

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

"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

The presence of optical activity and the carbon isotopic ratios also indicate a biological origin.

There is another hypothesis that suggests crude oil is derived from methane from the earth's interior. The current main proponent of this biotic theory is Thomas Gold, however biotic and extraterrestrial origins for fossil fuels were also considered at the turn of the century, and were discarded then. A large amount of additional evidence for the biological origin of crude oil has accumulated since then.

4.2 When will we run out of crude oil?

It has been estimated that the planet contains over 6.4×10^{15} tons of organic carbon that is cycled through two major cycles, but only about 18% of that contributes to petroleum production. The primary cycle (turnover of $2.7\text{-}3.0 \times 10^{12}$ tons of organic carbon) has a half-life of days to decades, whereas the large secondary cycle (turnover 6.4×10^{15} tons of organic carbon) has a half-life of several million years

Much of this organic carbon is too dilute or inaccessible for current technology to recover, however the estimates represent centuries to millennia of fossil fuels, even with continued consumption at current or increased rates

The concern about "running out of oil" arises from misunderstanding the significance of a petroleum industry measure called the Reserves/Production ratio (R/P). This monitors the production and exploration interactions. The R/P is based on the concept of "proved" reserves of fossil fuels. Proved reserves are those quantities of fossil fuels that 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 proved reserves quantity divided by the production in the last year, and the result will be the length of time that those remaining proved reserves would last if production were to continue at the current level

It is important to note the economic and technology component of the definitions, as the price of oil increases (or new technology becomes available), marginal fields become "proved reserves". We are unlikely to "run out" of oil, as more fields become economic. Note that investment in exploration is also linked to the R/P ratio, and the world crude oil R/P ratio typically moves between 20-40 years, however specific national incentives to discover oil can extend that range upward. Concerned people often refer to the "Hubert curves" that predict fossil fuel discovery rates would peak and decline rapidly. M. King Hubert calculated in 1982 that the ultimate resource base of the lower 48 states of the USA was 163+-2 billion barrels of oil, and the ultimate production of natural gas to be 24.6+-0.8 trillion cubic meters, with some additional qualifiers. As production and proved resources were 147 billion barrels of oil and 22.5 trillion cubic meters of gas, Hubert was implying that volumes yet to be developed could only be 16-49 billion barrels of oil and 2.1-4.5 trillion cubic meters. Technology has confounded those predictions for natural gas. The US Geological Survey has also just increased their assessment of US (not just the lower 48 states), inferred reserves crude oil by 60 billion barrels, and doubled the size of gas reserves to 9.1 trillion cubic meters. When combined with the estimate of undiscovered oil and gas, the totals reach 110 billion barrels of oil and 30 trillion cubic meters of gas

When the 1995 USGS estimates of undiscovered and inferred crude oil are calculated for just the lower 48 states, they totaled (in 1995) 68.9 billion barrels of oil, well above Hauberk's highest estimate made in 1982. The current price for Brent Crude is approx. \$22/bbl. The world R/P ratio has increased from 27 years (1979) to 43.1 years (1993). The 1995 BP Statistical Review of World Energy provides the following data

Crude Oil Proved Reserves R/P Ratio Middle East 89.4 billion tons 93.4 years USA 3.8 9.8 years USA - 1995 USGS data 10.9 33.0 years Total World 137.3 43.0 years.

Coal Proved Reserves R/P Ratio USA 240.56 billion tons 247 years Total World 1,043.864 235 years.

Natural Gas Proved Reserves R/P Ratio USA 4.6 trillion cubic meters 8.6 years USA - 1995 USGS data 9.1 17.0 years Total World 141.0 66.4 years.

One billion = 1×10^9 .

One trillion = 1×10^{12} .

One barrel of Arabian Light crude oil = 0.158987 m³ and 0.136 tons. If the crude oil 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

4.3 What is the history of gasoline?

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 gasoline's on residential properties, so Charles F. Kettering modified an IC engine to run on kerosene. However the kerosene-fuelled engine would "knock" and crack the cylinder head and pistons. He assigned Thomas Midgley Jr. to confirm that the cause was from the kerosene droplets vaporizing on combustion as they presumed. Midgley demonstrated that the knock was caused by a rapid rise in pressure after ignition, not during pre-ignition as believed.

This then led to the long search for antiknock agents, culminating in tetra ethyl lead. Typical mid-1920s gasoline's were 40 - 60 Octane. Because sulfur in gasoline inhibited the octane-enhancing effect of the alkyl lead, the sulfur content of the thermally-cracked refinery streams for gasoline's was restricted. By the 1930s, the petroleum industry had determined that the larger hydrocarbon molecules (kerosene) 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. Octane ratings, lead levels, and vapor pressure increased, whereas sulfur content and olefins decreased. 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 gasoline's were slowly changed as lead was phased out, lead levels plummeted, octane's initially decreased, and then remained 2-5 numbers lower, vapor pressures continued to increase, and sulfur and olefins remained constant, while aromatics increased. In 1990, the US Clean Air Act started forcing major compositional changes on gasoline, resulting in plummeting vapor pressure and increasing oxygenate levels. These changes will continue into the 21st Century, because gasoline use in SI engines is a major pollution source. Comprehensive descriptions of the changes to gasoline's this century have been provided by L.M.Gibbs

The move to unleaded fuels continues worldwide, however several countries have increased the aromatics content (up to 50%) to replace the alkyl lead octane enhancers. These highly aromatic gasoline's can result in damage to elastomers and increased levels of toxic aromatic emissions if used without exhaust catalysts.

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 (oxidized) to form water (H₂O) or carbon dioxide (CO₂). If the combustion is not complete, carbon monoxide (CO) may be formed. As CO can be burnt to produce CO₂, it is also a fuel. The way the hydrogen and carbons hold hands determines which hydrocarbon family they belong to. If they only hold one hand they are called

"saturated hydrocarbons" because they can not absorb additional hydrogen. If the carbons hold two hands they are called "unsaturated hydrocarbons" because they can be converted into "saturated hydrocarbons" by the addition of hydrogen to the double bond.

Hydrogen's are omitted from the following, but if you remember

C = 4 hands,

H = 1 hand, and

O = 2 hands,

You can draw the full structures of most HCs. Gasoline contains over 500 hydrocarbons that may have between 3 to 12 carbons, and gasoline used to have a boiling range from 30C to 220C at atmospheric pressure. The boiling range is narrowing as the initial boiling point is increasing, and the final boiling point is decreasing, both changes are for environmental reasons. Detailed descriptions of structures can be found in any chemical or petroleum text discussing gasoline's.

4.5 What are oxygenates?

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

Most oxygenates used in gasoline's are either alcohol's (Cx-O-H) or ethers (Cx-O-Cy), and contain 1 to 6 carbons. Alcohol's have been used in gasoline's since the 1930s, and MTBE was first used in commercial gasoline's in Italy in 1973, and was first used in the US by ARCO in 1979. The relative advantages of aromatics and oxygenates as environmentally-friendly and low toxicity octane-enhancers are still being researched.

Ethanol C-C-O-H C₂H₅OH C |

Methyl tertiary butyl ether C-C-O-C C₄H₉OCH₃ (Aka tertiary butyl methyl ether) they can be produced from fossil fuels e.g.

Methanol (MeOH),

Methyl tertiary butyl ether (MTBE),

Tertiary amyl methyl ether (TAME), or from biomass,

Ethanol (EtOH),

Ethyl tertiary butyl ether (ETBE)).

4.5.1 MTBE

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. MTBE production has increased at the rate of 10 to 20% per year, and the spot market price in June 1993 was around \$270/tonne

4.5.2 Ether.

Ether starting fluids for vehicles are usually diethyl ether (liquid) or dimethyl ether (aerosol). Note that " petroleum ethers " are volatile alkane hydrocarbon fractions, they are not a Cx-O-Cy compound. Oxygenates are added to gasoline's to reduce the reactivity of emissions, but they are only effective if the hydrocarbon fractions are carefully modified to utilize 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. Oxygenates do not necessarily reduce all exhaust toxins, nor are they intended to.

4.5.3 EPA Involvement

Oxygenates have significantly different physical properties to hydrocarbons, and the levels that can be added to gasoline's are controlled by the 1977 Clean Air Act amendments in the US. With the laws prohibiting the increase or introduction of a fuel or fuel additive that is not substantially similar to any fuel or fuel additive used to certify 1975 or subsequent years vehicles. Waivers can be granted if the product does not cause or contribute to emission device failures, and if the EPA does not specifically decline the application after 180 days, it is taken as granted.

In 1978 the EPA granted 10% by volume of ethanol a waiver, and having subsequently issued waivers for <10 vol. % ethanol

(1982), 7 vol. % tertiary butyl alcohol

(1979), 5.5 vol. % 1:1 MeOH/TBA

(1979), 3.5 mass % oxygen derived from 1:1 MeOH/TBA = ~9.5 vol. % of the alcohol's.

(1981), 3.7 mass % oxygen derived from methanol and cosolvents = 5 vol. % max MeOH and 2.5 vol. % min cosolvent - with some cosolvents requiring additional corrosion inhibitor

(1985,1988), 7.0 vol. % MTBE

(1979), and 15.0 vol. % MTBE

(1988). Only the ethanol waiver was exempted from the requirement to still meet ASTM volatility requirements

In 1981 the EPA ruled that fuels could contain aliphatic alcohol's (except MeOH) and/or ethers at concentrations until the oxygen content is 2.0 mass %. It also permitted 5.5 vol. % of 1:1 MeOH/TBA.

In 1991 the maximum oxygen content was increased to 2.7 mass %. To ensure sufficient gasoline base was available for ethanol blending, the EPA also ruled that gasoline containing up to 2 vol. % of MTBE could subsequently be blended with 10 vol. % of ethanol.

Initially, the oxygenates were added to hydrocarbon fractions that were slightly-modified unleaded gasoline fractions, and these were known as "oxygenated" gasoline's.

In 1995, the hydrocarbon fraction was significantly modified, and these gasoline's are called "reformulated gasoline's" (RFGs), and there are differing specifications for California (Phase 2) and Federal (simple model) RFGs,

however both require oxygenates to provide Octane. The California RFG requires the hydrocarbon composition of the RFG to be significantly more modified than the existing oxygenated gasoline's to reduce unsaturates, volatility, benzene, and the reactivity of emissions. Federal regulations only reduce vapor pressure and benzene directly, however aromatics are also reduced to meet emissions criteria

4.5.4 Function of Oxygenates in gasoline.

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%)

and other researchers have observed similar reductions also occur when oxygenates are added to reformulated gasoline's on older and newer vehicles, but have also shown that NO_x levels may increase, as also may some regulated toxins.

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 combustion efficiency that oxygenates provide on some engines usually do not completely compensate for the oxygen. 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 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 stabilized radicals such as allyl and methyl allyl, as well as stable species such as allene, which resist further oxidation

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. 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 kerosene to prevent knock, as it was apparent that engine development was being hindered. The kerosene 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 "antiknock". A higher octane aviation gasoline was required urgently

once the US entered WWI, and almost every possible chemical (including melted butter) was tested for antiknock ability

Originally, iodine was the best antiknock 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 antiknock, 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. 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 gasoline's must only use one theory. This ensures there is no excess bromine that could react with the engine. The alkyl leads rapidly became the most cost-effective method of enhancing octane. The introduction was not universally acclaimed, as the toxicity of TEL soon became apparent, and several eminent public health officials campaigned against the widespread introduction of alkyl leads

4.6.2 Percent of TEL in Gasoline.

We should be careful retrospectively applying judgement to the 1920s, as the increased octane of leaded gasoline provided major gains in engine efficiency and lower gasoline prices. 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 gasoline's 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 in 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 For Catalytic Reformat Straight Run Naphtha. Lead g/l Research Octane 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 antiknocks 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 HO₂ is the most important radical species. Lead oxide, either as solid particles, or in the gas phase, reacts with HO₂ and removes it from the available radical pool, thereby deactivating the major chain branching reaction sequence that results in undesirable, easily-auto-ignitable hydrocarbons

By the 1960s, the nature the toxicity of the emissions from gasoline-powered engines was becoming of increasing concern and extensive comparisons of the costs and benefits were being performed. By the 1970s, the failure to find durable, lead-tolerant exhaust catalysts would hasten the departure of lead, as the proposed regulated emissions levels could not be economically achieved without exhaust catalysts. A survey in 1995 indicated that over 50 countries (20 in Africa) still permit leaded fuels containing 0.8g Pb/l, whereas the European maximum is 0.15 g Pb/l.

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 , but is approved for use in Canada and Australia. Recently the EPA ban was overturned, and MMT can be used up to 0.031gMn/US Gal in all states except California (where it remains banned). The EPA has stated it intends to review the whole MMT situation and , if evidence supports removing MMT, they will revisit banning MMT. Automobile manufacturers believe MMT reduces the effectiveness of the latest emission control systems . Canada also contemplated banning MMT because of the same concerns, as well as achieving fuel supply uniformity with the lower 48 states of the USA . MMT is more expensive than alkyl leads and has been reported to increase unburned hydrocarbon emissions and block exhaust catalysts .

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. Germany used

ironpentacarbonyl($\text{Fe}(\text{CO})_5$) at levels of 0.5% or less in gasoline during the 1930s. While its cost was low, one of its major drawbacks was that the carbonyl decomposed rapidly when the gasoline was exposed to light. Ironoxide (Fe_3O_4) also deposited on the spark plug insulator causing short circuits, and the precipitation of iron oxides in the lubricating oil also led to excessive wear rates .

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 contains hydrocarbons with carbon atoms between 3 and 10, 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), liquefied gases (LPG), butane, aviation and automotive gasoline's, aviation and lighting kerosene's, 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 feedstock's for gasoline's.

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.
- * Hydro-cracking - 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.

The changes to the US 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 (containing benzene and benzene precursors) 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 hydro-cracked) from catalytic cracker product.

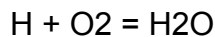
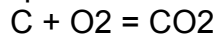
* Convert butane to isobutane or isobutylene for Alkylation or MTBE feed.

Some other countries are removing the alkyl lead compounds for health reasons, and replacing them with aromatics and oxygenates. If the vehicle fleet does not have exhaust catalysts, the emissions of some toxic aromatic hydrocarbons can increase. If maximum environmental and health gains are to be achieved, the removal of lead from gasoline should be accompanied by the immediate introduction of exhaust catalysts and sophisticated engine management systems,

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. The energy is released when the hydrogen and carbon are oxidized (burnt), to form water and carbon dioxide. 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 antiknock 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 [35].

Atomic masses used are:

Hydrogen = 1.00794,

Carbon = 12.011,

Oxygen = 15.994,

Nitrogen = 14.0067,

Sulfur = 32.066.

The composition of sea level air (1976 data, hence low CO₂ value) is

Gas Species	Fractional Volume	Molecular Weight kg/mole	Relative Mass
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N2	0.78084	28.0134	21.873983
O2	0.209476	31.9988	6.702981
Ar	0.00934	39.948	0.373114
CO2	0.000314	44.0098	0.013919
Ne	0.00001818	20.179	0.000365
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 C₇H₁₆ + 11O₂ = 7CO₂ + 8H₂O thus 1.000 kg of C₇H₁₆ requires 3.513 kg of O₂ = 15.179 kg of air.

The chemical stoichiometric combustion of hydrocarbons with oxygen can be written as:- C_xH_y + (x + (y/4))O₂ -> xCO₂ + (y/2)H₂O 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, where as maximum fuel economy is achieved at slightly lean.

The energy content of the gasoline is measured 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 vaporization, 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 as reported by API Project 45 using 60 octane base fuel, and the numbers in brackets are Blending Octane Numbers currently used for modern fuels. Typical Heats of Combustion are [36]:-

Fuel	State	Heat of Combustion MJ/kg	Research Octane	Motor 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* (111)	112* (94)

g 40.967
 2-methylbutene-2 44.720 176* (113) 141* (81)

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 cannot provide energy, they will have significantly lower energy contents. They are added to provide octane, not energy. For an engine that can be optimized 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 vaporize.

	Energy Content Nett MJ/kg	Heat of Vaporization MJ/kg	Oxygen Content 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 [37]:-

	Gross	Net
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
Liquefied petroleum gas	49.8	46.1
Aviation gasoline	46.0	44.0
Automotive gasoline	45.8	43.8
Kerosene	46.3	43.3
Diesel	45.3	42.5

Obviously, for automobiles, the Net calorific value is appropriate, as the water is emitted as vapor. The engine can not utilize the additional energy available when the steam is condensed back to water. The calorific value is the maximum energy that can be obtained from the fuel by combustion, but the reality of modern SI engines is that thermal efficiencies of only 20-40% may be obtained, this limit being due to engineering and material constraints that prevent optimum thermal conditions being used. CI engines can achieve higher thermal efficiencies, usually over a wider operating range as well. Note that combustion efficiencies are high, it is the thermal efficiency of the engine is low due to losses.

For a water-cooled SI engine with 25% useful work at the crankshaft, the losses may consist of 35% (coolant), 33% (exhaust), and 12% (surroundings).

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 pre-ignition) surfactants (prevent icing, improve vaporization, inhibit deposits, reduce NOx emissions) freezing point depressants (prevent icing) corrosion inhibitors (prevent gasoline corroding storage tanks) dyes (product color 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 than the injector deposits, in part because the 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 alcohol's 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. Intake valve deposits have also been shown to have significant adverse effects on emissions, and deposit control additives will be required to both reduce emissions and provide clean engine operation. A slightly 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 vapor phase to remove existing engine deposits without adversely affecting performance (as happens when water is poured into a running engine to remove carbon deposits). Chevron have also published data on the effectiveness of their additives, and successfully litigated to get Texaco to modify some of their claims. Most suppliers of quality Gasoline's will formulate similar additives into their products, and cheaper product lines are less likely to have such additives added. As different brands of gasoline use different additives and oxygenates, it is probable that important fuel parameters, such as octane distribution, are slightly 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 drivability is pathetic on the correct octane, try another brand. Remember that the

composition will change with the season, so if you lose derivability, try yet another brand. As various Clean Air Act changes are introduced over the next few years, gasoline will continue to change.

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. Major review papers on the carcinogenic, neurotic, reproductive and developmental toxicity of gasoline, additives, and oxygenates were presented, and interested readers should obtain the proceedings. The oxygenates are also being evaluated for carcinogenicity, and even ethanol and ETBE may be carcinogens. The introduction of oxygenated gasoline to Alaska and some other areas of the USA resulted in a range of complaints. Recent research has been unable to identify additional toxicity, but has detected increased levels of offensive smell. It should be noted that the oxygenated gasoline's were not initially intended to reduce the toxicity of emissions. The reformulated gasoline's will produce different emissions, and specific toxins must initially be reduced by 15% all year.

The removal of alkyl lead compounds certainly reduces the toxicity of exhaust gas emissions when used on engines with modern engine management systems and 3-way exhaust catalysts. If unleaded gasoline's are not accompanied by the introduction of catalysts, some other toxic emissions may increase. Engines without catalysts will produce increased levels of toxic carbonyls such as formaldehyde and acrolein when using oxygenated fuels, and increased levels of toxic benzene when using highly aromatic fuels.

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, and the relative hazards should always be kept in perspective. The major toxic risk from gasoline's comes from breathing the tailpipe, evaporative, and refueling emissions, rather than occasional skin contact from spills. Breathing vapors and skin contact should always be minimized.

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-importers with aromatic or olefin octane-importers without introducing exhaust catalysts. The aromatics contents may increase to around 40%, with high octane unleaded fuels reaching

50% in countries where oxygenates are not being used, and the producers have not reconfigured refineries to produce high octane paraffins. In general, aromatics are significantly more toxic than paraffins. Exhaust catalysts have a limited operational life, and will be immediately poisoned if misfueled with leaded fuel. Catalyst failure can result in higher levels of toxic emissions if catalysts or engine management systems are not replaced or repaired when defective. Maximum benefit of the switch to unleaded are obtained when the introduction of unleaded is accompanied by the introduction of exhaust catalysts and sophisticated engine management systems.

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, as leaded fuels typically contain around 30-40% aromatics. Other toxins and pollutants that are usually reduced by exhaust catalysts will be emitted at significantly higher levels if leaded fuels are used.

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 [55]. Alkyl lead additives can only substitute for some of the aromatics in gasoline, consequently they do not eliminate aromatics, which will produce benzene emissions [56]. Alkyl lead additives also require toxic organohalogen scavengers, which also react in the engine to form and emit other organohalogens, including highly toxic dioxin [57]. 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.

4.16 Is reformulated gasoline more toxic than unleaded?

The evidence so far indicates that the components of reformulated gasoline's (RFGs) are more benign than unleaded, and that the tailpipe emissions of hydrocarbons are significantly reduced for cars without catalysts, and slightly reduced for cars with catalysts and engine management systems. The emissions of toxic carbonyls such as formaldehyde, acetaldehyde and acrolein are increased slightly on all vehicles, and the emission of MTBE is increased about 10x on cars without catalysts and 4x on cars with catalysts. When all the emissions (evaporative and tailpipe) are considered, RFGs significantly reduce emissions of hydrocarbons, however the emissions of carbonyls and MTBE may increase. There has been an extensive series of reports on the emissions from RFGs, produced by the Auto/Oil Air Quality Improvement Research Program, who measured and calculated the likely effects

of RFG. More research is required before a definitive answer on toxicity is available.

The major question about RFGs is not the toxicity of the emissions, but whether they actually meet their objective of reducing urban pollution. This is a more complex issue, and most experts agree the benefits will only be modest.

4.17 Are all oxygenated gasoline's also reformulated gasoline's?

No. Oxygenates were initially introduced as alternative octane-enhancers in the 1930s, and are still used in some countries for that purpose. In the US the original "oxygenated gasoline's" usually had a slightly-modified gasoline as the hydrocarbon fraction. The US EPA also mandated their use to reduce pollution, mainly via the "enleanment" effect on engines without sophisticated management systems, but also because of the "aromatics substitution" effect. As vehicles with fuel injection and sophisticated engine management systems became pervasive, reformulated gasoline's could be introduced to further reduce pollution. The hydrocarbon component of RFGs is significantly different to the hydrocarbon fraction in earlier oxygenated gasoline's, having lower aromatics contents, reduced vapor pressure, and a narrower boiling range. RFGs do contain oxygenates as the octane-enhancer, but have different hydrocarbon composition profiles.

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, refueling emissions). The volatile organic carbon (VOC) emissions from these sources, along with nitrogen oxides (NOx) emissions from the tailpipe, will react in the presence of ultraviolet (UV) light (wavelengths of less than 430nm) to form ground-level (troposphere) ozone, which is one of the major components of photochemical smog . Smog has been a major pollution problem ever since coal-fired power stations were developed in urban areas, but 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 CO₂ that is added to the atmospheric burden. The effect of the additional CO₂ 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_x, SO_x, 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. The issue is whether it is natural, or induced by human activities and a large panel of scientific experts continues to review scientific data and models. Interested reader should seek out the various publications of the Intergovernmental Panel on Climate Change (IPCC). There are international agreements to limit CO₂ emissions 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.

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 vapor 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 drivability 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 gasoline's 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 gasoline's 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 gasoline's were introduced during 1970 to supplement the conventional gasoline's 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 gasoline's that would not adversely affect such catalytic devices has led to the large scale availability and growing use of unleaded gasoline's, with all late-model cars requiring unleaded gasoline.

There was a further reason why alkyl lead compounds were subsequently 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.

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 refueling, 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. 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 also attack evaporative and tailpipe emissions.

The health risks to service station workers, who are continuously exposed to refueling emissions remain a concern. Vehicles will soon be required to trap the refueling emissions in larger carbon canisters, as well as the normal evaporative emissions that they already capture. This recent decision went in favor 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 vapors, 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, but carbon canister systems can reduce evaporative emissions by 95% from uncontrolled levels.

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.

Tuning a carburetor 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 systems and fuel injection systems have developed, the volatility properties of the gasoline have been tuned to minimize 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 unburnt hydrocarbon emissions are related to the fuel composition (volatility, olefins, aromatics, final boiling point), as well as state of tune, engine condition, and condition of the engine lubricating oil. Particulate emissions, especially the size fraction smaller than ten micrometers, are a serious health concern. The current major source is from compression ignition (diesel) engines, and the modern SI engine system has no problem meeting regulatory requirements.

The ability of reformulated gasoline's 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 1/1/1998 Complex model specifications, that are based on several major ongoing government/industry gasoline and emission research programs, are more likely to provide unambiguous environmental improvements. One of the major problems is the nature of the ozone-forming reactions, which require several components (VOC, NOx, UV) to be present. Vehicles can produce the first two, but the their ratio is important, and can be affected by production from other natural (VOC = terpenes from conifers) or manmade (NOx from power stations) sources. The regulations for tailpipe emissions will continue to become more stringent as countries try to minimize local problems (smog, toxins etc.) and global problems (CO2). Reformulation does not always lower all emissions, as evidenced by the following aldehydes from an engine with an adaptive learning management system].

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.

FTP-weighted emission rates. (mg/mi)	
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 some compounds listed as toxics under the Clean Air Act, then the beneficial effects of catalysts are obvious. Note that hexane and iso-octane are the only alkanes listed as toxics, but benzene, toluene, ethyl benzene, o-xylene, m-xylene, and p-xylene are aromatics that are listed. The latter four are combined as C8 Aromatics below.

Aromatics	FTP-weighted emission rates. (mg/mi)					
	Benzene		Toluene		C8 Aromatics	
	Gas	Reform	Gas	Reform	Gas	Reform
Noncatalyst	156.18	138.48	338.36	314.14	425.84	380.44
Oxidation Cat.	27.57	25.01	51.00	44.13	52.27	47.07
3-way Catalyst	19.39	15.69	36.62	26.14	42.38	29.03
Adaptive Learn.	19.77	20.39	29.98	29.67	35.01	32.40

Aldehydes	FTP-weighted emission rates. (mg/mi)					
	Formaldehyde		Acrolein		Acetaldehyde	
	Gas	Reform	Gas	Reform	Gas	Reform
Noncatalyst	73.25	85.24	11.62	13.20	19.74	21.72
Oxidation Cat.	28.50	35.83	3.74	3.75	11.15	11.76
3-way Catalyst	7.27	7.61	1.11	0.74	4.43	3.64
Adaptive Learn.	4.87	8.43	0.81	1.16	3.07	4.71

Others	1,3 Butadiene		MTBE	
	Gas	Reform	Gas	Reform
	Noncatalyst	2.96	1.81	10.50
Oxidation Cat.	0.02	0.33	2.43	11.83
3-way Catalyst	0.07	0.05	1.42	4.59
Adaptive Learn.	0.00	0.14	0.84	3.16

The author reports analytical problems with the 1,3 Butadiene, and only Noncatalyst values are considered reliable. Other studies from the Auto/Oil research program indicate that lowering aromatics and olefins reduce benzene but increase formaldehyde and acetaldehyde.

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 (0.015g/mi.) and particulates (0.08g/mi), are omitted. The 1994 tests signal the federal transition from 50,000 to 100,000 mile compliance testing, and I have not listed the subsequent 50,000 mile limits.

Year	Federal			
	HCs g/mi	CO g/mi	NOx g/mi	Evap g/test
		+4.1		Before regs
add crankcase				
1966	6.3	51.0	6.0	
1968	6.3	51.0	6.0	
1970	4.1	34.0	4.1	34.0
1971	4.1	34.0	4.1	34.0
1972	3.0	28.0	4.0	
1973	3.0	28.0	3.0	
1974	3.0	28.0	3.0	
1975	1.5	15.0	3.1	2
1977	1.5	15.0	2.0	2
1980	0.41	7.0	2.0	6(SHED)
1981	0.41	3.4	1.0	2
1993	0.41	3.4	1.0	2
1994 50,000	0.26	3.4	0.3	2
1994 100,000	0.31	4.2	0.6	2
1997 LEV	0.08	3.4	0.2	
1997 ULEV	0.04	1.7	0.2	
1998 ZEV	0.0	0.0	0.0	0
2004		0.0		

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 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. 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.

Using the estimated fuel consumption, and about 10m³ of exhaust gas per liter of gasoline, the emissions are 2-40 Ng/km. These are 2-3 orders of magnitude lower than earlier reported work on palletized 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?

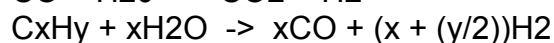
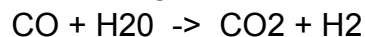
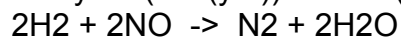
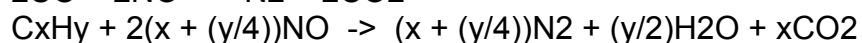
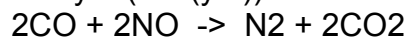
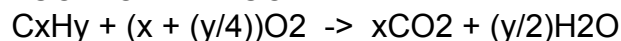
Modern adaptive learning engine management systems control the combustion stoichiometry by monitoring various ambient and engine parameters, including exhaust gas recirculation rates, the air flow sensor, and exhaust oxygen sensor outputs. This closed loop system using the oxygen sensor can compensate for changes in fuel content and air density. The oxygen sensor is also known as the lambda sensor because the actual air-fuel mass ratio divided by the stoichiometric air-fuel mass ratio is known as lambda or the air-fuel equivalence ratio.

The preferred technique for describing mixture strength is the fuel-air equivalence ratio (ϕ), which is the actual fuel-air mass ratio divided by the stoichiometric fuel-air mass ratio, however most enthusiasts use air-fuel ratio and lambda. Lambda is the inverse of the fuel-air equivalence ratio. The oxygen sensor effectively measures lambda around the stoichiometric mixture point. Typical stoichiometric air-fuel ratios are.

- 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 oxidizes about 80% of the H₂, CO, and HCs, and reduces the NO_x [76].

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%, was shown to increase formaldehyde by 45%, but testing in later model cars did not exhibit the same effect. This demonstrates that continuing changes to engine management system scan also change the response to fuel composition changes.

The requirement that the exhaust catalysts must now endure for 10 years or 100,000 miles will also encourage auto-makers to push for lower levels of elements that affect exhaust catalyst performance, such as sulfur and phosphorus, in both the gasoline and lubricant. Modern catalysts are unable to reduce the relatively high levels of NOx 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 auto-makers to move the fuel combustion towards the lean side, and different gasoline properties may be required to optimize the combustion and reduce pollution. Mazda claim that fuel efficiency is improved by 5-8%, while meeting all emission regulations, and some Japanese manufacturers have evaluated lean-burn catalysts in limited numbers of 1995 production models.

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, reducing available catalyst and thus increasing 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 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.

Reduced gasoline volatility and composition changes, along with cleanliness additives and engine management systems, can help minimize 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.

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

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. 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 gasoline's will enable the IC engine to continue well into the 21st century as the prime motive force for personal transportation. There have also been calls to use market forces to reduce pollution from automobiles, however most such suggestions (increased gasoline taxes, congestion tolls, and emission-based registration fees) are currently considered politically unacceptable. The issue of how to target the specific "gross polluters" is being considered, and is described in Section 5.14.

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.

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. 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, and aromatics has resulted in whole new families of compounds (ethers, alcohol's) 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 unraveled, the chemical precursors to toxic tailpipe emissions (such as higher aromatics that produce benzene emissions) are also controlled, even if they are not themselves toxic.

5.10 What does "renewable" fuel or oxygenate mean?

The general definition of "renewable" is that the carbon originates from recent biomass, and thus does not contribute to the increased CO₂ emissions. A truly "long-term" view could claim that fossil fuels are "renewable" on a 100 million year time scale. . There was 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. On 28 April 1995 a Federal appeals court permanently voided the EPA ruling requiring "renewable" oxygenates, thus fossil-fuel derived oxygenates such as MTBE are acceptable oxygenates.

Unfortunately, "renewable" ethanol is not cost competitive with crude oil. Ethanol and ETBE derived from ethanol, are still likely to be used in states where subsidies make them competitive with other oxygenates.

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 such as exhaust valve seat recession may 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 derivability and emissions problems occurred. Most reputable brands are now carefully formulated. Some older activated carbon canisters may not function efficiently with oxygenated gasoline's, 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 derivability.

Be prepared to try several different brands of oxygenated or reformulated gasoline's 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 aromatic and olefin content of the fuels. Cars later than 1990 should not experience compatibility problems, and cars later than 1994 should not experience derivability 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_x, and particulate contents. With the introduction of oxygenates and reformulated gasoline's, 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_x, 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 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 carboxylic acids can corrode metals. The emission of carbonyls can be controlled by combustion stoichiometry and exhaust catalysts, refer to section 5.5 for typical reductions for aldehydes.

Typical carbonyls are:-

- Aldehydes (containing -CHO),
 - Formaldehyde (HCHO) - which is formed in large amounts during lean combustion of methanol.
 - Acetaldehyde (CH₂CHO) - which is formed during ethanol combustion.
 - Acrolein (CH₂=CHCHO) - a very potent irritant and toxin.
- Ketones (containing C=O),
 - Acetone (CH₃COCH₃)
- Carboxylic acids (containing -COOH),
 - Formic acid (HCOOH) - formed during lean methanol combustion.
 - Acetic acid (CH₃COOH).

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. 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. There has recently been some unpublished studies that demonstrate that the current generation of remote sensing systems can not provide sufficient discrimination of gross polluters without also producing false positives for some acceptance vehicles - more work is required, and in some states I&M emissions testing using dynamometers is being introduced to identify gross polluters.

The most famous of the remote sensing systems is the FEAT (Fuel Efficiency Automobile Test) team from the University of Denver. This team is probably the world leader in remote sensing of auto emissions to identify grossly polluting vehicles. The system measures CO/CO₂ ratio, and the HC/CO₂ 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 license plate, date, time, calculated exhaust CO, CO₂, 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 invited to Provo, Utah to monitor vehicles, and gross polluters would be offered free repairs. 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.

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

Model year	Grams CO/gallon Vehicles	Number of Vehicles
92	40	247
91	55	1222
90	75	1467
89	80	1512
88	85	1651
87	90	1439
86	100	1563
85	120	1575
84	125	1206
83	145	719
82	170	639
81	230	612
80	220	551
79	350	667
78	420	584
77	430	430
76	770	317
75	760	163
Pre 75	920	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. No matter what changes are 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.

Thus, identifying and repairing or removing gross polluters can be far more cost-effective than playing around with reformulated gasoline's and oxygenates. A recent study has confirmed that gross polluters are not always older vehicles, and that vehicles have been scrapped that passed the 1993 new vehicle emission standards. The study also confirmed that if estimated costs and benefits of various emission reduction strategies were applied to the tested fleet, the identification and repair techniques are the most cost-effective means of reducing HC and CO. It should be noted that some strategies (such as the use of oxygenates to replace aromatics and alkyl lead compounds) have other environmental benefits.

Subject 6.0 Octane.

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 engine's. "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. They used a Dobbie-McInnes monograph to demonstrate that the knock did not arise from pre-ignition, as was commonly supposed, but arose from a violent pressure rise *after* ignition. The monograph 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. 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 1927 Graham Edgar suggested using two hydrocarbons that could be produced in sufficient purity and quantity. 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 we call it " iso-octane " or 2,2,4-trimethyl pentane. The octane had a high antiknock value, and he suggested using the ratio of the two as a reference fuel number. He demonstrated that all the commercially- available gasoline's 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	Heat of Boiling Point	Density	
Vaporization	C	C	g/ml	
MJ/kg				
normal heptane @ 25C	-90.7	98.4	0.684	0.365
ISO octane @ 25C	-107.45	99.3	0.6919	0.308

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 auto-ignite before the flame front arrives, knock will occur.

Simply put, the octane rating of the fuel reflects the ability of the unburnt end gases to resist spontaneous auto-ignition under the engine test conditions used. If auto-ignition occurs, it results in an extremely rapid pressure rise, as both the desired spark-initiated flame front, and the undesired auto-ignited 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 saw-tooth pattern of pressure oscillations that create the "knocking" sound.

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

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 auto-ignite before the flame-front arrives. Different reaction mechanisms, occurring at various stages of the pre-flame compression stroke, are responsible for the undesirable, easily-auto-ignitable, 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 HO₂), 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.

The octane rating of hydrocarbons is determined by the structure of the molecule, with long, straight hydrocarbon chains producing large amounts of easily-auto-ignitable 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 compression 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 HO₂ 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.

The addition of additives such as alkyl lead and oxygenates can significantly affect the pre-flame reaction pathways. Antiknock 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.

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

1. The energy content of fuel, this should be obvious, as oxygenates have lower energy contents, but high octanes.
2. 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.

The initial knock measurement methods developed in the 1920s resulted in a diverse range of engine test methods and conditions, many of which have been summarized by Campbell and Boyd. In 1928 the Co-operative Fuel Research Committee formed a sub-committee to develop a uniform knock-testing apparatus and procedure. They settled on a single-cylinder, valve-in-head, water-cooled, variable compression engine of 3.5"bore and 4.5" stroke. The knock indicator was the bouncing-pin type. They selected operating conditions for evaluation that most closely match the current Research Method, However correlation trials with road octane's in the early 1930s exhibited such large discrepancies that conditions were changed (higher engine speed, hot mixture temperature, and defined spark advance profiles), and a new tentative ASTM Octane rating method was produced. This method is similar to the operating conditions of the current Motor Octane procedure. Over several decades, a large number of alternative octane test methods appeared. These were variations to either the engine design, or the specified operating conditions. During the 1950-1960s attempts were made to internationally standardize and reduce the number of Octane Rating test procedures.

During the late 1940s 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 auto-makers 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.

The design of the engine and vehicle significantly affect the fuel octane requirement for both RON and MON. In the 1930s, most vehicles would have been sensitive to the Research Octane of the 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 changes of one RON is matched by an equal and opposite change of MON. I should note that the Research method was only formally approved in 1947, but used unofficially from 1942.

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 [104]
Engine	Cooperative Fuels Research (CFR)
Engine RPM	900 RPM
Intake air temperature	38 C
Intake air humidity	3.56 - 7.12 g H ₂ 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)
Carburetor 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 [105]
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 ₂ O / kg dry air
Intake mixture temperature.	Not specified
Coolant temperature.	100 C
Oil Temperature.	57 C
Ignition Advance - fixed .	13 degrees BTDC
Carburetor 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 recommended to have an 82+ MON, thus preventing very high sensitivity fuels. Recent changes in European gasoline's has caused concern, as high sensitivity unleaded fuels have been found that fail to meet the 85 MON requirement of the EN228 European gasoline specification.

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 cm³. 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 carburetor that can adjust individual bowl air-fuel ratios. This facilitates rapid switching between reference fuels and samples. A magnet orestrictive 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 [104,105]. 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 carburetor 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. 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.

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.

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 characterized, but it can be a major problem for the new, reformulated, low aromatic gasoline's, 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 behavior 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. 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. The difference between these is the delta RON (100C), usually just called the delta RON. The delta RON ratings are not particularly relevant to engines with injectors, and are not used in the US.

6.12 How do other fuel properties affect octane?

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 carburetor icing and increased evaporative emissions. Final Boiling Point, Decreases in the final boiling point increase fuel octane. Aviation gasoline's

have much lower final boiling points than automotive gasoline's. Note that final boiling points are being reduced because the higher boiling fractions are responsible for disproportionate quantities of pollutants and toxins. Pre-ignition tendency - both knock and pre-ignition can induce each other.

6.13 Can higher octane fuels give me more power?

On modern engines with sophisticated engine management systems, the engine can operate efficiently on fuels of a wider range of octane rating, but there remains an optimum octane for the engine under specific driving conditions. Older cars without such systems are more restricted in their choice of fuel, as the engine can not automatically adjust to accommodate lower octane fuel. Because knock is so destructive, owners of older cars must use fuel that will not knock under the most demanding conditions they encounter, and must continue to use that fuel, even if they only occasionally require the octane.

If you are already using the proper octane fuel, you will not obtain more power from higher octane fuels. The engine will be already operating at optimum settings, and a higher octane should have no effect on the management system. Your drivability 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 drivability.

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 realizing 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, as 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 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. Run-on is the tendency of an engine to continue running after the ignition has been switched off, and is

discussed in more detail in Section 8.2. 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 for most commercial gasoline's. 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 some oxygenates can have negative lead responses. 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. Will be losing both money and derivability. 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 utilize. The additive packages are matched to the engines using the fuel, for example intake valve deposit control additive concentrations may be increased in the premium octane grade. your vehicle does not have a knock sensor, then using a fuel with an octane rating significantly below the octane requirement of the engine 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 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 derivability 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 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). Refer to section 6.20 for a discussion on naphthalene (mothballs). It is preferable to purchase a higher octane fuel such as racing fuel, aviation gasoline's, 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 gasoline's were all highly leaded and graded using two numbers, with common grades being 80/87, 100/130, and 115/145. The first number is the Aviation rating (aka Lean Mixture rating), and the second number is the Supercharge rating (aka Rich Mixture rating). In the 1970s a new grade, 100 LL (low lead = 0.53mITEL/L instead of 1.06mITEL/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. 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 converted to an Aviation Number using a table in the method. Aviation

Numbers below 100 are Octane numbers, while numbers above 100 are Performance numbers. There is usually only 1 - 2 Octane units different to the Motor value up to 100, but Performance numbers varies significantly above that eg 110 MON = 128 Performance number.

The second Av gas 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 utilize 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.

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

6.20 Can mothballs increase octane?

The legend of mothballs as an octane enhancer arose well before WWII when naphthalene was used as the active ingredient. Today, the majority of mothballs use para-dichlorobenzene in place of naphthalene, so choose carefully if you wish to experiment). There have been some concerns about the toxicity of para-dichlorobenzene, and naphthalene mothballs have again become popular. In the 1920s, typical gasoline octane ratings were 40-60, and during the 1930s and 40s, the ratings increased by approximately 20 units as alkyl leads and improved refining processes became widespread].

Naphthalene has a blending motor octane number of 90 [52], so the addition of a significant amount of mothballs could increase the octane, and they were soluble in gasoline. The amount usually required to appreciably increase the octane also had some adverse effects. The most obvious was due to the high melting point (80C), when the fuel evaporated the naphthalene would precipitate out, blocking jets and filters. With modern gasoline's, naphthalene is more likely to reduce the octane rating, and the amount required for low octane fuels will also create operational and emissions problems.

Subject: 7. What parameters determine octane requirement?

7.1 What is the Octane Number Requirement of a Vehicle?

The actual octane requirement of a vehicle is called the Octane Number Requirement (ONR), and is determined by using series of standard octane fuels that can be blends of iso-octane and normal heptane (primary reference), or commercial gasoline's (full-boiling reference). In Europe, delta RON (100C) fuels are also used, but seldom in the USA. The vehicle is tested under a wide range of conditions and loads, using decreasing octane fuels from each series until trace knock is detected. The conditions that require maximum 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, which are usually performed on chassis dynamometers. Engine management systems that adjust the octane requirement may also reduce the power output on low octane fuel, resulting in increased fuel consumption, and adaptive learning systems have to be preconditioned prior to testing. The maximum ONR is of most interest, as that usually defines the recommended fuel, however it is recognized that the general public seldom drive as severely as the testers, and so may be satisfied by a lower octane fuel.

7.2 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 standard equation

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

Where γ = 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 for gasoline fuels in an SI engine.

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 carbureted engine, without engine management.

Compression Ratio	Octane Number Requirement	Brake Thermal Efficiency (Full Throttle)
5:1	72	-
6:1	81	25 %
7:	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.

7.3 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 air-fuel 12-13:1 (Rich), nor maximum thermal efficiency - which occurs around air-fuel 16-18:1 (Lean). The air-fuel ratio is controlled at part throttle by a 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 derivability. An average increase of 2 (R+M)/2 ON is required for each 1.0 increase (leaning) of the air-fuel ratio. 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.

7.4 What is the effect of changing the ignition timing?

The tendency to knock increases as spark advance is increased. For an engine with recommended 6 degrees BTDC (Before Top Dead Center) timing and 93 octane fuel, retarding the spark 4 degrees lowers the octane requirement to 91, whereas advancing it 8 degrees requires 96 octane fuel. It should be noted this requirement depends on engine design. 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 auto-igniting 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 auto-ignite, 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 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 BTDC.

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
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.

7.5 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.

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 alcohol's such as methanol can confuse the engine management system as they generate more hydrogen which can fool the oxygen sensor.

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 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.

7.6 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. Increasing the water jacket temperature from 71C to 82C, increases the $(R+M)/2$ ONR by two.

7.7 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.

7.8 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. 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 catalyze undesirable pre-flame reactions that produce end gases with low - temperatures.

7.9 What is the Road Octane Number of a Fuel?

The CFR 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 Union Town 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 trace knock ignition timing setting is read from the graph to provide the Road Octane Number. This is a rapid procedure but provides minimal information, and cars with engine management systems require sophisticated electronic equipment to adjust the ignition timing.

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 Union town Procedure, however trace knock is maintained throughout the run by adjustment of the spark advance. 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, however the technique is almost impossible to perform on vehicles with modern management systems.

The Road Octane Number lies between the MON and RON, and the difference between the RON and the Road Octane number is called 'depreciation'. Because nominally-identical new vehicle models display octane requirements that can range over seven numbers, a large number of vehicles have to be tested.

7.10 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. 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.

7.11 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. Other studies report the octane number requirement decreased by 1.0 - 1.9 RON/300m without specifying altitude. Modern engine management systems can accommodate this adjustment, and in some recent studies, the octane number requirement was reduced by 0.2 - 0.5 (R+M)/2 per 300m increase in altitude.

The larger 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.

7.12 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.

7.13 What does water injection achieve?.

Water injection, as a separate liquid or emulsion with gasoline, or as a vapor, has been thoroughly researched. If engines can be calibrated to operate with small amounts of water, knock can be suppressed, hydrocarbon emissions will slightly increase, NOx emissions will decrease, CO does not change significantly, and fuel and energy consumption are increased.

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 NOx by 25%. A decrease in combustion temperature will reduce the 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 vaporization, 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.

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 up rating 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.

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 neighborhood 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 (although the effect on well tuned engines is only 2-4%).

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.

Pre-ignition 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 pre-ignition 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 antiknock ability and pre-ignition tendency, however high combustion chamber temperatures favor both, and so one may lead to the other. An engine knocking during high-speed operation will increase in temperature and that can induce pre-ignition, and conversely any pre-ignition 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.PbSO₄; 3Pb₃(PO₄)₂.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 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. Obviously, engines with fuel injection systems do not have the problem, and idle speed is an important factor. Later model carburetors have an idle stop solenoid which partially closes the throttle blades when the ignition key was off, and thus (if set correctly) prevents run-on.

8.3 Can I prevent carburetor icing?

Yes, carburetor 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 vaporized gasoline in the carburetor, can be as much as 20C, perhaps dropping below the dew point of the charge. If this happens, water will condense on the cooler carburetor 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. In the US, anti-icing additives are seldom required because of the widespread use heated intake air and fuel injection.

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. Alcohol's (methanol, iso-propyl alcohol, etc) and glycol's (hexylene glycol, dipropylene glycol) are used at concentrations of 0.03% - 1%.

If you have icing problems, the addition of 100-200mls of alcohol to a full tank of dry gasoline will prevent icing under moderately-cold conditions. If you believe there is a small amount of water in the fuel tank, add 500mls of anhydrous isopropyl alcohol as the first treatment, and isopropyl alcohol is also preferred for more severe conditions. Oxygenated gasoline's using alcohol's can also be used. It's important to ensure the alcohol is anhydrous, as some grades contain up to 30% water.

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 drivability 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 drivability, providing the engines in reasonable condition.

8.5 Can I improve fuel economy by using quality gasoline's?

Yes, several manufacturers have demonstrated that their new gasoline additive packages are more effective than traditional gasoline formulations. Texaco claimed their new vapor-phase fuel additive can reduce existing deposits by up to 30%, improve fuel economy, and reduce NOx tailpipe emissions by 15%, when compared to other advanced liquid phase additives. The advertising claims have been successfully disputed in court by Chevron - who demonstrated that their existing fuel additive already offered similar benefits. Other reputable gasoline manufacturers will have similar additive packages in their premium quality gasoline's. Quality gasoline's, of whatever octane ratings, will include a full range of gasoline additives designed to provide consistent fuel quality.

Note that oxygenated gasoline's must decrease fuel economy for the same power. If your engine is initially well-tuned on hydrocarbon gasoline's, 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 catalyzing 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, but the blended fuel should be used immediately, otherwise the old fuel will catalyze rapid decomposition of the new, resulting in even larger quantities of stale fuel. 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 liter 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 drivability.

Water in fuel tanks can be minimized 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 gasoline's 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 lead, which lubricated the valve seat, causes the very hard oxidation products of the exhaust valve to wear down the seat. This valve seat recession is usually corrected by installing seat inserts, hardening the seats, or use of specific valve seat recession protection additives (such as Valve master). 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 gasoline's. If premium unleaded petrol containing relatively high levels of aromatics is used, some carburetor engines from the 1960s may experience spark plug fouling, however most vehicle manufacturers have guides to ensure careful engine tuning will eliminate most of the problem.

8.9 How serious is valve seat recession on older vehicles?

The amount of exhaust valve seat recession is very dependent on the load on the engine. There have been several major studies on valve seat recession, and they conclude that most damage occurs under high-speed, high-power conditions. Engine load is not a primary factor in valve seat wear for moderate operating conditions, and low to medium speed engines under moderate loads do not suffer rapid recession, as has been demonstrated on fuels such as CNG and LPG. Under severe conditions, damage occurs rapidly, however there are significant cylinder-to-cylinder variations on the same engine.

A 1970 engine operated at 70 mph conditions exhibited an average 1.5mm of seat recession in 12,000 km. The difference between cylinders has been attributed to different rates of valve rotation, and experiments have confirmed that more rotation does increase the recession rate. The mechanism of valve seat wear is a mixture of two major mechanisms. Iron oxide from the combustion chamber surfaces adheres to the valve face and becomes embedded. These hard particles then allow the valve act as a grinding wheel and cut into the valve seat . The significance of valve seat recession is that should it occur to the extent that the valve does not seat, serious engine damage can result from the localized hot spot.

There are a range of additives, usually based on potassium, sodium or phosphorus that can be added to the gasoline to combat valve seat recession. As phosphorus has adverse effects on exhaust catalysts, it is seldom used. The best long term solution is to induction harden the seats or install inserts, usually when the head is removed for other work, however additives are routinely and successfully used during transition periods.

Section: 9. Alternative Fuels and Additives

9.1 Do fuel additives work?

Most after market 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 after-market additive that may be cost-effective, the lubricity additive used with unleaded gasoline's to combat exhaust valve seat recession on engines that do not have seat inserts. This additive may be routinely added during the first few years of unleaded by the gasoline producers, but in the US this could not occur because they did not have EPA waivers, and also may be incompatible with 2-stroke engine oil additives and form a gel that blocks filters. The amount of recession is very dependent on the engine design and driving style. The long-term solution is to install inserts, or have the seats hardened, 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, and have often been subjected to decades-long evaluation and use.

A typical gasoline may contain.

- **Oil-soluble Dye**, initially added to leaded gasoline at about 10 ppm to prevent its misuse as an industrial solvent, and now also used to identify grades of product.
- **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**, 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 carburetor 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. Carburetor 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 carburetors.
 2. Fuel Injector tips operate about 100C, and deposits form in the annulus during hot soak, mainly from the oxidation and polymerization of the larger unsaturated hydrocarbons. The additives that prevent and unclog these tips are usually polybutene succinimides or poly-ether amines.
 3. Intake Valve Deposits caused major problems in the mid-1980s when some engines had reduced derivability 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 vapor, 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 alcohol's. 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 vapor phases to remove existing deposits that have resulted from the use of other additives, and prevent deposit formation. Note that these additives can not remove all deposits, just those resulting from the use of additives.

5. 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 octane's such as aromatics and olefins. These hydrocarbons are now being replaced by a mixture of saturated hydrocarbons and oxygenates.

6. 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 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 gasoline's have been shown to improve engine performance significantly. The new generation of additive packages for gasoline's include components that will dissolve existing carbon deposits, and have been shown to improve fuel economy, NOx emissions, and drivability. While there may be some disputes amongst the various producers about relative merits, it is quite clear that premium quality fuels do have superior additive packages that help to maintain engine condition,

9.3 What are the advantages of alcohol's 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 photo chemically-active emissions. Most vehicle manufacturers favored the use of liquid fuels over compressed or liquefied gases. The alcohol fuels have high research octane ratings, but also high sensitivity and high latent heats.

	Methanol	Ethanol	Unleaded Gasoline
RON	106	107	92 - 98
MON	92	89	80 - 90
Heat of Vaporization (MJ/kg)	1.154	0.913	0.3044
Nett Heating Value (MJ/kg)	19.95	26.68	42 - 44
Vapor 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
Auto-ignition 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 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.

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

CNG (Compressed Natural Gas) are usually around 70-90% methane with 10-20% ethane, 2-8% propane's, 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, SOx, and NOx, and the lean misfire limit is extended. 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 liter 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. Concerns about the safety of CNG have proved to be unfounded.

CNG has been extensively used in Italy and New Zealand (NZ had 130,000 dual-fuelled vehicles with 380 refueling stations in 198). 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 derivability 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 derivability 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 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 optimized (CR 12:1) for LPG, in which case there is no decrease in power or increase in fuel consumption. There have been several studies that have compared the relative advantages of CNG and LPG, and often LPG has been found to be a more suitable transportation fuel.

	methane	propane	iso-
octane			
RON	120	112	100
MON	120	97	100
Heat of Vaporization (MJ/kg)	0.5094		0.4253
0.2712			
Net Heating Value (MJ/kg)	50.0	46.2	44.2
Vapor 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			
Auto-ignition Temperature (C)	540 - 630		450
415			

9.5 Why are hydrogen-powered cars not available?

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 auto-ignition 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.

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 narrow inlet valve openings and cause back flash. This can be mitigated by the induction of fine mist of water, which also has the benefit of increasing thermal efficiency (although the water lowers the combustion

Temperature), the phase change creates voluminous gases that increase pressure and reduce NOx. An alternative technique is to use direct cylinder induction, which injects hydrogen once the cylinder has filled with an air charge, and because the volume required is so large, modern engines have two inlet valves, one for hydrogen and one for air. The advantage of a wide range of mixture strengths and high thermal efficiencies are matched by the disadvantages of pre-ignition and knock unless weak mixtures, clean engines, and cool operation are used.

9.6 What are "fuel cells" ?

Fuel cells are electrochemical cells that directly oxidize 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 net 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.

9.7 What is a "hybrid" vehicle?

A hybrid vehicle has three major systems.

1. A primary power source, either an IC engine driven generator where the IC engine only operates in the most efficient part of its performance map, or alternatives such as fuel cells and turbines.
2. A power storage unit, which can be a flywheel, battery, or ultra capacitor.
3. A drive unit, almost always now an electric motor that can be 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 derivability 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?

9.8.1 Ammonia (NH₃)

Anhydrous ammonia has been researched because it does not contain any carbon, and so would not release any CO₂. The high heat of vaporization requires a pre-vaporization 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. Ammonia fuel also produces copious quantities of undesirable oxides of nitrogen (NO_x) emissions.

9.8.2 Water

As water-gasoline fuels have been extensively investigated, interested potential investors may wish to refer to those papers for some background. Mr. Gunnerman advocates hydrocarbon/water emulsion fuels and promoted his A-55 fuel before the new A-21. A recent article claims a 29% gain in fuel economy, and he claims that mixing water with naphtha can provide as much power from an IC engine as the same flow rate of gasoline. He claims the increased efficiency is from catalyzed dissociation of A-21 into H₂ in the engine, because the combustion chamber of the test engines contain a "non-reactive" catalyst. For his fuel to provide power increases, he has to utilize heat energy that is normally lost. A-21 is just naphtha (effectively unleaded gasoline without oxygenates) and water (about 55%), with small amounts of winterizing and anti-corrosive additives. If the magic catalyst is not present, conventional IC

engines will not perform as efficiently, and may possibly be damaged if A-21 is used. The only modification is a new set of spark plugs, and it is also claimed that the fuel can replace both diesel and gasoline.

It has been claimed that test results of A-21 fuel emissions have shown significant reductions in CO₂ (50% claimed - who is surprised when the fuel is 55% water?), CO, HCs, NO_x and a 70% reduction in diesel particulates and smoke. It's claimed that 70% of the exhaust stream consists of water vapor. He has formed a joint venture company with Caterpillar called Advanced Fuels. U.S. patent #5,156,114 (Aqueous Fuel for Internal Combustion Engines and Combustion Method) was granted to Mr. Gunnerman in 1992.

9.8.3 Propylene Oxide

Propylene oxide ($\text{CH}_3\text{CH}(\text{O})\text{CH}_2$ = 1,2 epoxypropane) has apparently been used in racing fuels, and some racers erroneously claim that it behaves like nitrous oxide. It is a fuel that has very desirable volatility, flammability and auto-ignition properties. When used in engines tuned for power typically slightly rich), it will move the air-fuel ratio closer to stoichiometric, and the high volatility, high auto-ignition temperature (high octane), and slightly faster flame speed may improve engine efficiency with hydrocarbon fuels, resulting in increased power without major engine modifications. This power increase is, in part, due to the increase in volumetric efficiency from the requirement for less oxygen (air) in the charge. PO is a suspected carcinogen, and so should be handled with extreme care.

Relevant properties include Av. gas Propylene Oxide

Density (g/ml)	0.828
Boiling Point (C)	34
Stoichiometric Ratio (vol%)	4.97
Auto-ignition Temperature (C)	464
Lower Flammable Limit (vol%)	2.8
Upper Flammable Limit (vol%)	37
Minimum Ignition Energy (mJ)	0.14
Net Heat of Combustion (MJ/kg)	31.2
Flame Temperature (C)	2087
Burning Velocity (m/s)	0.67

9.8.4 Nitromethane

Nitromethane (CH_3NO_2) - usually used as a mixture with methanol to reduce peak flame temperatures - also provides excellent increases in volumetric efficiency of IC engines - in part because of the lower stoichiometric air-fuel ratio (1.7:1 for CH_3NO_2) and relatively high heats of vaporization (0.56 MJ/kg for

CH₃NO₂) result in dramatic cooling of the incoming charge. $4\text{CH}_3\text{NO}_2 + 3\text{O}_2 \rightarrow 4\text{CO}_2 + 6\text{H}_2\text{O} + 2\text{N}_2$

The Nitromethane Specific Energy at stoichiometric (heat of combustion divided by air-fuel ratio) of 6.6, compared to 2.9 for iso-octane, indicates that the fuel energy delivered to the combustion chamber is 2.3 times that of iso-octane for the same mass of air. Coupled with the higher flame temperature (2400C), and flame speed (0.5 m/s), it has been shown that a 50% blend in methanol will increase the power output by 45% over pure methanol, however knock also increased.

9.9 What about alternative oxidants?

9.9.1 Nitrous Oxide

Nitrous oxide (N₂O) contains 33 vol% of oxygen, consequently the combustion chamber is filled with less useless nitrogen. It is also metered in as a liquid, which 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). Nitrous oxide has also been readily available at a reasonable price, and is popular as a fast way to increase power in racing engines. The following data are for common premixed flames.

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
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 a 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 centered 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.

9.9.3 The myth of Triptane

This post is an edited version of several posts I made 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 post that claimed the unleaded octane was.

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 utilize 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 increases if the engine could handle 100+ PN fuel. 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.

Triptane was first shown to have high octane in 1926 as part of the General Motors Research Laboratories investigations. 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.

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 gasoline's. Significant design changes would have been required for engines to utilize the high antiknock rating.

As an unleaded additive, it was not that much different to other isoalkanes, consequently the modern manufacturing processes for aviation

gasoline's 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 antiknock 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. Triptane does not have a significantly different blending number for MON or RON, when compared to iso-octane. When TEL is 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.