it varies from a low about 10,000 gallons/month to about 1,000,000 gallons per month. Providing methanol refueling at all of these truck stops would cost about $250 million, one order of magnitude less than providing an adequate infrastructure for light duty vehicle. Furthermore, it is likely that the volumes sold would be substantially higher that in an infrastructure for LDV, even if a relatively small fraction of the trucks use it.

For the centrally fleet fueling, there are around 25,000 stations for heavy duty trucks. Although it should not necessarily be difficult to provide alcohol fuel distribution systems for centrally fueled fleets, the large number of stations implies a substantial cost for developing limited infrastructure, mostly to be borne by the fleet operators. The fuel use in these refueling stations is about 25,000 gallons per month per station, and it is necessary to provide for tanker-delivery of the methanol. If there is a 0.1 $/gallon price differential between methanol and diesel (on an equivalent energy basis), the payback time for the development of the infrastructure is 20 months (assuming an underground tank) About 16% of all on-road diesel is consumed by vehicles that are refilled at central fueling stations.

The present small distribution system for E85 is not particularly relevant to Heavy Duty long haul applications, as the stations are usually out of the way from the main freight routes.

F. **JOBS**

It is difficult to estimate the impact of the "methanol economy" on the labor market.

There are substantial jobs in the installation/construction of the plants. From Phillips and Dutta it is possible to determine that the cost of installation (mostly labor) is 40% more than the cost of the equipment and about half the total cost of the plant. Thus even if most of the components were purchased overseas, a substantial fraction of the costs of the plants would have a substantial

impact in the local labor market, although short-lasting during the construction phase. [Phillips, Dutta]

For the methanol manufacturing plants, it is estimated that there are 50 jobs per biomass-to-methanol plants [Phillips, Dutta]. The number of jobs in present-day megaplants is higher, about 120 jobs per plant. [Methanex] Thus, to displace 10% of the liquid fuels, between 5,000-10,000 highly-skilled jobs are created.

It is more difficult to estimate the number of indirect jobs created in the community. The job multiplier is between 5.3 (estimated for ethanol plant [Swenson]) to 9 for methanol plants [Dolan]. Thus, the number of jobs created in the community for 10% of the liquid fuel displacement is 25,000-90,000.

In addition, there are jobs for the collection and transport of the biomass. It is estimated that for every megawatt of power, there are 4 jobs created. [Perlack] For satisfying the biomass requirement for these plants, over 300,000 jobs would be created. At this scale, increases in productivity would decrease substantially the number of jobs and the cost of biomass (as highlighted in Table 6). As with ethanol job creation, these are rural jobs.

G. CONSUMER PERCEPTION

In California, there is erosion in support of methanol as a fuel, due to the negative impact of the use of methanol-derived MTBE as an oxygenate.

It is interesting to note that consumers are aware that alcohols are used in present windshield washer fluids. But most consumers do not know the difference between methanol and ethanol; for them, both are alcohols, and equivalent.

H. RESEARCH NEEDS:

Some of the pressing research needs for advancing methanol are:

- Perform study to quantify the benefits (economic, environmental, petroleum displacement) of using methanol and methanol blends in light and heavy duty applications.

- Develop and demonstrate FFV's that can operate with a wide range of liquid fuels (ethanol, methanol and gasoline) to fulfill the goals of the Open Fuel Standard.

- Develop and demonstrate high efficiency methanol engines for heavy duty applications.

- Continue to develop biomass-to-methanol processes to decrease the costs and improve the carbon efficiency.

- Compare pathways for near term energy independence/security

I. **METHANOL AS TRANSPORTATION FUEL IN THE US**

Methanol has attractive features of use in transportation:

- It is a liquid fuel which can be blended with gasoline and ethanol and can be used with today's vehicle technology at minimal incremental cost. THERE ARE NO TECHNICAL HURDLES.

- It is a high octane and safe fuel, and has combustion characteristics that allow engines to match the best efficiencies of diesels while meeting current pollutant emission regulations, although it has the drawback of reduced energy density.

- There is a very large potential supply of methanol since it can be made from natural gas, coal and biomass feedstocks

- It is currently produced from natural gas and coal at costs that are comparable to or less than gasoline and diesel fuel on an energy basis

- It is an attractive green house gas reduction option in the longer term, if produced from renewables/biomass. A bridging option is to use methanol derived from natural gas, with a CO_2 intensity that is no worse than conventional fuels. There is also the possibility of achieving greenhouse gas reduction by CO_2 sequestration in the methanol generation process.

- Multiple ways exist for introduction of methanol into the infrastructure (light blends or heavy blends) and into the vehicles (light duty or heavy duty applications). The optimal approaches are different in different countries and in different markets.

To be accepted as a transportation fuel, producers must price methanol at the pump to be competitive on an energy basis with gasoline or diesel. This price includes the bundled costs of production, distribution, fueling stations, taxes and engine efficiency. The 12-month U.S. average

pump price for gasoline and diesel are about $2.62 and $2.70 per gallon respectively (July 2010). To compete with gasoline and diesel on an energy equivalent basis, methanol would require a (maximum) pump price including taxes of $1.30 and $1.20 per gallon as a neat fuel (M100) respectively. The prices of methanol have been competitive with gasoline during the last decade. However prices of methanol have larger fluctuations than gasoline/diesel prices (at least in the last few years), due to spikes in the cost of natural gas.

An effective means to introduce methanol into the market place, is through a fleets, as employed in pilot programs in California. In order for the fleet approach to be attractive, vehicles cost become a significant factor, as fleet operators tend to buy the least expensive vehicles. Apart from the challenges of pricing the fuel, a sustainable market for methanol in a high level blend strategy will require the simultaneous and geographically matched deployment of infrastructure and vehicles, along with long-term plans for capturing fuel retail station owner interest. Because of the lower cost of methanol than other alternative liquid fuels and the smaller scale infrastructure changes requirements (either for local or long haul), the introduction of methanol fueled vehicles in the heavy duty market, where fuel cost is a predominant consideration, is particularly attractive.

In light-duty applications, methanol can also be used as M85 (85 percent methanol and 15 percent gasoline). In this case, M85 would need to be priced around $1.50 at the pump to compete with gasoline. Because of its higher octane, M85 would compete with premium gasoline.

Methanol in the reformulated gasoline markets would more likely displace ethanol than gasoline. Ethanol is currently blended into unleaded gasoline up to 10% by volume. The driver for ethanol use as an additive to gasoline is the Renewable Fuel Standard, as the excise tax credit for blenders is likely to expire at the end of 2010 (although there are efforts in Congress to extend it).

At the present time, there is limited production of methanol in the US but it can be increased rapidly if desired, in the near term from either natural gas or coal, and eventually from biomass. Ample reserves of fossil fuels and biomass exist in the US, and there is potential for meeting a substantial fraction of the liquid fuel demand by bio-methanol. There is a potential for methanol manufacturing from CO_2 already in the atmosphere or about to be discharged to the atmosphere.

The costs of deploying manufacturing facilities for producing 10% of the liquid fuel used in transportation in the US is 50-100 billion dollars which, although a large number, is addressing an

enormous problem. Further work is needed for a detailed comparison between methanol and the other alternative fuels, including those that provide energy security but not sustainability.

The "methanol economy" in the US has the potential to substantially decrease energy dependence, providing energy security using domestic feedstocks and labor, with substantially lower footprint to the environment (GHG), with a product that seems competitive in the present markets. However, substantial obstacles exist (lack of vehicle/infrastructure/manufacturing) which can be overcome with market incentives. In the US there is not enough biomass to displace all of the transportation fuels with methanol.

Methanol can be used directly in fuel cells. Although this technology is making inroads in electronics, with low power requirements, the technology is still too early in its development, unlikely to achieve significant commercialization in the transportation sector within the next 2 decades.

A full comparison between the different options has to be done, reflecting the present conditions. Although an attractive fuel, methanol is not a silver bullet that is better than the alternatives in all categories, and it is likely that a combination of the proposed solutions (including ethanol/methanol/gasoline mixtures and NG) is better suited to solve the massive transportation problem. The preferred solution may depend on the region, the market sector and other externalities, including past and present policies.

XI.   CLOSURE

- Methanol is a safe and viable transportation fuel, although it is not as good a fuel as ethanol in terms of energy density and ease of handling. While significant investment needs to be made for large-scale methanol deployment in the transportation sector, there is no technical hurdle both in terms of vehicle application and of distribution infrastructure.

- As a long term strategy to substantially replace petroleum fuel by renewable, methanol offers the following advantage

  - ➤ Thermo-chemical production of methanol from biomass is energetically efficient and the technology has been well developed.

  - ➤ In comparison, large-scale bio-chemical production of ethanol from cellulosic biomass is promising, but currently the technology is not sufficiently developed.

- Methanol from non-renewable could be used as a bridging option towards transition towards renewable methanol. Methanol can readily be made from natural gas or coal (there is plentiful supply of both feedstocks) so that large-scale production, infrastructure, and vehicle use could be developed. The system that is developed can then be applied to renewable methanol. It should be further noted that such system is also amenable to the use of renewable ethanol, should large scale bio-production of cellulosic ethanol be realized in the future.

- Non-crop based biomass derived fuels have the potential to supply a major part of the US transportation liquid fuel; this is especially so if substantial decrease of energy use in transportation is achieved. Renewable methanol from thermo-chemical biomass conversion is an attractive and viable future fuel option.

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