

## oxygenatedfuel

Last-modified: 18 Jan 1995

Version: 1.00

FAQ: Automotive Gasoline

Bruce Hamilton

B.Hamilton@irl.cri.nz

---

Subject: 1. Introduction and Intent

The intent of this FAQ is to provide some basic information on gasolines and other fuels for spark ignition engines used in automobiles. The toxicity and environmental reasons for recent and planned future changes to gasoline are discussed, along with recent and proposed changes in composition of gasoline. This FAQ intended to help readers choose the most appropriate fuel for vehicles, assist with the diagnosis of fuel-related problems, and to understand the significance of most gasoline properties listed in fuel specifications. I make no apologies for the fairly heavy emphasis on chemistry, it is the only sensible way to describe the oxidation of hydrocarbon fuels to produce energy, water, and carbon dioxide.

---

Subject: 2. Table of Contents

1. Introduction and Intent
2. Table of Contents
3. What Advantage will I gain from reading this FAQ?
4. What is Gasoline?
  - 4.1 Where does crude oil come from?.
  - 4.2 When will we run out of crude oil?.
  - 4.3 What is the history of gasoline?
  - 4.4 What are the hydrocarbons in gasoline?
  - 4.5 What are oxygenates?
  - 4.6 Why were alkyl lead compounds added?

## oxygenatedfuel

- 4.7 Why not use other organometallic compounds?
- 4.8 What do the refining processes do?
- 4.9 What energy is released when gasoline is burned?
- 4.10 What are the gasoline specifications?
- 4.11 What are the effects of the specified fuel properties?
- 4.12 Are brands different?
- 4.13 What is a typical composition?
- 4.14 Is gasoline toxic or carcinogenic?
- 4.15 Is unleaded gasoline more toxic than leaded?
5. Why is Gasoline Composition Changing?
  - 5.1 Why pick on cars and gasoline?
  - 5.2 Why are there seasonal changes?
  - 5.3 Why were alkyl lead compounds removed?
  - 5.4 Why are evaporative emissions a problem?
  - 5.5 Why control tailpipe emissions?
  - 5.6 Why do exhaust catalysts influence fuel composition?
  - 5.7 Why are "cold start" emissions so important?
  - 5.8 When will the emissions be "clean enough"?
  - 5.9 Why are only some gasoline compounds restricted?
  - 5.10 What does "renewable" fuel/oxygenate mean?
  - 5.11 Will oxygenated gasoline damage my vehicle?
  - 5.12 What does "reactivity" of emissions mean?
  - 5.13 What are "carbonyl" compounds?
  - 5.14 What are "gross polluters"?
6. What do Fuel Octane ratings really indicate?
  - 6.1 Who invented Octane Ratings?
  - 6.2 Why do we need Octane Ratings?
  - 6.3 What fuel property does the Octane Rating measure?
  - 6.4 Why are two ratings used to obtain the pump rating?
  - 6.5 What does the Motor Octane rating measure?
  - 6.6 What does the Research Octane rating measure?
  - 6.7 Why is the difference called "sensitivity"?
  - 6.8 What sort of engine is used to rate fuels?
  - 6.9 How is the Octane rating determined?
  - 6.10 What is the Octane Distribution of the fuel?
  - 6.11 What is a "delta Research Octane number"?
  - 6.12 How do other fuel properties affect octane?
  - 6.13 Can higher octane fuels give me more power?
  - 6.14 Does low octane fuel increase engine wear?

## oxygenatedfuel

- 6.15 Can I mix different octane fuel grades?
- 6.16 What happens if I use the wrong octane fuel?
- 6.17 Can I tune the engine to use another octane fuel?
- 6.18 How can I increase the fuel octane?
- 6.19 Are aviation gasoline octane numbers comparable?
- 7. What parameters determine octane requirement?
  - 7.1 What is the effect of Compression ratio?
  - 7.2 What is the effect of changing the air/fuel ratio?
  - 7.3 What is the effect of changing the ignition timing
  - 7.4 What is the effect of engine management systems?
  - 7.5 What is the effect of temperature and Load?
  - 7.6 What is the effect of engine speed?
  - 7.7 What is the effect of engine deposits?
  - 7.8 What is the Road octane requirement of an vehicle?
  - 7.9 What is the effect of air temperature?.
  - 7.10 What is the effect of altitude?.
  - 7.11 What is the effect of humidity?.
  - 7.12 What does water injection achieve?.
- 8. How can I identify and cure other fuel-related problems?
  - 8.1 What causes an empty fuel tank?
  - 8.2 Is knock the only abnormal combustion problem?
  - 8.3 Can I prevent carburettor icing?
  - 8.4 Should I store fuel to avoid the oxygenate season?
  - 8.5 Can I improve fuel economy by using quality gasolines?
  - 8.6 What is "stale" fuel, and should I use it?
  - 8.7 How can I remove water in the fuel tank?
  - 8.8 Can I use unleaded on older vehicles?
- 9. Alternative Fuels and Additives
  - 9.1 Do fuel additives work?
  - 9.2 Can a quality fuel help a sick engine?
  - 9.3 What are the advantages of alcohols and ethers?
  - 9.4 Why are CNG and LPG considered "cleaner" fuels.
  - 9.5 Why are hydrogen-powered cars not available?
  - 9.6 What are "fuel cells" ?
  - 9.7 What is a "hybrid" vehicle?
  - 9.8 What about other alternative fuels?
  - 9.9 What about alternative oxidants?
- 10. Historical Legends
  - 10.1 The myth of Triptane

## oxygenatedfuel

### 10.2 From Honda Civic to Formula 1 winner.

## 11. References

### 11.1 Books and Research Papers

### 11.2 Suggested Further Reading

---

Subject: 3. What Advantage will I gain from reading this FAQ?

This FAQ is intended to provide a fairly technical description of what gasoline contains, how it is specified, and how the properties affect the performance in your vehicle. The regulations governing gasoline have changed, and are continuing to change. These changes have made much of the traditional lore about gasoline obsolete. Motorists may wish to understand a little more about gasoline to ensure they obtain the best value, and the most appropriate fuel for their vehicle. There is no point in prematurely destroying your second most expensive purchase by using unsuitable fuel, just as there is no point in wasting hard-earned money on higher octane fuel that your automobile can not utilize. Note that this FAQ does not discuss the relative advantages of specific brands of gasolines, it is only intended to discuss the generic properties of gasolines.

---

Subject: 4. What is Gasoline?

4.1 Where does crude oil come from?. The generally-accepted origin of crude oil is from plant life up to 3 billion years ago, but predominantly from 100 to 600 million years ago [1]. "Dead vegetarian dino dinner" is more correct than "dead dinos". The molecular structure of the hydrocarbons and other compounds present in fossil fuels can be linked to the leaf waxes and other plant molecules of marine and terrestrial plants believed to exist during that era. There are various biogenic marker chemicals such as isoprenoids from terpenes, porphyrins and aromatics from natural pigments, pristane and phytane from the hydrolysis of chlorophyll, and normal alkanes from waxes, whose size and shape can not be explained by known geological processes [2]. The presence of optical activity and the carbon isotopic ratios also indicate a biological origin [3]. There is another hypothesis that suggests crude oil is derived from methane from the earth's interior. The current main proponent of this abiotic theory is Thomas Gold, however abiotic and extraterrestrial origins for fossil fuels were also considered at

oxygenated fuel

the turn of the century, and were discarded then.

#### 4.2 When will we run out of crude oil?

It has been estimated that the planet contains over  $1.4 \times 10^{15}$  tonnes of petroleum, however much of this is too dilute or inaccessible for current technology to recover [4]. The petroleum industry uses a measure called the Reserves/Production ratio (R/P) to monitor how production and exploration are linked. This is based on the concept of "proved" reserves of crude oil, which are generally taken to be those quantities which geological and engineering information indicate with reasonable certainty can be recovered in the future from known reservoirs under existing economic and operating conditions. The Reserves/Production ratio is the above reserves divided by the production in the last year, and the result is the length of time that those remaining reserves would last if production were to continue at the current level [5]. It is important to note those definitions, as the price of oil increases, marginal fields become "proved reserves", thus we are unlikely to "run out" of oil, as more fields will become economic as the price rises. If the price exceeds \$30/bbl then alternative fuels may become competitive, and at \$50-60/bbl coal-derived liquid fuels are economic, as are many biomass-derived fuels and other energy sources [6]. One barrel of oil equals 0.158987 m<sup>3</sup>. The current price for Brent Crude is approx. \$18/bbl. The R/P ratio has increased from 27 years (1979) to 43.1 years (1993) [5]. Now, some numbers.

( billion =  $1 \times 10^9$ . trillion =  $1 \times 10^{12}$  ).

Crude Oil	Proved Reserves	R/P Ratio
Middle East	89.6 billion tonnes	95.1 year
USA	4.0	9.9 years
Total World	136.7	43.1 years
Coal	Proved Reserves	R/P Ratio
USA	240.56 billion tonnes	267 years
Total World	1,039.182	236 years
Natural Gas	Proved Reserves	R/P Ratio
USA	4.7 trillion cubic metres	8.8 years
Total World	142.0	64.9 years.

#### 4.3 What is the history of gasoline?

## oxygenatedfuel

In the late 19th Century the most suitable fuels for the automobile were coal tar distillates and the lighter fractions from the distillation of crude oil. During the early 20th Century the oil companies were producing gasoline as a simple distillate from petroleum, but the automotive engines were rapidly being improved and required a more suitable fuel. During the 1910s, laws prohibited the storage of gasolines on residential properties, so Charles F. Kettering ( yes - he of ignition system fame ) modified an IC engine to run on kerosine. However the kerosine-fuelled engine would "knock" and crack the cylinder head and pistons. He assigned Thomas Midgley Jr. to confirm that the cause was from the kerosine droplets vaporising on combustion as they presumed . Midgley demonstrated that the knock was caused by a rapid rise in pressure after ignition, not during preignition as believed [7]. This then lead to the long search for anti-knock agents, culminating in tetra ethyl lead [8]. Typical mid-1920s gasolines were 40 - 60 Octane [9].

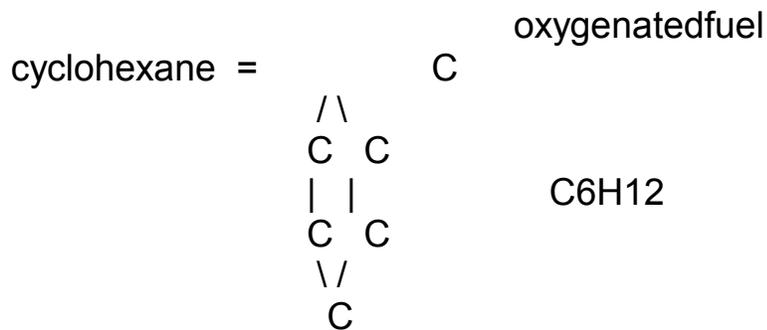
Because sulfur in gasoline inhibited the octane-enhancing effect of the alkyl lead, the sulfur content of the thermally-cracked refinery streams for gasolines was restricted. By the 1930s, the petroleum industry had determined that the larger hydrocarbon molecules (kerosine) had major adverse effects on the octane of gasoline, and were developing consistent specifications for desired properties. By the 1940s catalytic cracking was introduced, and gasoline compositions became fairly consistent between brands during the various seasons.

The 1950s saw the start of the increase of the compression ratio, requiring higher octane fuels. Lead levels were increased, and some new refining processes ( such as hydrocracking ), specifically designed to provide hydrocarbons components with good lead response and octane, were introduced. Minor improvements were made to gasoline formulations to improve yields and octane until the 1970s - when unleaded fuels were introduced to protect the exhaust catalysts that were also being introduced for environmental reasons. From 1970 until 1990 gasolines were slowly changed as lead was phased out. In 1990 the Clean Air Act started forcing major compositional changes on gasoline, and these changes will continue into the 21st Century because gasoline is a major pollution source.

### 4.4 What are the hydrocarbons in gasoline?

Hydrocarbons ( HCs ) are any molecules that just contain hydrogen and carbon, both of which are fuel molecules that can be burnt ( oxidised ) to form water ( H<sub>2</sub>O ) or carbon dioxide ( CO<sub>2</sub> ). If the combustion is not complete, carbon





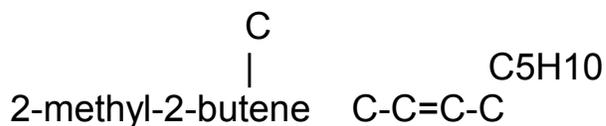
#### 4.4.2 Unsaturated Hydrocarbons

Unstable, are the remaining component of gasoline.

Tend to burn in air with a smoky flame.

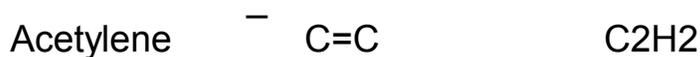
Alkenes ( aka olefins, have carbon=carbon double bonds )

These are unstable, and are usually limited to a few %.



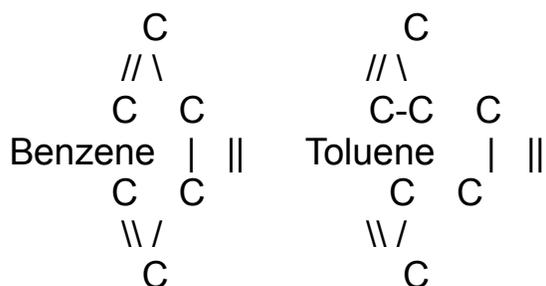
Alkynes ( aka acetylenes, have carbon-carbon triple bonds )

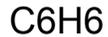
These are even more unstable, are only present in trace amounts, and only in some poorly-refined gasolines.



Arenes ( aka aromatics )

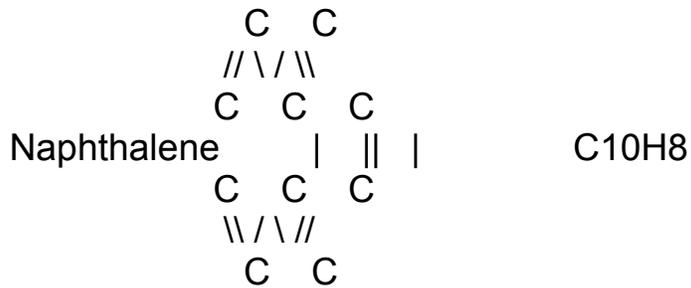
Used to be up to 40%, gradually being reduced to <20%.





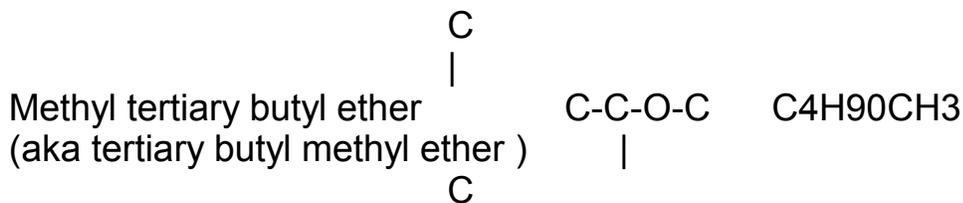
Polynuclear Aromatics ( aka PNAs or PAHs )

These are high boiling, and are only present in small amounts in gasoline. They contain benzene rings joined together, and the simplest is Naphthalene. The multi-ringed PNAs are highly toxic, and are not present in gasoline.



#### 4.5 What are oxygenates?

Oxygenates are just preused hydrocarbons :-). They contain oxygen, which can not provide energy, but their structure provides a reasonable anti-knock value, thus they are good substitutes for aromatics, and they may also reduce the smog-forming tendencies of the exhaust gases [11].



They can be produced from fossil fuels eg methanol (MeOH), methyl tertiary butyl ether (MTBE), tertiary amyl methyl ether (TAME), or from biomass, eg ethanol(EtOH), ethyl tertiary butyl ether (ETBE)). Most oxygenates used in gasolines are either alcohols (  $C_x-O-H$  ) or ethers (  $C_x-O-C_y$  ), and contain 1 to 6 carbons. MTBE is produced by reacting methanol ( from natural gas ) with isobutylene in the liquid phase over an acidic ion-exchange resin catalyst at 100C. The isobutylene was initially from refinery catalytic crackers or petrochemical olefin plants, but these days larger plants produce it from butanes. Production has increased at the rate of 10 to 20% per year, and the spot market

## oxygenatedfuel

price in June 1993 was around \$270/tonne [11]. The "ether" starting fluids for vehicles are usually diethyl ether ( liquid ) or dimethyl ether ( aerosol ). Note that " petroleum ether " is actually a volatile hydrocarbon fraction, it is not a C<sub>x</sub>-O-C<sub>y</sub> compound.

Oxygenates are added to gasolines to reduce the reactivity of emissions, but they are only effective if the hydrocarbon fractions are carefully modified to utilise the octane and volatility properties of the oxygenates. If the hydrocarbon fraction is not correctly modified, oxygenates can increase the undesirable smog-forming and toxic emissions. The major reduction in the reactivity of exhaust and evaporative emissions will occur with reformulated gasolines, due to be introduced in January 1995, which have oxygenates and major composition changes to the hydrocarbon component. Oxygenates do not necessarily reduce all individual exhaust toxins, nor are they intended to.

Oxygenates have significantly different physical properties to hydrocarbons, and the levels that can be added to gasolines are controlled by the EPA in the US, with waivers being granted for some combinations. The change to reformulated gasoline requires oxygenates, but also that the hydrocarbon composition must be significantly more modified than the existing oxygenated gasolines to reduce unsaturates, volatility, benzene, and the reactivity of emissions.

Oxygenates that are added to gasoline function in two ways. Firstly they have high blending octane, and so can replace high octane aromatics in the fuel. These aromatics are responsible for disproportionate amounts of CO and HC exhaust emissions. This is called the "aromatic substitution effect". Oxygenates also cause engines without sophisticated engine management systems to move to the lean side of stoichiometry, thus reducing emissions of CO ( 2% oxygen can reduce CO by 16% ) and HC ( 2% oxygen can reduce HC by 10%). However, on vehicles with engine management systems, the fuel volume will be increased to bring the stoichiometry back to the preferred optimum setting. Oxygen in the fuel can not contribute energy, consequently the fuel has less energy content. For the same efficiency and power output, more fuel has to be burnt, and the slight improvements in efficiency that oxygenates provide on some engines usually do not completely compensate for the oxygen [12].

There are huge number of chemical mechanisms involved in the pre-flame reactions of gasoline combustion. Although both alkyl leads and oxygenates are effective at suppressing knock, the chemical modes through which they act are

## oxygenatedfuel

entirely different. MTBE works by retarding the progress of the low temperature or cool-flame reactions, consuming radical species, particularly OH radicals and producing isobutene. The isobutene in turn consumes additional OH radicals and produces unreactive, resonantly stabilised radicals such as allyl and methyl allyl, as well as stable species such as allene, which resist further oxidation [13,14].

### 4.6 Why were alkyl lead compounds added?

The efficiency of a spark-ignited gasoline engine can be related to the compression ratio up to at least compression ratio 17:1 [15]. However any "knock" caused by the fuel will rapidly mechanically destroy an engine, and General Motors was having major problems trying to improve engines without inducing knock. The problem was to identify economic additives that could be added to gasoline or kerosine to prevent knock, as it was apparent that engine development was being hindered. The kerosine for home fuels soon became a secondary issue, as the magnitude of the automotive knock problem increased throughout the 1910s, and so more resources were poured into the quest for an effective "anti-knock". A higher octane aviation gasoline was required urgently once the US entered WWI, and almost every possible chemical ( including melted butter ) was tested for anti-knock ability [16].

Originally, iodine was the best anti-knock available, but was not a practical gasoline additive, and was used as the benchmark. In 1919 aniline was found to have superior antiknock ability to iodine, but also was not a practical additive, however aniline became the benchmark anti-knock, and various compounds were compared to it. The discovery of tetra ethyl lead, and the scavengers required to remove it from the engine were made by teams lead by Thomas Midgley Jr. in 1922 [7,8,16]. They tried selenium oxychloride which was an excellent antiknock, however it reacted with iron and "dissolved" the engine. Midgley was able to predict that other organometallics would work, and slowly focused on organoleads. They then had to remove the lead, which would otherwise accumulate and coat the engine and exhaust system with lead. They discovered and developed the halogenated lead scavengers that are still used in leaded fuels. The scavengers, ( ethylene dibromide and ethylene dichloride ), function by providing halogen atoms that react with the lead to form volatile lead halide salts that can escape out the exhaust. The quantity of scavengers added to the alkyl lead concentrate is calculated according to the amount of lead present. If sufficient scavenger is added to theoretically react with all the lead present, the amount is called one "theory". Typically, 1.0 to 1.5 theories are used, but aviation gasolines must only use one theory. This ensures there is no excess

### oxygenatedfuel

bromine that could react with the engine. The alkyl leads rapidly became the most cost-effective method of enhancing octane.

The development of the alkyl leads ( tetra methyl lead, tetra ethyl lead ) and the toxic halogenated scavengers meant that petroleum refiners could then configure refineries to produce hydrocarbon streams that would increase octane with small quantities of alkyl lead. If you keep adding alkyl lead compounds, the lead response of the gasoline decreases, and so there are economic limits to how much lead should be added.

Up until the late 1960s, alkyl leads were added to gasolines in increasing concentrations to obtain octane. The limit was 1.14g Pb/l, which is well above the diminishing returns part of the lead response curve for most refinery streams, thus it is unlikely that much fuel was ever made at that level. I believe 1.05 was about the maximum, and articles suggest that 1970 100 RON premiums were about 0.7-0.8 g Pb/l and 94 RON regulars 0.6-0.7 g Pb/l, which matches published lead response data [17] eg.

For Lead g/l	Catalytic Reformate Research Octane	Straight Run Naphtha. Number
0	96	72
0.1	98	79
0.2	99	83
0.3	100	85
0.4	101	87
0.5	101.5	88
0.6	102	89
0.7	102.5	89.5
0.8	102.75	90

The alkyl lead anti-knocks work in a different stage of the pre-combustion reaction to oxygenates. In contrast to oxygenates, the alkyl lead interferes with hydrocarbon chain branching in the intermediate temperature range where HO<sub>2</sub> is the most important radical species. Lead oxide, either as solid particles, or in the gas phase, reacts with HO<sub>2</sub> and removes it from the available radical pool, thereby deactivating the major chain branching reaction sequence that results in undesirable, easily-autoignitable hydrocarbons [13,14].

## oxygenatedfuel

### 4.7 Why not use other organometallic compounds?

As the toxicity of the alkyl lead and the halogenated scavengers became of concern, alternatives were considered. The most famous of these is methylcyclopentadienyl manganese tricarbonyl (MMT), which was used in the USA until banned by the EPA from 27 Oct 1978 [18], but is approved for use in Canada and Australia. It is more expensive than alkyl leads and has been reported to increase unburned hydrocarbon emissions and block exhaust catalysts [19]. Other compounds that enhance octane have been suggested, but usually have significant problems such as toxicity, cost, increased engine wear etc.. Examples include dicyclopentadienyl iron and nickel carbonyl.

### 4.8 What do the refining processes do?

Crude oil contains a wide range of hydrocarbons, organometallics and other compounds containing sulfur, nitrogen etc. The HCs contain between 1 and 60 carbon atoms. Gasoline requires hydrocarbons with carbon atoms between 3 and 12, arranged in specific ways to provide the desirable properties. Obviously, a refinery has to either sell the remainder as marketable products, or convert the larger molecules into smaller gasoline molecules.

A refinery will distill crude oil into various fractions and, depending on the desired final products, will further process and blend those fractions. Typical final products could be:- gases for chemical synthesis and fuel (CNG), liquified gases (LPG), butane, aviation and automotive gasolines, aviation and lighting kerosines, diesels, distillate and residual fuel oils, lubricating oil base grades, paraffin oils and waxes. Many of the common processes are intended to increase the yield of blending feedstocks for gasolines.

Typical modern refinery processes for gasoline components include

Catalytic cracking - breaks larger, higher-boiling, hydrocarbons into gasoline range product that contains 30% aromatics and 20-30% olefins.

Hydrocracking - cracks and adds hydrogen to molecules, producing a more saturated, stable, gasoline fraction.

Isomerisation - raises gasoline fraction octane by converting straight chain hydrocarbons into branched isomers.

Reforming - converts saturated, low octane, hydrocarbons into higher octane product containing about 60% aromatics.

Alkylation - reacts gaseous olefin streams with isobutane to produce liquid high octane iso-alkanes.

## oxygenatedfuel

The changes that the Clean Air Act and other legislation ensures that the refineries will continue to modify their processes to produce a less volatile gasoline with fewer toxins and toxic emissions. Options include:-

Reducing the "severity" of reforming to reduce aromatic production.

Distilling the C5/C6 fraction from reformer feeds and treating that stream to produce non-aromatic high octane components.

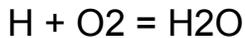
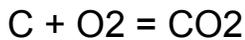
Distilling the higher boiling fraction ( which contains 80-100% of aromatics that can be hydrocracked ) from catalytic cracker product [20].

Convert butane to isobutane or isobutylene for alkylation or MTBE feed.

4.9 What energy is released when gasoline is burned?

It is important to note that the theoretical energy content of gasoline when burned in air is only related to the hydrogen and carbon contents. Octane rating is not fundamentally related to the energy content, and the actual hydrocarbon and oxygenate components used in the gasoline will determine both the energy release and the anti-knock rating.

Two important reactions are:-



The mass or volume of air required to provide sufficient oxygen to achieve this complete combustion is the "stoichiometric" mass or volume of air. Insufficient air = "rich", and excess air = "lean", and the stoichiometric mass of air is related to the carbon:hydrogen ratio of the fuel. The procedures for calculation of stoichiometric air/fuel ratios are fully documented in an SAE standard [21].

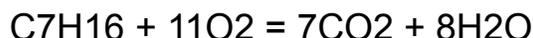
Atomic masses used are:- Hydrogen = 1.00794, Carbon = 12.011, Oxygen = 15.994, Nitrogen = 14.0067, and Sulfur = 32.066.

The composition of sea level air ( 1976 data, hence low CO<sub>2</sub> value ) is

Gas Species	Fractional Volume	Molecular Weight kg/mole	Relative Mass
N <sub>2</sub>	0.78084	28.0134	21.873983
O <sub>2</sub>	0.209476	31.9988	6.702981
Ar	0.00934	39.948	0.373114
CO <sub>2</sub>	0.000314	44.0098	0.013919
Ne	0.00001818	20.179	0.000365

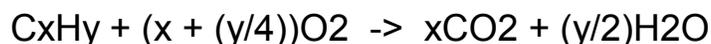
		oxygenatedfuel	
He	0.00000524	4.002602	0.000021
Kr	0.00000114	83.80	0.000092
Xe	0.000000087	131.29	0.000011
CH4	0.000002	16.04276	0.000032
H2	0.0000005	2.01588	0.000001
		-----	
Air		28.964419	

For normal heptane C7H16 with a molecular weight = 100.204



thus 1.000 kg of C7H16 required 3.513 kg of O2 = 15.179 kg air.

The chemical stoichiometric combustion of hydrocarbons with oxygen can be written as:-



Often, for simplicity, the remainder of air is assumed to be nitrogen, which can be added to the equation when exhaust compositions are required. As a general rule, maximum power is achieved at slightly rich, whereas maximum fuel economy is achieved at slightly lean.

The energy content of the gasoline is obtained by burning all the fuel inside a bomb calorimeter and measuring the temperature increase. The energy available depends on what happens to the water produced from the combustion of the hydrogen. If the water remains as a gas, then it cannot release the heat of vaporisation, thus producing the Nett Calorific Value. If the water were condensed back to the original fuel temperature, then Gross Calorific Value of the fuel, which will be larger, is obtained.

The calorific values are fairly constant for families of HCs, which is not surprising, given their fairly consistent carbon/hydrogen ratios. For liquid ( l ) or gaseous ( g ) fuel converted to gaseous products - except for the 2-methylbutene-2, where only gaseous is reported. \* = Blending Octane Number

Typical Heats of Combustion are [22]:-

Fuel	State	Heat of Combustion	Research	Motor
------	-------	--------------------	----------	-------

	MJ/kg	oxygenatedfuel	
		Octane	Octane
n-heptane l	44.592	0	0
g	44.955		
i-octane l	44.374	100	100
g	44.682		
toluene l	40.554	124*	112*
g	40.967		
2-methylbutene-2	44.720	176*	141*

Because all the data is available, the calorific value of fuels can be estimated quite accurately from hydrocarbon fuel properties such as the density, sulfur content, and aniline point ( which indicates the aromatics content ).

It should be noted that because oxygenates contain oxygen that can not provide energy, they will have significantly lower energy contents. They are added to provide octane, not energy. For an engine that can be optimised for oxygenates, more fuel is required to obtain the same power, but they can burn slightly more efficiently, thus the power ratio is not identical to the energy content ratio. They also require more energy to vaporise.

	Energy Content	Heat of Vaporisation	Oxygen Content
	Nett MJ/kg	MJ/kg	wt%
Methanol	19.95	1.154	49.9
Ethanol	26.68	0.913	34.7
MTBE	35.18	0.322	18.2
ETBE	36.29	0.310	15.7
TAME	36.28	0.323	15.7
Gasoline	42 - 44	0.297	0.0

Typical values for commercial fuels in megajoules/kilogram are [23]:-

	Gross	Nett
Hydrogen	141.9	120.0
Carbon to Carbon monoxide	10.2	-
Carbon to Carbon dioxide	32.8	-
Sulfur to sulfur dioxide	9.16	-
Natural Gas	53.1	48.0

		oxygenatedfuel
Liquified petroleum gas	49.8	46.1
Aviation gasoline	46.0	44.0
Automotive gasoline	45.8	43.8
Kerosine	46.3	43.3
Diesel	45.3	42.5

Obviously, for automobiles, the nett calorific value is appropriate. The calorific value is the maximum energy that can be obtained from the fuel, but the reality of modern SI engines is that efficiencies of 20-40% may be obtained, this limit being due to engineering and material constraints that prevent optimum combustion conditions being used. The CI engine can achieve higher efficiencies, usually over a wider operating range as well.

#### 4.10 What are the gasoline specifications?

Gasolines are usually defined by government regulation, where properties and test methods are clearly defined. In the US, several government and state bodies can specify gasoline properties. The US gasoline specifications and test methods are listed in several readily available publications, including the Society of Automotive Engineers (SAE) [24], and the American Society for Testing Materials (ASTM) [25]. The 1994 ASTM edition has:-

##### D4814-93a Specification for Automotive Spark-Ignition Engine Fuel.

This specification lists various properties that all fuels have to comply with, and may be updated throughout the year. Typical properties are:-

#### 4.10.1 Vapour Pressure and Distillation Classes.

6 different classes according to location and/or season.

As gasoline is distilled, the temperatures at which various fractions are evaporated are calculated. Specifications define the temperatures at which various percentages of the fuel are evaporated. Distillation limits include maximum temperatures that 10% is evaporated (50-70C), 50% is evaporated (110-121C), 90% is evaporated (185-190C), and the final boiling point (225C). A minimum temperature for 50% evaporated (77C), and a maximum amount of Residue (2%) after distillation. Vapour pressure limits for each class ( 54, 62, 69, 79, 93, 103 kPa ) are also specified. Note that the EPA has issued a waiver that does not require gasoline/ethanol blends to meet the required specifications.

## oxygenatedfuel

### 4.10.2 Vapour Lock Protection Classes

5 classes for vapour lock protection, according to location and/or season. The limit is a maximum Vapour/Liquid ratio of 20 at test temperatures of 41, 47, 51, 56, 60C.

### 4.10.3 Antiknock Index ( aka (RON+MON)/2, "Pump Octane" )

The ( Research Octane Number + Motor Octane Number ) divided by two. Limits are not specified, but changes in engine requirements according season and location are discussed. Fuels with an Antiknock index of 87, 89, 91 ( Unleaded), and 88 ( Leaded ) are listed as typical for the US.

### 4.10.4 Lead Content

Leaded = 1.1 g Pb / L maximum, and Unleaded = 0.013 g Pb / L maximum.

### 4.10.5 Copper strip corrosion

Ability to tarnish clean copper, indicating the presence of any corrosive sulfur compounds

### 4.10.6 Maximum Sulfur content

Sulfur adversely affects exhaust catalysts and fuel hydrocarbon lead response, and also may be emitted as polluting sulfur oxides.

Leaded = 0.15 %mass maximum, and Unleaded = 0.10 %mass maximum.

Typical US gasoline levels are 0.03 %mass.

### 4.10.7 Maximum Existent Gum

Limits the amount of gums present in fuel at the time of testing to 5 mg/100mls. The results do not correlate well with actual engine deposits caused by fuel vaporisation [26].

### 4.10.8 Minimum Oxidation Stability

This ensures the fuel remains chemically stable, and does not form additional gums during periods in distribution systems, which can be up to 3-6 months. The sample is heated with oxygen inside a pressure vessel, and the delay until significant oxygen uptake is measured.

### 4.10.9 Water Tolerance

Highest temperature that causes phase separation of oxygenated fuels. The

### oxygenated fuel

limits vary according to location and month. For Alaska - North of 62 latitude, it changes from -41C in Dec/Jan to 9C in July, but remains 10C all year in Hawaii.

As well as the above, there are various restrictions introduced by the Clean Air Act and state bodies such as California's Air Resources Board (CARB) that often have more stringent limits for the above properties, as well as additional limits. The Clean Air Act also specifies some regions that exceed air quality standards have to use reformulated gasolines (RFGs) all year, starting January 1995. Other regions are required to use oxygenated gasolines for four winter months, beginning November 1992. The RFGs also contain oxygenates. Metropolitan regions with severe ozone air quality problems must use reformulated gasolines in 1995 that;- contain at least 2.0 wt% oxygen, reduce 1990 volatile organic carbon compounds by 15%, and reduce specified toxic emissions by 15% (1995) and 25% (2000). Metropolitan regions that exceeded carbon monoxide limits were required to use gasolines with 2.7 wt% oxygen during winter months, starting in 1992.

Because phosphorus adversely affects exhaust catalysts, the EPA limits phosphorus in all gasolines to 0.0013 gP/L.

The 1990 Clean Air Act (CAA) amendments and CARB phase 2 (1996) specifications for reformulated gasoline establish the following limits, compared with typical 1990 gasoline. Because of a lack of data, the EPA were unable to define the CAA required parameters, so they instituted a two-stage system. The first stage, the "Simple Model" is an interim stage that run from 1/Jan/1995 to 1/May/1997. The second stage, the "Complex Model" would be developed, with the following parameters likely to be controlled - Reid vapour pressure, benzene, oxygen, sulfur, olefins distillation ( 90% Evaporated ), and aromatics. Each refiner must have their RFG recertified using the Complex model by 1/May/1997 [27].

	1990	Clean Air Act	CARB
benzene	2 %	1 % maximum	1.0 vol% maximum
oxygen	0.2 %	2 % minimum	1.8-2.0 mass%
sulfur	150 ppm	no increase	40 ppm
aromatics	32.0 %	25 % maximum	25 vol% maximum
olefins	9.9 %	5 % maximum	6 vol% maximum
Reid vapour pressure	60 kPa	56 kPa (north) 50 kPa (south)	48 kPa

		oxygenated fuel	
90% evaporated	170 C	-	149 C

These regulations also specify emissions criteria. eg CAA specifies no increase in nitric oxides (NOx) emissions, reductions in VOC by 15% during the ozone season, and specified toxins by 15% all year. These criteria indirectly establish vapour pressure and composition limits that refiners have to meet. Note that the EPA also can issue CAA Section 211 waivers that allow refiners to choose which oxygenates they use. In 1981, the EPA also decided that fuels with up to 2% alcohols and ethers (except methanol) were "substantially similar" to 1974 unleaded gasoline, and thus were not "new" gasoline additives. That level was increased to 2.7 wt% in 1991. Some other oxygenates have also been granted waivers, eg ethanol to 3.5 wt% in 1979/1982, and tert-butyl alcohol to 3.5 wt% in 1981.

#### 4.11 What are the effects of the specified fuel properties?

##### Volatility

This affects evaporative emissions and driveability, it is the property that must change with location and season. Fuel for mid-summer Arizona would be difficult to use in mid-winter Alaska. The US is divided into zones, according to altitude and seasonal temperatures, and the fuel volatility is adjusted accordingly. Incorrect fuel may result in difficult starting in cold weather, carburettor icing, vapour lock in hot weather, and crankcase oil dilution. Volatility is controlled by distillation and vapour pressure specifications. The higher boiling fractions of the gasoline have significant effects on the emission levels of undesirable hydrocarbons and aldehydes, and a reduction of 40C in the final boiling point will reduce the levels of benzene, butadiene, formaldehyde and acetaldehyde by 25%, and will reduce HC emissions by 20% [28].

##### Combustion Characteristics

As gasolines contain mainly hydrocarbons, the only significant variable between different grades is the octane rating of the fuel, as most other properties are similar. Octane is discussed in detail in Section 6. There are only slight differences in combustion temperatures ( most are around 2000C in isobaric adiabatic combustion [29]). Note that the actual temperature in the combustion chamber is also determined by other factors, such as load and engine design. The addition of oxygenates changes the pre-flame reaction pathways, and also reduces the energy content of the fuel. The levels of oxygen in the fuel is

oxygenated fuel  
regulated according to regional air quality standards.

## Stability

Motor gasolines may be stored up to six months, consequently they must not form gums which may precipitate. Gums are usually the result of copper-catalysed reactions of the unsaturated HCs, so antioxidants and metal deactivators are added. Existing Gum is used to measure the gum in the fuel at the time tested, whereas the Oxidation Stability measures the time it takes for the gasoline to break down at 100C with 100psi of oxygen. A 240 minutes test period has been found to be sufficient for most storage and distribution systems.

## Corrosiveness

Sulfur in the fuel creates corrosion, and when combusted will form corrosive gases that attack the engine, exhaust and environment. Sulfur also adversely affects the alkyl lead octane response and may poison exhaust catalysts. The copper strip corrosion test and the sulfur specification are used to ensure fuel quality. The copper strip test measures active sulfur, whereas the sulfur content reports the total sulfur present.

### 4.12 Are brands different?

Yes. The above specifications are intended to ensure minimal quality standards are maintained, however as well as the fuel hydrocarbons, the manufacturers add their own special ingredients to provide additional benefits. A quality gasoline additive package would include:-

- octane-enhancing additives ( improve octane ratings )
- anti-oxidants ( inhibit gum formation, improve stability )
- metal deactivators ( inhibit gum formation, improve stability )
- deposit modifiers ( reduce deposits, spark-plug fouling and preignition )
- surfactants ( prevent icing, improve vaporisation, inhibit deposits, reduce NOx emissions )
- freezing point depressants ( prevent icing )
- corrosion inhibitors ( prevent gasoline corroding storage tanks )
- dyes ( product colour for safety or regulatory purposes ).

During the 1980s significant problems with deposits accumulating on intake valve surfaces occurred as new fuel injection systems were introduced. These intake valve deposits (IVD) were different to the injector deposits, in part because the

## oxygenated fuel

valve can reach 300C. Engine design changes that prevent deposits usually consist of ensuring the valve is flushed with liquid gasoline, and provision of adequate valve rotation. Gasoline factors that cause deposits are the presence of alcohols or olefins. Gasoline manufacturers now routinely use additives that prevent IVD and also maintain the cleanliness of injectors. These usually include a surfactant and light oil to maintain the wetting of important surfaces. A more detailed description of additives is provided in Section 9.1.

Texaco demonstrated that a well-formulated package could improve fuel economy, reduce NOx emissions, and restore engine performance because, as well as the traditional liquid-phase deposit removal, some additives can work in the vapour phase to remove existing engine deposits without adversely affecting performance ( as happens when water is poured into a running engine to remove carbon deposits:-) )[30]. Most suppliers of quality gasolines will formulate similar additives into their products, and cheaper lines are less like to have such additives added. As different brands use different additives and oxygenates, it is probable that important parameters, such as octane distribution, are different, even though the pump octane ratings are the same.

So, if you know your car is well-tuned, and in good condition, but the driveability is pathetic on the correct octane, try another brand. Remember that the composition will change with the season, so if you lose driveability, try yet another brand. As various Clean Air Act changes are introduced over the next few years, gasoline will continue to change.

### 4.13 What is a typical composition?

There seems to be a perception that all gasolines of one octane grade are chemically similar, and thus general rules can be promulgated about "energy content", "flame speed", "combustion temperature" etc. etc.. Nothing is further from the truth. The behaviour of manufactured gasolines in octane rating engines can be predicted, using previous octane ratings of special blends intended to determine how a particular refinery stream responds to an octane-enhancing additive. Refiners can design and reconfigure refineries to efficiently produce a wide range of gasolines feedstocks, depending on market and regulatory requirements.

The last 10 years of various compositional changes to gasolines for environmental and health reasons have resulted in fuels that do not follow historical rules, and the regulations mapped out for the next decade also ensure

### oxygenatedfuel

the composition will remain in a state of flux. The reformulated gasoline specifications, especially the 1/May/1997 Complex model, will probably introduce major reductions in the distillation range, as well as the various limits on composition and emissions.

I'm not going to list all 500+ HCs in gasolines, but the following are representative of the various classes typically present in a gasoline. The numbers after each chemical are:- Research Blending Octane : Motor Blending Octane : Boiling Point (C): Density (g/ml @ 15C) : Minimum Autoignition Temperature (C). It is important to realise that the Blending Octanes are derived from a 20% mix of the HC with a 60:40 iC8:nC7 base, and the extrapolation of this 20% to 100%. This is different from rating the pure fuel, which often requires adjustment of the test engine conditions outside the acceptable limits of the rating methods. Generally the actual octanes of the pure fuel are similar for the alkanes, but are up to 30 octane numbers lower than the blending octanes for the aromatics and olefins [31].

A traditional composition I have dreamed up would be like the following, whereas newer oxygenated fuels reduce the aromatics and olefins, narrow the boiling range, and add oxygenates up to about 12-15% to provide the octane.

	RON	MON	BP	d	AIT
15% n-paraffins					
n-butane	113	114	-0.5	gas	370
n-pentane	62	66	35	0.626	260
n-hexane	19	22	69	0.659	225
n-heptane (0:0 by definition)	0	0	98	0.684	225
n-octane	-18	-16	126	0.703	220
( you would not want to have the following alkanes in gasoline, so you would never blend kerosine with gasoline )					
n-decane	-41	-38	174	0.730	210
n-dodecane	-88	-90	216	0.750	204
n-tetradecane	-90	-99	253	0.763	200
30% iso-paraffins					
2-methylpropane	122	120	-12	gas	460
2-methylbutane	100	104	28	0.620	420
2-methylpentane	82	78	62	0.653	306
3-methylpentane	86	80	64	0.664	-
2-methylhexane	40	42	90	0.679	-
3-methylhexane	56	57	91	0.687	-

	oxygenatedfuel
2,2-dimethylpentane	89 : 93 : 79 : 0.674 :
2,2,3-trimethylbutane	112 : 112 : 81 : 0.690 : 420
2,2,4-trimethylpentane	100 : 100 : 98 : 0.692 : 415
( 100:100 by definition )	
12% cycloparaffins	
cyclopentane	141 : 141 : 50 : 0.751 : 380
methylcyclopentane	107 : 99 : 72 : 0.749 :
cyclohexane	110 : 97 : 81 : 0.779 : 245
methylcyclohexane	104 : 84 : 101 : 0.770 : 250
35% aromatics	
benzene	98 : 91 : 80 : 0.874 : 560
toluene	124 : 112 : 111 : 0.867 : 480
ethyl benzene	124 : 107 : 136 : 0.867 : 430
meta-xylene	162 : 124 : 138 : 0.868 : 463
para-xylene	155 : 126 : 138 : 0.866 : 530
ortho-xylene	126 : 102 : 144 : 0.870 : 530
3-ethyltoluene	162 : 138 : 158 : 0.865 :
1,3,5-trimethylbenzene	170 : 136 : 163 : 0.864 :
1,2,4-trimethylbenzene	148 : 124 : 168 : 0.889 :
8% olefins	
2-pentene	154 : 138 : 37 : 0.649 :
2-methylbutene-2	176 : 140 : 36 : 0.662 :
2-methylpentene-2	159 : 148 : 67 : 0.690 :
cyclopentene	171 : 126 : 44 : 0.774 :
( the following olefins are not present in significant amounts in gasoline, but have some of the highest blending octanes )	
1-methylcyclopentene	184 : 146 : 75 : 0.780 :
1,3 cyclopentadiene	218 : 149 : 42 : 0.805 :
dicyclopentadiene	229 : 167 : 170 : 1.071 :

## Oxygenates

Published octane values vary a lot because the rating conditions are significantly different to standard conditions, for example the API Project 45 numbers used above for the hydrocarbons, reported in 1957, gave MTBE blending RON as 148 and MON as 146, however that was based on the lead response, whereas today we use MTBE in place of lead.

methanol	133 : 105 : 65 : 0.796 : 385
----------	------------------------------

	oxygenatedfuel
ethanol	129 : 102 : 78 : 0.794 : 365
iso propyl alcohol	118 : 98 : 82 : 0.790 : 399
methyl tertiary butyl ether	116 : 103 : 55 : 0.745 :
ethyl tertiary butyl ether	118 : 102 : 72 : 0.745 :
tertiary amyl methyl ether	111 : 98 : 86 : 0.776 :

There are some other properties of oxygenates that have to be considered when they are going to be used as fuels, particularly their ability to form very volatile azeotropes that cause the fuel's vapour pressure to increase, the chemical nature of the emissions, and their tendency to separate into a separate water/oxygenate phase when water is present. The reformulated gasolines address these problems more successfully than the original oxygenated gasolines.

Before you rush out to make a highly aromatic or olefinic gasoline to produce a high octane fuel, remember they have other adverse properties, eg the aromatics attack elastomers and generate smoke, and the olefins are unstable ( besides smelling foul ) and form gums. The art of correctly formulating a gasoline that does not cause engines to knock apart, does not cause vapour lock in summer - but is easy to start in winter, does not form gums and deposits, burns cleanly without soot/residues, and does not dissolve or poison the car catalyst or owner, is based on knowledge of the gasoline composition.

#### 4.14 Is gasoline toxic or carcinogenic?

There are several known toxins in gasoline, some of which are confirmed human carcinogens. The most famous of these toxins are lead and benzene, and both are regulated. The other aromatics and some toxic olefins are also controlled. Lead alkyls also require ethylene dibromide and/or ethylene dichloride scavengers to be added to the gasoline, both of which are suspected human carcinogens. In 1993 an International Symposium on the Health Effects of Gasoline was held [32]. Major review papers on the carcinogenic, neurotoxic, reproductive and developmental toxicity of gasoline, additives, and oxygenates were presented. The oxygenates are also being evaluated for carcinogenicity, and even ethanol and ETBE may be carcinogens. It should be noted that the oxygenated gasolines were not expected to reduce the toxicity of the emissions, however the reformulated gasolines will produce different emissions, and specific toxins must be reduced by 15% all year.

There is little doubt that gasoline is full of toxic chemicals, and should therefore be treated with respect. However the biggest danger remains the flammability,

## oxygenated fuel

and the relative hazards should always be kept in perspective. The major toxic risk from gasolines comes from breathing the tailpipe, evaporative, and refuelling emissions, rather than occasional skin contact from spills. Breathing vapours and skin contact should always be minimised.

### 4.15 Is unleaded gasoline more toxic than leaded?

The short answer is no. However that answer is not global, as some countries have replaced the lead compound octane-improvers with aromatic or olefin octane-improvers without introducing exhaust catalysts. Some aromatics are more toxic than paraffins. Unfortunately, the manufacturers of alkyl lead compounds have embarked on a worldwide misinformation campaign in countries considering emulating the lead-free US. The use of lead precludes the use of exhaust catalysts, thus the emissions of aromatics are only slightly diminished, and other pollutants can not be reduced by exhaust catalysts.

The use of unleaded on modern vehicles with engine management systems and catalysts can reduce aromatic emissions to 10% of the level of vehicles without catalysts [33]. Alkyl lead additives can only substitute for some of the aromatics in gasoline, consequently they do not eliminate aromatics, which will produce benzene emissions [34]. Alkyl lead additives also require toxic organohalogen scavengers, which also react in the engine to form and emit other organohalogens, including highly toxic dioxin [35]. Leaded fuels emit lead, organohalogens, and much higher levels of regulated toxins because they preclude the use of exhaust catalysts. In the USA the gasoline composition is being changed to reduce fuel toxins (olefins, aromatics) as well as emissions of specific toxins.

---

## Subject: 5. Why is Gasoline Composition Changing?

5.1 Why pick on cars and gasoline? Cars emit several pollutants as combustion products out the tailpipe, (tailpipe emissions), and as losses due to evaporation (evaporative emissions, refuelling emissions). The volatile organic carbon (VOC) emissions from these sources, along with nitrogen oxides (NO<sub>x</sub>) emissions from the tailpipe, will react in the presence of ultraviolet light (wavelengths of less than 430nm) to form ground-level (tropospheric) ozone, which is one of the major components of photochemical smog [36]. Smog has been a major pollution problem ever since coal-fired power stations were developed in urban areas, but

### oxygenatedfuel

their emissions are being cleaned up. Now it's the turn of the automobile.

Cars currently use gasoline that is derived from fossil fuels, thus when gasoline is burned to completion, it produces additional CO<sub>2</sub> that is added to the atmospheric burden. The effect of the additional CO<sub>2</sub> on the global environment is not known, but the quantity of man-made emissions of fossil fuels must cause the system to move to a new equilibrium. Even if current research doubles the efficiency of the IC engine/gasoline combination, and reduces HC, CO, NO<sub>x</sub>, SO<sub>x</sub>, VOCs, particulates, and carbonyls, the amount of carbon dioxide from the use of fossil fuels may still cause global warming. More and more scientific evidence is accumulating that warming is occurring [37]. The issue is whether it is natural, or induced by human activities. There are international agreements to limit CO<sub>2</sub> emissions to 1990 levels, a target that will require more efficient, lighter, or appropriately-sized vehicles, - if we are to maintain the current usage. One option is to use "renewable" fuels in place of fossil fuels. Consider the amount of energy-related CO<sub>2</sub> emissions for selected countries in 1990 [38].

	CO <sub>2</sub> Emissions ( tonnes/year/person )
USA	20.0
Canada	16.4
Australia	15.9
Germany	10.4
United Kingdom	8.6
Japan	7.7
New Zealand	7.6

The number of new vehicles provides an indication of the magnitude of the problem. Although vehicle engines are becoming more efficient, the distance travelled is increasing, resulting in a gradual increase of gasoline consumption. The world production of vehicles (in thousands) over the last few years was [39];-

### Cars

Region	1990	1991	1992	1993
Africa	222	213	194	201

	oxygenatedfuel			
Asia-Pacific	12,064	12,112	11,869	11,467
Central & South America	800	888	1,158	1,524
Eastern Europe	2,466	984	1,726	1,783
Middle East	35	24	300	377
North America	7,762	7,230	7,470	8,172
Western Europe	13,688	13,286	13,097	11,124
Total World	37,039	34,739	35,815	34,649

Trucks ( including heavy trucks and buses )

Region	1990	1991	1992	1993
Africa	133	123	108	109
Asia-Pacific	5,101	5,074	5,117	5,054
Central & South America	312	327	351	417
Eastern Europe	980	776	710	708
Middle East	36	28	100	110
North America	4,851	4,554	5,371	6,037
Western Europe	1,924	1,818	1,869	1,345
Total World	13,336	12,701	13,627	13,779

To fuel all operating vehicles, considerable quantities of gasoline and diesel have to be consumed. Major consumption in 1993 of gasoline and middle distillates ( which may include some heating fuels, but not fuel oils ) in million tonnes.

	Gasoline	Middle Distillates
USA	335.6	233.9
Canada	25.0	24.4
Western Europe	166.0	264.0
Japan	56.4	89.6
Total World	802.0	989.0

The USA consumption of gasoline increased from 294.4 (1982) to 335.6 (1989) then dipped to 324.2 (1991), and has continued to rise since then to reach 335.6 million tonnes in 1993. In 1993 the total world production of crude oil was 3164.8 million tonnes, of which the USA consumed 787.5 million tonnes [40]. Transport is a very significant user of crude oil products, thus improving the efficiency of utilisation, and minimising pollution from vehicles, can produce immediate

## oxygenated fuel

reductions in emissions of CO<sub>2</sub>, HCs, VOCs, CO, NO<sub>x</sub>, carbonyls, and other chemicals.

### 5.2 Why are there seasonal changes?

Only gaseous hydrocarbons burn, consequently if the air is cold, then the fuel has to be very volatile. But when summer comes, a volatile fuel can boil and cause vapour lock, as well as producing high levels of evaporative emissions. The solution was to adjust the volatility of the fuel according to altitude and ambient temperature. This volatility change has been automatically performed for decades by the oil companies without informing the public of the changes. It is one reason why storage of gasoline through seasons is not a good idea. Gasoline volatility is being reduced as modern engines, with their fuel injection and management systems, can automatically compensate for some of the changes in ambient conditions - such as altitude and air temperature, resulting in acceptable driveability using less volatile fuel.

### 5.3 Why were alkyl lead compounds removed?

" With the exception of one premium gasoline marketed on the east coast and southern areas of the US, all automotive gasolines from the mid-1920s until 1970 contained lead antiknock compounds to increase antiknock quality. Because lead antiknock compounds were found to be detrimental to the performance of catalytic emission control system then under development, U.S. passenger car manufacturers in 1971 began to build engines designed to operate satisfactorily on gasolines of nominal 91 Research Octane Number. Some of these engines were designed to operate on unleaded fuel while others required leaded fuel or the occasional use of leaded fuel. The 91 RON was chosen in the belief that unleaded gasoline at this level could be made available in quantities required using then current refinery processing equipment. Accordingly, unleaded and low-lead gasolines were introduced during 1970 to supplement the conventional gasolines already available.

Beginning with the 1975 model year, most new car models were equipped with catalytic exhaust treatment devices as one means of compliance with the 1975 legal restrictions in the U.S. on automobile emissions. The need for gasolines that would not adversely affect such catalytic devices has led to the large scale availability and growing use of unleaded gasolines, with all late-model cars requiring unleaded gasoline."[41].

There was a further reason why alkyl lead compounds were subsequently

## oxygenated fuel

reduced, and that was the growing recognition of the highly toxic nature of the emissions from a leaded-gasoline fuelled engine. Not only were toxic lead emissions produced, but the added toxic lead scavengers ( ethylene dibromide and ethylene dichloride ) could react with hydrocarbons to produce highly toxic organohalogen emissions such as dioxin. Even if catalysts were removed, or lead-tolerant catalysts discovered, alkyl lead compounds would remain banned because of their toxicity and toxic emissions [42].

### 5.4 Why are evaporative emissions a problem?

As tailpipe emissions are reduced due to improved exhaust emission control systems, the hydrocarbons produced by evaporation of the gasoline during distribution, vehicle refuelling, and from the vehicle, become more and more significant. A recent European study found that 40% of man-made volatile organic compounds came from vehicles [43]. Many of the problem hydrocarbons are the aromatics and olefins that have relatively high octane values. Any sensible strategy to reduce smog and toxic emissions will attack evaporative and tailpipe emissions.

The health risks to service station workers, who are continuously exposed to refuelling emissions remain a concern [44]. Vehicles will soon be required to trap the refuelling emissions in larger carbon canisters, as well as the normal evaporative emissions that they already capture. This recent decision went in favour of the oil companies, who were opposed by the auto companies. The automobile manufacturers felt the service station should trap the emissions. The activated carbon canisters adsorb organic vapours, and these are subsequently desorbed from the canister and burnt in the engine during normal operation, once certain vehicle speeds and coolant temperatures are reached. A few activated carbons used in older vehicles do not function efficiently with oxygenates.

### 5.5 Why control tailpipe emissions?

Tailpipe emissions were responsible for the majority of pollutants in the late 1960s after the crankcase emissions had been controlled. Ozone levels in the Los Angeles basin reached 450-500ppb in the early 1970s, well above the typical background of 30-50ppb [45].

Tuning a carburetted engine can only have a marginal effect on pollutant levels, and there still had to be some frequent, but long-term, assessment of the state of tuning. Exhaust catalysts offered a post-engine solution that could ensure pollutants were converted to more benign compounds. As engine management

### oxygenatedfuel

systems and fuel injection systems have developed, the volatility properties of the gasoline have been tuned to minimise evaporative emissions, and yet maintain low exhaust emissions.

The design of the engine can have very significant effects on the type and quantity of pollutants, eg unburned hydrocarbons in the exhaust originate mainly from combustion chamber crevices, such as the gap between the piston and cylinder wall, where the combustion flame can not completely use the HCs. The type and amount of unburned hydrocarbons are related to the fuel composition (volatility, olefins, aromatics, final boiling point), as well as state of tune, engine condition, and age/condition of the engine lubricating oil [46]. Particulate emissions, especially the size fraction smaller than ten micrometres, are a serious health concern. The current major source is from compression ignition ( CI = diesel ) engines, and the modern SI engine system has no problem meeting regulatory requirements.

The ability of reformulated gasolines to actually reduce smog has not yet been confirmed. The composition changes will reduce some compounds, and increase others, making predictions of environmental consequences extremely difficult. Planned future changes, such as the CAA 1997 Complex model specifications, that are based on several major ongoing government/industry gasoline and emission research programmes, are more likely to provide unambiguous environmental improvements. The rules for tailpipe emissions will continue to become more stringent as countries try to minimise local problems ( smog, toxins etc.) and global problems ( CO<sub>2</sub> ). Reformulation does not always lower all emissions, as evidenced by the following aldehydes from an engine with an adaptive learning management system [33].

	FTP-weighted emission rates (mg/mi)	
	Gasoline	Reformulated
Formaldehyde	4.87	8.43
Acetaldehyde	3.07	4.71

The type of exhaust catalyst and management system can have significant effects on the emissions [33].

FTP-weighted emission rates. (mg/mi)

	oxygenatedfuel			
	Total Aromatics		Total Carbonyls	
	Gasoline	Reformulated	Gasoline	Reformulated
Noncatalyst	1292.45	1141.82	174.50	198.73
Oxidation Catalyst	168.60	150.79	67.08	76.94
3-way Catalyst	132.70	93.37	23.93	23.07
Adaptive Learning	111.69	105.96	17.31	22.35

If we take the five compounds listed as toxics under the Clean Air Act, then the beneficial effects of catalysts are obvious [33].

	FTP-weighted emission rates. (mg/mi)					
	Benzene		Formaldehyde		Acrolein	
	Gas	Reform	Gas	Reform	Gas	Reform
Noncatalyst	156.18	138.48	73.25	85.24	11.62	13.20
Oxidation Cat.	27.57	25.01	28.50	35.83	3.74	3.75
3-way Catalyst	19.39	15.69	7.27	7.61	1.11	0.74
Adaptive Learn.	19.77	20.39	4.87	8.43	0.81	1.16

	Acetaldehyde		1,3 Butadiene	
	Gas	Reform	Gas	Reform
Noncatalyst	19.74	21.72	2.96	1.81
Oxidation Cat.	11.15	11.76	0.02	0.33
3-way Catalyst	4.43	3.64	0.07	0.05
Adaptive Learn.	3.07	4.71	0.00	0.14

The author reports analytical problems with the 1,3 Butadiene, and only Noncatalyst values are considered reliable.

## Emission Standards

There are several bodies responsible for establishing standards, and they promulgate test cycles, analysis procedures, and the % of new vehicles that must comply each year. The test cycles and procedures do change ( usually indicated by an anomalous increase in the numbers in the table ), and I have not listed the percentages of the vehicle fleet that are required to comply. This table is only intended to convey where we have been, and where we are going. It does not cover any regulation in detail - readers are advised to refer to the relevant regulations. Additional limits for other pollutants, such as formaldehyde and

oxygenatedfuel

particulates, are omitted. The 1994 tests signal the transition from 50,000 to 75,000 mile compliance testing, and I have not listed the subsequent 50,000 mile limits [47,48].

Year	Federal				California			
	HCs g/mi	CO g/mi	NOx g/mi	Evap g/test	HCs g/mi	CO g/mi	NOx g/mi	Evap g/test
Before regs	10.6	84.0	4.1	47	10.6	84.0	4.1	47
add crankcase	+4.1				+4.1			
1966				6.3	51.0	6.0		
1968	6.3	51.0	6.0					
1970	4.1	34.0			4.1	34.0		6
1971	4.1	34.0			4.1	34.0	4.0	6
1972	3.0	28.0			2.9	34.0	3.0	2
1973	3.0	28.0	3.0		2.9	34.0	3.0	2
1974	3.0	28.0	3.0		2.9	34.0	2.0	2
1975	1.5	15.0	3.1	2	0.90	9.0	2.0	2
1977	1.5	15.0	2.0	2	0.41	9.0	1.5	2
1980	0.41	7.0	2.0	6	0.41	9.0	1.0	2
1981	0.41	3.4	1.0	2	0.39	7.0	0.7	2
1993	0.41	3.4	1.0	2	0.25	3.4	0.4	2
1994 50,000	0.26	3.4	0.3	?	TLEV	0.13	3.4	0.4
1994 75,000	0.31	4.2	0.6	?				
1997				LEV	0.08	3.4	0.2	
1997				ULEV	0.04	1.7	0.2	
1998				ZEV	0.0	0.0	0.0	
2004	0.13	1.8	0.16	?				

It's also worth noting that exhaust catalysts also emit platinum, and the soluble platinum salts are some of the most potent sensitizers known. Early research [49] reported the presence of 10% water-soluble platinum in the emissions, however later work on monolithic catalysts has determined the quantities of water soluble platinum emissions are negligible [50]. The particle size of the emissions has also been determined, and the emissions have been correlated with increasing vehicle speed. Increasing speed also increases the exhaust gas temperature and velocity, indicating the emissions are probably a consequence of physical attrition.

## oxygenatedfuel

Speed km/h	Estimated Fuel		Median Aerodynamic	
	Consumption l/100km	Emissions ng/m-3	Particle Diameter um	
60	7	3.3	5.1	
100	8	11.9	4.2	
140	10	39.0	5.6	
US Cycle-75		6.4	8.5	

Using the estimated fuel consumption, and about 10m<sup>3</sup> of exhaust gas per litre of gasoline, the emissions are 2-40ng/km. These are 2-3 orders of magnitude lower than earlier reported work on pelletised catalysts. These emissions may be controlled directly in the future. They are currently indirectly controlled by the cost of platinum, and the new requirement for the catalyst to have an operational life of at least 100,000 miles.

### 5.6 Why do exhaust catalysts influence fuel composition?

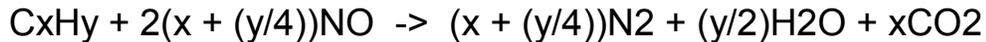
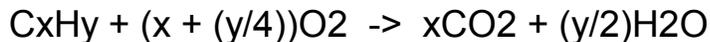
Modern adaptive learning engine management systems control the combustion stoichiometry by monitoring various ambient and engine parameters, including exhaust gas recirculation rates, the air flow sensor, and exhaust oxygen sensor outputs. This closed loop system using the oxygen sensor can compensate for changes in fuel content and air density. The oxygen sensor is also known as the lambda sensor, because the stoichiometric mass Air/Fuel ratio is known as lambda. Typical stoichiometric air/fuel ratios are [51]:-

- 6.4 methanol
- 9.0 ethanol
- 11.7 MTBE
- 12.1 ETBE, TAME
- 14.6 gasoline without oxygenates

The engine management system rapidly switches the stoichiometry between slightly rich and slightly lean, except under wide open throttle conditions - when the system runs open loop. The response of the oxygen sensor to composition changes is about 3 ms, and closed loop switching is typically 1-3 times a second, going between 50mV (lambda = 1.05 (Lean)) to 900mV (lambda = 0.99 (Rich)). The catalyst oxidises about 80% of the H<sub>2</sub>, CO, and HCs, and reduces the NO<sub>x</sub> [47].

### oxygenated fuel

Typical reactions that occur in a modern 3-way catalyst are:-



The use of exhaust catalysts have resulted in reaction pathways that can accidentally be responsible for increased pollution. An example is the CARB-mandated reduction of fuel sulfur. A change from 450ppm to 50ppm, which will reduce HC & CO emissions by 20%, may increase formaldehyde by 45% [19].

The requirement that the exhaust catalysts must now endure for 10 years or 100,000 miles will also encourage automakers to push for lower levels of known catalyst "poisons" such as sulfur and phosphorus in both the gasoline and lubricant. Modern catalysts are unable to reduce the relatively high levels of NO<sub>x</sub> that are produced during lean operation down to approved levels, thus preventing the application of lean-burn engine technology. Recently Mazda has announced they have developed a "lean burn" catalyst, which may enable automakers to move the fuel combustion towards the lean side, and different gasoline properties may be required to optimise the combustion and reduce pollution. Mazda claim that fuel efficiency is improved by 5-8% while meeting all emission regulations [52] .

Catalysts also inhibit the selection of gasoline octane-improving and cleanliness additives ( such as MMT and phosphorus-containing additives ) that may result in refractory compounds known to physically coat the catalyst and increase pollution.

#### 5.7 Why are "cold start" emissions so important?

The catalyst requires heat to reach the temperature ( >300-350C ) where it functions most efficiently, and the delay until it reaches operating temperature can produce more hydrocarbons than would be produced during the remainder of many typical urban short trips. It has been estimated that 70-80% of the non-methane HCs that escape conversion by the catalysts are emitted during the

## oxygenated fuel

first two minutes after a cold start. As exhaust emissions have been reduced, the significance of the evaporative emissions increases. Several engineering techniques are being developed, including the Ford Exhaust Gas Igniter ( uses a flame to heat the catalyst - lots of potential problems ), zeolite hydrocarbon traps, and relocation of the catalyst closer to the engine [47].

Reduced gasoline volatility and composition changes, along with cleanliness additives and engine management systems, can help minimise cold start emissions, but currently the most effective technique appears to be rapid, deliberate heating of the catalyst, and the new generation of low thermal inertia "fast light-up" catalysts reduce the problem, but further research is necessary [53].

As the evaporative emissions are also starting to be reduced, the emphasis has shifted to the refuelling emissions. These will be mainly controlled on the vehicle, and larger canisters may be used to trap the vapours emitted during refuelling.

### 5.8 When will the emissions be "clean enough"?

The California ZEV regulations effectively preclude IC vehicles, because they stipulate zero emissions. However, the concept of regulatory forcing of alternative vehicle propulsion technology may have to be modified to include hybrid or fuel-cell vehicles, as the major failing of EVs remains the lack of a cheap, light, safe, and easily-rechargeable electrical storage device [54,55]. There are several major projects intending to further reduce emissions from automobiles, mainly focusing on vehicle mass and engine fuel efficiency, but gasoline specifications and alternative fuels are also being investigated. It may be that changes to IC engines and gasolines will enable the IC engine to continue well into the 21st century as the prime motive force for personal transportation.

### 5.9 Why are only some gasoline compounds restricted?

The less volatile hydrocarbons in gasoline are not released in significant quantities during normal use, and the more volatile alkanes are considerably less toxic than many other chemicals encountered daily. The newer gasoline additives also have potentially undesirable properties before they are even combusted. Most hydrocarbons are very insoluble in water, with the lower aromatics being the most soluble, however the addition of oxygen to hydrocarbons significantly increases the mutual solubility with water.

	oxygenatedfuel			
	Compound in Water		Water in Compound	
	% mass/mass @ C		% mass/mass @ C	
normal decane	0.0000052	25	0.0072	25
iso-octane	0.00024	25	0.0055	20
normal hexane	0.00125	25	0.0111	20
cyclohexane	0.0055	25	0.010	20
1-hexene	0.00697	25	0.0477	30
toluene	0.0515	25	0.0334	25
benzene	0.1791	25	0.0635	25
methanol	complete	25	complete	25
ethanol	complete	25	complete	25
MTBE	4.8	20	1.4	20
TAME	-		0.6	20

The concentrations and ratios of benzene, toluene, ethyl benzene, and xylenes ( BTEX ) in water are often used to monitor groundwater contamination from gasoline storage tanks or pipelines. The oxygenates and other new additives may increase the extent of water and soil pollution by acting as co-solvents for HCs.

Various government bodies ( EPA, OSHA, NIOSH ) are charged with ensuring people are not exposed to unacceptable chemical hazards, and maintain ongoing research into the toxicity of liquid gasoline contact, water and soil pollution, evaporative emissions, and tailpipe emissions [56]. As toxicity is found, the quantities in gasoline of the specific chemical ( benzene ), or family of chemicals ( alkyl leads, aromatics, olefins ) are regulated.

The recent dramatic changes caused by the need to reduce alkyl leads, halogens, olefins, aromatics has resulted in whole new families of compounds ( ethers, alcohols ) being introduced into fuels without prior detailed toxicity studies being completed. If adverse results appear, these compounds are also likely to be regulated to protect people and the environment.

Also, as the chemistry of emissions is unravelled, the chemical precursors to toxic tailpipe emissions ( such as higher aromatics that produce benzene emissions ) are also controlled, even if they are not toxic.

#### 5.10 What does "renewable" fuel/oxygenate mean?

The general definition of "renewable" is that the carbon originates from recent

## oxygenatedfuel

biomass, and thus does not contribute to the increased CO<sub>2</sub> emissions. A truly "long-term" view could claim that fossil fuels are "renewable" on a 100 million year timescale :-). There is currently a major battle between the ethanol/ETBE lobby ( agricultural, corn growing ), and the methanol/MTBE lobby ( oil company, petrochemical ) over an EPA mandate demanding that a specific percentage of the oxygenates in gasoline are produced from "renewable" sources [57].

Unfortunately, "renewable" ethanol is not cost competitive when crude oil is \$18/bbl, so a federal subsidy ( \$0.54/US Gallon ) and additional state subsidies ( 11 states - from \$0.08(Michigan) to \$0.66(Tenn.)/US Gal.) are provided. A judgement on the use of "renewable" oxygenates is expected in early 1995.

### 5.11 Will oxygenated gasoline damage my vehicle?

The following comments assume that your vehicle was designed to operate on unleaded, if not, then damage like valve seat recession may also occur. Damage should not occur if the gasoline is correctly formulated, and you select the appropriate octane, but oxygenated gasoline will hurt your pocket. In the first year of mandated oxygenates, it appears some refiners did not carefully formulate their oxygenated gasoline, and driveability and emissions problems occurred. Most reputable brands are now carefully formulated. Some older activated carbon canisters may not function efficiently with oxygenated gasolines, but this is a function of the type of carbon used. How your vehicle responds to oxygenated gasoline depends on the engine management system and state of tune. A modern system will automatically compensate for all of the currently-permitted oxygenate levels, thus your fuel consumption will increase. Older, poorly-maintained, engines may require a tune up to maintain acceptable driveability.

Be prepared to try several different brands of reformulated gasolines to identify the most suitable brand for your vehicle, and be prepared to change again with the seasons. This is because the refiners can choose the oxygenate they use to meet the regulations, and may choose to set some fuel properties, such as volatility, differently to their competitors.

Most stories of corrosion etc, are derived from anhydrous methanol corrosion of light metals (aluminum, magnesium), however the addition of either 0.5% water to pure methanol, or corrosion inhibitors to methanol/gasoline blends will prevent this. If you observe corrosion, talk to your gasoline supplier. Oxygenated fuels may either swell or shrink some elastomers on older cars, depending on the

### oxygenated fuel

aromatic and olefin content of the fuels. Cars later than 1990 should not experience compatibility problems, and cars later than 1994 should not experience driveability problems, but they will experience increased fuel consumption, depending on the state of tune and engine management system.

#### 5.12 What does "reactivity" of emissions mean?

The traditional method of exhaust regulations was to specify the actual HC, CO, NO<sub>x</sub>, and particulate contents. With the introduction of oxygenates and reformulated gasolines, the volatile organic carbon (VOC) species in the exhaust also changed. The "reactivity" refers to the ozone-forming potential of the VOC emissions when they react with NO<sub>x</sub>, and is being introduced as a regulatory means of ensuring that automobile emissions do actually reduce smog formation. The ozone-forming potential of chemicals is defined as the number of molecules of ozone formed per VOC carbon atom, and this is called the Incremental Reactivity. Typical values (big is bad :-)) are [45]:

#### Maximum Incremental Reactivities as mg Ozone / mg VOC

	carbon monoxide	0.054
alkanes	methane	0.0148
	ethane	0.25
	propane	0.48
	n-butane	1.02
olefins	ethylene	7.29
	propylene	9.40
	1,3 butadiene	10.89
aromatics	benzene	0.42
	toluene	2.73
	meta-xylene	8.15
	1,3,5-trimethyl benzene	10.12
oxygenates	methanol	0.56
	ethanol	1.34
	MTBE	0.62
	ETBE	1.98

#### 5.13 What are "carbonyl" compounds?

Carbonyls are produced in large amounts under lean operating conditions, especially when oxygenated fuels are used. Most carbonyls are toxic, and the

## oxygenated fuel

carboxylic acids can corrode metals. The emission of carbonyls can be controlled by combustion stoichiometry and exhaust catalysts.

Typical carbonyls are:-

aldehydes ( containing -CHO ),

formaldehyde (HCHO) - which is formed in large amounts during lean combustion of methanol [58].

acetaldehyde (CH<sub>2</sub>CHO) - which is formed during ethanol combustion.

acrolein (CH<sub>2</sub>=CHCHO) - a very potent irritant.

ketones ( containing C=O ),

acetone (CH<sub>3</sub>COCH<sub>3</sub>)

carboxylic acids ( containing -COOH ),

formic acid (HCOOH) - formed during lean methanol combustion.

acetic acid (CH<sub>3</sub>COOH).

5.14 What are "gross polluters"?

It has always been known that the EPA emissions tests do not reflect real world conditions. There have been several attempts to identify vehicles on the road that do not comply with emissions standards. Recent remote sensing surveys have demonstrated that the highest 10% of CO emitters produce over 50% of the pollution, and the same ratio applies for the HC emitters - which may not be the same vehicles [59,60,61]. 20% of the CO emitters are responsible for 80% of the CO emissions, consequently modifying gasoline composition is only one aspect of pollution reduction. The new additives can help maintain engine condition, but they can not compensate for out-of-tune, worn, or tampered-with engines.

The most famous of these remote sensing systems is the FEAT ( Fuel Efficiency Automobile Test ) team from the University of Denver [62]. This team is probably the world leader in remote sensing of auto emissions to identify grossly polluting vehicles. The system measures CO/CO<sub>2</sub> ratio, and the HC/CO<sub>2</sub> ratio in the exhaust of vehicles passing through an infra-red light beam crossing the road 25cm above the surface. The system also includes a video system that records the licence plate, date, time, calculated exhaust CO, CO<sub>2</sub>, and HC. The system is effective for traffic lanes up to 18 metres wide, however rain, snow, and water spray can cause scattering of the beam. Reference signals monitor such effects and, if possible, compensate. The system has been comprehensively validated, including using vehicles with on-board emissions monitoring instruments.

They can monitor up to 1000 vehicles an hour and, as an example, they were

oxygenated fuel

invited to Provo, Utah to monitor vehicles, and gross polluters would be offered free repairs [63]. They monitored over 10,000 vehicles and mailed 114 letters to owners of vehicles newer than 1965 that had demonstrated high CO levels. They received 52 responses and repairs started in Dec 1991, and continued to Mar 1992. They offered to purchase two vehicles at blue book price. They were declined, and so attempted to modify those vehicles, even though their condition did not justify the expense.

The entire monitored fleet at Provo (Utah) during Winter 1991/1992

Model year	Grams CO/gallon		Number of
	(Median value)	(mean value)	Vehicles
92	40	80	247
91	55		1222
90	75		1467
89	80		1512
88	85		1651
87	90		1439
86	100	300	1563
85	120		1575
84	125		1206
83	145		719
82	170		639
81	230		612
80	220	500	551
79	350		667
78	420		584
77	430		430
76	770		317
75	760	950	163
Pre 75	920	1060	878

As observed elsewhere, over half the CO was emitted by about 10% of the vehicles. If the 47 worst polluting vehicles were removed, that achieves more than removing the 2,500 lowest emitting vehicles from the total tested fleet.

Surveys of vehicle populations have demonstrated that emissions systems had been tampered with on over 40% of the gross polluters, and an additional 20% had defective emission control equipment [64]. No matter what changes are

## oxygenatedfuel

made to gasoline, if owners "tune" their engines for power, then the majority of such "tuned" vehicle will become gross polluters. Professional repairs to gross polluters usually improves fuel consumption, resulting in a low cost to owners ( \$32/pa/Ton CO year ). The removal of CO in the Provo example above was costed at \$200/Ton CO, compared to Inspection and Maintenance programs (\$780/Ton CO ), and oxygenates ( \$1034-\$1264/Ton CO in Colorado 1991-2 ), and UNOCALs vehicle scrapping programme ( \$1025/Ton of all pollutants ).

Thus, identifying and repairing or removing gross polluters can be far more cost-effective than playing around with reformulated gasolines and oxygenates.

---

Subject: 6. What do Fuel Octane ratings really indicate?

### 6.1 Who invented Octane Ratings?

Since 1912 the spark ignition internal combustion engine's compression ratio had been constrained by the unwanted "knock" that could rapidly destroy engines. "Knocking" is a very good description of the sound heard from an engine using fuel of too low octane. The engineers had blamed the "knock" on the battery ignition system that was added to cars along with the electric self-starter. The engine developers knew that they could improve power and efficiency if knock could be overcome.

Kettering assigned Thomas Midgley, Jr. to the task of finding the exact cause of knock [16]. They used a Dobbie-McInnes manograph to demonstrate that the knock did not arise from preignition, as was commonly supposed, but arose from a violent pressure rise after ignition. The manograph was not suitable for further research, so Midgley and Boyd developed a high-speed camera to see what was happening. They also developed a "bouncing pin" indicator that measured the amount of knock [7]. Ricardo had developed an alternative concept of HUCF ( Highest Useful Compression Ratio ) using a variable-compression engine. His numbers were not absolute, as there were many variables, such as ignition timing, cleanliness, spark plug position, engine temperature. etc.

In 1926 Graham Edgar suggested using two hydrocarbons that could be produced in sufficient purity and quantity [9]. These were "normal heptane", that was already obtainable in sufficient purity from the distillation of Jeffrey pine oil, and " an octane, named 2,4,4-trimethyl pentane " that he first synthesized. Today

## oxygenated fuel

we call it " iso-octane " or 2,2,4-trimethyl pentane. The octane had a high anti-knock value, and he suggested using the ratio of the two as a reference fuel number. He demonstrated that all the commercially- available gasolines could be bracketed between 60:40 and 40:60 parts by volume heptane:iso-octane.

The reason for using normal heptane and iso-octane was because they both have similar volatility properties, specifically boiling point, thus the varying ratios 0:100 to 100:0 should not exhibit large differences in volatility that could affect the rating test.

	Melting Point C	Boiling Point C	Heat of Density g/ml	Vaporisation MJ/kg
normal heptane	-90.7	98.4	0.684	0.365 @ 25C
iso octane	-107.45	99.3	0.6919	0.308 @ 25C

Having decided on standard reference fuels, a whole range of engines and test conditions appeared, but today the most common are the Research Octane Number ( RON ), and the Motor Octane Number ( MON ).

### 6.2 Why do we need Octane Ratings?

To obtain the maximum energy from the gasoline, the compressed fuel/air mixture inside the combustion chamber needs to burn evenly, propagating out from the spark plug until all the fuel is consumed. This would deliver an optimum power stroke. In real life, a series of pre-flame reactions will occur in the unburnt "end gases" in the combustion chamber before the flame front arrives. If these reactions form molecules or species that can autoignite before the flame front arrives, knock will occur [13,14].

Simply put, the octane rating of the fuel reflects the ability of the unburnt end gases to resist spontaneous autoignition under the engine test conditions used. If autoignition occurs, it results in an extremely rapid pressure rise, as both the desired spark-initiated flame front, and the undesired autoignited end gas flames are expanding. The combined pressure peak arrives slightly ahead of the normal operating pressure peak, leading to a loss of power and eventual overheating. The end gas pressure waves are superimposed on the main pressure wave, leading to a sawtooth pattern of pressure oscillations that create the "knocking" sound.

## oxygenatedfuel

The combination of intense pressure waves and overheating can induce piston failure in a few minutes. Knock and preignition are both favoured by high temperatures, so one may lead to the other. Under high-speed conditions knock can lead to preignition, which then accelerates engine destruction [17].

### 6.3 What fuel property does the Octane Rating measure?

The fuel property the octane ratings measure is the ability of the unburnt end gases to spontaneously ignite under the specified test conditions. Within the chemical structure of the fuel is the ability to withstand pre-flame conditions without decomposing into species that will autoignite before the flame-front arrives. Different reaction mechanisms, occurring at various stages of the pre-flame compression stroke, are responsible for the undesirable, easily-autoignitable, end gases.

During the oxidation of a hydrocarbon fuel, the hydrogen atoms are removed one at a time from the molecule by reactions with small radical species (such as OH and HO<sub>2</sub>), and O and H atoms. The strength of carbon-hydrogen bonds depends on what the carbon is connected to. Straight chain HCs such as normal heptane have secondary C-H bonds that are significantly weaker than the primary C-H bonds present in branched chain HCs like iso-octane [13,14].

The octane rating of hydrocarbons is determined by the structure of the molecule, with long, straight hydrocarbon chains producing large amounts of easily-autoignitable pre-flame decomposition species, while branched and aromatic hydrocarbons are more resistant. This also explains why the octane ratings of paraffins consistently decrease with carbon number. In real life, the unburnt "end gases" ahead of the flame front encounter temperatures up to about 700C due to piston motion and radiant and conductive heating, and commence a series of pre-flame reactions. These reactions occur at different thermal stages, with the initial stage ( below 400C ) commencing with the addition of molecular oxygen to alkyl radicals, followed by the internal transfer of hydrogen atoms within the new radical to form an unsaturated, oxygen-containing species. These new species are susceptible to chain branching involving the HO<sub>2</sub> radical during the intermediate temperature stage (400-600C), mainly through the production of OH radicals. Above 600C, the most important reaction that produces chain branching is the reaction of one hydrogen atom radical with molecular oxygen to form O and OH radicals.

## oxygenated fuel

The addition of additives such as alkyl lead and oxygenates can significantly affect the pre-flame reaction pathways. Anti-knock additives work by interfering at different points in the pre-flame reactions, with the oxygenates retarding undesirable low temperature reactions, and the alkyl lead compounds react in the intermediate temperature region to deactivate the major undesirable chain branching sequence [13,14].

The antiknock ability is related to the "autoignition temperature" of the hydrocarbons. Antiknock ability is not substantially related to:-

The energy content of fuel, this should be obvious, as oxygenates have lower energy contents, but high octanes.

The flame speed of the conventionally ignited mixture, this should be evident from the similarities of the two reference hydrocarbons. Although flame speed does play a minor part, there are many other factors that are far more important. (such as compression ratio, stoichiometry, combustion chamber shape, chemical structure of the fuel, presence of antiknock additives, number and position of spark plugs, turbulence etc.) Flame speed does not correlate with octane.

6.4 Why are two ratings used to obtain the pump rating?

The correct name for the  $(RON+MON)/2$  formula is the "antiknock index", and it remains the most important quality criteria for motorists [25].

The initial octane method developed in the 1920s was the Motor Octane method and, over several decades, a large number of octane test methods appeared. These were variations to either the engine design, or the specified operating conditions [65]. During the 1950-1960s attempts were made to internationally standardise and reduce the number of Octane Rating test procedures.

During the late 1930s - mid 1960s, the Research method became the important rating because it more closely represented the octane requirements of the motorist using the fuels/vehicles/roads then available. In the late 1960s German automakers discovered their engines were destroying themselves on long Autobahn runs, even though the Research Octane was within specification. They discovered that either the MON or the Sensitivity ( the numerical difference between the RON and MON numbers ) also had to be specified. Today it is accepted that no one octane rating covers all use. In fact, during 1994, there have been increasing concerns in Europe about the high Sensitivity of some commercially-available unleaded fuels.

## oxygenated fuel

The design of the engine and car significantly affect the fuel octane requirement for both RON and MON. In the 1930s, most vehicles would run on the specified Research Octane fuel, almost regardless of the Motor Octane, whereas most 1990s engines have a 'severity' of one, which means the engine is unlikely to knock if a change of one RON is matched by an equal and opposite change of MON [19].

### 6.5 What does the Motor Octane rating measure?

The conditions of the Motor method represent severe, sustained high speed, high load driving. For most hydrocarbon fuels, including those with either lead or oxygenates, the motor octane number (MON) will be lower than the research octane number (RON).

Test Engine conditions	Motor Octane
Test Method	ASTM D2700-92 [66]
Engine	Cooperative Fuels Research ( CFR )
Engine RPM	900 RPM
Intake air temperature	38 C
Intake air humidity	3.56 - 7.12 g H <sub>2</sub> O / kg dry air
Intake mixture temperature	149 C
Coolant temperature	100 C
Oil Temperature	57 C
Ignition Advance - variable	Varies with compression ratio ( eg 14 - 26 degrees BTDC )
Carburettor Venturi	14.3 mm

### 6.6 What does the Research Octane rating measure?

The Research method settings represent typical mild driving, without consistent heavy loads on the engine.

Test Engine conditions	Research Octane
Test Method	ASTM D2699-92 [67]
Engine	Cooperative Fuels Research ( CFR )
Engine RPM	600 RPM
Intake air temperature	Varies with barometric pressure ( eg 88kPa = 19.4C, 101.6kPa = 52.2C )
Intake air humidity	3.56 - 7.12 g H <sub>2</sub> O / kg dry air
Intake mixture temperature	Not specified
Coolant temperature	100 C

	oxygenated fuel
Oil Temperature	57 C
Ignition Advance - fixed	13 degrees BTDC
Carburettor Venturi	Set according to engine altitude
	( eg 0-500m=14.3mm, 500-1000m=15.1mm )

6.7 Why is the difference called "sensitivity"?

RON - MON = Sensitivity. Because the two test methods use different test conditions, especially the intake mixture temperatures and engine speeds, then a fuel that is sensitive to changes in operating conditions will have a larger difference between the two rating methods. Modern fuels typically have sensitivities around 10. The US 87 (RON+MON/2) unleaded gasoline is required to have a 82+ MON, thus preventing very high sensitivity fuels [25].

6.8 What sort of engine is used to rate fuels?

Automotive octane ratings are determined in a special single-cylinder engine with a variable compression ratio ( CR 4:1 to 18:1 ) known as a Cooperative Fuels Research ( CFR ) engine. The cylinder bore is 82.5mm, the stroke is 114.3mm, giving a displacement of 612 cm<sup>3</sup>. The piston has four compression rings, and one oil control ring. The intake valve is shrouded. The head and cylinder are one piece, and can be moved up and down to obtain the desired compression ratio. The engines have a special four-bowl carburettor that can adjust individual bowl air/fuel ratios. This facilitates rapid switching between reference fuels and samples. A magnetorestrictive detonation sensor in the combustion chamber measures the rapid changes in combustion chamber pressure caused by knock, and the amplified signal is measured on a "knockmeter" with a 0-100 scale [66,67]. A complete Octane Rating engine system costs about \$200,000 with all the services installed. Only one company manufactures these engines, the Waukesha Engine Division of Dresser Industries, Waukesha. WI 53186.

6.9 How is the Octane rating determined?

To rate a fuel, the engine is set to an appropriate compression ratio that will produce a knock of about 50 on the knockmeter for the sample when the air/fuel ratio is adjusted on the carburettor bowl to obtain maximum knock. Normal heptane and iso-octane are known as primary reference fuels. Two blends of these are made, one that is one octane number above the expected rating, and another that is one octane number below the expected rating. These are placed in different bowls, and are also rated with each air/fuel ratio being adjusted for maximum knock. The higher octane reference fuel should produce a reading around 30-40, and the lower reference fuel should produce a reading of 60-70.

## oxygenated fuel

The sample is again tested, and if it does not fit between the reference fuels, further reference fuels are prepared, and the engine readjusted to obtain the required knock. The actual fuel rating is interpolated from the knockmeter readings [66,67].

### 6.10 What is the Octane Distribution of the fuel?

The combination of vehicle and engine can result in specific requirements for octane that depend on the fuel. If the octane is distributed differently throughout the boiling range of a fuel, then engines can knock on one brand of 87 (RON+MON/2), but not on another brand. This "octane distribution" is especially important when sudden changes in load occur, such as high load, full throttle, acceleration. The fuel can segregate in the manifold, with the very volatile fraction reaching the combustion chamber first and, if that fraction is deficient in octane, then knock will occur until the less volatile, higher octane fractions arrive [17].

Some fuel specifications include delta RONs, to ensure octane distribution throughout the fuel boiling range was consistent. Octane distribution was seldom a problem with the alkyl lead compounds, as the tetra methyl lead and tetra ethyl lead octane volatility profiles were well characterised, but it can be a major problem for the new, reformulated, low aromatic gasolines, as MTBE boils at 55C, whereas ethanol boils at 78C. Drivers have discovered that an 87 (RON+MON/2) from one brand has to be substituted with an 89 (RON+MON/2) of another, and that is because of the combination of their driving style, engine design, vehicle mass, fuel octane distribution, fuel volatility, and the octane-enhancers used.

### 6.11 What is a "delta Research Octane number"?

To obtain an indication of behaviour of a gasoline during any manifold segregation, an octane rating procedure called the Distribution Octane Number was used. The rating engine had a special manifold that allowed the heavier fractions to be separated before they reached the combustion chamber [17]. That method has been replaced by the "delta" RON procedure.

The fuel is carefully distilled to obtain a distillate fraction that boils to the specified temperature, which is usually 100C. Both the parent fuel and the distillate fraction are rated on the octane engine using the Research Octane method [68]. The difference between these is the delta RON(100C), usually just called the delta RON.

### 6.12 How do other fuel properties affect octane?

## oxygenated fuel

Several other properties affect knock. The most significant determinant of octane is the chemical structure of the hydrocarbons and their response to the addition of octane enhancing additives. Other factors include:-

Front End Volatility - Paraffins are the major component in gasoline, and the octane number decreases with increasing chain length or ring size, but increases with chain branching. Overall, the effect is a significant reduction in octane if front end volatility is lost, as can happen with improper or long term storage. Fuel economy on short trips can be improved by using a more volatile fuel, at the risk of carburettor icing and increased evaporative emissions.

Final Boiling Point.- Decreases in the final boiling point increase fuel octane.

Aviation gasolines have much lower final boiling points than automotive gasolines. Note that final boiling points are being reduced because the higher boiling fractions are responsible for disproportionate quantities of pollutants and toxins.

Preignition tendency - both knock and preignition can induce each other.

### 6.13 Can higher octane fuels give me more power?

Not if you are already using the proper octane fuel. The engine will be already operating at optimum settings, and a higher octane should have no effect on the management system. Your driveability and fuel economy will remain the same. The higher octane fuel costs more, so you are just throwing money away. If you are already using a fuel with an octane rating slightly below the optimum, then using a higher octane fuel will cause the engine management system to move to the optimum settings, possibly resulting in both increased power and improved fuel economy. You may be able to change octanes between seasons ( reduce octane in winter ) to obtain the most cost-effective fuel without loss of driveability.

Once you have identified the fuel that keeps the engine at optimum settings, there is no advantage in moving to an even higher octane fuel. The manufacturer's recommendation is conservative, so you may be able to carefully reduce the fuel octane. The penalty for getting it badly wrong, and not realising that you have, could be expensive engine damage.

### 6.14 Does low octane fuel increase engine wear?

Not if you are meeting the octane requirement of the engine. If you are not meeting the octane requirement, the engine will rapidly suffer major damage due to knock. You must not use fuels that produce sustained audible knock, engine damage will occur. If the octane is just sufficient, the engine management system will move settings to a less optimal position, and the only major penalty will be

## oxygenated fuel

increased costs due to poor fuel economy. Whenever possible, engines should be operated at the optimum position for long-term reliability. Engine wear is mainly related to design, manufacturing, maintenance and lubrication factors. Once the octane and run-on requirements of the engine are satisfied, increased octane will have no beneficial effect on the engine. The quality of gasoline, and the additive package used, would be more likely to affect the rate of engine wear, rather than the octane rating.

### 6.15 Can I mix different octane fuel grades?

Yes, however attempts to blend in your fuel tank should be carefully planned. You should not allow the tank to become empty, and then add 50% of lower octane, followed by 50% of higher octane. The fuels may not completely mix immediately, especially if there is a density difference. You may get a slug of low octane that causes severe knock. You should refill when your tank is half full. In general the octane response will be linear for most hydrocarbon and oxygenated fuels eg 50:50 of 87 and 91 will give 89.

Attempts to mix leaded high octane to unleaded high octane to obtain higher octane are useless. The lead response of the unleaded fuel does not overcome the dilution effect, thus 50:50 of 96 leaded and 91 unleaded will give 94. Some blends of oxygenated fuels with ordinary gasoline can result in undesirable increases in volatility due to volatile azeotropes, and that some oxygenates can have negative lead responses. Also note that the octane requirement of some engines is determined by the need to avoid run-on, not to avoid knock.

### 6.16 What happens if I use the wrong octane fuel?

If you use a fuel with an octane rating below the requirement of the engine, the management system may move the engine settings into an area of less efficient combustion, resulting in reduced power and reduced fuel economy. You will be losing both money and driveability. If you use a fuel with an octane rating higher than what the engine can use, you are just wasting money by paying for octane that you can not utilise. Forget the stories about higher octanes having superior additive packages - they do not. If your vehicle does not have a knock sensor, then using an octane significantly below the requirement means that the little men with hammers will gleefully pummel your engine to pieces.

You should initially be guided by the vehicle manufacturer's recommendations, however you can experiment, as the variations in vehicle tolerances can mean that Octane Number Requirement for a given vehicle model can range over 6

## oxygenated fuel

Octane Numbers. Caution should be used, and remember to compensate if the conditions change, such as carrying more people or driving in different ambient conditions. You can often reduce the octane of the fuel you use in winter because the temperature decrease and possible humidity changes may significantly reduce the octane requirement of the engine.

Use the octane that provides cost-effective driveability and performance, using anything more is waste of money, and anything less could result in an unscheduled, expensive visit to your mechanic.

### 6.17 Can I tune the engine to use another octane fuel?

In general, modern engine management systems will compensate for fuel octane, and once you have satisfied the optimum octane requirement, you are at the optimum overall performance area of the engine map. Tuning changes to obtain more power will probably adversely affect both fuel economy and emissions. Unless you have access to good diagnostic equipment that can ensure regulatory limits are complied with, it is likely that adjustments may be regarded as illegal tampering by your local regulation enforcers. If you are skilled, you will be able to legally wring slightly more performance from your engine by using a dynamometer in conjunction with engine and exhaust gas analyzers and a well-designed, retrofitted, performance engine management chip.

### 6.18 How can I increase the fuel octane?

Not simply, you can purchase additives, however these are not cost-effective and a survey in 1989 showed the cost of increasing the octane rating of one US gallon by one unit ranged from 10 cents ( methanol ), 50 cents (MMT), \$1.00 ( TEL ), to \$3.25 ( xylenes ) [69]. It is preferable to purchase a higher octane fuel such as racing fuel, aviation gasolines, or methanol. Sadly, the price of chemical grade methanol has almost doubled during 1994. If you plan to use alcohol blends, ensure your fuel handling system is compatible, and that you only use dry gasoline by filling up early in the morning when the storage tanks are cool. Also ensure that the service station storage tank has not been refilled recently. Retailers are supposed to wait several hours before bringing a refilled tank online, to allow suspended undissolved water to settle out, but they do not always wait the full period.

### 6.19 Are aviation gasoline octane numbers comparable?

Aviation gasolines were all highly leaded and graded using two numbers, with common grades being 80/87, 100/130, and 115/145 [70]. The first number is the

## oxygenatedfuel

Aviation rating ( aka Lean Mixture rating ), and the second number is the Supercharge rating ( aka Rich Mixture rating ). In the 1970s a new grade, 100LL ( low lead = 0.53mlTEL/L instead of 1.06mlTEL/L) was introduced to replace the 80/87 and 100/130. Soon after the introduction, there was a spate of plug fouling, and high cylinder head temperatures resulting in cracked cylinder heads [71]. The old 80/87 grade was reintroduced on a limited scale. The Aviation rating is determined using the automotive Motor Octane test procedure, and then corrected to an Aviation number using a table in the method - it's usually only 1 - 2 Octane units different to the Motor value up to 100, but varies significant above that eg 110MON = 128AN.

The second Avgas number is the Rich Mixture method Performance Number ( PN - they are not commonly called octane numbers when they are above 100 ), and is determined on a supercharged version of the CFR engine which has a fixed compression ratio. The method determines the dependence of the highest permissible power ( in terms of indicated mean effective pressure ) on mixture strength and boost for a specific light knocking setting. The Performance Number indicates the maximum knock-free power obtainable from a fuel compared to iso-octane = 100. Thus, a PN = 150 indicates that an engine designed to utilise the fuel can obtain 150% of the knock-limited power of iso-octane at the same mixture ratio. This is an arbitrary scale based on iso-octane + varying amounts of TEL, derived from a survey of engines performed decades ago. Aviation gasoline PNs are rated using variations of mixture strength to obtain the maximum knock-limited power in a supercharged engine. This can be extended to provide mixture response curves which define the maximum boost ( rich - about 11:1 stoichiometry ) and minimum boost ( weak about 16:1 stoichiometry ) before knock [71].

The 115/145 grade is being phased out, but even the 100LL has more octane than any automotive gasoline.

---

Subject: 7. What parameters determine octane requirement? 7.1 What is the effect of Compression ratio?

Most people know that an increase in Compression Ratio will require an increase in fuel octane for the same engine design. Increasing the compression ratio increases the theoretical thermodynamic efficiency of an engine according to the

## oxygenatedfuel

standard equation

$$\text{Efficiency} = 1 - (1/\text{compression ratio})^{\gamma-1}$$

where  $\gamma$  = ratio of specific heats at constant pressure and constant volume of the working fluid ( for most purposes air is the working fluid, and is treated as an ideal gas ). There are indications that thermal efficiency reaches a maximum at a compression ratio of about 17:1 [15].

The efficiency gains are best when the engine is at incipient knock, that's why knock sensors ( actually vibration sensors ) are used. Low compression ratio engines are less efficient because they can not deliver as much of the ideal combustion power to the flywheel. For a typical carburetted engine, without engine management [17,24]:-

Compression Ratio	Octane Number Requirement	Brake Thermal Efficiency ( Full Throttle )
5:1	72	-
6:1	81	25 %
7:1	87	28 %
8:1	92	30 %
9:1	96	32 %
10:1	100	33 %
11:1	104	34 %
12:1	108	35 %

Modern engines have improved significantly on this, and the changing fuel specifications and engine design should see more improvements, but significant gains may have to await improved engine materials and fuels.

### 7.2 What is the effect of changing the air/fuel ratio?

Traditionally, the greatest tendency to knock was near 13.5:1 air/fuel ratio, but was very engine specific. Modern engines, with engine management systems, now have their maximum octane requirement near to 14.5:1. For a given engine using gasoline, the relationship between thermal efficiency, air/fuel ratio, and power is complex. Stoichiometric combustion ( Air/Fuel Ratio = 14.7:1 for a typical non-oxygenated gasoline ) is neither maximum power - which occurs around A/F 12-13:1 (Rich), nor maximum thermal efficiency - which occurs around A/F 16-18:1 (Lean). The air-fuel ratio is controlled at part throttle by a

## oxygenated fuel

closed loop system using the oxygen sensor in the exhaust. Conventionally, enrichment for maximum power air/fuel ratio is used during full throttle operation to reduce knocking while providing better driveability [24]. If the mixture is weakened, the flame speed is reduced, consequently less heat is converted to mechanical energy, leaving heat in the cylinder walls and head, potentially inducing knock. It is possible to weaken the mixture sufficiently that the flame is still present when the inlet valve opens again, resulting in backfiring.

### 7.3 What is the effect of changing the ignition timing

The tendency to knock increases as spark advance is increased, eg 2 degrees BTDC requires 91 octane, whereas 14 degrees BTDC requires 96 octane. If you advance the spark, the flame front starts earlier, and the end gases start forming earlier in the cycle, providing more time for the autoigniting species to form before the piston reaches the optimum position for power delivery, as determined by the normal flame front propagation. It becomes a race between the flame front and decomposition of the increasingly-squashed end gases. High octane fuels produce end gases that take longer to autoignite, so the good flame front reaches and consumes them properly.

The ignition advance map is partly determined by the fuel the engine is intended to use. The timing of the spark is advanced sufficiently to ensure that the fuel/air mixture burns in such a way that maximum pressure of the burning charge is about 15-20 degree after TDC. Knock will occur before this point, usually in the late compression/early power stroke period. The engine management system uses ignition timing as one of the major variables that is adjusted if knock is detected. If very low octane fuels are used ( several octane numbers below the vehicle's requirement at optimal settings ), both performance and fuel economy will decrease.

The actual Octane Number Requirement depends on the engine design, but for some 1978 vehicles using standard fuels, the following (R+M)/2 Octane Requirements were measured. "Standard" is the recommended ignition timing for the engine, probably a few degrees before Top Dead Centre [24].

Vehicle	Basic Ignition Timing		
	Retarded 5 degrees	Standard	Advanced 5 degrees
A	88	91	93
B	86	90.5	94.5
C	85.5	88	90

			oxygenated fuel
D	84	87.5	91
E	82.5	87	90

The actual ignition timing to achieve the maximum pressure from normal combustion of gasoline will depend mainly on the speed of the engine and the flame propagation rates in the engine. Knock increases the rate of the pressure rise, thus superimposing additional pressure on the normal combustion pressure rise. The knock actually rapidly resonates around the chamber, creating a series of abnormal sharp spikes on the pressure diagram. The normal flame speed is fairly consistent for most gasoline HCs, regardless of octane rating, but the flame speed is affected by stoichiometry. Note that the flame speeds in this FAQ are not the actual engine flame speeds. A 12:1 CR gasoline engine at 1500 rpm would have a flame speed of about 16.5 m/s, and a similar hydrogen engine yields 48.3 m/s, but such engine flame speeds are also very dependent on stoichiometry.

#### 7.4 What is the effect of engine management systems?

Engine management systems are now an important part of the strategy to reduce automotive pollution. The good news for the consumer is their ability to maintain the efficiency of gasoline combustion, thus improving fuel economy. The bad news is their tendency to hinder tuning for power. A very basic modern engine system could monitor and control:- mass air flow, fuel flow, ignition timing, exhaust oxygen ( lambda oxygen sensor ), knock ( vibration sensor ), EGR, exhaust gas temperature, coolant temperature, and intake air temperature. The knock sensor can be either a nonresonant type installed in the engine block and capable of measuring a wide range of knock vibrations ( 5-15 kHz ) with minimal change in frequency, or a resonant type that has excellent signal-to-noise ratio between 1000 and 5000 rpm [72].

A modern engine management system can compensate for altitude, ambient air temperature, and fuel octane. The management system will also control cold start settings, and other operational parameters. There is a new requirement that the engine management system also contain an on-board diagnostic function that warns of malfunctions such as engine misfire, exhaust catalyst failure, and evaporative emissions failure. The use of fuels with alcohols such as methanol can confuse the engine management system as they generate more hydrogen which can fool the oxygen sensor [47] .

The use of fuel of too low octane can actually result in both a loss of fuel economy and power, as the management system may have to move the engine

## oxygenated fuel

settings to a less efficient part of the performance map. The system retards the ignition timing until only trace knock is detected, as engine damage from knock is of more consequence than power and fuel economy.

### 7.5 What is the effect of temperature and load?

Increasing the engine temperature, particularly the air/fuel charge temperature, increases the tendency to knock. The Sensitivity of a fuel can indicate how it is affected by charge temperature variations. Increasing load increases both the engine temperature, and the end-gas pressure, thus the likelihood of knock increases as load increases.

### 7.6 What is the effect of engine speed?

Faster engine speed means there is less time for the pre-flame reactions in the end gases to occur, thus reducing the tendency to knock. On engines with management systems, the ignition timing may be advanced with engine speed and load, to obtain optimum efficiency at incipient knock. In such cases, both high and low engines speeds may be critical.

### 7.7 What is the effect of engine deposits?

A new engine may only require a fuel of 6-9 octane numbers lower than the same engine after 25,000 km. This Octane Requirement Increase (ORI) is due to the formation of a mixture of organic and inorganic deposits resulting from both the fuel and the lubricant. They reach an equilibrium amount because of flaking, however dramatic changes in driving styles can also result in dramatic changes of the equilibrium position. When the engine starts to burn more oil, the octane requirement can increase again. ORIs up to 12 are not uncommon, depending on driving style [17,19]. The deposits produce the ORI by several mechanisms:-

- they reduce the combustion chamber volume, effectively increasing the compression ratio.
- they also reduce thermal conductivity, thus increasing the combustion chamber temperatures.
- they catalyse undesirable pre-flame reactions that produce end gases with low autoignition temperatures.

### 7.8 What is the Road Octane requirement of an vehicle?

The actual octane requirements of a vehicle is called the Octane Number Requirement ( ONR ), and is determined by using standard octane fuels that can be blends of iso-octane and normal heptane, or commercial gasolines. The vehicle is tested under a wide range of conditions and loads, using different octane fuels until trace knock is detected. The conditions that require maximum

## oxygenated fuel

octane are not consistent, but often are full-throttle acceleration from low starting speeds using the highest gear available. They can even be at constant speed conditions [17]. Engine management systems that adjust the octane requirement may also reduce the power output on low octane fuel, resulting in increased fuel consumption. The maximum ONR is of most interest, as that usually defines the recommended fuel.

The octane rating engines do not reflect actual conditions in a vehicle, consequently there are standard procedures for evaluating the performance of the gasoline in an engine. The most common are:- 1. The Modified Uniontown Procedure. Full throttle accelerations are made from low speed using primary reference fuels. The ignition timing is adjusted until trace knock is detected at some stage. Several reference fuels are used, and a Road Octane Number v Basic Ignition timing graph is obtained. The fuel sample is tested, and the ignition timing setting is read from the graph to provide the Road Octane Number. This is a rapid procedure but provides minimal information. 2. The Modified Borderline Knock Procedure. The automatic spark advance is disabled, and a manual adjustment facility added. Accelerations are performed as in the Modified Uniontown Procedure, however trace knock is maintained throughout the run. A map of ignition advance v engine speed is made for several reference fuels and the sample fuels. This procedure can show the variation of road octane with engine speed.

### 7.9 What is the effect of air temperature?

An increase in ambient air temperature of 5.6C increases the octane requirement of an engine by 0.44 - 0.54 MON [17,24]. When the combined effects of air temperature and humidity are considered, it is often possible to use one octane grade in summer, and use a lower octane rating in winter. The Motor octane rating has a higher charge temperature, and increasing charge temperature increases the tendency to knock, so fuels with low Sensitivity ( the difference between RON and MON numbers ) are less affected by air temperature.

### 7.10 What is the effect of altitude?

The effect of increasing altitude may be nonlinear, with one study reporting a decrease of the octane requirement of 1.4 RON/300m from sea level to 1800m and 2.5 RON/300m from 1800m to 3600m [17]. Other studies report the octane number requirement decreased by 1.0 - 1.9 RON/300m without specifying altitude [24]. Modern engine management systems can accommodate this adjustment, and in some recent studies, the octane number requirement was 0.2

## oxygenated fuel

- 0.5 Antiknock Index/300m. The reduction on older engines was due to:-

- reduced air density provides lower combustion temperature and pressure. - fuel is metered according to air volume, consequently as density decreases the stoichiometry moves to rich, with a lower octane number requirement. - manifold vacuum controlled spark advance, and reduced manifold vacuum results in less spark advance.

7.11 What is the effect of humidity?.

An increase of absolute humidity of 1.0 g water/ kg of dry air lowers the octane requirement of an engine by 0.25 - 0.32 MON [17,24].

7.12 What does water injection achieve?.

Water injection was used in WWII aviation engine to provide a large increase in available power for very short periods. The injection of water does decrease the dew point of the exhaust gases. This has potential corrosion problems. The very high specific heat and heat of vaporisation of water means that the combustion temperature will decrease. It has been shown that a 10% water addition to methanol reduces the power and efficiency by about 3%, and doubles the unburnt fuel emissions, but does reduce NO<sub>x</sub> by 25% [73]. A decrease in combustion temperature will reduce the theoretical maximum possible efficiency of an otto cycle engine that is operating correctly, but may improve efficiency in engines that are experiencing abnormal combustion on existing fuels.

Some aviation SI engines still use boost fluids. The water/methanol mixtures are used to provide increased power for short periods, up to 40% more - assuming adequate mechanical strength of the engine. The 40/60 or 45/55 water/methanol mixtures are used as boost fluids for aviation engines because water would freeze. Methanol is just "preburnt" methane, consequently it only has about half the energy content of gasoline, but it does have a higher heat of vaporisation, which has a significant cooling effect on the charge. Water/methanol blends are more cost-effective than gasoline for combustion cooling. The high Sensitivity of alcohol fuels has to be considered in the engine design and settings.

Boost fluids are used because they are far more economical than using the fuel. When a supercharged engine has to be operated at high boost, the mixture has to be enriched to keep the engine operating without knock. The extra fuel cools the cylinder walls and the charge, thus delaying the onset of knock which would otherwise occur at the associated higher temperatures.

## oxygenatedfuel

The overall effect of boost fluid injection is to permit a considerable increase in knock-free engine power for the same combustion chamber temperature. The power increase is obtained from the higher allowable boost. In practice, the fuel mixture is usually weakened when using boost fluid injection, and the ratio of the two fuel fluids is approximately 100 parts of avgas to 25 parts of boost fluid. With that ratio, the resulting performance corresponds to an effective uprating of the fuel of about 25%, irrespective of its original value. Trying to increase power boosting above 40% is difficult, as the engine can drown because of excessive liquid [71].

Note that for water injection to provide useful power gains, the engine management and fuel systems must be able to monitor the knock and adjust both stoichiometry and ignition to obtain significant benefits. Aviation engines are designed to accommodate water injection, most automobile engines are not. Returns on investment are usually harder to achieve on engines that do not normal extend their performance envelope into those regions. Water injection has been used by some engine manufacturers - usually as an expedient way to maintain acceptable power after regulatory emissions baggage was added to the engine, but usually the manufacturer quickly produces a modified engine that does not require water injection.

---

Subject: 8. How can I identify and cure other fuel-related problems? 8.1 What causes an empty fuel tank?

You forgot to refill it.

Your friendly neighbourhood thief "borrowed" the gasoline - the unfriendly one took the vehicle.

The fuel tank leaked.

Your darling child/wife/husband/partner/mother/father used the car.

The most likely reason is that your local garage switched to an oxygenated gasoline, and the engine management system compensated for the oxygen content, causing the fuel consumption to increase significantly.

8.2 Is knock the only abnormal combustion problem?

No. Many of the abnormal combustion problems are induced by the same conditions, and so one can lead to another.

## oxygenated fuel

Preignition occurs when the air/fuel mixture is ignited prematurely by glowing deposits or hot surfaces - such as exhaust valves and spark plugs. If it continues, it can increase in severity and become Run-away Surface Ignition (RSI) which prevents the combustion heat being converted into mechanical energy, thus rapidly melting pistons. The Ricardo method uses an electrically-heated wire in the engine to measure preignition tendency. The scale uses iso-octane as 100 and cyclohexane as 0.

Some common fuel components:-

paraffins	50-100
benzene	26
toluene	93
xylene	>100
cyclopentane	70
di-isobutylene	64
hexene-2	-26

There is no direct correlation between anti-knock ability and preignition tendency, however high combustion chamber temperatures favour both, and so one may lead to the other. An engine knocking during high-speed operation will increase in temperature and that can induce preignition, and conversely any preignition will result in higher temperatures than may induce knock.

Misfire is commonly caused by either a failure in the ignition system, or fouling of the spark plug by deposits. The most common cause of deposits was the alkyl lead additives in gasoline, and the yellow glaze of various lead salts was used by mechanics to assess engine tune. From the upper recess to the tip, the composition changed, but typical compounds ( going from cold to hot ) were PbClBr; 2PbO.PbClBr; PbO.PbSO<sub>4</sub>; 3Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.PbClBr.

Run-on is the tendency of an engine to continue running after the ignition has been switched off. It is usually caused by the spontaneous ignition of the fuel/air mixture, rather than by surface ignition from hotspots or deposits, as commonly believed. The narrow range of conditions for spontaneous ignition of the fuel/air mixture ( engine speed, charge temperature, cylinder pressure ) may be created when the engine is switched off. The engine may refire, thus taking the conditions out of the critical range for a couple of cycles, and then refire again, until overall cooling of the engine drops it out of the critical region. The octane rating of the

## oxygenated fuel

fuel is the appropriate parameter, and it is not rare for an engine to require a higher Octane fuel to prevent run-on than to avoid knock [17].

### 8.3 Can I prevent carburettor icing?

Yes, carburettor icing is caused by the combination of highly volatile fuel, high humidity and low ambient temperature. The extent of cooling, caused by the latent heat of the vaporised gasoline in the carburettor, can be as much as 20C, perhaps dropping below the dew point of the charge. If this happens, water will condense on the cooler carburettor surfaces, and will freeze if the temperature is low enough. The fuel volatility can not always be reduced to eliminate icing, so anti-icing additives are used.

Two types of additive are added to gasoline to inhibit icing:-

- surfactants that form a monomolecular layer over the metal parts that inhibits ice crystal formation. These are usually added at concentrations of 30-150 ppm. - cryoscopic additives that depress the freezing point of the condensed water so that it does not turn to ice. Alcohols ( methanol, ethanol, iso-propanol, etc. ) and glycols ( hexylene glycol, dipropylene glycol ) are used at concentrations of 0.03% - 1%. If you have icing problems, the addition of 100-200mls of methanol to a full tank of dry gasoline will prevent icing under most conditions. If you believe there is a small amount of water in the fuel tank, add 500mls of isopropanol as the first treatment. Oxygenated gasolines using alcohols can also be used.

### 8.4 Should I store fuel to avoid the oxygenate season?

No. The fuel will be from a different season, and will have significantly different volatility properties that may induce driveability problems. You can tune your engine to perform on oxygenated gasoline as well as it did on traditional gasoline, however you will have increased fuel consumption due to the useless oxygen in the oxygenates. Some engines may not initially perform well on some oxygenated fuels, usually because of the slightly different volatility and combustion characteristics. A good mechanic should be able to recover any lost performance or driveability, providing the engine is in reasonable condition.

### 8.5 Can I improve fuel economy by using quality gasolines?

Yes, several manufacturers have demonstrated that their new gasoline additive packages are more effective than traditional gasoline formulations. Texaco claim their new vapour phase fuel additive can reduce existing deposits by up to 30%,

## oxygenated fuel

improve fuel economy, and reduce NOx tailpipe emissions by 15%, when compared to other advanced liquid phase additives. These claims appear to have been verified in independent tests [30]. Other reputable gasoline brands will have similar additive packages in their quality products. Quality gasolines, of whatever octane ratings, will include a full range of gasoline additives designed to provide consistent fuel quality.

Note that oxygenated gasolines must decrease fuel economy for the same power. If your engine is initially well-tuned on hydrocarbon gasolines, the stoichiometry will move to lean, and maximum power is slightly rich, so either the management system ( if you have one ) or your mechanic has to increase the fuel flow. The minor improvements in combustion efficiency that oxygenates may provide, can not compensate for 2+% of oxygen in the fuel that will not provide energy.

### 8.6 What is "stale" fuel, and should I use it?

"Stale" fuel is caused by improper storage, and usually smells sour. The gasoline has been allowed to get warm, thus catalysing olefin decomposition reactions, and perhaps also losing volatile material in unsealed containers. Such fuel will tend to rapidly form gums, and will usually have a significant reduction in octane rating. The fuel can be used by blending with twice the volume of new gasoline. Some stale fuels can drop several octane numbers, so be generous with the dilution.

### 8.7 How can I remove water in the fuel tank?

If you only have a small quantity of water, then the addition of 500mls of dry isopropanol (IPA) to a near-full 30-40 litre tank will absorb the water, and will not significantly affect combustion. Once you have mopped up the water with IPA. Small, regular doses of any anhydrous alcohol will help keep the tank dry. This technique will not work if you have very large amounts of water, and the addition of greater amounts of IPA may result in poor driveability.

Water in fuel tanks can be minimised by keeping the fuel tank near full, and filling in the morning from a service station that allows storage tanks to stand for several hours after refilling before using the fuel. Note that oxygenated gasolines have greater water solubility, and should cope with small quantities of water.

### 8.8 Can I use unleaded on older vehicles?

Yes, providing the octane is appropriate. There are some older engines that cut the valve seats directly into the cylinder head ( eg BMC minis ). The absence of

## oxygenated fuel

lead, which lubricated the valve seat, causes the very hard oxidation products of the valve to wear down the seat. This valve seat recession is usually corrected by installing seat inserts. Most other problems arise because the fuels have different volatility, or the reduction of combustion chamber deposits. These can usually be cured by reference to the vehicle manufacturer, who will probably have a publication with the changes. Some vehicles will perform as well on unleaded with a slightly lower octane than recommended leaded fuel, due to the significant reduction in deposits from modern unleaded gasolines.

---

### Section: 9. Alternative Fuels and Additives 9.1 Do fuel additives work?

Most aftermarket fuel additives are not cost-effective. These include the octane-enhancer solutions discussed in section 6.18. There are various other pills, tablets, magnets, filters, etc. that all claim to improve either fuel economy or performance. Some of these have perfectly sound scientific mechanisms, unfortunately they are not cost-effective. Some do not even have sound scientific mechanisms. Because the same model production vehicles can vary significantly, it's expensive to unambiguously demonstrate these additives are not cost-effective. If you wish to try them, remember the biggest gain is likely to be caused by the lower mass of your wallet/purse.

There is one aftermarket additive that may be cost-effective, the lubricity additive used with unleaded gasolines to combat valve seat recession on engines that do not have seat inserts. The long-term solution is to install inserts at the next top overhaul.

Some other fuel additives work, especially those that are carefully formulated into the gasoline by the manufacturer at the refinery.

A typical gasoline may contain [17,19,24]:-

\* Oil-soluble Dye, initially added to leaded gasoline at about 10 ppm to prevent its misuse as an industrial solvent \* Antioxidants, typically phenylene diamines or hindered phenols, are added to prevent oxidation of unsaturated hydrocarbons. \* Metal Deactivators, typically about 10ppm of chelating agent such as N,N'-disalicylidene-1,2-propanediamine is added to inhibit copper, which can rapidly catalyze oxidation of unsaturated hydrocarbons. \* Corrosion Inhibitors,

## oxygenated fuel

about 5ppm of oil-soluble surfactants are added to prevent corrosion caused either by water condensing from cooling, water-saturated gasoline, or from condensation from air onto the walls of almost-empty gasoline tanks that drop below the dew point. If your gasoline travels along a pipeline, it's possible the pipeline owner will add additional corrosion inhibitor to the fuel. \* Anti-icing Additives, used mainly with carburetted cars, and usually either a surfactant, alcohol or glycol. \* Anti-wear Additives, these are used to control wear in the upper cylinder and piston ring area that the gasoline contacts, and are usually very light hydrocarbon oils. Phosphorus additives can also be used on engines without exhaust catalyst systems. \* Deposit-modifying Additives, usually surfactants.

1. Carburettor Deposits, additives to prevent these were required when crankcase blow-by (PCV) and exhaust gas recirculation (EGR) controls were introduced. Some fuel components reacted with these gas streams to form deposits on the throat and throttle plate of carburettors.
2. Fuel Injector tips operate about 100C, and deposits form in the annulus during hot soak, mainly from the oxidation and polymerisation of the larger unsaturated hydrocarbons. The additives that prevent and unclog these tips are usually polybutene succinimides or polyether amines.
3. Intake Valve Deposits caused major problems in the mid-1980s when some engines had reduced driveability when fully warmed, even though the amount of deposit was below previously acceptable limits. It is believed that the new fuels and engine designs were producing a more absorbent deposit that grabbed some passing fuel vapour, causing lean hesitation. Intake valves operate about 300C, and if the valve is kept wet deposits tend not to form, thus intermittent injectors tend to promote deposits. Oil leaking through the valve guides can be either harmful or beneficial, depending on the type and quantity. Gasoline factors implicated in these deposits include unsaturates and alcohols. Additives to prevent these deposits contain a detergent and/or dispersant in a higher molecular weight solvent or light oil whose low volatility keeps the valve surface wetted.
4. Combustion Chamber Deposits have been targeted in the 1990s, as they are responsible for significant increases in emissions. Recent detergent-dispersant additives have the ability to function in both the liquid and vapour phases to remove existing carbon and prevent deposit formation.

\* Octane Enhancers, these are usually formulated blends of alkyl lead or MMT compounds in a solvent such as toluene, and added at the 100-1000 ppm levels. They have been replaced by hydrocarbons with higher octanes such as aromatics and olefins. These hydrocarbons are now being replaced by a mixture of saturated hydrocarbons and oxygenates. If you wish to play with different fuels and additives, be aware that some parts of your engine management systems, such as the oxygen sensor, can be confused

## oxygenated fuel

by different exhaust gas compositions. An example is increased quantities of hydrogen from methanol combustion.

### 9.2 Can a quality fuel help a sick engine?

It depends on the ailment. Nothing can compensate for poor tuning and wear. If the problem is caused by deposits or combustion quality, then modern premium quality gasolines have been shown to improve engine performance significantly. The new generation of additive packages for gasolines include components that will dissolve existing carbon deposits, and have been shown to improve fuel economy, NO<sub>x</sub> emissions, and driveability.

### 9.3 What are the advantages of alcohols and ethers?

This section discusses only the use of high ( >80% ) alcohol or ether fuels. Alcohol fuels can be made from sources other than imported crude oil, and the nations that have researched/used alcohol fuels have mainly based their choice on import substitution. Alcohol fuels can burn more efficiently, and can reduce photochemically-active emissions. Most vehicle manufacturers favoured the use of liquid fuels over compressed or liquified gases. The alcohol fuels have high research octane ratings, but also high sensitivity and high latent heats [6,17,51,74].

	Methanol	Ethanol	Unleaded Gasoline	
RON	106	107	92 - 98	
MON	92	89	80 - 90	
Heat of Vaporisation (MJ/kg)	1.154	0.913	0.3044	
Nett Heating Value (MJ/kg)	19.95	26.68	42 - 44	
Vapour Pressure @ 38C (kPa)	31.9	16.0	48 - 108	
Flame Temperature ( C )	1870	1920	2030	
Stoich. Flame Speed. ( m/s )	0.43	-	0.34	
Minimum Ignition Energy ( mJ )	0.14	-	0.29	
Lower Flammable Limit ( vol% )	6.7	3.3	1.3	
Upper Flammable Limit ( vol% )	36.0	19.0	7.1	
Autoignition Temperature ( C )	460	360	260 - 460	
Flash Point ( C )	11	13	-43 - -39	

The major advantages are gained when pure fuels ( M100, and E100 ) are used, as the addition of hydrocarbons to overcome the cold start problems also significantly reduces, if not totally eliminates, any emission benefits. Methanol will

### oxygenated fuel

produce significant amounts of formaldehyde, a suspected human carcinogen, until the exhaust catalyst reaches operating temperature. Ethanol produces acetaldehyde. The cold-start problems have been addressed, and alcohol fuels are technically viable, however with crude oil at <\$30/bbl they are not economically viable, especially as the demand for them as precursors for gasoline oxygenates has elevated the world prices. Methanol almost doubled in price during 1994. There have also been trials of pure MTBE as a fuel, however there are no unique or significant advantages that would outweigh the poor economic viability [11].

#### 9.4 Why are CNG and LPG considered "cleaner" fuels.

CNG ( Compressed Natural Gas ) is usually around 70-90% methane with 10-20% ethane, 2-8% propanes, and decreasing quantities of the higher HCs up to butane. The fuel has a high octane and usually only trace quantities of unsaturates. The emissions from CNG have lower concentrations of the hydrocarbons responsible for photochemical smog, reduced CO, SO<sub>x</sub>, and NO<sub>x</sub>, and the lean misfire limit is extended [75]. There are no technical disadvantages, providing the installation is performed correctly. The major disadvantage of compressed gas is the reduced range. Vehicles may have between one to three cylinders ( 25 MPa, 90-120 litre capacity), and they usually represent about 50% of the gasoline range. As natural gas pipelines do not go everywhere, most conversions are dual-fuel with gasoline. The ignition timing and stoichiometry are significantly different, but good conversions will provide about 85% of the gasoline power over the full operating range, with easy switching between the two fuels [76].

CNG has been extensively used in Italy and New Zealand ( NZ had 130,000 dual-fuelled vehicles with 380 refuelling stations in 1987 ). The conversion costs are usually around US\$1000, so the economics are very dependent on the natural gas price. The typical 15% power loss means that driveability of retrofitted CNG-fuelled vehicles is easily impaired, consequently it is not recommended for vehicles of less than 1.5l engine capacity, or retrofitted onto engine/vehicle combinations that have marginal driveability on gasoline. The low price of crude oil, along with installation and ongoing CNG tank-testing costs, have reduced the number of CNG vehicles in NZ. The US CNG fleet continues to increase in size ( 60,000 in 1994 ).

LPG ( Liquefied Petroleum Gas ) is predominantly propane with iso-butane and

### oxygenated fuel

n-butane. It has one major advantage over CNG, the tanks do not have to be high pressure, and the fuel is stored as a liquid. The fuel offers most of the environmental benefits of CNG, including high octane. Approximately 20-25% more fuel is required, unless the engine is optimised ( CR 12:1 ) for LPG, in which case there is no decrease in power or increase in fuel consumption [17,76].

	methane	propane	iso-octane
RON	120	112	100
MON	120	97	100
Heat of Vaporisation (MJ/kg)	0.5094	0.4253	0.2712
Net Heating Value (MJ/kg)	50.0	46.2	44.2
Vapour Pressure @ 38C ( kPa )	-	-	11.8
Flame Temperature ( C )	1950	1925	1980
Stoich. Flame Speed. ( m/s )	0.45	0.45	0.31
Minimum Ignition Energy ( mJ )	0.30	0.26	-
Lower Flammable Limit ( vol% )	5.0	2.1	0.95
Upper Flammable Limit ( vol% )	15.0	9.5	6.0
Autoignition Temperature ( C )	540 - 630	450	415

#### 9.5 Why are hydrogen-powered cars not available?

The Hindenburg. The technology to operate IC engines on hydrogen has been investigated in depth since before the turn of the century. One attraction was to use the hydrogen in airships to fuel the engines instead of venting it. Hydrogen has a very high flame speed ( 3.24 - 4.40 m/s ), wide flammability limits ( 4.0 - 75 vol% ), low ignition energy ( 0.017 mJ ), high autoignition temperature ( 520C ), and flame temperature of 2050 C. Hydrogen has a very high specific energy ( 120.0 MJ/kg ), making it very desirable as a transportation fuel. The problem has been to develop a storage system that will pass all safety concerns, and yet still be light enough for automotive use. Although hydrogen can be mixed with oxygen and combusted more efficiently, most proposals use air [73,77].

Unfortunately the flame temperature is sufficiently high to dissociate atmospheric nitrogen and form undesirable NOx emissions. The high flame speeds mean that ignition timing is at TDC, except when running lean, when the ignition timing is advanced 10 degrees. The high flame speed, coupled with a very small quenching distance mean that the flame can sneak past inlet narrow inlet valve openings and cause backfiring. The advantage of a wide range of mixture strengths and high thermal efficiencies are matched by the disadvantages of

## oxygenated fuel

pre-ignition and knock unless weak mixtures, clean engines, and cool operation are used.

Interested readers are referred to the group [sci.energy.hydrogen](#) for details about this fuel.

### 9.6 What are "fuel cells" ?

Fuel cells are electrochemical cells that directly oxidise the fuel at electrodes producing electrical and thermal energy. The oxidant is usually oxygen from the air and the fuel is usually gaseous, with hydrogen preferred. There has, so far, been little success using low temperature fuel cells ( <200c ) to perform the direct oxidation of hydrocarbon-based liquids or gases. Methanol can be used as a source for the hydrogen by adding an on-board reformer. The main advantage of fuel cells is their high fuel-to- electricity efficiency of about 40-60% of the nett calorific value of the fuel. As fuel cells also produce heat that can be used for vehicle climate control. Fuel Cells are the most likely candidate to replace the IC engine as a primary energy source. Fuel cells are quiet and produce virtually no toxic emissions, but they do require a clean fuel ( no halogens, CO, S, or ammonia ) to avoid poisoning. They currently are expensive to produce, and have a short operational lifetime, when compared to an IC engine [78,79].

### 9.7 What is a "hybrid" vehicle?

A hybrid vehicle has three major systems [80].

A primary power source, either an IC engine driven generator where the IC engine only operates in the most efficient part of it's performance map, or alternatives such as fuel cells and turbines.

A power storage unit, which can be a flywheel, battery, or ultracapacitor.

A drive unit, almost always now an electric motor that can used as a generator during braking. Regenerative braking may increase the operational range about 8-13%.

Battery technology has not yet advanced sufficiently to economically substitute for an IC engine, while retaining the carrying capacity, range, performance, and driveability of the vehicle. Hybrid vehicles may enable this problem to be at least partially overcome, but they remain expensive, and the current ZEV proposals exclude fuel cells and hybrids systems, but this is being re-evaluated.

### 9.8 What about other alternative fuels?

## oxygenatedfuel

### 9.8.1 Ammonia

Anhydrous ammonia has been researched because it does not contain any carbon, and so would not release any CO<sub>2</sub>. The high heat of vaporisation requires a pre-vaporisation step, preferably also with high jacket temperatures ( 180C ) to assist decomposition. Power outputs of about 70% of that of gasoline under the same conditions have been achieved [73].

### 9.8.2 Water

Mr Gunnerman has been promoting his patents that claim mixing one part of gasoline with 2 parts water can provide as much power from an IC engine as the same flow rate of gasoline. He claims the increased efficiency is from catalysed dissociation of water to H<sub>2</sub> and O<sub>2</sub>, as the combustion chamber of the test engine contained a catalyst. It takes the same amount of energy to dissociate water, as you reclaim when you burn the H<sub>2</sub> with O<sub>2</sub>. So he has to use heat energy that is normally lost. He appears to have modified his claims a little with his new A55 fuel. A recent article claims a 29% increase in fuel economy for a test bus in Reno, but also claims that his fuel combusts so efficiently that it can pass an emissions test without requiring a catalytic converter [81]. Caterpillar are working with Gunnerman to evaluate his claims and develop the product.

## 9.9 What about alternative oxidants?

### 9.9.1 Nitrous Oxide

Nitrous oxide ( N<sub>2</sub>O ) contains 33 vol% of oxygen, consequently the combustion chamber is filled with less useless nitrogen. It is also metered in as a liquid, with can cool the incoming charge further, thus effectively increasing the charge density. With all that oxygen, a lot more fuel can be squashed into the combustion chamber. The advantage of nitrous oxide is that it has a flame speed, when burned with hydrocarbon and alcohol fuels, that can be handled by current IC engines, consequently the power is delivered in an orderly fashion, but rapidly. The same is not true for pure oxygen combustion with hydrocarbons, so leave that oxygen cylinder on the gas axe alone :-). The following are for common premixed flames [82].

Fuel	Oxidant	Temperature ( C )	Flame Speed ( m/s )
Acetylene	Air	2400	1.60 - 2.70
"	Nitrous Oxide	2800	2.60
"	Oxygen	3140	8.00 - 24.80

			oxygenated fuel
Hydrogen	Air	2050	3.24 - 4.40
"	Nitrous Oxide	2690	3.90
"	Oxygen	2660	9.00 - 36.80
Propane	Air	1925	0.45
Natural Gas	Air	1950	0.39

Nitrous oxide is not yet routinely used on standard vehicles, but the technology is well understood.

### 9.9.2 Membrane Enrichment of Air

Over the last two decades, extensive research has been performed on the use of membranes to enrich the oxygen content of air. Increasing the oxygen content can make combustion more efficient due to the higher flame temperature and less nitrogen. The optimum oxygen concentration for existing automotive engine materials is around 30 - 40%. There are several commercial membranes that can provide that level of enrichment. The problem is that the surface area required to produce the necessary amount of enriched air for an SI engine is very large. The membranes have to be laid close together, or wound in a spiral, and significant amounts of power are required to force the air along the membrane surface for sufficient enriched air to run a slightly modified engine. Most research to date has centred on CI engines, with their higher efficiencies. Several systems have been tried on research engines and vehicles, however the higher NOx emissions remain a problem [83,84].

---

Subject: 10. Historical Legends 10.1 The myth of Triptane

This post is an edited version of some posted after JdA posted some claims from a hot-rod enthusiast reporting that triptane + 4cc TEL had a rich power octane rating of 270. This was followed by another that claimed the unleaded octane was 150.

In WWII there was a major effort to increase the power of the aviation engines continuously, rather than just for short periods using boost fluids. Increasing the octane of the fuel had dramatic effects on engines that could be adjusted to utilise the fuel ( by changing boost pressure ). There was a 12% increase in cruising speed, 40% increase in rate of climb, 20% increase in ceiling, and 40% increase in payload for a DC-3, if the fuel went from 87 to 100 Octane, and further

## oxygenatedfuel

increases if the engine could handle 100+ PN fuel [85]. A 12 cylinder Allison aircraft engine was operated on a 60% blend of triptane ( 2,2,3-trimethylbutane ) in 100 octane leaded gasoline to produce 2500hp when the rated take-off horsepower with 100 octane leaded was 1500hp [10].

Triptane was first shown to have high octane in 1926 as part of the General Motors Research Laboratories investigations [86]. As further interest developed, gallon quantities were made in 1938, and a full size production plant was completed in late 1943. The fuel was tested, and the high lead sensitivity resulted in power outputs up to 4 times that of iso-octane, and as much as 25% improvement in fuel economy over iso-octane [10].

All of this sounds incredibly good, but then, as now, the cost of octane enhancement has to be considered, and the plant producing triptane was not really viable. The fuel was fully evaluated in the aviation test engines, and it was under the aviation test conditions - where mixture strength is varied, that the high power levels were observed over a narrow range of engine adjustment. If turbine engines had not appeared, then maybe triptane would have been used as an octane agent in leaded aviation gasolines. Significant design changes would have been required for engines to utilise the high anti-knock rating.

As an unleaded additive, it was not that much different to other isoalkanes, consequently the modern manufacturing processes for aviation gasolines are alkylation of unsaturated C4 HCs with isobutane, to produce a highly iso-paraffinic product, and/or aromatization of naphthenic fractions to produce aromatic hydrocarbons possessing excellent rich-mixture antiknock properties.

So, the myth that triptane was the wonder anti-knock agent that would provide heaps of power arose. In reality, it was one of the best of the iso-alkanes ( remember we are comparing it to iso-octane which just happened to be worse than most other iso-alkanes), but it was not that different from other members. It was targeted, and produced, for supercharged aviation engines that could adjust their mixture strength, used highly leaded fuel, and wanted short period of high power for takeoff, regardless of economy.

The blending octane number, which is what we are discussing, of triptane is designated by the American Petroleum Institute Research Project 45 survey as 112 Motor and 112 Research [31]. Triptane does not have a significantly different blending number for MON or RON, when compared to iso-octane. When TEL is

## oxygenatedfuel

added, the lead response of a large number of paraffins is well above that of iso-octane ( about +45 for 3ml TEL/US Gal ), and this can lead to Performance Numbers that can not be used in conventional automotive engines [10].

### 10.2 From Honda Civic to Formula 1 winner.

The following is edited from a post in a debate over the advantages of water injection. I tried to demonstrate what modifications would be required to convert my own 1500cc Honda Civic into something worthwhile :-).

There are many variables that will determine the power output of an engine. High on the list will be the ability of the fuel to burn evenly without knock. No matter how clever the engine, the engine power output limit is determined by the fuel it is designed to use, not the amount of oxygen stuffed into the cylinder and compressed. Modern engines designs and gasolines are intended to reduce the emission of undesirable exhaust pollutants, consequently engine performance is mainly constrained by the fuel available.

My Honda Civic uses 91 RON fuel, but the Honda Formula 1 turbocharged 1.5 litre engine was only permitted to operate on 102 Research Octane fuel, and had limits placed on the amount of fuel it could use during a race, the maximum boost of the turbochargers was specified, as was an additional 40kg penalty weight. Standard 102 RON gasoline would be about 96 R+M/2 if sold as a pump gasoline. The normally-aspirated 3.0 litre engines could use unlimited amounts of 102RON fuel. The F1 race duration is 305 km or 2 hours, and it's perhaps worth remembering that Indy cars run at 7.3 psi boost.

Engine	Standard	Formula One	
Year	1986	1987	1989
Size	1.5 litre	1.5 litre	1.5 litre
Cylinders	4	12	12
Aspiration	normal	turbo	turbo
Maximum Boost	-	58 psi	36.3 psi
Maximum Fuel	-	200 litres	150 litres
Fuel	91 RON	102 RON	102 RON
Horsepower @ rpm	92 @ 6000	994 @ 12000	610 @ 12500
Torque (lb-ft @ rpm)	89 @ 4500	490 @ 9750	280 @ 10000

## oxygenatedfuel

Lets consider the transition from Standard to Formula 1, without considering materials etc.

Replace the exhaust system. HP and torque climb to 100.

Double the rpm while improving breathing, you now have 200hp but still only about 100 torque.

Boost it to 58psi which equals 4 such engines, so 1000hp and 500 torque.

Simple?, not with 102RON fuel, the engine would detonate to pieces. so..

Lower the compression ratio to 7.4:1, and the higher rpm is a big advantage - there is much less time for the end gases to ignite and cause detonation.

Optimise engine design. 80 degree bank angles V for aerodynamic reasons and go to six cylinders = V-6

Cool the air. The compression of 70F air at 14.7psi to 72.7psi raises its temperature to 377F. The turbos churn the air and although they are about 75% efficient the air is now at 479F. The huge intercoolers could reduce the air to 97F, but that was too low to properly vaporise the fuel.

Bypass the intercoolers to maintain 104F.

Change the Air:Fuel ratio to 23% richer than stoichiometric to reduce combustion temperature.

Change to 84:16 toluene/heptane fuel, harder to vaporise, but complies with the 102 RON requirement

Add sophisticated electronic timing and engine manangement controls to ensure reliable combustion with no detonation.

You now have a six-cylinder, 1.5 litre, 1000hp Honda Civic.

For subsequent years the restrictions were even more severe, 150 litres and 36.3 maximum boost, in a still vain attempt to give the 3 litre, normally-aspirated engines a chance. Obviously Honda took advantage of the reduced boost by increasing CR to 9.4:1, and only going to 15% rich air/fuel ratio. They then developed an economy mode that involved heating the liquid fuel to 180F to improve vaporisation, and increased the air temp to 158F, and leaned out the air-fuel ratio to just 2% rich. The engine output dropped to 610hp @ 12,500 ( from 685hp @ 12,500 and about 312 lbs-ft of torque @ 10,000 rpm ), but 32% of the energy in the fuel was converted to mechanical work. The engine still had crisp throttle response, and still beat the normally aspirated engines that did not have the fuel limitation. So turbos were banned. No other F1 racing engine has ever come close to converting 32% of the fuel energy into work [87].

Subject: 11. References

11.1 Books and Research Papers

1. Modern Petroleum Technology - 5th edition.  
Editor, G.D.Hobson.  
Wiley. ISBN 0 471 262498 (1984).  
- Chapter 1. G.D.Hobson.
2. Hydrocarbons from Fossil Fuels and their Relationship with Living Organisms.  
I.R.Hills, G.W.Smith, and E.V.Whitehead.  
J.Inst.Petrol., v.56 p.127-137 (May 1970).
3. Reference 1.  
- Chapter 9. R.E.Banks and P.J.King.
4. Ullmann's Encyclopedia of Industrial Chemistry - 5th edition.  
Editor, B.Elvers.  
VCH. ISBN 3-527-20123-8 (1993).  
- Volume A23. Resources of Oil and Gas.
5. BP Statistical Review of World Energy - June 1994.  
- Proved Reserves at end 1993. p.2.
6. Kirk-Othmer Encyclopedia of Chemical Technology - 4th edition.  
Editor M.Howe-Grant.  
Wiley. ISBN 0-471-52681-9 (1993)  
- Volume 1. Alcohol Fuels.
7. Midgley: Saint or Serpent?.  
G.B.Kauffman.  
Chemtech, December 1989. p.717-725.
8. ?  
T.Midgley Jr., T.A.Boyd.  
Ind. Eng. Chem., v.14 p.589,849,894 (1922).

## oxygenatedfuel

9. Measurement of the Knock Characteristics of Gasoline in terms of a Standard Fuel.  
G. Edgar.  
Ind. Eng. Chem., v.19 p.145-146 (1927).
10. The Effect of the Molecular Structure of Fuels on the Power and Efficiency of Internal Combustion Engines.  
C.F.Kettering.  
Ind. Eng. Chem., v.36 p.1079-1085 (1944).
11. Experiments with MTBE-100 as an Automobile Fuel.  
K.Springer, L.Smith.  
Tenth International Symposium on Alcohol Fuels.  
- Proceedings, v.1 p.53 (1993).
12. Oxygenates for Reformulated Gasolines.  
W.J.Piel, R.X.Thomas.  
Hydrocarbon Processing, July 1990. p.68-73.
13. The Chemical Kinetics of Engine Knock.  
C.K.Westbrook, W.J. Pitz.  
Energy and Technology Review, Feb/Mar 1991. p.1-13.
14. The Chemistry Behind Engine Knock.  
C.K.Westbrook.  
Chemistry & Industry (UK), 3 August 1992. p.562-566.
15. A New Look at High Compression Engines.  
D.F.Caris and E.E.Nelson.  
SAE Paper 812A. (1958)
16. Problem + Research + Capital = Progress  
T.Midgley,Jr.  
Ind. Eng. Chem., v.31 p.504-506 (1939).
17. Reference 1.  
- Chapter 20. K.Owen.

oxygenatedfuel

18. Automotive Gasolines - Recommended Practice  
SAE J312 Jan93.  
- Section 3.  
SAE Handbook, volume 1. ISBN 1-56091-461-0 (1994).
19. Reference 6.  
- Volume 12. Gasoline and Other Motor Fuels
20. Refiners have options to deal with reformulated gasoline.  
G.Yepsin and T.Witoshkin.  
Oil & Gas Journal, 8 April 1991. p.68-71.
21. Stoichiometric Air/Fuel Ratios of Automotive Fuels - Recommended Practice.  
SAE J1829 May92.  
SAE Handbook, volume 1. ISBN 1-56091-461-0 (1994).
22. Chemical Engineers' Handbook - 5th edition  
R.H.Perry and C.H.Chilton.  
McGraw-Hill. ISBN 07-049478-9 (1973)  
- Chapter 3.
23. Alternative Fuels  
E.M.Goodger.  
MacMillan. ISBN 0-333-25813-4 (1980)  
- Appendix 4.
24. Automotive Gasolines - Recommended Practice.  
SAE J312 Jan93.  
SAE Handbook, volume 1. ISBN 1-56091-461-0 (1994).
25. Standard Specification for Automotive Spark-Ignition Engine Fuel.  
ASTM D 4814-93a.  
Annual Book of ASTM Standards v.05.03 (1994).
26. Criteria for Quality of Petroleum Products.  
Editor, J.P. Allinson.  
Applied Science. ISBN 0 85334 469 8  
- Chapter 5. K.A.Boldt and S.T.Griffiths.

## oxygenatedfuel

27. Meeting the challenge of reformulated gasoline.  
R.J. Schmidt, P.L.Bogdan, and N.L.Gilsdorf.  
Chemtech, February 1993. p.41-42.
28. The Relationship between Gasoline Composition and Vehicle Hydrocarbon Emissions: A Review of Current Studies and Future Research Needs.  
D. Schuetzle, W.O.Siegl, T.E.Jensen, M.A.Dearth, E.W.Kaiser, R.Gorse, W.Kreucher, and E.Kulik.  
Environmental Health Perspectives Supplements v.102 s.4 p.3-12. (1994)
29. Reference 23.  
- Chapter 5.
30. Texaco to introduce clean burning gasoline.  
Oil & Gas Journal, 28 February 1994. p.22-23.
31. Knocking Characteristics of Pure Hydrocarbons.  
ASTM STP 225. (1958)
32. Health Effects of Gasoline.  
Environmental Health Perspectives Supplements v.101. s.6 (1993)
33. Speciated Measurements and Calculated Reactivities of Vehicle Exhaust Emissions from Conventional and Reformulated Gasolines.  
S.K.Hoekman.  
Environ. Sci. Technol., v.26 p.1206-1216 (1992).
34. Effect of Fuel Structure on Emissions from a Spark-Ignited Engine.  
2. Naphthene and Aromatic Fuels.  
E.W.Kaiser, W.O.Siegl, D.F.Cotton, R.W.Anderson.  
Environ. Sci. Technol., v.26 p.1581-1586 (1992).
35. Determination of PCDDs and PCDFs in Car Exhaust.  
A.G.Bingham, C.J.Edmunds, B.W.L.Graham, and M.T.Jones.  
Chemosphere, v.19 p.669-673 (1989).
36. Volatile Organic Compounds: Ozone Formation, Alternative Fuels and  
Toxics.

oxygenatedfuel

B.J.Finlayson-Pitts and J.N.Pitts Jr..

Chemistry and Industry (UK), 18 October 1993. p.796-800.

37. The rise and rise of global warming.  
R.Matthews.  
New Scientist, 26 November 1994. p.6.
38. Energy-related Carbon Dioxide Emissions per Capita for OECD Countries during 1990.  
International Energy Agency. (1993)
39. Market Data Book - 1991, 1992, 1993 and 1994 editions.  
Automobile News  
- various tables
40. BP Statistical Review of World Energy - June 1994.  
- Crude oil consumption p.7.
41. Automotive Gasolines - Recommended Practice  
SAE J312 Jan93.  
- Section 4  
SAE Handbook, volume 1. ISBN 1-56091-461-0 (1994).
42. The Rise and Fall of Lead in Petrol.  
IDG Berwick  
Phys. Technol., v.18 p.158-164 (1987)
43. E.C. seeks gasoline emission control.  
Hydrocarbon Processing, September 1990. p.43.
44. Health Effects of Gasoline Exposure. I. Exposure assessment for U.S. Distribution Workers.  
T.J.Smith, S.K.Hammond, and O.Wong.  
Environmental Health Perspectives Supplements. v.101 s.6 p.13 (1993)
45. Atmospheric Chemistry of Tropospheric Ozone Formation: Scientific and Regulatory Implications.  
B.J.Finlayson-Pitts and J.N.Pitts, Jr.  
Air & Waste, v.43 p.1091-1100 (1993).

## oxygenatedfuel

46. Trends in Auto Emissions and Gasoline Composition.  
R.F.Sawyer  
Environmental Health Perspectives Supplements. v.101 s.6 p.5 (1993)
47. Reference 6.  
- Volume 9. Exhaust Control, Automotive.
48. Achieving Acceptable Air Quality: Some Reflections on Controlling Vehicle Emissions.  
J.G.Calvert, J.B.Heywood, R.F.Sawyer, J.H.Seinfeld  
Science v261 p37-45 (1993).
49. Radiometric Determination of Platinum and Palladium attrition from Automotive Catalysts.  
R.F.Hill and W.J.Mayer.  
IEEE Trans. Nucl. Sci., NS-24, p.2549-2554 (1977).
50. Determination of Platinum Emissions from a three-way catalyst-equipped Gasoline Engine.  
H.P.Konig, R.F.Hertel, W.Koch and G.Rosner.  
Atmospheric Environment, v.26A p.741-745 (1992).
51. Alternative Automotive Fuels - SAE Information Report.  
SAE J1297 Mar93.  
SAE Handbook, volume 1. ISBN 1-56091-461-0 (1994).
52. Lean-burn Catalyst offers market boom.  
New Scientist, 17 July 1993. p.20.
53. Catalysts in cars.  
K.T.Taylor.  
Chemtech, September 1990. p.551-555.
54. Advanced Batteries for electric vehicles.  
G.L.Henriksen, W.H.DeLuca, D.R.Vissers.  
Chemtech, November 1994. p.32-38.
55. The great battery barrier.

oxygenatedfuel

IEEE Spectrum, November 1992. p.97-101.

56. Exposure of the general Population to Gasoline.  
G.G.Akland  
Environmental Health Perspectives Supplements. v.101 s.6 p.27-32 (1993)
57. Court Ruling Spurs Continued Debate Over Gasoline Oxygenates.  
G.Peaff.  
Chemical & Engineering News, 26 September 1994. p.8-13.
58. The Application of Formaldehyde Emission Measurement to the Calibration of Engines using Methanol as a Fuel.  
P.Waring, D.C.Kappatos, M.Galvin, B.Hamilton, and A.Joe.  
Sixth International Symposium on Alcohol Fuels.  
- Proceedings, v.2 p.53-60 (1984).
59. Emissions from 200,000 vehicles: a remote sensing study.  
P.L.Guenther, G.A.Bishop, J.E.Peterson, D.H.Stedman.  
Sci. Total Environ., v.146/147 p.297-302 (1994)
60. Remote Sensing of Vehicle Exhaust Emissions.  
S.H.Cadle and R.D.Stephens.  
Environ. Sci. Technol., v.28 p.258A-264A. (1994)
61. Real-World Vehicle Emissions: A Summary of the Third Annual  
CRC-APRAC  
On-Road Vehicle Emissions Workshop.  
S.H.Cadle, R.A.Gorse, D.R.Lawson.  
Air & Waste, v.43 p.1084-1090 (1993)
62. IR Long-Path Photometry: A Remote Sensing Tool for Automobile Emissions.  
G.A.Bishop, J.R.Starkey, A.Ihlenfeldt, W.J.Williams, and D.H.Stedman.  
Analytical Chemistry, v.61 p.671A-677A (1989)
63. A Cost-Effectiveness Study of Carbon Monoxide Emissions Reduction Utilising Remote Sensing.  
G.A.Bishop, D.H.Stedman, J.E.Peterson, T.J.Hosick, and P.L.Guenther  
Air & Waste, v.42 p.978-985 (1993)

## oxygenatedfuel

64. A presentation to the California I/M Review Committee of results of a 1991 pilot programme.  
D.R.Lawson, J.A.Gunderson  
29 January 1992.
65. Methods of Knock Rating. 15. Measurement of the Knocking Characteristics of Automotive Fuels.  
J.M.Campbell, T.A.Boyd.  
The Science of Petroleum. Oxford Uni. Press. v.4 p.3057-3065 (1938).
66. Standard Test Method for Knock Characteristics of Motor and Aviation Fuels by the Motor Method.  
ASTM D 2700 - 92. IP236/83  
Annual Book of ASTM Standards v.05.04 (1994).
67. Standard Test Method for Knock Characteristics of Motor Fuels by the Research Method.  
ASTM D 2699 - 92. IP237/69  
Annual Book of ASTM Standards v.05.04 (1994).
68. Preparation of distillates for front end octane number ( RON 100C ) of motor gasoline  
IP 325/82  
Standard Methods for Analysis and Testing of Petroleum and Related Products. Wiley. ISBN 0 471 94879 9 (1994).
69. Octane Enhancers.  
D.Simanaitis and D.Kott.  
Road & Track, April 1989. p.82,83,86-88.
70. Specification for Aviation Gasolines  
ASTM D 910 - 93  
Annual Book of ASTM Standards v.05.01 (1994).
71. Reference 1.  
- Chapter 19. R.A.Vere
72. Automotive Sensors Improve Driving Performance.

oxygenatedfuel

L.M.Sheppard.

Ceramic Bulletin, v.71 p.905-913 (1992).

73. Reference 23.

- Chapter 7.

74. Investigation of Fire and Explosion Accidents in the Chemical, Mining and Fuel-Related Industries - A Manual.

Joseph M. Kuchta.

US Dept. of the Interior. Bureau of Mines Bulletin 680 (1985).

75. Natural Gas as an Automobile Fuel, An Experimental study.

R.D.Fleming and J.R.Allsup.

US Dept. of the Interior. Bureau of Mines Report 7806 (1973).

76. Comparative Studies of Methane and Propane as Fuels for Spark Ignition and Compression Ignition Engines.

G.A.Karim and I.Wierzba.

SAE Paper 831196. (198?).

77. The Outlook for Hydrogen.

N.S.Mayersohn.

Popular Science, October 1993. p.66-71,111.

78. Reference 6.

- Volume 11. Fuel Cells.

79. The Clean Machine.

R.H.Williams.

Technology Review, April 1994. p.21-30.

80. Hybrid car promises high performance and low emissions.

M. Valenti.

Mechanical Engineering, July 1994. p.46-49.

81. ?

Automotive Industries Magazine, December 1994.

82. Instrumental Methods of Analysis - 6th edition.

### oxygenatedfuel

H.H.Willard, L.L.Merritt, J.A.Dean, F.A.Settle.  
D.Van Nostrand. ISBN 0-442-24502-5 (1981).

83. Research into Asymmetric Membrane Hollow Filter Device for Oxygen-Enriched Air Production.  
A.Z.Gollan. M.H.Kleper.  
Dept.of Energy Report DOE/ID/12429-1 (1985).
84. New Look at Oxygen Enrichment. I. The diesel engine.  
H.C.Watson, E.E.Milkins, G.R.Rigby.  
SAE Technical Paper 900344 (1990)
85. Thorpe's Dictionary of Applied Chemistry - 4th edition.  
Longmans. 1949.  
- Petroleum
86. Detonation Characteristics of Some Paraffin Hydrocarbons.  
W.G.Lovell, J.M.Campbell, and T.A.Boyd.  
Ind. Eng. Chem., v.23 p.26-29. (1931)
87. Secrets of Honda's horsepower heroics.  
C. Csere.  
Road & Track/Car & Driver?, May 1991. p.29.

### 11.2 Suggested Further Reading

1. Modern Petroleum Technology - any edition.  
Editor, G.D.Hobson.  
Wiley. ISBN 0 471 262498 (5th=1984).
2. Hydrocarbon Fuels.  
E.M.Goodger.  
MacMillan. (1975)
3. Alternative Fuels  
E.M.Goodger.  
MacMillan. ISBN 0-333-25813-4 (1980)
4. Kirk-Othmer Encyclopedia of Chemical Technology - 4th edition.

## oxygenatedfuel

Editor, M.Howe-Grant.

Wiley. ISBN 0-471-52681-9 (1993)

- especially Alcohol Fuels, Gasoline and Other Motor Fuels, and Fuel Cells chapters.

5. The Automotive Handbook. - any edition.  
Bosch.
6. SAE Handbook, volume 1. - issued annually.  
SAE. ISBN 1-56091-461-0 (1994).  
- especially J312, and J1297.
7. Proceedings of the xxth International Symposium on Alcohol Fuels.  
- Held every two years and most of the 10 conferences have lots of good technical information, especially the earlier ones.  
- various publishers.
8. Alternative Transportation Fuels - An Environmental and Energy solution.  
Editor, D.Sperling.  
Quorum Books. ISBN 0-89930-407-9 (1989).
9. The Gasohol Handbook.  
V. Daniel Hunt.  
Industrial Press. ISBN 0-8311-1137-2 (1981).

Home page

<script type="te