

Alcohol Fuels (Ethanol and Methanol): Safety (Submitted by Harry Stokes, Project Gaia)

The CleanCook stove has been designed for safety. One of the reasons the Dometic stoves are safe is because they employ alcohol, not kerosene or a flammable gas, as their fuel. Alcohol fuels can be evaluated for their safety by considering the following issues: toxicity, flammability and fire hazard, environmental impacts and products of combustion or impact on air quality when burned, particularly in the close environment of the home.

Toxicity: When used as a domestic fuel, both ethanol and methanol, whether blended or separate, should be denatured with a colorant, an odorizing agent and a bittering (tasting) agent to clearly identify them and render them unpalatable for ingestion. The Dometic stoves are used in Europe and North America with fuel blends of ethanol and methanol that have been denatured for safety. A denaturing protocol has been developed by Dometic for use in denaturing ethanol and methanol. The denaturing agents help to color alcohol's clear blue flame to make it more visible in the daylight. This provides an additional safety measure.

Ethanol is used in the chemical, pharmaceutical and food industries, where long experience has shown that it is neither a serious hazard nor requires elaborate or unusual means to handle safely. As indicated above, it is a volatile compound, but it has a vapor pressure lower than most other liquid fuels. When straightforward ventilation practices are used, worker inhalation can be kept quite low. Moderate exposures to the vapors produce only temporary irritation of the eyes and respiratory tract. As airborne concentrations increase, the discomfort becomes intolerable well before a level that could cause suffocation or other dangerous effects. The threshold limit value (TLV) for prolonged exposure has been set at 1000 ppm by various U.S. and European regulatory agencies, while the corresponding TLVs for methanol, gasoline and kerosene are 200, 300 and ~20 ppm respectively. Five thousand to 10,000 ppm of ethanol in the atmosphere causes uncomfortable irritation, and eventual stupor or drowsiness. Intoxication, in the sense of drunkenness, from industrial inhalation is rare.¹

Methanol is toxic, but it is less toxic than the petroleum fuels. In 1991, the U.S. Department of Energy concluded gasoline to be more hazardous to human health than neat (pure) methanol.² Methanol poses no known cumulative health hazard and is not classified as carcinogenic, mutagenic or teratogenic. The petroleum fuels are a complex blend of chemicals that include, for example, benzene, a chemical that is considered to be extremely toxic and carcinogenic. The U.S. EPA's Office of Air Quality Planning and Standards has determined that methanol offers little threat of chronic toxicity and it gives methanol a composite score of 7 on a scale of 1-100 (100 being the most toxic). EPA has likewise concluded that momentary dermal contact with methanol is not of significant concern.³ Because methanol evaporates quickly and cleanly, it does not adhere to the skin or leave a residue on the skin.

¹ Kirk-Othmer Encyclopedia of Chemical Technology, Third Ed., 1980. Ethanol. Volume 9, p. 366.

² IdaTech "Tech Brief", January 2001. US DOE, October 1991. Technical Report No. 7.

³ US EPA Office of Pollution Prevention and Toxics, 1994. Chemical Summary for Methanol.

Flammability & Fire Hazard: There are several ways to compare and contrast the fire hazard of alcohol fuels—ethanol and methanol—versus the fire hazard of hydrocarbon fuels—kerosene, gasoline and diesel. First, the lower flammability (or explosion) limit (LFL) can be considered for each fuel. Accidental fires often occur because flammable vapor increases from a low level to the minimum concentration at which ignition will occur. The higher the value for the LFL, the less likely a fire will result. Thus, a high value for LFL is considered to be safer than a low LFL value. Ethanol has a LFL value of 3.3% in air at room temperature and methanol a value of 6.0%. These values are significantly greater than for kerosene at 1.7% and gasoline at 1.4%. Depending upon the nature or composition of the kerosene, its LFL can sometimes be lower—as low as 0.7%. The LFL of diesel is 0.6%. (Values are from Material Safety Data Sheets and Lange's Handbook of Chemistry—See **Table 3** below).

Consistent with these values for the LFL of alcohols and hydrocarbon fuels is the minimum temperature at which the lighter hydrocarbon fuels will ignite (flash point). The flash point of methanol is 11° C and that of ethanol is 14° C, while the flash point of gasoline is – 45° C, and that of benzene, – 11° C. The flash point for kerosene and for grades of jet fuel is a more complex matter. The flash point may range between 21° and 82° C.⁴ (The same situation exists for diesel fuel. Diesel fuel extended with light naphtha or light crude can reach flashpoints as low as 22° C, well below its normal prescribed range of 60° to 80° C.⁵)

Many developing nations buy aviation grade kerosene for their domestic kerosene market. Aviation kerosene fuels are complex mixtures, containing hundreds of species of chemicals in varying amounts, depending on the crude oil and the refinement process, among other factors. Typically Jet A will contain 18 to 20% aromatics including many lighter fractions. The vapor composition of kerosene fuel is different from that of the liquid and depends strongly on temperature and, to a lesser extent, on the amount of liquid fuel in the fuel tank. The explosion hazard of kerosene vapor will also depend in part on the ignition source.⁶ Kerosene is no longer the relatively safe household fuel that it was in the past.

Gasoline, kerosene and diesel vapors are denser than ethanol or methanol vapor, and therefore are more likely to accumulate at the lower levels of a room near the floor where ignition sources are commonly encountered. A similar situation exists for propane, butane and LPG. They will seek the lowest space if they escape from their pressure cylinder. As they escape, they expand rapidly and cool. The very cold gas sinks.

The auto ignition temperature of kerosene is low, at 210° C, while those of ethanol and methanol are 363° and 460° respectively. Considering these higher auto ignition temperatures and the higher concentrations required to reach LFL for ethanol and methanol, as discussed above, the explosion hazard of the alcohols is substantially less than that of gasoline and kerosene.

⁴ Shepherd, J.E., Nuyt, C.D. and Lee, J.J., May 2000. Flash Point and Chemical Composition of Aviation Kerosene (Jet A), Explosion Dynamics Laboratory Report FM99-4, CA Institute of Technology, ARCO Products Co. and Univ. Nevada, for NTSB.

⁵ Queensland Government, Dept. of Training and Industrial Relations, May 1996. Health and Safety Alert, Alleged Illegal and Dangerous Practices in the Petroleum Industry, Queensland, Australia.

⁶ Shepherd, Nuyt and Lee, May 2000.

Another fuel property to consider is latent heat of evaporation. More heat is required to evaporate ethanol than gasoline and more again to evaporate methanol than ethanol. When a liquid fuel evaporates, it is cooled. The CleanCook fuel canister is designed to evaporate its fuel into the heat of a flame that burns above—not on—the evaporative surface of the fuel canister. As the fuel evaporates from the fuel canister into the flame, the alcohol in the canister is cooled, because of the high latent heat of evaporation of the ethanol and methanol. Thus, the fuel in the canister and the canister itself stay cool.

Another way to evaluate relative fire hazard is to compare the severity of fires. Severity refers here to the amount of heat released during combustion, including radiated heat from the flames. In this respect gasoline and kerosene again compare unfavorably with the alcohol fuels. The hydrocarbon fuels burn with enormous release of heat. Much of this heat is radiated by the flames, making it difficult to approach the fire to extinguish it. Methanol and ethanol flames radiate less heat. As previously mentioned, when they burn outside of a controlled environment like the stove chimney, they burn in excess air, which produces the typical “lazy” flame of a can of sterno. For this reason, an alcohol flame can often simply be blown out. Since alcohol is 100% miscible in water, it is extinguished by water. Hydrocarbon fuels are not miscible in and their flames will only be spread by water.

Hydrocarbon fuels are also not miscible in ethanol, methanol or other alcohols. Mixtures of gasoline or kerosene with alcohol carry risks of phase separation, which can lead to nonoptimal performance and even danger when used in devices designed for either one or the other homogeneous fuel. The safest approach to using alcohols or hydrocarbon fuels in distributed, “low-tech” applications is to stay with a stable single-phase fuel, having a minimum of hazardous or incompatible additives.

The mixing of ethanol and methanol with hydrocarbon fuels for household use is strongly advised against. Not only does this project not mix fuels, it is premised on the fact that alcohol fuels do not need to be and should not be mixed to be used effectively. It will educate the participants in the pilot study and the consumer in general not to mix alcohols with hydrocarbon fuels. The CleanCook stove has been designed to discourage the use of any fuel other than alcohol.

If ethanol is mixed with kerosene and used in a kerosene stove, whether by accident or through ignorance, the results can be very dangerous. In contrast, if kerosene is used in a CleanCook stove, while the results would be very unsatisfactory, they would be only minimally dangerous. Loose kerosene, if ignited, will flare up as kerosene does, but the stove cannot be made to explode.

The fuel tank of a kerosene wick stove will pressurize and is not designed to handle pressure. Normally, the vapor pressure of kerosene is low and remains so during the normal operation of a wick stove. Ethanol in a wick stove would very likely raise the vapor pressure in the fuel tank and promote ignition and possibly an explosion. In contrast, filling the CleanCook stove with kerosene might result in a flare up (if one could even succeed in lighting the stove), but it would not result in an explosion. This is so because the CleanCook fuel canister is open and cannot be made to pressurize.

If kerosene is placed in the CleanCook fuel canister it can be burned or evaporated out to clean the canister. This would have to be done before the canister could be used again for normal, safe operation with ethanol or methanol fuel.

A Note about the Hygroscopicity of Alcohol: Ethanol's attraction of water creates a problem when blending with gasoline for motor fuel use, namely, the separation of an alcohol-gasoline blend into an aqueous alcohol phase and a gasoline-hydrocarbon phase. This not only means that the alcohol to be blended must be anhydrous, but also that great care must be taken to assure that storage, transport and service-station tankage is free of water. A small amount of water is enough to cause phase separation, even in blends containing as much as 25% alcohols.

Even the best precautions at the refinery, in transit and at service stations cannot prevent the possibility of water-phase separation in automobile fuel tanks. Such separation can cause corrosion, rough engine operation, starting problems and fuel-line plugging.

In contrast, the hygroscopicity of alcohol poses no problems for its use as a stove fuel. Indeed, some water in the alcohol is beneficial. Alcohol containing as much as 10% water can be burned without problem in the CleanCook stove. The ethanol-water azeotrope (or the mixture which nature seeks), is 95% alcohol, which is quite desirable as a stove fuel but cannot be used for gasoline blending. Thus, the hygroscopicity of alcohol, while it presents a problem for the use of alcohol in internal combustion engines, does not present a problem for use as a stove fuel.

Environmental Hazards: Ethanol and methanol mix readily with water and quickly degrade in the environment. Hydrocarbon fuels do not mix with water and do not degrade rapidly in the environment. For these reasons, the U.S. Department of Energy determined that the environmental hazards created by gasoline, kerosene and diesel fuel spills were greater than those created by ethanol and methanol releases.⁷ Moreover, studies have determined that ethanol and methanol are essentially non-toxic to a variety of aquatic of plants and animals tested,⁸ while gasoline and petroleum fuels in general are very toxic to aquatic life.⁹

Products of Combustion/Air Quality: Health benefits accruing as a result of the cleanliness of ethanol and methanol when burned as compared to the smoke, particulate matter and complex mix of organic compounds produced by the burning of biomass fuels and kerosene are very significant. The long list of products of combustion of wood and kerosene include smoke and soot (particulate matter), benzene, butadiene, formaldehyde, carbon monoxide, polycyclic aromatic hydrocarbons, dioxins, furans and so

⁷ IdaTech "Tech Brief", January 2001. US DOE, October 1991. Assessment of Costs and Benefits of Flexible and Alternative Fuel Use in the US Transportation Sector. Technical Report No. 7: Environmental, Health and Safety Concerns.

⁸ US Environmental Protection Agency, Office of Pollution Prevention and Toxics, 1994. Report No. EPA 749-F-94-013a.

⁹ Machiele, Paul A., 1989. A Perspective on the Flammability, Toxicity and Environmental Safety Distinctions Between Methanol and Conventional Fuels. Prepared for the AIChE. USEPA. Ann Arbor, Michigan.

on. Extensive study has been devoted to the health impacts of smoke and fumes from biomass and kerosene fires. Sufficient here is simply to document the cleanliness of alcohol when it burns.

Below are the emissions data from a laboratory report produced for Dometic and its South African agent by Chemtaur Technologies Laboratory (Johannesburg) in 2001. This study was completed in conjunction with a small pilot study that was conducted in the town of eMbalenhle near Johannesburg by NOVA Institute, a South African non-governmental organization specializing in household energy and community health, using fuel methanol provided by SASOL. This study shows that the primary products of combustion of ethanol and methanol are CO₂ and water vapor, with only parts per million of formaldehyde or acetaldehyde (<1), carbon monoxide (<20) and uncombusted ethanol and methanol vapors (<5), all well under the published exposure standards. No measurable NO_x (<1) was produced.

Analyte	Unit	Test 1	Test 2	Test 3	Test 4
Time to burn ~500mL fuel	minutes	129	127	130	125
Water left from 2500mL	mL	509	899	412	738
Carbon monoxide, CO	ppm	19	17	20	20
Carbon dioxide, CO ₂	ppm	2050	2100	2450	2400
Nitrous fumes, NO _x	ppm	<1	<1	<1	<1
Formaldehyde, HCHO	ppm/hrs	<1	<1	<1	<1
Ethanol, C ₂ H ₆ O	mg/m ³	2.97	<0.01	3.77	<0.01
Methanol, CH ₄ O	mg/m ³	<0.01	6.54	<0.01	11.15

Table 1: Test Methods used were as follows: The tests were performed by burning the stove in a tightly closed room of a volume approximated at 35m³. Test 1 was performed with ethanol with one burner burning. Test 2 was methanol with one burner burning. Tests 3 and 4 were with two burners burning, ethanol and methanol respectively. The nitrous fumes, carbon monoxide and carbon dioxide were determined with Dräger color-tubes. The methanol and ethanol concentrations were analyzed by GC/MS and the formaldehyde was determined using a KLM color comparator. The mg/m³ measure is approximately equivalent to a ppm measure.

Table 3: Properties of Basic Fuels (following page)

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Property	Value					
	Methanol CH ₃ OH	Ethanol C ₂ H ₅ OH	Propane C ₃ H ₈ (Butane is C ₄ H ₁₀)	Gasoline C ₄ -C ₁₂ (up to C???)	Kerosene C ₉ -C ₁₆ (down to C ₅)	Diesel C ₁₂ -C ₂₃ (down to C ₅)
Molecular Weight	32	46	44	~114	~170 average	
Specific Gravity	0.789 (25C)	0.788 (25C)	0.585 (-40C)	0.739(15.5C)	0.820(15.5C)	
Vapor Density Rel. to Air	1.10	1.59	1.56	3.0 to 4.0	4.5 to 5.9	4.5
Liquid Density (g cm ⁻³ at 25°C)	0.79	0.79	0.50	0.74	0.79 to 0.84	
Boiling Point (°C)	65C (149F)	78C (172.4F)	-42.5	27 to 245	200 to 250 spec 148 to 325	150 to 355
Melting Point (°C)	-98	-144				
Vapor Pressure@38°C (psia)	4.6	2.5	208	8-10	~1 and up	~1and up
Heat of Evaporation (Btu/lb)	472	410		135		
Heating Value (kBTU gal ⁻¹)						
Lower	58	74	81	111	121	130
Upper	65	85	88	122	130	
Tank Design Pressure (psig)	15	15	325	15	5	
Viscosity (cp)	0.54	1.20		0.56	2.37	1.7 to 3.4
Flash Point (°C)	11	14	-104	- 45	~38 ASTM spec 21 to 82	38 to 55 ASTM 21 to 82
Flammability/Explosion Limits						
(%) Lower (LFL)	6.7	3.3	2.1	1.3	0.6 to 1.7	0.5
(%) Upper (UFL)	36	19	9.6	7.6	5	7.5
Auto ignition Temp. (°C)	460	363	450	250 to 460	210	254 to 446
Solubility in H ₂ O (%)	Miscible(100%)	Miscible(100%)		Negl. (~. 001)	Negl. (~. 001)	Negl. (~. 001)
Azeotrope with H ₂ O	None	95% EtOH Hygroscopic	Immiscible	Immiscible	Immiscible	Immiscible
Peak Flame Temperature °C	1870	1920	1925	2030	2038	2054
Minimum Ignition Energy In Air (mJ)	0.14		0.26	0.23	0.23	0.23
TLV for Exposure (ppm)	200	1000	1000	300 1ppm only for benzene	20 to 100 .01 to 25 for particulate matter in air	10 to 100 .01 to 25 for particulate matter in air

Table 4: Properties of basic fuels that influence safety of manufacture, transport, storage, and use. Values for gasoline, kerosene and diesel reflect a typical base-fuel value and the potential for variability. (Data compiled from standard chemical engineering reference works and representative industry Material Safety Data Sheets.)