Subject: Gasoline FAQ - Part 1 of 4

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              FAQ: Automotive Gasoline
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This FAQ is posted monthly to the Usenet groups news.answers, rec.answers,
and rec.autos.tech. The latest copy should be available on the WWW from sites
that automatically convert those FAQs, such as www.faqs.org.

Changes:
- added a little more data on US crude oil resources.

Subject: 1. Introduction, Intent, Acknowledgements, and Abbreviations

1.1 Introduction and Intent.

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

1.2 Acknowledgements.

Thanks go to all the posters in sci.energy and rec.autos.tech who spend
valuable time responding to questions. I would also like to acknowledge
the considerable effort of L.M.Gibbs of Chevron, who has twice spent his
valuable time courteously detailing errors and providing references
for his corrections. All remaining errors and omissions are mine.

1.3 Abbreviations.

AKI = Antiknock Index of Gasoline ((RON+MON)/2)
CI = Compression Ignition (Diesel)
Gasoline = Petrol (Yes, complaints were received :-))
IC = Internal Combustion
MON = Motor Octane Rating
Octane = The Octane Rating of the Gasoline
RFG = Reformulated Gasoline (as defined by US Clean Air Act)
RON = Research Octane Rating
SI = Spark Ignition (Gasoline)

Subject: 2. Table of Contents

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

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

Subject: 4. What is Gasoline?

4.1 Where does crude oil come from?.

The generally-accepted origin of crude oil is from plant life up to 3
billion years ago, but predominantly from 100 to 600 million years ago [1].
"Dead vegetarian dino dinner" is more correct than "dead dinos".
The molecular structure of the hydrocarbons and other compounds present
in fossil fuels can be linked to the leaf waxes and other plant molecules of
marine and terrestrial plants believed to exist during that era. There are
various biogenic marker chemicals (such as isoprenoids from terpenes,
porphyrins and aromatics from natural pigments, pristane and phytane from
the hydrolysis of chlorophyll, and normal alkanes from waxes), whose size
and shape can not be explained by known geological processes [2]. The
presence of optical activity and the carbon isotopic ratios also indicate a
biological origin [3]. There is another hypothesis that suggests crude oil
is derived from methane from the earth's interior. The current main
proponent of this abiotic theory is Thomas Gold, however abiotic and
extraterrestrial origins for fossil fuels were also considered at 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} tonnes 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
$2.7-3.0 \times 10^{12}$ tonnes of organic carbon) has a half-life of days to
decades, whereas the large secondary cycle (turnover 6.4×10^{15} tonnes of
organic carbon) has a half-life of several million years [4]. Much of this
organic carbon is too dilute or inaccessible for current technology to
recover, however the estimates represent centuries to millenia of fossil
fuels, even with continued consumption at current or increased rates [5].

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 [6]. 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 " Hubbert curves" that predict fossil fuel discovery rates would peak and decline rapidly. M. King Hubbert 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 metres, with some additional qualifiers. As production and proved resources were 147 billion barrels of oil and 22.5 trillion cubic metres of gas, Hubbert was implying that volumes yet to be developed could only be 16-49 billion barrels of oil and 2.1-4.5 trillion cubic metres. Technology has confounded those predictions for natural gas [6a].

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 metres. When combined with the estimate of undiscovered oil and gas, the totals reach 110 billion barrels of oil and 30 trillion cubic metres of gas [7]. When the 1995 USGS estimates of undiscovered and inferred crude oil are calculated for just the lower 48 states, they totalled (in 1995) 68.9 billion barrels of oil, well above Hubbert'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 [6,7].

Crude Oil	Proved Reserves	R/P Ratio
Middle East	89.4 billion tonnes	93.4 year
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 tonnes	247 years
Total World	1,043.864	235 years

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

One billion = 1 x 10^9. One trillion = 1 x 10^12.
One barrel of Arabian Light crude oil = 0.158987 m3 and 0.136 tonnes.

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 [8].

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 gasolines
on residential properties, so Charles F. Kettering (yes - he of ignition
system fame) modified an IC engine to run on kerosine. However the
kerosine-fuelled engine would "knock" and crack the cylinder head and
pistons. He assigned Thomas Midgley Jr. to confirm that the cause was
from the kerosine droplets vaporising on combustion as they presumed.
Midgley demonstrated that the knock was caused by a rapid rise in
pressure after ignition, not during preignition as believed [9]. This
then lead to the long search for antiknock agents, culminating in
tetra ethyl lead [10]. Typical mid-1920s gasolines were 40 - 60 Octane [11].

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

The 1950s saw the start of the increase of the compression ratio, requiring
higher octane fuels. Octane ratings, lead levels, and vapour 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 gasolines were slowly changed as lead was
phased out, lead levels plummetted, octanes initially decreased, and then
remained 2-5 numbers lower, vapour 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 vapour pressure and increaing 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 gasolines this century have been provided by L.M.Gibbs [12,13].

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 gasolines can result in
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 (oxidised)
to form water (H_2O) or carbon dioxide (CO_2). If the combustion is
not complete, carbon monoxide (CO) may be formed. As CO can be burnt
to produce CO_2, 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. Hydrogens 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 gasolines [14].

4.4.1 Saturated hydrocarbons (aka paraffins, alkanes)

- stable, the major component of leaded gasolines.
- tend to burn in air with a clean flame.
- octane ratings depend on branching and number of carbon atoms.

```
alkanes
  normal = continuous chain of carbons ( Cn H2n+2 )
  - low octane ratings, decreasing with carbon chain length.

    normal heptane     C-C-C-C-C-C-C                     C7H16

  iso = branched chain of carbons  ( Cn H2n+2 )
  - higher octane ratings, increasing with carbon chain branching.

    iso octane =                    C    C
    ( aka 2,2,4-trimethylpentane )  |    |
                                  C-C-C-C-C           C8H18
                                    |
                                    C

  cyclic = circle of carbons  ( Cn H2n )
  ( aka Naphthenes )
  - high octane ratings.

    cyclohexane  =               C
                               /  \
                              C    C
                              |    |                 C6H12
                              C    C
                               \  /
```

C

4.4.2 Unsaturated Hydrocarbons

- Unstable, are the remaining component of gasoline.
- Tend to burn in air with a smoky flame.

Alkenes (aka olefins, have carbon=carbon double bonds)
- These are unstable, and are usually limited to a few %.
- tend to be reactive and toxic, but have desirable octane ratings.

```
                              C
                              |                        C5H10
         2-methyl-2-butene    C-C=C-C
```
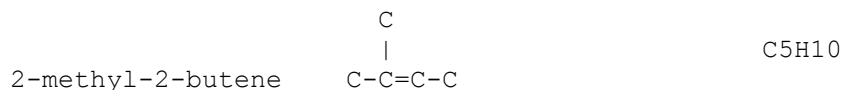
Alkynes (aka acetylenes, have carbon-carbon triple bonds)
- These are even more unstable, are only present in
  trace amounts, and only in some poorly-refined gasolines.

```
                                    _
         Acetylene               C=C                      C2H2
```

Arenes (aka aromatics)
- Used to be up to 40%, gradually being reduced to <20% in the US.
- tend to be more toxic, but have desirable octane ratings.
- Some countries are increasing the aromatic content (up to 50% in some
  super unleaded fuels) to replace the alkyl lead octane enhancers.

```
                      C                        C
                    // \                      // \
                   C    C                  C-C    C
         Benzene   |    ||      Toluene     |    ||
                   C    C                  C    C
                    \\ /                    \\ /
                     C                        C

               C6H6                      C7H8
```
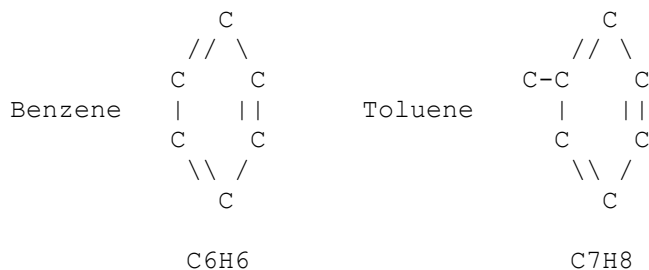
Polynuclear Aromatics   (aka PNAs or PAHs)
- These are high boiling, and are only present in small amounts in gasoline.
  They contain benzene rings joined together. The simplest, and least toxic,
  is Naphthalene, which is only present in trace amounts in traditional
  gasolines, and even lower levels are found in reformulated gasolines.
  The larger multi-ringed PNAs are highly toxic, and are not present in
  gasoline.

```
                       C   C
                     // \ / \\
                    C   C   C
         Naphthalene |   ||   |               C10H8
                    C   C   C
                     \\ / \ //
                      C   C
```
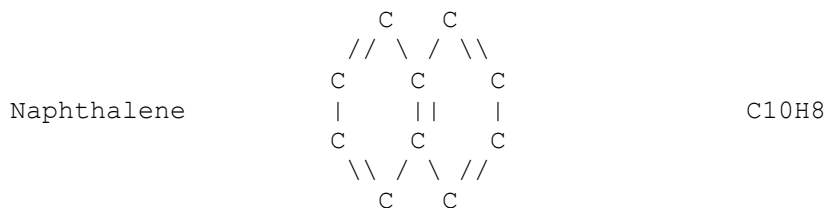
4.5 What are oxygenates?

Oxygenates are just preused 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 [15]. Most oxygenates used
in gasolines are either alcohols (Cx-O-H) or ethers (Cx-O-Cy), and contain
1 to 6 carbons. Alcohols have been used in gasolines since the 1930s, and
MTBE was first used in commercial gasolines 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 )             |
                                                     C
```
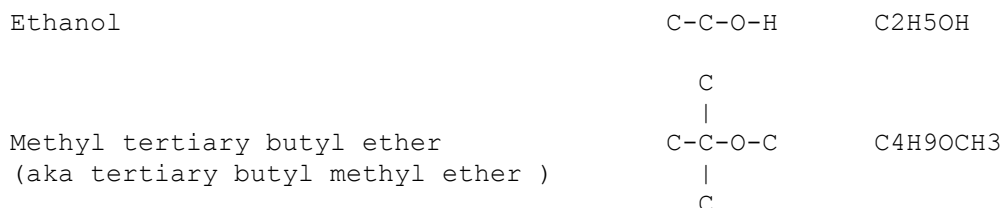
They can be produced from fossil fuels eg methanol (MeOH), methyl tertiary
butyl ether (MTBE), tertiary amyl methyl ether (TAME), or from biomass, eg
ethanol(EtOH), ethyl tertiary butyl ether (ETBE)). MTBE is produced by
reacting methanol (from natural gas) with isobutylene in the liquid phase
over an 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 [15]. The "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 gasolines to reduce the reactivity of emissions,
but they are only effective if the hydrocarbon fractions are carefully
modified to utilise the octane and volatility properties of the oxygenates.
If the hydrocarbon fraction is not correctly modified, oxygenates can
increase the undesirable smog-forming and toxic emissions. Oxygenates do not
necessarily reduce all exhaust toxins, nor are they intended to.

Oxygenates have significantly different physical properties to hydrocarbons,
and the levels that can be added to gasolines are controlled by the 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 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 have 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 alcohols (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 [16].

In 1981 the EPA ruled that fuels could contain aliphatic alcohols (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 [16].

Initially, the oxygenates were added to hydrocarbon fractions that were slightly-modified unleaded gasoline fractions, and these were known as "oxygenated" gasolines. In 1995, the hydrocarbon fraction was significantly modified, and these gasolines are called "reformulated gasolines" (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 gasolines to reduce unsaturates, volatility, benzene, and the reactivity of emissions. Federal regulations only reduce vapour pressure and benzene directly, however aromatics are also reduced to meet emissions criteria [16].

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%) [17], and other researchers have observed similar reductions also occur when oxygenates are added to reformulated gasolines on older and newer vehicles, but have also shown that NOx levels may increase, as also may some regulated toxins [18,19,20].

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 stabilised radicals such as allyl and methyl allyl, as well as stable species such as allene, which resist further oxidation [21,22].

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 [23]. However any "knock" caused by the fuel will rapidly mechanically destroy an engine, and General Motors was having major problems trying to improve engines without inducing knock. The problem was to identify economic additives that could be added to gasoline or kerosine to prevent knock, as it was apparent that engine development was being hindered. The kerosine for home fuels soon became a secondary issue, as the magnitude of the automotive knock problem

increased throughout the 1910s, and so more resources were poured into the quest for an effective "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 [24].

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 [9,10,24]. They tried selenium oxychloride which was an excellent antiknock, however it reacted with iron and "dissolved" the engine. Midgley was able to predict that other organometallics would work, and slowly focused on organoleads. They then had to remove the lead, which would otherwise accumulate and coat the engine and exhaust system with lead. They discovered and developed the halogenated lead scavengers that are still used in leaded fuels. The scavengers, (ethylene dibromide and ethylene dichloride), function by providing halogen atoms that react with the lead to form volatile lead halide salts that can escape out the exhaust. The quantity of scavengers added to the alkyl lead concentrate is calculated according to the amount of lead present. If sufficient scavenger is added to theoretically react with all the lead present, the amount is called one "theory". Typically, 1.0 to 1.5 theories are used, but aviation gasolines must only use one theory. This ensures there is no excess 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 [25]. Their cause was assisted by some major disasters at TEL manufacturing plants, and although these incidents were mainly attributable to a failure of management and/or staff to follow instructions, they resulted in a protracted dispute in the chemical and public health literature that even involved Midgley [25,26]. 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 gasolines in increasing concentrations to obtain octane. The limit was 1.14g Pb/l, which is well above the diminishing returns part of the lead response curve for most refinery streams, thus it is unlikely that much fuel was ever made at that level. I believe 1.05 was about the maximum, and articles suggest that 1970 100 RON premiums were about 0.7-0.8 g Pb/l and 94 RON regulars 0.6-0.7 g Pb/l, which matches published lead response data [27,28] eg.

For	Catalytic Reformate	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 HO_2 is the most important radical species. Lead oxide, either as
solid particles, or in the gas phase, reacts with HO_2 and removes it from
the available radical pool, thereby deactivating the major chain branching
reaction sequence that results in undesirable, easily-autoignitable
hydrocarbons [21,22].

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 [29]. 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 [29a].

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 [30], 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
siuation and , if evidence supports removing MMT, they will revisit banning
MMT. Automobile manufacturers believe MMT reduces the effectiveness of the
latest emission control systems [31]. 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 [31]. MMT is more expensive
than alkyl leads and has been reported to increase unburned hydrocarbon
emissions and block exhaust catalysts [32].

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
iron pentacarbonyl $(Fe(CO)_5)$ 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. Iron
oxide (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 [33].

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 12, arranged in specific ways to provide the desirable properties. Obviously, a refinery has to either sell the remainder as marketable products, or convert the larger molecules into smaller gasoline molecules.

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

Typical modern refinery processes for gasoline components include
* Catalytic cracking - breaks larger, higher-boiling, hydrocarbons into gasoline range product that contains 30% aromatics and 20-30% olefins.
* Hydrocracking - cracks and adds hydrogen to molecules, producing a more saturated, stable, gasoline fraction.
* Isomerisation - raises gasoline fraction octane by converting straight chain hydrocarbons into branched isomers.
* Reforming - converts saturated, low octane, hydrocarbons into higher octane product containing about 60% aromatics.
* Alkylation - reacts gaseous olefin streams with isobutane to produce liquid high octane iso-alkanes.

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 precusers) from reformer feeds and treating that stream to produce non-aromatic high octane components.
* Distilling the higher boiling fraction (which contains 80-100% of aromatics that can be hydrocracked) from catalytic cracker product [34].
* 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 oxidised (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:-

```
          C + O2 = CO2
          H + O2 = H2O
```
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, and 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
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.
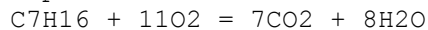
The chemical stoichiometric combustion of hydrocarbons with oxygen can be
written as:-
CxHy + (x + (y/4))O2 -> xCO2 + (y/2)H2O
Often, for simplicity, the remainder of air is assumed to be nitrogen,
which can be added to the equation when exhaust compositions are required.
As a general rule, maximum power is achieved at slightly rich, whereas
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 vaporisation, thus producing the Nett Calorific Value.
If the water were condensed back to the original fuel temperature, then
Gross Calorific Value of the fuel, which will be larger, is obtained.

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

		MJ/kg	Octane	Octane
n-heptane	l	44.592	0	0
	g	44.955		
i-octane	l	44.374	100	100
	g	44.682		
toluene	l	40.554	124* (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 can not provide energy, they will have significantly lower energy contents. They are added to provide octane, not energy. For an engine that can be optimised for oxygenates, more fuel is required to obtain the same power, but they can burn slightly more efficiently, thus the power ratio is not identical to the energy content ratio. They also require more energy to vaporise.

	Energy Content Nett MJ/kg	Heat of Vaporisation 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	Nett
Hydrogen	141.9	120.0
Carbon to Carbon monoxide	10.2	-
Carbon to Carbon dioxide	32.8	-
Sulfur to sulfur dioxide	9.16	-
Natural Gas	53.1	48.0
Liquified petroleum gas	49.8	46.1
Aviation gasoline	46.0	44.0
Automotive gasoline	45.8	43.8
Kerosine	46.3	43.3
Diesel	45.3	42.5

Obviously, for automobiles, the nett calorific value is appropriate, as the water is emitted as vapour. The engine can not utilise 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).

4.10 What are the gasoline specifications?

Gasolines are usually defined by government regulation, where properties and test methods are clearly defined. In the US, several government and state bodies can specify gasoline properties, and they may choose to use or modify consensus minimum quality standards, such as American Society for Testing Materials (ASTM). The US gasoline specifications and test methods are listed in several readily available publications, including the Society of Automotive Engineers (SAE) [38], and the Annual Book of ASTM Standards [39].

The 1995 ASTM edition includes:-
D4814-94d Specification for Automotive Spark-Ignition Engine Fuel.
This specification lists various properties that all fuels have to comply with, and may be updated throughout the year. Typical properties are:-

4.10.1 Vapour Pressure and Distillation Classes.
6 different classes according to location and/or season.
As gasoline is distilled, the temperatures at which various fractions are evaporated are calculated. Specifications define the temperatures at which various percentages of the fuel are evaporated. Distillation limits include maximum temperatures that 10% is evaporated (50-70C), 50% is evaporated (110-121C), 90% is evaporated (185-190C), and the final boiling point (225C). A minimum temperature for 50% evaporated (77C), and a maximum amount of Residue (2%) after distillation. Vapour pressure limits for each class (54, 62, 69, 79, 93, 103 kPa) are also specified. Note that the EPA has issued a waiver that does not require gasoline with 9-10% ethanol to meet the required specifications between 1st May - 15 September.

4.10.2 Vapour Lock Protection Classes
5 classes for vapour lock protection, according to location and/or season.
The limit for each class is a maximum Vapour-Liquid ratio of 20 at one of the specified testing temperatures of 41, 47, 51, 56, 60C.

4.10.3 Antiknock Index   (aka (RON+MON)/2, "Pump Octane")
The (Research Octane Number + Motor Octane Number) divided by two. Limits are not specified, but changes in engine requirements according season and location are discussed. Fuels with an Antiknock index of 87, 89, 91 (Unleaded), and 88 (Leaded) are listed as typical for the US at sea level, however higher altitudes will specify lower octane numbers.

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

4.10.5 Copper strip corrosion
Ability to tarnish clean copper, indicating the presence of any corrosive sulfur compounds

4.10.6 Maximum Sulfur content
Sulfur adversely affects exhaust catalysts and fuel hydrocarbon lead response, and also may be emitted as polluting sulfur oxides.
Leaded = 0.15 %mass maximum, and Unleaded = 0.10 %mass maximum.
Typical US gasoline levels are 0.03 %mass.

4.10.7 Maximum Solvent Washed Gum (aka Existent Gum)
Limits the amount of gums present in fuel at the time of testing to 5 mg/100mls. The results do not correlate well with actual engine deposits caused by fuel vaporisation [40].

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

4.10.9 Water Tolerance
Highest temperature that causes phase separation of oxygenated fuels. The limits vary according to location and month. For Alaska - North of 62 latitude, it changes from -41C in Dec-Jan to 9C in July, but remains 10C all year in Hawaii.

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

As well as the above, there are various restrictions introduced by the Clean Air Act and state bodies such as California's Air Resources Board (CARB) that often have more stringent limits for the above properties, as well as additional limits. More detailed descriptions of the complex regulations can be found elsewhere [16,41,42] - I've just included some of the major changes, as some properties are determined by levels of permitted emissions, eg the toxics reduction required for fuel that has the maximum permitted benzene (1.0%), means total aromatics are limited to around 27%. There have been some changes in early 1996 to the implementation timetable, and the following timetable has not yet been changed.

The Clean Air Act also specifies some regions that exceed air quality standards have to use reformulated gasolines (RFGs) all year, starting January 1995. Other regions are required to use oxygenated gasolines for four winter months, beginning November 1992. The RFGs also contain oxygenates. Metropolitan regions with severe ozone air quality problems must use reformulated gasolines in 1995 that;- contain at least 2.0 wt% oxygen, reduce 1990 volatile organic carbon compounds by 15%, and reduce specified toxic emissions by 15% (1995) and 25% (2000). Metropolitan regions that exceeded carbon monoxide limits were required to use gasolines with 2.7 wt% oxygen during winter months, starting in 1992.

The 1990 Clean Air Act (CAA) amendments and CARB Phase 2 (1996) specifications for reformulated gasoline establish the following limits, compared with typical 1990 gasoline. Because of a lack of data, the EPA were unable to define the CAA required parameters, so they instituted a two-stage system. The first stage, the "Simple Model" is an interim stage that run from 1/Jan/1995 to 31/Dec/1997. The second stage, the "Complex Model" has two phases, Phase I (1995-1999) and Phase II (2000+), and there are different limits for EPA Control Region 1 (south) and Control Region 2 (north). Each refiner must have their RFG recertified to the Complex model prior to the 1/Jan/1998 implementation date. The following are some of the criteria for RFG when complying on a per gallon basis, more details are available elsewhere, including the details of the baseline fuel compositions to be used for testing [16,41,42,43,43a].

	1990	Clean Air Act			CARB Phase 2	
		Simple	Complex			
			I	II	Limit	Average
benzene (max.vol.%)	2	1.00	1.00	1.00	1.00	0.8
oxygen (min.mass %)	0.2	2.0	2.0	2.0	1.8	-
(max.mass %)	-	2.7	-	-	2.2	-

Property						
sulfur (max.mass ppm)	150	no increase	-	-	40	30
aromatics (max.vol.%)	32	toxics reduction	-	-	25	22
olefins (max.vol.%)	9.9	no increase	-	-	6.0	4.0
reid vapour pressure (kPa) (during VOC Control Period)	60	55.8 (north) 49.6 (south)	-	-	48.3	-
50% evaporated (max.C)	-	-	-	-	98.9	93
90% evaporated (max.C)	170	-	-	-	148.9	143
VOC Reductions - Region I (min.%)			35.1	27.5	-	-
(VOC Control Period only) - Region II (min.%)			15.6	25.9	-	-
NOx Reductions - VOC Control Period (min.%)			0	5.5	-	-
- Non-VOC Control Period (min.%)			0	0	-	-
Toxics Reductions (min.%)			15.0	20.0	-	-

These regulations also specify emissions criteria. eg CAA specifies no increase in nitric oxides (NOx) emissions, reductions in VOC by 15% during the ozone season, and specified toxins by 15% all year. These criteria indirectly establish vapour pressure and composition limits that refiners have to meet. Note that the EPA also can issue CAA Section 211 waivers that allow refiners to choose which oxygenates they use. In 1981, the EPA also decided that fuels with up to 2% weight of oxygen (from alcohols and ethers (except methanol)) were "substantially similar" to 1974 unleaded gasoline, and thus were not "new" gasoline additives. That level was increased to 2.7 wt% in 1991. Some other oxygenates have also been granted waivers, eg ethanol to 10% volume (approximately 3.5 wt%) in 1979 and 1982, and tert-butyl alcohol to 3.5 wt% in 1981. In 1987 and 1988 further waivers were issued for mixture of alcohols representing 3.7% wt of oxygen.

4.11 What are the effects of the specified fuel properties?

Volatility
This affects evaporative emissions and driveability, it is the property that must change with location and season. Fuel for mid-summer Arizona would be difficult to use in mid-winter Alaska. The US is divided into zones, according to altitude and seasonal temperatures, and the fuel volatility is adjusted accordingly. Incorrect fuel may result in difficult starting in cold weather, carburetter icing, vapour lock in hot weather, and crankcase oil dilution. Volatility is controlled by distillation and vapour pressure specifications. The higher boiling fractions of the gasoline have significant effects on the emission levels of undesirable hydrocarbons and aldehydes, and a reduction of 40C in the final boiling point will reduce the levels of benzene, butadiene, formaldehyde and acetaldehyde by 25%, and will reduce HC emissions by 20% [44].

Combustion Characteristics
As gasolines contain mainly hydrocarbons, the only significant variable between different grades is the octane rating of the fuel, as most other properties are similar. Octane is discussed in detail in Section 6. There are only slight differences in combustion temperatures (most are around 2000C in isobaric adiabatic combustion [45]). Note that the actual temperature in the combustion chamber is also determined by other factors, such as load and engine design. The addition of oxygenates changes the pre-flame reaction pathways, and also reduces the energy content of the fuel. The levels of oxygen in the fuel is regulated according to regional air quality standards.

Stability
Motor gasolines may be stored up to six months, consequently they must not

form gums which may precipitate. Reactions of the unsaturated HCs may produce gums (these reactions can be catalysed by metals such as copper), so antioxidants and metal deactivators are added. Existent Gum is used to measure the gum in the fuel at the time tested, whereas the Oxidation Stability measures the time it takes for the gasoline to break down at 100C with 100psi of oxygen. A 240 minute test period has been found to be sufficient for most storage and distribution systems.

Corrosiveness
Sulfur in the fuel creates corrosion, and when combusted will form corrosive gases that attack the engine, exhaust and environment. Sulfur also adversely affects the alkyl lead octane response, and will adversely affect exhaust catalysts, but monolithic catalysts will recover when the sulfur content of the fuel is reduced, so sulfur is considered an inhibitor, rather than a catalyst poison. The copper strip corrosion test and the sulfur content specification are used to ensure fuel quality. The copper strip test measures active sulfur, whereas the sulfur content reports the total sulfur present.

Manufacturers many also add additional tests, such as filterability, to ensure no distribution problems are encountered.

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4.12 Are brands different?
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Yes. The above specifications are intended to ensure minimal quality
standards are maintained, however as well as the fuel hydrocarbons, the
manufacturers add their own special ingredients to provide additional
benefits. A quality gasoline additive package would include:-
* octane-enhancing additives (improve octane ratings)
* anti-oxidants (inhibit gum formation, improve stability)
* metal deactivators (inhibit gum formation, improve stability)
* deposit modifiers (reduce deposits, spark-plug fouling and
  preignition)
* surfactants (prevent icing, improve vaporisation, inhibit deposits,
  reduce NOx emissions)
* freezing point depressants (prevent icing)
* corrosion inhibitors (prevent gasoline corroding storage tanks)
* dyes (product colour for safety or regulatory purposes).

During the 1980s significant problems with deposits accumulating on intake
valve surfaces occurred as new fuel injection systems were introduced.
These intake valve deposits (IVD) were different 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 alcohols or olefins [46]. 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 [47], and
deposit control additives will be required to both reduce emissions and
provide clean engine operation [48]. A slighty more detailed description
of additives is provided in Section 9.1.

Texaco demonstrated that a well-formulated package could improve fuel
economy, reduce NOx emissions, and restore engine performance because, as
well as the traditional liquid-phase deposit removal, some additives can
work in the vapour phase to remove existing engine deposits without adversely
affecting performance (as happens when water is poured into a running engine
to remove carbon deposits :-))[49]. Chevron have also published data on the
effectiveness of their additives [50], and successfully litigated to get
Texaco to modify some of their claims [51]. Most suppliers of quality
```

gasolines 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 driveability is pathetic on the correct octane, try another brand. Remember that the composition will change with the season, so if you lose driveability, try yet another brand. As various Clean Air Act changes are introduced over the next few years, gasoline will continue to change.

4.13 What is a typical composition?

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

It is important to note that "oxygenated gasolines" have a hydrocarbon fraction that is not too different to traditional gasolines, but that the hydrocarbon fraction of "reformulated gasolines" ( which also contain oxygenates ) are significantly different to traditional gasolines.

The last 10 years of various compositional changes to gasolines for environmental and health reasons have resulted in fuels that do not follow historical rules, and the regulations mapped out for the next decade also ensure the composition will remain in a state of flux. The reformulated gasoline specifications, especially the 1/Jan/1998 Complex model, will probably introduce major reductions in the distillation range, as well as changing the various limits on composition and emissions.

I'm not going to list all 500+ HCs in gasolines, but the following are representative of the various classes typically present in a gasoline. The numbers after each chemical are:- Research Blending Octane : Motor Blending Octane : Boiling Point (C): Density (g/ml @ 15C) : Minimum Autoignition Temperature (C). It is important to realise that the Blending Octanes are derived from a 20% mix of the HC with a 60:40 iC8:nC7 ( 60 Octane Number ) base fuel, and the extrapolation of this 20% to 100%. These numbers result from API Project 45, and are readily available. As modern refinery streams have higher base octanes, these Blending Octanes are higher than those typically used in modern refineries. For example, modern Blending Octane ratings can be much lower ( toluene = 111RON and 94MON, 2-methyl-2-butene = 113RON and 81MON ), but detailed compilations are difficult to obtain.

The technique for obtaining Blending Octanes is different from rating the pure fuel, which often requires adjustment of the test engine conditions outside the acceptable limits of the rating methods. Generally, the actual octanes of the pure fuel are similar for the alkanes, but are up to 30 octane numbers lower than the API Project 45 Blending Octanes for the

aromatics and olefins [52].

A traditional composition I have dreamed up would be like the following,
whereas newer oxygenated fuels reduce the aromatics and olefins, narrow the
boiling range, and add oxygenates up to about 12-15% to provide the octane.
The amount of aromatics in super unleaded fuels will vary greatly from
country to country, depending on the configuration of the oil refineries
and the use of oxygenates as octane enhancers. The US is reducing the levels
of aromatics to 25% or lower for environmental and human health reasons.

Some countries are increasing the level of aromatics to 50% or higher in
super unleaded grades, usually to avoid refinery reconfiguration costs or
the introduction of oxygenates as they phase out the toxic lead octane
enhancers. An upper limit is usually placed on the amount of benzene
permitted, as it is known human carcinogen.

```
15% n-paraffins                        RON   MON    BP      d      AIT
      n-butane                         113 : 114 :  -0.5:  gas  : 370
      n-pentane                         62 :  66 :  35  : 0.626 : 260
      n-hexane                          19 :  22 :  69  : 0.659 : 225
      n-heptane (0:0 by definition)      0 :   0 :  98  : 0.684 : 225
      n-octane                         -18 : -16 : 126  : 0.703 : 220
   ( you would not want to have the following alkanes in gasoline,
     so you would never blend kerosine with gasoline )
      n-decane                         -41 : -38 : 174  : 0.730 : 210
      n-dodecane                       -88 : -90 : 216  : 0.750 : 204
      n-tetradecane                    -90 : -99 : 253  : 0.763 : 200
30%  iso-paraffins
      2-methylpropane                  122 : 120 : -12  :  gas  : 460
      2-methylbutane                   100 : 104 :  28  : 0.620 : 420
      2-methylpentane                   82 :  78 :  62  : 0.653 : 306
      3-methylpentane                   86 :  80 :  64  : 0.664 :  -
      2-methylhexane                    40 :  42 :  90  : 0.679 :
      3-methylhexane                    56 :  57 :  91  : 0.687 :
      2,2-dimethylpentane               89 :  93 :  79  : 0.674 :
      2,2,3-trimethylbutane            112 : 112 :  81  : 0.690 : 420
      2,2,4-trimethylpentane           100 : 100 :  98  : 0.692 : 415
         ( 100:100 by definition )
12% cycloparaffins
      cyclopentane                     141 : 141 :  50  : 0.751 : 380
      methylcyclopentane               107 :  99 :  72  : 0.749 :
      cyclohexane                      110 :  97 :  81  : 0.779 : 245
      methylcyclohexane                104 :  84 : 101  : 0.770 : 250
35% aromatics
      benzene                           98 :  91 :  80  : 0.874 : 560
      toluene                          124 : 112 : 111  : 0.867 : 480
      ethyl benzene                    124 : 107 : 136  : 0.867 : 430
      meta-xylene                      162 : 124 : 138  : 0.868 : 463
      para-xylene                      155 : 126 : 138  : 0.866 : 530
      ortho-xylene                     126 : 102 : 144  : 0.870 : 530
      3-ethyltoluene                   162 : 138 : 158  : 0.865 :
      1,3,5-trimethylbenzene           170 : 136 : 163  : 0.864 :
      1,2,4-trimethylbenzene           148 : 124 : 168  : 0.889 :
8% olefins
      2-pentene                        154 : 138 :  37  : 0.649 :
      2-methylbutene-2                 176 : 140 :  36  : 0.662 :
      2-methylpentene-2                159 : 148 :  67  : 0.690 :
```

```
        cyclopentene                       171 : 126 :  44  : 0.774 :
    ( the following olefins are not present in significant amounts
      in gasoline, but have some of the highest blending octanes )
        1-methylcyclopentene               184 : 146 :  75  : 0.780 :
        1,3 cyclopentadiene                218 : 149 :  42  : 0.805 :
        dicyclopentadiene                  229 : 167 : 170  : 1.071 :
```

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

```
        methanol                           133 : 105 :  65  : 0.796 : 385
        ethanol                            129 : 102 :  78  : 0.794 : 365
        iso propyl alcohol                 118 :  98 :  82  : 0.790 : 399
        methyl tertiary butyl ether        116 : 103 :  55  : 0.745 :
        ethyl tertiary butyl ether         118 : 102 :  72  : 0.745 :
        tertiary amyl methyl ether         111 :  98 :  86  : 0.776 :
```

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

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

4.14 Is gasoline toxic or carcinogenic?

There are several known toxins in gasoline, some of which are confirmed
human carcinogens. The most famous of these toxins are lead and benzene, and
both are regulated. The other aromatics and some toxic olefins are also
controlled. Lead alkyls also require ethylene dibromide and/or ethylene
dichloride scavengers to be added to the gasoline, both of which are
suspected human carcinogens. In 1993 an International Symposium on the Health
Effects of Gasoline was held [53]. Major review papers on the carcinogenic,
neurotoxic, 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 [54]. It should be noted
that the oxygenated gasolines were not initially intended to reduce the
toxicity of emissions. The reformulated gasolines 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 gasolines 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 gasolines comes from breathing the tailpipe, evaporative, and refuelling emissions, rather than occasional skin contact from spills. Breathing vapours and skin contact should always be minimised.

4.15 Is unleaded gasoline more toxic than leaded?

The short answer is no. However that answer is not global, as some countries have replaced the lead compound octane-improvers with aromatic or olefin octane-improvers without introducing exhaust catalysts. 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 misfuelled 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 [55].

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 gasolines

(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 [55].
When all the emissions (evaporative and tailpipe) are considered, RFGs
significantly reduce emissions of hydrocarbons, however the emissions of
carbonyls and MTBE may increase [55]. 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 [18,19,20,58,59,60,61]. 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 [18,19,20,61,62].

4.17 Are all oxygenated gasolines also reformulated gasolines?

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 gasolines" 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 gasolines could be
introduced to further reduce pollution. The hydrocarbon component of RFGs is
significantly different to the hydrocarbon fraction in earlier oxygenated
gasolines, having lower aromatics contents, reduced vapour pressure, and a
narrower boiling range. RFGs do contain oxygenates as the octane-enhancer,
but have different hydrocarbon composition profiles [34,41,42,43,44].

Subject: 5. Why is Gasoline Composition Changing?

5.1 Why pick on cars and gasoline?

Cars emit several pollutants as combustion products out the tailpipe,
(tailpipe emissions), and as losses due to evaporation (evaporative
emissions, refuelling emissions). The volatile organic carbon (VOC)
emissions from these sources, along with nitrogen oxides (NOx) emissions
from the tailpipe, will react in the presence of ultraviolet (UV) light
(wavelengths of less than 430nm) to form ground-level (tropospheric) ozone,
which is one of the major components of photochemical smog [63]. 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, NOx, SOx, 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 [64,65]. The issue is whether it is natural, or induced by human activities and 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 CO_2 emissions to 1990 levels, a target that will require more efficient, lighter, or appropriately-sized vehicles, - if we are to maintain the current usage. One option is to use "renewable" fuels in place of fossil fuels. Consider the amount of energy-related CO_2 emissions for selected countries in 1990 [66].

	CO2 Emissions (tonnes/year/person)
USA	20.0
Canada	16.4
Australia	15.9
Germany	10.4
United Kingdom	8.6
Japan	7.7
New Zealand	7.6

The number of new vehicles provides an indication of the magnitude of the problem. Although vehicle engines are becoming more efficient, the distance travelled is increasing, resulting in a gradual increase of gasoline consumption. The world production of vehicles (in thousands) over the last few years was [67];-

Cars

Region	1990	1991	1992	1993	1994
Africa	222	213	194	201	209
Asia-Pacific	12,064	12,112	11,869	11,463	11,020
Central & South America	800	888	1,158	1,523	1,727
Eastern Europe	2,466	984	1,726	1,837	1,547
Middle East	35	24	300	390	274
North America	7,762	7,230	7,470	8,172	8,661
Western Europe	13,688	13,286	13,097	11,141	12,851
Total World	37,039	34,739	35,815	34,721	36,289

Trucks (including heavy trucks and buses)

Region	1990	1991	1992	1993	1994
Africa	133	123	108	101	116
Asia-Pacific	5,101	5,074	5,117	5,057	5,407
Central & South America	312	327	351	431	457
Eastern Europe	980	776	710	600	244
Middle East	36	28	100	128	76
North America	4,851	4,554	5,371	6,037	7,040
Western Europe	1,924	1,818	1,869	1,718	2,116
Total World	13,336	12,701	13,627	14,073	15,457

To fuel all operating vehicles, considerable quantities of gasoline

and diesel have to be consumed. Major consumption in 1994 of gasoline
and middle distillates (which may include some heating fuels, but
not fuel oils) in million tonnes.

	Gasoline	Middle Distillates
USA	338.6	246.3
Canada	26.8	26.1
Western Europe	163.2	266.8
Japan	60.2	92.2
Total World	820.4	1029.0

The USA consumption of gasoline increased from 294.4 (1982) to 335.6 (1989)
then dipped to 324.2 (1991), and has continued to rise since then to reach
338.6 million tonnes in 1994. In 1994 the total world production of crude oil
was 3209.1 million tonnes, of which the USA consumed 807.9 million tonnes
[68]. Transport is a very significant user of crude oil products, thus
improving the efficiency of utilisation, and minimising pollution from
vehicles, can produce immediate reductions in emissions of CO_2, HCs, VOCs,
CO, NOx, carbonyls, and other chemicals.

5.2 Why are there seasonal changes?

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

5.3 Why were alkyl lead compounds removed?

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

Beginning with the 1975 model year, most new car models were equipped
with catalytic exhaust treatment devices as one means of compliance with
the 1975 legal restrictions in the U.S. on automobile emissions. The need
for gasolines that would not adversely affect such catalytic devices has
led to the large scale availability and growing use of unleaded gasolines,
with all late-model cars requiring unleaded gasoline."[69].

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 [70,71].

5.4 Why are evaporative emissions a problem?

As tailpipe emissions are reduced due to improved exhaust emission control systems, the hydrocarbons produced by evaporation of the gasoline during distribution, vehicle refuelling, and from the vehicle, become more and more significant. A recent European study found that 40% of man-made volatile organic compounds came from vehicles [72]. 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 refuelling emissions remain a concern [73]. Vehicles will soon be required to trap the refuelling emissions in larger carbon canisters, as well as the normal evaporative emissions that they already capture. This recent decision went in favour of the oil companies, who were opposed by the auto companies. The automobile manufacturers felt the service station should trap the emissions. The activated carbon canisters adsorb organic vapours, and these are subsequently desorbed from the canister and burnt in the engine during normal operation, once certain vehicle speeds and coolant temperatures are reached. A few activated carbons used in older vehicles do not function efficiently with oxygenates, but carbon cannister 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 [74].

Tuning a carburetted engine can only have a marginal effect on pollutant levels, and there still had to be some frequent, but long-term, assessment of the state of tuning. Exhaust catalysts offered a post-engine solution that could ensure pollutants were converted to more benign compounds. As engine management systems and fuel injection systems have developed, the volatility properties of the gasoline have been tuned to minimise evaporative emissions, and yet maintain low exhaust emissions.

The design of the engine can have very significant effects on the type and quantity of pollutants, eg unburned hydrocarbons in the exhaust originate mainly from combustion chamber crevices, such as the gap between the piston and cylinder wall, where the combustion flame can not completely use the HCs. The type and amount of 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 [75]. Particulate emissions, especially the size fraction

smaller than ten micrometres, 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 gasolines to actually reduce smog has not yet been confirmed. The composition changes will reduce some compounds, and increase others, making predictions of environmental consequences extremely difficult. Planned future changes, such as the CAA 1/1/1998 Complex model specifications, that are based on several major ongoing government/industry gasoline and emission research programmes, are more likely to provide unambiguous environmental improvements. 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 [62,63]. The regulations for tailpipe emissions will continue to become more stringent as countries try to minimise local problems (smog, toxins etc.) and global problems (CO_2). Reformulation does not always lower all emissions, as evidenced by the following aldehydes from an engine with an adaptive learning management system [55].

	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 [55].

	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 [55].

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   130.30
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 [20]

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 [28,76,77].

Year		Federal				California		
	HCs g/mi	CO g/mi	NOx g/mi	Evap g/test		HCs g/mi	CO g/mi	NOx g/mi	Evap g/test
Before regs	10.6	84.0	4.1	47		10.6	84.0	4.1	47
add crankcase	+4.1					+4.1			
1966						6.3	51.0	6.0	
1968	6.3	51.0	6.0						
1970	4.1	34.0				4.1	34.0		6
1971	4.1	34.0		6(CC)		4.1	34.0	4.0	6
1972	3.0	28.0		2		2.9	34.0	3.0	2
1973	3.0	28.0	3.0			2.9	34.0	3.0	2
1974	3.0	28.0	3.0			2.9	34.0	2.0	2
1975	1.5	15.0	3.1	2		0.90	9.0	2.0	2
1977	1.5	15.0	2.0	2		0.41	9.0	1.5	2
1980	0.41	7.0	2.0	6(SHED)		0.41	9.0	1.0	2
1981	0.41	3.4	1.0	2		0.39	7.0	0.7	2
1993	0.41	3.4	1.0	2		0.25	3.4	0.4	2
1994 50,000	0.26	3.4	0.3	2	TLEV	0.13	3.4	0.4	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	0.125	1.8	0.16	2					

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 [78] 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 [79]. 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.

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

Using the estimated fuel consumption, and about 10m3 of exhaust gas per
litre of gasoline, the emissions are 2-40 ng/km. These are 2-3 orders
of magnitude lower than earlier reported work on pelletised catalysts.
These emissions may be controlled directly in the future. They are currently
indirectly controlled by the cost of platinum, and the new requirement for
the catalyst to have an operational life of at least 100,000 miles.

5.6 Why do exhaust catalysts influence fuel composition?

Modern adaptive learning engine management systems control the combustion
stoichiometry by monitoring various ambient and engine parameters, including
exhaust gas recirculation rates, the air flow sensor, and exhaust oxygen
sensor outputs. This closed loop system using the oxygen sensor can
compensate for changes in fuel content and air density. The oxygen sensor
is also known as the lambda sensor because the 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 (phi), 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
[80]:-
     6.4 methanol
     9.0 ethanol
    11.7 MTBE
    12.1 ETBE, TAME
    14.6 gasoline without oxygenates

The engine management system rapidly switches the stoichiometry between
slightly rich and slightly lean, except under wide open throttle conditions
- when the system runs open loop. The response of the oxygen sensor to
composition changes is about 3 ms, and closed loop switching is typically
1-3 times a second, going between 50mV (lambda = 1.05 (Lean)) to 900mV
(lambda = 0.99 (Rich)). The catalyst oxidises about 80% of the H2, CO,
and HCs, and reduces the NOx [76].

Typical reactions that occur in a modern 3-way catalyst are:-
$$2H_2 + O_2 \rightarrow 2H_2O$$
$$2CO + O_2 \rightarrow 2CO_2$$
$$C_xH_y + (x + (y/4))O_2 \rightarrow xCO_2 + (y/2)H_2O$$

```
                  2CO + 2NO   ->  N2 + 2CO2
    CxHy + 2(x + (y/4))NO  ->  (x + (y/4))N2 + (y/2)H2O + xCO2
                 2H2 + 2NO   ->  N2 + 2H2O
                  CO + H20   ->  CO2 + H2
             CxHy + xH2O   ->  xCO + (x + (y/2))H2
```

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 [32,58,
59]. This demonstrates that continuing changes to engine management systems
can 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 automakers 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 automakers to move the
fuel combustion towards the lean side, and different gasoline properties may
be required to optimise the combustion and reduce pollution [81]. 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 [76].

Reduced gasoline volatility and composition changes, along with cleanliness
additives and engine management systems, can help minimise cold start
emissions, but currently the most effective technique appears to be rapid,
deliberate heating of the catalyst, and the new generation of low thermal
inertia "fast light-up" catalysts reduce the problem, but further research
is necessary [76,82].

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

during refuelling.

5.8 When will the emissions be "clean enough"?

The California ZEV regulations effectively preclude IC vehicles, because
they stipulate zero emissions. However, the concept of regulatory forcing
of alternative vehicle propulsion technology may have to be modified to
include hybrid or fuel-cell vehicles, as the major failing of EVs remains
the lack of a cheap, light, safe, and easily-rechargeable electrical
storage device [83,84]. There are several major projects intending to
further reduce emissions from automobiles, mainly focusing on vehicle mass
and engine fuel efficiency, but gasoline specifications and alternative
fuels are also being investigated. It may be that changes to IC engines and
gasolines will enable the IC engine to continue well into the 21st century
as the prime motive force for personal transportation [77,85]. There have
also been calls to use market forces to reduce pollution from automobiles
[86], 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.

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

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

Various government bodies (EPA, OSHA, NIOSH) are charged with ensuring
people are not exposed to unacceptable chemical hazards, and maintain
ongoing research into the toxicity of liquid gasoline contact, water and soil
pollution, evaporative emissions, and tailpipe emissions [87]. 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, alcohols) being introduced into fuels without prior detailed toxicity studies being completed. If adverse results appear, these compounds are also likely to be regulated to protect people and the environment.

Also, as the chemistry of emissions is unravelled, the chemical precursors to toxic tailpipe emissions (such as higher aromatics that produce benzene emissions) are also controlled, even if they are not 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 timescale :-). 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 [88]. 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 [89].

Unfortunately, "renewable" ethanol is not cost competitive when crude oil is $18/bbl, so a federal subsidy ($0.54/US Gallon) and additional state subsidies (11 states - from $0.08(Michigan) to $0.66(Tenn.)/US Gal.) are provided. 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 driveability and emissions problems occurred. Most reputable brands are now carefully formulated. Some older activated carbon canisters may not function efficiently with oxygenated gasolines, but this is a function of the type of carbon used. How your vehicle responds to oxygenated gasoline depends on the engine management system and state of tune. A modern system will automatically compensate for all of the currently-permitted oxygenate levels, thus your fuel consumption will increase. Older, poorly-maintained, engines may require a tune up to maintain acceptable driveability.

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

Most stories of corrosion etc, are derived from anhydrous methanol corrosion of light metals (aluminum, magnesium), however the addition of either 0.5%

water to pure methanol, or corrosion inhibitors to methanol-gasoline blends
will prevent this. If you observe corrosion, talk to your gasoline supplier.
Oxygenated fuels may either swell or shrink some elastomers on older cars,
depending on the aromatic and olefin content of the fuels. Cars later than
1990 should not experience compatibility problems, and cars later than 1994
should not experience driveability problems, but they will experience
increased fuel consumption, depending on the state of tune and engine
management system.

5.12 What does "reactivity" of emissions mean?

The traditional method of exhaust regulations was to specify the actual HC,
CO, NOx, and particulate contents. With the introduction of oxygenates and
reformulated gasolines, the volatile organic carbon (VOC) species in the
exhaust also changed. The "reactivity" refers to the ozone-forming potential
of the VOC emissions when they react with NOx, 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 [74]:

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 [90].
  - acetaldehyde (CH2CHO) - which is formed during ethanol combustion.
  - acrolein (CH2=CHCHO) - a very potent irritant and toxin.
* ketones (containing C=0),
  - 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 [91-102]. 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 acception 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 [99]. 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 licence 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 [100]. 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		Number of
	(Median value)	(mean value)	Vehicles
92	40	80	247
91	55		1222
90	75		1467
89	80		1512
88	85		1651
87	90		1439
86	100	300	1563
85	120		1575
84	125		1206
83	145		719
82	170		639
81	230		612
80	220	500	551
79	350		667

```
78                    420                              584
77                    430                              430
76                    770                              317
75                    760          950                 163
Pre 75                920          1060                878
```

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

Surveys of vehicle populations have demonstrated that emissions systems had been tampered with on over 40% of the gross polluters, and an additional 20% had defective emission control equipment [101]. 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, resulting in a low cost to owners ($32/pa/Ton CO year). The removal of CO in the Provo example above was costed at $200/Ton CO, compared to Inspection and Maintenance programs ($780/Ton CO), and oxygenates ($1034-$1264/Ton CO in Colorado 1991-2), and UNOCALs vehicle scrapping programme ($1025/Ton of all pollutants).

Thus, identifying and repairing or removing gross polluters can be far more cost-effective than playing around with reformulated gasolines and oxygenates. 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 [102]. 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.

Action	Vehicles Affected (millions)	Estimated Cost ($billion)	% reduction		% reduction per $billion	
			HC	CO	HC	CO
Reformulated Fuels	20	1.5	17	11	11	7.3
Scrap pre-1980 vehicles	3.2	2.2	33	42	15	19
Scrap pre-1988 vehicles	14.6	17	44	67	2.6	3.9
Repair worst 20% of vehicles	4	0.88	50	61	57	69
Repair worst 40% of vehicles	8	1.76	68	83	39	47

Subject: Gasoline FAQ - Part 3 of 4

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All FAQs posted in: rec.autos.tech
Source: Usenet Version

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

6.1 Who invented Octane Ratings?

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

Kettering assigned Thomas Midgley, Jr. to the task of finding the exact
cause of knock [24]. They used a Dobbie-McInnes manograph to demonstrate
that the knock did not arise from preignition, as was commonly supposed, but
arose from a violent pressure rise *after* ignition. The manograph was not
suitable for further research, so Midgley and Boyd developed a high-speed
camera to see what was happening. They also developed a "bouncing pin"
indicator that measured the amount of knock [9]. 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 [11]. 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 gasolines could be bracketed between 60:40 and 40:60 parts by
volume heptane:iso-octane.

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

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

Having decided on standard reference fuels, a whole range of engines and

test conditions appeared, but today the most common are the Research Octane Number (RON), and the Motor Octane Number (MON).

6.2 Why do we need Octane Ratings?

To obtain the maximum energy from the gasoline, the compressed fuel-air mixture inside the combustion chamber needs to burn evenly, propagating out from the spark plug until all the fuel is consumed. This would deliver an optimum power stroke. In real life, a series of pre-flame reactions will occur in the unburnt "end gases" in the combustion chamber before the flame front arrives. If these reactions form molecules or species that can autoignite before the flame front arrives, knock will occur [21,22].

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

The combination of intense pressure waves and overheating can induce piston failure in a few minutes. Knock and preignition are both favoured by high temperatures, so one may lead to the other. Under high-speed conditions knock can lead to preignition, which then accelerates engine destruction [27,28].

6.3 What fuel property does the Octane Rating measure?

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

During the oxidation of a hydrocarbon fuel, the hydrogen atoms are removed one at a time from the molecule by reactions with small radical species (such as OH and 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 [21,22].

The octane rating of hydrocarbons is determined by the structure of the molecule, with long, straight hydrocarbon chains producing large amounts of easily-autoignitable pre-flame decomposition species, while branched and aromatic hydrocarbons are more resistant. This also explains why the octane ratings of paraffins consistently decrease with carbon number. In real life, the unburnt "end gases" ahead of the flame front encounter temperatures up to about 700C due to 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 [21,22].

The antiknock ability is related to the "autoignition 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 [39].

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 summarised by Campbell and Boyd [103]. 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 octanes 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 [12,103]. 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 [103]. During the 1950-1960s attempts were made to internationally standardise 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 automakers discovered their engines were destroying themselves on long Autobahn runs, even though the Research Octane was within specification. They discovered that either the MON or the Sensitivity (the numerical difference between the RON and MON numbers) also had to be specified. Today it is accepted that no one octane rating covers all use. In fact, during 1994, there have been increasing concerns in Europe about the high

Sensitivity of some commercially-available unleaded fuels.

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 [32]. 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 H2O / kg dry air
Intake mixture temperature          149 C
Coolant temperature                 100 C
Oil Temperature                      57 C
Ignition Advance - variable    Varies with compression ratio
                              ( eg 14 - 26 degrees BTDC )
Carburettor Venturi                 14.3 mm
```

6.6 What does the Research Octane rating measure?

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

```
Test Engine conditions             Research Octane
Test Method                     ASTM D2699-92 [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 H2O / kg dry air
Intake mixture temperature       Not specified
Coolant temperature                 100 C
Oil Temperature                      57 C
Ignition Advance - fixed        13 degrees BTDC
Carburettor Venturi        Set according to engine altitude
                         ( eg 0-500m=14.3mm, 500-1000m=15.1mm )
```

6.7 Why is the difference called "sensitivity"?

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

[39]. Recent changes in European gasolines 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 [106].

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 carburettor that can adjust individual bowl air-fuel ratios. This facilitates rapid switching between reference fuels and samples. A magnetorestrictive detonation sensor in the combustion chamber measures the rapid changes in combustion chamber pressure caused by knock, and the amplified signal is measured on a "knockmeter" with a 0-100 scale [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 carburettor bowl to obtain maximum knock. Normal heptane and iso-octane are known as primary reference fuels. Two blends of these are made, one that is one octane number above the expected rating, and another that is one octane number below the expected rating. These are placed in different bowls, and are also rated with each air-fuel ratio being adjusted for maximum knock. The higher octane reference fuel should produce a reading around 30-40, and the lower reference fuel should produce a reading of 60-70. 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 [104,105].

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 [27,28].

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

(RON+MON)/2 of another, and that is because of the combination of their driving style, engine design, vehicle mass, fuel octane distribution, fuel volatility, and the octane-enhancers used.

6.11 What is a "delta Research Octane number"?

To obtain an indication of behaviour of a gasoline during any manifold segregation, an octane rating procedure called the Distribution Octane Number was used. The rating engine had a special manifold that allowed the heavier fractions to be separated before they reached the combustion chamber [27]. 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 [107]. 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 carburettor icing and increased evaporative emissions.
Final Boiling Point.- Decreases in the final boiling point increase fuel octane. Aviation gasolines have much lower final boiling points than automotive gasolines. Note that final boiling points are being reduced because the higher boiling fractions are responsible for disproportionate quantities of pollutants and toxins.
Preignition tendency - both knock and preignition can induce each other.

6.13 Can higher octane fuels give me more power?

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 driveability and fuel economy will remain the same. The higher octane fuel costs more, so you are just throwing money away. If you are already using a fuel with an octane rating slightly below the optimum, then using a higher octane fuel will cause the engine management system to move to

the optimum settings, possibly resulting in both increased power and improved fuel economy. You may be able to change octanes between seasons (reduce octane in winter) to obtain the most cost-effective fuel without loss of driveability.

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

6.14 Does low octane fuel increase engine wear?

Not if you are meeting the octane requirement of the engine. If you are not meeting the octane requirement, the engine will rapidly suffer major damage due to knock. You must not use fuels that produce sustained audible knock, 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 gasolines. 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. You will be losing both money and driveability. If you use a fuel with an octane rating higher than what the engine can use, you are just wasting money by paying for octane that you can not utilise. 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. If 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 driveability and performance, using anything more is waste of money, and anything less could result in an unscheduled, expensive visit to your mechanic.

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

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

6.18 How can I increase the fuel octane?

Not simply, you can purchase additives, however these are not cost-effective and a survey in 1989 showed the cost of increasing the octane rating of one US gallon by one unit ranged from 10 cents (methanol), 50 cents (MMT), $1.00 (TEL), to $3.25 (xylenes) [108]. 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 gasolines, or methanol. Sadly, the price of chemical grade methanol has almost doubled during 1994. If you plan to use alcohol blends, ensure your fuel handling system is compatible, and that you only use dry gasoline by filling up early in the morning when the storage tanks are cool. Also ensure that the service station storage tank has not been refilled recently. Retailers are supposed to wait several hours before bringing a refilled tank online, to allow suspended undissolved water to settle out, but they do not always wait the full period.

6.19 Are aviation gasoline octane numbers comparable?

Aviation gasolines were all highly leaded and graded using two numbers, with common grades being 80/87, 100/130, and 115/145 [109,110]. 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, 100LL (low lead = 0.53mlTEL/L instead of 1.06mlTEL/L) was introduced to replace the 80/87 and 100/130. Soon after the introduction, there was a

spate of plug fouling, and high cylinder head temperatures resulting in cracked cylinder heads [110]. 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 Avgas number is the Rich Mixture method Performance Number (PN - they are not commonly called octane numbers when they are above 100), and is determined on a supercharged version of the CFR engine which has a fixed compression ratio. The method determines the dependence of the highest permissible power (in terms of indicated mean effective pressure) on mixture strength and boost for a specific light knocking setting. The Performance Number indicates the maximum knock-free power obtainable from a fuel compared to iso-octane = 100. Thus, a PN = 150 indicates that an engine designed to utilise the fuel can obtain 150% of the knock-limited power of iso-octane at the same mixture ratio. This is an arbitrary scale based on iso-octane + varying amounts of TEL, derived from a survey of engines performed decades ago. Aviation gasoline PNs are rated using variations of mixture strength to obtain the maximum knock-limited power in a supercharged engine. This can be extended to provide mixture response curves which define the maximum boost (rich - about 11:1 stoichiometry) and minimum boost (weak about 16:1 stoichiometry) before knock [110].

The 115/145 grade is being phased out, but even the 100LL 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 [11], and during the 1930s and 40s, the ratings increased by approximately 20 units as alkyl leads and improved refining processes became widespread [12].

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 gasolines, 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 gasolines (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 [27,28,111]. 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 recognised that the general public seldom drive as severely as the testers, and so may be satisfied by a lower octane fuel [28].

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

Efficiency = 1 - (1/compression ratio)^gamma-1

where gamma = ratio of specific heats at constant pressure and constant volume of the working fluid (for most purposes air is the working fluid, and is treated as an ideal gas). There are indications that thermal efficiency reaches a maximum at a compression ratio of about 17:1 for gasoline fuels in an SI engine [23].

The efficiency gains are best when the engine is at incipient knock, that's why knock sensors (actually vibration sensors) are used. Low compression ratio engines are less efficient because they can not deliver as much of the ideal combustion power to the flywheel. For a typical carburetted engine, without engine management [27,38]:-

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

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

7.3 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 driveability [38]. An average increase of 2 (R+M)/2 ON is required
for each 1.0 increase (leaning) of the air-fuel ratio [111]. 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 Centre) 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 [27]. 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 autoigniting species to form before
the piston reaches the optimum position for power delivery, as determined by
the normal flame front propagation. It becomes a race between the flame front
and decomposition of the increasingly-squashed end gases. High octane fuels
produce end gases that take longer to autoignite, so the good flame front
reaches and consumes them properly.

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

The actual Octane Number Requirement depends on the engine design, but for
some 1978 vehicles using standard fuels, the following (R+M)/2 Octane
Requirements were measured. "Standard" is the recommended ignition timing
for the engine, probably a few degrees BTDC [38].

| | Basic Ignition Timing | | |
Vehicle	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 [112].

A modern engine management system can compensate for altitude, ambient air temperature, and fuel octane. The management system will also control cold start settings, and other operational parameters. There is a new requirement that the engine management system also contain an on-board diagnostic function that warns of malfunctions such as engine misfire, exhaust catalyst failure, and evaporative emissions failure. The use of fuels with alcohols such as methanol can confuse the engine management system as they generate more hydrogen which can fool the oxygen sensor [76] .

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 [111].

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 [27,28,32,111]. The deposits produce
the ORI by several mechanisms:-
 - they reduce the combustion chamber volume, effectively increasing the
   compression ratio.
 - they also reduce thermal conductivity, thus increasing the combustion
   chamber temperatures.
 - they catalyse undesirable pre-flame reactions that produce end gases with
   low autoignition temperatures.

7.9 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 Uniontown Procedure. Full throttle accelerations are made
   from low speed using primary reference fuels. The ignition timing is
   adjusted until trace knock is detected at some stage. Several reference
   fuels are used, and a Road Octane Number v Basic Ignition timing graph is
   obtained. The fuel sample is tested, and the 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 [28].
2. The Modified Borderline Knock Procedure. The automatic spark advance is
   disabled, and a manual adjustment facility added. Accelerations are
   performed as in the Modified Uniontown Procedure, however trace knock is
   maintained throughout the run 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 [28].

The Road Octane Number lies between the MON and RON, and the difference
between the RON and the Road Octane number is called 'depreciation" [111].
Because nominally-identical new vehicle models display octane requirements
that can range over seven numbers, a large number of vehicles have to be
tested [28,111].

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 [27,38]. 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 [27]. Other studies report the octane number requirement decreased by 1.0 - 1.9 RON/300m without specifying altitude [38]. 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 [27,28,38].

7.13 What does water injection achieve?.

Water injection, as a separate liquid or emulsion with gasoline, or as a vapour, has been thoroughly researched. If engines can 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 [113].

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% [114]. A decrease in combustion temperature will reduce the theoretical maximum possible efficiency of an otto cycle engine that is operating correctly, but may improve efficiency in engines that are experiencing abnormal combustion on existing fuels.

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

Boost fluids are used because they are far more economical than using the fuel. When a supercharged engine has to be operated at high boost, the

mixture has to be enriched to keep the engine operating without knock. The extra fuel cools the cylinder walls and the charge, thus delaying the onset of knock which would otherwise occur at the associated higher temperatures.

The overall effect of boost fluid injection is to permit a considerable increase in knock-free engine power for the same combustion chamber temperature. The power increase is obtained from the higher allowable boost. In practice, the fuel mixture is usually weakened when using boost fluid injection, and the ratio of the two fuel fluids is approximately 100 parts of avgas to 25 parts of boost fluid. With that ratio, the resulting performance corresponds to an effective uprating of the fuel of about 25%, irrespective of its original value. Trying to increase power boosting above 40% is difficult, as the engine can drown because of excessive liquid [110].

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

Subject: 8. How can I identify and cure other fuel-related problems?

8.1 What causes an empty fuel tank?

* You forgot to refill it.
* Your friendly neighbourhood thief "borrowed" the gasoline - the unfriendly
  one took the vehicle.
* The fuel tank leaked.
* Your darling child/wife/husband/partner/mother/father used the car.
* The most likely reason is that your local garage switched to an oxygenated
  gasoline, and the engine management system compensated for the oxygen
  content, causing the fuel consumption to increase (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.

Preignition occurs when the air-fuel mixture is ignited prematurely by glowing deposits or hot surfaces - such as exhaust valves and spark plugs. If it continues, it can increase in severity and become Run-away Surface Ignition (RSI) which prevents the combustion heat being converted into mechanical energy, thus rapidly melting pistons. The Ricardo method uses an electrically-heated wire in the engine to measure preignition tendency. The scale uses iso-octane as 100 and cyclohexane as 0.
Some common fuel components:-
          paraffins   50-100
          benzene   26
          toluene   93

```
      xylene           >100
      cyclopentane       70
      di-isobutylene     64
      hexene-2          -26
```

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

Misfire is commonly caused by either a failure in the ignition system, or
fouling of the spark plug by deposits. The most common cause of deposits
was the alkyl lead additives in gasoline, and the yellow glaze of various
lead salts was used by mechanics to assess engine tune. From the upper
recess to the tip, the composition changed, but typical compounds (going
from cold to hot) were $PbClBr$; $2PbO.PbClBr$; $PbO.PbSO4$; $3Pb3(PO4)2.PbClBr$.

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 [27,28].
Obviously, engines with fuel injection systems do not have the problem, and
idle speed is an important factor. Later model carburettors 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 carburetter icing?

Yes, carburettor icing is caused by the combination of highly volatile fuel,
high humidity and low ambient temperature. The extent of cooling, caused by
the latent heat of the vaporised gasoline in the carburettor, can be as much
as 20C, perhaps dropping below the dew point of the charge. If this happens,
water will condense on the cooler carburettor surfaces, and will freeze if
the temperature is low enough. The fuel volatility can not always be reduced
to eliminate icing, so anti-icing additives are used. In the US, anti-icing
additives are seldom required because of the widespread use heated intake
air and fuel injection [28].

Two types of additive are added to gasoline to inhibit icing:-
- surfactants that form a monomolecular layer over the metal parts that
  inhibits ice crystal formation. These are usually added at concentrations
  of 30-150 ppm.
- cryoscopic additives that depress the freezing point of the condensed water
  so that it does not turn to ice. Alcohols (methanol, iso-propyl alcohol,
  etc.) and glycols (hexylene glycol, dipropylene glycol) are used at
  concentrations of 0.03% - 1%.

If you have icing problems, the addition of 100-200mls of 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 gasolines using alcohols 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 driveability problems. You can tune your engine to perform on oxygenated gasoline as well as it did on traditional gasoline, however you will have increased fuel consumption due to the useless oxygen in the oxygenates. Some engines may not initially perform well on some oxygenated fuels, usually because of the slightly different volatility and combustion characteristics. A good mechanic should be able to recover any lost performance or driveability, providing the engine is in reasonable condition.

8.5 Can I improve fuel economy by using quality gasolines?

Yes, several manufacturers have demonstrated that their new gasoline additive packages are more effective than traditional gasoline formulations. Texaco claimed their new vapour-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 [49]. 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 gasolines [50]. Quality gasolines, of whatever octane ratings, will include a full range of gasoline additives designed to provide consistent fuel quality.

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

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

"Stale" fuel is caused by improper storage, and usually smells sour. The gasoline has been allowed to get warm, thus catalysing olefin decomposition reactions, and perhaps also losing volatile material in unsealed containers. Such fuel will tend to rapidly form gums, and will usually have a significant reduction in octane rating. The fuel can be used by blending with twice the volume of new gasoline, but the blended fuel should be used immediately, otherwise teh old fuel will catalyse 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 litre tank will absorb the water, and will not significantly affect combustion. Once you have mopped up the

water with IPA, small, regular doses of any anhydrous alcohol will help
keep the tank dry. This technique will not work if you have very large
amounts of water, and the addition of greater amounts of IPA may result in
poor driveability.

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

8.8 Can I used 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 Valvemaster). Most other problems arise because the fuels have
different volatility, or the reduction of combustion chamber deposits.
These can usually be cured by reference to the vehicle manufacturer, who
will probably have a publication with the changes. Some vehicles will
perform as well on unleaded with a slightly lower octane than recommended
leaded fuel, due to the significant reduction in deposits from modern
unleaded gasolines. If premium unleaded petrol containing relatively
high levels of aromatics is used, some carburetted 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.

Subject: Gasoline FAQ - Part 4 of 4

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All FAQs in Directory: autos/gasoline-faq
All FAQs posted in: rec.autos.tech
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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 12,000km. 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 [29].
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 [115]. 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 localised 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 aftermarket fuel additives are not cost-effective. These include the
octane-enhancer solutions discussed in section 6.18. There are various other
pills, tablets, magnets, filters, etc. that all claim to improve either fuel
economy or performance. Some of these have perfectly sound scientific
mechanisms, unfortunately they are not cost-effective. Some do not even have
sound scientific mechanisms. Because the same model production vehicles can
vary significantly, it's expensive to unambiguously demonstrate these
additives are not cost-effective. If you wish to try them, remember the
biggest gain is likely to be caused by the lower mass of your wallet/purse.

There is one aftermarket additive that may be cost-effective, the lubricity

additive used with unleaded gasolines to combat 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 [12,13].

A typical gasoline may contain [16,27,32,38,111]:-
* 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 carburetted cars, and usually either
        a surfactant, alcohol or glycol.
* Anti-wear Additives, these are used to control wear in the upper cylinder
        and piston ring area that the gasoline contacts, and are usually
        very light hydrocarbon oils. Phosphorus additives can also be used
        on engines without exhaust catalyst systems.
* Deposit-modifying Additives, usually surfactants.
  1. Carburettor Deposits, additives to prevent these were required when
        crankcase blow-by (PCV) and exhaust gas recirculation (EGR) controls
        were introduced. Some fuel components reacted with these gas streams
        to form deposits on the throat and throttle plate of carburettors.
  2. Fuel Injector tips operate about 100C, and deposits form in the
        annulus during hot soak, mainly from the oxidation and polymerisation
        of the larger unsaturated hydrocarbons. The additives that prevent
        and unclog these tips are usually polybutene succinimides or
        polyether amines.
  3. Intake Valve Deposits caused major problems in the mid-1980s when
        some engines had reduced driveability when fully warmed, even though
        the amount of deposit was below previously acceptable limits. It is
        believed that the new fuels and engine designs were producing a more
        absorbent deposit that grabbed some passing fuel vapour, causing lean
        hesitation. Intake valves operate about 300C, and if the valve is
        kept wet, deposits tend not to form, thus intermittent injectors
        tend to promote deposits. Oil leaking through the valve guides can be
        either harmful or beneficial, depending on the type and quantity.
        Gasoline factors implicated in these deposits include unsaturates and
        alcohols. Additives to prevent these deposits contain a detergent
        and/or dispersant in a higher molecular weight solvent or light oil
        whose low volatility keeps the valve surface wetted [46,47,48].

4. Combustion Chamber Deposits have been targeted in the 1990s, as they
        are responsible for significant increases in emissions. Recent
        detergent-dispersant additives have the ability to function in both
        the liquid and vapour phases to remove existing 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.
* Octane Enhancers, these are usually formulated blends of alkyl lead
        or MMT compounds in a solvent such as toluene, and added at the
        100-1000 ppm levels. They have been replaced by hydrocarbons with
        higher octanes such as aromatics and olefins. These hydrocarbons
        are now being replaced by a mixture of saturated hydrocarbons and
        and oxygenates.

If you wish to play with different fuels and additives, be aware that
some parts of your engine management systems, such as the oxygen sensor,
can be confused by different exhaust gas compositions. An example is
increased quantities of hydrogen from methanol combustion.

9.2 Can a quality fuel help a sick engine?

It depends on the ailment. Nothing can compensate for poor tuning and wear.
If the problem is caused by deposits or combustion quality, then modern
premium quality gasolines have been shown to improve engine performance
significantly. The new generation of additive packages for gasolines include
components that will dissolve existing carbon deposits, and have been shown
to improve fuel economy, NOx emissions, and driveability [49,50,111]. 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 [16,28,111],

9.3 What are the advantages of alcohols and ethers?

This section discusses only the use of high (>80%) alcohol or ether fuels.
Alcohol fuels can be made from sources other than imported crude oil, and the
nations that have researched/used alcohol fuels have mainly based their
choice on import substitution. Alcohol fuels can burn more efficiently, and
can reduce photochemically-active emissions. Most vehicle manufacturers
favoured the use of liquid fuels over compressed or liquified gases. The
alcohol fuels have high research octane ratings, but also high sensitivity
and high latent heats [8,27,80,116].

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

The major advantages are gained when pure fuels (M100, and E100) are used,
as the addition of hydrocarbons to overcome the cold start problems also

significantly reduces, if not totally eliminates, any emission benefits. Methanol will 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 then 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 [15].

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

CNG (Compressed Natural Gas) is usually around 70-90% methane with 10-20% ethane, 2-8% propanes, and decreasing quantities of the higher HCs up to butane. The fuel has a high octane and usually only trace quantities of unsaturates. The emissions from CNG have lower concentrations of the hydrocarbons responsible for photochemical smog, reduced CO, SOx, and NOx, and the lean misfire limit is extended [117]. There are no technical disadvantages, providing the installation is performed correctly. The major disadvantage of compressed gas is the reduced range. Vehicles may have between one to three cylinders (25 MPa, 90-120 litre capacity), and they usually represent about 50% of the gasoline range. As natural gas pipelines do not go everywhere, most conversions are dual-fuel with gasoline. The ignition timing and stoichiometry are significantly different, but good conversions will provide about 85% of the gasoline power over the full operating range, with easy switching between the two fuels [118]. Concerns about the safety of CNG have proved to be unfounded [119,120].

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

LPG (Liquified 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 optimised (CR 12:1) for LPG, in which case there is no decrease in power or increase in fuel consumption [27,118]. 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 [118,120].

		methane	propane	iso-octane
RON		120	112	100
MON		120	97	100
Heat of Vaporisation	(MJ/kg)	0.5094	0.4253	0.2712
Net Heating Value	(MJ/kg)	50.0	46.2	44.2
Vapour Pressure @ 38C	(kPa)	–	–	11.8
Flame Temperature	(C)	1950	1925	1980

```
Stoich. Flame Speed.     ( m/s  )        0.45            0.45            0.31
Minimum Ignition Energy  ( mJ )          0.30            0.26              -
Lower Flammable Limit    ( vol% )        5.0             2.1             0.95
Upper Flammable Limit    ( vol% )        15.0            9.5             6.0
Autoignition Temperature ( C )        540 - 630          450             415
```

9.5 Why are hydrogen-powered cars not available?

The Hindenburg.

The technology to operate IC engines on hydrogen has been investigated in
depth since before the turn of the century. One attraction was to
use the hydrogen in airships to fuel the engines instead of venting it.
Hydrogen has a very high flame speed (3.24 - 4.40 m/s), wide flammability
limits (4.0 - 75 vol%), low ignition energy (0.017 mJ), high autoignition
temperature (520C), and flame temperature of 2050 C. Hydrogen has a very
high specific energy (120.0 MJ/kg), making it very desirable as a
transportation fuel. The problem has been to develop a storage system that
will pass all safety concerns, and yet still be light enough for automotive
use. Although hydrogen can be mixed with oxygen and combusted more
efficiently, most proposals use air [114,119,121-124].

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 backflash. 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 creases voluminous gases that increase
pressure), and reducing NOx [124]. 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 [124]. 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.

Interested readers are referred to the group sci.energy.hydrogen and the
" Hydrogen Energy" monograph in the Kirk Othmer Encyclopedia of Chemical
Technology [124], for recent information about this fuel.

9.6 What are "fuel cells" ?

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

ammonia) to avoid poisoning. They currently are expensive to produce, and have a short operational lifetime, when compared to an IC engine [125-127].

9.7 What is a "hybrid" vehicle?

A hybrid vehicle has three major systems [128].
1. A primary power source, either an IC engine driven generator where the IC engine only operates in the most efficient part of it's performance map, or alternatives such as fuel cells and turbines.
2. A power storage unit, which can be a flywheel, battery, or ultracapacitor.
3. A drive unit, almost always now an electric motor that can used as a generator during braking. Regenerative braking may increase the operational range about 8-13%.

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

9.8 What about other alternative fuels?

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 vaporisation requires a pre-vaporisation step, preferably also with high jacket temperatures (180C) to assist decomposition. Power outputs of about 70% of that of gasoline under the same conditions have been achieved [114]. Ammonia fuel also produces copious quantities of undesirable oxides of nitrogen (NOx) emissions.

9.8.2 Water

As water-gasoline fuels have been extensively investigated [113,129], 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 [130], 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 catalysed 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 utilise heat energy that is normally lost. A-21 is just naphtha (effectively unleaded gasoline without oxygenates) and water (about 55%), with small amouts 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, NOx and a 70% reduction in diesel particulates and smoke. It's claimed that 70% of the exhaust stream consists of water vapour. 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 (CH3CH(O)CH2 = 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 autoignition 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 autoignition temperature (high octane), and slightly faster flamespeed 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.

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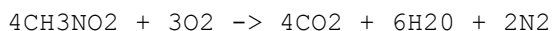Relevant properties include [116]:-                              Avgas
                                Propylene Oxide    100/130  115/145
Density                 (g/ml)       0.828          0.72     0.74
Boiling Point            (C)          34           30-170   30-170
Stoichiometic Ratio     (vol%)        4.97          2.4      2.2
Autoignition Temperature (C)          464           440      470
Lower Flammable Limit   (vol%)        2.8           1.3      1.2
Upper Flammable Limit   (vol%)        37            7.1      7.1
Minimum Ignition Energy  (mJ)         0.14          0.2      0.2
Nett Heat of Combustion (MJ/kg)       31.2          43.5     44.0
Flame Temperature        (C)         2087          2030     2030
Burning Velocity        (m/s)         0.67          0.45     0.45
```

9.8.4 Nitromethane

Nitromethane (CH3NO2) - 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 CH3NO2) and relatively high heats of vaporisation (0.56 MJ/kg for CH3NO2) result in dramatic cooling of the incoming charge.

    4CH3NO2 + 3O2 -> 4CO2 + 6H20 + 2N2

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 [28].

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 [131].

```
                              Temperature      Flame Speed
  Fuel          Oxidant          ( C )           ( 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 an
SI engine is very large. The membranes have to be laid close together, or
wound in a spiral, and significant amounts of power are required to force
the air along the membrane surface for sufficient enriched air to run a
slightly modified engine. Most research to date has centred on CI engines,
with their higher efficiencies. Several systems have been tried on research
engines and vehicles, however the higher NOx emissions remain a problem
[132,133].

Subject: 10. Historical Legends

10.1 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 150.]

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

to 100 Octane, and further increases if the engine could handle 100+ PN fuel [134]. 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 [14].

Triptane was first shown to have high octane in 1926 as part of the General Motors Research Laboratories investigations [135]. 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 [14].

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

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

So, the myth that triptane was the wonder 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 [52]. 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 [14].

10.2 From Honda Civic to Formula 1 winner.

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

There are many variables that will determine the power output of an engine. High on the list will be the ability of the fuel to burn evenly without knock. No matter how clever the engine, the engine power output limit is determined by the fuel it is designed to use, not the amount of oxygen

stuffed into the cylinder and compressed. Modern engines designs and gasolines are intended to reduce the emission of undesirable exhaust pollutants, consequently engine performance is mainly constrained by the fuel available.

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

Engine	Standard	Formula One	Formula One
Year	1986	1987	1989
Size	1.5 litre	1.5 litre	1.5 litre
Cylinders	4	6	6
Aspiration	normal	turbo	turbo
Maximum Boost	-	58 psi	36.3 psi
Maximum Fuel	-	200 litres	150 litres
Fuel	91 RON	102 RON	102 RON
Horsepower @ rpm	92 @ 6000	994 @ 12000	610 @ 12500
Torque (lb-ft @ rpm)	89 @ 4500	490 @ 9750	280 @ 10000

The details of the transition from Standard to Formula 1, without considering engine materials, are:-

1. Replace the exhaust system. HP and torque both climb to 100.
2. Double the rpm while improving breathing, you now have 200hp but still only about 100lb-ft of torque.
3. Boost it to 58psi - which equals four such engines, so you have 1000hp and 500lb-ft of torque.

Simple?, not with 102 RON fuel, the engine/fuel combination would knock the engine into pieces, so....

4. Lower the compression ratio to 7.4:1, and the higher rpm is a big advantage - there is much less time for the end gases to ignite and cause detonation.
5. Optimise engine design. 80 degree bank angles V for aerodynamic reasons, and go to six cylinders = V-6
6. Cool the air. The compression of 70F air at 14.7psi to 72.7psi raises its temperature to 377F. The turbos churn the air, and although they are about 75% efficient, the air is now at 479F. The huge intercoolers could reduce the air to 97F, but that was too low to properly vaporise the fuel.
7. Bypass the intercoolers to maintain 104F.
8. Change the air-fuel ratio to 23% richer than stoichiometric to reduce combustion temperature.
9. Change to 84:16 toluene/heptane fuel - which complies with the 102 RON requirement, but is harder to vaporise.
10.Add sophisticated electronic timing and engine management controls to ensure reliable combustion with no detonation.

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

For subsequent years the restrictions were even more severe, 150 litres
and 36.3 maximum boost, in a still vain attempt to give the 3 litre,
normally-aspirated engines a chance. Obviously Honda took advantage
of the reduced boost by increasing CR to 9.4:1, and only going to 15%
rich air-fuel ratio. They then developed an economy mode that involved
heating the liquid fuel to 180F to improve vaporisation, and increased
the air temp to 158F, and leaned out the air-fuel ratio to just 2% rich.
The engine output dropped to 610hp @ 12,500 (from 685hp @ 12,500 and
about 312 lbs-ft of torque @ 10,000 rpm), but 32% of the energy in
the fuel was converted to mechanical work. The engine still had crisp
throttle response, and still beat the normally aspirated engines that
did not have the fuel limitation. So turbos were banned. No other
F1 racing engine has ever come close to converting 32% of the fuel
energy into work [136].

In 1995 the FIA listed a detailed series of acceptable ranges for
typical components in racing fuels for events such as F1 races, along
with the introduction of detailed chromatographic "fingerprinting" of
the hydrocarbon profile of the fuel [137]. This was necessary to prevent
novel formulations of fuels, such as produced by Honda for their turbos.

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