

**HEALTH AND SAFETY OF  
COMPETING FUEL OPTIONS  
FOR FUEL CELLS IN THE  
ROAD TRANSPORT SECTOR**

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## **EXECUTIVE SUMMARY**

This report presents a critical analysis of the health and safety issues surrounding competing transport fuel options, including those for possible future fuel-cell powered vehicles.

The fuels considered in this report are gasoline (unleaded and reformulated), diesel, hydrogen (H<sub>2</sub>), methanol, natural gas and liquefied petroleum gas (LPG). The analysis presented here is based on available information in peer-reviewed, published papers and other sources such as government department or research laboratory reports and websites. An overall evaluation of the fuels in terms of their toxicity and health effects, environmental fate, and fire and explosion safety aspects is presented. The report is based on current knowledge and makes no assumptions as to how fuels may change in the future if they are to be used in fuel-cell vehicles.

The report identifies the hazards of the fuels but does not estimate the risks likely to be associated with their eventual use in fuel-cell vehicles. The focus is on the fuels themselves and not their exhaust or reaction products. No assessment has been made of the environmental effects data for the fuels. Broad environmental considerations such as ozone forming potential and also global warming are not considered. Basic information on environmental fate is included to provide an understanding of migratory pathways, environmental compartmentalisation and potential routes of human exposure. Other factors such as economics, government incentives or disincentives and public attitudes may have a bearing on which of the fuels are considered most appropriate for future fuel-cell vehicles; these factors are not considered in any detail in this report.

### **Gasolines**

A number of potential health hazards are associated with exposure to gasoline fuels. Inhalation of gasoline at very high concentrations can cause coma and death; at lower concentrations the effects resemble alcoholic inebriation and mainly affect the central nervous system (CNS). Exposure to levels of gasoline vapour sufficient to cause such effects is unlikely in normal use. Aspiration of liquid fuel causes irritation and damage to the lung. Ingestion leads to irritation of the throat and digestive system, vomiting, colic and diarrhoea but is only likely to occur in accidental situations or following intentional ingestion. Dermal contact causes defatting of the skin. Repeated or prolonged exposure causes drying, cracking and dermatitis. Gasoline has been evaluated as possibly carcinogenic to humans, primarily based on its benzene and 1,3-butadiene content. Although studies in rats show gasoline induces kidney tumours, the mechanism by which this occurs is not thought to be predictive of human cancer risk.

Of the many compounds which may be found in current motor gasolines, six (benzene, xylene, toluene, methyl tertiary-butyl ether (MTBE), ethyl tertiary-butyl ether (ETBE) and ethanol) are considered in detail here. Benzene exposure has been linked (often in occupational settings) with bone marrow depression and leukaemias, particularly acute non-lymphoblastic leukaemia (ANLL). Relating low-level, long-term benzene exposure to leukaemia incidence is made difficult by the small number of leukaemia cases

encountered, even in occupational settings, and by uncertainties in exposure assessment. The benzene content of gasoline is being reduced gradually and in Europe is now less than 1%.

Exposure to high levels of xylene and toluene (alkylbenzenes) can cause CNS dysfunction. Most studies are occupationally based and, due to the lack of available information, the chronic effects of exposure to alkylbenzenes in gasoline remain uncertain. There is inadequate evidence for the carcinogenicity of either compound in humans and experimental animals.

Exposure to very high levels of MTBE (eg accidental exposure) can cause acute effects including headache, eye, nose and throat irritation and a range of other systemic effects. However, published studies on human populations do not indicate that exposures to MTBE in either occupational or environmental scenarios would cause acute or medium-term health effects in normal circumstances. Animal studies indicate that MTBE induces tumours at various sites but whether this is indicative of a human cancer risk is uncertain. It is thought that there is no case for assuming that inhalation of low levels of MTBE would be associated with a risk of cancer. During the preparation of this report no literature on the health effects of MTBE ingestion was identified. Dermal contact with MTBE can cause skin and eye irritation.

Acute exposure to ETBE in a single small volunteer study has shown that the compound causes throat and airway irritation, a bad taste in the mouth and slightly impaired lung function.

Ethanol affects the CNS and can cause mucous membrane irritation. Ingestion over long periods increases the risk of certain cancers but it is unlikely that such effects would be associated with exposure to ethanol as a gasoline constituent.

Gasoline is a complex mixture of hydrocarbon compounds which have differing properties and therefore different behaviours in the environment. If released to the open environment, the majority of compounds present in gasoline will evaporate to the atmosphere where they will be degraded by reaction with hydroxyl radicals in a matter of days. If gasoline is lost below ground, volatilisation will be much less significant and there is the potential for toxic compounds such as benzene to contaminate groundwater. The majority of gasoline released to soil will be biodegraded, although some higher molecular weight compounds with highly branched alkyl-chain components are recalcitrant. The oxygenates MTBE and TAME, present in reformulated gasoline, are readily transported in water and are not degraded, leading to concern about groundwater contamination.

Gasolines are extremely flammable and combustible liquids that can be ignited by heat, sparks or flames. The gasoline flashpoint is less than  $-40^{\circ}\text{C}$ , which means that, at normal temperatures, the fuel emits sufficient vapour to support combustion. Static charges built-up during bulk fuel transfer may be sufficient to ignite a fuel-air mixture within the flammable range, but normal vehicle re-fuelling is unlikely to build-up such charges. Also, effective mitigating measures such as equipment grounding and anti-static additives are commonly used.

## **Diesel**

Inhalation of high concentrations of diesel vapour can cause CNS depression but, because diesel is not particularly volatile (unless temperatures are high) inhalation exposure will normally be low. Based on the findings of a case study, it is evident that long-term exposure to high levels of diesel vapours can cause a range of gastrointestinal symptoms and renal failure. Aspiration of liquid diesel has been found to cause coughing, lung damage and other respiratory effects; in certain circumstances death may result. Ingestion of diesel is unlikely due to its odour and taste; however, possible effects are mouth, throat and gastrointestinal tract irritation. Dermal contact with diesel causes skin irritation, defatting and, over longer exposures, acne, folliculitis, eczema and hyperkeratosis; very high level exposure may reversibly affect renal function. A link between diesel exposure and cancer is uncertain; an epidemiological study of occupationally exposed workers found an increased risk of a lung and prostatic cancer but the study did not adequately account for other chemical exposures. Another study found no association between diesel exposure and renal-cell cancer.

Diesel is a complex mixture of hydrocarbons which have differing behaviours in the environment. If released to the environment the lower molecular weight fraction of diesel will partition to air where these compounds will be degraded by reaction with hydroxyl radicals in a matter of days. Aromatic and polar components of diesel can dissolve in water to varying extents and higher molecular weight compounds are anticipated to adsorb to soil and sediment. All components of diesel are biodegradable to varying extents but some polycyclic aromatic hydrocarbons (PAHs) can persist for a number of years. Some compounds in diesel would be anticipated to have a high potential for bioaccumulation, but the measured bioconcentration factors (BCFs) are generally lower than predicted.

Like all other fuels, diesel is flammable but its low volatility, low ignitability and high flashpoint mean it is potentially less hazardous than the other fuels considered in this report.

## **Hydrogen**

The extremely low boiling point of liquefied hydrogen ( $H_2$ ) presents particular difficulties for storing, transporting and handling this fuel. However, the primary attraction of  $H_2$  as a fuel is that the only product of its combustion or use in fuel cells is water (although nitrogen oxides ( $NO_x$ ) may be produced if the fuel is used in an internal combustion engine).

There are no known toxic effects, whether acute or chronic, associated with  $H_2$  exposure. However, if present in sufficient quantities, the gas can exclude enough oxygen to cause asphyxiation. The main health concerns relate to cryogenic burns from the liquid.

Any emissions of  $H_2$  to the atmosphere will be photo-oxidised to water and a small amount will escape through the atmosphere into space.

From a fire, explosion and general safety viewpoint, concerns relate to its high flammability across a wide range of fuel-air concentrations, its low minimum ignition energy (MIE), meaning it is easily ignited, and its propensity to

explode. A further safety concern relates to the low temperature at which liquefied H<sub>2</sub> must be stored and the high pressures at which compressed H<sub>2</sub> is stored (13.9 to 34.6MPa). This increases the need for careful engineering, maintenance and operating procedures in relation to its storage and distribution. Even a small leak from a pressure vessel may release a large volume of gas. A failure of an above-ground pressure vessel could cause damage to nearby properties and people. Current safety regulations and procedures mitigate the hazard of pressure vessel failures and boiling liquid expanding vapour explosions (BLEVEs). Furthermore, because pressure vessels must withstand high internal pressures, their mechanical strength makes them relatively more resistant to physical impacts. However, hydrogen can diffuse into the materials (particularly steel) in which it is stored and reduce their mechanical strength (hydrogen embrittlement).

Hydrogen is less dense than air and will naturally dissipate, unless confined by roofs or other constructions. Releases of liquefied H<sub>2</sub> may linger at or near ground level until sufficiently warm to rise and dissipate. The low temperature at which liquefied H<sub>2</sub> is stored necessitates particular health and safety precautions. The flame of burning H<sub>2</sub> is only visible at night making fire detection difficult. The gas is also odourless making leak detection difficult. However, it is currently not technically possible to add an odorant to liquefied H<sub>2</sub>, meaning leaks may go undetected.

### **Natural gas**

Natural gas is a simple asphyxiant with no other recorded toxic properties. From a health viewpoint, greater concern relates to the potential for cryogenic burns from liquefied natural gas (LNG).

The major component of natural gas, methane, is persistent in the atmosphere and has a lifetime of up to 12 years.

Any pressurised gas escaping from a container will undergo cooling, a hazard associated with compressed natural gas (CNG). In addition, CNG must be stored at high pressures (20-25MPa). At such high pressures, even a small leak can release a large volume of gas into the environment. Failure of an above ground pressure vessel could cause damage to nearby properties and people. Current safety regulations and procedures mitigate the hazard of pressure vessel failures and BLEVEs. Furthermore, because pressure vessels must withstand high internal pressures, their mechanical strength makes them relatively more resistant to physical impacts. Natural gas contains small amounts of CO<sub>2</sub>, hydrogen sulphide and water which, particularly under high pressure (ie with CNG), may be corrosive to steel storage vessels. Before compressing the gas it is necessary to treat and dry it to remove as much of these trace constituents as practicable.

Natural gas is less dense than air and will naturally dissipate, unless confined by roofs or other constructions. Cold, dense gaseous releases of LNG or CNG (if the latter has undergone pressure-release cooling) may linger at or near ground level for a time until sufficiently warmed to dissipate. The low temperature at which LNG is stored necessitates particular health and safety precautions.

The flame of burning natural gas is poorly distinguishable in bright light. The gas is also odourless, making leak detection difficult unless, as is now the case for natural gas supplies, an odorant is added. However, it is not technically possible to add an odorant to LNG, meaning leaks may go undetected.

### **Methanol**

Acute exposure to methanol, whether by inhalation, ingestion or dermal contact, produces a well-defined set of symptoms: CNS depression followed by an asymptomatic period of usually 12 to 24h and, finally, visual effects (blurred vision, changes to visual fields and, in severe cases, blindness). The acute toxicity of methanol is such that accidental ingestion (eg as a result of siphoning fuel from a vehicle) may be sufficient to cause acute effects and even death. Intentional ingestion would carry even greater risks. Chronic effects are qualitatively similar to acute effects. Whether toxic effects occur depends on whether methanol absorption exceeds the body's capacity to metabolise it. Methanol can be abused as an ethanol (alcohol) substitute.

Methanol is released to the atmosphere by evaporative emissions. Once there, methanol is estimated to have a half-life of 17.8d due to its reaction with hydroxyl radicals. Methanol is completely miscible with water, resulting in ready dilution in the presence of water, and is considered to be readily biodegradable in natural waters and soil.

The main safety concerns regarding methanol are its high flammability, wide flammability limits and relatively high flashpoint and low MIE. However, its lower flammability limit is greater than gasoline (7% compared with 1.4%) and it is also less volatile. Together, these attributes make methanol less likely to produce flammable fuel-air mixtures than the other liquid fuels. However, the high upper flammability limit of methanol means it is more likely to produce flammable fuel-air mixtures in air spaces above the fuel in storage tanks. Static charges built-up during bulk fuel transfer may be sufficient to ignite a fuel-air mixture within the flammable range, but normal vehicle re-fuelling is unlikely to build-up such a charge. Also, effective mitigating measures such as equipment grounding and anti-static additives are commonly used.

Methanol vapour is much heavier than air and, if accidentally released, may accumulate at floor level or in pockets in low lying areas. Furthermore, it is possible for the vapour to travel considerable distances to an ignition source and then flash back towards the source. In daylight, methanol burns with an invisible flame, unless a fuel additive is added or another combustible material is affected by the flame. Methanol is also corrosive, which necessitates careful decisions about the materials used for storing, transporting and transferring the fuel.

### **Liquefied petroleum gas (LPG)**

The health effects associated with exposure to LPG or its constituents (propane and butane) at high concentrations include direct asphyxia causing hypoxia, anaesthetic effects and cardiac sensitisation with the associated risk of sudden death. At concentrations above 100,000ppm (10%), effects include weakness, headache, light-headedness, nausea and other narcotic effects. Limited information is available on the chronic effects of LPG. Direct dermal contact with LPG presents a high risk of cryogenic burns.

Emissions of LPG will lead to the presence of propane and butane in the atmosphere where they are anticipated to be degraded relatively rapidly by reaction with hydroxyl radicals; propane and butane have half-lives of 13d and 6d respectively.

LPG is denser than air and thus will accumulate in places such as drains, trenches or other depressions. Because LPG is stored at pressure, a leak from a storage vessel may release a large volume of gas. A failure of an above ground pressure vessel could cause damage to nearby properties and people. Current safety regulations and procedures mitigate the hazard of pressure vessel failure and BLEVEs. Furthermore, because pressure vessels must withstand high internal pressures, their mechanical strength makes them relatively more resistant to physical impacts. Propane is odourless, making leak detection difficult unless, as is currently the case for LPG supplies, an odorant is added.

### **Overall evaluation**

All of the fuels considered in this report have inherent health and safety hazards but it is also the case that they are all currently used for a range of purposes. Regulations and standards are in place to help ensure their safe handling and use. However, introduction of some of the fuels into the road transport sector will require careful consideration to ensure they can be used safely by, for instance, individuals re-fuelling private vehicles.

Exposure to high levels of any of the fuels can cause acute health effects. These range from asphyxia associated with H<sub>2</sub>, natural gas and LPG (if levels are sufficient to exclude oxygen), to effects on the central nervous, respiratory and gastrointestinal systems associated with gasolines, diesel and methanol. Accidental or intentional ingestion of methanol can cause acute effects and even death at relatively low doses. The asymptomatic period that usually follows methanol exposure means that appropriate medical attention is often not sought.

Information is lacking on the chronic effects associated with the gaseous fuels, whereas the liquid fuels have been shown to potentially cause a range of chronic effects. Overall, however, health effects would only be expected in accidental situations, when health and safety procedures are not correctly applied, or when exposure is intentional, such as abuse of methanol as an alcohol substitute or the abuse of gasoline as a cleansing agent.

There is a large information base on the environmental fate of these fuels. However, the broad range of parameters that influence their environmental fate

and behaviour precludes an overall conclusion being reached as to the relative environmental hazards they may present. Situation-specific information would be necessary to consider the environmental risks associated with their widespread use in road transport. Gasoline and diesel losses to the environment will affect all environmental compartments while the gaseous fuels will only affect air. Methane and H<sub>2</sub> are the longest-lived of the fuels and may persist in the atmosphere for years. However, H<sub>2</sub> is not regarded as a hazardous pollutant as it is benign and naturally present at low concentrations. The other fuels (methanol and LPG) are less persistent, with half-lives measured in days. Only gasolines and diesel show any bioaccumulative potential.

All the fuels considered carry with them the inherent hazard of fire and explosion. Some also pose hazards due to the low temperature at which they must be stored (liquefied H<sub>2</sub> and LNG). For the compressed gases (CNG, LPG and H<sub>2</sub>), pressure is another hazard. Methanol is corrosive and H<sub>2</sub> can cause embrittlement, which requires careful consideration of the materials used in their storage, transport and use. Natural gas is not in itself corrosive, but trace constituents of the raw gas can be corrosive under pressure, unless they are removed before the gas is compressed. In addition, H<sub>2</sub>, natural gas and methanol all burn with poor flame visibility. For most of the alternative fuels (particularly the liquefied and compressed gases), introducing them into mainstream use, perhaps with members of the public re-fuelling vehicles, is an unknown scenario that will require careful consideration regarding the control of the hazards. It will be necessary to explore technological or operational ways in which to minimise the potential for exposure to these hazards. It should be noted, however, that there is a growing number of cars in the UK that run on Autogas (LPG) and an increasing number of Autogas re-fuelling points nationwide; to date the handling and use of LPG by members of the public has not given rise to serious concern.



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## **1 INTRODUCTION**

The aim of this report is to analyse critically the health and safety issues surrounding competing transport fuel options, including those for possible future fuel cell powered vehicles. This project has been conducted under the auspices of the Department of Trade and Industry (DTI) New and Renewable Energy Programme (NREP). A series of reports on the technological and economic aspects of fuel cells have also been produced within this programme and the reader is directed to the NREP website for further information<sup>1</sup>.

This report presents an assessment of the health and safety and environmental fate aspects of individual fuels, augmented by an overall evaluation of the fuels and recommendations for future work. The fuels included within the remit of the project are:

- unleaded and reformulated gasolines;
- diesel;
- compressed and liquid hydrogen (H<sub>2</sub>);
- compressed and liquid natural gas;
- methanol; and
- liquefied petroleum gas (LPG).

This report is based on peer-reviewed, published papers and articles identified through extensive literature searches conducted using the Medline, Toxline, Cancerlit and Embase on-line databases. The searches were primarily focused on literature published from 1995 onwards, although some relevant information from before this date was also used. Information presented in the report has been supplemented from other sources including company reports, government department websites and from internet searches.

A glossary of terms is provided at the end of this report. Information is presented in Appendix A on health and safety-related initiatives that may impact on the future uptake of specific fuels.

Experts representing fuel suppliers/distributors and motor manufacturers, independent scientists and Government Department representatives met to discuss the key issues relating to the health and safety of competing fuel options at a workshop held in Leicester on 13 September 2000. This report reflects those discussions but assumes no endorsement from any individual or group represented at the meeting for the conclusions and recommendations contained here. A list of the workshop participants is given in Appendix B.

### **1.1 Scope of the report**

This report is a first step in the process of assessing the relative health and safety risks associated with the use of various fuel options for fuel-cell vehicles. The report considers the health and safety hazards of the fuels listed above but makes no attempt at estimating the risks likely to be associated with

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<sup>1</sup> Information on the DTI New and Renewable Energy Programme available [June 2000] from <http://www.dti.gov.uk/renewable/index.html>

their eventual use in fuel-cell vehicles. The focus is on the fuels themselves rather than on exhaust or reaction products. As will be shown in subsequent sections, all the candidate fuels have inherent health and safety hazards some of which are well known and familiar. For detailed risk assessment, information is required on exposure scenarios (eg exposure levels resulting from vehicle re-fuelling activities), production volumes and use patterns, the composition of the fuels themselves, and so on. The current uncertainty about these issues precludes a risk assessment at this stage.

It is worth noting that all the fuels discussed in this report are currently in use, either as road transport, domestic heating or electricity generation fuels or for other purposes such as chemical feedstocks, and regulations and standards are in place to help to ensure their safe use.

The report does not address the detailed technology of fuel-cell vehicles, unless it has a bearing on the health and safety of the fuels themselves (eg the use of odorants and bitterants to aid detection of leaking fuels or colorants for fuel excise duty purposes may be incompatible with fuel cell technology).

While important in determining the relative hazards (and consequent risks) of the various fuels, broad environmental considerations (eg ozone forming and global warming potential) are not within the scope of this report. However, as a starting point, basic information about environmental fate is presented. This helps to inform our understanding of migratory pathways, environmental compartmentalisation and likely routes of human exposure to the fuels and their breakdown products.

As technical developments take place and regulatory requirements evolve, the exact composition, and hence hazards, of the fuels that may be used in the future will be different from that of today (this is particularly so for gasolines and diesel fuel). The report presents hazard information based on current knowledge and literature but does recognise that the situation is changing. For instance, gasolines for fuel-cell vehicles are unlikely to require additives such as MTBE to improve their combustion and exhaust emission performance. Furthermore, owing to regulatory requirements, the sulphur and benzene content of gasoline and diesel will also be reduced over time.

## **1.2 The fuel cell**

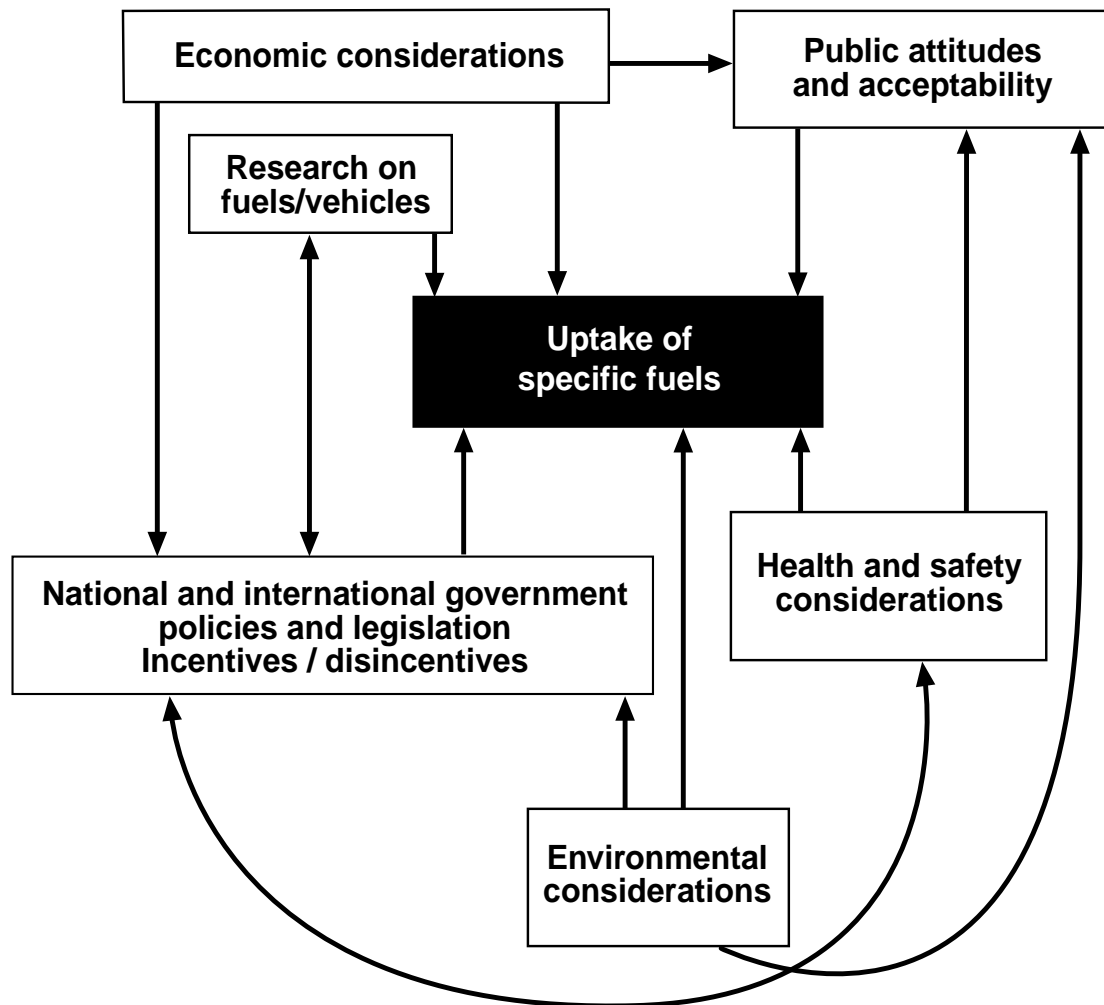
Like ICEs and batteries, fuel cells convert energy from one form to another. Fuel cells convert the chemical energy of a fuel directly into usable electricity and heat without combustion and produce a direct current but, unlike batteries, they use reactants (usually hydrogen and oxygen) that are external to the device and operate continuously as long as there is a supply of fuel. Like batteries, fuel cells have two electrodes separated by an electrolyte. As hydrogen flows into the fuel cell on the anode side, a platinum catalyst facilitates the separation of the gas into protons (hydrogen ions) and electrons. The hydrogen ions pass through the electrolyte between the electrodes while the electrons, which cannot pass through the electrolyte, flow through an external circuit (for instance a motor) to the cathode. At the cathode, hydrogen ions, oxygen and electrons combine, producing water. Each individual cell

produces less than 1v so a number of cells are combined in a stack to produce sufficient energy for the given application.

### **1.3 Factors affecting uptake of specific fuels**

This report focuses on the health and safety considerations that may affect the uptake of specific fuels. Figure 1.1 sets out a range of other factors that will also play a role in deciding which of the competing fuels is or are most appropriate for future fuel-cell vehicles.

**Figure 1.1 Factors that may influence the uptake of specific fuels for fuel-cell vehicles**



There is a large amount of on-going research in Europe and the US, both academic and commercial, that is exploring how fuel cell technology may be applied in the road transport sector<sup>2</sup>. As this research progresses and overcomes the hurdles inherent in developing new technologies, so there will come a point when it is necessary to establish standards to which commercial fuel-cell vehicles will be produced. This does not mean the technologies should be standardised, but that agreed codes may be required to which

<sup>2</sup> Researchers are also looking into other applications such as fixed power sources and combined heat and power systems.

vehicles and test procedures should comply. For instance, fuel cells are very different from internal combustion engines (ICEs), and the drive cycles used in establishing fuel efficiency and emissions for the purposes of government regulations may differ.

Legislative and regulatory actions by governments, both nationally and internationally, could have an impact by either encouraging or discouraging the use of particular fuels. For instance, as an incentive to increase its uptake in the UK, LPG is currently taxed at a lower rate than other fuels. Disincentives may also be used, such as the recent increase in vehicle excise duty for diesel-powered cars introduced on health grounds.

Although likely to be more efficient than conventional vehicles using ICEs, fuel-cell vehicles will, for the foreseeable future, emit pollutants in the same way. These pollutants have environmental and health impacts that will also have a bearing on which fuels are seen as more or less advantageous. Such health, safety and environmental considerations will affect to a degree how consumers view each fuel and thus their confidence in buying and using them.

It is clear that issues beyond those of health, safety and environmental fate (as considered in this report) will affect the uptake of specific fuels. These broader issues will need consideration before fuel-cell vehicles become commercial reality. Current estimates put this at around the year 2004.

#### **1.4 Report structure**

Each fuel is addressed in a separate section containing the following sub-sections.

##### **1.4.1 Background**

This sets out a brief summary of the characteristics of each fuel, its current use and degree of exploitation as a road transport fuel.

##### **1.4.2 Toxicity and health effects**

There are three main routes of exposure to the fuels considered in this report: inhalation, ingestion and dermal (skin) contact. Of the fuels covered, three are gases at ambient temperatures and the liquid fuels, other than diesel, are highly volatile. Therefore, inhalation is a major exposure route for all fuels. However, specific differences between the fuels mean that other exposure routes may be important. For instance, petrol and diesel are sometimes inadvisably used for removing oil and grease from skin and hair and can thereby enter the body through the skin. The most important exposure routes for each fuel are discussed in more detail in the respective sections.

This section critically evaluates the available information on the health effects associated with acute and chronic exposure to the respective fuels. The fuels display a range of toxic properties and include simple asphyxiants (such as H<sub>2</sub>) and more toxic or carcinogenic compounds such as those found in gasolines.

##### **1.4.3 Environmental fate**

A particular hazard associated with the storage and transport of fuels is that, through unforeseen circumstances or error, they may be released to the environment from storage facilities, distribution sites or vehicles. It is necessary to understand the physicochemical behaviour of each fuel and its

constituents in order to predict potential environmental sinks and migratory pathways. This knowledge is important because it helps to inform an understanding of likely routes of exposure to the fuels and their breakdown products. For instance, loss of gasoline from an underground storage tank could impact on underlying groundwater through mass movement of liquid fuel. Alternatively, vapour migration from the released fuel may take it from the spill site towards nearby properties or underground services such as utility ducts or drains. Each particular fuel-use scenario will have its own environmental hazards, which must be considered on a case-by-case basis.

With regard to the rate of removal of chemicals from the atmosphere, measurements and estimates are presented in the literature for half-lives and atmospheric lifetimes and residence times. The half-life of a chemical is the time it takes for the concentration to fall to half its initial value; for fuels and fuel components, this usually refers to a substance's reaction rate with hydroxyl (OH) radicals, the dominant process for the removal of pollutants from the atmosphere. Atmospheric lifetime is equal to the global mean abundance of a compound divided by its emission rate and therefore considers all removal processes (Seinfeld & Pandis, 1998). Averaging the life histories of all molecules of a substance yields an average lifetime or residence time for that substance (Seinfeld & Pandis, 1998). It should be borne in mind that half-life and residence time are not necessarily directly comparable.

#### 1.4.4 Fire, explosion and other safety aspects

This section presents a discussion of the properties of each fuel with regard to flammability, flame luminescence and other safety issues (eg pressurised storage). Fuels are by their nature flammable, but the fire and explosion-related hazards associated with them depend on the various properties described below (Baker *et al.*, 1983; Energy Information Administration, 1994; Murphy *et al.*, 1995; Owen & Coley, 1995):

- *Flashpoint* — the lowest temperature, under specific conditions, at which a liquid produces enough vapour to flash on the application of an ignition source; below this temperature, fuels will not produce sufficient vapour to form ignitable fuel-air mixtures.
- *Fuel volatility* — (liquid fuels at reference temperature) — described by the Reid Vapour Pressure (RVP; the pressure exerted by fuel vapour over the liquid fuel in a sealed container at 38°C).
- *Autoignition temperature* — the minimum temperature that causes self sustained combustion in air due to heat alone, without an additional spark or flame; this tends to be higher than the ignition temperature.
- *Flammability limit* — the range of fuel concentrations in air (expressed as a percentage) that will support combustion; below this limit the mixture is too lean to combust, above it the mixture is too rich.
- *Electrical conductivity* — materials with low conductivity will have a greater propensity to build up static charges and thereby produce static sparks which may act as ignition sources. Ignition will only occur if such a



discharge is in the presence of an air-fuel mixture that is within the combustible range.

- *Minimum ignition energy (MIE)* — the smallest amount of energy that can be deposited in a gas mixture from a very low inductance capacitance spark which will cause a flame to propagate away from the spark. If the spark energy is less than the minimum, a small quantity of the material will burn but the energy will not be enough to set up a sustained flame propagation. Sparks with sufficient energy to ignite most hydrocarbons are barely audible and can be generated by static electricity.

The difference between fires, deflagrations and detonations is an important facet of the safety considerations for each fuel. A fire is a non-explosion fuel-oxygen combustion event in which a flame front is relatively stationary and produces heat but no pressure effects (unless in an enclosed space). A deflagration has a more rapid energy release than a fire and the flame front is subsonic producing some overpressure effects (pressure greater than ambient). In a detonation event the flame front is supersonic and produces both more energy and occurs over a shorter timescale than either a fire or deflagration and produces greater overpressure effects. Overpressure can cause structural damage and injuries to nearby properties and people (Baker *et al.*, 1983; Cadwallader & Herring, 1999).

#### 1.4.5 Summary

Individual sections conclude with a summary of the main points concerning the health and safety and environmental aspects of each fuel.

### **1.5 Overall evaluation and recommendations**

The final section of this report presents an overall evaluation of the fuels in terms of their toxicity and health effects, environmental fate, and fire, explosion and other safety issues. This is followed by recommendations for further research to feed into subsequent risk assessments of the fuels in fuel cell applications.

## **2 GASOLINE**

### **2.1 Background**

Although unleaded and reformulated gasoline differ in their detailed composition, their toxicity, health effects, and fire, explosion and other health and safety aspects are sufficiently similar to enable them to be considered together under the general term 'gasoline'. Any specific differences are made explicit throughout this section.

Gasoline typically contains more than 150 individual chemical constituents; the specific fuel composition varies according to the crude petroleum source, manufacturer and time of year (see Section 2.3 for more detailed information on gasoline composition). Until recently, gasolines were blended primarily for optimum engine performance. Before the advent of unleaded gasolines, the fuel composition was basic hydrocarbon gasoline plus a lead additive to increase the fuel octane rating. Vapour pressure adjustments were made to account for seasonal changes in ambient temperatures (Stern & Kneiss, 1997). These adjustments increased vapour pressure in the winter months and reduced it in the summer to limit evaporative losses and improve engine performance. Currently, concerns about evaporative and exhaust emissions also drive the design and formulation of gasolines.

The development of reformulated gasolines came in response to concerns about the contribution to air pollution made by cars and other road transport (Stern & Kneiss, 1997). Oxygenated fuel (usually referred to as 'oxyfuel') has been introduced to reduce carbon monoxide (CO) emissions to the ambient air and to enhance the octane number (Saarinen *et al.*, 1998). Reformulated gasolines have a minimum oxygen content of 2% by weight and benzene and heavy metal additives are limited. Oxygenated gasolines contain 2.7% oxygen by weight, which is achieved by adding, most commonly, 15% (by volume) methyl-tertiary-butyl ether (MTBE) or 7.8% (by volume) ethanol (Stern & Kneiss, 1997). In the UK, petrol typically contains up to 5% MTBE, the EC regulatory limit being 15%.

The oxygenates used in reformulated gasolines are either alcohols (methanol and ethanol) or ethers derived from these alcohols. Methanol is the feedstock for MTBE and tertiary-amyl methyl ether (TAME, also known as methyl tertiary-amyl ether, MTAE) and ethanol is the feedstock for ethyl tertiary-butyl ether (ETBE) and tertiary-amyl ethyl ether (TAEE). The alcohols (methanol and ethanol) can be blended directly into gasolines but, due to their higher volatility compared with the gasolines, can have a detrimental effect on engine performance, particularly in the summer months. Their higher water solubility also introduces problems during transport and distribution. The ethers (MTBE, TAME, ETBE and TAEE) are less volatile and less soluble than their feedstock alcohols, making them more suited to year-round use (Stern & Kneiss, 1997). It is worth noting that, in the US, the Environmental Protection Agency, the main instigator of efforts to introduce oxygenates into fuels, has recently set about reducing or eliminating the use of

MTBE in gasolines and boosting the use of alternatives such as ethanol<sup>3</sup>, primarily because of environmental concerns and for taste and odour considerations (MTBE can give drinking water an unpleasant odour and taste, said to resemble turpentine<sup>4,5</sup>).

## **2.2 Toxicity and health effects**

### **2.2.1 Gasolines**

Inhalation and dermal contact are the usual routes of exposure to gasolines, although accidental ingestion may also occur.

#### **Inhalation**

##### *Acute effects*

Inhaled gasoline vapour is absorbed faster than ingested gasoline, if aspiration of liquid gasoline does not occur (Reese & Kimbrough, 1993). The principal target following inhalation of gasoline vapour is the central nervous system (CNS) with the main systemic effect being CNS depression that mimics ethanol inebriation. Exposure results in flushing of the face, ataxia, staggering, vertigo, mental confusion, headaches, blurred vision, slurred speech, and difficulty in swallowing (Reese & Kimbrough, 1993). At high concentrations, coma and death may result in a few minutes without any accompanying respiratory struggle or post-mortem signs of anoxia. Little information is available on dose-response relationships in humans (Reese & Kimbrough, 1993). Exposure to concentrations of gasoline sufficient to cause such acute effects is unlikely in normal use.

Aspiration of only small amounts of gasoline can cause irritation of the respiratory tract which can lead to breathing difficulties and development of a potentially fatal pneumonitis (CONCAWE, 1992a); other effects include pulmonary epithelial damage, haemorrhagic pneumonia, and pleurisy (Reese and Kimbrough, 1993). Aspiration of liquid gasolines normally occurs only in accidental situations or following ingestion (see ingestion section below).

##### *Chronic effects*

In relation to possible carcinogenicity, the International Agency for Research on Cancer (IARC) evaluated gasoline and concluded that there was limited evidence for the carcinogenicity of gasoline in experimental animals but inadequate evidence in humans. Their overall evaluation was that gasoline is possibly carcinogenic to humans (IARC, 1989), primarily based on its benzene and 1,3-butadiene content (Owen & Coley, 1995). No epidemiological investigations have looked at leaded and unleaded gasoline separately (IARC, 1999a).

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<sup>3</sup> EPA Headquarters press release “EPA Administrator Browner and Agriculture Secretary Glickman to announce steps to eliminate MTBE and to increase use of renewable additives” 20 March 2000 [available at <http://yosemite.epa.gov/opa/admpress.nsf/>]

<sup>4</sup> USGS. Methyl Tertiary-Butyl Ether (MTBE). Available [October 2000] from <http://water.wr.usgs.gov/mtbe/>

<sup>5</sup> San Mateo Courts. Final Report: Use of MTBE as a Fuel Additive. Available [October 2000] from <http://www.co.sanmateo.ca.us/sanmateocourts/98mtbe.htm>.

Gasoline, along with a number of other compounds, has been shown to induce nephropathy and renal tumours in male rats. Recently, IARC attempted to produce a consensus report on a number of chemically induced rodent tumours (IARC, 1999a). Its focus was the mechanism of tumour induction and its relevance to human health risk assessment. There was general agreement that  $\alpha_{2u}$ -globulin nephropathy, and its associated renal cell carcinoma, is a lesion event unique to male rats that, if caused by non-genotoxic substances, is not predictive of a human cancer risk. The report noted that a series of pathophysiological events need to be observed before it can be concluded that a rodent renal cancer is due to the  $\alpha_{2u}$ -globulin mechanism. Unleaded gasoline-induced renal tumours fulfil these requirements (IARC, 1999a) and hence are not predictive of a human cancer risk.

### Ingestion

#### *Acute effects*

Ingestion usually only occurs accidentally, for instance when siphoning fuel from vehicles. Taste and smell will usually limit ingestion to small amounts. Spontaneous vomiting is common following ingestion and can lead to aspiration of fuel into the lungs (see inhalation section above). Local effects caused by ingestion of undiluted gasoline include a burning sensation in the mouth, pharynx and chest, gastrointestinal irritation, vomiting, colic and diarrhoea (Reese and Kimbrough, 1993).

#### *Chronic effects*

See inhalation section, above.

### Dermal contact

#### *Acute effects*

Gasoline causes defatting of the skin and prolonged exposure reportedly leads to chemical burns (CONCAWE, 1992a). Splash contact with eyes causes slight, transient corneal epithelial damage. The amount of gasoline absorbed dermally is unknown (Reese and Kimbrough, 1993).

#### *Chronic effects*

Repeated exposure to gasolines causes drying, cracking and dermatitis. This can also make the skin more susceptible to irritation and penetration by other materials (CONCAWE, 1992a). See also inhalation section, above.

### 2.2.2 Benzene

Until recently benzene comprised on average 2% by volume of gasoline in the UK, but from 1 January 2000, EU legislation required that it be below 1% (DETR, 2000). In the past, benzene content has been as high as 30% (Coggon, 1992).

Benzene can be inhaled and the liquid form can be absorbed through the skin. Total absorbed doses of benzene have been estimated by measuring its concentration in blood and exhaled breath, and by monitoring urinary excretion of phenol. In general these measures have correlated well with

airborne levels, suggesting that inhalation is the major route of occupational exposure.

### Inhalation

#### *Acute effects*

Inhalation of benzene produces acute toxic effects on the CNS in humans, which clear once exposure ceases (IEH, 1999).

#### *Chronic effects*

The most important toxic effects of high level benzene exposure are depression of bone marrow function and leukaemogenesis (IEH, 1999). Most of the evidence for these effects comes from studies of occupationally exposed populations (Coggon, 1992). Chronic occupational exposure to benzene (with inhalation as the main route of absorption) causes bone marrow injury and haemopoietic toxicity, including leukopenia, lymphocytopenia, aplastic anaemia and leukaemia (acute myelogenous leukaemia) (Caprino & Togna, 1998). Unlike leukopenia and lymphocytopenia, benzene-induced leukaemia has only been observed in humans; no satisfactory animal model exists that can consistently reproduce the human disease (Caprino & Togna, 1998).

In terms of the risk from long-term low level exposure, acute non-lymphoblastic leukaemia (ANLL) is the critical outcome. Other haematological malignancies have not been consistently linked with benzene and, if there is an association, the risk is almost certainly much lower than for ANLL. Severe bone marrow depression has only been reported at exposures in excess of 25ppm, and epidemiological studies indicate that any risk of serious aplasia at lower exposure levels is also smaller than the risk of ANLL (Coggon, 1992).

Attempts to quantify the risk of leukaemia associated with low level occupational exposure to benzene have usually been based on a small number of occupational studies that are limited by the small number of leukaemia cases and by uncertainties about exposure estimates in the absence of complete industrial hygiene records (Coggon, 1992). Among occupationally exposed workers, the lowest observable adverse effect level for the development of all leukaemia combined, acute myelocytic and monocytic leukaemia and ANLL appears to be in the range of 10-25ppm. However, some studies of workers exposed to lower estimated levels of benzene have found some evidence for increased risk of leukaemia, although it has not been possible to determine clear estimates of risk (IEH, 1999). At low exposure levels, smoking is an important confounder because benzene is present in cigarette smoke (Coggon, 1992).

The major determinant of benzene dose in the general population is smoking habit. The influence of driving and re-fuelling cars with petrol is smaller. Any risk of leukaemia from environmental exposure to benzene is likely to be lower among non-smokers than smokers, and may well be orders of magnitude less than that from occupational exposure (Coggon, 1992). Occupational settings provide scenarios for higher exposures than environmental exposures.

### Ingestion

#### *Acute effects*

Acute oral toxicity of benzene is low. It has been estimated that ingestion of 10ml (8.8g) would be an acute lethal dose in humans. Gastrointestinal ulceration has been observed following benzene ingestion (IEH, 1999).

#### *Chronic effects*

No information is available on chronic effects due to ingestion but, depending on absorption, may be qualitatively similar to effects seen following inhalation. However, it is unlikely that repeated ingestion of benzene would occur.

### Dermal contact

#### *Acute effects*

Benzene can be absorbed through and irritate the skin. Systemic effects, depending on the bioavailable levels, will be the same as in the case of inhalation.

#### *Chronic effects*

See inhalation section, above.

### 2.2.3 Toluene and xylene

#### Inhalation

##### *Acute effects*

These alkylbenzenes cause irritation of the respiratory tract. Exposure to vapour irritates the eyes (Caprino & Togna, 1998). CNS dysfunction is the principal consequence of exposure to alkylbenzenes. The effects may vary from neurological disorder to deficit in neurobehavioural function in occupationally exposed groups (Caprino & Togna, 1998).

##### *Chronic effects*

Because of the wide industrial use of alkylbenzenes, studies continue to investigate the effects of these compounds in occupationally exposed groups. However, due to the scarcity of information specific to gasolines, the long-term effects on human health from the use of alkylbenzenes as constituents of gasoline remain uncertain. The International Agency for Research on Cancer recently reviewed the data for toluene (IARC, 1999b) and xylene (IARC, 1999c) and concluded that there was inadequate evidence of carcinogenicity for both compounds in humans and in experimental animals; thus, toluene and xylene are not classifiable regarding their carcinogenicity in humans (IARC, 1999b, c).

### Ingestion

#### *Acute and chronic effects*

No information is available on either acute or chronic effects due to alkylbenzene ingestion.

## Dermal contact

### *Acute effects*

These alkylbenzenes are absorbed through the skin. Xylene is a more potent skin irritant than benzene or toluene (Caprino & Togna, 1998).

### *Chronic effects*

Direct skin contact promotes defatting of the keratin layer, vasodilation, erythema, and dry, scaly dermatitis (Caprino & Togna, 1998). Chronic effects are as for long-term inhalation.

## 2.2.4 Methyl tertiary-butyl ether (MTBE)

Information on the effects of human exposure to MTBE is available from clinical applications, population studies and laboratory experiments with volunteers. The clinical data are of limited value as they describe effects observed using MTBE to dissolve gallstones *in situ*. Accidental exposures (case reports) provide some information regarding the fate of MTBE in the human body, but the data quality is limited (ECETOC, 1997).

## Inhalation

### *Acute effects*

Inhalation is the major exposure route for exposure to MTBE used in gasoline. MTBE is only slightly acutely toxic (Reese & Kimbrough, 1993). Exposure to high levels of MTBE causes acute symptoms (headache, eye, nose and throat irritation, cough, nausea and vomiting, dizziness and disorientation) only in some individuals and, on the basis of current data, volunteer studies do not reveal adverse effects of MTBE on humans for either subjective or objective end-points (ECETOC, 1997). Although studies in rats reveal neurotoxicity at relatively high levels, neurotoxicity is unknown at the lower levels to which most people are exposed (HEI, 1996).

Symptoms such as nausea, headache and sensory irritation were reported in some communities after oxyfuel and reformulated gasoline containing MTBE were introduced. Studies on human populations do not indicate that exposure to MTBE in either occupational or environmental scenarios would cause acute health effects (ECETOC, 1997). Even in areas with requirements for the use of at least 12% MTBE in motor fuels, occupational exposures (eg service station attendants) are likely to be low (Hartle, 1993). Findings by Nihlèn *et al.* (1998a), suggested no or minimal acute effects of MTBE vapour following short-term exposure at relatively high levels.

### *Chronic effects*

Studies on human populations do not indicate that exposure to MTBE in either occupational or environmental scenarios would cause medium-term health effects (ECETOC, 1997).

Tumours have been observed at multiple sites in rats and mice after exposure to high levels of MTBE. Although these findings are of concern, the HEI Committee noted that the mechanisms causing these tumours, and the likelihood that these or other tumours will occur in humans exposed to MTBE at substantially lower levels, are unknown (HEI, 1996). The Department of

Health Committee on the Medical Effects of Air Pollution (COMEAP<sup>6</sup>) recently stated that there is no case for assuming that inhalation of low concentrations of MTBE would be associated with a risk of cancer. However, there is the contrasting view that, in the absence of adequate data on humans, it is biologically plausible and prudent to regard MTBE, for which there is sufficient evidence of carcinogenicity in experimental animals, as a probable human carcinogen (Mehlman, 1996).

### Ingestion

#### *Acute and chronic effects*

During the preparation of this report no literature relating to the health effects of MTBE ingestion was identified.

### Dermal contact

#### *Acute effects*

Skin and eye irritation have been described as acute effects of MTBE exposure (ECETOC, 1997).

#### *Chronic effects*

No information is available on chronic effects due to dermal contact with MTBE.

## 2.2.5 Ethyl tertiary-butyl ether (ETBE)

### Inhalation

#### *Acute effects*

In a volunteer study (Nihlèn *et al.*, 1998b), it was observed that healthy subjects exposed to ETBE for only 2h, but to high levels (concentration not known), may feel irritation in the throat and airways, a bad taste in the mouth, and slightly impaired lung function. However, the low number of participants in this study reduced its power and no firm conclusions can be drawn.

#### *Chronic effects*

No information is available on chronic effects due to inhalation of ETBE.

### Ingestion and dermal contact

No information was available regarding the ingestion and dermal effects of ETBE.

## 2.2.6 Ethanol

### Inhalation

#### *Acute effects*

Ethanol vapours, even at low concentrations, may cause irritation of the mucous membranes of the eyes and respiratory tract (Reese & Kimbrough, 1993). The primary target for ethanol toxicity is the CNS (see ingestion section below). It is thought unlikely that these effects would result from the low

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<sup>6</sup> COMEAP. Methyl tertiary-butyl ether (MTBE). Available [October 2000] from <http://www.doh.gov.uk/comeap/mtbe.htm>



exposure levels (by inhalation) associated with re-fuelling situations, particularly if ethanol is used as a fuel constituent rather than as a fuel in its own right.

#### *Chronic effects*

No information was available on the chronic effects of ethanol inhalation.

#### Ingestion

##### *Acute effects*

The principal target for acute alcohol poisoning is the CNS, and the primary route of human exposure is ingestion. However, ingestion is an unlikely path for ethanol exposure if the fuel is used as a constituent in gasolines. If used as a fuel in its own right, abuse would be a possible hazard.

Ethanol is a CNS depressant that induces all stages of anaesthesia. As the level of ethanol in the blood increases, effects progress from decreased inhibition, poor coordination, slow reaction time, and blurred vision to definite visual impairment, slurred speech, hypoglycaemia, and staggering. At very high blood levels, marked incoordination, stupor, hypoglycaemia, convulsions, coma and death can be observed. At such elevated levels, the greater the amount of ethanol in the blood, the shorter the time of survival (Reese & Kimbrough, 1993).

##### *Chronic effects*

Extensive evidence indicates that ingesting ethanol at moderate to high levels affects the nervous system and prenatal development processes, and that ingestion over long periods of time increases the risk of certain cancers (HEI, 1996). However, these findings relate to recreational consumption of alcohol and it is not possible to assess the possible effects of ingestion of ethanol as a constituent in reformulated gasolines.

#### Dermal contact

No information is available on the dermal effects of ethanol exposure.

## **2.3 Environmental fate**

### 2.3.1 General

Gasoline is a complex mixture of hydrocarbons that is primarily made up of C<sub>5</sub>-C<sub>10</sub> alkanes but which also contains aromatic compounds such as benzene, toluene, ethylbenzene and xylene (collectively known as the BTEX compounds). A summary of the composition of a typical automotive gasoline by hydrocarbon type is presented in Table 2.1.

**Table 2.1 Automotive gasoline composition**

Component	Average composition (% wt)	Range in composition (% wt)
Total straight chain and iso-alkanes	47	45-50 (29-48) <sup>a</sup>
Total cycloalkanes	3.2	2.4-4.3 (3-7) <sup>a</sup>
Alkenes	10	8.4-12 (2-5) <sup>a</sup>
Benzene	1.9 <sup>b</sup>	1.6-2.3 (0.5-2.5) <sup>a</sup>
Total mono-aromatics (BTXs) <sup>c</sup>	19	16-24
Total aromatics	35	29-38 (20-50)

From TPHCWG, 1999 except <sup>a</sup>adapted from CONCAWE, 1985, 1987 in IARC, 1989; <sup>b</sup> recent EU legislation requires that benzene content be below 1% (DETR, 2000); <sup>c</sup>BTXs — benzene, toluene and xylenes (commonly classified as BTEXs, which includes ethylbenzene)

King (1992) described a typical unleaded gasoline (non-oxygenated) as containing 28% aromatics, 9% alkenes (all forms) and 63% saturates (all forms of alkanes) by volume. An antioxidant and a metal deactivator are also added in small quantities (20ppm and 10ppm, respectively). Other performance enhancing additives added to unleaded fuel include detergents, anti-rust agents and anti-icing agents (King, 1992). However, the composition of gasolines for use in fuel-cell engines may be different from that used in ICEs.

The constituents of gasoline have different physical and chemical characteristics, which means that they will behave differently in the environment. Physicochemical and environmental fate data are presented for the range of compounds present in gasoline. Individual assessments are also made for benzene and the ethers MTBE and TAME. Methanol, an alcohol constituent of some reformulated gasolines, is discussed in Section 6.3.

### 2.3.2 Physicochemical properties

Table 2.2 presents the principal physicochemical properties of gasoline.

**Table 2.2 Physicochemical properties of gasoline**

Property	Value
Molecular weight	~100 (mean molecular weight) <sup>a</sup>
Melting point	-90.5 to -95.4°C <sup>b</sup>
Boiling point	39-200°C <sup>b</sup>
Vapour pressure	35-90kPa (at 37.8°C) <sup>c</sup> = 263-675mmHg
Henry's Law constant	n/a
Water solubility	30-100mg/l <sup>c</sup> , 120mg/l <sup>d</sup>
Relative density	0.68-0.79 (at 15°C) <sup>c</sup>
Vapour density	3-4 (air = 1) <sup>b</sup>
Log K <sub>ow</sub>	2.1-6 <sup>c</sup>

Notes: <sup>a</sup>Squillace *et al.* (1991); <sup>b</sup>HSDB<sup>7</sup>; <sup>c</sup>IUCLID (1996a); <sup>d</sup>USGS Fact Sheet<sup>8</sup>; n/a — not available in literature identified

<sup>7</sup> HSDB. Gasoline. Produced by National Library of Medicine, Bethesda, USA. Accessed via Datarstar [May 2000]

<sup>8</sup> USGS Fact Sheet FS-203-96 (Revised 2/98). Environmental Behaviour and Fate of Methyl tert-Butyl Ether (MTBE). Available [March 2000] from <http://water.wr.usgs.gov/mtbe/fs20396>

Gasoline is liquid at typical environmental temperatures but an increasing amount will evaporate at higher temperatures, as the lower molecular weight compounds have boiling points starting at 39°C. Due to the volatility of the compounds in gasoline, significant amounts will be lost to the atmosphere during storage and transfer and from leaks in road vehicles. Leaks and spills occur from sites such as petrol stations and underground storage tanks and can cause pollution of groundwater.

### 2.3.3 Environmental accumulation

The range of log  $K_{ow}$  values shown in Table 2.2 suggests that a number of compounds found in gasoline (those with log  $K_{ow} > 4$ ) will have the potential to bioaccumulate significantly in aquatic and/or terrestrial organisms, or accumulate in organic carbon-rich soils or sediments. Information in the literature, however, does not indicate whether gasoline constituents bioaccumulate to a significant extent.

### 2.3.4 Environmental degradation and fate

In the event of a spillage, the more volatile components of gasoline will rapidly evaporate with concurrent dissolution of the more water soluble compounds, such as the mono-aromatics (eg benzene, toluene and xylene). Mackay level I distribution modelling suggests that in general most of the components of gasoline will partition to air with 0.4-1.1% of mono-aromatics partitioning to water (IUCLID, 1996a). As molecular weight increases, mono-aromatics will show an increasing tendency to adsorb to soil (IUCLID, 1996a). Volatilised gasoline components will photodegrade in the atmosphere at varying rates; calculations from reaction rates with hydroxyl radicals (12h daytime average concentration of  $1.6 \times 10^6$  molecules per  $\text{cm}^3$ ) indicate a range of atmospheric lifetimes from 7h for *m*-xylene to 12d for benzene (Atkinson, 1994). However, it has been estimated that combined evaporative and photodegradative losses may account for only about 1-2% of land spills of petroleum hydrocarbons (Ridgway *et al.*, 1989); these figures are presumed to refer to underground spills, such as those that occur from gasoline storage tanks.

Compounds in gasoline are not susceptible to hydrolysis under environmental conditions but many hydrocarbon components of unleaded gasoline are rapidly degraded by soil bacteria (IUCLID, 1996a). A study of gasoline biodegradation in soil demonstrated that n-paraffins and the BTEX compounds were degraded by day 4. However more complex substituted aromatic hydrocarbons such as 1,3,5-trimethylbenzene, and iso-paraffins such as 2,2,4-trimethylpentane had not degraded by day 60 (IUCLID, 1996a). The rate of biodegradation of gasoline hydrocarbons in soil and water will depend upon the indigenous microbial community, prevailing environmental conditions and the availability of nutrients such as oxygen, nitrogen and phosphorus. Inactivation of gasoline degrading bacteria can occur and is possibly due to the formation of toxic metabolites (Ridgway *et al.*, 1989).

*Benzene (CAS no. 71-43-2)*

The volatility (vapour pressure of 99.8mmHg) and solubility in water (1.8g/l) of benzene are the most important properties influencing its environmental transport (WHO, 1993). A Henry's Law constant of  $5.5 \times 10^{-3} \text{ atm.m}^3/\text{mol}$  suggests that benzene will partition to the atmosphere from surface water (WHO, 1993). Benzene can enter the atmosphere via direct evaporation or volatilisation from water or surface soil; partitioning to groundwater will occur if benzene is released well below the surface (WHO, 1993). Benzene in air is fairly soluble in water and is removed from the atmosphere by rain but once it has been deposited on soil or water, volatilisation will return a portion back to the atmosphere (WHO, 1993). Benzene is not expected to bioconcentrate in aquatic or terrestrial organisms to any great extent or adsorb strongly to soil or sediment (WHO, 1993). Benzene in the atmosphere has a lifetime of 12d (Atkinson, 1994) and is biodegraded with half-lives of 28d and 16d in groundwater and river water, respectively. Benzene is usually only slowly degraded under anaerobic conditions (WHO, 1993).

*Methyl tertiary-butyl ether (MTBE; CAS no. 1634-04-4) and tertiary-amyl methyl ether (TAME; CAS no. 994-05-8)*

Methyl tertiary-butyl ether is a major component of reformulated gasolines. It has generated considerable environmental concern because of its potential to contaminate groundwater owing to its high solubility in water (51g/l)<sup>9</sup>. When gasoline oxygenated with MTBE comes into contact with water, as in instances of leakage from underground storage, large amounts of MTBE can dissolve (5g/l at 25°C) (Squillace *et al.*, 1991). Because MTBE only sorbs weakly to subsurface solids, sorption does not significantly retard its transport in groundwater; MTBE is also resistant to biodegradation in groundwater (Squillace *et al.*, 1991). MTBE is not expected to bioaccumulate in surface water aquatic organisms (Squillace *et al.*, 1991). It has a vapour pressure of 250mmHg (at 25°C)<sup>5</sup> indicating that a significant amount can be lost by evaporative emissions from sources of pure MTBE or gasoline. However, a Henry's Law constant value (which describes a compound's air/water partitioning) of  $5.28 \times 10^{-4} \text{ atm.m}^3/\text{mol}$  indicates that MTBE does not volatilise from water and explains why the fuel oxygenates partition into atmospheric water (eg precipitation) and are somewhat difficult to remove from water by aeration (Squillace *et al.*, 1991). MTBE reacts with hydroxyl (OH) radicals in the atmosphere and, assuming a concentration of  $1 \times 10^6$  radicals per  $\text{cm}^3$ , the half-life of MTBE can be as short as 3d (Squillace *et al.*, 1991).

Another gasoline oxygenate, tertiary-amyl methyl ether (TAME), has similar environmental characteristics to that of the structurally related MTBE in that it is volatile (vapour pressure of 67.5mmHg at 20°C), non-hydrophobic (log  $K_{ow}$  of 1.55), water soluble (10.7g/l) and is not readily biodegradable (Huttunen *et al.*, 1997). The Henry's Law constant for TAME is  $8.9 \times 10^{-4} \text{ atm.m}^3/\text{mol}$  (Huttunen *et al.*, 1997). If spilled into the ground in large volumes TAME is

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<sup>9</sup> SRC PhysProp Database information available [May 2000] from <http://esc.syrres.com/interkow/PhysProp.htm>

expected to be mobile in soil (relative mobility of 0.69; MTBE = 1) and persistent (Huttunen *et al.*, 1997).

#### **2.4 Fire, explosion and other safety aspects**

Gasolines are flammable and combustible and may be ignited by heat, sparks or flames. Gasoline has a minimum ignition energy (MIE) of 0.24mJ. There is the potential during bulk transfer of gasoline at high pumping rates for a static charge to build up which could provide an ignition source. Normal re-fuelling of vehicles is unlikely to build up such an excessive static charge. Anti-static additives are occasionally added to the fuel even though equipment is almost always grounded (Owen & Coley, 1995).

Gasoline containers may explode in heat or fire. The vapour is heavier than air and does not disperse easily in still air conditions. Due to its density, it tends to sink to the lowest possible level of its surroundings and may accumulate in tanks, cavities, drains, pits or other depressions. Vapours may travel to a source of ignition, for instance through drainage or other service ducts, and then flash back to the vapour source. Furthermore, because gasoline floats on water, it may be carried for long distances from the initial source by water courses, sewers, drains or groundwater (HSE, 1996). The autoignition temperature for gasoline is approximately 255°C; its flashpoint is less than -40°C meaning that at normal ambient temperatures, the fuel will emit sufficient vapour to support combustion and will therefore burn if there is an ignition source. The fuel's upper and lower flammability limits are 7.6% and 1.4%, respectively (IUCLID, 1996a).

#### **2.5 Summary**

A number of potential health effects are associated with exposure to gasoline fuels. Inhalation of gasoline at very high concentrations can cause coma and death; at lower concentrations the effects resemble alcoholic inebriation and mainly affect the CNS. Exposure to levels of gasoline sufficient to cause such effects is unlikely in normal use. Aspiration of the fuel causes irritation and damage to the lung. Ingestion leads to irritation of the throat and digestive system, vomiting, colic and diarrhoea but is only likely in accidental situations or following intentional ingestion. Dermal contact causes defatting of the skin. Repeated or prolonged exposure causes drying, cracking and dermatitis.

Gasoline has been evaluated as possibly carcinogenic to humans, primarily based on its benzene and 1,3-butadiene content. Although studies in rats show gasoline induces kidney tumours, the mechanism by which this occurs is not thought to be predictive of human cancer risk.

Of the many components of modern fuels, six (benzene, xylene, toluene, MTBE, ETBE and ethanol) are considered in detail here. Benzene exposure has been linked (often in occupational settings) with bone marrow depression and leukaemias, particularly ANLL. Relating low-level benzene exposure to leukaemia incidence is made difficult by the small number of leukaemia cases encountered, even in occupational settings, and by uncertainties in exposure assessment. The benzene content of gasoline is being reduced gradually and is now less than 1% in Europe.

Xylene and toluene (alkylbenzenes) cause CNS dysfunction. Most studies are occupationally based and, due to the lack of available information, the long-term effects of alkylbenzenes in gasoline remain uncertain. There is inadequate evidence for the carcinogenicity of either compound in humans and experimental animals; neither compound is classifiable as to its carcinogenicity in humans.

Published studies on human populations do not indicate that exposures to MTBE in either occupational or environmental scenarios would cause acute or medium-term health effects. Exposure to high levels of MTBE can cause acute effects including headache, eye, nose and throat irritation and a range of other systemic effects. Animal studies indicate that MTBE induces tumours at various sites. Whether this is indicative of a human cancer risk is uncertain but it is thought that there is no case for assuming that inhalation of low levels of MTBE would be associated with a risk of cancer. There is no information available on the effects of MTBE ingestion. Dermal contact causes skin and eye irritation.

Acute exposure to ETBE in a single small volunteer study has shown that the compound causes throat and airway irritation, a bad taste in the mouth and slightly impaired lung function.

Ethanol also affects the CNS and can cause mucous membrane irritation. Ingestion over long periods increases the risk of certain cancers but it is unlikely that such effects would be associated with exposure to ethanol as a gasoline constituent.

Gasoline is a complex mixture of hydrocarbon compounds which have differing properties and therefore different behaviours in the environment. If released to the open environment, the majority of compounds present in gasoline will evaporate to the atmosphere where they will be degraded by reaction with hydroxyl radicals in a matter of days. If gasoline is lost below ground, volatilisation will be much less significant and there is the potential for toxic compounds such as benzene to contaminate groundwater. The majority of gasoline released to soil will be biodegraded, although some higher molecular weight compounds with highly branched alkyl-chain components are recalcitrant. The oxygenates MTBE and TAME, present in reformulated gasoline, are readily transported in water and are not degraded, leading to concern about groundwater contamination.

Gasolines are flammable and combustible liquids that can be ignited by heat, sparks or flames. The gasoline flashpoint is less than  $-40^{\circ}\text{C}$ , which means that, at normal temperatures, the fuel emits sufficient vapour to support combustion. Static charges built-up during bulk fuel transfer may be sufficient to ignite a fuel-air mixture within the flammable range, but normal vehicle refuelling is unlikely to build-up such a charge. Also, effective mitigating measures such as equipment grounding and anti-static additives are used.



## **3 DIESEL**

### **3.1 Background**

Diesel fuel (also known as DERV or automotive gas oil) is a complex mixture of hydrocarbons, mainly falling in the range C<sub>9</sub> to C<sub>25</sub> (see Section 3.3 for more detailed information on diesel composition). It has traditionally been used in heavy duty engines in applications such as lorries, buses and marine engines, but recently has seen an increasing popularity as a fuel for small passenger vehicles. Like gasolines, the composition of diesel varies with manufacturer, crude petroleum source and time of year. In winter, manufacturers increase the proportion of volatile components to reduce the formation of waxy deposits that might affect engine performance. This is illustrated by the different melting points of the fuel in winter and summer shown in Table 3.1.

### **3.2 Toxicity and health effects**

#### **3.2.1 Inhalation**

##### *Acute effects*

In general, the middle distillates such as diesel demonstrate relatively low acute toxicity by any route of exposure (Koschier, 1999). Due to its low vapour pressure, exposure to diesel by inhalation is likely to be low. If temperatures are high and ventilation is poor, inhalation exposures can induce CNS depression characterised by ataxia, hypoactivity and prostration (CONCAWE, 1996).

Aspiration may occur directly or result from spontaneous vomiting of ingested diesel (see Section 3.2.2). The effects of diesel aspiration include coughing, damage to lung tissue, breathing difficulties, dyspnoea, cyanosis, loss of consciousness and a potentially fatal pneumonitis (CONCAWE, 1996; WHO, 1996). Effects on the liver may also result as shown by changes in levels of particular enzymes (WHO, 1996).

##### *Chronic effects*

In a case-control study conducted in Montreal, Canada, an increased risk for squamous-cell carcinoma of the lung was observed in men exposed to diesel fuel. However, the possible effects of exposure to combustion products were not taken into consideration. An association with prostatic cancer was also observed, although there was no apparent dose-response relationship. In another case-control study, no association was found between the occurrence of renal-cell cancer and occupational exposure to fuel oils, including diesel fuel (WHO, 1996).

#### **3.2.2 Ingestion**

##### *Acute effects*

Ingestion of diesel is only likely to occur accidentally such as when siphoning fuel. The taste and smell of the fuel will limit ingestion to small amounts. Irritation of the mouth, throat and gastrointestinal tract would be expected following ingestion (CONCAWE, 1996). A case report (WHO, 1996) describes abdominal pain and vomiting following ingestion (presumably with suicidal intent) of 1.5 litres of diesel fuel (WHO, 1996).



### Chronic effects

No information is available on any effects due to long-term exposure.

### 3.2.3 Dermal contact

#### Acute effects

Diesel will remove natural fat from the skin following dermal exposure. If such exposure is repeated or prolonged the result will be drying, cracking, irritation and dermatitis (CONCAWE, 1996). Case reports indicate that reversible renal effects can result from using diesel as a skin and hair cleanser (WHO, 1996).

#### Chronic effects

The kerosene range middle distillates are generally inactive in genetic toxicity tests although some positive studies have been reported. Recent studies have demonstrated that tumorigenic effects depend on chronic dermal irritation; in the absence of skin irritation, tumours do not develop (Nessel, 1999)<sup>10</sup>.

Long-term exposure and poor personal hygiene when working with diesel may lead to oil acne, eczema, hyperkeratosis and folliculitis (CONCAWE, 1996; Bruynzeel & Verburch, 1996; WHO, 1996).

### **3.3 Environmental fate**

#### 3.3.1 General

Diesel gas oils are a complex mixture of hydrocarbons falling in the range of C<sub>9</sub> to C<sub>25</sub>. The major hydrocarbon types are iso- and cyclo-alkanes (paraffins), but gas oils may contain a significant amount of aromatic hydrocarbons including alkylbenzenes, alkyl-naphthalenes, alkylanthracenes and other polycyclic compounds. Custance *et al.* (1992) describe the composition of diesel fuel no. 2 (CAS no. 68476-34-6), which is used in motor vehicles, as n-alkanes (37.6%), iso- and cyclo-alkanes (37.6%), highly branched isoalkanes (3.5%), aromatics (20.2%) and polar compounds (1%). Sulphur, olefins (alkenes), and nitrogen- and oxygen-containing compounds are also present as impurities in diesel fuels (Custance *et al.*, 1992).

#### 3.3.2 Physicochemical properties

Table 3.1 presents the principal physicochemical properties of diesel in general and diesel fuel no. 2.

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<sup>10</sup> It is understood that IARC is soon to publish a monograph on the carcinogenicity of diesel which was unavailable at the time of writing

**Table 3.1 Physicochemical properties of diesel**

Property	Value	
	Diesel	Diesel fuel no. 2
Molecular weight	n/a	
Melting point (pour point)	-12°C (winter); -3°C (summer) <sup>a</sup>	18°C <sup>c</sup>
Boiling point	182-374°C <sup>a</sup>	282-338°C <sup>c</sup>
Vapour pressure	0.03mmHg <sup>b</sup>	21.2-264mmHg <sup>c</sup>
Henry's Law constant	0.042atm.m <sup>3</sup> /mol <sup>b</sup>	6.03-7.5×10atm.m <sup>3</sup> /mol <sup>c</sup>
Water solubility	0.2 <sup>b</sup> -5 <sup>c</sup> mg/l	n/a
Relative density	0.84 (at 15°C) <sup>a,b</sup>	0.87-0.95 (at 20°C) <sup>c</sup>
Vapour density	n/a	n/a
Log K <sub>ow</sub>	3.9-6.0 <sup>a</sup>	3.3-7.06 <sup>c</sup>

Data from <sup>a</sup>IUCLID (1996b); <sup>b</sup>Custance *et al.*, (1992); <sup>c</sup>WHO (1996); n/a — not available from identified literature

Diesel oil is liquid at normal ambient temperatures but may solidify at low temperatures.

### 3.3.3 Environmental accumulation

The high log K<sub>ow</sub> values of some compounds in diesel indicate a high potential for bioaccumulation. However, the measured bioconcentration factors (BCFs) are lower than predicted because many compounds of low relative molecular mass (eg substituted benzenes) are readily metabolised and the actual bioaccumulation of compounds of high relative molecular mass is limited by their low water solubility and large molecular size (WHO, 1996). In a continuous-flow system, containing diesel fuel at 200-400µg/l, mussels (*Mytilus edulis*) had hydrocarbon tissue levels 1000 times higher after 41d exposure than before (WHO, 1996). The bioaccumulation factor (BAF) for methyl naphthalenes in clams has been measured at 2.3-26.7 and increased with increasing alkylation of the naphthalene ring (WHO, 1996).

The different components of diesel exhibit varying degrees of adsorption and mobility in soil (WHO, 1996). The highly mobile compounds in diesel fuel include benzene, quinoline and cresols, which exhibit relatively weak adsorption to soil particles, although the actual degree of adsorption will depend upon the organic matter content of the soil (WHO, 1996). Compounds with low mobility include phenanthrene, pyrene and benzantracene which will adsorb strongly to soil particles and exhibit little penetration through the soil column (WHO, 1996).

### 3.3.4 Environmental degradation and fate

Lower molecular weight alkanes and aromatic hydrocarbons will mainly partition to air, with increasing distribution to soil and sediment as the molecular weight rises (IUCLID, 1996b). Those diesel components which volatilise will be readily photodegraded by reaction with hydroxyl radicals and other species within hours or days (IUCLID, 1996b; WHO, 1996). Higher molecular weight hydrocarbon components of diesel will have little or no tendency to partition to air and, depending on the circumstances, will become dispersed in the water column or adsorbed to soil or sediment (CONCAWE, 1996). When diesel fuels are released into the environment, water and land (soils and sediments) are the affected compartments (WHO, 1996).

On release into the aquatic environment diesel oil will tend to float and, although generally insoluble, the most soluble components will dissolve and be dispersed (CONCAWE, 1996) and the more volatile compounds will evaporate (WHO, 1996). The higher molecular weight, hydrophobic compounds, such as the polycyclic aromatic hydrocarbons (PAHs), will sorb to suspended particulate matter. In marine environments, oils and fuels are generally delivered to bottom sediments on settling particles (WHO, 1996).

The different components of diesel sorb to soil particles to varying extents and, in effect, soil contaminated with diesel fuel acts like a chromatographic column, separating individual constituents by their adsorption (WHO, 1996). The mobility of these compounds in soil and therefore their ability to contaminate groundwater ranges from low (fluorene, pyrene, benzanthracene) to high (eg benzene, cresols and phenols) (WHO, 1996).

The individual components of diesel are inherently degradable to varying degrees and at different rates. The n-alkanes and n-alkylaromatics are the most readily biodegradable whilst the PAHs are the compounds most recalcitrant to microbial degradation (WHO, 1996). The calculated half-lives for the toxicologically relevant PAH components of diesel range from one week to two months in water, and eight months to six years in sediment for naphthalene and dibenz[a,h]anthracene, respectively (WHO, 1996). A study in sandy soils found that 50-85% of the hydrocarbons in diesel were degraded within a few weeks, depending on the experimental conditions, and degradation efficiency increased with additional soil inoculation (WHO, 1996).

### **3.4 Fire, explosion and other safety aspects**

Diesel fuel is a combustible liquid but does not ignite readily, unless provided with a wick or aerosolised. Its minimum ignition energy (MIE) is approximately 0.5mJ, depending on the specific properties of the diesel in question (Stuart Hawksworth, personal communication). The fuel will greatly increase the spread and severity of already established fires (Energy Information Administration, 1994) and if ignited can burn fiercely (CONCAWE, 1996). The autoignition temperature for diesel is 315°C (600°F). Its flashpoint is between 55°C and 70°C (IUCLID, 1996b), the highest flashpoint temperature of any fuel considered in this report. Lower and upper flammability limits for diesel are 0.6% and 6.5%, respectively (IUCLID, 1996b). Its low volatility (vapour pressure; Table 3.1), relatively high MIE and high flashpoint make diesel potentially less hazardous than gasoline or the other fuels considered (Energy Information Administration, 1994).

### **3.5 Summary**

Inhalation of diesel causes CNS depression but, because it is not volatile (unless temperatures are high) inhalation exposure will be low. From a case study, long-term exposure to high levels of diesel vapours can cause a range of gastrointestinal symptoms and renal failure. Aspirated diesel has been found to cause coughing, lung damage and other respiratory effects; in certain circumstances death may result. Diesel ingestion is unlikely due to its odour and taste; likely effects are mouth, throat and gastrointestinal tract irritation. Dermal contact with diesel causes skin irritation, defatting and, over longer

exposures, acne, folliculitis, eczema and hyperkeratosis; very high level exposure may reversibly affect renal function. An epidemiological study of occupationally exposed workers found an increased risk of a specific lung cancer but the study did not adequately account for other chemical exposures. Another study found no association between diesel exposure and renal-cell cancer.

Diesel, like gasoline, is a complex mixture of hydrocarbons which have differing behaviours in the environment. If released to the environment the lower molecular weight fraction of diesel will partition to air where these compounds will be degraded by reaction with hydroxyl radicals in a matter of days. Aromatic and polar components of diesel can dissolve in water to varying extents and higher molecular weight compounds are anticipated to adsorb to soil and sediment. All components of diesel are biodegradable to varying extents but some PAHs can persist for a number of years. Some compounds in diesel would be anticipated to have a high potential for bioaccumulation, but the measured BCFs are lower than predicted.

Like all other fuels, diesel is flammable but its low volatility, low ignitability and high flashpoint mean it is potentially less hazardous than the other fuels considered in this report.



## **4 HYDROGEN**

### **4.1 Background**

Hydrogen (H<sub>2</sub>) is gaining in popularity as a potential fuel for road transport and other energy applications. However, being a gas at normal temperatures, it presents greater difficulties in transportation and storage than are encountered with liquid fuels for road transport applications. The gas has a density one-fifteenth that of air and must be compressed or liquefied for use in vehicles. The extremely low boiling point of liquefied H<sub>2</sub> at ambient pressures (-253°C) makes storage of the liquefied gas problematic (Murphy *et al.*, 1995) and also presents health and safety concerns during transport, storage, transfer and use.

The over-riding positive quality that sets H<sub>2</sub> apart from other fuels is that the only product from its combustion or use in fuel cells is water. Although nitrogen oxides (NO<sub>x</sub>) may be produced if H<sub>2</sub> is used in normal internal combustion engines (ICEs), owing to the oxidation of nitrogen in the air, NO<sub>x</sub> would not be produced in fuel cell applications (Energy Information Administration, 1994). However, other pollutants (most notably carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO) and a small amount of NO<sub>x</sub>) may be produced if H<sub>2</sub> is re-formed from hydrocarbon feedstocks, whether within the vehicle or at a remote location. In the longer term, the ideal would be to manufacture H<sub>2</sub> by electrolysis of water, using renewable energy as the power source (Murphy *et al.*, 1995). Other technologies for H<sub>2</sub> storage, such as the use of metal hydrides, are being explored but are not considered here.

### **4.2 Toxicity and health effects**

Liquefied H<sub>2</sub> in the ambient environment rapidly gasifies and the two forms of fuel are not considered separately for either inhalation or ingestion.

#### **4.2.1 Inhalation**

##### **Acute effects**

Hydrogen is classed as a simple non-toxic asphyxiant. High concentrations in air may exclude an adequate supply of oxygen to the lungs.

##### **Chronic effects**

There is no information available on the potential effects of chronic exposure to H<sub>2</sub>; however, toxic effects are unlikely.

#### **4.2.2 Ingestion**

Ingestion of either gaseous or liquefied H<sub>2</sub> is unlikely.

#### **4.2.3 Dermal contact**

##### **Acute effects**

##### ***Liquefied hydrogen***

Evaporating liquefied H<sub>2</sub> may cause frostbite or cryogenic burns in the eye and surrounding skin. Eye irritation also may be experienced<sup>11</sup>. Skin contact causes

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<sup>11</sup> BOC (1996) *Material Safety Data Sheet: Hydrogen, Refrigerated Liquid*. Available [May 2000] from <http://www.boc.com>

frostbite; there is a change in colour of the skin to grey or white, sometimes followed by blistering. These vesicles may become inflamed and painful.

#### *Compressed hydrogen*

For gaseous H<sub>2</sub>, there are no known effects of contact with the gas on the eye or skin<sup>12</sup>.

#### Chronic effects

There is no information available on the potential effects of chronic dermal exposure to H<sub>2</sub>; however, toxic effects are unlikely.

### **4.3 Environmental fate**

#### 4.3.1 General

The following assessment focuses on gaseous H<sub>2</sub> because liquefied H<sub>2</sub>, the other form in which this compound may be used as a fuel, will vaporise rapidly on release.

#### 4.3.2 Physicochemical properties

Table 4.1 presents the principal physicochemical properties of molecular hydrogen (CAS no. 1333-74-0).

**Table 4.1 Physicochemical properties of hydrogen**

<b>Property</b>	<b>Value</b>
Molecular weight	2.016
Melting point	-259.2°C
Boiling point	-252.77°C
Vapour pressure	1.24×10 <sup>6</sup> mmHg
Henry's Law constant	n/a
Water solubility	1.62mg/l (at 21°C)
Relative density	n/a
Vapour density	0.069 (air = 1)
Log K <sub>ow</sub>	0.45

All data from SRC PhysProp Database<sup>13</sup> except vapour density (HSDB)<sup>14</sup>; n/a — not available in the identified literature

Hydrogen is a colourless, odourless and tasteless gas (HSDB)<sup>13</sup>.

#### 4.3.3 Environmental degradation and fate

Due to its extremely low boiling point, all H<sub>2</sub> emitted will be present in the gaseous state.

Little information is available on environmental aspects of H<sub>2</sub>. It does not appear to be regarded as a potentially hazardous pollutant and is a natural, minor component of the atmosphere at levels of 0.5ppm (Brimblecombe, 1996).

<sup>12</sup> BOC (1996) *Material Safety Data Sheet: Hydrogen*. Available [May 2000] from <http://www.boc.com>

<sup>13</sup> SRC PhysProp Database information available [May 2000] from <http://esc.syrres.com/interkow/PhysProp.htm>

<sup>14</sup> HSDB. Hydrogen. Produced by National Library of Medicine, Bethesda, USA. Accessed via Datastar [May 2000]

Hydrogen is the lightest element and has the capacity to escape the earth's gravitational field and so be lost to space. However, little molecular H<sub>2</sub> is lost in this way as the gas is photo-oxidised to water in the atmosphere, where its residence time is in the range 5-10 years (Bowen, 1979; Brimblecombe, 1996). A major loss process for H<sub>2</sub> is its reaction with excited atomic oxygen:

$\text{H}_2 + \text{O}(^1\text{D}) \rightarrow \text{H} + \text{OH} + 182\text{kJ}$  which has a rate constant ( $k$ ) of  $\sim 1 \times 10^{-10} \text{ cm}^3/\text{molecule}\cdot\text{s}$  (McEwan & Phillips, 1975).

#### **4.4 Fire, explosion and other safety aspects**

Hydrogen is a highly flammable and explosive gas which forms ignitable mixtures with air over a wide range of concentrations. The gas is also odourless, making leaks from storage vessels or other equipment difficult to detect. It is buoyant and may collect under roofs or ceilings, forming pockets of potentially ignitable gaseous mixtures. In unconfined areas, the fuel will rise and dissipate into the atmosphere.

If a hydrogen-air mixture develops following a release, the gas can either combust as a fire, a deflagration or a detonation (Cadwallader & Herring, 1999). It may be easily ignited by low-energy sparks (the minimum ignition energy (MIE) for hydrogen is  $0.02\text{mJ}^{15}$  (Cadwallader & Herring, 1999)) and can also be ignited by contact with catalytic substances at temperatures considerably below its autoignition temperature ( $574^\circ\text{C}$ ) (Energy Information Administration, 1994; Murphy *et al.*, 1995). Static charges developed during a loss of H<sub>2</sub> may have enough energy to ignite a hydrogen-air mixture within hydrogen flammability limits (Cadwallader & Herring, 1999). Deflagrations are more likely than detonations because the MIE is lower and the flammable range is wider. In some circumstances (for instance confinement or obstruction), deflagrations can undergo a transition to detonations (Cadwallader & Herring, 1999).

The flame of burning H<sub>2</sub> is virtually invisible, being visible only in darkness (Energy Information Administration, 1994; Cadwallader & Herring, 1999). Hydrogen has the highest autoignition temperature, and widest flammability range (between 4.1% and 74% for deflagration; 18.3% and 59% for detonation) of any of the fuels discussed here (Cadwallader & Herring, 1999). Its flashpoint is less than  $-150^\circ\text{C}$  (IUCALID, 1996c).

The fact that liquefied and compressed H<sub>2</sub> is stored at pressure in a vessel may increase the risk of leaks from fittings, valves and joints; however, regulations and safety requirements, such as pressure relief systems, mitigate the hazard. The need for the tanks to be able to withstand high internal pressures also makes them resistant to damage from impacts such as vehicle collisions. Hydrogen can diffuse into the materials (particularly steel) in which it is stored and reduce their mechanical strength, a phenomenon known as hydrogen embrittlement (Murphy *et al.*, 1995).

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<sup>15</sup> The MIE for hydrogen detonation is 10kJ (Cadwallader & Herring, 1999)



#### 4.4.1 Compressed hydrogen

At ambient temperatures, gaseous hydrogen has typically been stored at pressures of 13.9MPa (2000psi) up to 34.6MPa (5000psi) (Cadwallader & Herring, 1999). The fact that the vessel is pressurised means large volumes of gas can be released if a leak does occur. Although such pressures may increase the potential for leaks from fittings, valves and joints, regulations and safety procedures, such as pressure relief systems, mitigate this hazard. The need for the tanks to be able to withstand high pressures also makes them resistant to damage from impacts such as vehicle collisions.

#### 4.4.2 Liquefied hydrogen

The low temperature of liquefied H<sub>2</sub> means it is not technically possible to add an odorant to aid leak detection. Therefore, other means of detecting leaks will be required. Bulk transport of H<sub>2</sub> is most often in the liquid form in double-skinned, highly insulated tankers. A loss of insulation will lead to rapid temperature rises and increases in pressure. Like other stored liquefied gases, there must be pressure-relief and venting mechanisms to control this situation. Any spill of liquefied H<sub>2</sub> will produce flammable air-fuel mixtures which, due to the coldness of the liquid, may linger at or near ground level before dissipating. Dealing with an extremely cold, flammable gas necessitates stringent precautions and complex safety systems when transferring fuel between bulk, retail and vehicle storage systems (Murphy *et al.*, 1995).

A potential hazard with liquefied H<sub>2</sub> storage is the boiling liquid expanding vapour explosion (BLEVE). If a vessel containing a liquid whose vapour pressure is well above atmospheric pressure ruptures, a BLEVE may occur (Baker *et al.*, 1983). Expansion from liquid to vapour could potentially occur if a liquefied H<sub>2</sub> storage vessel is ruptured. The contents can then flash evaporate, imparting large amounts of energy into vessel fragments. If radiant heat or flames heat a storage vessel containing liquefied H<sub>2</sub>, its contents will warm and may begin to boil. If the vessel ruptures, the contained liquid will be released, leading to an explosive, rapid phase change from liquid to gas and a buoyant fireball (Baker *et al.*, 1983; Papazoglou & Aneziris, 1999). Such events are rare and can be further mitigated by using materials for the vessel that fail predictably and non-catastrophically and by fitting pressure release valves or safety devices to allow controlled releases of stored product if the internal pressure increases. Furthermore, the need for the tanks to be able to withstand high pressures also makes them resistant to damage from impact such as in vehicle collisions.

#### 4.5 Summary

The extremely low boiling point of liquefied H<sub>2</sub> presents particular difficulties for storing, transporting and handling this fuel. However, the primary attraction of H<sub>2</sub> as a fuel is that the only product of its combustion or use in fuel cells is water (although NO<sub>x</sub> may be produced if the fuel is used in an ICE).

There are no known toxic effects, whether acute or chronic, associated with H<sub>2</sub> exposure. However, if present in sufficient quantities, the gas can exclude

enough oxygen to cause asphyxiation. The main health concerns relate to cryogenic burns from the liquid.

Any emissions of H<sub>2</sub> to the atmosphere will be photo-oxidised to water and a small amount will escape through the atmosphere into space.

From a fire, explosion and general safety viewpoint, concerns relate to its high flammability across a wide range of fuel-air concentrations and its low MIE, meaning it is easily ignited. A further safety concern relates to the low temperature at which liquefied H<sub>2</sub> must be stored and the high pressures at which compressed H<sub>2</sub> are stored (13.9 to 34.6MPa). This increases the need for careful engineering, maintenance and operating procedures. Even a small leak from a pressure vessel may release a large volume of gas. A failure of an above ground pressure vessel could cause damage to nearby properties and people. Safety regulations and procedures mitigate the hazard of pressure vessel failures and BLEVEs. Furthermore, because pressure vessels must withstand high internal pressures, their mechanical strength makes them relatively more resistant to physical impacts.

Hydrogen is less dense than air and will naturally dissipate, unless confined by roofs or other constructions. Releases of liquefied H<sub>2</sub> may linger at or near ground level until sufficiently warm to rise and dissipate. The low temperature at which liquefied H<sub>2</sub> is stored necessitates particular health and safety precautions. The flame of burning H<sub>2</sub> is only visible at night making fire detection difficult. The gas is also odourless making leak detection difficult. However, it is not technically possible to add an odorant to liquefied H<sub>2</sub>, meaning leaks may go undetected.



## **5 NATURAL GAS**

### **5.1 Background**

Natural gas comprises a variety of hydrocarbon and other gases in varying proportions depending on the source. North sea gas typically contains 93.7% methane, 3.2% ethane, 2% nitrogen, 0.6% propane, 0.3% other hydrocarbons and 0.2% carbon dioxide (CO<sub>2</sub>). An odourising agent (mercaptan) is added to all piped supplies of the gas in order that leaks can be readily detected (Jerome, 1994). Natural gas may be used either as a compressed gas (CNG) with essentially the same composition as the raw gas or, by cooling, as a liquefied natural gas (LNG) that, with treatment, can comprise up to 99% methane.

The primary advantage of using LNG is that it can be stored at relatively low pressures of between 140 and 1030kPa compared to CNG which is stored at pressures of between 20 and 25MPa (Murphy *et al.*, 1995). This need to be stored under pressure makes CNG, like other alternative fuels such as H<sub>2</sub> and to a lesser degree liquefied petroleum gas (LPG), more difficult to store than the traditional liquid fuels. The interest in natural gas as an alternative fuel stems from its inherently clean-burning properties, its domestic resource base (North Sea reserves) and widespread commercial availability (Energy Information Administration, 1994).

### **5.2 Toxicity and health effects**

For inhalation and ingestion exposures, LNG and CNG are considered together.

#### **5.2.1 Inhalation**

##### *Acute effects*

Methane, the main constituent of natural gas, is classed as a simple asphyxiant.

##### *Chronic effects*

There is no information available on the chronic effects of exposure to either CNG or LNG.

#### **5.2.2 Ingestion**

##### *Acute and chronic effects*

Ingestion of either CNG or LNG is unlikely.

#### **5.2.3 Dermal contact**

##### *Acute effects*

##### *Compressed natural gas*

Eye and skin effects resulting from exposure to CNG are not anticipated<sup>16</sup>.

##### *Liquefied natural gas*

As with other cryogenic gases (such as liquefied H<sub>2</sub>) the major health hazard associated with LNG is cryogenic burns from contact with the liquid itself or

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<sup>16</sup> BOC (1996) *Material Safety Data Sheet: Methane*. Available [May 2000] from <http://www.boc.com>

components of fuel storage or delivery systems that are in contact with the fuel. Although a lesser hazard, cold gas may also injure individuals in the vicinity of gas releases (Murphy *et al.*, 1995).

### Chronic effects

There is no information available on the chronic effects of exposure to either CNG or LNG.

## **5.3 Environmental fate**

### 5.3.1 General

Natural gas (CAS no. 8006-14-2) is primarily made up of methane and a small amount of ethane. These compounds will be the main consideration in this section. Liquefied natural gas released to the environment will vaporise to its gaseous state. Therefore, this section focuses on the environmental fate of the gases.

### 5.3.2 Physicochemical properties

Table 5.1 summarises the principal physicochemical properties of methane and ethane.

**Table 5.1 Physicochemical properties of methane and ethane**

Property	Value	
	Methane	Ethane
Formula	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>
CAS number	74-82-8	74-84-0
Molecular weight	16.04 <sup>a</sup>	30.07 <sup>b</sup>
Melting point	-182.47°C <sup>a</sup>	-183.3°C <sup>b</sup>
Boiling point	-161.45°C <sup>a</sup>	-88.6°C <sup>b</sup>
Vapour pressure	4.66×10 <sup>5</sup> mmHg (at 25°C) <sup>c</sup>	3.15×10 <sup>4</sup> mmHg (at 25°C) <sup>d</sup>
Henry's Law constant	0.66atm.m <sup>3</sup> /mol (at 25°C) <sup>c</sup>	0.50atm.m <sup>3</sup> /mol (at 25°C) <sup>d</sup>
Water solubility	22mg/l (at 25°C) <sup>c</sup>	60.2mg/l (at 25°C) <sup>d</sup>
Relative density	0.7168g/l (density) <sup>e</sup>	n/a
Vapour density	0.555 (air = 1) <sup>a</sup>	1.05 (air = 1) <sup>b</sup>
Log K <sub>ow</sub>	1.09 <sup>c</sup>	1.81 <sup>d</sup>

Notes: <sup>a</sup>Chemfinder [methane]<sup>17</sup>; <sup>b</sup>Chemfinder [ethane]<sup>17</sup>; <sup>c</sup>esc [methane]<sup>18</sup>; <sup>d</sup>esc [ethane]<sup>18</sup>, <sup>e</sup>HSDB [methane]<sup>19</sup>; n/a — not available in literature identified

Both compounds are colourless and odourless, and gaseous at ambient temperatures.

<sup>17</sup> Chemfinder information available [April 2000] from <http://www.chemfinder.com>

<sup>18</sup> esc information available [May 2000] from SRC PhysProp Database <http://esc.syrres.com/interkow/PhysProp.htm>

<sup>19</sup>HSDB. Methane. Produced by National Library of Medicine, Bethesda, USA. Accessed via Datastar [May 2000]

### 5.3.3 Environmental degradation and fate

Methane is less dense than air so any that is emitted due to a release of natural gas will dissipate into the atmosphere.

The main loss process for atmospheric methane is the reaction with hydroxyl (OH) radicals (Vaghjiani & Ravishankara, 1991). Methane has an atmospheric hydroxyl radical reaction rate constant ( $k$ ) of  $8.36 \times 10^{-15} \text{ cm}^3/\text{molecule.s}$  at  $25^\circ\text{C}$  (IUCLID, 1996d) in the troposphere under the influence of sunlight, and the estimated half-life ranges from 960d (IUCLID, 1996d) to 1908d (HSDB<sup>20</sup>). However, Vaghjiani and Ravishankara (1991) measured rate constants at lower temperatures as temperatures in the troposphere range from 20 to  $-55^\circ\text{C}$  ( $k = 9.0 \times 10^{-16} \text{ cm}^3/\text{molecule.s}$  at  $-50^\circ\text{C}$ ), and suggested a 25% longer lifetime for methane than previously accepted. The Intergovernmental Panel on Climate Change, as cited by Wallington and Nielsen (1999), give the atmospheric lifetime of methane as 12.2 years.

Ethane has an atmospheric hydroxyl radical reaction rate constant of  $2.68 \times 10^{-13} \text{ cm}^3/\text{molecule.s}$  (at  $25^\circ\text{C}$ ) (IUCLID, 1996e) and an estimated half-life of 30d in the troposphere under the influence of sunlight (IUCLID, 1996e).

A  $K_{oc}$  (solids/water partition coefficient normalised to organic carbon) of 753 for methane indicates low mobility with water in soil (HSDB<sup>19</sup>); however, its high vapour pressure suggests that the gas would permeate through soil in the event of an underground leak

The ability of bacteria to metabolise  $\text{C}_1\text{-C}_4$  hydrocarbons has been demonstrated in a number of studies (IUCLID, 1996d) and the utilisation of methane by some bacteria, such as *Methylococcus*, as a carbon source suggests that methane is biodegradable (HSDB<sup>19</sup>). Utilisation of methane by soil microorganisms has been detected in five soil samples collected from sites near Adelaide, South Australia (HSDB<sup>19</sup>). Methane has also been demonstrated to be 'inherently biodegradable' in a 35d adaptation of the normal biochemical oxygen demand (BOD) test. After 35d, 65.7% of the 1mg of methane placed in a BOD vessel was degraded (IUCLID, 1996d). A similar test with 1mg of ethane resulted in 72.6% degradation after 35d (IUCLID, 1996e).

### 5.4 Fire, explosion and other safety aspects

Natural gas is highly flammable and explosive and forms ignitable mixtures with air over a relatively wide range of concentrations (from 5 to 15% by volume in air). The minimum ignition energy (MIE) of methane has been reported as 0.28 to 0.29mJ (Baker, *et al.*, 1983; Ringland, 1994). The flashpoint of methane is  $-187.7^\circ\text{C}$ ; the autoignition temperature of natural gas is between 450 and  $500^\circ\text{C}$ . It is also buoyant and may collect under roofs or ceilings, forming pockets of potentially ignitable gaseous mixtures (Energy Information Administration, 1994). In unconfined areas, the fuel will rise and dissipate. Natural gas has no odour and for safety reasons an odorant is added

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<sup>20</sup> HSDB. Methane. Produced by National Library of Medicine, Bethesda, USA. Accessed via Dastar [May 2000]

to all piped supplies in such amounts that the gas is detectable by smell at a fifth of the lower flammable concentration (ie at approximately 1% gas in air) (Murphy *et al.*, 1995). Natural gas burns with a pale blue flame which may not be easily distinguished in bright light.

Although the fact that both LNG and CNG are stored at pressure in a vessel may increase the risk of leaks from fittings, valves and joints (Murphy *et al.*, 1995), regulations and safety procedures, such as pressure relief systems, mitigate this hazard. Furthermore, the need for the tanks to be able to withstand high pressures also makes them resistant to damage from impacts such as vehicle collisions.

#### 5.4.1 Compressed natural gas (CNG)

A major safety consideration, particularly with CNG, is pressure. The vessels storing CNG must be manufactured to withstand great pressures (between 20 and 25MPa). As for other compressed gaseous fuels, the high pressures encountered in re-fuelling or otherwise maintaining CNG-powered vehicles require safety precautions and training (Murphy *et al.*, 1995), particularly for consumer retail situations. Furthermore, any fire that occurs in a CNG vehicle that impinges on the storage tank will lead to increased venting of its contents, introducing more fuel to the fire in a potential cascade effect.

The fact that CNG is stored at pressure means that even small leaks can lead to large volumes of gas being released. A unit volume of compressed gas produces approximately 200 times that volume when it is released. A leak from a CNG storage vessel will produce a cloud of cold dense gas due to the cooling effect of the drop in pressure from the vessel to ambient conditions (temperatures of  $-100^{\circ}\text{C}$  or less may be reached (Murphy *et al.*, 1995)). Therefore, although CNG is lighter than air, there is the opportunity for such cold and therefore dense fuel to collect in low lying areas, drains or trenches (Murphy *et al.*, 1995).

A final safety consideration for CNG is that natural gas contains small amounts of  $\text{CO}_2$ , hydrogen sulphide and water which, particularly under high pressure, may be corrosive to steel storage vessels. Before compressing the gas it is necessary to treat and dry it to remove as much of these trace constituents as practicable (Murphy *et al.*, 1995). Therefore, consideration should be given to the choice of material used in CNG storage.

#### 5.4.2 Liquefied natural gas (LNG)

The main disadvantage of LNG as a fuel is the low temperature ( $-160^{\circ}\text{C}$ ) at which it must be stored. At such low temperatures, it is not technically possible to add an odorant to the gas, which means that leaks from LNG storage may go undetected and thereby pose a hazard and will require other means of detecting leaks. Another problem with low temperatures is that the materials used in fuel applications from production through to use must withstand repeated cycling between ambient and extremely low temperatures, which can lead to stress-related failures (Murphy *et al.*, 1995).

Storage of LNG is usually in double-skinned, highly insulated tanks that are able to contain an internal pressure of 1.6-1.7MPa (Owen & Coley, 1995). Should an incident, such as a collision with a vehicle, reduce or remove the

insulation, rapid warming of the contents will lead to pressure build up and increased venting from pressure relief systems designed to maintain the tank integrity. Complete failure of the tank and an associated explosion is unlikely unless these pressure relief systems fail.

If a vessel containing a liquid whose vapour pressure is well above atmospheric pressure ruptures, a boiling liquid expanding vapour explosion (BLEVE) may occur (Baker *et al.*, 1983). Although no instances of LNG BLEVEs have been reported in the literature reviewed, it is possible that it may occur with an LNG storage vessel (Murphy *et al.*, 1995). If radiant heat or flames heat a storage vessel containing liquefied LNG, its contents will warm and may begin to boil. If the vessel ruptures, the contained liquid will be released, leading to an explosive, rapid phase change from liquid to gas and a buoyant fireball (Baker *et al.*, 1983; Leslie & Birk, 1991; Papazoglou & Aneziris, 1999). Such events are rare and can be further mitigated by using materials for the vessel that fail predictably and non-catastrophically and by fitting pressure release valves or safety devices to allow controlled releases of product if the internal pressure increases.

Any spillage of LNG produces a fire risk. As the released liquid is so cold, the vaporising gas above it will be denser than air. The gas may then travel along the ground or into drains, utility ducts and other low lying areas until ambient conditions warm it sufficiently for it to rise and dissipate. If such a spill is ignited, its heat release rate is 60% greater than that from an equivalent spill of gasoline (Murphy *et al.*, 1995).

Finally, if a spillage of LNG enters a water body there will be a rapid phase change from liquid to gas. The rapidity of the change is such that an apparent explosion can result (Murphy *et al.*, 1995).

## **5.5 Summary**

Natural gas is a simple asphyxiant with no other recorded toxic properties. From a health viewpoint, greater concern relates to the potential for cryogenic burns from LNG.

The major component of natural gas, methane, is persistent in the atmosphere and has a lifetime of up to 12 years.

Any pressurised gas escaping from a container will undergo cooling, a hazard associated with CNG. In addition, CNG must be stored at high pressures (20-25MPa). At such high pressures, even a small leak can release a large volume of gas into the environment. A failure of an above ground pressure vessel could cause damage to nearby properties and people. Safety regulations and procedures mitigate the hazard of pressure vessel failure and BLEVEs. Furthermore, because pressure vessels must withstand high internal pressures, their mechanical strength makes them relatively more resistant to physical impacts.

Natural gas is less dense than air and will naturally dissipate, unless confined by roofs or other constructions. Cold, dense gaseous releases of LNG or CNG (if the latter has undergone pressure-release cooling) may linger at or near ground level for a time until sufficiently warmed to dissipate. The low



temperature at which LNG is stored necessitates particular health and safety precautions.

The flame of burning natural gas is poorly distinguishable in bright light. The gas is also odourless, making leak detection difficult unless, as is now the case for natural gas supplies, an odorant is added. However, it is not technically possible to add an odorant to LNG, meaning leaks may go undetected.

## **6 METHANOL**

### **6.1 Background**

Methanol has been used since the beginning of the 20th century as a solvent, and more recently as a fuel for racing cars (Costantini, 1993). In the last few years in the US, efforts have been made by government, state regulators, and others to promote the use of methanol to replace gasoline and diesel fuels for passenger cars, buses, and other fleet vehicles in order to improve air quality. Although its use would indeed reduce the levels of some pollutants, this practice could increase exposure of the general public to methanol itself and to formaldehyde, a product of methanol combustion (Costantini, 1993), although this will not be a concern with methanol as a fuel in fuel-cell vehicles.

### **6.2 Toxicity and health effects**

#### **6.2.1 Inhalation**

##### *Acute effects*

Nearly all the available information about methanol toxicity in humans concerns the consequences of acute exposures (Kavet & Nauss, 1990). Acute methanol toxicity has a fairly well-defined pattern. There is an initial transient depression of the central nervous system (CNS) followed by an asymptomatic period lasting from several hours to two or more days (12 to 24 hours is more common). The final stage involves a metabolic acidosis with associated visual effects (blurred or indistinct vision, changes to the visual field and, in severe cases, blindness). Other physical effects include headache, dizziness, nausea and vomiting; coma and death may result, usually from respiratory failure (Kavet & Nauss, 1990). It is unlikely, other than in accidental or intentional inhalation of large amounts of methanol vapour, that such effects would occur from exposure to methanol as a fuel (Kavet & Nauss, 1990; Costantini, 1993).

Acute exposure of healthy people to low concentrations of methanol has little effect on measures of neurobehavioural performance (Chuwers *et al.*, 1996).

##### *Chronic exposure*

Long-term human exposures to methanol may cause effects qualitatively similar to those from relatively high levels of acute exposure, but to a lesser degree (Kavet & Nauss, 1990). These effects consist of CNS and visual disorders. There is limited information on the effects of repeated exposure to methanol concentrations similar to those that would result from the introduction of methanol fuels (Costantini, 1993). Whether toxic effects occur depends on whether methanol metabolism can proceed at a faster rate than methanol absorption (Kavet & Nauss, 1990).

There is some evidence from epidemiological studies of workers exposed to methanol from duplicating machines that repeated exposures may cause headache, dizziness, nausea, and blurred vision, indicating that methanol exposure can result in CNS depression (Costantini, 1993). These conclusions, however, were based on self-reporting of symptoms. The dose-effect relationships for the chronic effects of methanol in humans are not well described (Kavet & Nauss, 1990). Human and animal studies provide weak evidence that protracted exposures to methanol vapours may damage the CNS

and visual system, but additional work is required to define the clear dose-response relationship (Costantini, 1993).

Studies on developmental effects of methanol have been conducted in rodents. These have indicated that fetal methanol exposure at high doses during gestation can be teratogenic and may produce developmental effects; however, no such effects have been observed in humans (Costantini, 1993).

### 6.2.2 Ingestion

#### Acute effects

Historically, ingestion has been the predominant route of poisoning. Methanol has been recognised as a toxic agent for humans since the end of the nineteenth century (Costantini, 1993). Early manifestations of intoxication by ingestion are similar to those for ethanol (Reese & Kimbrough, 1993) but later sequelae differ (eg delayed visual effects; see inhalation section above). The most important initial symptom of methanol poisoning is visual disturbance (Becker, 1983). Blurred vision, with other senses remaining relatively undisturbed, is strongly suggestive of methanol poisoning.

The appearance of clinical symptoms in methanol poisoning is affected by the amount of ethanol simultaneously ingested (ethanol slows the progression of methanol toxicity), by associated medical conditions and by the dietary sufficiency of folate (which is involved in methanol metabolism) (Kavet & Nauss, 1990; Becker, 1983). Methanol may be ingested by alcoholics as an alcohol substitute, and sporadic cases in chronic alcoholics present special problems for clinical diagnosis because evidence of acidosis may be misinterpreted as alcoholic ketoacidosis.

#### Chronic effects

No specific information is available on effects due to chronic ingestion, but in common with chronic exposure by inhalation, the health effects are likely to be qualitatively similar to those from acute exposure.

### 6.2.3 Dermal contact

#### Acute effects

Although ingestion has been the predominant route of poisoning, percutaneous absorption of methanol liquids has also been shown to produce toxic effects (see inhalation and ingestion sections above).

#### Chronic effects

No specific information is available on chronic effects due to dermal contact with methanol, but in common with chronic exposure by inhalation and ingestion, the health effects are likely to be qualitatively similar to those from acute exposure.

## **6.3 Environmental fate**

### **6.3.1 General**

Methanol, CH<sub>3</sub>OH (CAS no. 67-56-1), unlike gasoline and diesel, is highly water soluble. Therefore, measures such as the use of interceptors<sup>21</sup> on surface drainage from fuel retail sites will be ineffective in preventing the fuel from entering drainage courses, and alternative means of containing spillages of methanol would be required. It may be necessary to confine the entire contents of storage tanks in the event of an accidental loss. Methanol is both volatile and biodegradable (Murphy *et al.*, 1995) and does not bioaccumulate.

### **6.3.2 Physicochemical properties**

Table 6.1 presents the principal physicochemical properties of methanol.

**Table 6.1 Physicochemical properties of methanol**

<b>Property</b>	<b>Value</b>
Molecular weight	32.04 <sup>a</sup>
Melting point	-98°C <sup>a</sup>
Boiling point	64.6°C <sup>a</sup>
Vapour pressure	96mmHg; 12.8kPa (at 20°C) <sup>a</sup>
Henry's Law constant	4.55×10 <sup>-6</sup> atm.m <sup>3</sup> /mol <sup>c</sup>
Water solubility	Miscible in all proportions with water <sup>a,b,c</sup>
Relative density	0.791 <sup>a</sup>
Vapour density	1.11 (air = 1) <sup>a,c</sup>
Log K <sub>ow</sub>	-0.77 <sup>b,c</sup>

Notes: <sup>a</sup>Chemfinder<sup>22</sup>; <sup>b</sup>IUCLID (1996f), <sup>c</sup>HSDB<sup>23</sup>

Methanol is a colourless liquid at room temperature with an 'alcoholic' odour<sup>23</sup>.

### **6.3.3 Environmental accumulation**

Methanol has a low adsorptive capacity on soils (adsorption coefficient: 0.13-0.61) and due to its miscibility with water is highly mobile in the terrestrial environment in the presence of water (IUCLID, 1996f). The bioaccumulation factor (BAF) of methanol has been determined to be 1 in fish (carp, *Cyprinus carpio*) (IUCLID, 1996f), indicating that the concentration of methanol is the same in the fish as in the surrounding water. The bioconcentration factor (BCF) is <10 in golden ide (fish) and has been estimated to be 0.2 using a recommended regression-derived equation<sup>23</sup>.

### **6.3.4 Environmental degradation and fate**

The high vapour pressure of methanol indicates that evaporative emissions would be a major concern and any methanol released to a dry surface would volatilise relatively rapidly. The values quoted for Henry's Law constant also indicate that volatilisation from water may be significant (IUCLID, 1996f). Volatilisation half-lives of 4.8d and 51.7d have been estimated for a model

<sup>21</sup> Interceptors are currently installed on petrol station forecourts as a measure to prevent spills of diesel and gasoline from reaching the surface water drainage beyond the station boundary

<sup>22</sup> Chemfinder information available [April 2000] from <http://www.chemfinder.com>

<sup>23</sup> HSDB. Methanol. Produced by National Library of Medicine, Bethesda, USA. Accessed via Dastar [May 2000]

river (1m deep) and an environmental pond, respectively<sup>24</sup>. Methanol present in the atmosphere has a half-life of up to 17.8d and is removed by reaction with hydroxyl radicals (HSDB<sup>25</sup>; IUCLID, 1996f).

Methanol released to waterways would be rapidly diluted and a large number of screening tests indicate that it is readily biodegradable<sup>24</sup>, although no data are available from tests using river water inocula. One test reported 70% degradation of methanol in seawater at a concentration of 2.56ppm (IUCLID, 1996f) while another test, following OECD guideline 301D (Ready Biodegradability: closed bottle test), reported 99% degradation. Methanol has also been reported to be readily degraded in subsurface soil and groundwater; concentrations of 1-1000mg/l have degradation rates of 0.8-20.4mg/l/d (IUCLID, 1996f). The rate of degradation of methanol was higher in samples incubated under anaerobic as opposed to aerobic conditions (IUCLID, 1996f). An anaerobic water die-away test using marinewater and sediment inocula from San Francisco Bay gave 83-91% degradation after 3d<sup>26</sup>. Numerous bacterial strains have been isolated that are capable of degrading methanol as a sole source of carbon<sup>24,25</sup> and 90% removal has been reported after 1d in an acclimated wastewater batch reactor (IUCLID, 1996f). Methanol degraded readily in test tube microcosms simulating subsurface soils and groundwaters from sites in Virginia and New York. Significant biodegradation has also been observed in field tests involving the injection of organic waste (comprising methanol, acetic acid and formic acid) into wells of 850-1000ft depth; biodegradation was confirmed by concentration monitoring and microbial population counts<sup>26</sup>.

Modelling the transport and fate of methanol introduced into surface water and groundwater environments in various scenarios indicates that approximately all of the released methanol would be removed fairly quickly through volatilisation, advection or degradation (Katsumata & Kastenberg, 1996). Due to dilution and the natural processes mentioned above, significant concentrations of methanol are not likely to occur much beyond the immediate vicinity of the release or to persist long after the release period (Katsumata & Kastenberg, 1996).

#### **6.4 Fire, explosion and other safety aspects**

Methanol is a highly flammable liquid and therefore poses a fire and explosion hazard. Due to its volatility, it readily forms explosive mixtures with air at normal room temperatures (Energy Information Administration, 1994). The fuel's minimum ignition energy (MIE) is 0.14mJ (Jerome, 1994) and it also has a wide flammability range (from 7.3 to 36%), which present greater safety concerns than for other fuels with more narrow flammability ranges and MIEs. In partially filled or empty storage tanks, methanol is more likely than other hydrocarbon fuels to produce a combustible mixture above the fuel. However,

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<sup>24</sup> ChemFate Database information available [May 2000] from <http://esc.syrres.com/efdb/Chemfate.htm>

<sup>25</sup> HSDB. Methanol. Produced by National Library of Medicine, Bethesda, USA. Accessed via Datastar [May 2000]

<sup>26</sup> Chemfinder information available [April 2000] from <http://www.chemfinder.com>

concerns over the flammability range in methanol are offset by its relatively high lower flammability limit (7.3% compared with 1.4% for gasoline), higher flashpoint temperature (approximately 11°C; IUCLID, 1996f), higher autoignition temperature (approximately 470°C; Merck, 1989) and lower vapour pressure than gasoline (Energy Information Administration, 1994).

Methanol vapour is much heavier than air and, if accidentally released, may accumulate at floor level or in pockets in low lying areas. Furthermore, it is possible for the vapour to travel considerable distances to an ignition source and then flash back towards the source (Energy Information Administration, 1994). In daylight, methanol burns with an invisible flame, unless a fuel additive is added or another combustible material is affected by the flame, in which case a colour may be seen.

There are no appreciable differences, from a fire hazard viewpoint, between road tanker transport of methanol and equivalent transport of gasoline. However, it is important for those transporting and storing methanol to consider the greater corrosive potential of methanol over other fuels when specifying materials for fuel storage and transfer (Murphy *et al.*, 1995). Furthermore, and in contrast to gasoline, methanol will form flammable air-fuel mixtures in the air space above fuel in tanks. Gasoline stored in tanks produces an air-fuel mixture that is too rich to support combustion whereas the air-fuel mixture in diesel tanks is too lean. To reduce the hazards associated with the transfer and storage of methanol, vapour recovery and earthing of tanks and delivery vehicles is necessary to minimise the opportunity for ignition of fuel-air mixtures (Murphy *et al.*, 1995).

### **6.5 Summary**

Acute exposure to methanol, whether by inhalation, ingestion or dermal contact, produces a well-defined set of symptoms: CNS depression followed by an asymptomatic period of usually 12 to 24h and, finally, visual effects (blurred vision, changes to visual fields and, in severe cases, blindness). The acute toxicity of methanol is such that accidental ingestion (eg as a result of siphoning fuel from a vehicle) may be sufficient to cause acute effects and even death. Intentional ingestion would carry greater risks. The asymptomatic period that may follow methanol exposure means that appropriate medical attention is often not sought. Chronic effects are qualitatively similar to acute effects. Whether toxic effects occur depends on whether methanol absorption exceeds the body's metabolic capacity. Methanol can be abused as an ethanol (alcohol) substitute.

Methanol can be released to the atmosphere by evaporative emissions. Once there, methanol is estimated to have a half-life of 17.8d due to its reaction with hydroxyl radicals. Methanol is completely miscible with water, resulting in ready dilution in the presence of water and is considered to be readily biodegradable in natural waters and soil.

The main safety concerns regarding methanol are its high flammability, wide flammability limits and relatively high flashpoint and low MIE. However, its lower flammability limit is greater (7% compared with 1.4%) and it is less volatile than gasoline. Together, these attributes make methanol less likely to

produce flammable fuel-air mixtures than the other liquid fuels. However, the high upper flammability limit of methanol means it is more likely to produce flammable fuel-air mixtures in air spaces above the fuel in storage tanks. Static charges built-up during bulk fuel transfer may be sufficient to ignite a fuel-air mixture within the flammable range, but normal vehicle re-fuelling is unlikely to build-up such a charge. Also, effective mitigating measures such as equipment grounding and anti-static additives are used. Methanol is also corrosive, which necessitates careful decisions about the materials used for storing, transporting and transferring the fuel.

## **7 LIQUEFIED PETROLEUM GAS**

### **7.1 Background**

Liquefied petroleum gas (LPG) is a generic term to describe liquefiable gases consisting mainly of C<sub>3</sub> and C<sub>4</sub> hydrocarbons (propane and butane, with lesser quantities of propene and butene). Automotive grade LPG in the UK is typically greater than 90% propane with lesser quantities of iso-butane and n-butane. Other countries such as France, Italy and the Netherlands use propane/butane mixtures. At normal temperatures and pressure, these hydrocarbons exist as gases but under moderate pressure (690 to 2070kPa; 100 to 300psi) they exist as liquids, making them suitable for storage and transport. When the pressure is released, the liquid hydrocarbons again become gaseous.

### **7.2 Toxicity and health effects**

#### **7.2.1 Inhalation**

##### *Acute effects*

While there are few reports in the published literature of studies on LPG (CONCAWE, 1997), information published on the major components (propane and butane) is useful for predicting the likely toxicity of LPG. Propane is classed as a simple asphyxiant.

Brief exposure to low concentrations of propane and butane does not cause any systemic effects. At sufficiently high concentrations these gases are anaesthetics; such exposures are mainly associated with intentional inhalation (for instance of aerosol propellants). A particular hazard in such a situation is cardiac sensitisation with the subsequent risk of sudden death. Inhalation of high concentrations (above 10%) will result in narcotic effects such as weakness, headache, light-headedness, nausea, confusion, blurred vision and increased drowsiness. Exposure to high concentrations may result in loss of consciousness, convulsions and even asphyxiation as a consequence of oxygen deficiency, in addition to cardiac sensitisation. The narcotic effect of butane is greater than that of propane and exposure to a concentration of 1% (10,000ppm) can cause drowsiness after a few minutes.

##### *Chronic effects*

Limited information is available on the chronic effects of LPG exposure. Occupationally exposed workers in an LPG bottling plant complained of dry throat, dry cough, a high degree of excitation and sometimes dizziness (BUA, 1997).

#### **7.2.2 Ingestion**

##### *Acute and chronic effects*

Ingestion of LPG is unlikely.

#### **7.2.3 Dermal contact**

##### *Acute effects*

Direct contact with liquefied propane causes erythema, oedema and deep necrosis (ie cryogenic burns; BUA, 1997).



### Chronic effects

No irritant effects have been detected on the skin and mucous membranes (BUA, 1997).

## **7.3 Environmental fate**

### 7.3.1 General

Liquefied petroleum gas (CAS no. 68476-85-7) primarily comprises propane and butane (n- and iso-) and these compounds will be the main consideration in this section. The physical properties of a specific commercial LPG will depend on the relative proportions of its constituents and will be intermediate between those of propane and n-butane (CONCAWE, 1992b); in the UK, LPG is 90% propane. The following assessment focuses on LPG components in the gaseous state.

### 7.3.2 Physicochemical properties

Table 7.1 presents the principal physicochemical properties of propane and n-butane.

**Table 7.1 Physicochemical properties of propane and n-butane**

Property	Value		
	Propane	Isobutane <sup>h</sup>	n-Butane
Formula	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	C <sub>4</sub> H <sub>10</sub>
CAS number	74-98-6	72-28-5	106-97-8
Molecular weight	44.10 <sup>a</sup>	58.12	58.12 <sup>b</sup>
Melting point (°C)	-187.7 <sup>a</sup>	-159.6	-138.35 <sup>b</sup>
Boiling point (°C)	-42.1 <sup>a</sup>	-11.7	-0.45 <sup>b</sup>
Vapour pressure (mmHg)	7152 (at 25°C) <sup>d</sup> 11,326 (at 40°C) <sup>c</sup> 760 (at 25°C) <sup>f</sup>	2280 (at 20°C)	1823 (at 25°C) <sup>e</sup> 2813 (at 40°C) <sup>c</sup> 760 (at 25°C) <sup>g</sup>
Henry's Law constant (atm.m <sup>3</sup> /mol)	0.7067 <sup>d</sup>		0.9497 <sup>e</sup>
Water solubility (mg/l)	62.4 <sup>d</sup>	48.9	61.2 <sup>e</sup>
Relative density	0.585 (at -45°C) <sup>f</sup>	0.594 (at -11.7°C)	0.601 (at 0°C) <sup>g</sup>
Vapour density (air=1)	1.56 (at 0°C) <sup>f</sup>	2.05	2.07 (at 0°C) <sup>g</sup>
Log K <sub>ow</sub>	2.36 <sup>d</sup>	2.76	2.89 <sup>e</sup>

Notes: <sup>a</sup>Chemfinder [propane]<sup>27</sup>; <sup>b</sup>Chemfinder[butane]<sup>27</sup>; <sup>c</sup>CONCAWE (1992); <sup>d</sup>SRC[propane]<sup>28</sup>; <sup>e</sup>SRC[n-butane]<sup>27</sup>; <sup>f</sup>HSDB[propane]<sup>29</sup>; <sup>g</sup>HSDB[butane]<sup>30</sup>; <sup>h</sup>BUA, 1997

Both compounds are colourless; propane is odourless<sup>29</sup> while butane is described as having a faint, gasoline-like odour<sup>30</sup>. The components of LPG are normally gaseous at commonly encountered environmental temperatures, although n-butane will exist as a liquid at temperatures below 0°C.

<sup>27</sup> Chemfinder information available [April 2000] from <http://www.chemfinder.com>

<sup>28</sup> SRC information available [May 2000] from SRC PhysProp Database <http://esc.syrres.com/interkow/PhysProp.htm>

<sup>29</sup> HSDB. Propane. Produced by National Library of Medicine, Bethesda, USA. Accessed via Dastar [May 2000]

<sup>30</sup> HSDB. Butane. Produced by National Library of Medicine, Bethesda, USA. Accessed via Dastar [May 2000]

### 7.3.3 Environmental accumulation

Bioconcentration factors (log BCF) for propane have been estimated to range from 1.56 to 1.78<sup>29</sup> and those for butane from 1.78 to 1.79<sup>30</sup>, suggesting bioconcentration is not an important factor for organisms in aquatic systems<sup>31,32</sup>. Estimated  $K_{oc}$  values range from 450 to 460 for propane<sup>31</sup> and 450 to 900<sup>32</sup> for butane indicating that some of the primary constituents of LPG may partition from the water column to organic matter contained in sediments and suspended materials. However, volatilisation is expected to be the dominant fate process<sup>31,32</sup>.

### 7.3.4 Environmental distribution and fate

The high vapour pressures of propane, isobutane and butane suggest that almost all of any LPG released will enter the atmosphere (BUA, 1997). Mackay level 1 distribution modelling indicates that C<sub>1</sub> to C<sub>4</sub> hydrocarbons will be present exclusively in air (IUCLID, 1996g). Propane and butane in the atmosphere are degraded by reaction with photochemically produced hydroxyl radicals. Reaction with hydroxyl radicals under the influence of sunlight is estimated to result in half-lives of 13d for propane<sup>30</sup> and 6d for butane<sup>31</sup>.

The Henry's Law constants for propane and butane, presented in Table 7.1, suggest rapid volatilisation from aquatic environments. The volatilisation half-lives from a model river and a model pond (the latter considering the effects of adsorption) have been estimated to be 1.9h and 2.3d for propane, and 2.2h and 2.6d for butane.

These hydrocarbons are not sensitive to hydrolysis under environmental conditions but are considered readily biodegradable (IUCLID, 1996g). It has been reported that bacterial degradation of propane readily occurs in soil (IUCLID, 1996g), and it has been observed that ethane, propane and butane promote the growth of *Mycobacterium vaccae*, suggesting that these hydrocarbons are biodegradable (IUCLID, 1996g). *Mycobacterium crassa* and *M. phlei* also grow on butane. Over 24h, propane and n-butane were observed to be oxidised to their corresponding methyl ketones and the corresponding alcohols by cell suspensions of over 20 methylotrophic organisms isolated from lake water and soil samples<sup>25,26</sup>.

## 7.4 Fire, explosion and other safety aspects

In gaseous form, the constituents of LPG are approximately 50% more dense than air and do not disperse easily. Therefore, it is likely that releases of LPG will sink to the lowest possible level and form pockets in such places as drains, depressions and other low lying areas. If the gas migrates, it is possible for it to encounter an ignition source some distance from the release point and the flame may then travel back to the source (HSE, 1997). Although the gas is odourised to aid detection, the fact that it is denser than air means it may go undetected in low lying areas (Murphy *et al.*, 1995).

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<sup>31</sup> HSDB. Propane. Produced by National Library of Medicine, Bethesda, USA. Accessed via Datastar [May 2000]

<sup>32</sup> HSDB. Butane. Produced by National Library of Medicine, Bethesda, USA. Accessed via Datastar [May 2000]

Liquefied petroleum gas forms flammable mixtures with air at concentrations between 2% and 10% and, therefore, poses a fire and explosion hazard. The minimum ignition energy (MIE) of propane has been reported to range from 0.26 to 0.31mJ (Baker *et al.*, 1983; Ringland, 1994); the reported MIE for n-butane is 0.26mJ (Baker *et al.*, 1983). Releases of LPG into confined spaces and subsequent ignition may result in an explosion; if unconfined, fires are the major hazard (HSE, 1997). Propane, one of the main constituents of LPG, burns with a luminous, smoky flame. The flashpoints of propane and butane are -104°C and -60°C, respectively (Royal Society of Chemistry, 1992).

As for the other pressurised liquefied gaseous fuels with vapour pressure well below atmospheric pressure, boiling liquid expanding vapour explosions (BLEVEs) can occur with vessels containing LPG. If a vessel tears, its contents may flash evaporate and impart a great deal of energy into fragments of the vessel. If the vessel is subjected to heating for sufficient time and subsequently fails, a similar process can occur with flash evaporation of the LPG and an associated buoyant fireball (Baker *et al.*, 1983; Papazoglou & Aneziris, 1999). The explosive part of the release is caused by a rapid change from liquid phase to gas phase (Leslie & Birk, 1991). Such events are rare and all pressure vessels in the UK are fitted with pressure release valves or safety devices to allow controlled releases of product and reduce the risk of vessel failure.

Bulk storage of LPG can be in either above or below ground storage vessels. A potential safety concern for above ground storage vessels is that should there be a failure, it will impart a great deal of energy into tank fragments and fittings that may then cause severe injury to nearby individuals or damage to nearby equipment and properties. However, the pressures encountered in LPG storage are lower than those in compressed natural gas (CNG) or liquefied hydrogen (H<sub>2</sub>) storage, for example, and can be further mitigated by using materials that fail predictable or non-catastrophically. Uncontrolled releases of the gas from its pressurised state to ambient pressure will result in cooling and an associated potential for cold burns, but this is a lesser concern than the cryogenic hazard associated with liquefied H<sub>2</sub> and liquefied natural gas (LNG) (Murphy *et al.*, 1995). Although the fact that LPG is stored at pressure in a vessel may increase the risk of leaks from fittings, valves and joints (Murphy *et al.*, 1995), regulations and safety procedures, such as pressure relief valves, mitigate the hazard. Furthermore, the need for the tanks to be able to withstand high internal pressures also makes them resistant to damage from impacts such as in vehicle collisions.

### **7.5 Summary**

The health effects associated with exposure to LPG or its constituents (propane and butane) at high concentrations include direct asphyxia causing hypoxia, anaesthetic effects and cardiac sensitisation with the associated risk of sudden death. At concentrations above 100,000ppm (10%), effects include weakness, headache, light-headedness, nausea and other narcotic effects. Only limited information is available on the chronic effects of LPG. Direct dermal contact with LPG can cause damage to the skin.

Emissions of LPG will lead to the presence of propane and butane in the atmosphere where they are anticipated to be degraded relatively rapidly by reaction with hydroxyl radicals; propane and butane have half-lives of 13d and 6d, respectively.

LPG is denser than air and thus will accumulate in places such as drains, trenches or other depressions. Because LPG is stored at pressure, a leak from a storage vessel may release a large volume of gas. A failure of an above ground pressure vessel could cause damage to nearby properties and people. Safety regulations and procedures mitigate the hazard of pressure vessel failure and BLEVEs. Furthermore, because pressure vessels must withstand high internal pressures, their mechanical strength makes them relatively more resistant to physical impacts. Propane is odourless, making leak detection difficult unless, as is currently the case for LPG supplies, an odorant is added.



## **8 OVERALL EVALUATION AND RECOMMENDATIONS**

### **8.1 Introduction**

All the fuels discussed in this report have inherent health and safety hazards. As a society we are familiar with using gasoline and diesel fuels and have come to accept, choose to ignore, or are unaware of the hazards associated with their use. Similarly, the alternative fuels discussed in this report carry with them specific health and safety concerns. This does not mean they are necessarily more (or less) hazardous than conventional fuels, but that new engineering solutions will need to be developed to reduce these health, safety and environment risks in a consumer retail fuel market. What must be emphasised is the need for forethought, sound engineering, training and education before the widespread introduction of alternative fuels (Murphy *et al.*, 1995). The use of some fuels, particularly pressurised or refrigerated gases, in road vehicles will require careful consideration to ensure they can be used safely by, for instance, members of the public re-fuelling private cars.

The aim of this section is to present, as far as is practicable, an overall hazard evaluation of the fuels in terms of their toxicity, health effects and environmental fate, as well as fire, explosion and other safety issues. It is not possible to present a *risk* ranking since this requires situation-specific information which falls outside the remit of this report. However, where possible, the fuels have been ranked in terms of hazard.

### **8.2 Toxicity and health effects**

Table 8.1 summarises the health effects of all the fuels considered in this report. Because these fuels have long been used, though not necessarily as vehicle fuels, there is a battery of knowledge on their safe use. Based on current knowledge, accidental exposures (ie when health and safety procedures are not correctly applied), or intentional exposures resulting from, for example, the abuse of methanol as an alcohol substitute or the use of gasoline/diesel as a cleaning agent could pose the greatest risks to health and safety.

Diesel and gasoline are known to cause both acute and chronic effects, observed in experimental and epidemiological studies. Although animal studies have shown that gasoline induces kidney tumours, the mechanism is not thought to be predictive of human cancer risk. Benzene, present as a constituent in gasoline at less than 1%, has been implicated in malignant diseases of the blood and blood-forming tissues. However, the major determinant of benzene exposure in the general population is smoking habit.

Although methanol can cause both acute and chronic health effects, available evidence indicates that adverse effects will not occur at the levels anticipated to result from exposure to automotive methanol vapour. However, methanol can be abused as an ethanol (alcohol) substitute with potentially severe health consequences, including blindness.

**Table 8.1 Acute and chronic health effects associated with fuels**

<b>Fuel (constituent)</b>	<b>Route of exposure</b>	<b>Acute health effects</b>	<b>Chronic health effects</b>	<b>Comments</b>
Gasolines	Inhalation	Central nervous system effects, coma and death, lung effects	Inadequate evidence for carcinogenicity in humans, limited evidence in animals; mechanism of tumour induction in rats not indicative of human cancer risk	Exposure sufficient to cause acute effects is unlikely in normal use scenarios.
	Ingestion	Ingestion will cause local damage to the gastrointestinal tract	No specific information is available	Ingestion unlikely other than by accident or from intentional abuse
	Dermal exposure	Skin defatting, transient corneal epithelial damage	Drying, cracking and dermatitis	Accidental exposure or abuse of gasoline as a cleansing agent, or through poor working hygiene
(Benzene)	Inhalation	Reversible effects on the CNS	Bone marrow depression and leukaemogenesis	Benzene content in gasoline is declining, now less than 1%
	Ingestion	Gastrointestinal ulceration	No information is available	Ingestion unlikely other than by accident or from intentional abuse of gasoline
	Dermal exposure	Reversible effects on the CNS	No information is available	Accidental exposure or abuse of gasoline as a cleansing agent, or through poor working hygiene
(Toluene and xylene)	Inhalation	Irritation of respiratory tract; CNS dysfunction	Long-term effects due to these additives in gasoline are uncertain; not classifiable as to carcinogenicity in humans	Unknown whether effects attributable to alkylbenzenes could occur from gasoline exposure

<b>Fuel (constituent)</b>	<b>Route of exposure</b>	<b>Acute health effects</b>	<b>Chronic health effects</b>	<b>Comments</b>
(Toluene and xylene)	Ingestion	No information is available	No information is available	Ingestion unlikely other than by accident or from intentional abuse of gasoline
	Dermal exposure	Skin irritation	Defatting, dermatitis	Accidental exposure or abuse of gasoline as a cleansing agent, or through poor work hygiene
	Inhalation	Nausea, headaches and sensory irritation, gastrointestinal symptoms and disorientation.	Evidence for tumours in rats and mice at high levels but whether indicative of human cancer risk unknown	Unknown whether effects attributable to MTBE could occur from gasoline exposure
	Ingestion	No information was identified during the preparation of this report	No information is available	Ingestion unlikely other than by accident or from intentional abuse of gasoline
	Dermal exposure	Skin and eye irritation	No information is available	Accidental exposure or abuse of gasoline as a cleansing agent, or through poor work hygiene
Diesel	Inhalation	CNS depression, coughing, lung damage and other respiratory effects, renal failure, liver effects, loss of consciousness	Possible evidence for lung cancer and prostatic cancer	Low volatility limits exposure, hence acute effects only occur at high exposure levels; the study showing lung cancer did not adequately account for other exposures
	Ingestion	Irritation of mouth, throat and gastrointestinal tract	No information is available	Ingestion unlikely other than by accident or from intentional abuse of diesel as a cleansing agent



<b>Fuel (constituent)</b>	<b>Route of exposure</b>	<b>Acute health effects</b>	<b>Chronic health effects</b>	<b>Comments</b>
Diesel	Dermal exposure	Skin irritation and defatting; reversible renal effects following high exposure	Acne and hyperkeratosis and other effects on the skin; tumour induction depends on chronic dermal irritation	Accidental exposure or abuse of diesel as a cleansing agent, or through poor work hygiene
Hydrogen	Inhalation	A simple asphyxiant, liquefied H <sub>2</sub> causes cryogenic burns	No information is available on chronic effects but are considered unlikely	Predominant exposure route; gas easily dissipates, reducing the opportunity for exposure
	Ingestion	No information is available	No information is available but chronic effects are considered unlikely	Ingestion is unlikely
	Dermal exposure	Liquefied H <sub>2</sub> may cause frostbite and cryogenic burns	No information is available but chronic effects are considered unlikely	Accidental exposure only
Natural gas	Inhalation	A simple asphyxiant; LNG can cause cryogenic burns	No information on chronic effects	Predominant exposure route; gas easily dissipates, reducing the opportunity for exposure
	Ingestion	No information is available	No information is available	Ingestion is unlikely
	Dermal exposure	Cryogenic burns	No information is available	Accidental exposure only
Methanol	Inhalation	CNS depression, metabolic acidosis, loss of motor coordination visual disturbances	CNS and visual disorders	

<b>Fuel (constituent)</b>	<b>Route of exposure</b>	<b>Acute health effects</b>	<b>Chronic health effects</b>	<b>Comments</b>
Methanol	Ingestion	Apart from gastrointestinal symptoms due to irritation, symptoms as for inhalation	No specific information but likely to be similar to inhalation chronic effects	Predominant route of exposure, whether through accident or from intentional abuse. Misuse of methanol as an ethanol substitute may be a concern; exposure may be followed by an asymptomatic period of up to two days
	Dermal exposure	Symptoms similar to other routes	No specific information but likely to be similar to inhalation chronic effects	Accidental exposure only unless used as a skin cleansing agent or through poor work hygiene
LPG	Inhalation	Asphyxiation, anaesthesia, cardiac sensitisation	Limited information from occupational study: dry throat, dry cough, excitation and occasional dizziness	Predominant exposure route
	Ingestion	No information is available	No information is available	Ingestion is unlikely
	Dermal exposure	Erythema, oedema and deep necrosis (ie cryogenic burns)	No irritant effects on skin and mucous membranes	Accidental exposure only

Notes: MTBE — methyl tertiary-butyl ether; LNG — liquefied natural gas; LPG - liquefied petroleum gas

Of the gaseous fuels (whether liquefied or compressed), both H<sub>2</sub> and methane (the main constituent of natural gas) are classed as simple asphyxiants with no other identified acute or chronic toxic effects. Liquefied petroleum gas (LPG) is also an asphyxiant but at high levels can also cause anaesthetic effects, cardiac sensitisation and central nervous system (CNS) effects. From a toxicity viewpoint, it may be said that these fuels present a lesser health hazard than gasoline, diesel or methanol. Furthermore, because they are gases at ambient temperatures and pressures, they will tend to disperse (unless in a confined space), reducing opportunities for prolonged exposure. However, liquefied gaseous fuels pose a health hazard owing to the low temperatures at which they must be stored, ie they can cause cryogenic burns on contact with body tissues. Losses of compressed gases from storage vessels can also present a low temperature hazard due to the cooling effect that occurs when the gas pressure falls (fire, explosion and other safety issues are addressed in Section 8.4).

There are many areas of uncertainty in assessing the potential health impacts of alternative fuels, due mostly to data limitations, particularly regarding the possible chronic effects of H<sub>2</sub>, natural gas and LPG.

### **8.3 Environmental fate**

The broad range of parameters that influence the environmental fate and behaviour of these fuels precludes an overall conclusion being reached as to the relative environmental hazard they present. For instance, they may be present as liquids or gases and, if released, will be found in different environmental compartments. Therefore, this assessment identifies the affected compartments for each fuel, attempts to rank the fuels in terms of persistence, and indicates bioaccumulative potential. Ecotoxicological considerations are not included within the remit of this report.

#### **8.3.1 Environmental compartments affected**

Table 8.2 presents a summary of the environmental compartments most likely to be affected by the various fuels. This has been produced by examining the physicochemical properties of the fuels and using the measurements and results of modelling exercises reported in the literature. This assessment shows that gasoline and diesel have the potential to affect all environmental compartments while methanol, due to its low affinity for soils and sediments, high volatility and miscibility with water, is most likely to affect air and water. The gaseous fuels are only a concern in air.

**Table 8.2 Environmental compartments affected by each fuel**

<b>Fuel</b>	<b>Environmental compartment</b>		
	<b>Air</b>	<b>Water</b>	<b>Soil/sediment</b>
Gasoline	√	√	√
Diesel	√	√	√
Hydrogen	√		
Natural gas	√		
Methanol	√	√	
LPG	√		

#### **8.3.2 Persistence**

In Table 8.3, the fuels are presented in order of decreasing environmental persistence. The fuels (and components thereof) that occur in a number of different environmental compartments will have different half-lives in each compartment; by default, the

longest half-life or lifetime reported in the literature has been used in this ranking exercise. The figures quoted in Table 8.3 are half-lives except for methane (natural gas) and H<sub>2</sub>, for which atmospheric lifetimes and residence time are used respectively. A half-life value was not found for hydrogen and those suggested for methane may be inaccurate (see Section 5.3.3). Hydrogen ranks second in this list, but is not regarded as a hazardous pollutant as it is benign and naturally present in the atmosphere at low levels (0.5ppm). This comparison of persistence demonstrates that the longest-lived fuels are methane, H<sub>2</sub> and diesel, persisting in the environment for periods in the order of years. The other fuels, gasoline, methanol and LPG, have half-lives measurable in days to months.

**Table 8.3 Environmental persistence**

<b>Fuel</b>	<b>Persistence</b>
Natural gas	Methane — 12y <sup>a</sup> ; ethane — 13d <sup>c</sup>
Hydrogen	10y <sup>b</sup>
Diesel	Up to 6y <sup>c</sup> (sediment)
Gasolines	>60d <sup>c</sup> (soil)
Methanol	18d <sup>c</sup> (atmosphere)
LPG	Propane — 13d <sup>c</sup> ; butane — 6d <sup>c</sup>

Notes: y — year; d — day

<sup>a</sup> Atmospheric lifetime, <sup>b</sup> atmospheric residence time, <sup>c</sup> half-lives

### 8.3.3 Bioaccumulation potential

Table 8.4 summarises the fuels' bioaccumulative potential. Of the fuels considered, only diesel and gasoline might conceivably have any significant bioaccumulative potential. It is generally accepted that values of log K<sub>ow</sub> greater than four indicate a potential for bioaccumulation; the log K<sub>ow</sub> of some components in diesel and gasoline exceed this value. However, none of the literature reviewed for this project reports any measurements of bioaccumulation for gasoline components with high log K<sub>ow</sub> and the measured bioaccumulation for diesel compounds is less than anticipated from its log K<sub>ow</sub> value.

**Table 8.4 Bioaccumulative potential**

<b>Fuel</b>	<b>Bioaccumulative potential</b>
Diesel	√
Gasolines	√
Hydrogen	x
Natural gas	x
Methanol	x
LPG	x

### 8.4 Fire, explosion and other safety aspects

The fuels considered in this report are a mixture of gases and liquids (whether at ambient or cryogenic temperatures). Therefore, each has a particular set of hazards that makes cross comparison difficult. However, it has been possible to consider the fuels in terms of four aspects: fire and explosion (ignition potential), pressure, temperature, corrosion and embrittlement.

#### 8.4.1 Fire and explosion

There are essentially two aspects to fire hazard: the potential for the fuel to ignite, and the size and intensity of a fire or explosion resulting from an ignition. There are three main potential sources of ignition: electrical, hot surfaces and naked flames. Having ignited, there are three main scenarios: fire, deflagration or detonation. Any ignition source can lead to any scenario and the energy imparted by an ignition source affects to a degree whether a fuel will burn, deflagrate or detonate.

The consequences of a leak or spill will be specific to the incident (eg volume of fuel released; closeness and density of nearby populations; prevailing meteorological conditions and the physical nature of the surroundings). The most important factors are the amount of fuel released and the thermal radiation resulting from the fire or explosion (which is specific to the fuel in question). Predicting the consequences of an ignition of a leak or spill requires a detailed (quantified) risk assessment, which falls outside the remit of this report. However, in simple terms, the greater the volume of fuel released in a spill or leak, the greater the potential consequences should the fuel be ignited.

Fuels can also be considered in terms of their ignition potential. For this aspect, the primary issue is the minimum ignition energy (MIE). Table 8.5 lists the fuels in order of their MIE. The lower the MIE, the greater the potential for an ignition source of sufficient energy to be able to ignite a fuel-air mixture. The MIE varies depending on the fuel-air ratio. Other important aspects are fuel volatility, flammable range and flashpoint. Of the fuels that are liquid at ambient temperatures, gasoline and methanol have the greatest potential to ignite. Gasoline is more volatile and has a lower flashpoint than methanol and diesel, but methanol has a lower MIE. Furthermore, gasoline has a relatively wide flammable range (1.4-7.6%) but this is surpassed by that of methanol (7.3 to 36%). A wide flammable range increases the potential for flammable air-fuel mixtures to form. Diesel has the highest flashpoint and lowest volatility of any of the fuels and its flammability range is comparable to gasoline. The first two criteria mean that, at ambient temperatures, diesel vapour cannot build up to sufficient levels to support combustion; it is necessary to raise the temperature or aerosolise the fuel for diesel ignition to occur.

The compressed and liquefied gaseous fuels (natural gas, LPG, and H<sub>2</sub>) have flashpoints well below ambient temperatures, increasing their ignition potential compared with the liquid fuels. Other than H<sub>2</sub>, the gaseous fuels have MIEs comparable to the liquid fuels. The low MIE of H<sub>2</sub> increases the possibility of a fuel-air mixture within the flammable range being ignited. In terms of flammability ranges, H<sub>2</sub> has the widest (4.1-74%), which increases the opportunity for flammable air-fuel mixtures to develop. Liquefied petroleum gas has the narrowest flammability range (2-10%), slightly narrower than natural gas (5-15%). However, the fact that these fuels are gaseous increases the rate at which they can dissipate, and thereby acts as a counterpoint to their greater ignition potential. Table 8.5 lists the fuels in descending order of ignition potential.

**Table 8.5 Fuel minimum ignition energies**

Liquid	Minimum ignition energy (mJ)	Gas	Minimum ignition energy (mJ)
Methanol	0.14	Hydrogen	0.02
Gasoline	0.24	Natural gas (methane)	0.28
Diesel	0.50	LPG (propane)	0.26-0.31

Note: n/a - not available in the identified literature, but assumed to be greater than gasoline or methanol

A further safety consideration is flame luminescence. Of the fuels considered, methanol, H<sub>2</sub> and natural gas burn with an invisible or poorly distinguishable flame. Although it may be possible to include additives in these fuels to increase their flame visibility, the need for high purity fuels for fuel cells may make this problematic.

#### 8.4.2 Pressure

The potential for a leak or spill increases with the pressure at which a fuel is stored. However, the corollary of this is that the transport and storage vessels used for pressurised fuels (ie compressed natural gas (CNG), LPG and compressed H<sub>2</sub>) need to have greater mechanical strength than liquid fuel containers to counter the internal pressures and are therefore relatively more resistant to physical impact. Furthermore, safety systems such as pressure relief valves mitigate the hazard.

A factor to consider in assessing the hazard associated with pressurised fuels is that relatively more material can be lost from a pressurised than from an unpressurised container in the event of a spill or leak. Table 8.6 lists the fuels in descending order of pressure hazard and shows that the compressed gaseous fuels present a greater hazard than the liquefied or liquid fuels.

**Table 8.6 Relative pressure hazard**

Fuel
Hydrogen (compressed)
Natural gas (compressed)
LPG
Natural gas (liquid)
Hydrogen (liquid)
Gasolines/Methanol/ Diesel

#### 8.4.3 Temperature

Fuel temperature is an important safety consideration for both the liquefied and pressurised gaseous fuels. When handling liquefied gases such as H<sub>2</sub> or LNG, more complex maintenance and operation systems must be employed to minimise the opportunity for contact between personnel and the liquefied gas. This may increase the opportunity for human errors or equipment failures and malfunctions. There is also the consideration of thermal cycling (the repeated change from ambient to low temperature and *vice versa*), which can lead to mechanical fatigue in storage and transfer equipment such as hoses and couplings.

An indirect temperature consideration relates to the cooling effect associated with releases of pressurised gases, whether intentional or accidental. As the gas expands from its pressurised state to ambient pressure, it undergoes cooling which may lead to potentially hazardous low temperatures, either from a human health viewpoint (ie skin contact with cold components; see Section 8.2) or a mechanical fatigue viewpoint.

Table 8.7 lists the fuels in order of descending low temperature hazard and shows the liquefied gaseous fuels present a greater hazard than the compressed gases or liquid fuels.

**Table 8.7 Relative low temperature hazard**

<b>Fuel</b>
Hydrogen (liquid)
Natural gas (liquid)
Hydrogen (compressed)
Natural gas (compressed)
LPG
Gasolines/Methanol/Diesel

#### 8.4.4 Corrosion and embrittlement

Methanol presents a potential hazard due to its corrosiveness. Although natural gas itself is not corrosive, moisture and other trace constituents in the raw gas may be corrosive if not removed before the gas is compressed. Liquefied hydrogen can, under certain circumstances, cause embrittlement of steel storage vessels. Thus, it is important to consider the choice and application of materials for storage, transport and end-use that can withstand the corrosive or embrittlement action of these fuels. In the case of CNG, drying and treating the gas to remove trace constituents is a practical measure to ensure that corrosion is not a major issue. For methanol, the primary consideration is the corrosion resistance of materials in contact with the fuel.

#### 8.5 Significant hazards and other issues

In September 2000, a workshop on the health and safety of alternative fuels was held in Leicester. This was attended by representatives of fuel producers, users (such as vehicle manufacturers), regulators and independent scientists. The aim of the workshop was to discuss the findings presented in a previous draft of this report. Based on discussions at the workshop, the following hazards and other issues (including positive considerations) have been highlighted for each fuel. These lists are not exhaustive, but serve to highlight those hazards and/or other issues felt to be of most importance for each fuel. They are intended to focus possible future research and technological developments

##### 8.5.1 Gasolines and diesel

###### Toxicity and health effects

- Carcinogenicity of some constituents

###### Environmental fate

- Bioaccumulative potential
- Potential to affect all environmental compartments

###### Fire, explosion and other safety issues

- Vapour dispersal impaired by vapour density

##### 8.5.2 Hydrogen

###### Toxicity and health effects

- Chronic toxicity data lacking
- Cryogenic hazard (liquefied H<sub>2</sub>)



### Environmental fate

- Persistent in the environment, but considered benign

### Fire, explosion and other safety issues

- Boiling liquid expanding vapour explosions (BLEVEs; liquefied H<sub>2</sub>)
- Leak detection difficult because gas is odourless (compressed and liquefied H<sub>2</sub>)
- Adding an odorant is not technically possible (liquefied H<sub>2</sub>)
- Odorants may not be compatible with fuel-cell technology (compressed and liquefied H<sub>2</sub>)
- Low ignition energy (compressed and liquefied H<sub>2</sub>)
- Wide flammable/detonable limits (compressed and liquefied H<sub>2</sub>)
- High storage pressure (compressed H<sub>2</sub>)
- Over pressure generation after ignition (compressed and liquefied H<sub>2</sub>)
- Dispersal of released fuel enhanced by low density
- Container integrity may be affected by heat cycling (liquefied H<sub>2</sub>)
- Invisible flame (compressed and liquefied H<sub>2</sub>)
- Stored fuel requires controlled venting to maintain safety (liquefied H<sub>2</sub>)

### 8.5.3 Natural gas

#### Toxicity and health effects

- Chronic toxicity data lacking
- Cryogenic hazard (LNG)

#### Environmental fate

- Persistent in the environment

#### Fire, explosion and other safety issues

- BLEVEs (LNG)
- Leak detection difficult because gas is odourless (LNG and CNG)
- Adding an odorant is not technically possible (LNG)
- Odorants may not be compatible with fuel-cell technology (LNG and CNG)
- Low ignition energy (LNG and CNG)
- Wide flammable/detonable limits (LNG and CNG)
- High storage pressure (CNG)
- Over pressure generation after ignition (LNG and CNG)
- Dispersal of released fuel enhanced by low vapour density (LNG and CNG)
- Container integrity may be affected by heat cycling (LNG and CNG)

- Poorly visible flame (LNG and CNG)
- Stored fuel requires controlled venting to maintain safe pressure (LNG)

#### 8.5.4 Methanol

##### Toxicity and health effects

- Acute toxicity and delayed onset of serious toxic effects
- Chronic toxicity data lacking
- Potential for abuse for intoxicating effects
- Potential for misuse as a solvent or cleaning agent for skin

##### Environmental fate

- Interceptors on retail sites ineffective in controlling/containing liquid spills

##### Fire, explosion and other safety issues

- Low ignition energy
- Wide flammable limits
- Poorly visible flame
- Corrosive
- Not all fire-fighting foams compatible with methanol fuel fires
- Tank headspace may be within flammable limits

#### 8.5.5 Liquefied petroleum gas

##### Toxicity and health effects

- Chronic toxicity data lacking
- Cryogenic hazard

##### Environmental fate

##### Fire, explosion and other safety issues

- BLEVEs
- Leak detection difficult because gas is odourless (propane)
- Odorants may not be compatible with fuel-cell technology
- Dispersal of released fuel impaired by low vapour density
- Container integrity may be affected by heat cycling

### **8.6 Conclusions and recommendations**

The aim of this project has been to analyse critically the health and safety issues surrounding competing transport fuel options, including those for possible future fuel cell powered vehicles. Of course, other factors like cost, energy efficiency, availability, need for proper storage and transport facilities, pollution caused by the products of combustion, safety from major accidents etc, will also govern decisions about the uptake of alternative fuels.

Hydrogen has the potential to be the least environmentally damaging of the fuels considered, but new, sustainable means of production must be developed. Furthermore, liquefied H<sub>2</sub> presents a particular health and safety concern owing to its low temperature. From an environmental viewpoint, methanol is the most attractive liquid fuel because it is easily diluted by water, is biodegradable and can be produced by sustainable means. However, methanol carries with it concerns about health effects (mostly from deliberate ingestion) and fire and explosion risks.

None of the fuels considered here could be termed experimental. All are in use as fuels, industrial chemical feedstocks or bulk chemicals and there is an extensive battery of knowledge regarding their safe handling. However, there are some aspects, such as the chronic toxicity of the alternative fuels, flame visibility and leak detection for odourless gases used in fuel cells, that require particular attention before widespread adoption of the alternative fuels could be considered. The technical needs of fuel cell technology must also be considered. For instance, using an additive that increases a fuel's flame luminescence, gives an odour to a gas or acts as a fuel excise marker may be incompatible with the needs of fuel cells, which currently require high purity fuels.

#### 8.6.1 Toxicity and health effects

As far as health effects of the fuels are concerned, available information shows that H<sub>2</sub> and natural gas pose a lesser health hazard than gasolines or diesel, if carefully handled. Anticipated levels of exposure to methanol vapour, during automotive use, suggest that methanol may also be less harmful. For none of the fuels (other than gasoline or diesel) is there information on their long-term effects in humans. **If these alternative fuels are to be used in large quantities as alternatives to gasoline and diesel, there is a need to conduct experimental and epidemiological studies to evaluate the health risks they pose in both occupational and environmental exposure settings.**

Introducing alternative fuels that are cryogenic liquids into mainstream use, with members of the public re-fuelling vehicles, increases the potential for cryogenic burns to occur. **Therefore, it will be necessary to explore technical and operational means of minimising such hazards.**

There remain many uncertainties surrounding likely exposure scenarios for the fuels considered in this report (eg the composition of fuels for use in fuel-cell vehicles, storage and re-fuelling options, etc). **There is, therefore, a need to consider carefully future patterns of exposure (levels, frequency, duration) to allow qualitative and/or quantitative risk assessments to be conducted for the exposure scenarios that may be expected in the future for all stages of fuel use.**

#### 8.6.2 Environmental issues

There is a large information base regarding the environmental fate of these fuels. **However, situation-specific information will be necessary to evaluate the risks associated with their widespread use in road vehicles.**

In order to make fully informed decisions about the relative hazards of the alternative fuels, **detailed ecotoxicological assessments will need to be undertaken.**

#### 8.6.3 Fire, explosion and other safety aspects

Introducing most of the alternative fuels (particularly the liquefied and compressed gases) into mainstream use, perhaps with members of the public re-fuelling vehicles, is an unknown scenario that will require careful consideration to minimise the hazards. **It will be necessary to review and/or explore technological or operational ways in which to minimise the potential for fire and explosion hazards.**

In common with the use of normal internal combustion engines, it is an intrinsic part of using fuel cells that ignitable fuels will be in close proximity to potential sources of ignition, such as sparks. **Therefore, it will be necessary to explore technical means of minimising the associated fire and explosion hazards.**

## **ADDENDUM**

If radiant heat or flames heat a storage vessel containing a liquid fuel whose vapour pressure is well above atmospheric pressure, its contents will warm and may begin to boil. If the vessel ruptures, the contained liquid will be released, leading to an explosive, rapid phase change from liquid to gas and a buoyant fireball. This phenomenon is known as a boiling liquid expanding vapour explosion (BLEVE).

The BLEVE is a rare event that is usually associated with liquefied petroleum gas (LPG). However, it has been reported that liquefied natural gas (LNG) may also be subject to the BLEVE phenomenon, and by extension, it has been suggested that liquefied hydrogen (H<sub>2</sub>) may also undergo a BLEVE. However, it is not clear whether a BLEVE could indeed occur with cryogenic gases (eg LNG and liquefied H<sub>2</sub>). Because LNG and liquefied H<sub>2</sub> are liquefied by reducing their temperature, rather than by increasing their storage pressure as is the case with LPG, their vapour pressure is not above atmospheric pressure at the temperature at which they are stored. If the contents of a vessel containing cryogenic gases are released by a sudden loss of containment, the liquid will boil off rapidly as it makes contact with heated surfaces. However, as this process occurs outside the vessel some argue that this results in a flammable vapour cloud rather than a BLEVE as normally defined.

## **GLOSSARY**

**$\alpha_{2u}$ -globulin:** A type of protein unique to the male rat that indicates kidney damage and is found in damaged kidney tubules.

**Acne:** A chronic inflammatory disease of the skin generally associated with adolescence. Occupational acne is observed in those occupationally exposed to a wide variety of chemicals including tars and oils, waxes and chlorinated hydrocarbons.

**Acute health effect:** A health effect with a short time course, occurring quickly after exposure to the causative agent.

**Acute myeloid leukaemia:** A rapidly progressing cancer of the blood affecting immature cells of the bone marrow, usually white cells. It is much more common in adults than in children.

**Acute non-lymphoblastic leukaemia:** A form of leukaemia which is characterised by the proliferation of immature bone marrow precursor cells and immature white blood cells (granulocytes) in the bloodstream. Occurs primarily in adults and in infants under 1 year old. Complications include abnormal bleeding and susceptibility to infections.

**Adenocarcinoma:** Carcinoma (malignant growth) derived from glandular tissue or in which tumour cells form recognisable glandular structures.

**Adsorption:** Attachment of 'foreign' molecules or atoms to a surface.

**Alcoholic ketoacidosis:** A form of ketoacidosis (increase in the acidity of blood) that results from the abuse of alcohol.

**Anaemia:** A reduction of the normal number of red blood cells in the blood which occurs when there is a disturbance in the normal balance between blood production and blood loss (whether through bleeding, normal metabolism or some other cause).

**Anaesthesia:** The loss of the ability to feel pain or any other sensation, usually caused by the administration of a drug during medical interventions but which may also result from exposure to other chemicals.

**Anoxia:** A total lack of oxygen; often used interchangeably with hypoxia to mean a reduced supply of oxygen to the tissues of the body.

**Aplasia:** A lack of development of an organ or tissue or of the cellular products from an organ or tissue.

**Asphyxiant:** A substance which causes suffocation (asphyxia) by reducing the concentration of oxygen in inhaled air.

**Ataxia:** Failure of muscular coordination or irregularity of muscular action.

**Autoignition temperature:** The minimum temperature to cause self sustained combustion in air due to heat alone, without an additional spark or flame; this tends to be higher than the ignition temperature.

**Bioaccumulation:** Increased concentration of a chemical in an organism as a net result of the uptake, distribution and elimination of a substance due to all routes of exposure (ie air, water, soil/sediment and food). A bioaccumulation factor (BAF) is a partition coefficient for the distribution of a chemical between an organism exposed through all possible routes and an environmental compartment (air, water, soil or sediment) or food.

**Bioconcentration:** Net result of the uptake, distribution and elimination of a substance in an organism due to waterborne exposure. A bioconcentration factor (BCF) is the ratio of a compound's concentration in the test organism to the concentration in the test water at steady state conditions (i.e. when the rates of uptake and clearance are equal).

**Biodegradation:** Breakdown of a substance catalysed by enzymes. Biodegradation is commonly the result of bacterial activity.

**BLEVE:** A boiling liquid expanding vapour explosion (BLEVE) is mainly associated with liquefied petroleum gas storage but may also occur in liquefied natural gas storage. Such explosions occur when there is a rapid change from the liquid to the gas phase when radiant heat or flames heat a storage vessel until it ruptures. The hazards associated with BLEVEs are greatest with large storage vessels but small cylinders can explode when subjected to direct heat, even when fitted with pressure release valves.

**BOD test:** Biochemical Oxygen Demand test to assess the biodegradability of a substance.

**Cardiac sensitisation:** Sensitisation of heart muscles, usually by an external agent (chemical) in the blood.

**Carcinogenic:** Producing carcinoma.

**Carcinoma:** A malignant new growth that tends to infiltrate the surrounding tissues and give rise to the transfer of disease from one part of the body to another.

**Chronic health effect:** A health effect that persists over a prolonged period of time.

**Confounder:** A third variable that indirectly distorts the relationship between two other variables.

**Cryogenic burn:** Cryogenic liquids and their associated cold vapours and gases can produce effects on the skin similar to a thermal (heat) burn. Brief exposures that would not affect skin on the face or hands can damage delicate tissues such as the eyes. Prolonged exposure of the skin or contact with cold surfaces can cause frostbite. The skin appears waxy yellow. There is no initial pain, but there is intense pain when frozen tissue thaws.

**Cyanosis:** A bluish discolouration, especially of the skin and mucous membranes due to an excessive concentration of reduced haemoglobin (containing less oxygen and more carbon dioxide) in the blood.

**Defatting:** Removal of fat.

**Deflagration:** A deflagration has a subsonic flame front and releases energy more rapidly than a fire.

**Dermal route of exposure:** Exposure to a substance via the skin.

**Detonation:** In a detonation, the flame front is supersonic and produces more energy and occurs over a shorter timescale than either a fire or deflagration; overpressure is also greater than in deflagrations or fires.

**Dyspnoea:** Difficulty in breathing.

**Electrical conductivity:** The ability of a material to allow an electric current to flow through it. Materials with low conductivity will have a greater propensity to build up static charges and thereby produce static sparks which may act as ignition sources.

**Electrolysis:** The decomposition of a substance by the application of an electric current.

**Erythema:** A term to describe redness of the skin produced by congestion of the capillaries.

**Feedstock:** The raw material supplying an industrial process.

**Fire:** A non-explosion fuel-oxygen combustion event in which a flame is relatively stationary and produces heat by no pressure effects (unless in a confined space).

**Flame luminescence:** A means to assess the visibility of flames from different fuels; certain fuels burn invisibly in air, which has important implications from a health and safety viewpoint.

**Flammable:** A description of solids, liquids, gases or vapours indicating that they are easily ignited in air. The term flammable is synonymous with inflammable but the former is preferred because inflammable may be mistaken for a negative. The opposite of flammable is non-flammable.

**Flammability limits:** The range of fuel concentrations in air (expressed as a percentage) that will support combustion; below this limit the mixture is too lean to combust, above it the mixture is too rich (also referred to as upper and lower flammability, explosion or explosive limits).

**Flashpoint:** The lowest point, under specific conditions, at which a liquid produces enough vapour to flash on the application of an ignition source; below this temperature, fuels will not produce sufficient vapours to form ignitable fuel-air mixtures.

**Folate:** The anionic form of folic acid. The formation and development of blood cells relies on folic acid which is found in liver, green vegetables and yeast.

**Folliculitis:** Inflammation of a follicle or follicles, used ordinarily in reference to hair follicles.

**Free radical:** A free radical is a highly reactive chemical molecule that has at least one unpaired electron.

**Fuel cell:** A device used to convert the electrochemical energy in the reaction between oxygen and hydrogen directly into electrical energy.

**Fuel octane rating:** The octane rating is a measure of a fuel's resistance to knocking. Knock, also known as 'pinking', occurs during combustion when the fuel-air mixture explodes ahead of the flame front rather than burning smoothly, causing a knocking noise.

**Fuel volatility:** Measured by the Reid Vapour Pressure (RVP; the pressure exerted by fuel vapour over the liquid fuel in a sealed container at 38°C). The ease with which a fuel vapourises in an internal combustion engine improves the driveability of the fuel/vehicle combination. Vehicles using less volatile fuels such as diesel may operate ineffectively at extremely low ambient temperatures; conversely, at high ambient temperatures, vehicles using more volatile fuels such as gasoline may also operate poorly.

**Groundwater:** Groundwater is water sitting in the spaces between rock particles in special rock layers known as 'aquifers'.

**Haematological malignancy:** Malignant disease located in the blood and blood-forming tissue (the bone marrow and lymphatic tissue), the commonest forms of which are the various types of leukaemia, lymphoma and myelodysplastic syndrome (a group of related bone marrow disorders preceding the development of leukaemia).

**Haemorrhagic pneumonia:** Lung damage with associated bleeding.

**Hazard:** A property or situation that in certain circumstances could lead to harm.

**Henry's Law constant:** The ratio of the aqueous-phase concentration of a chemical to its equilibrium partial pressure in the gas phase. This indicates a compound's tendency to volatilise from solution in water.

**Heavy metal additives:** Fuel additives incorporated into a fuel blend to increase its octane rating.

**Hydrocarbon:** A compound containing only carbon and hydrogen.

**Hydroxyl radical:** One of the most toxic and reactive of the free radical species. In the atmosphere, the hydroxyl radical is the main driving force behind the daytime reactions of hydrocarbons in the troposphere.

**Hyperkeratosis:** Enlargement or overgrowth of the corneous (keratin) layer of the skin.

**Hypoglycaemia:** An abnormally low concentration of glucose in the blood.

**Internal combustion engine (ICE):** an engine which burns fuel in a confined space and may employ a wide variety of fuels, including, but not limited to, gasoline, diesel fuel, gasohol (a mixture of gasoline and alcohol), LNG (liquefied natural gas), CNG (compressed natural gas) or LPG (liquefied propane gas). Ignition can either be by spark or compression.

**Leukaemia:** A progressive, malignant disease of the blood-forming organs (bone marrow and lymphatic tissue) which is classified according to the type of cell involved and the degree of cell differentiation.



**Leukaemogenesis:** The development of leukaemia.

**Log  $K_{ow}$ :** A logarithmic presentation of the octanol/water partition coefficient that measures a compound's hydrophobicity. As a general guide, compounds with a low Log  $K_{ow}$  will tend to concentrate in the aqueous phase while compounds with a high Log  $K_{ow}$  will tend to concentrate in lipophilic phases such as biota or sediments.

**Mackay level 1 distribution modelling:** Modelling based on a compound's physicochemical properties to assess its partitioning between the environmental compartments air, water and soil/sediment. Level 1 modelling assumes complete mixing, the attainment of equilibrium and no removal processes.

**Metabolic acidosis:** A metabolic derangement of acid-base balance where the blood pH is abnormally low.

**Molecular weight:** The weight of one molecule referred to the standard of  $^{12}\text{C} = 12.000$  atomic mass units.

**Mono-aromatics:** Compounds containing one aromatic (benzene) ring.

**Mutagenic:** Inducing genetic mutation.

**Myeloma:** A malignant tumour composed of plasma cells of the type normally found in the bone marrow.

**Nephropathy:** Disease of the kidneys.

**Neurotoxic:** Poisonous or destructive to nerve tissue.

**Neurobehavioural:** Relating to neurological status as assessed by observation of behaviour.

**Oxygenated fuel:** A fuel that, through the addition of oxygen-rich compounds, burns more cleanly through improved fuel combustion.

**Partition:** Distribution of a compound between different phases.

**Percutaneous absorption:** Absorption through the skin.

**Photodegradation:** Breakdown of a compound by the action of sunlight (or more accurately by the influence of a high energy photon).

**Pleurisy:** Inflammation of the membranes surrounding the lungs.

**Polycyclic compounds:** Compounds containing more than one aromatic (benzene) ring.

**Polycyclic aromatic hydrocarbons (PAHs):** A large group of chemical compounds with a similar structure comprising two or more joined aromatic rings.

**Prenatal development process:** Development process prior to birth, in utero.

**Pulmonary epithelial damage:** Damage of the epithelial (surface) layers of the lung tissue.

**Pulmonary infiltrates:** Penetration of the lung tissue by disease tissue (eg cancer) or other substances (eg metals/foreign bodies) or infection (eg bacteria and inflammatory cells).

**Relative density:** Density (mass per unit volume) of a substance relative to that of water at  $4^{\circ}\text{C}$  (1 kg/l).

**Renal tubular necrosis:** Death of kidney tubules.

**Risk:** A combination of the probability, or frequency, of occurrence of a defined hazard and the magnitude of the consequences of the occurrence.

**Squamous-cell carcinoma:** A malignant growth originating from a squamous cell. This form of cancer can be seen on the skin, lips, inside the mouth, throat or oesophagus.

**Steam re-formation:** A process whereby gasoline and other carbonaceous fuels are converted to hydrogen-rich fuels for use in fuel-cells. The main reaction products are  $\text{H}_2$ , CO and  $\text{CO}_2$ . Depending on the fuel-cell technology, further processing may be required to reduce the concentration of CO to acceptable levels.

**Systemic effect:** Pertaining to or affecting the body as a whole.

**Teratogenic:** Tending to produce physical defects in embryos and fetuses (ie formation defects).

**Transient corneal epithelial damage:** A damage of the corneal (outer surface of the black area of the eye) epithelial cells.

**Troposphere:** The lowest part of the atmosphere in which clouds and weather phenomena occur. The troposphere is defined as the region in which temperature generally decreases with height.

**Tumorigenic:** Capable of causing tumours. Can refer either to a carcinogenic substance or agent such as radiation that affects cells or to transformed cells themselves.

**Vapour pressure:** The pressure of the vapour of a compound at equilibrium with its pure condensed phase, be it a liquid or solid. This is a factor in a substance's partitioning and transport between environmental media. The higher a substance's vapour pressure, the more likely it is to be found in air.

**Vapour density:** Vapour density is the weight per unit volume of a pure gas or vapour. The vapour density is commonly given as the ratio of the density of the gas or vapour to the density of air. Gases denser than air will tend to accumulate in low lying areas.

**Vasodilation:** The increase in the internal diameter of a blood vessel that results from relaxation of smooth muscle within the wall of the vessel. This causes an increase in blood flow, but a decrease in systemic vascular resistance.

**Vesicular eczema:** An itchy inflammation of the skin with associated blisters that occurs as a reaction to many agents; characterised in the acute stage by oozing, blistering, crusting and scaling.

**Volatility:** Volatility is the ability of a material to evaporate. The term volatile is commonly understood to mean that a material evaporates easily.

**Water solubility:** Ability of a material to dissolve in water.



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## **APPENDIX A: INITIATIVES**

This report has been produced under the auspices of the Department of Trade and Industry (DTI) New and Renewable Energy Programme (NREP)<sup>33</sup>. Such programmes do not operate in isolation and the purpose of this Appendix is to identify and summarise briefly the aims of initiatives and other activities that may have an impact on the uptake of specific fuels, focusing on health and safety issues. Furthermore, the development and projected introduction of vehicles using non-conventional (ie non-gasoline/diesel) fuels, whether in fuel cells or not, introduces issues of whether current regulatory regimes are sufficiently targeted. This is addressed in Section A.2.

### **A.1 Research and development initiatives**

There is a great and burgeoning interest in the application of fuel cells in the transport sector. Much of this research focuses on technological aspects of fuel cells, whether for vehicles, portable equipment or stationary power generation, rather than the health and safety issues surrounding the fuels that they will employ. Such technological research is being supported though government and research council initiatives, both in the UK and across Europe and the USA. Research on health and safety issues of specific fuels is more limited and available information is summarised below.

#### **A.1.1 UK initiatives**

##### ***Department of the Environment, Transport and the Regions (DETR) Research***

The Vehicle Standards and Engineering Division of DETR is currently funding research on identifying vehicle construction standards necessary to ensure the safe operation of alternatively fuelled vehicles. This work is being performed by an external consultancy, Frazer Nash Consulting and will have the following elements:

- a literature study to identify the range of fuels currently under development;
- a description of the fuel system for each advanced fuel;
- identification of the safety considerations needed when using each advanced fuel;
- development of a benchmarking system that can be used to ensure that future applications for licences to use advanced fuels adequately cover base construction and safety standards, and
- a final report describing the findings of the study.

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<sup>33</sup> DTI *New and Renewable Energy Programme* information available [June 2000] from <http://www.dti.gov.uk/renewable/>



*Health and Safety Executive (HSE) mainstream research*

The HSE has an extensive mainstream research programme dealing with occupational health and safety topics across the range of the HSE's responsibilities. The following research activities are particularly relevant to the issues discussed in this report (Table A.1).

**Table A.1 Health and Safety Executive (HSE) mainstream research**

Project area	Project title	Research objectives
Explosions — vapour release	Ignition parameters of mists and sprays	To explore the ease with which mists and sprays from a range of flammable liquids will ignite by both electrical sparks and heated surfaces or small bodies.
Fires	Size effect of impact/fire on flammable liquid receptacles	To compare the effects of impact and fire on flammable liquid receptacles of different sizes and materials. To determine whether current receptacle sizes allowed under international road transport regulations may be safely increased.
	Fire risk assessment for workplaces containing flammable substances	To consider how current UK legislation and guidance relates to the control of fire hazards in workplaces containing flammable substances. To propose a risk-based methodology for assessing the hazards consequent from the storage and handling of such substances. To provide a comparison with the requirements of UK legislation and guidance.
Ignition from electricity	Methodology for on-site ignition probability at installations where flammable liquids and gases are stored	To review data for on-site ignition and methods for control of ignition sources. To collate data for on-site ignition sources, incorporate this data into an ignition probability model and implement the result within risk assessment.
Engineering — mechanical	Safety categories for electrical equipment in explosive atmospheres Probabilistic fracture risk assessment method	To produce a harmonised system for the categorisation of safety-related devices used in electrical equipment intended for use in potentially explosive atmospheres. To develop an assessment procedure which can be used to assess the conditions under which steel pressure containment vessels and pipework can be operated with a minimum risk of brittle failure at temperatures below the original design temperature.
Engineering — electrical	[No specific project titles available]	To investigate electrical safety of machines and electrical installations including methods of preventing electric shock.
Work environment — monitoring of gases	Chemical sensors for pollution monitoring	To provide a scientific and technological basis for the manufacture of optical sensors for toxic gases. To carry out a systematic investigation into the preparation, treatment and analysis of surfaces of thin films of a novel sensor material (for the detection of organic gases such as methane) and their potential industrial importance.
Chemical hazards	Factors influencing the dermal absorption of vapours	To investigate the parameters which affect the dermal absorption potential of vapours, such as temperature, humidity, clothing and air velocity. To determine whether these factors could significantly enhance the uptake of vapours across the skin.

Project area	Project title	Research objectives
	Uncertainty factors for chemical risk assessment	To categorise the physiological and metabolic processes which can determine critical toxicokinetic parameters. To use the scientific and clinical literature to define the extent of human variability, and the scientific scrutiny based on available human kinetic and response data and to explore the extent of differences between humans and other species, in toxicokinetic and toxicodynamic parameters. To develop data-derived uncertainty factors relating to the different toxicokinetic processes and toxicodynamic parameters defined by the previous steps.
	<i>In vitro</i> dermal absorption of liquids	To measure dermal penetration of a range of solvents using human skin preparations under various conditions to understand better both the physicochemical factors governing dermal uptake of liquids and the effects of different dose regimes on dermal uptake. To use the results to validate further and refine the knowledge-based system.
	<i>In vitro</i> dermal absorption of vapours	To investigate the feasibility of measuring <i>in vitro</i> penetration of solvent vapours through viable human skin. To measure the penetration of various solvent vapours across skin <i>in vitro</i> . To elucidate the effect on this penetration (through hydrated skin) of intra-individual variation. To compare the results obtained with published <i>in vitro</i> data, so as to assess the validity of the <i>in vitro</i> method. To use the above results to assess and, if possible, refine a quantitative structure permeability relationship model.
Risk assessment — general methodologies and criteria	Experimental data acquisition for validation of a new vapour cloud fire modelling approach	To develop mathematical models, that have been adequately validated by a series of clearly defined experimental data and field trials, that enable assessment of the consequences and associated risks from vapour cloud fires.
Risk assessment tools	Current dense gas dispersion models at low wind speeds	To obtain a measure of the uncertainty associated with the use of different dense gas dispersion models in low wind speeds, especially for risks in the far field. To provide an independent validation of three currently used dense gas dispersion models, especially at low wind speeds.
	Dense gas dispersion studies using the most likely failure point method with HSE software	To investigate the performance of the MLFP methodology when interfaced with dense gas dispersion models used by HSE. To calculate data importances for a range of chlorine releases. To investigate representation of weather data by continuous functions.
Risk assessment for the storage of refrigerated flammable liquids	Risk assessment for the storage of refrigerated flammable liquids	To develop and record risk assessment methodologies for refrigerated liquefied petroleum gas (LPG) and liquefied natural gas (LNG).

Project area	Project title	Research objectives
	Scientific model evaluation of dense gas dispersal models	To develop further the protocol published by the EC Model evaluation group on Dense Gas Dispersion (DGD) and test a protocol for a Scientific Model Evaluation (SME) of DGD models. To carry out a SME on all current DGD models in Europe, using this protocol with particular emphasis on the complex effects of aerosol formation, complex terrain and obstacles. To leave in place a methodology for scientific model evaluation.
	Efficacy of water spray tank protection against butane jet fires	To understand better the behaviour and performance of water sprays on an LPG tank during butane jet fire impingement. To incorporate the knowledge gained into CHID's site-specific boiling liquid expanding vapour explosion (BLEVE) frequency assessment tool.
Mitigation	Blast wave sheltering and amplification: effects on off-site hazard	To quantify the effects of intervening terrain and structures on the off-site consequences of blast from onshore major hazard installations, using a combined CFD and experimental modelling approach. To provide a methodology for incorporation of these effects in HSE's consequence modelling tools.

### A.1.2 European initiatives

#### European Union-funded research

The following information has been identified by a search of the EU Community Research and Development Information Service (CORDIS) website database<sup>34</sup>. The most relevant studies are summarised below. It is recommended that the reader seek supplementary information from the CORDIS website<sup>35</sup>.

#### *Risk assessment for occupational dermal exposure to chemicals (on-going)*

This project aims to develop two tools for the management of dermal exposure and prevention of ill-health: a validated predictive model for estimating dermal exposure for use in risk assessment of single chemicals and a practical dermal exposure risk management tool for use in workplace situations.

#### *Low emission vehicle with integrated natural gas storage system (LEVINGS) (completed August 2000)*

Although primarily focused on technological facets of using natural gas in road vehicles, part of this project explored gas storage technologies that would operate at lower pressures (3.5MPa as opposed to 20MPa). The objective was to reduce the pressure hazard associated with natural gas storage.

#### *European integrated hydrogen project (EIHP) (completed April 2000)*

The aim of this project was to come to a harmonised approach for the licensing and approval of hydrogen-related vehicles, infrastructure equipment and components. The project involved:

- surveying and evaluating existing European rules and regulations for licensing of such vehicles;
- identifying rules and regulations already eligible for harmonisation;
- identifying deficits in licensing practices;
- research and safety studies as preparation for standardisation activities, and
- investigation of high strength steel tanks and re-fuelling systems.

#### *Fuel cell powered electric vehicle for efficiency and range (completed May 1998)*

The project aimed to develop and construct a small fuel cell driven passenger car using hydrogen as a fuel. One of the main topics addressed within the project was safety. Other topics included component integration and system optimisation.

#### *Investigation of flame propagation, influence of repeated obstacles and partial confinement (completed December 1989) and Investigation of flame propagation, influence of turbulence (completed June 1990)*

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<sup>34</sup> The search terms employed were 'fuel and safety, not nuclear'. Using the term health made the search too narrow and omitted relevant projects.

<sup>35</sup> CORDIS information available [October 2000] from <http://www.cordis.lu/>

These related projects, using propane and ethylene as examples, explored how obstacles and their arrangement affect flame propagation. Slow laminar combustion can develop into an intense explosive blast generating process, caused by turbulence. Obstacles and confinement can increase this turbulence in fuel-air mixtures and hence increase the explosive intensity.

#### European Pressure Equipment Research Council (EPERC)

The EPERC<sup>36</sup> was set up in 1995 to foster co-operative research, ensure technology transfer (particularly towards small and medium enterprises) and liaise with the services of the European Commission and Comité Européen de Normalisation (CEN) in the field of non-nuclear pressure equipment. The projects funded by EPERC cover design, testing and inspection, materials and joining, and operation and maintenance of pressure equipment.

#### European Chemicals Bureau (ECB)

Within ECB<sup>37</sup>, the Existing Chemicals Work Area is responsible for data collection, priority setting and risk assessment of existing chemicals following Council Regulation (EEC) 793/93 (the Existing Substances Regulation). Information on the human health and environmental effects of all the fuels discussed in this report has been gathered on the International Uniform Chemical Database (IUCLID). Furthermore, it is understood that research on LPG and hydrogen is on-going under the auspices of the ECB high production volume chemicals programme.

#### A.1.3 US activities

There is a great deal of activity in the US in alternative fuels and fuel-cell development. Of particular relevance are the US Department of Energy (DOE) Energy Efficiency and Renewable Energy Network (EREN)<sup>38</sup> and Office of Transportation Technologies (OTT)<sup>39</sup>. The main focus of their research is on fuel-cell technology, rather than fuel health and safety. Within EREN, the US DOE focuses on specific technologies and fuels, among them H<sub>2</sub> through the Hydrogen Program<sup>40</sup>. Part of the program supports the introduction of safe and dependable H<sub>2</sub>-based energy systems, including the development of codes and standards for H<sub>2</sub> technologies. A project of particular relevance is being performed jointly by the National Renewable Energy Laboratory and Oak Ridge National Laboratory to develop sensors able to detect hydrogen leaks.

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<sup>36</sup> European Pressure Equipment Research Council information available [October 2000] from <http://www.eperc.jrc.nl/>

<sup>37</sup> European Chemicals Bureau information available [October 2000] from <http://ecb.ei.jrc.it/>

<sup>38</sup> EREN information available [June 2000] from <http://www.eren.doe.gov/EE/transportation.html>

<sup>39</sup> OTT information available [June 2000] from <http://www.ott.doe.gov/>

<sup>40</sup> EREN Hydrogen Program information available [June 2000] from <http://www.eren.doe.gov/hydrogen/program.html>

## **A.2 Regulatory considerations**

Concerns about the impact of road transport on air quality and climate change have resulted in a range of initiatives to develop cleaner, more efficient road vehicles, including the development of fuel-cell-powered vehicles (FCVs). The evaluation of alternative fuel options for FCVs requires consideration to be given to possible legislative and other regulatory constraints that might affect their uptake.

A number of environmental and health and safety issues arise in relation to fuel-cell-powered vehicles that are already (or will be) subject to some form of regulatory controls including:

- the manufacture of the fuel cells themselves;
- the production of the primary energy source;
- the transportation/distribution and storage of the fuels;
- re-fuelling options (retail or domestic);
- the storage and use of the fuel on board the vehicle; and
- emissions (re-fuelling and use).

While specific regulatory details can only be addressed once the fuel-cell technology is sufficiently advanced, a number of control arrangements already exist that might impact on the development and uptake of specific fuel options. Because many of these have already been discussed in other reports produced under the DTI's NREP (Scott, 1997; Wilcox, 1999), only a brief summary of the key points is presented here.

### **A.2.1 Manufacture of fuel cells**

The health and safety aspects associated with the manufacture of fuel cells are outside the scope of this document. However, because certain types of fuel cell lend themselves towards particular fuel options, regulatory constraints at this point of the production-distribution-use chain may impact on the ultimate choice of fuel to be used in the road transport sector. As with other industrial processes, the manufacture of fuel cells will be subject to a broad raft of regulatory constraints and Codes of Practice including, for example, compliance with the Health and Safety at Work Act (1974), the Environmental Protection Act (1990), the Environment Act (1995) and the new requirements of integrated pollution prevention and control (IPPC) under the EU IPPC Directive (EC/61/96) which .

### **A.2.2 Existing fuels (gasolines, diesel, natural gas, LPG)**

The vast majority of existing road vehicles in the UK use gasoline or diesel fuel, with a small number of LPG- or compressed natural gas (CNG)-fuelled vehicles.

- The infrastructure for the manufacture and distribution of gasoline and diesel is well established in the UK. Because of their existing widespread application, these fuels are already covered by comprehensive safety and planning controls. From a production and distribution view there would, therefore, be no significant regulatory barriers to the uptake of gasoline or

diesel for fuel-cell-powered vehicles with on-board re-forming facilities. However, it is pertinent to note that gasoline, as currently dispensed, contains impurities that make it unsuitable for use in fuel cells and a relatively pure grade would need to be introduced that may require changes to some regulatory controls such as the Motor Fuel (Composition and Content) Regulations 1994.

- LPG- and CNG-fuelled vehicles are still relatively uncommon in the UK (about 20,000 cars are converted to run on LPG in the UK) although technical and safety issues are well understood because of their use in other countries such as the Netherlands and Italy. LPG is produced as a by-product of natural gas production and crude oil refining. Because natural gas production and supply is already covered by comprehensive safety and planning controls it is unlikely that there will be any significant barriers to the uptake of LPG or CNG for on-board re-forming in relation to the production and distribution of the fuels.
- Retail site re-forming of existing fuels to H<sub>2</sub> is technically feasible. However, because this would require re-forming facilities (essentially a small petrochemical plant) to be in place at the point of retail, there would clearly be regulatory implications and a significant change to planning and licensing legislation would be required. In addition, retail site re-forming would require the storage of H<sub>2</sub> (either as a liquid or high pressure gas), which would again have regulatory implications, particularly from a health and safety viewpoint (see below).
- Currently the Road Vehicles (Construction and Use) Regulations 1986 effectively prohibit the use of gaseous fuel-powered vehicles except for those using LPG. These Regulations prohibit the routine use of CNG and would thus limit its widespread uptake for use in fuel-cell-powered vehicles unless they were changed.

#### A.2.3 New fuels (hydrogen, methanol)

- Significant quantities of H<sub>2</sub> are produced and traded world-wide. Currently H<sub>2</sub> is delivered both by pipeline and road transport and the safety procedures relating to its production, storage and transport are well understood and regulated. A significant increase in demand for H<sub>2</sub> as a road vehicle fuel is most likely to emerge among the fleet sector. In this case H<sub>2</sub> would be supplied by industrial gas companies by road tanker. These activities are already covered by regulatory controls and Codes of Practice.
- Hydrogen is usually manufactured from fossil fuels; this process produces a range of pollutants, including CO<sub>2</sub>, that are comprehensively regulated, for example, under air quality and climate change controls. Compliance with these regulations may constrain a significant increase in the production of H<sub>2</sub> by this process.
- The major issue regarding the widespread use of H<sub>2</sub> as a road vehicle fuel relates to its storage and handling at retail sites. Safe storage and handling facilities would require approval of the HSE, local authorities and national planning authorities such as the Environment Agency. In addition, the re-fuelling of vehicles with H<sub>2</sub> (either as a high pressure gas or cryogenic



liquid) by the public would require the careful development and stringent regulation of 'fail-safe' vehicle re-fuelling systems. The need to develop rigorous storage and handling controls at retail sites may impede the widespread application of H<sub>2</sub> for use among the private-use vehicle sector.

- Methanol is produced and distributed in large quantities and there is also substantial experience in the US of using methanol as a road vehicle fuel. The safety issues relating to its storage, transportation and re-fuelling techniques are well understood. While new storage and filling facilities would need to be developed at retail sites for private-use vehicles, there appear to be no significant regulatory constraints to its uptake as a fuel for vehicles with on-board re-forming facilities from a production and distribution viewpoint.
- The dispensing of methanol fuel to the public would be similar to that of gasoline and methanol dispensing sites are already in operation in the US. However, concerns about the toxicity of methanol and certain emissions, most notably formaldehyde, would need to be addressed through stringent health and safety controls, particularly in relation to handling and re-fuelling at retail sites.

## **APPENDIX B: WORKSHOP PARTICIPANTS**

Table B.1 lists the participants who attended a workshop in Leicester on 13 September 2000 to discuss a previous draft of this report. The Institute gratefully acknowledges the contribution of all those who attended the workshop and provided material or information to include in this report. We assume no endorsement from these individuals for the findings presented in this report.

**Table B.1 Workshop participants**

<b>Participant</b>	<b>Affiliation</b>
Dr Jane Alcock	Shell Research Limited, Shell Research Centre, P O Box 1, Chester CH1 3SH
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