

CHAPTER 2

THEORETICAL CONSIDERABLE

Motor gasoline has, until recent years, consisted almost entirely of a complex mixture of hydrocarbons derived from crude oil and boiling between about 30°C and 220°C, i.e. containing compounds in the range C₄ to C₁₂. Gasoline can vary widely in composition even if they are of the same grade. This is because refineries differ in the range of products they supply and so differ in the processes that they have available. The hydrocarbons which make up the bulk of a gasoline are normally categorized into three general types: paraffins, olefins, and aromatics. A motor gasoline must have an odour that is acceptable to consumers and so must be essentially free of any constituent that has an unpleasant smell.

Gasoline Properties (1-3,14)

The performance of the engine depends very much on the quality of the gasoline, the most important properties

in this respect being knock characteristics (or anti-knock value), volatility and stability.

Volatility

Gasoline should have the proper vaporizing characteristics for the climate and altitude where it will be used. Otherwise, the gasoline may cause vapor lock. (Partial vapour lock reduces the top speed and power of and engine by restricting the flow of fluid and, by making the fuel-air mixture " lean ", may cause knocking combustion. Complete vapor lock chokes off the engine's feed supply, stalling it and making it difficult to restart until the fuel system has cooled for sometime.

Antiknock quality

To prevent annoying, fuel-wasting, potentially damaging engine knock at all engine speeds and loads, gasoline must have high antiknock quality (octane number) throughout its entire distillation range. The anti-knock quality of a fuel is determined primarily by its hydrocarbon composition, but this quality can be increased by the addition of anti-knock agents.

Gum

Gasoline should be free of gum-forming materials in order to avoid clogging of engine fuel systems, carburettor malfunction, sticking of engine intake valves, and manifold deposits that would cause exhaust smoke and loss of engine power.

Corrosion

Corrosion of untreated or improperly treated gasoline is ordinarily caused by free sulfur or sulfur compounds that consist of hydrogen sulfide, sulfuric acid, or any of a number of organic sulfur compounds. Many compounds of sulfur are not corrosive, but the combustion gases from sulfur compounds are particularly corrosive in the presence of moisture. For these reasons, a number of refinery processes have been developed either to remove sulfur compounds from petroleum products or to convert them to inoffensive forms.

Cost

The fuel should be inexpensive and find easily.

Gasoline additive

Additives are used in gasoline for two main reasons. The first is to help ensure the satisfactory performance of engines (e.g. by minimizing deposits in carburettors, on valves, etc.) and the second is by supplementing refinery processing (e.g. by the use of anti-knock agents and anti-oxidants). Many of the additives used are summarized in table 2.1.



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Table 2.1 Additives used in gasoline.

Additive	Function	Composition
Anti-knock compounds	To improve octane quality	Lead alkyls, Methylcyclopentadienylmanganese tricarbonyl
anti-icing additives	To minimize engine stalling and power loss due to ice formation in carburettors and fuel lines	Freezing point depressants such as alcohols glycols
Anti-oxidants	To minimize gum formation and improve storage stability	Phenylene diamine and alkyl phenol compounds

Table 2.1 (continue)

Additive	Function	Composition
Metal deactivators	To prevent catalysis of oxidation process by deactivating metal ions such as copper	N,N-diamine derivatives
Combustion chamber deposit modifiers	To minimize misfire due to lead fouling of spark plugs and to reduce surface ignition and preignition	Organophosphorus compounds
Detergents and dispersants	To minimize deposits the fuel intake system and to supplement the sludge dispersant quality of the lubricant	Alkyl amine phosphates

Table 2.1 (continue)

Additive	Function	Composition
Antirust additives	To prevent rust and corrosion arising from water (and air)	Fatty-acid amines, sulfonates or alkyl phosphates

Normal Combustion (1,3)

Spark ignition engines operate on the otto cycle, which is composed of the following steps:

-Intake stroke: the air fuel mixture is drawn into the cylinder, the fuel being present partly as a vapor and partly as small liquid dropets;

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

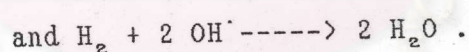
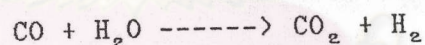
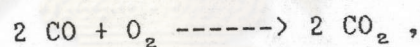
-Combustion: the spark ignites the mixture, combustion being essentially at constant volume;

-Power stroke: the hot combustion gases expand,

the work of expansion being transmitted to the crankshaft of the engine; and

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

Combustion of the fuel is practically complete within the narrow flame front, yielding carbon monoxide, carbon dioxide, and water(15). 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 (e.g. C-H and C-C) superimposed on a background of continuous emission; its ultra-violet spectrum shows CO and OH bands(16); its infrared emission indicates the presence of carbon dioxide and water.

In normal combustion the pressure increases to its maximum value in a smooth, continuous manner without

pulsations or vibration.

However, in practice a number of abnormal combustion characteristics can intrude (Figure 2.1):

- Knocking combustion (also known colloquially as pinking) occurs when the gas mixture most remote from the flame initiation autoignites before the flame can reach it. This end-gas explosion causes a rapid rise in local pressure, this expanding gas meets the advancing turbulent flame with its expanding gas behind it, with the result that very high oscillatory pressures are set up. The effect is easily audible, but can also be picked up by accelerometers as vibrations are set up in the whole engine structure. High temperatures are rapidly reached as heat transfer is increased many times, and engine damage can soon take place.
- Run-on combustion occurs when the engine continues to fire even after the electrical spark-ignition is switched off. The fuel-air mixture is inducted into the hot combustion chamber by the momentum of the engine, and because of high enough heat transfer processes, the mixture can auto-ignite (or diesel) for a short time until the engine cools.

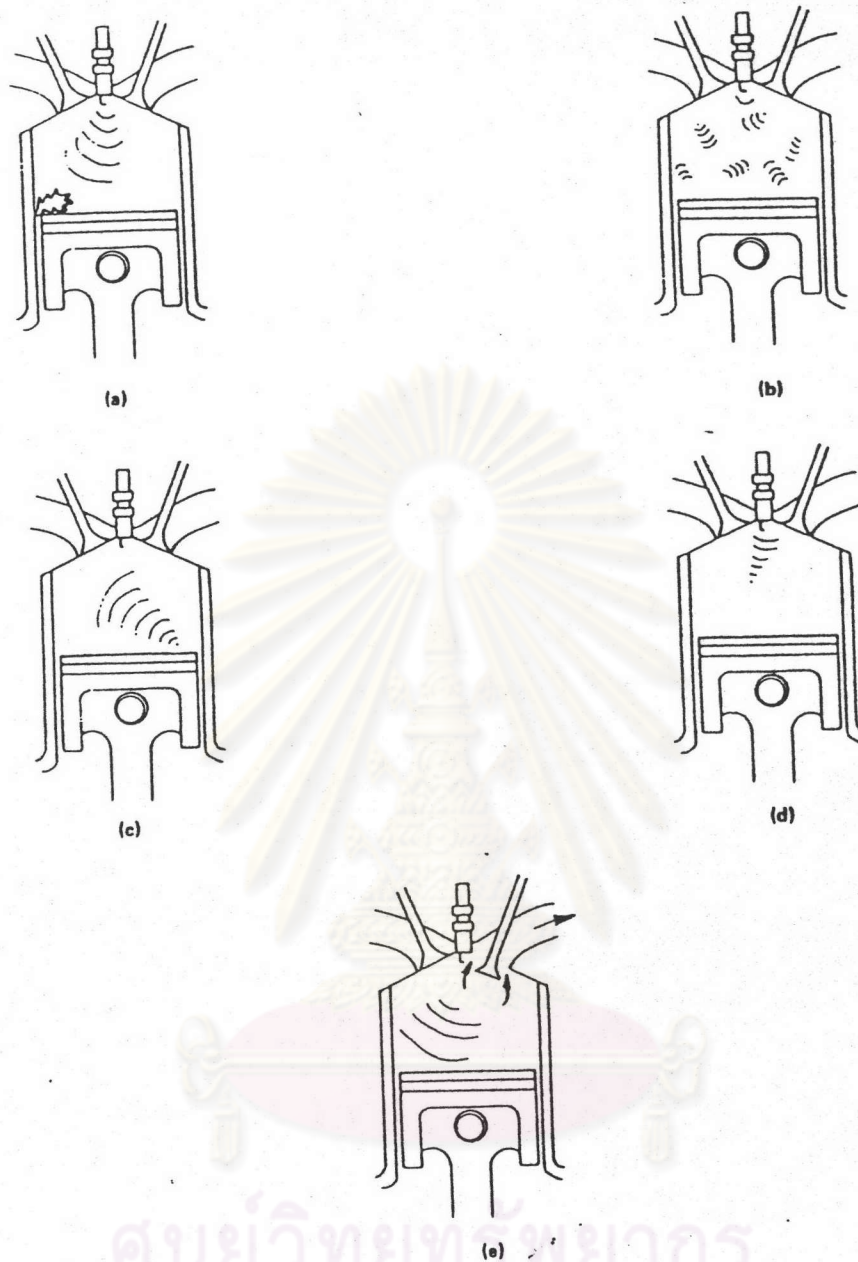


Figure 2.1 (a) Knock (an end-gas explosion); (b) run-on (a compression ignition at idle); (c) pre-ignition (a surface ignition before spark-ignition can occur); (d) misfire (flame kernel too weak and so the flame dies early); (e) exhaust valve seat recession (VSR) (environment too hostile for the 'soft' metallurgy).

-Pre-ignition can take place in more than one way, thereby establishing a flame before the main spark ignition event has occurred. One common source is the hot spark plug itself, thus locating the pre-ignited flame in the same place as usual. Another is the surface of the piston, whereby hot metal or a hot layer of piston deposit can also pre-ignite the incoming gases. The problem with pre-ignition is that very often it can become a runaway process, leading to catastrophic overheating and engine damage.

-Misfire, totally or partially, is a relatively common abnormality that is more of an inconvenience than a source of engine damage. It occurs, for example, when the fuel-air mixture is poorly mixed (giving rise to fuel maldistribution among the cylinders) or is not fuel-rich enough (giving rise to a lean-limit extinction of the flame), or the electrical spark is unable to deliver enough energy (as a consequence of deposits or fouling on the spark plugs). In each case the newly formed flame kernel is not allowed to grow and develop into a self-sustaining flame. Instead, the flame merely dies out after only a few millimetres of travel. The engine is felt to

stumble or hesitate or give other symptoms of poor driveability. In the extreme, bad misfire leads to considerable power loss and nowadays can also give rise to exhaust catalyst burnout.

-Exhaust-valve seating damage can occur under certain circumstances, and while this is not strictly a combustion abnormality in itself it can be attributed to the activity of certain combustion products. Exhaust valve seat wear is a phenomenon that occurs if too high temperatures are reached and at the same time certain "solid-lubricant" combustion products (e.g. lead products) are not present in significant quantities. The phenomenon has been resolved by use of resistant steels for the exhaust valves and seats, but recurred when lead was removed from gasoline without the exhaust valves and seats being made of improved, resistant metallurgy.

Of the various kinds of irregular of abnormal combustion which may occur in an engine, the most importance from both the theoretical and practical points of view is the type variously known as knock, ping or detonation. Knock may be defined as an abnormally rapid explosion of a certain portion of the charge which is the

last to burn in an internal combustion engine, resulting in the formation of pressure-waves in the gas.

In non-knocking operation no indication is found of any extensive chemical change in the end gas. When the fuel of operating conditions 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 knocking combustion, absorption spectra of the end gas begin to show the presence of formaldehyde about 0.001 sec. before the knock in an engine running at 600 rpm. The concentration of formaldehyde increases up to the point of inflammation. The chemical analysis of the end gas show the presence of aldehydes and substances of the peroxide type when operating under knocking conditions. In non-knocking operation no peroxides are detected; aldehydes may or may not be found.

It seems probable that the original fuel molecules

are partially oxidized, giving active or energy-rich products. These may subsequently, on a favourable collision with other reactants, bring about further oxidation and the formation of additional active products, thus continuing a reaction chain. On the other hand, an unfavourable type of collision will cause a deactivation of these chain carriers and a termination of the chain, the energy of the carriers being distributed throughout the gas in the form of heat. In the absence of knock, this condition prevails in the end gas until the arrival of the flame front and the subsequent inflammation of the gas at about the normal rate.

In 1918 Ricardo (16) stated that knock resulted not from mechanical defects in the engines, but from a simultaneous and spontaneous ignition of the last part of the charge to burn. Migley and Boyd (17) announced in 1920 and 1922, the discovery of the antiknock effect of very small amounts of different compounds. The ideas of theory knock were based upon experimental facts which, in large part, had been obtained under conditions more or less different from those found in an engine, and a considerable degree of confusion and several distinctly erroneous

conclusions resulted therefrom.

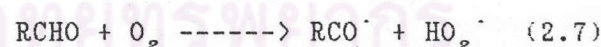
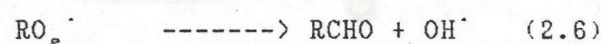
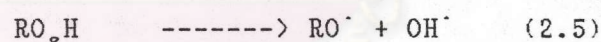
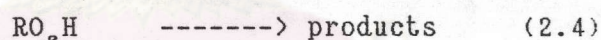
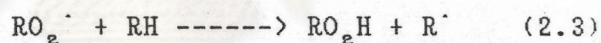
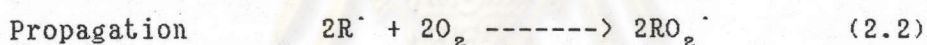
The series of fact which brought out by the experiments conducted directly with engines or in closely related apparatus indicated that the development of the chain-reaction theory of the slow oxidation and explosion of gases provided a reasonable basis for the explanation of the phenomena observed.

Chain-reaction theory

The investigations about the actual mechanisms indicate that the reaction products which can be isolated and, in part, identified, such as aldehydes, alcohols, peroxides, etc. are no more than the end products of the reaction chain; they are chemically too stable to play an active role in the reaction mechanism. The chain carriers and the chemically active products which are responsible for such phenomena as autocatalysis and induced oxidation appear to exist as such for no more than a fraction of a second, and are probably best described by the general designation of free radicals.

Semenov (18) suggested the most widely accepted explanation of gas-phase oxidation of hydrocarbons

behavior. This mechanism proposed that, during reaction, a product was formed which reacted after a time (very long compared with the normal life of a chain carrier), to initiate two new chains carriers, except at very high temperatures, were taken to be free radicals or atoms. Thus the reaction may be represented by the following general scheme for the oxidation of an alkane (where RH represents an alkane and X \cdot represents an initiating species):



In this scheme, reaction (2.4) is the normal fate of, for example, the hydroperoxide formed during propagation. Occasionally, however, decomposition occurs which yields two chains centers (reaction (2.5)) and brings about chain branching. Reaction (2.5) is not the

only step by which branching occurs; thus in reaction (2.6) an aldehyde is formed which reacts further to effect chain branching. The radicals are terminated by surface destruction.

Elbe and Lewis (15) 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.

Knock rating of gasoline (1-4)

The knock rating of a gasoline is found by comparing the knock with that of a blend of primary reference fuels (PRF). These fuels are n-heptane with an octane number (ON) of 0; and 2,2,4-trimethylpentane (called isooctane) with an octane number of 100. The CFR (Cooperative Fuel Research) knock-test engine has been adopted as the standard for determining octane number. Basically, it is a single cylinder, four-stroke engine in which the compression ratio can be varied at will. Briefly, the procedure followed is to vary the compression ratio to

obtain a standard knock intensity as measured by an electronically controlled knock meter, using an air/fuel ratio that gives maximum knock. When this knock meter reading is bracketed by two reference fuels differing by two octane numbers, the rating of the sample is calculated by interpolation.

Nowadays it is normal to define the antiknock quality of a fuel by three different octane parameters: research octane number (RON), motor octane number (MON), and a number concerned with the octane distribution through the boiling range of the gasoline. The most important of these from a commercial viewpoint is the research octane number (RON), since this is widely used to define octane quality in the market. It is determined by the research or F-1, rating method and relates mainly to relatively mild operating conditions such as are found during cruising and low-speed driving. The motor, or F-2, rating method relates to more severe driving, conditions such as high-speed, high load operation. Most gasolines show a higher research octane number than motor octane number, and the difference between these two octane ratings is called the sensitivity since it affords a

measure of the sensitivity of the fuel to changes in operating conditions, i.e.

$$\text{Sensitivity} = \text{RON} - \text{MON}$$

Sensitivity (S) is often used instead of MON and together with RON to define road octane performance. The third octane parameter used gives a measure of the distribution of octane number through the distillation range of the gasoline. The importance of octane distribution in a fuel is that some cars, particularly during full throttle acceleration, tend to segregate the high-boiling from the low-boiling components in the inlet manifold. Octane distribution of a fuel can be measured by a number of different methods in the laboratory. One type of test measures the octane number of the lighter fractions that distill off under standard conditions; the most common fraction used is the percentage distilling upto 100°C. The difference between the RON of this fraction and the RON of the total fuel is a measure of octane distribution and is designated as $\Delta R_{100 \text{ } ^\circ\text{C}}$ -often shortened to ΔR . Another method not now used very widely in the oil industry, employs a CFR engine fitted with a special manifold which allows some of the heavier fractions to be segregated

before they reach the engine.

Antiknock Compounds and Their Mechanism

These are compounds which, when added to gasoline in small amounts, cause a marked increase in octane number. The ideal requirements for an antiknock are:

- Low cost per unit increase in octane rating.
- No deposits left in the engine.
- Relatively low boiling temperature to ensure good distribution in multicylinder engines.
- Complete solubility.
- Nontoxic.
- Stable.

Antiknock agents fall into two distinct classes: metallic elements and non-metallic organic compounds. They exhibit a difference in relative effectiveness so marked as to suggest a fundamental distinction between their respective modes of action. Egerton (19) attributes the antiknock effect of the metallic agents to the fact that the metals in question are capable of forming two or more oxides in equilibrium at the end gas in an engine, and

that the oxide is the active agent which breaks the reaction chains. Other evidence suggests that the free metal atom is involved. On the other hand, the relatively unstable organic antiknock compounds probably cannot undergo such reactions in an engine. They usually are, in act of chain-breaking, oxidized, decomposed or otherwise rendered ineffective for further inhibitory action.

In the case of organometallic compounds, it is stated by Egerton (19) that the molecule must be dissociated before the metal atom can be effective; correspondingly, metals in the form of compounds which are chemically stable under the conditions existing in an engine are inactive as antiknock agents. Sims & Mardless (20) established that the metal rather than the organic radical is the active constituent of antiknock compound.

The causes of knock and the mode of action of antiknock agents are not yet fully understood. Many experiments have been performed to show that the two-stage ignition occurring in an engine parallels that at low pressures. All the evidence indicates that if particles of metal oxide with adequate surface were to be formed in an engine, such surfaces could then inhibit the reaction in

the end gas zone to prevent knock. Recent experiments performed by V.K.Rao and C.R.Prasad (21) has been shown that the total extent of effectiveness of TEL can be completely accounted for if some of the TEL decomposes forming PbO, in the end gas zone is the chief criterion that decides its effectiveness.

Preparation of Organotin Compound (14,22-24)

In this study the selected organotin compound was a compound which tend 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.

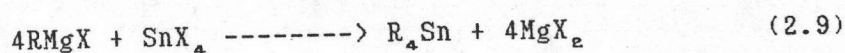
The tetraalkyltins are colorless, and the compounds of lower molecular weight are liquids at room temperature and are soluble in the common organic solvents. They are quite stable in the presence of air or water and are unreactive in such organometallic reactions as addition to a carbonyl group. They 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.

These compounds were prepared by various kinds of synthetic methods such as the Grignard reaction, Wurtz reaction, reactions with organoaluminums and direct reaction (14,22,23). The Grignard reaction, Wurtz reaction and reaction with organoaluminums are generally suitable for the preparation of R_4Sn and, on the other hand, direct reaction are suitable for the preparation of R_2SnX_2 .

Grignard Reaction (14,22,23)

The Grignard reaction has been used for a long time as the synthetic method for organotin compounds, and now it is widely used both experimentally and industrially. 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 by 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 eqn. (2.9).



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 prepared tetraorganotin (R_4Sn) only. 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 solvent and they give improved yields. (22)

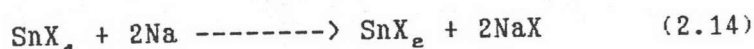
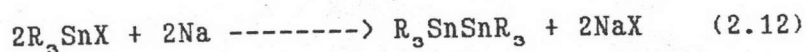
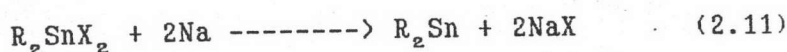
Wurtz Reaction (14,22,23)

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 $R-R$.



The yields are usually only fair, and, as shown in eqns.

(2.11)-(2.14), various kinds of side reactions also proceed.

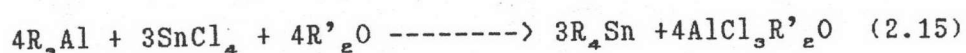


The basic Wurtz reaction is applicable to almost all simple alkyl and aryl chlorides. But, there are many disadvantages: degradation of solvent through further alkylation or arylation, formation of high boiling hydrocarbon by-products, the required control of sodium granulation, formation of R_2Sn and 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.

Organoaluminums (14,22,23)

Alkylation of tin tetrachloride with organoaluminium compounds has the advantage that it can be carried out in the absence of solvent but the aluminium chloride which is formed during the reaction forms a complex with the dialkyltin dichloride and trialkyltin chloride which inhibits further alkylation;

this can be avoided by carrying out the reaction in the presence of a strong complexing agent such as ether or amine.



This method is useful for syntheses of higher alkyltin compounds because the yield of the Grignard method is lower. Tetraethyltin and tetraoctyltin are prepared industrially by this method.

Direct Reaction (14,22,23)

The organotins may be synthesized directly from tin metal, tin alloys or tin (II) and tin (IV) halides and this method was first used by Frankland in 1849. The direct synthesis of organotin halides has been reviewed by Murphy and Poller (24).

The reaction of the tin metal with an alkylhalide has obvious attractions as an industrial process, but in practice is rather limited, since the dominant product is most commonly the diorganotin dihalide. The order of reactivity of the alkylhalide is $RI > RBr > RCl$. A catalyst is also required and this is typically a quaternary halide or trialkyl derivative of the Group V

element, R_4MX or R_3M ($M = N, P$ or Sb). The direct synthesis is employed for the industrial manufacture of dimethyltin dichloride.

Literature Review

In 1921, the lead alkyls as a group were discovered to be the most effective antiknock compound, and of these TEL (tetraethyllead) proved to be the most effective (2,5,10). Then in the 1960's and early 1970's, concern about the effect of auto emissions led to legislative restrictions on automotive exhaust emissions. Nobel metal exhaust catalyst systems, which are poisoned by lead, were proposed as one way to meet the legislation requiring gradual removal of lead compounds from gasoline caused renewed interest in nonlead octane quality improvers.

Due to worldwide lead phaseout in gasoline, many attempts have been made to find other compounds which can replace lead as efficient octane improvers. Such compounds as MMT (methylcyclopentadienyl manganese tricarbonyl) (1,3,5,11,14) and iron pentacarbonyl (13,14) were used in Europe and the United States, but they were banned later for the reason that MMT aggravated the emission and air

pollution and iron pentacarbonyl reduced the lifetime of valve and other parts of the engine because of its combustion product, iron oxide. Materials that received significant attention are oxygenates such as alcohols and ethers because they conserve crude oil, supply antiknock quality, and offer potential for pollution reduction. Oxygenates, which are important as gasoline blending components, include methanol (MeOH), ethanol (EtOH), isopropyl alcohol (IPA), tert-butyl alcohol (TBA), and methyl-tert-butyl ether (MTBE) (1,8-14). MTBE, which is widely used now must be blended in high proportion with gasoline (10-20% by volume) to meet the octane required but it is expensive. MeOH is the most attractive oxygenates from a strictly economic point of view but the most serious problem is the separation of blends into hydrocarbon and methanol phases when their water content exceeds a critical level, i.e. water tolerance (8). This problem is exacerbated at low ambient temperatures. Then the use of more molecular weight alcohols should solve this problem. Today, a higher alcohol such as TBA, IBA, SBA or IPA practically can be blended with MeOH, increase the water solubility of gasoline containing MeOH and increase the

equilibrium concentration of MeOH in gasoline phase, should the solubility be exceeded. In this study we evaluated C_{3-4} alcohols as a high octane blending component which could be used in place of MTBE because they are cheaper than MTBE. Another class of compounds is suitable non-toxic organometallic compounds which could be used in place of lead as octane dope in gasoline would be very useful (5,14). This was organotin compound which selected for detailed investigation. This compound should have many advantages, firstly, tin is in the same group as lead in the periodictable, they should have similar chemical properties. Such compounds as TET (tetraethyltin) (5), TBT (tetrabutyltin) (14), TOT (tetraoctyltin) (14) were used in selected base oil and showed that the antiknock property was improved. Secondly, organotin compounds can solve the pollution problem for its decomposition products, inorganic tin compounds, are non-toxic and very inert (14). Thirdly, tin metal is an excellent lubricant when allowed to come into contact with moving parts in the engine, thus providing the necessary lubrication and compensated for the loss of lead's lubricating qualities (14,23). This study tetrahexyltin

was synthesized from the Grignard reaction because this reaction gives yield higher than among the others.



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