Paper No. 43b

A Perspective on the Flammability, Toxicity, and Environmental Safety Distinctions Between Methanol and Conventional Fuels

Paul A. Machiele
U.S. Environmental Protection Agency
2565 Plymouth Rd, Ann Arbor, Mi, 48105

Prepared for Presentation at the American Institute of Chemical Engineers 1989 Summer National Meeting
Philadelphia, Pennsylvania
August 22, 1989

ABSTRACT

Methanol is one fuel increasingly being considered as a prime candidate to replace petroleum as our primary transportation fuel. Due to the widespread availability of methanol resulting from such a use, it is important that the flammability, toxicity, and environmental concerns of methanol fuels be assessed and compared to those of the fuels which it may replace. This paper describes these concerns with pure methanol (M100) and compares them with the other high level methanol fuels (M85) as well as gasoline and diesel fuel. Since the intent of this paper is to provide a broad discussion of methanol fuel safety, detailed discussion of specific situations and concerns is not included. As such, this paper best serves as a general reference for gaining an overall perspective on the issues related to methanol fuel safety.

INTRODUCTION

For a variety of reasons, methanol has received attention during the last few years as a promising replacement for gasoline and diesel fuel as our Nation's primary transportation fuels. The automotive industry has been looking at methanol due to its excellent combustion characteristics.[1] EPA and various other state and local air quality agencies have been considering methanol as a means of addressing the nations air quality problems. The Department of Energy has for some time been studying methanol due to the ability to produce it from natural gas, coal, and renewable sources.[2] The racing industry has been using methanol for its power and safety benefits.

Transportation fuels affect many aspects of our lives, and as a result, safety concerns with them are very important. Gasoline and diesel fuel were selected as transportation fuels long ago with little concern over their human and environmental safety. Instead, safety concerns were subsequently minimized

by implementing vehicle design changes or special fuel handling procedures. What risks could not be eliminated have merely been accepted by the American public in order to maintain effective transportation. The substitution of gasoline and diesel fuel with alternative fuels such as methanol could alter the human and environmental safety situation that currently exists. The nature of this change is what is discussed in the following paper.

In the discussion which follows, the four fuels: diesel fuel, gasoline, M100, and M85 are compared by their flammability, human toxicity, and environmental hazards. Flammability discussion focuses on the likelihood of a fire occurring followed by the hazard which the fire represents once it does occur. Human toxicity discussion first considers the toxic symptoms of exposure to the different fuels, followed by discussion of the severity of expected exposures and an assessment of overall risk. Environmental hazard discussion includes consideration of air toxics emissions as well as leaks and spills of the different fuels to water, land, and groundwater. These discussions are followed by an overall summary.

FLAMMABILITY

The risk of fire with today's transportation fuels is probably the greatest safety risk with the fuels. It is estimated that there are 15,000 to 20,000 fires annually resulting from motor vehicle accidents, the majority of which are fuel related.[3] Associated with these fires are approximately 1700 deaths, 3700 serious injuries, 3600 moderate injuries, and personal injury and property damage costs of well over three billion dollars.[3,4] There are an additional 2553 reported service station fires annually resulting in approximately 4 deaths and 115 injuries.[3] In addition, there are many more fuel related fires which are not included in these data bases.

Diesel fuel, gasoline, M100, and M85 are all flammable materials; the characteristic prompting their use as fuels. But the likelihood that each fuel will ignite under similar circumstances, and the hazard which it poses is significantly different depending on the particular properties of each fuel. The properties in Table 1 are those thought to be most important in assessing the hazard of the different fuels.

Ease of Ignition in Open Air

Open air refers to situations in which there is typically a significant amount of natural or artificial ventilation to make accumulation of fuel vapor to flammable concentrations difficult except in relatively close proximity to the vapor source (spill, open fuel container, etc.). In these

Table 1

Fuel Properties

Property	Diesel Fuel		Gasoline		M100		M85	
Volatility (RVP-kPa)	0.28 - 2.8	[5,6]	55 - 110 (79)	[7]	31.7	[5]	50 - 70 (59)	
Flammability Limits:								
Lower (LFL)								
Volume Percent	0.6	[6,8]	1.4	[9]	6.0	[10]	2*	
Temperature (°C)	21 - 96 (53)	[11]	-43		7		-43 to -37	
Upper (UFL)								
Volume Percent	7.5	[8]	7.6	[12,13]	36.5	[10]	8.55	[14]
Temperature (°C)	?		-30 to -12 (-21)		43		-20 to -10	
Flash Point (°C)	52	[9]	- 43	[9,12]	11	[10,12]	-36	[15]
Vapor Density (relative to air)	5-6		2-5 (3.5)		1.11		2*	
Diffusion Coefficient (m^2hr)	0.02**		0.02		0.05		0.04*	
Heat of Combustion (kJ/kg)	41,870		43,030		19,930	[12]	23,400*	
(kJ/l)	35,680		31,970		15,860		18,270*	
Latent Heat of Vaporization (kJ/kg)	267	[16]	349	[12]	1177	[12]	1047*	
Pool Burn Rate (cm/min)	4.0	[17]	4.8	[17]	2.1	[17]	2.5*	
Flame Spread Rate (m/s)	0.02-0.08	[16]	4-6	[16]	2-4	[16]	3-5*	
Boiling Point (°C)	188 - 343	[18]	27-225	[12]	64	[10]	27-225*	
Electrical Conductivity (cu)	50-100	[19]	3-10	[19]	3×10^7	[19]	3×10^7***	
Minimum Ignition Energy(mJ)	0.24**		0.24	[20]	0.14	[16]	0.24**	
NFPA Classification	2		1		1		1	

* estimated based on combination of gasoline and methanol
** estimated based on equivalency with gasoline
*** estimated based on equivalency with M100

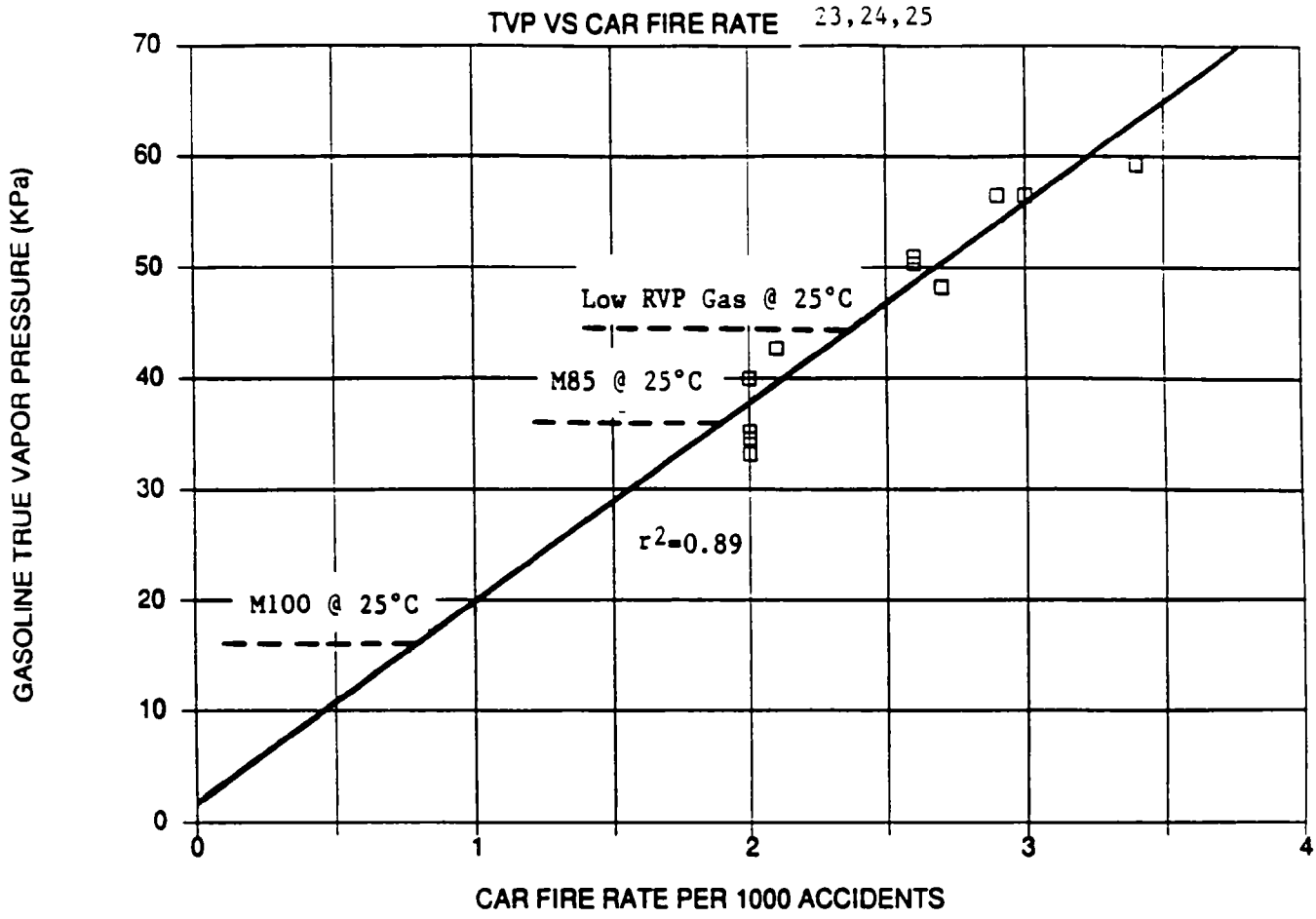
situations, the fuel volatility, and lower flammability limit (LFL) play the most important roles in assessing the likelihood of ignition, but as ventilation is diminished, the vapor density and diffusion coefficient also become important. The surface ignition temperature is not expected to result in any significant difference between the fuels since their surface ignition temperatures are near or above the temperatures expected on vehicles in-use.[21,22]

Diesel fuel is the least likely of the four fuels to ignite in both well and poorly ventilated open air situations primarily due to its extremely low volatility. Sufficient vapor is not produced to achieve a combustible mixture even at the fuel surface until the fuel reaches a temperature of approximately 53°C (ranging from 21 to 96°C depending on the particular blend).[11] If an ignition source enters the liquid fuel itself, however, it may generate sufficient vapor, and ignition is possible.

Gasoline represents a serious flammability hazard in open air situations. Its volatility allows for the production of combustible concentrations of fuel vapor when the fuel is exposed to the atmosphere at any temperature above approximately -43°C. Meanwhile, its LFL is such that only 1.4 volume percent of gasoline vapor in air is adequate for ignition to occur. Thus, not only is gasoline a flammability hazard from an ignition source entering the fuel, but also from ignition sources in the area near the exposed fuel. If ventilation is limited such as in mechanic pits, stationary-vehicle engine compartments, and buildings or rooms without special air handling systems, then gasoline is even more likely to ignite. Its low diffusion rate limits the dispersion of the vapors to safe levels. In addition, the high vapor density allows the vapors to travel readily to ignition sources. Unlike in enclosed spaces, the dilution and ventilation in open air situations typically prevent vapor concentrations above the UFL (rich limit) from forming, so ignition is not precluded.

In open air situations, M100 is much less likely to ignite than gasoline. Its low volatility means that compared to gasoline approximately 30 percent (50 percent if fuel volume is increased in proportion to methanol's heat of combustion and combustion efficiency - assumed to be 30 percent more efficient for future dedicated M100 vehicles due to higher compression ratios and lean burn operation) of the volume of vapor is emitted per unit time. As shown in Figure 1, based on volatility alone, M100 is expected to result in significantly lower incidences of fire following motor vehicle accidents than with gasoline. In addition, M100's LFL is such that a concentration more than 4 times greater than that for gasoline is required before ignition is possible. In well ventilated open air situations this LFL is not likely to be reached except

FIGURE 1


TVP VS CAR FIRE RATE 23,24,25
GASOLINE TRUE VAPOR PRESSURE (KPa)
70
60
50
40
30
20
10
0
Low RVP Gas @ 25°C
M85 @ 25°C
M100 @ 25°C
r2=0.89
0
1
2
3
4
CAR FIRE RATE PER 1000 ACCIDENTS

for very near to the vapor source. At temperatures below 7°C, as are typical for much of the country in winter months, methanol acts very similar to diesel fuel in that not enough vapor is produced to form a flammable mixture even at the fuel surface. Thus, on the basis of the fuel volatility and LFL alone, methanol vapor is much less likely to exist in flammable concentrations in open air situations than either gasoline or M85 (See Table 2). In addition, in situations where ventilation is limited, the high diffusivity of 2-1/2 times that of gasoline causes methanol vapor to disperse more rapidly, and the low vapor density of just 1.11 times that of air makes accumulation of vapor in low areas much less likely than for gasoline.

M85 is expected to act very similar to gasoline in open air situations. It has a volatility which ranges between 50 and 70 kPa RVP depending on the blend gasoline volatility. This relatively high volatility produces approximately 77 percent (127 percent if fuel volume is increased in proportion to M85's heat of combustion and combustion efficiency - assumed to be 10 percent more efficient for future dedicated M85 vehicles) of the volume of vapor that is produced from gasoline, and roughly 2.7 times the volume produced by M100. Since roughly 2/3 of the volume of vapor produced by M85 is composed of gasoline hydrocarbons, the LFL is estimated to be most similar to that of gasoline, approximately 2.0 volume percent.[26] As a result, M85 is flammable at any temperature above approximately -40°C. Based on this analysis, and as shown in Table 2, M85 can be considered to be nearly as prone to ignition in open areas as is gasoline. In addition to having a volatility and LFL similar to those of gasoline, since roughly two-thirds of "M85 vapor" is gasoline hydrocarbon, the vapor density and diffusion coefficient are also estimated to be most similar to those of gasoline. Thus, in situations where ventilation is limited, M85 should also act similar to gasoline.

Enclosed Space Flammability

Enclosed space flammability refers to fires and/or explosions which can occur within sealed containers and fuel tanks. These are unique situations in that there is no dilution or ventilation, and thus fuel vapor can easily accumulate to potentially flammable concentrations. They are also unique in that since the fuel is unexposed to the environment, there are a limited number of ignition sources. Malfunctioning electrical in-tank fuel pumps and fuel level sending units, static discharges, and friction sparks during tank puncture represent potential ignition sources. Friction sparks and tank puncture, however, are seldom of sufficient energy to achieve ignition.[27,28] The most likely source of ignition of a fuel tank is probably exposing an open fill pipe to ignition sources such as cigarettes. In addition to the

Table 2

Lower Flammability Limit and Available Concentration

Fuel	LFL (V%)	Equil Conc (V%) @ 0°C*	Equil Conc (V%) @ 25°C**	Ratio (EC/LFL) @ 0°C*	Ratio (EC/LFL) @ 25°C**
M100	6.0	3.9	16.3	0.65	2.7
M85***	2.0	18.0	38.8	9.0	19.4
Gasoline	1.4	27.2	50.7	19.4	36.2
Diesel	0.6	0.01****	0.2****	0.02	0.3

* Assumes base gasoline of 90 kPa RVP (winter fuel)
** Assumes base gasoline of 72 kPa RVP (summer fuel)
*** Properties approximated based on the proportions of its constituents
**** Rough approximation

properties of the container, the flammability in these situations is a function of the fuel volatility, the flammability limits, and the ignition properties.

Diesel fuel represents a small, but significant hazard with respect to enclosed space flammability. Although typically diesel fuel's LFL is above 53°C due to its extremely low volatility, and as a result seldom exists in a flammable condition in an enclosed space, its LFL (flash point) can range from as low as 21°C to as high as 96°C.[11] As a result, depending on the batch of fuel, it is possible to have an explosive diesel fuel vapor/air mixture inside an enclosed space at high ambient temperatures. In addition, excess uninjected diesel fuel is typically recirculated back to the fuel tank after passing it through the engine in heavy-duty vehicles causing the fuel temperatures in the tanks to be well over 16°C above ambient in certain circumstances.[29] Despite the expected frequency with which flammable concentrations might be expected to occur in fuel tanks with diesel fuel, in-use testing, as well as historical fire data, does not seem to support it, possibly due to rapid weathering of the fuel.[29] Rapid weathering during vehicle operation can quickly raise the LFL above 65°C, causing diesel fuel tanks in-use not to be flammable under normal operating conditions.

Gasoline is virtually incombustible in enclosed space situations. The fuel volatility is so high, and the upper flammability limit so low (7.6 volume percent in air), that except at temperatures below approximately -26°C, the fuel/air mixture is too rich for ignition to occur. Thus, even though ignition sources might be available in the fuel tank under some situations, the fuel vapor concentration will almost always be too rich and preclude ignition. In extreme northern areas of the U.S. and Canada in mid-winter such temperatures are possible but, apparently, since ignition sources are typically rare inside fuel tanks, explosions are not known to occur. Other situations where ignition of gasoline fuel tanks is possible occur when vapor/air equilibrium is not maintained, such as in nearly empty fuel tanks, or when venting has taken place. Occurrences such as these, however, are rare.

M100 represents the most significant flammability concern of the four fuels in enclosed spaces. The volatility and flammability limits of M100 allow a combustible mixture in the fuel tank between approximately 7°C and 45°C. Thus, although much of the U.S. would experience temperatures too low for ignitable vapor/air mixtures to exist in fuel tanks during the winter months, during most of the rest of the year fuel tank ignition is possible.

Despite the fact that M100 typically exists at a flammable concentration inside a fuel tank, the probability of ignition is still low due to the fact that the vapor is separated from

most ignition sources. Shorting electrical fuel level sending units and friction sparks during tank rupture in an accident are not considered to be sufficient to ignite methanol vapor.[27,28,30,31] Static discharges, although a possible ignition source (a means of grounding gasoline and diesel fuel refueling nozzles is required to eliminate static buildup), are not as likely to occur with M100 due to its high electrical conductivity. In-tank fuel pumps are possible ignition sources, but only if they are exposed to the vapor space (the tank is empty), and the use of diodes across the terminals of the pump may prevent ignition altogether.[30] Exposing the fill neck to a flame such as a cigarette is also a potential ignition source. But, here again, it is expected to result in ignition only under certain conditions, and there are a number of means of virtually eliminating the chance of ignition.[28] Two of the simplest would be to install flame arresters on the fill pipe and tank vents, and/or to extend the fill pipe to the bottom of the tank to separate the vapor space from the atmosphere. Thus, due to the lack of available ignition sources, and the possibility to minimize the chance of ignition, fuel tank explosions are expected to remain rare events with the use of M100 as a fuel. The most common fuel tank fires will be from fuel which leaks out of the tank and ignites. In this case, methanol is less flammable as described in the open air situations earlier.

M85 is similar to gasoline in that it too is typically not flammable in enclosed space situations due to its low UFL of approximately 8.55 volume percent, and its relatively high volatility. These two properties combine such that above approximately -10°C the vapor concentration in an enclosed space is too rich to allow ignition. This limit is not so low as to prevent ignition under extreme wintertime conditions, but it is, nevertheless, a lower concern relative to M100. However, vehicles which are not used frequently or vehicles such as most heavy-duty diesel vehicles which do not have closed fuel systems, will contain fuel with a vapor space very similar to that of M100 due to the rapid weathering that can be expected with a fuel which contains such a small fraction of volatile components. Thus, it seems prudent that M85 be treated the same as M100 with regard to fuel tank flammability even though the likelihood of ignition is probably lower.

Hazard if a Fire Occurs

The overall flammability hazard of a fuel is not only a function of the probability of a fire, but is also dependent on the danger which that fire represents. The following discussion will attempt to define the hazards of fires with the four different fuels.

Severity of the Fire

The severity of a fuel related fire determines, in large part, the magnitude of the fire hazard associated with that fuel. This involves not just the violence with which the fuel burns, but also the heat given off by that fire, and the amount of smoke which it produces. All three help determine how easily the flame will spread, or how dangerous that fire will be to person and property.

Diesel fuel fires begin slowly, due to its extremely low volatility, with a flame spread rate over a pool of fuel of only 0.02 to 0.08 m/s (See Table 1). At the same time, its high heat of combustion and low heat of vaporization (a ratio of 156:1) combine to quickly vaporize additional fuel; causing the burn to progress much more violently. The only controlling factor is the high boiling points of diesel fuel's constituents. As a result, as seen in Table 3, the relative heat release rate from a diesel fuel fire is very high. This high heat release rate results in a high probability that a diesel fuel fire will spread to other nearby flammable substances, and cause serious burns to exposed individuals.

Gasoline's high volatility enables immediate eruption of a fully developed fire. The flame spread rate over a pool of gasoline is nearly 100 times that for diesel fuel, or approximately 4 to 6 m/s. Once ignition occurs, the high heat of combustion provides more than adequate heat to overcome the low heat of vaporization (a ratio of 123:1) and low boiling point of many of its constituents. The pool burn rate for gasoline is thus the highest of all the fuels, and when coupled with its high heat of combustion causes the heat release rate for gasoline also to be the highest of all the fuels (See Table 3). As a result, gasoline represents the greatest hazard of the four fuels for the fire to spread to other flammable substances nearby, and represents the greatest hazard for serious burns to individuals in the vicinity of the fire.

M100's low volatility causes a flame to spread over a pool of fuel at a speed just slightly more than half that of gasoline; and M100's low heat of combustion and high heat of vaporization combine to cause the burn to progress much more slowly. (The ratio of the heat of combustion to the heat of vaporization is only 17:1 for M100.) For this reason, a pool of M100 burns at the slowest rate of all four fuels, and as shown in Table 3, the heat release rate (ignoring situational effects such as flame geometry) is nearly one-fifth that for gasoline. In addition, the fraction of heat emitted in the form of radiation is less with methanol than with the other fuels.[22] Since this is the main source of heat exposure to persons and objects near a fire, the relative heat release rate is even more favorable to methanol than the values in Table 3 suggest.

Table 3

Relative Heat Release Rates*

Fuel	Heat of Combustion (kJ/l)	Heat of Vaporization (kJ/l)	Burn Rate (mm/min)	Relative Rate Release Rate
M100	15860	936	2.1	1.0
M85**	18270	817	2.5	1.4
Gasoline	31970	259	4.8	4.9
Diesel	35680	228	4.0	4.5

* Ignores differences in flame geometry and radiative heat loss

** Properties approximated based on proportions of the constituents

As a result of the low heat release from the methanol fire, the likelihood that the fire will spread to other nearby combustible substances or cause injury to people located nearby is much lower than with gasoline. As shown in Figure 2, the distance from the center of a burning pool of M100 where the incident heat radiation is adequate to cause a one percent fatality among people located near the fire (7.5 kw/m^2) is just slightly larger than the radius of the fuel itself, while for gasoline it is 4 to 5 times the radius of the fuel spill.[16]

Also of importance in avoiding personal injury with methanol is the fact that it does not produce the suffocating clouds of black smoke that both gasoline and diesel fuel do. However, since methanol vapor itself is toxic, not all risk is avoided. In addition, as discussed later, pure methanol has the unique property of burning with an invisible flame in daylight conditions which increases the hazard of the fire.

In situations of fuel tank explosion, the additional hazard results from the pressure wave associated with the explosion. Direct biological damage to humans occurs when they are exposed to an overpressurization of about 310 kPa, while structural damage results with an overpressurization as low as 41 kPa.[17] A methanol fuel tank if ignited will result in a maximum pressure rise under ideal conditions as high as 620 kPa (825 kPa for gasoline hydrocarbons) at the fuel tank surface (decreasing to 310 kPa at 12 feet from the tank), but under typical in-use conditions the pressure rise could be significantly lower.[17] Any hazard resulting from this explosion may be minimized, however, by designing the fuel tank to withstand the pressure. Testing has shown that M100 tanks may not need to be significantly stronger than today's gasoline tanks to withstand the pressures generated.[28]

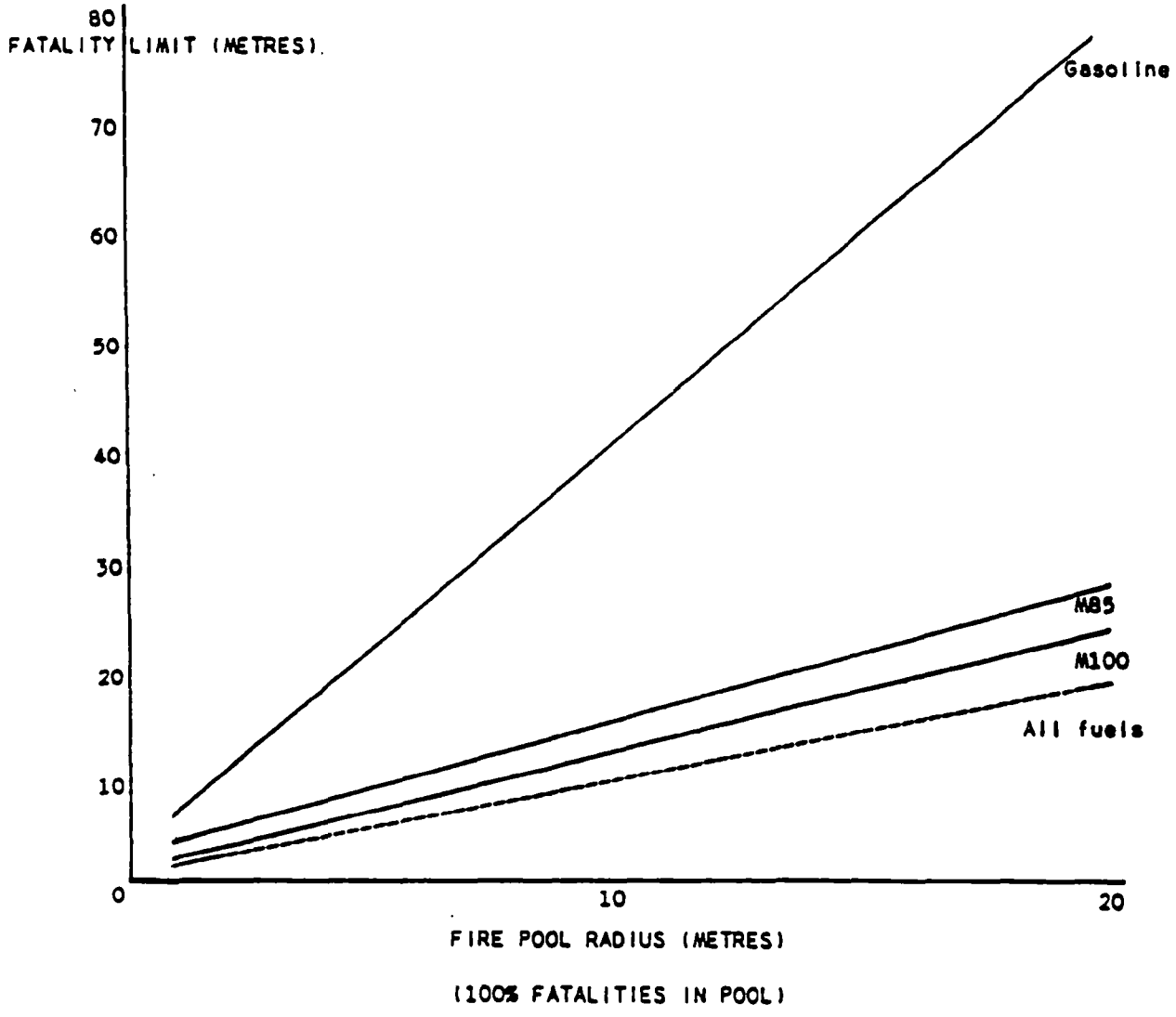
M85 likely represents a compromise between methanol and gasoline in aspects related to the hazard of a fire once it occurs. Its volatility is high enough to cause the fire to develop fully immediately following ignition, but its other properties tend to limit the severity with which it burns. Its heat of combustion is just slightly more than that of methanol, while its heat of vaporization is just slightly less (a ratio of 22:1). As a result, the rate at which a pool of M85 burns and the rate at which heat is released from the fire are estimated to be just slightly greater than for M100 (See Table 3). Thus, as seen in Figure 2 the area effected by a pool fire of M85 is estimated to be just slightly greater than for M100.

Ease of Extinguishing

Given enough time, and proximity to combustible materials, any fire can cause personal injury and extensive property damage. For this reason, the ease with which a fire can be extinguished also becomes important.

FIGURE 2

Fatality and Damage Distances for Methanol & Gasoline Pool Fires [16]



Key: ——— 1% fatality distance

- - - - 100% fatality

Note: This figure was taken in its entirety from reference 16

The main difference between M100 and gasoline and diesel fuel is that M100 can be extinguished much easier with water. Gasoline and diesel fuel are not water soluble and are both lighter than water. Thus, a fire with these fuels is difficult to extinguish with water as the fuel floats to the surface where it reignites. Only by means of spraying water as a fog and driving the fire off of the fuel can it be extinguished with water. However, with diesel fuel, due to its high flash point, water may be of some benefit in getting a fire under control if it can be used to cool the fuel below its flash point. Unlike gasoline and diesel fuel, methanol is infinitely water soluble. Thus, it does not float on the water, and can be extinguished by diluting it. Large quantities of water are necessary, however, since a methanol/water mixture is flammable down to 21 volume percent methanol. Since water is the most abundant and readily available substance for fire fighting, this can be a significant benefit with methanol, especially when fires develop in remote areas. Since M85 has only limited solubility in water before it will separate into the two phases of gasoline and a methanol/water blend, water may be even less effective as an extinguishing agent for M85 than for gasoline.

An additional benefit with methanol is the low amount of heat given off by the fire. Fire fighting personnel are thus able to approach a methanol fire with less chance for burn injuries, fire stroke, and heat exhaustion, and should be able to extinguish the fire more readily.[16] In addition, due to the lack of smoke and typically low levels of products of incomplete combustion (PICs) produced when methanol burns, the hazard to fire and rescue teams due to smoke inhalation should be greatly reduced below that for gasoline and diesel fuel.[16] An added concern with fighting a methanol fire, however, is that the fire itself is considered invisible during daylight if it involves no other combustible materials or contaminants. This could hinder fire fighting efforts, and represents a serious safety concern. (This topic will be discussed further in the following section.) The main benefit of M85 over M100 is that, as discussed below, the flame is typically visible in daylight.

Visibility of the Flame

As alluded to above, the lack of luminosity of an M100 flame is a significant issue relative to both the severity of a fire, and the ease with which it can be extinguished. Gasoline and diesel fuel burn with dark yellow flames clearly visible under any conditions. In addition, they give off large clouds of thick black smoke which can be seen for long distances. Thus, there is little chance that even small fires with these fuels will go unnoticed. Methanol, however, burns with a smokeless blue flame, which is considered to be invisible in daylight, since it contains no carbon-carbon bonds and, therefore, does not produce unoxidized carbon particles or

precursors to soot particles when it burns.[32] For comparison, M100 burns with a luminance of 0.39 foot-lamberts, while gasoline burns with a luminance typically exceeding 300 foot-lamberts.[33] The only way of knowing that a fire exists in which only M100 is burning (no other combustible materials or contaminants are involved) under well lit conditions is by seeing the heat waves or feeling the heat radiation given off by the fire. This creates the potential of people entering the fire without realizing it. However, the heat radiated from the fire and any other substances which become involved in the fire may provide some warning. Testing done on actual vehicle engine compartments revealed that within a short period of time after ignition of the M100 fire, combustion of underhood materials (plastics, rubbers, etc.) provided sufficient luminosity and smoke.[30] This should also be the case in spills outdoors as vegetation burns, and possibly also in garage areas where minor oil spills are commonplace.

To avoid possible problems due to methanol's low luminosity, there are a number of additives which have been tested for use to make the flame visible. Many additives will provide luminosity, but few provide luminosity throughout the entire burn (i.e., they burn off faster than the methanol). However, recent efforts with various organic dyes have yielded more positive results at concentrations in the hundreds of ppm range.[34]

To date, the simplest and most successful additive for obtaining a luminous flame has been 15 percent of a high aromatic, high volatility gasoline as selected by Ford.[36] Testing has shown that this results in an adequate amount of flame visibility even in broad daylight throughout the burn; thus, the emergence of M85.[35,37] Despite this there are still some concerns with regard to its flame luminosity. Although the addition of gasoline provides luminosity, it is still not very intense, and its blue and yellow flame tends to diminish in luminosity as the burn progresses, especially if not properly blended.[35,37] For this reason, if all of its luminosity benefits are to be realized, care must be taken to ensure that M85 is blended properly. In addition to concerns over its effectiveness as a flame luminosity additive, 15 percent gasoline also changes significantly the other safety characteristics of the fuel as discussed in this paper. As a result, additives which provide luminosity without significantly altering the nature of methanol may be preferable.

TOXIC RISK OF FUEL TO HUMANS

Fuel toxicity to humans is an issue of great importance when assessing the safety of a given fuel. There are many situations in which a person may come into contact with the fuel either through inhalation, ingestion, or dermal contact. Thus, if the fuel causes any acute, chronic, subchronic, or carcinogenic toxic effects to humans, the risks due to toxicity may far outweigh any other safety concerns.

Fuel Toxicity

The acute toxicity of diesel fuel relative to ingestion is such that acute exposure may cause nausea, vomiting, cramping, liver and kidney damage, lung irritation, and central nervous system depression ranging from a mild headache to coma, and death.[8] If the lethal dose to rats (LD50) is extrapolated to humans, death would result from ingestion of just 63 ml (1/4 cup) for the average adult male.[38] Since diesel fuel will often cause regurgitation, large quantities of ingested fuel will often not stay in the stomach, thus avoiding the acute toxicity discussed above. Unfortunately, when regurgitation occurs, aspiration into the lungs of even small amounts of diesel fuel may result in severe irritation with coughing, gagging, difficulty breathing, chest pain, and chemical pneumonitis, and bronchopneumonia.[8,39]

In addition to ingestion, acute effects with diesel fuel can also result from dermal contact. Diesel fuel is considered to be a moderate to severe skin irritant, causing irritation of hair follicles and blockage of sebaceous glands resulting in a rash of pimples and spots.[8,40] More importantly, prolonged or repeated exposure may result in defatting of the lipid components of the skin. Prolonged exposure may also result in a state of stupor (narcosis) as a result of absorption through the skin. No information was found in the literature which quantified the exposure necessary to result in these toxic symptoms, however, and as a result it is difficult to make comparisons with the other fuels. Based on what information was available, diesel fuel would appear to be the mildest of the four fuels in relation to skin contact. Eye contact may result in irritation and redness; with prolonged exposure resulting in inflammation of the eye's mucous membranes.

Acute inhalation exposure to diesel fuel vapor, though extremely rare, may cause respiratory tract irritation, and high levels may cause giddiness, headache, dizziness, nausea, vomiting, incoordination, and unconsciousness.[8] The concentration in air which is considered to be immediately dangerous to life and health (IDLH) is 10,000 ppm.[17] Long term chronic exposure to diesel fuel vapor is not known to be carcinogenic. However, skin painting carcinogenesis bioassay tests reveal that diesel fuel may be weakly to moderately carcinogenic, and mutagenesis assays have yielded mixed results.[38,40]

The acute toxicity of gasoline relative to ingestion is such that even small amounts (5 to 10 ml) may cause a burning sensation in the mouth, throat, and chest, and intense irritation and burning in the gastro intestinal tract, with nausea, vomiting, diarrhea, and abdominal pain. Ingestion of 27 to 40 ml of gasoline will typically result in additional more serious symptoms including central nervous system

depression, headache, dizziness, drowsiness, fever, and transient liver damage.[13,38] Severe intoxication may result in unconsciousness and coma or convulsions with seizures.[13,38] Estimates for the dose which is typically fatal to the average adult range from 115-180 ml to 470 ml, but death has been reported at a dose as low as 13 ml.[38,41] In children, the normally fatal dose is approximately 13 to 20 ml.[38] In addition to the potentially severe systemic toxicity of gasoline, it is probably even more hazardous if aspirated into the lungs following regurgitation or belching. Once in the lungs, even small amounts may cause severe chemical pneumonitis, and death from lung insufficiency.[13,41]

The acute toxicity of gasoline skin contact is such that minor direct contact can result in irritation, drying and cracking of the skin, and dermatitis.[13] A more severe or repeated exposure can cause chemical burns and blistering, and defatting of the skin due to gasoline's lipid (fatty tissue) soluble characteristic.[13] In addition, prolonged exposure can result in absorption into the body causing systemic toxic effects such as weight loss and lung, heart, neurologic, kidney, and liver problems with potentially life threatening consequences.[42] As with diesel fuel, since no information was found in the literature which quantified the exposure necessary to result in these toxic symptoms or the rate at which gasoline is absorbed into the skin, comparisons with the other fuels are difficult. Eye contact with gasoline may result in mild irritation and redness.[13]

The acute toxicity of gasoline vapor inhalation is such that exposure to low concentrations may cause eye irritation, respiratory tract irritation and burning with cough and sore throat, central nervous system depression with headache, dizziness, drowsiness, nausea, or mental confusion.[13,43,44] Higher concentrations may cause respiratory difficulty, accumulation of fluid in the lungs, bronchial pneumonia with fever, and heart damage. Further central nervous system depression may occur with muscular incoordination, blurred vision, unconsciousness, or convulsions. Even brief exposure to high concentrations may cause narcosis, coma, or death from severe central nervous system depression resulting in respiratory failure. Extremely high concentrations may cause asphyxiation.[13,45]

The chronic effects of gasoline exposure are less well known. It is believed that chronic exposure to gasoline results in pathological changes in the lung and central nervous system disturbances, and may result in gradual irreversible eye damage, but other effects are uncertain.[46] Information is inconclusive regarding any mutagenic, reproductive, or teratogenic effects. EPA has classified gasoline vapors as being a group 2B probable human carcinogen.[47] Despite more recent information which questions the applicability of the rat

and mouse studies on which this classification is based, EPA has retained the B2 classification.[40,47,48,49] The fact that gasoline contains benzene, a proven carcinogen, lends support to the carcinogenicity of gasoline vapor. In fact, gasoline's threshold limit value (TLV) of 300 ppm and short term exposure limit (STEL) of 500 ppm were set at least in part to protect against the cumulative toxic effects of benzene.[16]

With few exceptions, the acute toxic effects of methanol exposure are the same regardless of the route of exposure.[50] These symptoms, all related to systemic toxicity, occur in three stages.

1st: Depending on the amount ingested, the first symptom is intoxication similar to that with ethanol.

2nd: This is followed by a latent period of 10-48 hours in which no symptoms occur.

3rd: If the exposure was significant (large) enough, and treatment was not received, the latent period is followed by a variety of symptoms including: headache, nausea, vomiting, violent abdominal pain, leg and back pain, blurred vision, sensitivity to light, and pain in the eyes. If the exposure were severe, symptoms can progress to severe impairment of vision, temporary or permanent blindness, coma, and possibly death as a result of respiratory failure or rarely circulatory collapse. If death does not occur, these symptoms may be followed by a prolonged recovery period with loss of strength, blindness, and impaired kidney function.[50,51,52]

The initial symptoms of overexposure to methanol result in a manner similar to that for ethanol. However, the symptoms following the latent period result from methanol's metabolites in the body.[53] Methanol is metabolized to formate, which is in turn oxidized to form CO_2 which is then exhaled.[50,54] However, the rate of metabolism of formate is slower than for methanol. Thus, if the level of methanol exposure is severe enough and/or of long enough duration, the body's ability to metabolize the formate is overwhelmed, causing formate buildup and acidosis of the blood with the subsequent symptoms of methanol exposure.[53,54] The minimum exposure to methanol which is estimated to challenge formate's rate of metabolism and, thus, the point at which the toxic symptoms following the latent period are expected to occur in humans, is approximately 210 mg/kg of body weight.[55] Correspondingly the minimum lethal dose of methanol in the absence of medical treatment generally ranges between 300 and 1000 mg/kg, while the dose often causing death ranges between 800 and 5000 mg/kg.[55]

Ingestion is the most common form of methanol poisoning in humans. There are no additional unique symptoms relative to ingestion. Metabolism of the methanol may be slowed and the

latent period extended if ethanol is ingested along with the methanol or within the first few hours thereafter. For the average adult male weighing 70 kg, toxic effects can begin with ingestion of as little as 18 ml (approximately 3 to 4 teaspoons) of methanol. Ingestion of larger amounts can cause blindness, and as little as 26 to 70 ml can be fatal. However, there are cases described where as little as 6 ml proved fatal while in other cases 500 ml has not resulted in any permanent damage, and the normally fatal dose ranges from 60 to 240 ml.

Methanol is considered to be a moderate skin and eye irritant.[56] Additional symptoms of acute toxicity relative to skin contact include defatting and a mild dermatitis on the skin, and prolonged or repeated exposure may cause eczema, redness, and scaling. The most severe symptoms occur if methanol is absorbed into the skin in significant quantities to result in the systemic toxicity discussed above. Methanol will absorb through the skin readily at an estimated rate of 0.2 mg/cm^2 per minute.[57] Momentary contact with it is not a large concern, but frequent or long term exposure can be. Immersion of a hand (with a surface area of roughly 440 cm^2) in methanol for three hours may cause toxic effects (roughly equivalent to a body concentration of 220 mg/kg), and immersion for four hours could potentially cause death. Acute eye contact with methanol has caused superficial corneal lesions, but the real hazard to the eyes is to the optic nerve as a result of methanol's metabolism as described above.

The symptoms related to acute inhalation of methanol vapor include irritation of the mucous membranes, headache, and mild eye irritation. Headaches have been reported to occur at concentrations between 17 and 385 ppm, while the first sign of eye irritation, eye sensitivity to light, may begin at concentrations as low as 2.5 ppm.[57] Prolonged exposure to high concentrations can result in the systemic toxic effects discussed above. In order for these toxic symptoms to occur, the ambient concentration of methanol for eight hours a day must typically be about 3000 ppm.[58] The TLV, however, is set much lower than this at 200 ppm, while the STEL is 250 ppm, and the level immediately dangerous to life or health is 25,000 ppm. To put inhalation into perspective with the other modes of exposure (assuming total absorption of the inhaled vapor), a 70 kg person breathing at twice the resting rate (20 m^3/day), who is exposed to 150 ppm of methanol vapor for 15 minutes accumulates a methanol body concentration of 0.6 mg/kg, which is at least 500 times less than the minimum lethal dose.[55] For comparison, the average person consumes anywhere from one-half to two and one-half times this amount through the consumption of fruits, vegetables, and alcoholic beverages in the diet everyday.[55] Using similar assumptions, the concentration would have to be nearly 20,000 ppm in order to achieve the minimum fatal dose (300 mg/kg) with exposure for 1 hour. The majority of methanol taken into the body is purged within a few hours, and usually completely gone in 10 to 16 hours.[59]

Available peer-reviewed literature does not provide conclusive evidence of any long-term low-level chronic effects associated with exposure to methanol.[53] The belief that methanol is not toxic with low-level, long-term chronic exposure is supported by the fact that methanol occurs naturally in the body at a level of approximately 0.5 mg/kg (ranging from 0.2 to 5.0 mg/kg) as a result of natural metabolic processes, occurs naturally in the atmosphere in minute concentrations, and is present in our daily diet.[55] The average daily intake of methanol in the diet through ingestion of fruits, vegetables, and alcoholic beverages is estimated at 0.3 to 1.1 mg/kg with a 99th percentile as high as 3.4 mg/kg. In addition, just one can of a diet softdrink sweetened with aspartame amounts to the ingestion of roughly 0.3 mg/kg (See Table 4).[55]

A few studies have suggested possible neurobehavioral, central nervous system, reproductive, or developmental effects of exposure to methanol at concentrations at or substantially above methanol's TLV.[62] The most plausible chronic effects of methanol exposure are probably reproductive and developmental due to methanol's similarity to ethanol, and the known effects of ethanol in these areas.

M85, due to its newcomer status, has not been studied in any detail, but its toxicity is expected to be merely a combination of that for gasoline and methanol, with the precise effects dependent on the type of exposure.[56] Since both methanol and gasoline are central nervous system depressants, the methanol may serve to enhance the toxic effects of gasoline just as ethanol does.[40]

Relative to ingestion, since gasoline comprises only 15 percent of the volume of M85, only if extremely large amounts are ingested will the acute systemic toxic effects of gasoline ingestion be expected to occur. However, it may be possible in some situations, especially if regurgitation occurs, for enough gasoline to be aspirated into the lungs where it could potentially result in death (See discussion of gasoline toxicity). Typically, the main concern with M85 ingestion will result from the 85 percent of it which is methanol, for which the discussion above applies. In instances where regurgitation occurs shortly after ingestion, however, the chances of any methanol poisoning are greatly reduced.

The area of skin contact is an area where synergistic effects of methanol and gasoline on the toxicity of M85 are currently expected to occur. Testing done with M85 has shown that methanol's rate of absorption into the skin is higher than with M100 alone, thus representing a higher likelihood for systemic toxic effects.[63] It is hypothesized that this may be due to the gasoline content drying out the skin allowing the methanol to be absorbed more readily. Aside from this aspect M85 is not known to cause any unique effects with respect to skin or eye contact.

Table 4

Methanol Body Burden for Selected Situations
Extracted from Health Effects Institute Information[55]

Exposure Scenario	Assumed Condition	Added Body Burden of Methanol
Minimum Lethal Dose		300 mg/kg
Personal Garage	600 mg/m^3, 15 min. Twice resting breathing rate	1.8 mg/kg[a]
	100 mg/m^3, 5 min. Twice resting breathing rate	0.1 mg/kg
	100 mg/m^3, 5 min. Resting breathing rate	0.03 mg/kg
Self-Service Refueling	50 mg/m^3, 4 min., Twice resting breathing rate	0.04 mg/kg
12-Ounce Diet Beverage	555 mg aspartame/l	0.3 mg/kg[b]
Dietary Intake of Aspartame (w/o diet beverages)	Normal Diet	0.3-1.1 mg/kg/day
Background Body Burden		0.5 mg/kg[c]

a. Assumes all inhaled methanol absorbed across respiratory epithelium; in all probability, less (appx. 60 percent of inhaled) is absorbed.[60]
b. Assumes all aspartame-derived methanol crosses gut mucosa instantaneously; because of the time required for hydrolysis and transport, peak measured levels reach 70-75 percent of the value in the table.[61]
c. Based on value of 0.73 mg/l of blood.[60]

With respect to inhalation, since roughly two-thirds of the vapor produced by M85 exposed to the atmosphere is gasoline hydrocarbon (See flammability discussion), the acute toxic effects of M85 are expected to most closely resemble those of gasoline. Nevertheless, if the exposure is severe enough, it is possible that symptoms caused by both exposure to gasoline and methanol may develop.

Long-term chronic effects of exposure to M85 is also expected to be most similar to that for gasoline. Due to the limited amount of work done with M85, there is not a TLV specified strictly for M85.

Exposure and Overall Risk Assessment

As discussed above, all of the fuels are toxic to humans, but in order to perform an appropriate comparison between the fuels it is necessary to take into account not only the fuel toxicity itself, but also the potential exposure to the fuel. In addition, traits of the fuel such as odor, taste, and color all become important for immediate detection of possible toxic hazards.

Ingestion

Ingestion represents the most likely cause of serious acute toxicity due to the ability to get large quantities of fuel into the body quickly. All of the fuels pose a toxic threat if a sufficient amount of fuel is ingested.

Despite its wide use as a fuel, little information was found in the literature relative to ingestion of diesel fuel, possibly due to the fact that it is handled by a limited number of people in a limited number of applications. In addition, its strong taste, color, and odor may tend to discourage accidental and intentional ingestion.

Due to the offensive nature of gasoline (i.e., taste and odor), one would not expect gasoline ingestion to be common. However, due to its widespread use and large number of applications there are many instances in which accidental ingestion occurs. It has been estimated based on American Association of Poison Control Centers (AAPCC) information that there are 35,000 incidences of gasoline ingestion annually.[64] Roughly 39 percent of these instances are as a result of siphoning accidents, while an additional 36 percent occur as a result of accidental exposure to children under 6 years of age.[64] Most of the pediatric exposures are related to improper storage of gasoline in and around the home or to storage of fuel for use in lawn and garden applications. Despite the large number of ingestions, the amount typically ingested is apparently small since only 16.4 percent of reported incidents are managed by a health care facility, and

only 2 percent experience a "moderate" or "major" (life threatening) medical outcome.[64] Despite the number of severe exposures, only one known death occurred in 1987 which may have been attributable to gasoline ingestion.[64] Siphoning accidents, though likely to result in toxic symptoms, are not likely to result in death (unless aspiration occurs), since the average "mouthful" of fluid is only approximately 80 ml (range of 55 to 110) while the usually fatal dose ranges from 115 - 180 ml to 470 ml.[38,41,64]

AAPCC data reveal that in 1987 there were 1601 reported incidences of acute exposure to methanol (all exposures, no differentiation was made in the data between ingestion and other types of exposure).[64] These exposures are likely to have resulted from ingestion or skin contact to canned heat, de-icers, duplicator fluid, gas-line antifreeze, paint strippers and removers, model airplane fuels, pipe sweeteners, or windshield washing fluids. Roughly 53.2 percent of these exposures were treated in a health care facility, however, only 5.575 percent resulted in "moderate" or "major" health effects (0.375 percent in death).[64] Since these exposures are not related to the use of fuel in motor vehicles, it is difficult to compare these data with that for gasoline.

Based on the available information, it has been estimated that the number of fatalities due to ingestion of motor fuels would increase by as much as 195 per year if methanol were to replace gasoline.[64] It was further assumed, however, that this number could be significantly reduced if certain precautions are taken in the implementation of methanol as a fuel.[64] Some of these precautions will require specific action on the part of authorities, but others will likely be an automatic part of a methanol fuel program. If methanol vehicles are equipped with flame arresters on the fill pipe and vents to minimize the ignition hazard, most siphoning accidents should be precluded. If methanol is not used in lawn mower applications (or marine applications) then the exposures associated with such a use should also not occur. These include siphoning exposures to adults attempting to obtain fuel for lawn mower use, and pediatric exposures associated with lawn mower refueling containers located in areas accessible to small children. In addition, methanol being a polar substance is not an effective solvent for oils and greases which are non-polar. As a result, the ingestions resulting from gasoline stored in and around the home for this purpose should also not occur as frequently with M100. Educational efforts, fuel additives to provide distinguishing characteristics such as taste, odor, and/or color to pure methanol, and other methods may also be effective at minimizing the risks associated with methanol fuel ingestion.

As historical data have shown, however, methanol may be more likely to be ingested intentionally than the other fuels. Although it causes a burning sensation in the mouth and

irritates the gastro-intestinal system, M100 does not have an unpleasant odor or taste, nor will it typically cause regurgitation. Therefore, M100 presents no natural barriers to intentional drinking. In addition, since methanol has no taste, color, or odor to identify it, it has the potential to be ingested unintentionally more readily than the other fuels. Although there is an effective treatment for methanol ingestion, it will not be given unless the person knows he/she has the need for it. For these reasons there have been a number of different additives proposed for M100 to give it taste, odor, and color.[19,65,66] To date, the most common additives to methanol for fuel use in the United States have been the addition of various hydrocarbons as in M85. Much smaller amounts than 15 percent gasoline can accomplish this task, however, with some estimates stating that as little as 1 to 2 percent hydrocarbon can deter against its ingestion.[67]

M85 possesses a taste, color and odor similar to that of gasoline. However, for many of the same reasons as for M100, it is not as likely to be ingested. Siphoning from motor vehicles should be prevented if flame arresters are used, and its presumed lack of use in lawn/garden applications will reduce the frequency of ingestion by children. It is expected that M85 will not be as good a solvent for oils and greases as gasoline since most of it is methanol (a polar substance vs non-polar for oils and greases). Thus, its availability in and around the home is likely to be less than with gasoline today. As a result, despite the fact that toxic concerns with M85 result from both its methanol and gasoline fractions, as long as appropriate precautions are taken, the frequency of exposures is expected to be lower than for gasoline today.

Skin and Eye Contact

There are many possible instances in which people may come into direct bodily contact with these fuels. Some are accidental such as spitback while filling a fuel tank, while others involve negligent use of the fuel such as use as solvent to clean oil stained hands. As discussed earlier, all of the fuels can result in toxic effects, but due to the short term nature of most skin contact, acute effects tend to be much more rare than with ingestion. In addition, for the general public, skin contact is not likely to be a frequent enough event to result in chronic effects.

Little information was found in the available literature concerning the frequency of skin and eye contact with diesel fuel. It has been suggested by persons involved with the heavy-duty diesel vehicle industry that diesel fuel tends to be handled rather carelessly due to its low flammability. If this is indeed the case, then the incidences of skin contact may be unproportionately high compared to its sales volume. However, the toxicity information presented earlier suggests that the

effects of skin and eye contact tend to be less severe with diesel fuel than with the other fuels and, thus, the overall hazard may nevertheless be small.

Due to gasoline's wide use, any situation which allows for skin contact may represent a significant problem nationwide. Of the 13,028 exposures to gasoline reported to the AAPCC in 1987, roughly 11.4 percent were due to skin contact, and 19.5 percent due to eye contact.[64] However, only 1.6 percent of the dermal exposures and 1.1 percent of the ocular exposures resulted in "moderate" effects, and only 1 dermal and 1 ocular exposure resulted in "major" effects (no deaths were reported).[64] The most likely event leading to acute dermal toxic effects (or even possibly chronic) with gasoline is its misuse as a solvent for cleaning oils and greases from the hands. Splashes on the skin evaporate quickly and, if infrequent tend to be of little concern. (Some components of gasoline evaporate slowly, but these are often washed off due to the unpleasant odor of gasoline.) Except in the case of a severe accident resulting in massive and prolonged dermal contact (in which case all the fuels would be likely to cause death), only with continued and/or severe misuse as a solvent is exposure likely to be severe enough or frequent enough to result in the toxic effects discussed above.

Methanol's use as a motor vehicle fuel will also result in skin and eye exposures. However, since it is not a good solvent for cleaning oils and greases due to its polar nature, and since it is not as likely to be used in other applications (lawn mowers, boats, etc.), the frequency with which skin and eye contact occur is likely to be less than with gasoline. In addition, since its toxicity relative to the skin or eye is not significantly greater than that of gasoline, the number of cases with "moderate" or "major" effects seen with gasoline in the AAPCC data is not expected to be significantly greater with methanol. Splashes on the skin evaporate quickly, and as a result are not of long enough duration to be of concern. Only if methanol is maintained in contact with the skin such as with methanol soaked clothing are concerns likely to arise. Nevertheless, since methanol does not have a distinctive odor or color which might tend to deter against frequent intentional or careless skin contact, or speed cleanup of accidental skin contact, additives such as odorants, colors, or dyes to methanol in addition to educational efforts, may be beneficial.

The situation relative to skin and eye contact with M85 should be virtually the same as with M100. As discussed above, M85 may be absorbed through the skin slightly faster than M100, but in most situations this is not a significant difference. Also, M85 may be a slightly better solvent for greases and oils, and as a result possibly also more likely to be used on the hands for this purpose. However, M85 possesses the odor of gasoline, and as a result an additive for this purpose may not be necessary.

Inhalation

Inhalation of fuel vapors can represent a serious health hazard. Although the number of exposures by inhalation is large, seldom is it to a high enough concentration or of a long enough duration to result in acute toxicity. The most common instances where acute inhalation exposure to motor vehicle fuels are known to occur today are in intentional abuse situations such as "gas sniffing", and in personal accident or spill situations where exposure to high concentration is maintained for long periods of time. The largest risk from inhalation of motor vehicle fuels may come as a result of possible long-term chronic exposure. Thus, even low concentrations in the background air we breathe can conceivably be a toxic hazard.

The extremely low volatility of diesel fuel causes there to be concern of acute toxicity due to inhalation only in situations such as an individual lying in or near a pool of diesel fuel, or if a heating source is vaporizing the fuel. Thus, only chronic concerns are likely with diesel fuel. Although it may be possible that diesel fuel is a weak to moderate carcinogen with long-term chronic exposure based on skin painting bioassay tests, once again, due to the extremely low volatility, exposures tend to be very minor, and any possibility of chronic effects is minimized.[38,40]

The properties of gasoline (high volatility, low diffusion coefficient, and high vapor density) suggest that acutely toxic concentrations of vapor would be more common with it than with the other fuels. Despite this, natural ventilation apparently limits exposures except in the most severe circumstances. Sampling performed in the breathing zones of persons at service stations revealed that time weighted exposures were 8.2 ppm or less, and when averaged over the entire working day were less than 2 ppm.[68] Only approximately 8.3 percent of the 13,028 exposures to gasoline reported to AAPCC in 1987 were inhalation related, and of these just 5.1 percent (60) resulted in "moderate" effects and 0.4 percent (5) resulted in "major effects". In addition, one death was reported as a result of gasoline "sniffing", and one death possibly related to inhalation.[64] Most reported instances of severe inhalation exposure are as a result of either intentional abuse as with gasoline sniffing or direct exposure to spills.[64]

Low concentration exposures to gasoline are extremely common (refueling, vehicle exhaust, ambient air, etc.). While these events are typically not of an acutely toxic concern, they may be of a chronic concern. Gasoline vapor is considered by EPA to be a group B2 probable human carcinogen which was estimated to result in as many as 68 incidences in 1986, and is suspected of causing various other chronic effects (See earlier discussion).[69] In addition, gasoline vapor contains benzene,

a group A human carcinogen which was estimated to cause as many as 155 cancer incidences in 1986 (as will be discussed later, roughly 70 percent of these are projected to be due to benzene in vehicle exhaust, with the remainder due to evaporative and refueling emissions and other direct emissions).[73] As a result, the chronic effects of gasoline inhalation exposure far outweigh the acute effects.

Due to a similar use pattern, the frequency of inhalation exposure with M100 may be similar to that with gasoline today. Due to methanol's much lower volatility, however, the level of exposure is expected to be much lower; 30 percent by volume of that for gasoline based on volatility alone. (The actual concentration will be a strong function of the specific situation.) In addition, the high diffusion coefficient and low vapor density of methanol tend to limit concentrations and speed their dispersion. Based on this information, and discussion of the AAPCC data on gasoline earlier, it appears that the situations most likely to result in acute exposure with gasoline are less likely to occur with M100. It is not expected to be abused as is gasoline (gasoline sniffing), and it should be less prone to flow into low areas where it may accumulate, or stay along the ground where already unconscious people may be exposed. Most other likely exposures, as with gasoline, are not expected to be significant enough to lead to acute toxic effects. The time weighted average methanol concentration in the breathing space of attendants refueling methanol vehicles is roughly just 2 ppm.[50] The results of modelling done for a variety of other situations (street canyons, roadways, tunnels, personal garages) using emission rates from malfunctioning methanol vehicles (first generation, low technology vehicles compared to the vehicles likely to be introduced in the future) reveal that only in the worst case situation (malfunction idle in a personal garage) is the ambient concentration expected to exceed the STEL. However, since the TLV is based on an 8 hour exposure, and the garage scenario exposure lasts for only approximately 15 minutes, the TLV is not exceeded.[70] Thus, as shown in Table 4 the expected body burden caused by even the worst case scenario still only produces an exposure less than one-hundredth the minimum lethal dose. In addition, it is much more likely that the TLV for carbon monoxide (CO) will be reached before that for methanol. Testing done in the LA garage where M85 vehicles have been operated for a number of years demonstrated that concentrations of CO reached levels as high as 30 percent of the TLV, while those for methanol were less than 1 percent.[71,74]

Since chronic effects are not presently considered to result from exposure to low levels of methanol, and since it is not considered to be carcinogenic, even though some exposures related to vehicle exhaust emissions may be slightly more severe with methanol, the toxic risk is expected to be much

less. In the few studies which have suggested that some chronic effects may exist with methanol similar to those that exist with ethanol, the concentration has typically been well above normal exposures, and has greatly exceeded the expected ambient concentration of less than 1 ppm.[74]

Despite the lack of situations leading to toxic exposure, a unique concern with methanol is that it does not have a distinctive odor at the concentrations at which it can be a health hazard. Thus, a person could be inhaling a toxic concentration of methanol without knowing it until the symptoms (mucous membrane irritation, eye irritation, headache - refer to earlier discussion) began to show. Estimates vary widely on what the odor threshold is for methanol with some estimates as low as 3.3 ppm and other estimates as high as 6000 ppm, but a reasonable estimate is probably approximately 2000 ppm.[57] This is ten times the level of methanol's TLV, but is still below the minimum concentration thought to be capable of causing acute methanol toxicity (3000 ppm). To alleviate this potential problem, there has been some consideration of the addition to the fuel of odorants. A wide variety of possible odorants exist; including gasoline in very low concentrations.

M85, once again, appears to represent a compromise between M100 and gasoline. Due to a similar usage pattern the types of exposures may be similar to those for gasoline, but due to its lower volatility, the level of exposure should be lower; 77 percent by volume of that for gasoline based on volatility alone. Roughly two-thirds of "M85 vapor" is composed of gasoline hydrocarbon, and as a result, exposed M85 fuel produces roughly 90 percent by volume of the methanol vapor as does M100, and 50 percent by volume of the gasoline hydrocarbon vapor as does gasoline.[73] (Note that actual emissions can be quite different from these estimates as they will vary depending on the specific situation.) M85 also represents a compromise in its vapor dispersion properties, but is probably most similar to gasoline due to the large fraction of "M85 vapor" which is gasoline hydrocarbon.

Also, as a result of the large fraction of vapor which is gasoline hydrocarbon, the practice of "gasoline sniffing" is not eliminated. In addition, high concentrations of gasoline hydrocarbon may build up in low areas or along the ground. But since less gasoline hydrocarbon is given off from M85 than from gasoline, acute effects from exposure are less likely than with gasoline.

Chronic effects resulting from exposure to M85 may be of greater concern than the acute effects. The cancer risk of M85 is expected to be in proportion to the fraction of emissions which are gasoline hydrocarbon. Based on the above discussion, the hydrocarbon portion of "M85 vapor" is estimated to be approximately 50 percent of that from gasoline, thus, roughly

50 percent of the cancer incidences estimated to result each year from exposure to gasoline vapor may also be expected with M85. Due to the high aromatic content of M85's gasoline fraction (roughly 40 percent compared to approximately 30 for standard gasoline), benzene emissions from M85 should represent a proportionately greater fraction of the hydrocarbon emissions. Incorporating the greater fuel volume requirement for M85 (roughly 65 percent) results in the conclusion that roughly 68 percent of the evaporative and refueling benzene emissions from gasoline and 68 percent of the cancer incidences associated with them should also be expected to occur with M85. The actual number could be even higher due to the greater tendency for benzene to evaporate when mixed with methanol.[40,75]

ENVIRONMENTAL HAZARD

Each year billions of dollars are spent in an effort to clean or maintain various aspects of the environment. Without such expenditures we would pay a penalty either in public health or quality of life. Of this money, a significant amount goes toward cleaning up the land, water and air due to leaks, spills and emissions from petroleum fuel sources. If another fuel is to replace petroleum, it too will have to be evaluated on this basis. If it proves much less hazardous, it could be a great economic and social benefit. If it proves much more hazardous, it may deter its implementation.

Emissions

Motor vehicle emissions are a primary source of air pollution, particularly in metropolitan areas, and the problems which they cause are a real concern when considering a new fuel. In fact, the ability of methanol to reduce one of our most severe air quality problems today, ozone, is the main reason why EPA is interested in methanol as an alternative fuel. The effectiveness of methanol at reducing the ambient levels of ozone is currently the focus of a great deal of effort both within EPA and elsewhere. Due to the complexity of the topic, it will not be addressed further in this report, but the reader is instead referred to references 74, 76, and 77 for further information. Other emissions such as carbon monoxide (CO), carbon dioxide (CO_2), the oxides of nitrogen (NO_x), and the oxides of sulfur (SO_x) will also be impacted to some degree with the use of methanol instead of gasoline or diesel fuel. In most cases the impacts are favorable toward methanol. The discussion of these emissions, however, is also left for other studies. The emissions which will be briefly discussed here, are those which are considered to be air toxics (particulate, benzene, formaldehyde, and 1,3 butadiene). Since a large portion of the exposures of the general public to motor fuels is from inhalation of the products of combustion in the exhaust of the vehicles, these emissions are of great importance in assessing the toxicity of the different fuels (evaporative emissions were addressed earlier).

Particulate

Particulate emissions lead to poor visibility, soiling of anything it precipitates on, and more importantly can cause premature mortality, aggravation of bronchitis, and reversible declines in lung function. For these reasons EPA has set a national ambient air quality standard for particulates smaller than 10 microns in diameter.[78] Particulate emissions from mobile sources represent approximately 15 percent of the national emission inventory, and are likely the most troublesome emissions from diesel vehicles. Particulate emissions from diesel vehicles are typically 20 to 100 times greater than from gasoline, M100, or M85 vehicles, and are a particular concern from buses and trucks that operate primarily in urban areas where public exposure is very high. Particulate in the exhaust of diesel vehicles results from the incomplete combustion of the heavy hydrocarbons in the fuel, and is composed of elemental carbon and a wide variety of condensed and/or adsorbed fuel and lubricant components and other varied combustion products.[69] Over 90 percent of diesel particulate is less than 1 micron in diameter and is thus small enough to be inhaled and deposited deep within the lungs.[69] The organics adsorbed onto diesel particulate have been found to be mutagenic in a variety of bioassays. In addition, testing with rats has shown that when diesel exhaust is inhaled chronically at high concentrations it results in lung cancer in rats. Based on these studies, diesel particulate was estimated to have resulted in 176 to 860 incidences of cancer in 1986, but as shown in Table 5 this is expected to decrease substantially already by 1995 as a result of EPA's more stringent particulate standards.[69] To add additional perspective to the problem of diesel particulate, it is worth pointing out that diesel fuel represents only approximately 20 percent of the total motor fuel consumption in the United States.

A gasoline vehicle emits far less particulate than a diesel vehicle, and what is emitted is far less noticeable since it is difficult to see with the naked eye. Nevertheless, particulate emissions from gasoline (also known as the products of incomplete combustion) are considered to be mutagenic and possibly carcinogenic, and were estimated to cause from 1 to 176 cancer incidences in 1986 depending on the method used (See Table 5).[69]. The main concern with gasoline particulate emissions appears to result from high molecular weight organics such as polycyclic aromatic hydrocarbons (PAHs) including benzo(a)pyrene.

Due to M100's simple chemical structure, and lack of impurities and additives, carbonaceous particles, PAHs, and other products of incomplete combustion (PICs) are not as likely to form with the combustion of M100 as with gasoline and diesel fuel. In fact, it is mainly the potential for significant particulate emission reductions which is causing

Table 5

Summary of Risk Estimates.[a, 69]

Motor Vehicle Pollutant	U.S Cancer Incidences/Year[b] 1986	1995[c]
Diesel Particulate	178 - 860	106 - 662
Formaldehyde	46 - 86	24 - 43
Benzene	100 - 155	60 - 107
Gasoline Vapors	17 - 68	24 - 95
Other Gas Phase Organics		
1,3-Butadiene	236 - 269	139 - 172
Acetaldehyde	2	1
Gasoline Particulate	1 - 176	1 - 156
Dioxins	ND[d]	ND
Asbestos	5 - 33	ND
Vehicle Interior Emissions	ND	ND
Cadmium	<1	<1
Ethylene Dibromide	1	<1
Total	586 - 1650	355 - 1236

---

a The risk estimates are 95% upper confidence limits.

b The risk estimates for asbestos, cadmium and ethylene dibromide are for urban exposure only. Risks for the other pollutants include both urban and rural exposure.

c The total risk in 1995 is slightly underestimated. Due to inadequate information and the sensitivity of future risk to control decisions which have not yet been made, projected risk estimates were not made for some of the pollutants.

d ND = Not Determined.

NOTE: The risk estimates are upper bound estimates; therefore, they are not intended to represent actual numbers of cancer cases but rather can be used to rank the mobile source pollutants and to guide further study.

Taken in its entirety from reference 69.

the heavy-duty industry (particularly the urban transit bus industry) to consider methanol as an alternative fuel. Some particulate emissions may occur with methanol due to factors such as the incomplete combustion of lubricating oils, but the magnitude of these emissions (as well as those resulting from any potential additives) in production vehicles and their carcinogenic risk is yet to be determined. Due to the concentration of gasoline in M85 and the particulate emissions associated with it, a fraction (as of yet not completely established) of the cancer incidences associated with gasoline can also be associated with M85.

Benzene

As discussed briefly earlier in the paper, benzene emissions represent a serious health hazard due to their carcinogenic potential. Based on several epidemiology studies which demonstrated its potential to cause leukemia in humans, EPA has classified benzene as a group A human carcinogen. Annual incidence estimates associated with all motor vehicle related benzene emissions range from 100 to 155 for 1986 (95th percentile confidence limit) but are projected to decrease to 60 to 107 by 1995 as hydrocarbon emissions are controlled (See Table 5).[69]

Eighty-five percent of all benzene emissions (and hence also incidence estimates) are estimated to be motor vehicle related, and 97 percent of these are estimated to be gasoline related (only 3 percent diesel fuel related).[69] Of the 85 percent, roughly 70 percent comes from the exhaust, while 14 percent are evaporative emissions, and 1 percent refueling emissions. Benzene occurs in the exhaust of gasoline vehicles mainly as a result of the incomplete combustion of benzene and other aromatics in the liquid fuel. Hence, any fuel which contains either benzene or aromatics is expected to result in significant benzene exhaust emissions.

M100 contains no benzene or other aromatics, and therefore is not expected to cause any benzene related cancer incidences.

M85 contains 15 percent of a highly volatile, high aromatic gasoline. Thus, M85 contains approximately 6 volume percent aromatics of which approximately 0.3 volume percent is benzene. In addition, due to the lower heat of combustion of M85, roughly 65 percent more fuel will have to be used to get the same mileage. Based on this and the fuel concentrations, as much as 35 percent of the benzene emissions and related cancer incidences that occur as a result of the exhaust of gasoline vehicles may also occur if M85 vehicles replace gasoline vehicles. Actual benzene emissions and related cancer incidences, however, will be a strong function of the design of the production M85 vehicles.

Formaldehyde

Formaldehyde, a colorless pungent gas, is a common emission from many different combustion processes. Even small concentrations of formaldehyde may irritate exposed membranes of the eyes, nose, and respiratory tract, and may cause various other acute effects including headaches, nausea, and possible death. Formaldehyde is not expected to result in systemic toxic effects under any expected exposure scenarios. Due to its potency as an irritant, formaldehyde has a very low TLV of 1 ppm, and a STEL set at 2 ppm. However, a level of concern of 0.5 ppm has been chosen by EPA for future work.[72] Since formaldehyde's odor threshold for most individuals ranges from 0.08 to 0.4 ppm, concentrations of a toxic concern should be detectable. Based on various animal and human epidemiology studies formaldehyde is classified by EPA as a group B1 probable human carcinogen.

Roughly 50 to 90 percent of ambient formaldehyde is estimated to result from photooxidation in the atmosphere of other hydrocarbons from motor vehicles (including exhaust, evaporative, and refueling emissions). Approximately 35 percent of this is estimated to occur as a result of the combustion of fuels in motor vehicles, since motor vehicles are responsible for about 35 percent of total hydrocarbon emissions.[69] Only 10 to 50 percent of ambient formaldehyde is estimated to be directly emitted formaldehyde.[79] However, since 91 percent of the human exposure to formaldehyde is estimated to be due to indoor formaldehyde (formaldehyde is used in many industrial applications and is emitted from many common construction materials and home furnishings), current mobile sources are estimated to contribute only about 3 to 4 percent to an individual's total exposure to formaldehyde, and direct motor vehicle emissions of formaldehyde less than 2 percent.[79] Despite the small fraction of formaldehyde exposure which is attributable to mobile sources, the annual incidences of cancer associated with that exposure is estimated to be rather large. As shown in Table 5, all mobile source (both gasoline and diesel) related formaldehyde was estimated to result in 46 to 86 incidences in 1986 (decreasing to 24 to 43 by 1995).[69]

Formaldehyde emissions from gasoline vehicles are roughly 1 to 4 percent of the total hydrocarbon emissions depending on vehicle class.[69] For well maintained, late model, light-duty gasoline vehicles this corresponds to approximately 4.4 mg/km.[79] Despite this relatively low emission rate, modelling of public and private garage scenarios indicates that concentrations approaching and exceeding levels capable of causing acute toxic symptoms are possible. However, exposures in these situations are typically of short duration and thus not usually a serious concern. As discussed above, much of the ambient formaldehyde (and thus carcinogenic hazard) associated

with gasoline vehicle emissions occurs as a result of the photooxidation of the other highly reactive hydrocarbons emitted in the exhaust (as well as evaporative, and refueling emissions).

Despite the fact that overall hydrocarbon emissions are lower with diesel vehicles than with gasoline vehicles, the direct formaldehyde emissions in the exhaust are estimated to be roughly 2 to 3 times those from gasoline vehicles because they do not utilize catalysts.[79] However, due to the decrease in total hydrocarbon emissions, the total ambient formaldehyde contribution (including photochemically generated formaldehyde) of a diesel vehicle may not be significantly greater than that for a gasoline vehicle.

Very little information exists on formaldehyde emissions from production M100 vehicles. One data source that does exist is on heavy-duty bus engines. This information suggests that engine-out formaldehyde emissions from current technology M100 vehicles may be as much as 10 times that from comparable diesel vehicles (i.e., as much as 20 to 30 times that from comparable gasoline vehicles), but with the use of a proper catalyst (possible with methanol due to the small amount of particulate matter in the exhaust), the formaldehyde emissions can be as low or lower than from comparable diesel vehicles.[79] On the other hand, if formaldehyde emissions from M100 vehicles are assumed to be similar to those from M85 vehicles (for which most LDV information exists), then formaldehyde emissions from light-duty M100 vehicles is roughly 3 to 7 times that of comparable gasoline vehicles.[79]

Despite the increase in engine out formaldehyde emissions from methanol vehicles over that from gasoline vehicles, modelling suggests that the low reactivity of methanol in the atmosphere causes ambient concentrations of formaldehyde to be similar with M100 and M85 vehicles to those with gasoline vehicles.[74] Thus, there is not expected to be a significant change in mobile source formaldehyde related cancer incidences with the substitution of methanol for gasoline as the primary motor fuel.

1,3-Butadiene

1,3-Butadiene is a photochemically reactive compound which is estimated to comprise 0.35 percent of gasoline vehicle exhaust.[69] Based on animal data, 1,3-butadiene is classified by EPA as a group B2, probable human carcinogen. As shown in Table 5, mobile source 1,3-butadiene emissions were estimated to result in 236 to 269 cancer incidences in 1986, but this number is projected to decrease to 139 to 172 by 1995.

Due to the difficulty in measuring 1,3-butadiene separately from n-butane, until recently data on actual emissions from current gasoline vehicles was extremely scarce,

and it remains scarce with diesel vehicles. In addition, nothing has yet been published as to the concentration of 1,3-butadiene in the exhaust of M100 and M85 vehicles. However, due to the general lack of hydrocarbon emissions in the exhaust of methanol vehicles, 1,3-butadiene is not expected to represent as large of a fraction of methanol vehicle exhaust as gasoline vehicle exhaust.

Leaks and Spills into Water

Leaks and spills of hazardous materials into water are a common occurrence and represent a potentially significant environmental hazard. Often spills on land drain into lakes, rivers, and streams, where the effect is the same as if the spill had occurred directly into the water. In addition, since much of the transportation of petroleum fuels is done over oceans and rivers, the chance for massive spills from tankers and barges also exists.

The effects of petroleum spills and petroleum-derived fuels on aquatic environments are fairly well known - oil films stretching for miles, ruined beaches, surface fires, dead fish and water fowl, and many more.[80] While petroleum fuels are for the most part not soluble in water and, as a result, spread out over long distances on the surface in a thin layer, some components are soluble in water and are extremely toxic to aquatic life.[81] In 1957, a tanker spill of diesel fuel in a small bay in Mexico resulted in near total destruction of the bay, and other spills have resulted in destruction of commercial fishing grounds.[81] In addition, many of the toxic effects of petroleum fuels on aquatic life not killed by exposure are not reversible and remain for years. An estimate of the retention time of soluble petroleum components in coastal marshlands of France following a tanker spill is considered conservative at 7 to 12 years.[81] These long-term effects follow extensive cleanup operations involving containment of the spill using physical barriers, suction-pump recollection, chemical surfactant dispersal, detergent application, or absorption to straw, floating pellets, or other material, and later removal or degradation of larger residue. Since the majority of gasoline components evaporate readily, the need for extensive spill cleanup may not be as necessary as with other petroleum fuels; however the heavier components evaporate much more slowly.

In general, methanol is significantly less toxic to marine life than petroleum fuels, and many of the effects of short-term exposure are temporary and reversible.[82] Most aquatic life can survive concentrations of less than one volume percent of methanol for brief periods of time (some as high as 10 percent), although few can survive long term exposure to 500 ppm.[82,83] Since methanol is infinitely soluble in water, a spill in open water disperses rapidly, especially in situations

with strong currents, tidal action, and wave action. As a result, concentrations outside the immediate spill area tend to remain below toxic concentrations, and even in the spill area, the toxic concentrations are short-lived (although severe). Simulation of a large-scale (10,000 ton), open-sea, methanol spill revealed that the concentration near the spill site would be reduced to less than 0.36 percent within an hour of the spill.[84] A similar simulation of a 10,000 kl/hr spill on a coast (at a pier) revealed that even in the severe case where the wind was blowing toward the coast, the concentration was less than 1 percent at the spill site within 2 hours after the spill was stopped and 0.13 percent after 3 hours.[84] If these results are extrapolated to rivers, the methanol concentration can be expected to be reduced even faster due to the greater effects of currents and eddys.

In addition to its rapid dispersion, complete elimination from the environment occurs as a result of methanol's rapid biodegradation (decomposition of methanol as a result of natural processes). There is a wide variety of naturally occurring marine and terrestrial microbes which metabolize methanol.[85] As a result, recolonization of methanol spill sites is very rapid (a matter of months) with no long-term effects, while the effects of petroleum spills may require years to disappear.[82] Part of the explanation for the comparative resilience of aquatic habitats to methanol may be due to the fact that methanol occurs naturally in both drinking and surface water and, as such, is not a foreign substance to these environments.

Cleanup of methanol spills on water should not require the extensive efforts and costs associated with petroleum fuel cleanup and is generally much more effective. Small spills usually do not require cleanup, but rather require only monitoring and isolation of the area for several days, allowing natural biodegradation to complete the task.[82] Larger spills require the removal of dead organisms, and cleanup may be accelerated by aerating the water to promote aerobic (as opposed to anaerobic) degradation and/or inoculating the water with nonpathogenic bacteria, such as the naturally occurring Pseudomonas fluorescens, which metabolize methanol.[81,82]

M85 has not been studied in any detail, but it is not likely to be an advantage over M100. When spilled in the water, the methanol portion will dissolve into the water and quickly disperse as with M100 while the majority of the gasoline components will rise to the surface where they can evaporate (and/or be cleaned up). Those gasoline components that are water soluble will act exactly as with gasoline with the exception that there is much less of them (although a greater fraction of the gasoline in M85 will likely dissolve in the water due to the cosolubility with methanol [18]).

Leaks and Spills on Land

Leaks and spills on land arise from a wide variety of sources. Many of these are minor, involving the spillage of only a few gallons or less of fuel such as from small fuel containers or vehicle fuel tanks. Other instances which are of more concern involve spills from overturned tanker trucks, leaks from pipelines, or leaks at refineries, fuel terminals, or well sites. Among the more frequent spills on land are those from underground storage tanks. These alone accounted for 12,444 reported incidences of release between 1984 and 1986, and most releases are never reported.[85,87]

Gasoline and diesel fuel are very toxic to terrestrial plant and animal life. Since they are composed of many different compounds including many additives, their toxicity, fate, and transport in soil is extremely variable. Once spilled, they are retained in the soil by capillary forces, by adsorption onto soil particles, by evaporation in soil air, and by dissolution in soil water.[88] Their main route of dissipation is through evaporation. Since diesel fuel evaporates much more slowly relative to gasoline, much more of the spilled fuel will be absorbed into the soil tending to make its effects of longer duration. A wide variety of organisms exist in the soil which can degrade hydrocarbons. Degradation rates vary depending on the soil acidity, nutrient content, temperature, moisture content, and oxygen content.[88] Oxygen content is the dominant variable, since, although some studies indicate that anaerobic degradation occurs, it is at a significantly slower rate than aerobic degradation.[88] Aerobic conditions can quickly become anaerobic once degradation begins and the available oxygen is used up, especially if the soil is near saturation with water. In addition, the products of anaerobic degradation may themselves be toxic.[88] Thus, absolute recovery of soil ecosystems contaminated with gasoline or other petroleum fuels is a very slow process which can last for years as a result of slow degradation and disruption of successional organisms.[89]

Because of the slowness of the natural processes, damage from leaks and spills of petroleum fuels is in large part a function of the rate and extent to which cleanup efforts are undertaken.[40] However, the cleanup of a petroleum spill site is difficult, and itself can last for years. The most common technique for land cleanup is excavation of the contaminated soil with subsequent disposal at a land fill site.[88] Although still controversial, the use of biorestoration may be a preferable alternative since it eliminates the contamination, not merely transferring it to a new medium. It also does not require massive soil removal, but may instead require extremely long periods to complete cleanup. Due to the expense of such spill cleanup processes, many spills in the past have not been cleaned up and have merely been left to the natural processes of dissipation.

M100, like the petroleum fuels, is very toxic to plant and animal life. Grasses, mosses, and other plants are quickly killed by surface saturation with methanol; and few of the organisms in the spill area can withstand even brief exposure to high concentrations of methanol.[81,83] However, the toxic effects of an M100 spill are much shorter lived than for petroleum fuels for a variety of reasons. First, M100 evaporates completely much more quickly than diesel fuel and even quicker than gasoline (gasoline's heavier components evaporate slowly). This causes less fuel to be absorbed into the soil, and thus, less fuel must undergo decomposition. Second, M100 is completely water soluble, and as a result, disperses to non-toxic concentrations much faster than petroleum fuels. Third, M100 is easily decomposed both aerobically and anaerobically by naturally occurring micro-organisms living in the soil which move into the area following a spill.[90,91] As a result, analysis of the lateral and vertical movement of methanol spills shows penetration to be limited to the immediate spill area.[81] Fourth, M100 occurs naturally in the environment in low concentrations, causing many organisms to be more tolerant of it than of petroleum fuels. As a result, growth can return to a spill site before the methanol is entirely dissipated.

Experimental information shows that much of the subsoil life has returned to a spill site just one week following surface saturation with M100.[81] As much as 90 percent recovery of subsoil life is possible within 3 weeks with M100, as opposed to 50 percent recovery in 3 to 12 months with gasoline spills.[20] In a field study, methanol applied to the surface of a scattered black-spruce heath community disappeared within one week as a result of evaporation, percolation, and biodegradation.[91] In an effort to assess just the biodegradation rate of methanol, soil samples taken at various depths at three different locations in the United States were contaminated with methanol. Results indicated that methanol concentrations of 1000 mg/l added to soil placed in sealed tubes (no dispersion, or influx of oxygen or additional microbes) would degrade to non-measurable levels in less than a year, and complete degradation of 100 mg/l in 30 to 60 days.[92] As with gasoline, aerobic degradation of methanol is more rapid than anaerobic, but both are apparently much faster than with gasoline.

Since the effects of a methanol spill are generally of short duration, nothing is typically done to clean up a spill site. If, however, the spill is massive, and a cleanup period faster than that of the natural process is required, the techniques used for cleanup of petroleum spills on land should also be effective (as long as groundwater is not affected), including injections of the various methanol decomposing bacteria.[89]

Unfortunately, since M85 is a new fuel there have been no studies conducted to determine its actual impacts on land. However, M85 would appear to be more hazardous than M100 and possibly even gasoline. This is evidenced by the results of a field study in which the return of vegetation was slower following a low level methanol blend spill than with either gasoline or M100.[19] Not only may the methanol carry the gasoline further distances, causing more to enter the soil rather than evaporating, but also some of the methanol decomposing bacteria may be totally intolerant of gasoline.[82,90] The result is a larger area which may be affected by both the gasoline and the methanol and a longer time over which both components remain toxic.

Groundwater and Drinking Water Contamination

One of the major threats of spills to both land and water is that the fuel will contaminate groundwater and other drinking water supplies. Roughly half of the United States' drinking water is supplied by groundwater, including all or part of the drinking water for 34 of the 100 largest cities.[87,93] Although spills have been one of the more visible environmental threats, leaks from underground storage tanks is probably of greater importance to groundwater. There are an estimated 796,000 underground storage tanks in the U.S. today.[86] New York state and Maine have estimated that at one point as many as 19 and 25 percent respectively of their underground gasoline tanks were leaking.[93] Of the 12,444 reported incidences of release of material from underground storage tanks between 1984 and 1986, an estimated 45 percent involved leaks to the groundwater.[86] Thus, more than 70,000 underground storage tanks may be leaking to groundwater, and an estimated 29 percent of the drinking water supplied to large cities is contaminated with volatile organic compounds.[93]

Due to the strong odor and taste of petroleum fuels, even concentrations as low as 1 ppm can render drinking water supplies unpalatable.[93] Thus, even small leaks or spills can ruin large water supplies. In addition, thirteen compounds commonly found in gasoline are regulated as hazardous chemicals under the Comprehensive Emergency Response, Compensation and Liability Act (CERCLA) due to their toxic nature.[88] Most gasoline and diesel fuel components are not soluble in water (only 25 to 250 mg/l for gasoline) and, as a result, float on top of the water in the underground aquifer. However, benzene, toluene, and xylene, (BTX), three of the hazardous chemicals regulated under CERCLA, represent the majority of the soluble fraction of gasoline in water.[18] Although expected to occur, biodegradation of gasoline and diesel fuel in the relatively anaerobic conditions of an underground aquifer is very slow.[88] Therefore, contaminated areas will remain so for long periods of time.

Cleanup of petroleum spills to groundwater takes two forms, both of which are necessary if groundwater is to be used as a drinking source. The first stage of cleanup consists of removing undissolved gasoline from the upper level of the aquifer (free product plume) through the use of trenching with skimmers or filter separators, or the use of a pumping well system with oil/water separators.[88] The second stage consists of removing hydrocarbons dissolved in the water through the use of air stripping towers or carbon adsorption, or both, although biorestoration is also receiving increased attention for this purpose.[88] Given proper design and implementation, all of these techniques can ideally remove greater than 99 percent of the spilled fuel, however, it may be years before the effectiveness approaches this level. Carbon adsorption also lends itself for use in removing small concentrations of dissolved hydrocarbons in the water at the point of entry into homes.[88] The level of cleanup necessary is that which will achieve compliance with the current and proposed drinking water standards for benzene, toluene, and xylene are 5 ug/l (5.65 ppb), 2.0 mg/l (2.3 ppm), and 0.44 mg/l (0.51 ppm), respectively.

Biorestoration of groundwater involves the addition to the contaminated aquifer of indigenous microorganisms that have been selectively adapted or genetically altered to degrade gasoline components dissolved in groundwater (at present still a very controversial technique). Biorestoration tends to be oxygen limited and, as a result, various pumping, injection, and circulation pumping systems that mix the contaminated water with oxygen, nitrogen, phosphorus, and growth substrates are needed in addition to the microorganisms.[88]

Due to its relatively short-term effects on aquatic and terrestrial life, the main concern of methanol spills relates to the possibility that concentrations toxic to humans may occur in groundwater and other water supplies used for drinking water. Unlike the petroleum fuels, since methanol is not considered to be carcinogenic and is not presently known to result in long-term effects due to chronic exposure to low level concentrations, high concentrations in groundwater capable of causing acute toxic effects are the major concern, although EPA is evaluating possible adverse effects of low concentrations. Since methanol dissolves completely in water, high concentrations may be possible; and, since M100 has no odor, taste, or color, potentially toxic concentrations will be undetectable (although drinking water supplies are not rendered unpalatable). If it is assumed that toxic effects begin with exposure to 210 mg/kg of methanol, that the maximum average water intake of an adult is two liters per day, and that this is all ingested in 8 hours, then the methanol concentration in the drinking water would have to be roughly 9200 ppm in order for toxic symptoms to occur. To receive the minimum lethal dose of 300 mg/kg, the corresponding water concentration would

have to be roughly 13,000 ppm. Methanol concentrations of this magnitude in drinking water derived from either surface water or groundwater are not expected under any credible scenario, however.[90] As discussed above with open water spills, methanol's complete solubility in water combined with naturally occurring currents, dispersion, and biodegradation cause concentrations to fall below 1300 ppm within 3 hours in even the most severe situations. In cases where drinking water supplies are derived from groundwater, due to the rapid evaporation and biodegradation of methanol, spills on land tend to remain localized and, due to its susceptibility to aerobic and anaerobic biodegradation, groundwater contamination problems should be minimal.[81,92]

With the exception of biorestoration, the cleanup techniques used for groundwater contamination with gasoline are not expected to be effective for cleaning up methanol contamination.[18,94] Because methanol is completely soluble in water, there is not expected to be a large free product plume that can be removed with the use of trenches or pumping techniques. In addition, methanol's water solubility, polarity, and low molecular weight render air stripping and carbon adsorption techniques ineffective.[88] Fortunately, due to its speed of biodegradation, methanol contamination may often be removed naturally faster than gasoline contamination using active cleanup techniques. In addition, biorestoration techniques similar to those being developed with gasoline may cause methanol cleanup to be even quicker.

While these findings are encouraging, it is clear that further study is necessary to determine if in fact under certain extreme conditions concentrations toxic to humans may be possible in groundwater. If this possibility cannot be precluded, it may be necessary to add components to the fuel such as a dye to provide an identifiable characteristic to drinking water if it contains a toxic concentration of methanol.

Due to the uncertainty in our understanding of groundwater processes and the lack of information with M85, it is difficult to assess the relative hazard of M85 to that of the other fuels. Once in the groundwater, M85 should separate into free gasoline, which floats on top of the groundwater, and methanol (along with small concentrations of certain gasoline components) dissolved in the groundwater itself.[94] For a number of reasons, the actual gasoline contamination may be greater than might first be expected. In limited testing the addition of just 20 percent methanol to gasoline caused the amount of naphthalene (a component of gasoline) retained in the soil (and thus able to move to groundwater) to decrease by more than half.[18] In addition, since methanol is water soluble and gasoline is cosoluble with methanol in water at low concentrations of water, the gasoline in M85 may be carried further distances, causing groundwater to be affected more

frequently.[86,90] Limited testing has also demonstrated that the solubility of xylene and naphthalene in water is increased by 266 percent and 335 percent, respectively, with the addition of just 20 percent methanol to gasoline.[18] Thus, the effect of M85 on groundwater may be more severe than with either M100 or gasoline.

Cleanup techniques for removing M85 contamination from groundwater will likely involve the techniques used for gasoline. Due to the presence of the gasoline, the potential problem related to the inability to detect even toxic concentrations of methanol in groundwater should no longer be of concern. Although not yet confirmed, the taste and odor of the gasoline should serve as an adequate warning and is likely to persist in the groundwater at least as long as the methanol.

SUMMARY AND CONCLUSIONS

Transportation fuels affect many aspects of our lives. As a result, safety concerns with those fuels are important when considering changes to the Nation's transportation system. Thus, the recent emphasis on methanol as an alternative to gasoline and diesel fuel raises questions as to the effect methanol would have on public and environmental safety.

The largest public safety and environmental health concerns with transportation fuels today result from the flammability of gasoline and long-term inhalation exposure to air toxic emissions from gasoline and diesel vehicles.

Methanol fuels (particularly M100) can go a long way in reducing the risks associated with today's fuels. Only a fraction of the fires that occur with gasoline today are likely to occur with M100, and the frequency and severity of serious personal injury and property damage with the fires which do occur will tend to be lower. In addition, available information suggests that a large share of the cancer incidences estimated to occur as a result of emissions from today's motor fuels would also not occur with methanol fuels (especially M100).

Despite these safety advantages, there are also safety concerns and uncertainties unique to methanol which will need to be addressed if methanol is used as a fuel. One such concern is the lack of a luminous flame when M100 burns in certain situations. Based on available information, the fraction of M100 fuel fires which will be invisible is not expected to be large, but further study is necessary to properly quantify this. In addition, the added hazard which an invisible flame represents and the effectiveness of additives to enhance the luminosity of M100 fires also need to be studied further in order to properly quantify the hazards of methanol fires. Recent research has produced promising results with luminosity additives, which if successful could completely eliminate any concern over flame invisibility.

A second unique concern with M100 is that due to its low volatility and high flammability limits it is flammable inside fuel tanks. Although a valid concern, it is nevertheless a concern with solutions. Available information suggests that, since ignition sources are limited in fuel tanks, ignition is not expected to be a frequent occurrence, and that a number of fuel tank design precautions, such as the use of flame arresters and modified in-tank electrical devices, can be taken to limit even further the chance for ignition. Additional information suggests that, were ignition to occur, the severity of the explosion is much milder than might be expected, and once again proper fuel tank designs may be able to minimize much of the risk. For these reasons, any potential increase in risk with M100 resulting from fuel tank flammability can be minimized through the utilization of proper vehicle design considerations on the part of motor vehicle manufacturers.

The third area where concern may arise with the substitution of M100 for petroleum fuels is accidental ingestion of the fuel. M100 is tasteless, odorless, and colorless, and toxic if small amounts are ingested. These properties have led to projections of large increases in injuries and fatalities resulting from accidental ingestion if M100 replaces gasoline unless certain precautions are taken. Precautions likely to be part of any methanol fuel program include: requiring the use of flame arresters on vehicles to prevent many siphoning related exposures; preventing the use of pure methanol in lawn and garden applications to eliminate many siphoning and pediatric exposures; adding compounds to methanol to provide a taste, color, or odor; and instituting a public education program. In addition, properties of methanol itself such as its low solubility with oils and greases will limit its misuse for these purposes and reduce accidental exposures. Thus, the societal risk of ingestion of motor fuels should not be significantly greater with M100 than with gasoline.

In addition to human health and safety concerns, there are a number of environmental safety concerns which exist today with petroleum fuels. Spills of fuel onto land and into the water result in serious disruption of plant and animal life in the spill areas, sometimes for many years. Spills which impact groundwater can prevent its use as a drinking water supply for many years due to palatability, long-term toxicity concerns, and slow natural biodegradation. Although cleanup is possible, cleanup to EPA's current and proposed drinking water standards may also take years and incur great costs.

In comparison, although also toxic to plant and animal life, the effects of M100 spills onto land and into water are comparatively short lived, especially with spills into water. Relative to spills which effect drinking water, it would appear that there is a tradeoff between the long-term toxic effects and palatability concerns with gasoline and the potential for

severe short-term toxic effects if high concentrations of methanol occur in groundwater which is used as a drinking water supply. Due to the lack of hydrogeologic information relative to methanol, it is not yet known whether its concentration in groundwater would be likely to reach toxic concentrations, but the speed at which it biodegrades may result in faster natural cleanup of M100 contamination than invasive cleanup of gasoline contamination. In addition, it may be possible to add compounds such as dyes to methanol to provide a recognizable characteristic to groundwater should a potentially toxic concentration exist.

Based on the available information, in all the areas discussed above M85 would appear to represent a compromise between gasoline and M100. M85 is not nearly as effective as M100 at decreasing the frequency of fire which exists today with gasoline, and its concern relative to air toxics, while less than for gasoline and diesel fuel, is greater than with M100. However, M85 burns with a luminous flame, and is not expected to be flammable in fuel tanks in typical situations. Relative to ingestion, accidental ingestion patterns will likely be similar to those of M100, with the added benefit that the gasoline fraction serves as an effective odorant and taste deterrent. Less toxic additives, however, can be found to serve the same purposes in M100. In groundwater most concerns with M85 are likely to result from the long-term effects of its gasoline fraction. The lack of available information, however, limits the certainty of these conclusions.

The most important conclusion to be drawn is that the magnitude of the potential safety benefits with M100 coupled with the ability to minimize many of the concerns should result in improved overall public and environmental safety with the use of M100 instead of petroleum. The difference between M100 and M85 is less clear, but M100 is likely more advantageous in terms of overall risk. Although a significant amount of work remains to be done in many areas before firm conclusions can be drawn, the unresolved issues do not appear to be serious enough to prohibit the use of methanol as an alternative fuel to petroleum.

REFERENCES

1. Statements by Ford Motor Company, General Motors, and Chrysler Motors before the House Subcommittee on Energy and Power, June 17, 1987.

2. "Is There a Government Role in Methanol Market Development," Barry D. McNutt, E. Eugene Ecklund, SAE Paper No. 861571.

3. "Summary and Analysis of Comments Regarding the Potential Safety Implications of Onboard Vapor Recovery Systems," Office of Mobile Sources, U.S. EPA, August, 1988.

4. Memorandum: "Analysis of Fuel Tank-Related Fires," from Kathleen A. Steilen, Standards Development and Support Branch, to Charles L. Gray, Jr., Director, Emission Control Technology Division, U.S. EPA, April, 1987.

5. "A Technical Assessment of Alcohol Fuels," Alternative Fuels Committee of the Engine Manufacturers Association, SAE Paper No. 820261, February, 1982.

6. "Methanol Fuel Manual: General Guidelines for the Use of Methanol Fuel by Transit Properties, Draft," ABACUS Enterprises LTD for the Florida Dept. of Transportation, March, 1986.

7. MVMA Gasoline Surveys, 1982-1988.

8. "Material Safety Data Sheet: Diesel Fuel Oil No. 2-D", Occupational Health Services, Inc., September, 1985.

9. Safe Handling and Testing of Alternative Fuels," Mueller Associates for the U.S. DOE Alternative Fuels Utilization Program, January, 1982.

10. "Methanol: Technical Literature," Arco Chemical Co., 1983.

11. MVMA Diesel Fuel Surveys, 1982-1988.

12. "The Transport of Methanol by Pipeline", U.S. Department of Transportation, April, 1985.

13. "Material Safety Data Sheet: Gasoline/Automotive". Occupational Health Services, Inc., September, 1985.

14. Explosibility of High Methanol Fuel Blends," Sebastian I. Amadi and E. Earl Graham, Dept. of Chem Engr, Pennsylvania State University, Ind. Eng. Chem. Prod. Res. Dev., 1983, 22, 500-505.

15. "Tag Closed Cup Flash Points and Lower Flammable Limits of Nearly Neat Methanol Fuels," D.J. Gordon, Celanese Chemical Company, Inc., March 1985.

16. Assessment of the Safety of Transportation, Distribution and Storage of Methanol Fuels," R.F. Webb for Transport Canada, September, 1988.

17. "Comparative Safety of Methanol-Fueled Buses in a Tunnel Environment," Arthur D. Little Inc., for Triborough Bridge and Tunnel Authority, ADL Ref. 60219, December, 1987.

18. "Groundwater Contamination by Methanol Fuels," Bruce J. Bauman, Ph.D., Presentation at the Methanol Health and Safety Workshop, South Coast Air Quality Management District, November 2, 1988.

19. "Alcohol and Alcohol Blends as Motor Fuels", Vol. IIA, IIB, Swedish National Board for Technical Development, 1986.

20. "Assessment of Methane-Related Fuels for Automobile Fleet Vehicles," Energy Conservation Directorate, The Aerospace Corporation, For U.S. DOE, DOE/CE-50179-1, February, 1982.

21. "Recent Canadian Research Initiatives on Methanol Safety," Pat Hallett, Canadian Dept. of Transport, Presentation at the Methanol Health and Safety Workshop, South Coast Air Quality Management District, November 2, 1988.

22. "Ignition Risks of Hot Surfaces in Open Air," API, API PSD 2216, July 1980.

23. "Study of Motor Vehicle Fires," Prepared by Data Link Inc., for the National Highway Traffic Safety Administration, February, 1988.

24. MVMA Gasoline Fuel Survey, 1984.

25. "A Predictive Study for Defining Limiting Temperatures and their Application in Petroleum Product Specifications," John P. Doner, Coating and Chemical Laboratory, NTIS AD-756420, November, 1972.

26. "Characterization of Emissions from a Methanol Fueled Motor Vehicle," Richard Snow, et. al., 39, 48-54, 1989.

27. "Spilled Fuel Ignition Sources and Countermeasures", N. Johnson, et. el, Ultrasystems Inc., Prepared for NHTSA. September, 1975.

28. "Comparative Safety of Methanol and Conventional Fuels," Presentation by Vittoria Battista, Transport Canada, at the Fifth Windsor Workshop on Alternative Fuels, June, 1989.

29. "An In-Depth Study of Truck Fire Accident Data," James O'Day, Robin Ruthazer, Tom Gonzalez, The University of Michigan Transportation Research Institute, UMTRI-85-17-1, April, 1985.

30. Presentation by Vittoria Battista, Transport Canada, at the Fourth Windsor Workshop on Alternative Fuels, June, 1988.

31. Fire Protection Manual, Ed. C.H. Vervalin, 3rd edition.

32. "Methanol as a Fuel: A Review with Bibliography," David L. Hagen, University of Minnesota, SAE Paper No. 770792.

33. "Investigation into Methanol Fuel Formulations," Morrie Kirshenblatt and Matthew A. Bol, Sypher Mueller International Inc., SAE Paper No. 881599.

34. BP Oil Company, June, 1989.

35. "Feasibility Study on the Utilization of Neat Methanol (M80-M100) Fuel for Automobile in FY1985 (Abstract)", Volumes 1 and 2, Nomura Research Institute, January, 1986.

36. Letter to Richard D. Wilson, Director of Office of Mobile Sources, from Donald R. Buist, Director, Automotive Emissions and Fuel Economy Office, Ford Motor Company. November 26, 1986.

37. "Safety Aspects of the Use of Alcohol Fuels in Road Vehicles," A. Larson, E.W. Simmons, J.A.B. Athey, Ontario Research Foundation, Final Report No. 4439, September 12, 1986.

38. Information supplied by Chevron in response to the November, 1987 Draft Technical Report, "Methanol Fuel Safety: A Comparative Study of M100, M85, Gasoline, and Diesel Fuel as Motor Vehicle Fuels", Paul Machiele, EPA/OMS/ECTD/SDSB.

39. "Toxicology: The Basic Science of Poisons," Gasarett and Doulls. 2nd Edition, 1980.

40. Information supplied by API in response to the November, 1987 Draft Technical Report, Methanol Fuel Safety: A Comparative Study of M100, M85, Gasoline, and Diesel Fuel as Motor Vehicle Fuels, by Paul Machiele, EPA/OMS/ECTD/SDSB.

41. "Incidence of Siphoning-Related Gasoline Ingestion," Draft report, Battelle for EPA/OAR/OMS/ECTD/SDSB, February, 1989.

42. "Hydrocarbon Contact Injuries," J.F. Hansbrough et. al., The Journal of Trauma, Vol 25, No.3, March, 1985.

43. "Potential Health and Safety Impacts from Distribution and Storage of Alcohol Fuels," S.E. Rosenberg, J.R. Gasper, Argonne National Laboratory for U.S. DOE, June, 1980.

44. "Gasoline Intoxication," W. Machle, J. Amer. Med. Assoc., [1]: 1967-1971, 1941.

45. "Facts and Issues Associated with the Need for a Hydorcarbon Criteria Document," EPA/ORD Environmental Criteria and Assessment Office Internal Document, February, 1980.

46. "Toxicology of the Eye", Second Edition, W. Morton Grant, M.D.

47. Memorandum, "Review of MVMA comments on Gasoline Vapor Risk Assessment," From William Pepelko, Ph.D., Carcinogen Assessment Group, To Charles L. Gray, Jr., Director, Emission Control Technology Division, December 23, 1987.

48. "Kidney-Specific DNA Repair Assay: An Evaluation of Unleaded Gasoline," Chemical Industry Institute of Toxicology, Volume 6, No. 4, April, 1986.

49. "Gasoline Vapor Exposure and Human Cancer: Evaluation of Existing Scientific Information and Recommendations for Future Research" Special Supplementary Report, Health Effects Institute, January, 1988.

50. "Health Aspects when Dealing with Methanol," Dr. K. Hanisch, Presentation during the 27th DGMK-Main Assembly in Aachen.

51. "Material Safety Data Sheet: Methyl Alcohol", Occupational Health Services Inc., September, 1985.

52. "Clinical Toxicology of Commercial Products", Robert E. Gosselin, M.D., Ph.D., Harold C. Hodge, Ph.D., D.Sc., Roger P. Smith, Ph.D., Marion N. Gleason, M.Sc., Fourth Edition, 1976.

53. "An Evaluation of the Human Health Effects of Automotive Methanol Vapors," Dr. Kathleen Nauss, Health Effects Institute, Presentation at the Methanol Health and Safety Workshop, South Coast Air Quality Management District, November 2, 1988.

54. "Metabolism, Ocular Toxicity and Possible Chronic Effects of Methanol," Dr. Kenneth McMartin, Presentation at the Methanol Health and Safety Workshop, South Coast Air Quality Management District, November 2, 1988.

55. "Automotive Methanol Vapors and Human Health: An Evaluation of Existing Scientific Information and Issues for Future Research," Health Effects Institute, May 1987.

56. "A Critical Review of the Toxicity of Methanol Fuel," Dr. John Clary, Presentation at the Methanol Health and Safety Workshop, South Coast Air Quality Management District, November 2, 1988.

57. "Methanol Health Effects," Midwest Research Institute for EPA, EPA-460/3-81-032, December, 1981.

58. "Alcohols Toxicology", William W. Wimer, John A. Russell, Harold L. Kaplan, Southwest Research Institute, 1983.

59. "A Review of the Toxicity of Methanol", Dr. John J. Clary, Presented at the First International Conference on Methanol, May, 1983.

60. "Biological Monitoring of Persons Exposed to Methanol Vapors," V. Sedivec, et.al., Int. Arch. Occup. Environ. Health, 48: 257-271, 1981.

61. "Blood Methanol Concentrations in Normal Adult Subjects Administered Abuse Doses of Aspartame," L.D. Stegink, et.al., J. Toxicol, Environ. Health, 7: 281-290, 1981.

62. "Risk Assessment for Health Effects of Methanol Vapor," J. Michael Davis, Ph.D., EPA, Presentation at the Methanol Health and Safety Workshop, South Coast Air Quality Management District, November 1-2, 1988.

63. "The Percutaneous Absorption of Methanol after Dermal Exposure to Mixtures of Methanol and Petrol", D.G. Ferry, W.A. Temple, and E.G. McQueen, Proceedings, Fifth International Alcohol Fuel Technology Symposium, Volume 3, 1982.

64. "Acute Exposure to Methanol in Fuels: A Prediction of Ingestion Incidence and Toxicity," Dr. Toby Litovitz, National Capitol Poison Center, October 31, 1988.

65. Conversation with Ake Brandberg, Dr. Eng., Svensk Drivmedelsteknik AB, June 25, 1987.

66. Briefing to Charles L. Gray Jr., Director Emission Control Technology Division, EPA/OAR/OMS, by Angela Linder, Chemical Engineer, EPA/OAR/OMS/ECTD/SDSB, May, 1989.

67. "Methanol Fuel Modification for Highway Vehicle Use," Union Oil Company of California for U.S. Department of Energy, Final Report, HCP/W3683-18, July, 1978.

68. "Gasoline Vapor Exposures at a High Volume Service Station," Christine A. Kearney and David B. Dunham, Mobil Oil Corporation, Am. Ind. Hyg. Assoc. J. 47(8): 535-539, 1986.

69. "Air Toxics Emissions and Health Risks from Motor Vehicles," Jonathan M. Adler and Penny M. Carey, U.S. EPA, AWMA Paper No. 89-34A.6, July, 1989.

70. "Projected Air Concentrations of Methanol," Presentation by Penny M. Carey, U.S. EPA at the Health Effects Institute Workshop on Fetal Toxicity of Methanol and Carbon Monoxide, October 3, 1988.

71. "LA County Mall Garage Emissions Study," Ken Smith, Californian Energy Commission, Presentation to the Advisory Board on Air Quality and Fuels, December 1, 1988.

72. "Regulatory Support Document: Proposed Organic Emission Standards and Test Procedures for 1988 and Later Methanol Vehicles and Engines," EPA/OMS/ECTD/SDSB, July 1986.

73. "Characterization of Emissions from Vehicles Using Methanol and Methanol-Gasoline Blended Fuels," Peter A. Gabele, James O. Baugh, Frank Black, Richard Snow, JAPCA 35: 1168-1175, 1985.

74. "Quantitative Estimate of the Air Quality Impacts of Methanol Use," Armistead Russel, et.al., Carnegie Mellon University, for the California Air Resources Board, April, 1989.

75. Methanol Informational Brochure, Alberta Gas Chemicals Ltd.

76. "Motor Vehicle Emission Characteristics and Air Quality Impacts of Methanol and Compressed Natural Gas," Jeffrey A. Alson, Jonathan M. Adler, Thomas M. Baines, U.S. EPA, Office of Mobile Sources, Chapter 8 of a book published by Greenwood Press and Edited by Daniel Sperling, January, 1989.

77. "Effects of Emission Standards on Methanol Vehicle-Related Ozone, Formaldehyde, and Methanol Exposure," Michael D. Gold, Charles E. Moulis, EPA/OAR/OMS/ECTD/SDSB, APCA Paper No. 88-41.4, June, 1988.

78. "Revisions to the National Ambient Air Quality Standards for Particulate Matter," EPA Federal Register Vol 52, No. 126, pp. 24634-24750, July 1, 1987.

79. "Formaldehyde Emissions From Mobile Sources and Potential Human Exposures," Charles E. Moulis, U.S. EPA, AWMA Paper No. 89-34A.1.

80. "Preliminary Perspective on Pure Methanol Fuel for Transportation," EPA 460/3-83-003, September, 1982.

81. "Overview of Environmental Impacts from Methanol Fuel Spills", Dr. Peter D'Eliscu, West Valley College, 1981.

82. "An Environmental Assessment of the Use of Alcohol Fuels in Highway Vehicles," Argonne National Laboratory, December, 1980.

83. "Environmental Consequences of Methanol Spills and Methanol Fuel Emissions on Terrestrial and Freshwater Organisms," Dr. Peter Neal D'Eliscu, Department of Biology, University of Santa Clara.

84. "Toxicological Research of Methanol as a Fuel Power Station: Demonstration Tests for the Environmental Safety of Methanol," New Energy Development Organization.

85. Methanol as a Transportation Fuel: Assessment of Environmental and Health Research," Lawrence Livermore Laboratory, June 18, 1979.

86. "Technical Support Document: Methyl Tert-Butyl Ether," Draft Final, Michael W Neal, et. al., Syracuse Research Corporation for the Office of Toxic Substances, Feb, 1987.

87. "Underground Leakage of Hydrocarbons, An Overview of a Potential Fire Problem," Martin F. Henry, Fire Journal, March, 1981.

88. "Cleanup of Releases of Petroleum USTs: Selective Technologies," EPA/530/UST-88/001, April, 1988.

89. Letter to Charles R. Imbrecht, Chairman, California Energy Commission, from Dr. Peter D'Eliscu, Department of Biology, West Valley College, April 28, 1987.

90. Conversation with Dr. Peter D'Eliscu, West Valley College, July 20, 1987.

91. "Summary Review of Health Effects Associated with Methanol: Health Issue Assessment," Bryant and Parkinson, EPA/OAQPS, September, 1987.

92. "Biodegradation of Methanol and Tertiary Butyl Alcohol in Subsurface Systems," J.T. Novak et.al., Water Sci Tech, Vol 17, pp 71-85, 1985.

93. "Update on the Underground Leakage Problem,"Martin F. Henry, Fire Journal, January, 1986.

94. "Storage and Handling of Gasoline-Methanol/Cosolvent Blends at Distribution Terminals and Service Stations," API recommended practice, API Publication No. 1627, First Edition, August, 1986.

420-S-89-101