

Methanol Fuel Safety – Practical Guide

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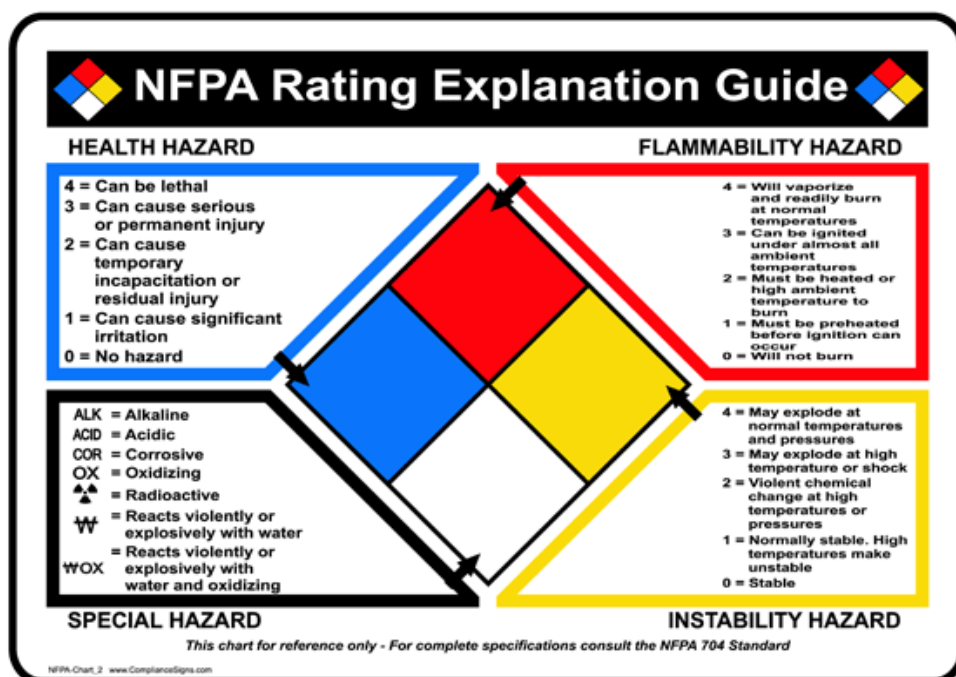
This guide was written initially for the students at Cal Poly engaged in the conversion of IC engines to methanol fuel, especially my students working on methanol projects in my course “Automotive Technologies for a Sustainable Future”. It may be of interest to anyone considering the conversion or operation of an engine on methanol, or to those that handle methanol for other purposes. Most precautions and conclusions are equally applicable to E85 fuel.

In General

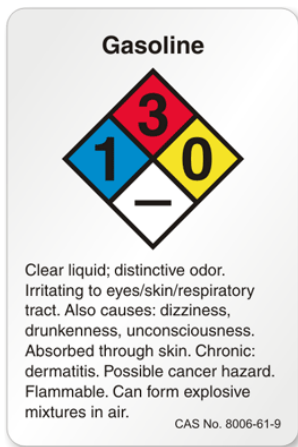
Methanol (methyl alcohol) is a hazardous material, in the same flammability, toxicity and reactivity hazard classes as gasoline. Since every automobile driver is familiar with the handling of gasoline fuel, a realistically discussion of the potential hazards of methanol fuel might best be accomplished by relating it to the comparable hazards associated with gasoline for which there exists a vast amount of experience, accident data and pragmatic lessons learned.

OSHA, NIOSH, NFPA, US DOT, and the US CDC rate hazardous substances and require placard labeling to identify to first responders the risks of health hazards, flammability, reactivity (instability), and ‘other’ or ‘special’ risks. A comprehensive NFPA (National Fire Protection Association) reference for all hazardous liquids and gases can be found at:

http://www.nmsu.edu/safety/programs/chem_safety/NFPA-ratingJ-R.htm . The required placards (diamond) for gasoline or methanol are shown below, preceded by the “NFPA Explanation Guide”, from http://www.compliancesigns.com/media//ZOOM/NFPA-Chart_2_600.gif



Gasoline, from http://cdn.compliancesigns.com/media/NFPA/NFPA-Gasoline-Signs-NFPA_PRINTED_1300_300.gif



Methanol, from http://www.cdc.gov/niosh/ershdb/EmergencyResponseCard_29750029.html



Here's an online MSDS (Material Safety Data Sheet) for methanol:

http://www.midi-inc.com/pdf/MSDS_Methanol.pdf

A comprehensive web site describing emergency response procedures for methanol accidents can be found at www.methanol.org/Health-And.../Methanol-Emergency-Response.aspx

What follows is a relative assessment of the safety issues associated with methanol compared with gasoline, based upon the chemical properties and selected case histories for each fuel:

Flammability Risk (the top or red quadrant of the hazard placard):

1. Gasoline contains more than twice the energy per unit mass or per unit volume compared with gasoline:

Gasoline: 41.2 – 41.9 MJ/kg (depends on summer vs winter, and regional blending)

Methanol: 19.7 MJ/kg

This means that a given quantity of methanol releases less than half the heat energy of the equivalent quantity of gasoline.

2. The range of flammability *A/F limits for methanol are about the same* as gasoline, with methanol requiring a much richer mixture before it will ignite. Measured as a *volume* percentage of fully vaporized fuel in air from http://www.engineeringtoolbox.com/explosive-concentration-limits-d_423.html :

Gasoline: 1.4% to 7.6% ratio: 5.43:1

Methanol: 6.7% to 36% ratio: 5.37:1

This means that significantly more methanol vapor must be present in air before ignition can occur, but that methanol combustion will occur with much richer mixtures of methanol. However, gasoline vapor at typical temperatures in a fuel tank is so rich that it is non-flammable, while methanol vapor under the same conditions could be.

3. The volatility (an indicator of the flammable vapor concentration at a given temperature and pressure) for methanol is much less than gasoline. A good indicator of volatility is the specific heat of vaporization – the energy required to vaporize a given mass of a liquid. From the SAE Automotive Handbook, 7th ed., by Robert Bosch, 2007:

Methanol: 1,110 kJ/kg

Gasoline: 380 – 500 kJ/kg

Combined with the higher minimum ignition A/F limit, this means that vapor ignition a given distance from exposed liquid fuel (such as a storage tank vent) is much less probable for methanol than for gasoline.

4. Risk of spontaneous combustion. Like any volatile solvent, there is a risk of spontaneously combustion, possibly long after you have left the area. On a relative scale, however, methanol is no more prone to spontaneous combustion than gasoline, and less prone than oils such as diesel fuel or (most notoriously) linseed oil used in many wood stain products.

If you have rags soaked in methanol, do not leave them in a pile, box or regular trash can. Dispose of them in an approved sealed metal "solvent rag storage can" until they can be taken to a hazardous material disposal service.

However, methanol, because it evaporates completely, allows an option for reuse/recycling of rags *if it is the only chemical soaked into the rag material*. This is from my personal experience alone, not approved practice: Leave them overnight outdoors on a concrete surface in a protected area (inaccessible to dogs, children or smokers), far from anything that could catch fire if they should for some reason ignite. After a night outdoors (or as little as a few minutes in sunshine), the methanol will evaporate completely, allowing you to reuse them.

In brief, methanol is not high-risk for spontaneous combustion, but take the same precautions that you would for gasoline anyway.

5. Methanol combustion emits almost no light, and creates no smoke. Methanol burns in air so cleanly that it emits almost no visible light compared with all conventional hydrocarbon fuels. Its lack of a carbon-carbon bond is primarily responsible for the complete lack of soot or particulate emissions from methanol combustion. By comparison, gasoline combustion in air is brightly luminescent, generates much infrared radiation, and creates heavy visible smoke, especially in oxygen-depleted situations such as large burning gas spills

In the absence of contaminants (such as gasoline in M85), it may be difficult to observe visually a methanol fire – no light, no smoke and very little infrared radiation. This can be a potential hazard for first responders in a methanol fire incident, as will be illustrated in the next section.

However, it should be mentioned that in most methanol fire situations, other contaminants are present, such as lube oil, paint, combustible fabric, or the asphalt on which the methanol may have spilled. These contaminants impart some visibility to the flame, and generate some smoke.

6. Methanol is soluble in water. The water solubility of methanol allows methanol fires to be extinguished by conventional firefighting equipment via water dilution. By comparison, gasoline is not soluble in water, and being less dense than water, will float on the surface of water, continuing to burn unaffected by the volume of water. Training manuals in military aviation emphasize the importance of a survivor of a water crash getting as far away as possible from a burning aircraft, since the aviation fuel (gasoline or jet fuel) will form a burning layer on the surface of water.
7. Methanol safety experience is heavily extrapolated from auto racing. Gasoline is widely considered by professional racers to be more hazardous than methanol. In some venues, gasoline is not allowed for safety reasons – only methanol or ethanol. For example, from http://en.wikipedia.org/wiki/Methanol_fuel :

“A seven-car crash on the second lap of the 1964 Indianapolis 500 resulted in USAC's decision to encourage, and later mandate, the use of methanol. Eddie Sachs and Dave MacDonald died in the crash when their gasoline-fueled cars exploded. The gasoline-triggered fire created a dangerous cloud of thick black smoke that completely blocked the view of the track for oncoming cars. Johnny Rutherford, one of the other drivers involved, drove a methanol-fueled car, which also leaked following the crash. While this car burned from the impact of the first fireball, it formed a much smaller inferno than the gasoline cars, and one that burned invisibly. That testimony, and pressure from Indianapolis Star writer George Moore, led to the switch to alcohol fuel 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.

In 2006, in partnership with the ethanol industry, the IRL used a mixture of 10% ethanol and 90% methanol as its fuel. Starting in 2007, the IRL switched to "pure" ethanol, E100."

However, in the same racing venue that outlawed gasoline due to its extreme fire hazard, a methanol fire occurred following a collision in 1981 in which the invisibility of methanol combustion played a major part in a confused response by the pit crew: From:

http://en.wikipedia.org/wiki/1981_Indianapolis_500

"When Rick Mears pitted on lap 58, fuel began to gush from the refueling hose before it had been connected to the car. Fuel sprayed over the car, Mears and his mechanics, then ignited when it contacted the engine. Methanol burns with a transparent flame and no smoke, and panic gripped the pit as crew members and spectators fled from the invisible fire. Mears, on fire from the waist up, jumped out of his car and ran to the pit wall, where a safety worker, not seeing the fire, tried to remove Mears' helmet. Meanwhile, Mears' fueller, covered in burning fuel, waved his arms frantically to attract the attention of the fire crews already converging on the scene. By this time the safety worker attending to Mears had fled, and Mears, in near panic at being unable to breathe, leaped over the pit wall toward another crewman carrying a fire extinguisher, who dropped the extinguisher and also fled. Mears tried to turn the extinguisher on himself, but at this point his father, Bill Mears, having already pulled Rick's wife Deena to safety, grabbed the extinguisher and put out the fire. His mechanics had also been extinguished, and the pit fire crew arrived to thoroughly douse Mears' car.

Thanks to quick action by safety workers and the fact that methanol burns at a much lower temperature than gasoline, no one was seriously hurt in the incident."

Unreported by the author of the above article was the fact that the driver wore a fire-proof Nomex driving suit. While this definitely helped to limit his burn injuries, the non-flammable suit imparted no luminescence to the burning methanol. The vehicle itself, and conventional clothing soaked in methanol will yield some luminescence and smoke as they burn.

8. In general, methanol may be considered less of a fire hazard and less consequential in the event of a fire compared with gasoline. The previous reference http://en.wikipedia.org/wiki/Methanol_fuel concludes:

"Methanol is far more difficult to ignite than gasoline and burns about 60% slower. A methanol fire releases energy at around 20% of the rate of a gasoline fire, resulting in a much cooler flame. This results in a much less dangerous fire that is easier to contain with proper protocols. Unlike gasoline, water is acceptable and even preferred as a fire suppressant, since this both cools the fire and rapidly dilutes the fuel below the

concentration where it will maintain self-flammability. These facts mean that, as a vehicle fuel, methanol has great safety advantages over gasoline.”

As matter of practice, exercise the same cautionary measures when handling methanol that you would with gasoline. Don't have ANY ignition source nearby when handling methanol or any fuel, e.g., a torch, cigarette, source of electrical sparks, heat-shrink gun, even a hot soldering iron. If there is a methanol fire, a ***dry chemical fire extinguisher is preferred*** over a CO2 extinguisher. Or just plain water is effective as long as there is not also gasoline, diesel fuel or engine lube oil involved in the combustion. Methanol burns so cleaning that you can accidentally walk right into the flames. Watch for the heat waves in the air rather than visible flame. Have a safety person standing by when you are starting an engine for the first time, or in an experimental configuration. Use common sense.

Health Hazard or Toxicity Risk (the left or blue quadrant of the hazard placard):

Methanol is highly toxic if ingested, inhaled as a vapor or if in contact with your skin for an extended period of time. Much has been said and written to emphasize this risk, but it is rarely put into perspective with other common toxins. Again, I will compare the health hazard effects of methanol with a well-known and understood fuel, gasoline.

9. Ingestion: Methanol is potent neurotoxin. Methanol toxicity is more insidious than you would normally expect, e.g., blindness comes in a few days. 2 to 8 ounces can be deadly for an adult. History records countless cases of accidental or homicidal ingestion of methanol in blends with ethanol. These represent the overwhelming majority of methanol toxicity cases. I could not find any recorded cases of poisoning from *methanol fuel* during refueling or handling. Gasoline is also toxic, and in similar concentrations, although the physiological mechanisms are different. Aside from the direct toxicity of gasoline, it is also a known carcinogen, unlike methanol. That means it may kill you years later from cancer. But the accidental or homicidal presence of gasoline in an ingested beverage is easy to detect due to the insolubility of gasoline in water, and the greater volatility of gasoline which provides an easily recognizable odor. By contrast, lethal levels of methanol can be added to ethanol beverages undetected. Among the many tragic examples are mass poisonings of drinkers of alcoholic beverages by unscrupulous beverage producers, distributors or vendors, since methanol is much less expensive than taxed beverage ethanol. For example, in 2003, <http://www.ncbi.nlm.nih.gov/pubmed/17849250>

From: Vale A (2007). "Methanol". *Medicine* **35** (12): 633–4. and other credible root sources reported in <http://en.wikipedia.org/wiki/Methanol#Toxicity> :

“Methanol has a high toxicity in humans. If as little as 10 mL of pure methanol is ingested, for example, it can break down into formic acid, which can cause permanent blindness by destruction of the optic nerve, and 30 mL is potentially fatal, although the median lethal dose is typically 100 mL (4 fl oz) (i.e. 1–2 mL/kg body weight of pure

methanol). Reference dose for methanol is 0,5 mg/kg/day. Toxic effects take hours to start, and effective antidotes can often prevent permanent damage. Because of its similarities in both appearance and odor to ethanol (the alcohol in beverages), it is difficult to differentiate between the two (such is also the case with denatured alcohol).

In summary, DON'T DRINK methanol in ANY quantity. Don't ever siphon methanol or any fuel by mouth (unlike the author at an alternative fuel vehicle competition in 1981, requiring the 'ethanol treatment'). Other than that, there's pretty much no way to accidentally ingest methanol unless you confuse it with ethanol. If you accidentally ingest even a small amount of methanol, call a poison control center immediately, and follow their advice, which will differ depending on the expected concentration and time since ingestion.

The National Poison Control Center number is: 1-800-222-1222.

They will probably recommend one of two remedial actions, based upon the quantity ingested and the time since ingestion:

First, do not induce vomiting. If you think straight vodka burns your mouth and esophagus, methanol is worse and can do damage going up as well as going down.

- a. From: <http://emedicine.medscape.com/article/1174890-treatment>
"Like methanol, ethanol is metabolized by ADH, but the enzyme's affinity for ethanol is 10-20 times higher than it is for methanol." What this means is that for small to moderate risks of methanol poisoning, the appropriate treatment is to ingest a quantity of ethanol – e.g., a complete 1L bottle of 100 proof vodka. This is not a joke. There are, of course, the obvious hazards associated with ingesting such a large amount of ethanol. For a more rigorous protocol and description of symptoms to distinguish moderate from severe methanol poisoning, see <http://www.ncbi.nlm.nih.gov/pmc/articles/PMC1306022/>
- b. For suspected higher concentrations of ingested methanol, Fomepizole (commercial name Antizol) is the last resort. <http://www.ncbi.nlm.nih.gov/pubmed/12522524> It is very expensive and may not be available in some emergency rooms or urgent care centers.

If ingestion is suspected, seek help immediately, *even though you do not feel any immediate symptoms*. This is because by the time that visible symptoms occur, sufficient neurological damage may already have occurred.

If it matters, methanol blended with ethanol is slightly less toxic than pure methanol because of the above properties of ethanol. But it is still lethal in small quantities. M85, a methanol blend with gasoline, was used extensively as a government-sanctioned alternative fuel from 1990-2000 during the AFUP (Alternative Fuel Utilization program). Well-publicized concerns about M85 toxicity abounded prior to and during the AFUP. Some, although true, were politically motivated. I cannot find any recorded incidents of ingestion toxicity from M85 during this period, even though the 15% addition of gasoline in methanol probably creates an even more toxic liquid than neat methanol.

10. Inhalation: Like most fuels, methanol vapors can be absorbed through the lungs, with the potential for toxicity.

OSHA standards for maximum allowed continuous exposure to methanol vapor in air (40 hours/week) is 900 mg/m³ for gasoline, and 1260 mg/m³ for methanol. This suggests a slightly lower risk when handling methanol fuel compared with handling gasoline. However, it is much less volatile than gasoline, and therefore has lower evaporative emissions, producing a significantly lower risk of exposure risk during vehicle refueling and in the event of a minor spill.

Gasoline has such a characteristic odor that the presence of gasoline vapor in air, even at low concentrations, serves as a very effective warning – at least initially since sensitivity to a particular odor diminishes rapidly with continuous exposure. And while methanol does have a characteristic pungent odor, it is considerably less aromatic than the easily-vaporized components of gasoline, reducing this advanced warning advantage compared with gasoline. . At concentrations greater than 2,000 ppm (0.2%), methanol vapor is generally quite noticeable, however lower concentrations may remain undetected while still being potentially toxic over longer exposures.

What about the exhaust emissions of methanol fueled engines? With respect to all EPA or CARB-regulated emissions, methanol burned at stoichiometric A/F ratios (aspirated correctly) is overall a cleaner fuel than gasoline, even in engines not optimized for methanol. Some early examples of this ‘clean air’ advantage came from work in the 1980’s, e.g., <https://courseware.ee.calpoly.edu/~amaccarl/H2&MethanolPublications/DOE%201981%20-%20Development%20of%20a%20Dual%20Fuel%20Alcohol-Gasoline%20Vehicle%20Using%20Electronic%20Fuel%20Injection.pdf> . In general, CO, HC, NMOG and VOC emissions are consistently lower, while NO_x is similar or slightly higher than gasoline. Methanol eliminates the emission of aromatic carcinogens found in gasoline such as benzene and 1,3 butadiene. However, during cold starting, when overly rich fuel-air mixtures are used, methanol engines produce aldehyde vapors, notably formaldehyde, unlike gasoline engines. The highly irritating exhaust of a methanol-fueled race car is primarily due to this emission, caused by the grossly over-rich A/F ratios used in competition. Catalyst efficiency for methanol combustion is similar to gasoline. Evaporative emissions from methanol fuel systems are lower than gasoline, due to the much lower volatility. Extensive experience during the AFUP 1990-2000 confirmed these observations, with the 15% gasoline component in M85 believed to be responsible for the majority of the regulated exhaust emissions. (Ref: Alternative Fuels Utilization Program Quarterly Report, Fourth Quarter FY 1996, US Dept of Energy Contract DE-AC36-36CH10093, National Renewable Energy Laboratory, Golden Colorado, 1996). In terms of greenhouse gases, the combustion of methanol produces 12% more CO₂ than gasoline for the same quantity of usable energy (same number of miles traveled). For supporting calculations please see http://www.loragen.com/AltFuels/students/EE470_Lecture/Lecture%20Notes/10a%20Efficiency%20and%20Power%20Output.pdf

In sum, inhalation safety protocols are nearly identical between methanol and gasoline. When normally refueling a methanol vehicle, there is no need to wear a respirator. Just observe common sense to avoid breathing fuel vapor. If potential overexposure should occur, follow the same remedial process as described for ingestion above. When operating an engine on methanol, make sure the area is well-ventilated, especially if the engine is running rich like during cold start. You'll know immediately - that's when it may generate aldehydes, which are really irritating to the eyes, so much so that it's hard to reach the TLV (Threshold level value) for airborne toxicity.

11. Skin contact: Methanol, like gasoline, can be absorbed through the skin, and this is a particularly common vector for low-level methanol toxicity.

When handling methanol, like any liquid fuel, you are likely to get it on your skin. If a small area remains in contact with the skin for under about 30 seconds, there should be no toxicity effects. If a larger area or exposure time is involved, the potential for toxicity exists, up to the point of concentrations approaching those of oral ingestion. Direct methanol or gasoline contact with an open wound could pose a significant health hazard. These are reasons to seek medical assistance. Methanol, like gasoline, is also a powerful solvent that even in very small quantities will strip all the natural oils from your skin, leaving it irritated and dry.

In practice, if a small amount gets on your skin during refueling or work on a methanol fuel system, just wipe it off with a rag quickly and wash the skin soon after. If working on the fuel system and anticipating the possibility of fuel contact with your skin, take the precaution of wearing nitrile rubber mechanics gloves. If you get it on your clothes, remove the article and give it a few minutes for the alcohol to fully evaporate. Unlike gasoline, it will evaporate completely, and the only possible residue will be the lubricity additive (if added to the fuel) such as castor oil or other polar lubricant, probably not contact-toxic. Methanol will not damage any natural fibers. Wear a shop coat if possible.

Wear eye protection – methanol in the eyes is *always* a cause for immediate concern – get to an eye-wash station or lavatory quickly and continuously flush the eye for at least a full minute. Seek medical attention if the eye exposure was more than trivial. Formal treatment advice from the CDC (Center for Disease Control) can be found at:
http://www.cdc.gov/niosh/ersbdb/EmergencyResponseCard_29750029.html

Treat methanol like gasoline and you'll generally be safe.

Reactivity (or Stability) Risk (the right or yellow quadrant of the hazard placard):

12. Methanol is given a rating of zero for reactivity, since it is not prone under any conditions to explosion in the absence of air, or violent chemical change. No special concerns for methanol. Gasoline has the same rating.

Environmental Risk

Methanol, like gasoline, is toxic to most biological organisms (exceptions are some natural and several bioengineered microorganism's capable of metabolizing or even thriving on methanol). It can be used as a disinfectant, although this is rare in deference to isopropyl alcohol or other germicides. If released accidentally into the environment, methanol biodegrades rapidly and causes dramatically less long-term groundwater pollution. A methanol spill is therefore considered much less egregious than a gasoline spill of equivalent volume or energy content. The fact that it is infinitely soluble in water is also a big plus for methanol compared with gasoline, since it can be easily diluted below the level at which it could cause direct environmental harm. There have been few reported cases of significant methanol spills on land or sea. One example (60% methanol) is http://www.huffingtonpost.com/2011/07/18/bp-spill-pipeline-alaska_n_901601.html.

By comparison, gasoline released into the environment can cause serious harm. Gasoline or the crude oil from which it is made floats on the surface or water, with the spreading slick requiring major and rapid intervention to reduce the wide range of environmental consequences. Cases and related studies of environmental impacts abound, for example <http://www.cnn.com/2010/US/05/03/oil.spill.environmental.impact/index.html> .

Overall Risk Conclusions

Based upon the discussion above, and over 30 years experience handling methanol as a vehicle fuel on a nearly daily basis, I conclude that overall, methanol is a safer fuel than gasoline. But this is a relative assessment - gasoline itself is a highly hazardous substance. So is this comparison fair as an absolute assessment of the safety of methanol fuel?

In 2011, US automobile drivers purchased an average of 367 million gallons of gasoline each day (<http://www.eia.gov/tools/faqs/faq.cfm?id=23&t=10>). Assuming an average fill volume of 12 gallons, that's 24.5 million fills per day at gas stations across the country, by people with little to no awareness of fuel safety, some even smoking or driving off with the fill hose still in the tank, tearing the hose from the gas pump. Yet the Petroleum Equipment Institute reports only 100 gas station accidents per year, most due to grossly improper or illegal dispensing of fuel. We have no such statistics for methanol; even the scant use of M85 in flex fuel vehicles during the AFUP years resulted in no reported accident data that I could access.

In perspective, I believe that widespread adoption (or re-adoption) of methanol as a motor fuel, either neat or in blends with gasoline, would not present a significant risk to the public. As an intermediary in the production of other fuels such as synthetic gasoline or dimethyl ether (DME), there would be even less concern since the public would not be involved in handling methanol. Intuition suggests that one area of legitimate concern is the increased availability of a potential poison that can be mixed undetectably with an alcoholic beverage (only for neat methanol, not M85). In experimental work with methanol fuel, I suggest common sense and mindfulness that you are working with a flammable and toxic liquid. Use the same precautions that you would use for handling gasoline and you will face a level of risk no worse than with gasoline.