

CHAPTER 2

THEORETICAL CONSIDERATION

2.1 Gasoline (13)

2.1.1 General Characteristics

Gasolines are a complex mixture of hydrocarbons of four basic types differing in their properties according to the number of carbon and hydrogen atoms in the molecule and in the arrangement of the atoms, having a boiling range from 30 to 210°C, containing compounds in the range C₅ to C₁₂ (14). The four basic types of hydrocarbons are paraffins, olefins, naphthenes, and aromatics. With the processes available today the refiner can use hydrocarbon compounds of these four types to tailor his gasoline to commercial requirements.

By using high resolution capillary gas chromatography (HRCGC), chromatogram of a single commercial gasoline obtained on a squalane column shows probably more than 400 detectable components. In a typical gasoline, 100 to 150 compounds account for 90% of the volume (15).

In the internal combustion engines, gasoline is mixed with air and the mixture burned in the engine cylinder at the proper time in the engine cycle. Theoretically, the proper ratio of air to gasoline for perfect combustion is 15 parts by weight of air to 1 part of

gasoline. However, when burned in an engine this mixture generally does not give either maximum power or maximum economy. S. Bennett Hill and John G. Moxey, Jr.,⁽¹⁶⁾ pointed out that to function satisfactorily in the internal combustion engines, the gasoline must:

1. Burn smoothly and quietly in the cylinder without detonation or knocking.

2. Evaporate readily enough to supply a combustible mixture of fuel vapor and air to the cylinder when the engine is started cold.

3. Not be so volatile that it boils in the fuel pump or fuel lines when the engine is hot, resulting in vapor lock.

4. Under normal running, with the engine warm, it must be sufficiently volatile so that a considerable portion is vaporized in the intake manifold and the disturbing effects of liquid in the manifold are minimized.

5. It must not contain components of such low volatility that they are not vaporized and burned in the hot cylinder.

6. It must evaporate completely and cleanly without leaving solid or gummy deposits in either the fuel or the induction system.

Most refiners produce and market more than one grade of motor gasoline. The difference in these grades, a regular and a premium grade, is based on the octane rating of the fuels, differing principally in antiknock quality. Refiners also change the volatility properties of their motor fuels, depending on the atmospheric temperatures at which the vehicle is to operate.

2.1.2 Performance Requirements

Antiknock Quality

This tendency to knock, or "ping", or explode on compression in internal combustion engines is quantified by the octane number. Two laboratory methods, the Research and the Motor method, have been standardized for obtaining octane numbers of motor fuels by comparing their knock tendencies in standard test engines with reference fuels blended from n-heptane and isooctane. The proportion of "isooctane" in the reference fuel which matches the knock tendency of the fuel under test is termed its octane number (13). Because "isooctane" has better antiknock properties than most commercial gasolines, it is arbitrarily assigned an octane number of 100. A poor fuel, n-heptane, is assigned an octane rating of zero. Generally, n-paraffins have lower octane numbers than branched paraffins, while olefins and aromatics have high octane numbers. Olefins do not occur in significant concentrations in most petroleum, but are formed during refining operations and are important in increasing the octane number of fuels now that the use of lead-containing additives is being phased out (14).

The Research and the Motor method use the same basic test engine but operate under different conditions. The Research octane number (RON) is accepted as a better guide of antiknock quality of fuels when vehicles are operated under mild conditions associated with low engine speeds. When operation is at high engine speed or under heavy load conditions, the Motor octane number (MON) may become of equal or greater importance.

Table 2.1 Operating conditions for Research and Motor methods (17)

Conditions	Motor method	Research method
Inlet temperature	149 °C (300 °F)	52 °C (125 °F)
Inlet pressure	Atmospheric	
Humidity	0.0036-0.0072 kg/kg dry air	
Coolant temperature	100 °C (212 °F)	
Engine speed	900 rpm	600 rpm
Spark advance	19-26 °Btc (varies with comp. ratio)	13 °Btc (constant)
Air - fuel ratio	Adjusted for maximum knock	

The difference between RON and MON of a given fuel is known as its sensitivity. A high difference is taken to indicate greater sensitivity of the fuel to changes in severity of operating conditions of the engine.

Surface Ignition

This is another form of abnormal combustion in an automobile engine that is associated closely with knock but is actually a separate phenomenon. It is defined as the initiation of a flame front by any hot surface other than the spark discharge (such as overheated exhaust valves, spark-plug electrodes, or porcelains) prior to the arrival of the normal flame front. Principle offenders are combustion chamber deposits. Gasolines have been improved to remedy this

condition by more careful control of tail-end volatility and by use of additives that alter the chemical composition of deposits.

Volatility

Gasolines differ in their distillation range, or volatility, since they are a mixture of a large number of hydrocarbons with different boiling points. Gasoline volatility controls its performance for starting, vapor lock, warm-up, and crankcase dilution.

Starting

Approximately 10% of the gasoline in the fuel-air stream must evaporate and reach the cylinder as a vapor in order to give prompt starting.

Starting requirements in a motor fuel are of significance when the problem of vapor lock is considered. If too much of light hydrocarbons is included to give satisfactory starting characteristics, the motorist may encounter vapor lock on warmer days. On the other hand, if the proportion of the light hydrocarbons is kept low to protect against vapor lock, the motorist may have difficulty in starting.

Vapor Lock

This is a complex problem resulting from the fact that gasoline boils and forms vapor somewhere in the fuel system between the fuel tank and the carburetor discharge nozzle. Boiling may take place in the line to the pump, in the pump, in the line from the

pump to the carburetor, in the carburetor bowl, or even in the carburetor fuel passages. The vapor formed interrupts the normal flow of liquid fuel, and the engine will lose power and may misfire or stall completely.

Oxidation Stability

In certain gasolines, particularly those produced by cracking, easily oxidizable hydrocarbons may be present which have a tendency to form gummy materials at the carburetor float valve, in the venturi area of the carburetor nozzle, around the throttle, or on valve stems. Today the refiner removes the small amounts of undesirable, oxidizable hydrocarbons present in the raw gasoline. Most retail gasolines also contain an oxidation-inhibitor additive.

Odor and Colour

While these properties have no effect on the performance of motor gasoline, they are objectionable to the motorist. Refiners remove or neutralize the sulfur compounds known as mercaptans, which are the principle sources of offensive odor. Most motor gasolines are artificially coloured with gasoline-soluble dyes.

2.1.3 Gasoline Additives

Components are blended to promote high antiknock quality, ease of starting, quick warm-up, low tendency to vapor lock, and low engine deposits. For the purposes of preliminary plant design, however, the compounds used in blending motor gasoline can be limited to light straight-run gasoline, catalytic reformat,

catalytically cracked gasoline, hydrocracked gasoline, polymer, alkylate, and n-butane to achieve the desired Reid vapor pressure. The quantity and cost of antiknock agents, if used, must be determined by making octane blending calculations (18).

Antiknock Compounds

Tetraethyl lead (TEL) was first introduced in 1922. The exact mechanism by which TEL works to suppress knock is not known. In simple terms, it is visualized that the compound is decomposed by the heat in the combustion chamber, giving rise to particles which then influence the chemical reactions involved in the combustion of the fuel in such a way as to promote smooth combustion to the exclusion of knock. TEL is used in concentrations up to 3 ml per gal, which is equivalent to 0.08 percent by volume of the fuel into which it is blended.

TEL has certain well recognized disadvantages such as tending to increase deposits in the combustion chamber, tending to increase exhaust valve burning, tending to foul spark plugs, and resulting in exhaust gases that endanger health. In the absence of TEL it is possible to improve the antiknock rating by increasing, relative to straight chain hydrocarbons, the proportion of branched, cyclic, and aromatic hydrocarbons, but this results in a decrease in the extraction rate of useful fuel from petroleum. These disadvantages have been minimized through improved engine design, improved gasolines, and the use of other additives. The use of oxygenates in motor fuels were recognized as octane boosters and were accredited with giving "no knock" and "smoother burning".

Dyes

Dyes used in gasoline are the oil-soluble type. They are present to the extent of about 5 ppm.

Antioxidants

Antioxidants are used widely to inhibit the oxidation reaction which forms gums and thereby tend to improve the stability of gasoline in use or in storage. There are two major classes of antioxidant compounds, aromatic amines and alkyl-substituted phenols, used in concentrations of about 50 ppm.

Metal Deactivators

Metal deactivators are used in addition to antioxidants to destroy the catalytic effect of copper in promoting the gum-forming oxidation reaction. The concentration used is about 4 ppm.

Antirust Agents

Antirust agents are added to gasoline at the refinery to protect pipelines and storage tanks from the corrosive condition caused by the minute amounts of water usually present in gasoline.

Antipreignition Agents

This class of additives, also known as deposit modifiers, acts to change the character of the combustion-chamber deposits to give less tendency to induce preignition, thus reducing the tendency

of the engine to knock as the car builds up mileage. Phosphorus compounds are increasingly used as antipreignition agents in concentrations of around 200 ppm.

Upper-cylinder Lubricants

Many refiners incorporate from 0.2 to 0.5 percent of light lubricating oil or similar materials into their gasolines to provide extra lubrication for the engine intake valves and the top ring belt area. This light oil serves to prevent the deposition of gummy deposits in the intake system but may contribute to combustion-chamber deposits.

2.2 Combustion and Theory of Knock (1,2)

Spark ignition engines are operated by the following steps:

1. **Intake stroke** : the air-fuel mixture is drawn into the cylinder, the fuel being present partly as a vapor and partly as small liquid droplets.

2. **Compression stroke** : the air-fuel mixture is rapidly compressed and the magnitude of the compression ratio of the engine depends on the engine.

3. **Combustion** : the spark ignites the mixture, combustion being essentially at constant volume.

4. **Power stroke** : the hot combustion gases expand, the work of expansion being transmitted to the crankshaft of the engine.

5. **Exhaust stroke** : the combustion gases are pushed out of the cylinder and the above cycle is repeated.

2.2.1 Normal Combustion (17)

Normal combustion occurs in a spark-ignited automobile engine whenever a mixture of hydrocarbon fuel and air burns in a controlled fashion within the combustion chamber.

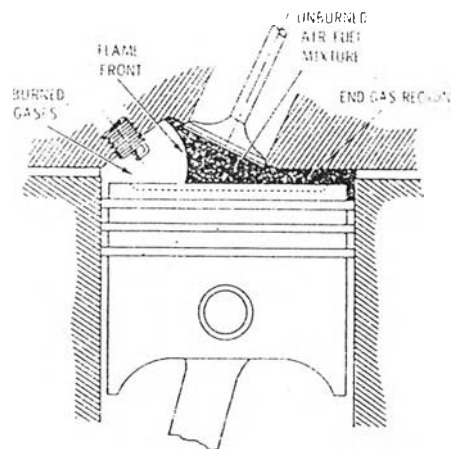


Figure 2.1 Schematic of normal combustion process (17)

A flame created at the spark plug advances into the unburned mixture so that the flame front propagates throughout the chamber until it is quenched near the wall surfaces. The chemical reaction between fuel and oxygen liberates energy that causes a rise in temperature. This temperature rise is primarily responsible for the pressure rise that drives the piston. Part of this energy is converted to usable work by the expanding gases acting against the piston top. The remainder is lost by heat rejection to the coolant and in the exhaust gases.

2.2.2 Abnormal Combustion (12,17)

Abnormal combustion in a spark ignition engine can be described as any chemical reaction of an air-fuel mixture that occurs in the absence of a spark and that results in a sudden release of chemical energy causing a rapid rise in temperature and pressure. This self-ignition process encompasses a general category which can describe such phenomena as (Figure 2.2) :

1. **knock** : an end-gas explosion.
2. **run-on** : a compression ignition at idle, sometimes referred to as "dieseling" or "after-run".
3. **pre-ignition** : a surface ignition before spark-ignition can occur.
4. **misfire** : flame kernel too weak and so the flame dies early.
5. **exhaust valve seat recession** : environment too hostile for the 'soft' metallurgy.

Knock and run-on are probably the forms of abnormal combustion most often noted by drivers in today's engines. Knock or detonation is usually identified by an audible "pinging" sound emanating from the engine during part-load or full-load operation. This sound is caused by high-frequency (about 500 cycles/sec) vibration of the engine structure induced by gas pressure waves within the combustion chamber. These pressure waves are generated by "autoignition" of the gas ahead of the normal flame front. Knock causes increased heat rejection to the coolant and a loss of engine power. In severe cases of sustained knock, failure of pistons and connecting rods can also occur.

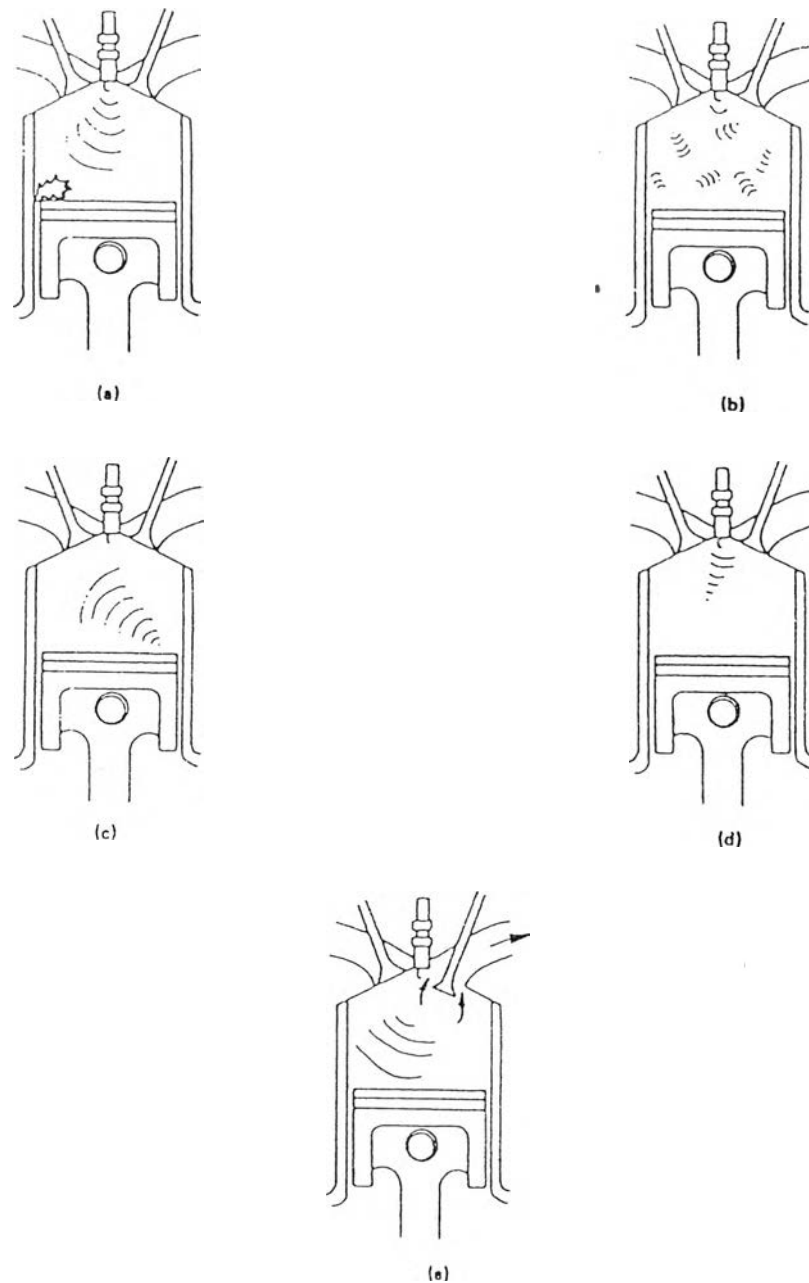


Figure 2.2 Abnormal combustion characteristics

(a) Knock (an end-gas explosion)

(b) Run-on (a compression ignition at idle)

(c) Pre-ignition (a surface ignition before spark-ignition can occur)

(d) Misfire (flame kernel too weak and so the flame dies early)

(e) Exhaust valve seat recession (VSR) (environment too hostile for the 'soft' metallurgy) (12)

Several engine design and operating variables affect knock. In general, the tendency to knock usually changes with changes in the variables listed in Table 2.2.

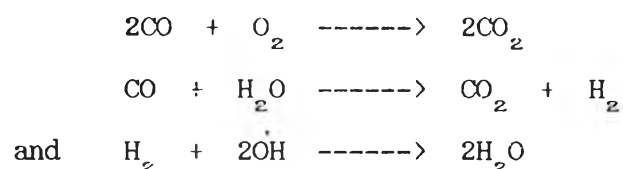
Table 2.2 Engine variables which affect knock (17)

Knock tendency increases	Knock tendency decreases
1. Higher compression ratio	1. Increased quench area
2. Advanced spark timing	2. Increased turbulence
3. Higher inlet air temperature	3. Higher engine speed
4. Increased barometric pressure	4. Higher humidity
5. Higher coolant temperature	5. Increased charge dilution (i.e. exhaust gas recirculation)
6. Increased load (throttle opening)	6. A/F richer or leaner than stoichiometric

Another abnormal combustion problem is run-on, caused by compression ignition and occurs when a spark ignition engine continues to run after the ignition is turned off. Recent investigations (19) have shown that run-on increases as the throttle opening at the idle increases, and decreases with increased octane quality of the fuel.

2.2.3 Characteristics of Knock (20)

Combustion of the fuel is practically complete within the narrow flame front, yielding carbon monoxide, carbon dioxide, and water (21). The traces of hydrocarbons found in exhaust gases result from the thermal decomposition of unvaporized fuel and oil on the cylinder walls. When the gases behind the flame front begin to cool down, readjustments occur in the equilibria:



The spectrum of the flame front in an engine similar to that of a Bunsen burner, comprising a number of well-known bands (eg. C-H and C-C) superimposed on a background of continuous emission; its ultra-violet spectrum shows CO and OH bands (22); its infrared emission indicates the presence of carbon dioxide and water.

The occurrence of knock in the engine is marked by flame and pressure characteristics distinctly different from those of normal combustion. These characteristics are confined to a portion of the charge, which is the last to burn; so called "end gas".

In non-knocking operation no indication is found of any extensive chemical change in the end gas. When the fuel of operating condition are changed in the direction to produce knock, absorption spectra show the presence of formaldehyde in the non-inflamed end gas, in amounts which increase as the threshold of knock is approached. Concurrently, the flame spectra show a decrease in the

emission of C-C and C-H bands, suggesting that the original fuel molecules have been partially oxidized or dissociated before the arrival of the flame front.

In 1918 Ricardo (22) stated that knock resulted from a simultaneous and spontaneous ignition of the last part of the charge to burn. Elbe and Lewis (21) presented the theory of hydrocarbon combustion reactions in the internal combustion engine. The combustion process is pictured to involve a race between combustion by a moving flame and the spontaneous ignition of the unburnt charge ahead of the flame.

The series of fact which brought out by the experiments conducted directly with engines or in closely related apparatus indicated that the development of the chain-reaction theory of the slow oxidation and explosion of gases provided a reasonable basis for the explanation of the phenomena observed. Detailed discussions of chain-reaction theory are available (5,12,23). Generally, it appears that the oxidizability of the fuel is the basic factor in determining its knocking tendency.

2.3 Oxygenates in Motor Gasolines (24)

With the phasing out of lead additives from gasoline, oxygenated supplements, covering a range of alcohol and ether types, have been recognized as a means of easing the octane burden on refiners, fuel blenders and marketers. However, Since these materials are not hydrocarbons their behaviour in terms of blending and vehicle performance is different from hydrocarbon-only gasolines. Furthermore, although many alcohols and ethers have high octane

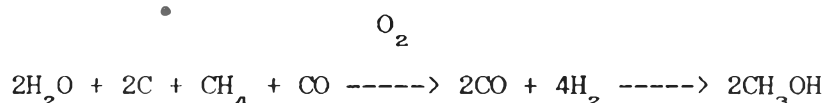
numbers they are not as effective as lead in raising base fuel octane numbers nor do they offer any valve seat protection. Therefore they cannot be regarded as a means of total lead replacement. Thus there is a need to evaluate the performance of oxygenates in blends with gasoline in order to define their scope, to establish credibility with existing gasoline specifications and to ensure acceptable market satisfaction.

Technically, Therefore, oxygenates may be regarded as the means of fulfilling three basic needs: extending the gasoline pool; boosting octane values; and providing the refiner with additional blending flexibility to meet ever-increasing demands on quality.

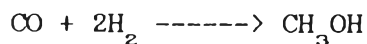
2.3.1 Manufacture of Oxygenates

Methanol

The first and oldest process for the production of methanol was the destructive distillation of wood, hence "wood alcohol". However, methanol is now produced synthetically using natural gas, coal gas, water gas or sewage gas at high pressure and temperature in the presence of metallic catalysts, and can be described by the general reaction equations:

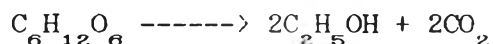


Direct synthesis from carbon monoxide and hydrogen (the intermediate product above) may also be performed at elevated temperatures and pressures as follows:

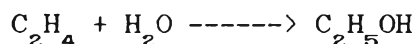


Ethanol

Commercially, there are two major manufacturing routes to the production of ethanol, namely "natural" and "synthetic". The natural route involves the fermentation of carbohydrates. These reactions come under the general heading of "bio-ethanol" and generally follow the equation:



"Bio-ethanol" is wet and requires drying before it can be considered as a motor gasoline supplement. The synthetic route generally involves the hydration of ethylene to ethanol, i.e.:



Ethylene is readily available from steam cracking where the primary use is in the manufacture of polyethylene.

Tertiary butyl alcohol

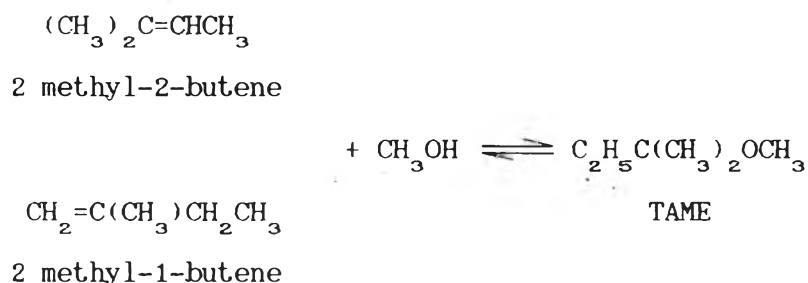
Tertiary butyl alcohol (TBA), the most commonly used of the methanol cosolvents, is produced and marketed by Arco Chemicals Inc. in the form of gasoline grade tertiary butyl alcohol (GTBA). The Arco process consists of a controlled oxidation of isobutane to TBA and tertiary butyl hydroperoxide (TBHP). The TBHP is reacted with propylene to produce propylene oxide (PO) and additional TBA. The ratio of TBA to PO is approximately 2.0-2.5 : 1, and the general

The MTBE formation reaction is equilibrium limited. Higher temperatures increase the reaction rate, but the conversion level is lower. Lower temperatures shift the equilibrium toward ether production, but more catalyst inventory is required. Therefore, conventional MTBE units are designed with two reactors in series. Most of the etherification reaction is achieved at elevated temperature in the first reactor and then finished at a thermodynamically advantageous lower temperature in the second reactor.

The main differences among the licensors are found in the reaction section. The reaction sections are designed to effectively control the exothermic heat of reaction.

Tertiary-amyl methyl ether

Tertiary-amyl methyl ether (TAME) is produced commercially by reacting an isoamylene, in which the double bond is on the tertiary carbon atom, with methanol. The exothermic reaction is reversible and catalysed by an acidic cation exchange resin:



Commercially, the feed for this process is either the C₅ fraction of a light catalytically cracked gasoline stream or a partially hydrogenated light steam-cracked gasoline stream.

Mixed ethers (26)

A number of processes, including the BP "Etherol" process, use mixed C_4 , C_5 , C_6 and C_7 olefins derived from catalytically cracked or steam-cracked streams and etherify the iso-olefins in the presence of methanol to produce mixtures of MTBE, TAME as well as C_6 and C_7 ethers. This process is particularly successful in upgrading the motor octane qualities of cracked naphthas and gives a product known as "etherified spirits" (24).

The isobutanol is advantageously not separated from the other higher alcohols but rather the whole higher alcohol mixture is subjected to dehydration and the resulting mixture of olefins is used to form ethers. This gives rise to a mixture of MTBE and other ethers. These mixtures are particularly useful gasoline additives: in some cases, RON of the gasoline containing the additive ether mixture is greater than that which would be expected from the use of the individual ethers. Also, by using a mixture of ethers, the boiling range of the octane enhancing components of the gasoline is advantageously broadened.

It has been proposed in published British Patent Application 2031886 to employ mixtures of MTBE and t-amyl methyl ether as gasoline additives. However such mixtures were obtained from a C_4 - C_5 hydrocarbon refinery fraction and were essentially only binary mixtures.

In UK Patent Application GB 2123411A (26) provided a process for the manufacture of a mixture of ethers useful as gasoline additives comprising:

i) synthesising, from synthesis gas comprising hydrogen, carbon monoxide and, optionally, carbon dioxide, a mixture of alcohols consisting of methanol, ethanol and higher alcohols.

ii) dehydrating said higher alcohols to give a mixture of olefins, and

iii) etherifying said olefin mixture by reaction with

a) methanol, and optionally ethanol, including at least part of methanol, and optionally ethanol, in alcohol mixture, and/or with

b) di-alkyl ethers resulting from dehydration of methanol, and optionally ethanol, including at least part of methanol, and optionally ethanol, in alcohol mixture.

2.3.2 Materials Compatibility

Materials compatibility studies are concerned with metal corrosion, elastomer and plastic attack and the effect on tank linings. In general terms, for both corrosion and elastomer compatibility it was found that the antagonistic effect of the oxygenated gasolines towards the test specimens showed the order of attack to be

methanol > ethanol > TBA > MTBE

However, increasing oxygenate content, temperature and, in the corrosion tests, water content increased the magnetude of the attack.

2.3.3 Distribution of Fuels Containing Oxygenates

From point of manufacture to point of sale, most gasolines have to be transported significant distances by various means. At any point in the distribution system, the motor gasoline may come

into contact with water. With wholly hydrocarbon gasolines this presents few problems, as hydrocarbons and water are virtually immiscible. However, alcohols are miscible with water, and in the presence of hydrocarbon tend to show a greater affinity for water than for the hydrocarbons. Hence, if a distribution network is too wet, alcohols tend to be leached out by "free" water, with two oxygenate-rich phases forming. These may either be in the form of distinct layers or as a hazy or cloudy product. Either way, product quality is adversely affected.

Methanol is infinitely miscible with water and in the presence of hydrocarbons has a low water tolerance, that is, the methanol/hydrocarbon blend cannot retain very much water without separating into two distinct layers. Higher alcohols such as tertiary butanol, isobutanol and isopropanol have high water tolerances and, when added to methanol/hydrocarbon blends, increase the water tolerance of the methanol. Hence higher alcohols of this type are often called cosolvents.

There are a number of ways to increase the water tolerance of an oxygenated blend, thereby reducing the probability of phase separation. These include increasing the aromatic content of the blend, the oxygenate concentration and/or the bulk temperature of the product. It is essential therefore, when distributing oxygenated/hydrocarbon blends (especially alcohols), that the pipe and tankage network should be as water-free as possible. Ethers (e.g. MTBE) are soluble in water but only at low levels and exhibit characteristics similar to hydrocarbons rather than alcohols.

2.3.4 Vehicle Performance with Fuels Containing Oxygenates

The following aspects of vehicle performance can be influenced by the presence of oxygenates in the gasoline:

1. Road anti-knock performance
2. Driveability (hot and cold weather)
3. Exhaust emissions
4. Fuel economy
5. Inlet system detergency
6. Evaporative emissions
7. Intake system icing

Detailed discussions are available (24).

Exhaust Emissions

Oxygenate supplements in gasoline can affect exhaust emission levels largely through "leaning effects". This is a particularly useful feature in "older" vehicles, which tend to run with progressively richer fuel mixtures with mileage. This is probably due to the fact that older cars were generally set to richer mixture settings and, with general trends in engine tune with mileage, etc., the mixture enrichment that would ensure could be counteracted by the leaning effects of oxygenates.

The net effects from refinery blending of oxygenates must be estimated from the knowledge of reducing aromatic content of the gasoline. Since reductions of gasoline properties such as aromatics content, heat of vaporization and boiling points of gasoline will also contribute in lower CO and HC emissions, refinery blending of high octane oxygenates such as ethers are expected to have a much

greater overall emission reduction benefit than just splash blending of oxygenates as typically done with ethanol (27).

In the case of MTBE, with its lower oxygen content, it appears that the enleanment effect plays a smaller role. MTBE's lower flame temperature effect begins to dominate in apparently lowering NOX emissions when the volume percent of MTBE exceeds 11 volume percent (2 wt% oxygen) in the fuel (27).

Fuel Economy

This is borne out by Figure 2.3 and 2.4, which show that the fuel economy of commercial oxygenated gasolines is essentially unchanged by increasing amounts of oxygenates. Indeed, Figure 2.4 show that there could be marginal benefits in terms of reduced energy consumption with increased fuel oxygen content.

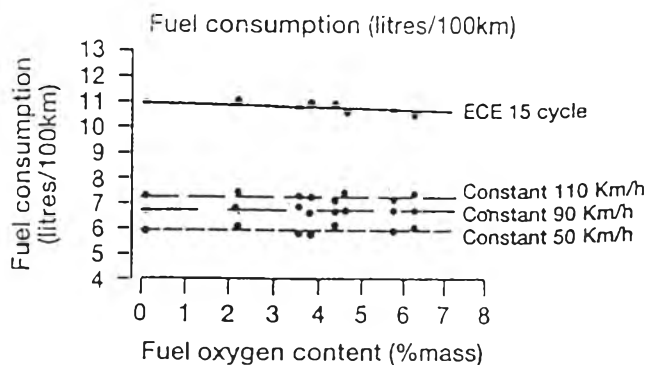


Figure 2.3 Volumetric fuel consumption (average of five vehicles) (24)

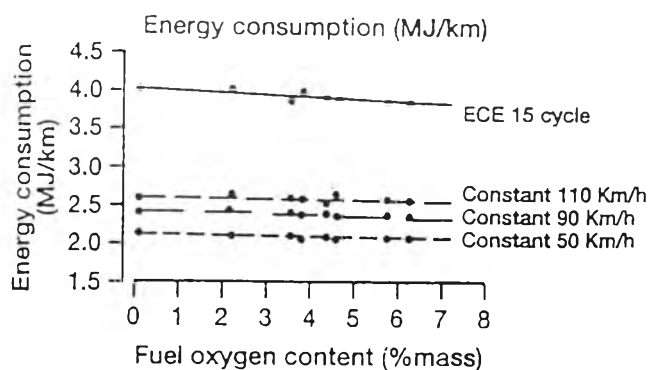
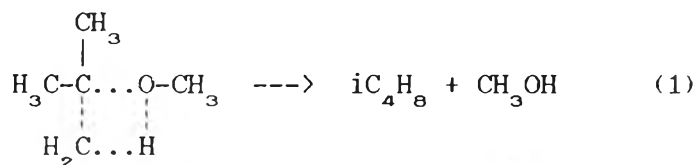


Figure 2.4 Fuel energy consumption (average of five vehicles) (24)

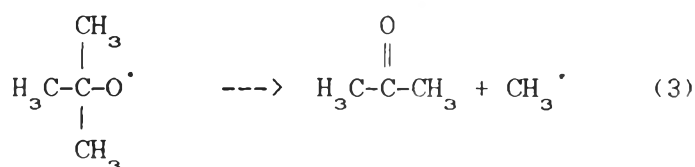
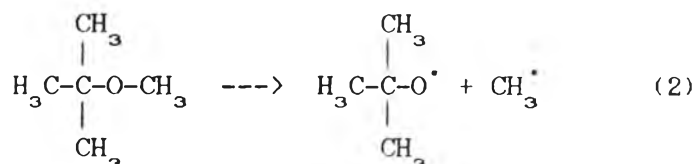
2.4 Oxidation of Methyl tert-Butyl Ether (28)

The oxidation of MTBE is studied in the Princeton atmospheric pressure flow reactor at initial temperatures of 1028K and 1119K, and equivalence ratios near one. The reaction is primarily governed by the formation of a four centered complex which decomposes to form isobutene and methanol, as previously determined by static reactor, lower temperature experiments (below 800K) (29-33).

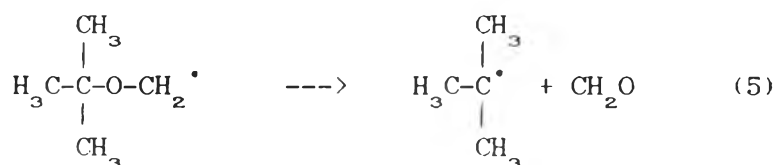
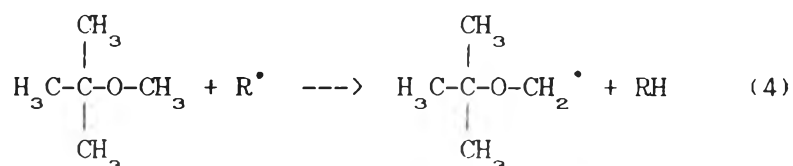


The existence of alternative unimolecule decomposition reactions and hydrogen abstraction reactions is supported by the appearance of acetone as an intermediate, and by the formation of larger quantities of isobutene than methanol.

Acetone formation can be accounted for by the cleavage of the methyl-ether C-O bond in MTBE. This is a relatively weak bond (ca.83 kcal/mol (34)), and the resulting molecule can then β -scission to form acetone and a methyl radical:



The C-H bond strengths of the methyl-ether group on MTBE are approximately 93 kcal/mol (34), which is the same as for a tertiary C-H bond. Thus, it is not surprising that a considerable quantity of MTBE might react through abstraction of these hydrogen atoms. The resulting radical would undergo β -scission at these temperatures, and form the tert-butyl radical and formaldehyde:



Finally, the tert-butyl radical is unstable at high temperatures, and rapidly decomposes to form isobutene and H radical, thus accounting for the appearance of larger quantities of isobutene than methanol, since no methanol is formed in this route.

The implications are that although MTBE acts as an anti-knock agent by introducing two chemical species with high blending octane rating, isobutene and methanol, its effect is less than would be expected than if only Reaction (1) were present. This is due to the production of formaldehyde, an extremely reactive compound, via Reaction (5). Of course, the present results are for atmospheric pressure, and other mechanistic changes may also occur as the pressure is increased to magnitudes similar to that in engines.

2.5 Tin Chemicals (35)

Tin is one of the world's most valuable metals. Although its annual consumption is quite small compared to many industrial metals, its importance lies in the fact that it is a vital component in a large number of fields. Major uses include tin plate associated with can-making and food-packing industries, an integral part of the electrical and electronic industries. Tin chemicals represent a growing use of tin, and in particular, the growth in consumption of the type of compounds known as organotins has increased dramatically.

Tin chemicals become so important because they exhibit a wide range of properties that can often be tailored to meet the requirements of specific end users. This is particularly true of the organotin class of compound, where changing the number or nature of the organic moiety can have a dramatic effect on the chemical and/or

biological properties. Tin compounds are often effective in very low concentrations in many applications, which is advantageous from a formulation and cost effectiveness point of view. In addition, there are particularly favourable environmental aspects that often give a decisive advantage over alternative materials (35). Inorganic tin compounds in particular are regarded as not presenting any health or environmental problems because, at physiological pH, the metal does not react and the oxides are insoluble (36).

Tin(IV) chloride [SnCl₄]

Tin (IV) chloride is colourless liquid which freezes at -30.2°C and boils at 114°C . It reacts vigorously with water, and hence fumes in moist air due to hydrolysis. By adding the anhydrous liquid to water under carefully controlled conditions, white solid crystals of the pentahydrate, SnCl₄.5H₂O, are formed. The pentahydrate is a deliquescent solid, very soluble in water or alcohol. Anhydrous tin(IV) chloride is prepared industrially by the reaction of dry chlorine with metallic tin at 110°C - 115°C .

An important use for the compound is as a starting material for the manufacture of organotin compounds, and for other tin(IV) compounds generally. In this research, it is used as a starting material for the synthesis of tetrahexyltin compound.

Tin(IV) oxide [SnO₂]

Tin(IV) oxide is one of the most industrially important tin compounds, and has found applications in many different areas as described below.

- Ceramics industry

Anhydrous tin(IV) oxide has been used as an opacifier in ceramic glazes.

- Glass applications

A major application of tin(IV) oxide is for surface films on glass. Transparent SnO_2 films are employed to strengthen glassware such as returnable and non-returnable bottles and jars, and catering glassware subjected to rigorous use.

- Catalytic applications

Tin(IV) oxide is one of the components of a number of binary oxide systems which find extensive use as heterogeneous catalysts in industry. The ability of SnO_2 to oxidise carbon monoxide has also led to air purification applications, for example in submarines and safety masks.

- Gas sensors

The semiconductor properties of tin(IV) oxide form the basis of its well-established use in gas sensors. The increase in conductivity is a measure of the gas concentration, and such gas sensors are available for the detection of hydrocarbons, other combustible gases, alcohol, carbon monoxide, ammonia, etc.

- Other uses such as ion-exchange resins.

Unlike lead, tin(IV) oxide produced in the combustion of tetraorganotin-blended gasolines is regarded as not presenting any health or environmental problems.

Organotin Compounds

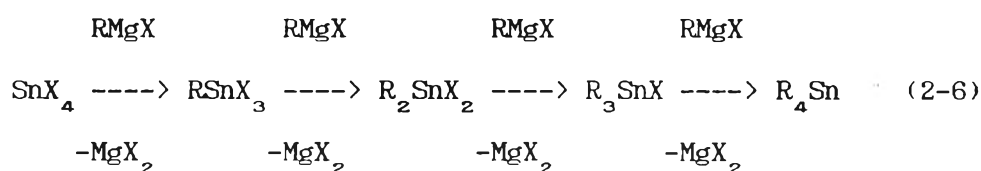
Organotin compounds are defined as those which contain at least one direct tin-carbon bond. The great majority of such compounds, and all the industrially important ones, have tin in the tetravalent state, and hence they can be conveniently divided into four classes: the mono-, di-, tri-, and tetraorganotins. The tin-carbon bond is more polar than carbon bonds to carbon, silicon, or germanium in Group (IV), and hence is more reactive. However, the tin-carbon bond is stable to water and atmospheric oxygen at normal temperatures. The number and nature of the organic groups attached to the tin atom dramatically affect the properties of the compound particularly its bioactivity, and this has resulted in organotins finding applications in a wide range of areas.

Tetraorganotin Compounds R_4Sn

Tetraorganotins are the first organotin products formed by the Wurtz, aluminium alkyl, and Grignard synthesis and hence they are an important intermediate in the manufacture of most other organotin compounds. This is their main use, and there are no other significant commercial applications at present, although they have been suggested as catalysts in various processes. Tetrabutyltin, $(nC_4H_9)_4Sn$, is marketed as an esterification catalyst. Tetramethyltin, $(CH_3)_4Sn$, is another precursor used to produce conductive tin(IV) oxide films on glass.

This is probably because the Grignard reaction easily gives R_4Sn in high yield in excess Grignard reagent, and the other organotin derivatives are produced the Kocheskov reaction. In general the yields of the organotin compounds are between 50 and 95 percent except in cases where they are influenced by steric factors.

In the Grignard reaction, a four-fold excess of Grignard reagent as an alkylating agent over stannic halide is theoretically required as shown in eq.(2-5), and the stannic halides are alkylated stepwise as shown in eq.(2-6), But actually, the resulting product is a mixture of R_4Sn , R_3SnX , R_2SnX_2 , and $RSnX_3$ when a four molar ratio of Grignard reagent to SnX_4 is used. So, generally, by using more than a four molar ratio of Grignard reagent to SnX_4 , the Grignard reaction can be used to prepare tetraorganotin (R_4Sn) only.



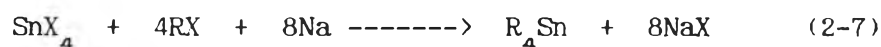
Chlorinated or brominated hydrocarbons are usually used as the starting materials. On the other hand, iodides are rarely used because of the low yield.

The conventional solvent for the Grignard reaction is ethyl ether or an ethyl ether-hydrocarbon mixture. But recently tetrahydrofuran and butyl ether have been found to be good solvents and they give improved yields. Phenyltin compounds and vinyltin compounds have been easily synthesized in tetrahydrofuran. The Grignard reaction can be carried out in high yield in toluene containing the minimum amount of ether needed to dissolve the

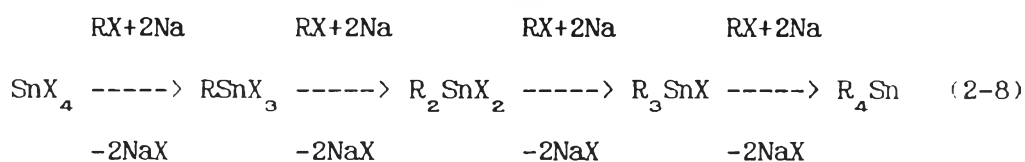
Grignard reagent on an industrial scale.

2.6.2 Wurtz Reaction

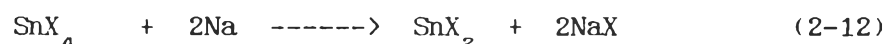
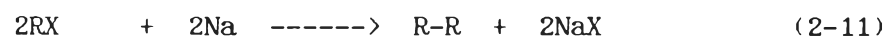
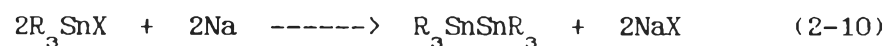
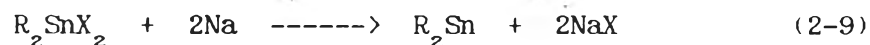
The Wurtz reaction, which relies on in situ formation of an active organosodium species, is a reaction for synthesizing R_4Sn by the reaction of stannic halide with a halogenated hydrocarbon and sodium metal. One disadvantage is that large volumes of solvent have to be used to suppress the conversion of the alkyl chloride RCl to the hydrocarbon $R-R$.



This reaction proceeds stepwise by the reaction of SnX_4 with alkylating agents and finally R_4Sn forms in the same way as in the Grignard reaction.



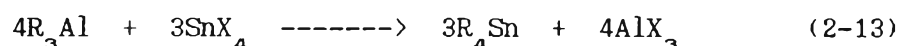
Various kinds of side reactions also proceed.



The basic Wurtz reaction is applicable to almost all simple alkyl and aryl chlorides. But, there are many disadvantages: degradation of solvent through further alkylation or arylation, formation of high boiling hydrocarbon by-products, the required control of sodium granulation, formation of R_2Sn and R_3SnSnR_3 compounds which are difficult to convert economically to the desired products, the hazard of excess sodium (because any reagent used to destroy excess sodium tends to also destroy some products) and difficulty in controlling temperatures.

2.6.3 Organoaluminums

Organotin compounds are prepared by reaction of organoaluminums with stannic halides as shown in eq.(2-13)

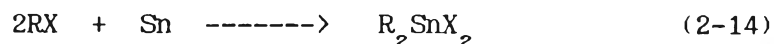


This reaction is also always accompanied by the formation of R_3SnX , R_2SnX_2 and $RSnX_3$. Koster (39) reported that the AlX_3 , formed by alkylation of the organoaluminum compound as shown in eq. (2-13), prevents stepwise alkylation with R_3Al because of the reaction of AlX_3 with the intermediate products R_nSnX_{4-n} , $n=1-3$, similar to the reactions shown in eq.(2-6) and (2-8).

The reaction of an organoaluminum gives R_4Sn easily in the presence of a complexing agent such as an ether, amine or sodium chloride. This method is useful for syntheses of higher alkyltin compounds because the yield of the Grignard method is lower. Alkylation with an organoaluminum compound has the advantage that it can be carried out in the absence of solvent.

2.6.4 Direct Reaction

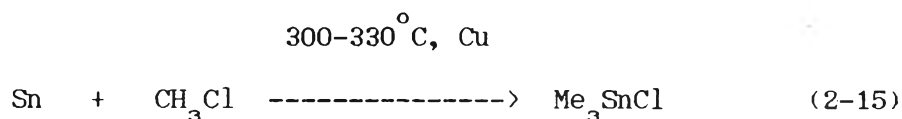
The organotin halide may be synthesized directly from tin metal.



The order of reactivity of the alkyl halide is RI > RBr > RCl and, for a given halogen, MeX > EtX > PrX, etc.

Rochow method

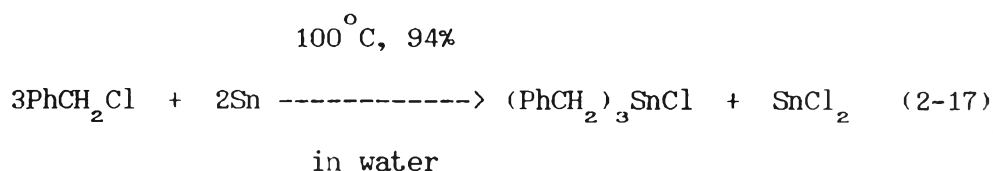
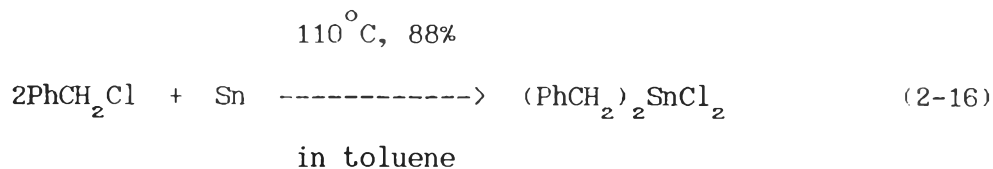
The direct reaction of organosilicon compounds, discovered by Rochow in 1944, was applied to the preparation of methyltin (eq. 2-15) and phenyltin compounds in 1953.



Sisido method

In 1953, Sisido and his co-workers found that dibenzyltin dichloride, tribenzyltin chloride and diallyltin dibromide were prepared in high yields by refluxing reactive halides such as benzyl chloride or allyl bromide with tin powder in water, or in toluene in the presence of a trace amount of water. The reaction in a strongly polar solvent gives the triorganotin compounds; on the other hand, that in a weakly polar solvent gives diorganotin compounds. The interconversion reaction proceeds in the respective solvent. For example, treatment at higher temperatures of the diorganotin

compound in water gives the triorganotin compound.

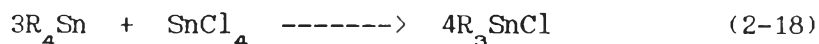


Matsuda-Matsuda method

Sumio Matsuda and Haruo Matsuda extensively studied the direct reaction of alkyltin halides with tin foil. The reactivity of alkyl chlorides with metallic tin is lower than that of alkyl bromides. The butyltin compounds are useful for industrial applications, but the reaction yield with butyl chloride is low. On the other hand, the reactivity of lower alkyl chlorides such as methyl chloride and ethyl chloride is high.

2.6.5 Redistribution Reaction (Kocheskov Reaction)

The redistribution reaction consists of the following three basic reactions of a tetraorganotin with anhydrous tin(IV) chloride. It is applied industrially since the desired pure organotin chloride is easily prepared.



In this reaction, which runs at elevated temperatures (>150°C), no solvent is used but it requires the presence of catalysts such as aluminum chloride and magnesium butanoate.

2.6.6 Industrial Preparations

Organotin compounds have been prepared industrially, usually by the Matsuda-Matsuda process in Japan, on the other hand, by the Grignard process and organoaluminum process in the United States and Europe.

In this study the selected organotin compound is a compound which tends to decompose readily forming tin metal or tin oxide particles in the combustion chamber. Therefore, tetraalkyltin was investigated in order to determine the antiknock property.

The tetraalkyltins are colorless, and the compounds of lower molecular weight are liquids at room temperature and are soluble in the common organic solvents. They are quite stable in the presence of air or water and are unreactive in such organometallic reactions as addition to a carbonyl group. They are not highly sensitive toward strong aqueous bases, but cleavage of the carbon-tin bond occurs readily with halogens, hydrogen halides, or strong aqueous acids (12).