CHAPTER II

THEORY AND LITERATURE REVIEW

Fundamental Principles of Engine Operation

Reciprocating internal combustion engines operate on either the four-stroke or the two-stroke cycle. The four-stroke cycle engine is the most commonly used for automotive purposes especially in road vehicles. The two-stroke engine is sometimes used in small passenger cars, motor cycles, and as outboard marine engines (9).

In the four-stroke cycle engine as well as the two-stroke cycle engine the following four processes take place during the cycle of operation:

1) Charging the cylinder with a fresh charge. This charge is composed of a mixture of fuel and air in the gasoline engine and air only in the diesel engine.

2) Compression of this charge to a temperature suitable for the proper combustion process which usually starts before the maximum compression pressure is reached. In the gasoline engine the combustion process starts by ignition from a spark plug. In the diesel engine auto-ignition occurs when the fuel is injected in the air which is compressed to a high temperature enough to cause self-ignition. The pressure of combustion results in a substantial increase into the gas temperature and pressure.

3) Expansion of the high pressure gas.

4) Discharging the exhaust gas.

1. The Four-Stroke Cycle Engine (10-11)

Foul-stroke cycle internal combustion engines utilize the reciprocating piston principle shown in Figure 2.1, wherein a piston slides back and forth in a cylinder and transmits power through, usually, a simple connecting-rod and crank mechanism to the drive shaft. The four-strokes of these engines are:

1) An intake stroke to draw a mixture of fuel and air from the carburetor into the cylinder of the engine through an open intake valve by the down-stroke of a piston (Figure 2.1 a).

2) A compression stroke to compress the fuel-air mixture by the up-stroke of the piston. Both intake and exhaust valves are closed. (Figure 2.1 b)

3) Ignition and consequent burning of a homogeneous mixture at the end of the compression stroke, with the liberation of energy raising the temperature and pressure of the gases; the piston then descends downward on the expansion or power stroke, Figure 2.1 c. (both valves closed)

4) An exhaust stroke to sweep the cylinder free of burned gases, Figure 2.1 d. (exhaust valve opened)

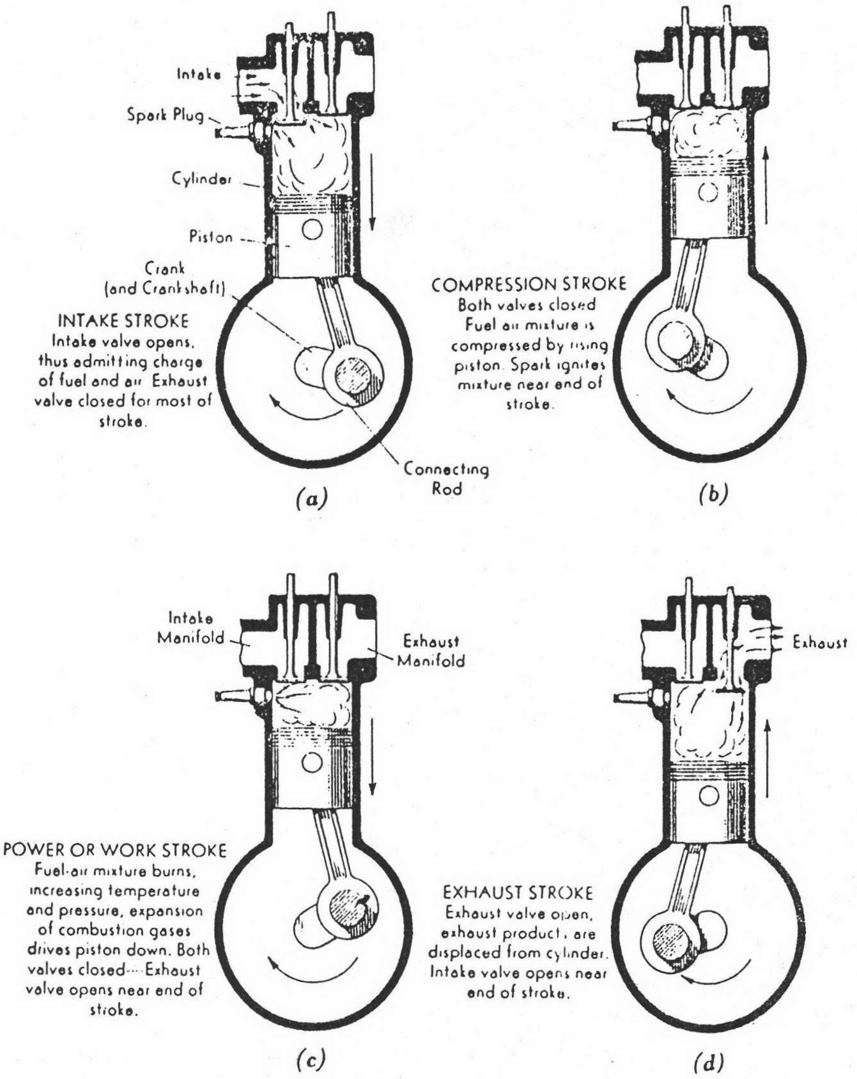


Figure 2.1 The four-stroke spark-ignition (SI) cycle (10)

The indicator diagram shown in Figure 2.2 gives the pressure-volume relationship during a complete four-stroke cycle. The pressure in the cylinder during the intake stroke, in naturally aspirated engines, is always lower than atmospheric pressure. The difference between the two pressures causes the flow of the charge into the cylinder. The intake valve is closed after bottom dead center at point 2 in Figure 2.2, 2.3, and 2.4 to improve the volumetric efficiency of the engine. The pressure rise due to compression starts a slow rate before the closing of intake valve during the piston motion from bottom dead center (B.D.C.) to top dead center (T.D.C.) on the compression stroke.

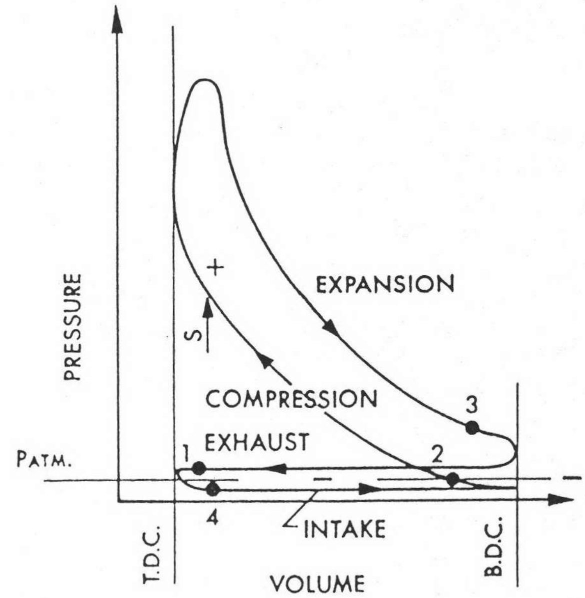


Figure 2.2 Pressure-volume diagram for a four-stroke cycle engine (9)

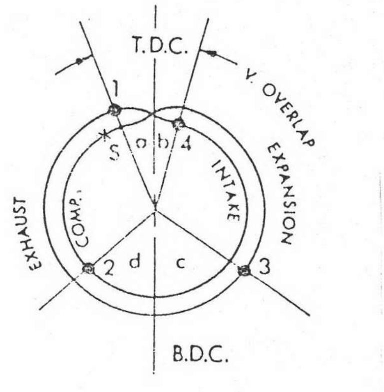


Figure 2.3 Valve-timing diagram (9)

List of events :

1. intake valve opens

2. intake valve closes

S. spark

3. exhaust valve opens

4. exhaust valve closes

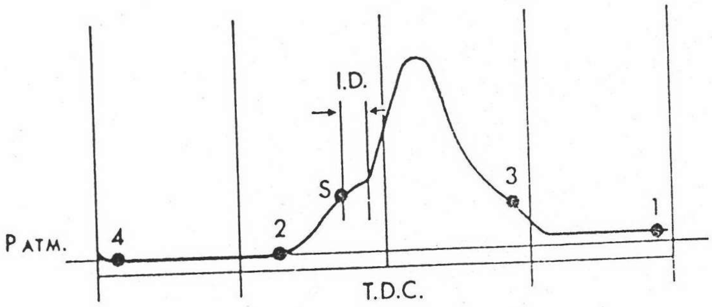


Figure 2.4 Pressure-time diagram (9)

Combustion (12)

Gasoline is a mixture of hydrocarbon compounds which have been distilled from petroleum. The composition of raw petroleum varies among oil fields. However, the saturated hydrocarbons dominate. Sulfur is also a constituent in oil (as well as in coal); low-sulfur oil is now in great demand as a fuel because the SO_2 emission is reduced. Low-sulfur oil is called "sweet".

While gasoline is a mixture it is convenient to consider it as a single hydrocarbon usually taken as octane or isooctane, C_8H_{18}. Then, gasoline is burned in the cylinders of an automobile engine which is expected to have the following reaction:

$$\underbrace{C_8H_{18} + xO_2 + x(3.76)\,N_2}_{\text{Reactants}} \longrightarrow \underbrace{aCO_2 + bH_2O + 3.76(x)N_2}_{\text{Products}} \qquad (2.1)$$

Substituting the values for x, a, and b to balance the equation gives:

$$C_8H_{18} + 12.5O_2 + 12.5(3.76)N_2 \longrightarrow 8CO_2 + 9H_2O + 47.0N_2 \qquad (2.2)$$

If the reaction occurred in this manner it would be a stoichiometric combustion process, that is, all the oxygen atoms in the oxidizer react chemically to appear in the products. The nitrogen appears to go along for the ride.

The correct air-fuel ratio (AFR) to provide stoichiometric combustion is:

$$AFR = N\ air/N\ fuel = (12.5+3.76(12.5)/1)$$

$$AFR = 59.5\ \text{moles air/mole fuel}$$

(N is the number of moles)

On a weight basis this becomes.

$$AFR = 59.5(28.95)/114 = 15\ \text{unit air/unit fuel}$$

(Air can be treated as a mixture of 1 mole of O_2 to 3.76 mole of N_2)

This is a very typical AFR for hydrocarbons. Thus, this combustion needs to use about 15 lb of air for each pound of fuel burned, or 15 grams for each gram of fuel burned.

Equation (2.1) assumes that combustion is complete, that is, all of the reactants are used up and no CO or NO_x is produced in the combustion process. The real fact is that the combustion process is usually incomplete and therefore noxious products can result. The unburned hydrocarbon or partially burned ones, along with the oxides of nitrogen and carbon monoxide are the major emission problem from automobiles. Thus, the more general combustion equation for isooctane would be:

$$C_8H_{18} + xO_2 + yN_2 \longrightarrow aCO_2 + bH_2O + cO_2 + dH_2 + eCO + fH + gOH + hO + iN_2 + jN + kNO + \ldots\ldots\ldots \qquad (2.3)$$

To investigate why combustion dose not go to completion requires knowledge of both the equilibrium conditions and the kinetics of the competing reactions. A reaction at a certain temperature and pressure, given a sufficiently long time (long compared to the residence time say, in the piston cylinder of the automobile engine) will reach an equilibrium state which may include products of combustion other than just CO_2 and H_2O. High temperature combustion processes can thus produce CO even if given time to reach equilibrium since the equilibrium state may include CO as one of the products. Usually, however, the combustion process does not have sufficient time to reach equilibrium and thus the process becomes kinetically limited. That is, it is limited not only by equilibrium considerations but also by the fact that reactions take time to proceed to completion, whether the completion state is one of stoichiometric combustion or not.

Pollutants from Engine (13)

There are three sources of emissions from most automotive vehicles, as shown in Figure 2.5. The fuel systems emission comes from the fuel tank and the carburetor and consists exclusively of hydrocarbons. Crankcase emission, also hydrocarbon (HC), comes mainly from the gas-air mixture which blows by the piston rings. The primary emissive source of automotive vehicles is the exhaust. Combustion is not complete. In addition to the exhaust products of water, nitrogen, and carbon dioxide, other products including carbon monoxide, unburned hydrocarbons, partially burned hydrocarbons, hydrogen, oxides of nitrogen, and various particulates such as lead and sulfur compounds.

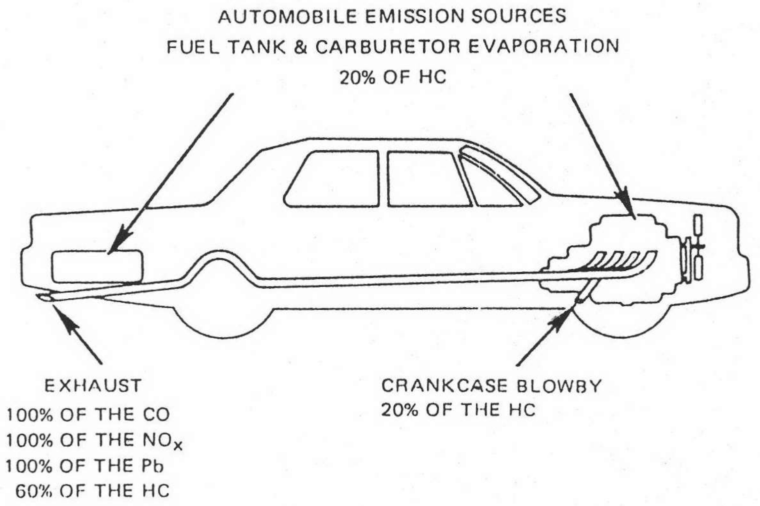


Figure 2.5 Sources of pollution from automobiles (12)

Water is not generally considered undesirable and therefore is not considered as a pollutant. Likewise, carbon dioxide is not normally considered as a pollutant, although it appears that about one-half of the carbon dioxide which is put into the atmosphere via combustion is remaining in the atmosphere with consequent increasing concentration. Since CO_2 in the atmosphere has the potential of affecting the weather (Green House Effect) it may ultimately be considered as pollutant.

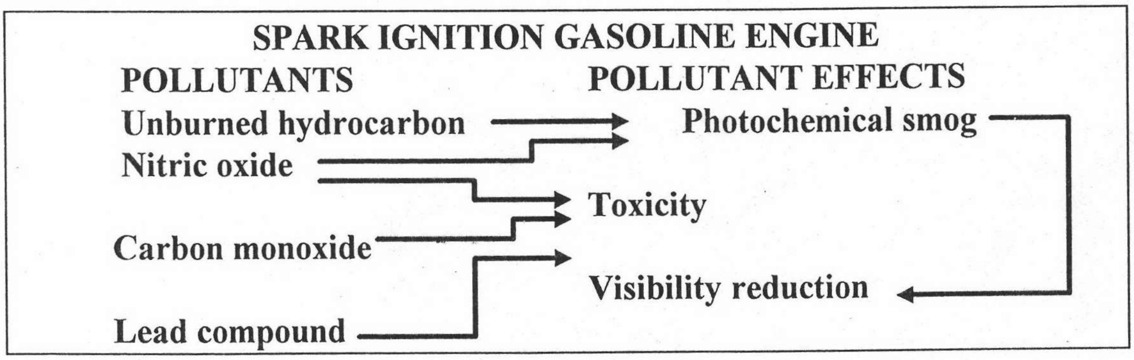


Figure 2.6 Pollutants and their harmful effects (13)

Figure 2.6 shows those automotive vehicle emission which are usually considered to be pollutants and the basis on which they are considered to be pollutants

1. Carbon Monoxide (CO)

The appearance of carbon monoxide in the combustion process is generally a simple result of oxygen insufficiency either on an overall or local basis. In principle, the concentration of carbon monoxide contained in exhaust products should correspond to a chemical equilibrium state represented by the water gas equation.

$$H_2O + CO \rightleftharpoons H_2 + CO_2 \qquad (2.4)$$

At high flame temperature, this equilibrium yields significant quantities of CO relative to CO_2 - even for fuel-lean mixture ratios. However, as the combustion gas as cool from peak flame temperatures to the much lower temperatures characteristic of exhaust products, this equilibrium shifts in the direction favoring oxidation of CO to CO_2. Consequently, for a fuel-lean or a chemically correct mixture ratio, relatively small quantities of carbon monoxide ultimately appear in combustion exhaust products. For fuel-rich mixture ratios, however, due to the simple insufficiency of oxygen, significant concentrations of carbon monoxide persist even in cool exhaust product.

Figure 2.7 illustrates the behavior of carbon monoxide in the spark-ignition engine cycle. Here the variation of carbon monoxide concentrations within the engine cylinder is plotted against time following completion of combustion. As previously indicated, CO is formed in large quantities in the early high temperature portion of the combustion process, and as the products expand and cool oxidation of CO to CO_2 occurs. The dashed line of Figure 2.7 represents CO concentrations that would result if chemical equilibrium prevailed throughout expansion. However, at the lower temperatures during expansion, chemical reaction rates lag after equilibrium leading to the solid curve of Figure 2.7 representing the actual situation.

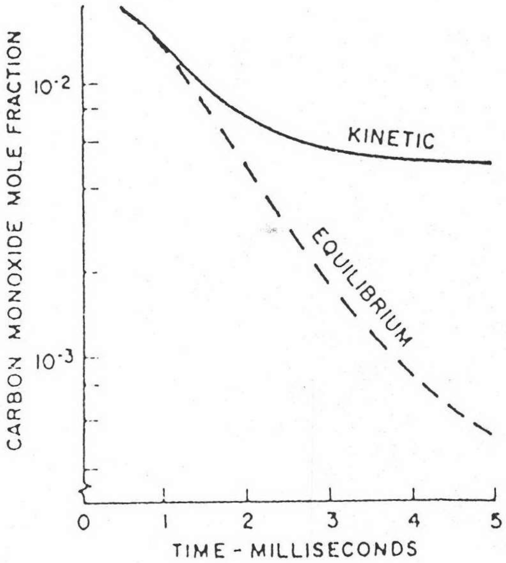


Figure 2.7 Carbon monoxide concentration as a function of time following combustion (13)

The influence of fuel-air ratio on this behavior is demonstrated by Figure 2.8 which compares theoretical calculations with experimental exhaust measurements. Here it is observed that real exhaust concentrations of CO fall between the peak temperature and exhaust temperature equilibrium values.

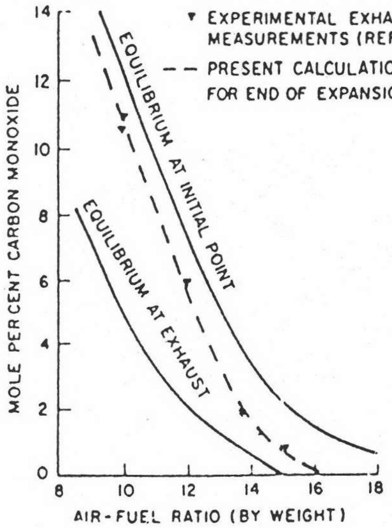


Figure 2.8 Carbon monoxide concentration as a function of air-fuel ratio (13)

The toxicity of carbon monoxide is well known. It occurs because the hemoglobin in the blood, which carries oxygen to the different parts of the body, has a higher affinity for carbon monoxide than for oxygen. The toxic effects of carbon monoxide are dependent upon both time and concentration, as shown in Figure 2.9.

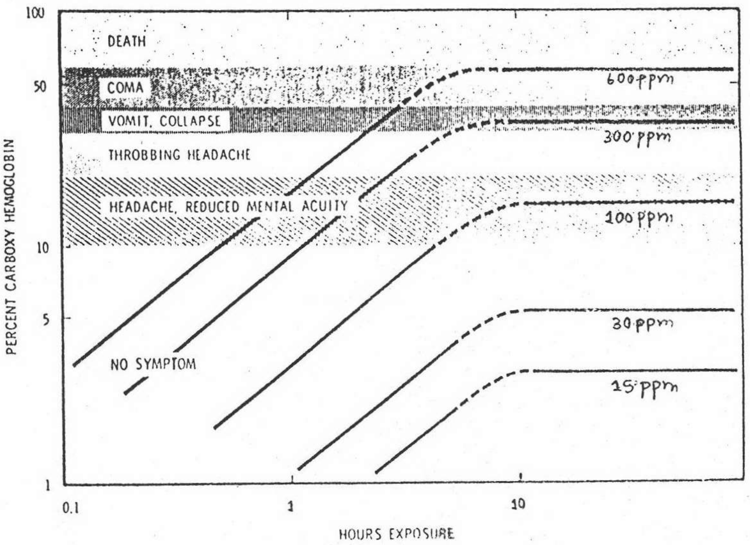


Figure 2.9 Toxicity of carbon monoxide (13)

2. Hydrocarbons

The hydrocarbon emissions come from the crankcase, the fuel system, and the exhaust. The case of incomplete combustion would be of major importance. Clearly, the presence of relatively cool combustion chamber walls can result in large heat losses from the adjacent fuel-air mixture. As a consequence, a quantity of unburned fuel-air mixture next to the walls will fail to ignite and will therefore persist throughout the combustion process. In a definitive study of this problem optical methods were used to experimentally confirm the role of combustion chamber surfaces in quenching the combustion reaction. It is generally considered that the thickness of this quench layer is a function of the fuel-air ratio and pressure, among other things (Figure 2.10 (a) and (b)).

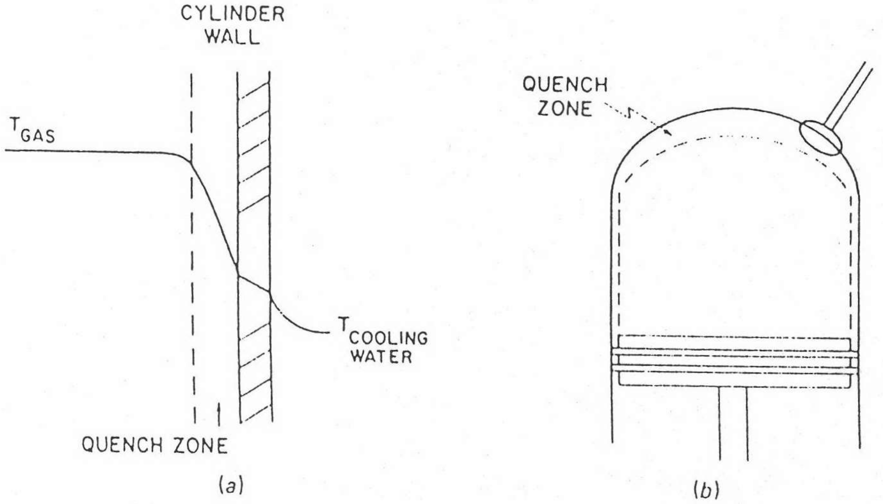


Figure 2.10 The quench zone in the piston-cylinder engine, (a) and (b) (12)

For this reason, both temperature and oxygen concentration in the exhaust gases are important to the final concentrations of hydrocarbons emitted from the exhaust system. The importance of oxygen concentration is illustrated by Figure 2.11 showing the variation of hydrocarbon emission with air-fuel ratio.

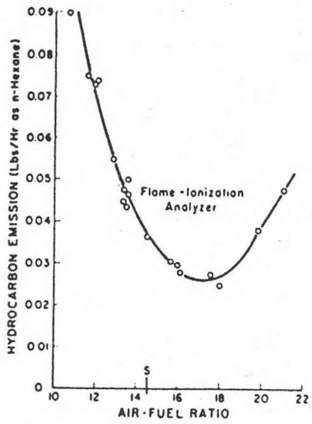


Figure 2.11 Variation of hydrocarbon emissions with air-fuel ratio (13)

The thickness of the quench zone is probably minimum when the fuel- air mixture is slightly on the rich side. However, as the engine mixture is made leaner more oxygen is available during the expansion and exhaust processes to help destroy the increased hydrocarbons present because of the increased quench thickness. Thus for lean mixtures, even though the quench-zone thickness has increased, very few hydrocarbons survive the expansion and exhaust processes until the mixture is so lean that erratic flame propagation occurs. On the rich side the quench thickness increases again with no offsetting increase in the destruction of hydrocarbon as on the lean side. The result is a very rapid increase in hydrocarbons in the exhaust when the mixture is made rich as shown in Figure 2.11

Fuel system HC emissions are due to evaporation of the fuel when the car is sitting after use (hot soak) or when the fuel tank heats during the day. The hot soak period is that which follows vehicle use and is caused by the heat release from the engine and exhaust systems. This increases fuel evaporation. The regular diurnal solar cycle results in hydrocarbon emission because of evaporation during the day which release fuel vapor from the fuel tank.

Crankcase emissions are mainly hydrocarbon blowby which goes past the piston rings into the crankcase. Since the blowby is largely from the quench zone it is not surprising that it is high in hydrocarbon content.

There are some unburned or partially burned hydrocarbons in the exhaust in addition to the small amount that escapes even when evaporation controls are used. The amount is insignificant from an energy standpoint, but may be objectionable from an odor, photochemical smog, or conceivably a carcinogen standpoint.

As will be pointed out later, odor is observed primarily when extremely lean mixtures are present during combustion, typically in diesel or stratified charge engines. The oders are believed to be a result of incomplete oxidation. It is not known specifically which compounds cause oders.

While the mechanistic details are not completely established, it is known that unburned or partially burned hydrocarbons in the gaseous form plus oxides of nitrogen and sunlight combine together to form what is called photochemical smog. The products of photochemical smog cause watering and burning of the eyes, and affect the respiratory system, especially when the respiratory system is marginal for other reasons. Hydrocarbons differ in their tendency to form photochemical smog. The reactive tendency of a hydrocarbon to cause photochemical smog is currently described by a reactivity index. The unsaturated hydrocarbons have the highest reactivity with the reactivity depending on the location of the double or triple bond.

Some of the high molecular weight aromatic hydrocarbons have been shown to be carcinogenic in animals and thus are suspect from this standpoint. As lead is removed from gasoline, a major environmental concern is that refiners will increase reforming severity to make up for lost octane. This would result in increased amounts of aromatics in gasoline, including benzene which is a known carcinogen. Current EEC legislation sets a maximum benzene level of 5 %volume in unleaded gasoline. Lower levels of 3 %volume, or less, are currently being considered in West Germany, California is now proposing to reduce the average benzene content to 0.6 %volume in the 1990s.

Typically, 80 to 90% of all benzene found in the atmosphere comes from gasoline powered motor vehicles (Figure 2.12). For European vehicles, 85% of the total benzene is emitted from the exhaust. Evaporative and refueling losses make up the remainder. Even with no benzene in a gasoline other aromatics, such as toluene, have been found to increase motor vehicle benzene emissions.

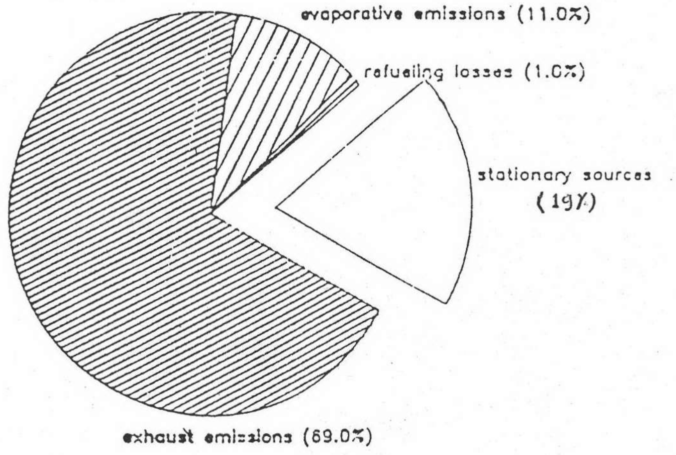


Figure 2.12 Sources of atmospheric benzene (West Germany) (3)

3. Oxides of Nitrogen

The principal oxide of nitrogen formed in combustion processes is nitric oxide, NO. Nitric oxide is a high-enthalpy species relative to N_2 and O_2 from the standpoint of basic thermodynamics. The emissions of nitric oxide, NO, are governed by two parameters: the availability of O_2 for the reaction

$$1/2N_2 + 1/2O_2 \rightleftharpoons NO \qquad (2.4)$$

(really $O + N_2 \rightleftharpoons NO + N$ and $N + O_2 \rightleftharpoons NO + O$) and high enough temperature to promote this reaction.

Like carbon monoxide, the oxides of nitrogen tend to settle on the hemoglobin in blood. However, probably the most undesirable toxic effect of oxides of nitrogen is their tendency to join with the moisture in the lungs to form dilute nitric acid. As already mentioned, oxides of nitrogen also seem to be a necessary component of photochemical smog.

4. Particulates

Particulate materials may be formed at a solid surface or in the gas phase. In general in spark-ignition engines operating with a relativity homogeneous mixtures, particulate matter in the gas phase is not observable unless extremely rich mixture are used.

As previously indicated particulate matter comes from hydrocarbons, lead additive and sulphur oxides. If lead is used with the fuel to control combustion about 70% of the lead is airborne with the exhaust gases.

Almost half (30%) of lead particulates are sufficiently large to rapidly settle to the ground while the remainder (40%) are smaller in size and remain in the atmosphere for an appreciable time. Lead is well known as a toxic compound. However, that man continuously takes in significant quantities of lead via food and drink as shown in Figure 2.13, and that the ingested airborne lead is small in comparison.

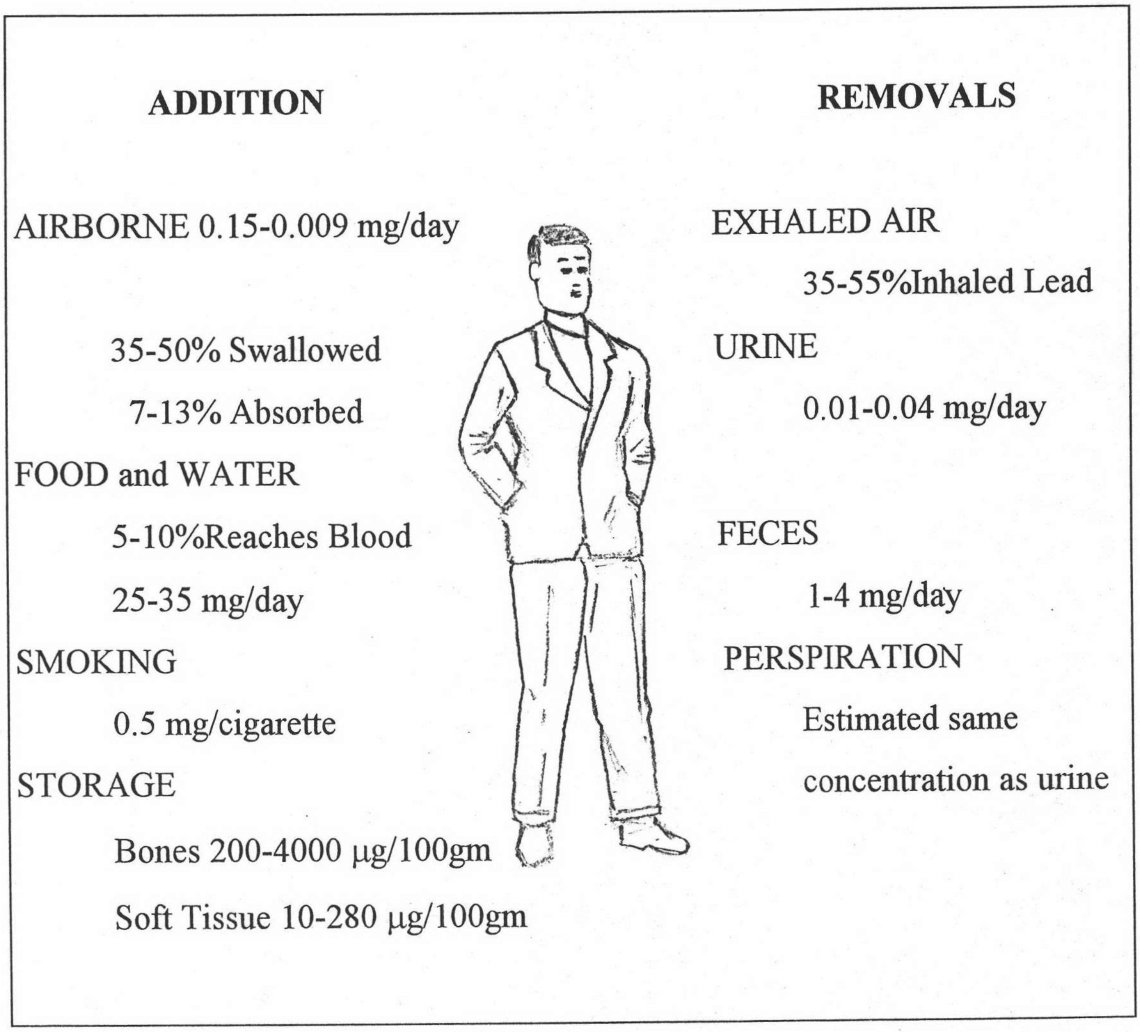


Figure 2.13 Mass rate balance for lead for an individual (13)

5. Odor

Effect of Operating Variables on Gasoline Engine Exhaust Emissions (9)

The exhaust emission of hydrocarbon, carbon monoxide, and nitric oxide can be minimized by the control of several interrelated engine design and operating parameters. Fuel preparation etc. includes 1, 2, and 3.These factor include:

1. Air-fuel Ratio (AFR)

Both CO and HC emissions can be reduced by increasing the air-fuel ratio. Figure 2.14 indicates typical results for CO, HC, and NO_x emissions as a function of AFR. Although increasing the AFR did reduce the CO and HC it markedly increased the No_x emissions.

To reduce HC, the cylinder was also redesigned reducing the crevices (such as between the piston top and combustion chamber) where unburned hydrocarbon could exist. In general the surface to volume ratio of the combustion chamber is an important variable. Large surface areas mean large quench areas and therefore higher HC emissions. The surface to volume ratio can be decreased by reducing the compression ratio or by changing the chamber to a more spherical shape, that is, short and fat.

Retarding the spark can also reduce the emissions. this is probably effective since it decreases the wall quench effect. Also the exhaust gas temperature is raised so that completion of the hydrocarbon reactions can occur in the exhaust.

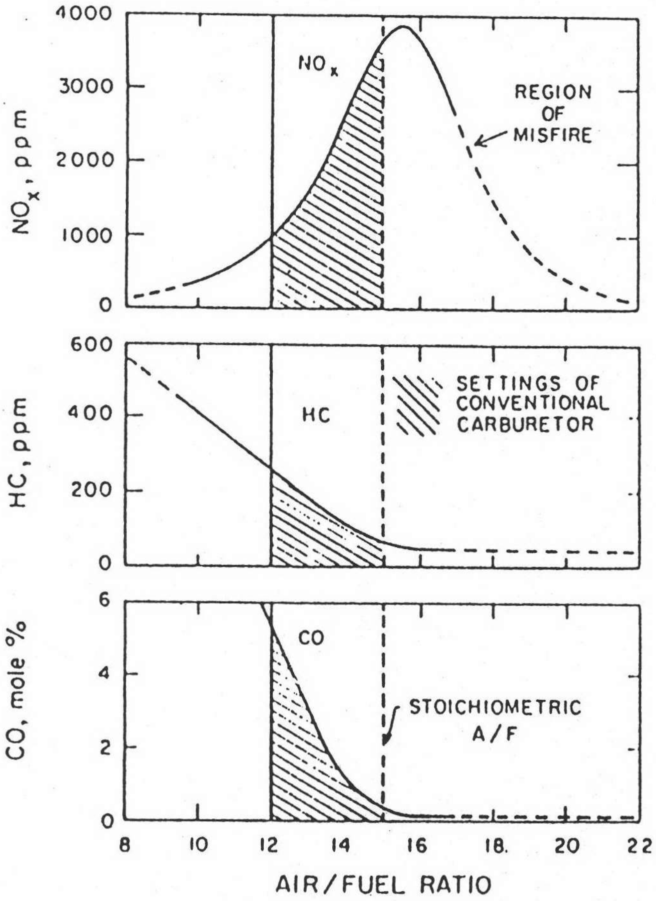


Figure 2.14 Typical concentrations of unburned hydrocarbons, carbon monoxide, and nitrogen oxides as a function of air-fuel ratio at 60 mph (2)

2. Engine Speed (14-15)

Emissions concentrations are markedly reduced at higher engine speeds. Primarily the increase in engine speed improves the combustion process within the cylinder by increasing turbulent mixing and eddy diffusion, thus promoting after-oxidation of the quenched layer. In addition, increased exhaust port turbulence at higher speeds promotes exhaust system oxidation reactions through better mixing. Speed has no effect on CO concentration because oxidation of CO in exhaust is kinetically limited rather than mixing limited at normal exhaust temperatures. Figure 2.15 shows the effect of engine speed on hydrocarbon concentration in the range between 1500 and 2500 rpm.

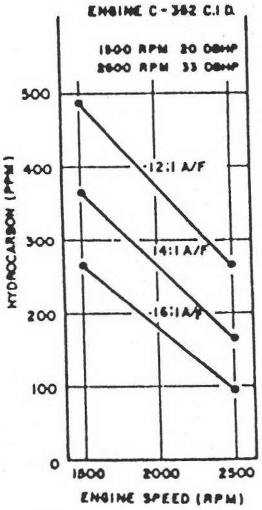


Figure 2.15 Effect of engine speed on exhaust gas hydrocarbon concentrations at 12:1, 14:1, and 16:1 air-fuel ratios (9)

Table 2.1 Relative emission rates for various engine-operating modes (4)

Mode	**Exhaust flow volume**	**Pollutant concentration**		
		HC	**CO**	**NO_x**
Idle	**Very low**	**High**	**High**	**Very low**
Cruise				
Low speed	**Low**	**Low**	**Low**	**Low**
High speed	**High**	**Very low**	**Very low**	**Moderate**
Accerelate				
Moderate	**High**	**Low**	**Low**	**High**
Heavy	**Very high**	**Moderate**	**High**	**Moderate**
Decelerate	**Very low**	**Very high**	**High**	**Very low**

Table 2.1 shows the effect of driving modes on exhaust emissions. During idle, the control valve remains seated. the distributor vacuum advance unit, now being exposed to only a weak carburetor vacuum signal, retards the ignition timing.

During acceleration and normal cruising speeds the increased carburetor vacuum causes the distributor vacuum advance unit to advance the spark timing in the conventional manner. Intake manifold vacuum still is not strong enough to overcome the control valve spring so the valve remains seated.

During deceleration, the period of highest CO and HC exhaust emission, carburetor vacuum is weak due to a closed throttle, but intake manifold vacuum is very strong. The high manifold vacuum unseats the control valve and full manifold vacuum is exerted on the distributor vacuum advance unit pulling it into a position of maximum spark advance. As deceleration progresses and engine speed falls to idle, intake manifold vacuum drops, the control valve spring seats the valve, and the distributor vacuum advance unit returns to a retard position. In this manner the exhaust emissions are held to an acceptable level.

3. Spark Timing

The effect of spark timing on HC emission reduction arises primarily from an increase in exhaust temperature, which promotes CO and HC oxidation, and a decrease in surface to volume ratio during combustion, emitted HC as a function of spark advance is illustrated in Figure 2.16.

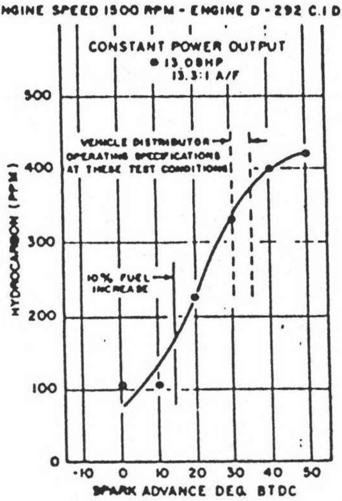


Figure 2.16 Effect of spark advance on exhaust gas hydrocarbon concentrations at constant load-engine speed 1500 rpm (9)

In a vehicle the emission reduction achieved by spark retard must be compromised by fuel economy loss considerations. Figure 2.17 shows the effect of spark timing at 30 mph on fuel economy.

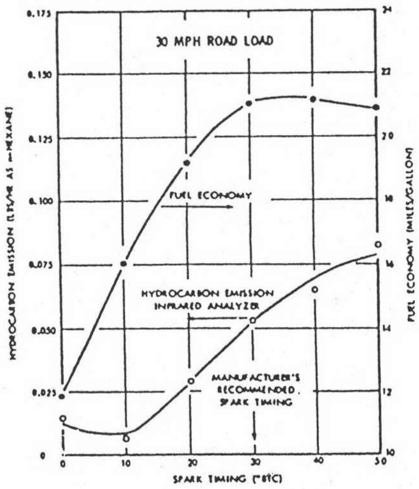


Figure 2.17 Effect of spark timing on exhaust hydrocarbon emissions and fuel economy in car at 30 mph road load (9)

Spark retard has little effect on CO concentration except at very retarded timing where the lack of time to complete CO oxidation leads to increased CO emissions. Because of the increased air flow required to maintain the power level constant, the mass of CO emitted from the cylinder tends to increase. The increase is offset to some extent by higher exhaust temperatures resulting in improved CO cleanup in the exhaust system. Figure 2.18 shows the CO emission for the engine as a function of spark timing for constant power output.

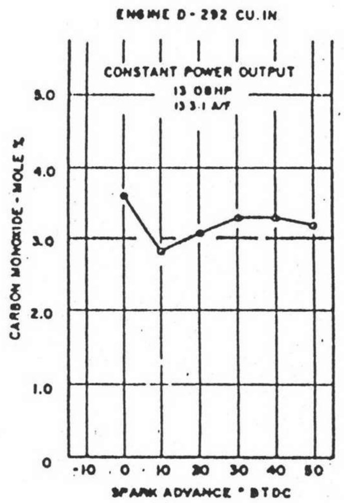


Figure 2.18 Effect of spark advance on exhaust gas carbon monoxide concentration for fixed throttle versus constant load at 1500 rpm

It is a common occurrence in vehicle tests that as a result of retarded timing the throttle must be opened and the carburetor operated at a point where the power enrichment valve is open. Where this happens CO increases markedly.

The effect of the many design and operating variables on hydrocarbons and carbon monoxide emissions is summarized in Table 2.2.

Table 2.2 Effect of design and operating variables on exhaust emissions and engine air flow (9)

Variable increased	HC concentration	CO concentration	Intake mass flow constant load
Air-fuel ratio	Ψ	Ч	↑
Load	-	-	↑
Speed	↓	-	↑
Spark retard	↓	↓	↑
Exhaust back pressure	↓	-	↑
Intake manifold pressure	-	-	↑
Combustion chamber deposits	↑	-	-
Surface to volume ratio	↑	-	-
Combustion chamber area	↑	-	-
Stroke to bore ratio	↓	-	↑
displacement per cylinder	↓	-	-
Compression ratio	↑	-	↓
Air injection	↓	↓	↑
Fuel injection	↓	↓	-
Coolant temperature	-↓	-↓	-

Gasoline

1. General Characteristics (16-18)

Gasolines are complex mixtures of hydrocarbons of four basic types differing in their properties according to the number of carbon and hydrogen atoms in the molecules and in the arrangement of the atoms. They have a boiling range from 30 to 210 °C and contain compounds in the range C_5 to C_{12}. The four basic types of hydrocarbons are paraffins, olefins, naphthalenes, and aromatics. With the processes available today the refiner can use hydrocarbon compounds of these four types to make his gasoline meet commercial requirements.

High resolution capillary gas chromatography (HRCGC), of a single commercial gasoline on a squalane column showed more than 400 detectable components. In a typical gasoline, 100 to 150 compounds account for 90% of the volume.

In internal combustion engines, gasoline is mixed with air and the mixture burned in the engine cylinders 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 that mixture is burned in an engine it generally does not give either maximum power or maximum economy. S. Bennet Hill and John G. Moxey, Jr., pointed out that to function satisfactorily in internal combustion engines, 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) Not contain components of such low volatility that they are not vaporized and hence, not burned in the hot cylinder.

6) 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. Performance Requirements (19-20)

2.1 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 method 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 blend 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 it octane number. Isooctane is arbitrarily assigned on octane number of 100. A poor fuel, n-heptane, is assigned on octane rating of zero. Generally, n-paraffins have lower octane numbers than branched paraffins, while olefins and aromatics have high octane numbers. Olefins are formed during refining operations and are important in increasing the octane number of fuels now that the use of lead-containing additive is being phased out

The Research and the Motor method use the same test procedures and equipment but operate under different conditions (shown in Table 2.3). 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 2.3 Operating conditions for Research and Motor methods (20)

	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	500 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.

2.2 Surface Ignition

This is another form of abnormal combustion (called "wild ping" or as low-frequency noises, similar to those produced by bad main bearings, called "rumble") in an automobile engine that occurs when the fuel-air charge is ignited by hot spots within the combustion chamber, including glowing deposits.

Wild ping results when the surface-ignited flame front causes the pressure and temperature in the unburned portion of the fuel-air charge to rise much faster than in normal combustion. Consequently, the unburned fuel-air mixture is stressed far beyond its antiknock quality and knock results. Rumble, on the other hand, is a form of nonknocking combustion. It occurs when ignition from a number of sources produces a very rapid pressure rise and high peak pressure during the compression stroke of the engine cycle.

In extreme cases, surface ignition can heat deposits and engine parts to the point where ignition occurs progressively earlier in the cycle. Such run away pre-ignition can quickly burn holes in pistons or exhaust valve face. 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 (as an example phosphorus compounds).

2.3 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 it performance for starting vapor lock, warm up and crankcase dilution.

2.4 Starting

The gasoline property which is most important in engine starting and performance is volatility. The volatility of a gasoline affects engine operation in a number of ways. If it is too low, insufficient vapor may be drawn into the cylinder to allow easy starting from cold, and warm-up will also be slow. On the other hand, a gasoline with too high a volatility is apt to cause carburetor icing and also vapor lock under adverse atmospheric conditions. The volatility is controlled and measured by a laboratory distillation test and by a Ried vapor pressure test.

In summer, oil companies blend their gasolines so "volatility"-its tendency to evaporate-is low. In winter, the engine will be slow to start unless the gasoline vaporizes readily; so oil companies blend gasolines for higher volatility.

2.5 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 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.

2.6 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 venture 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.

2.7 Odor and Color

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 gasoline are artificially colored with gasoline-soluble dyes.

3. Gasoline Additives

Components are blended to promote high antiknock quality, easy starting, quick warm up, tendency to vaporize, 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 reformate, 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.

3.1 Antiknock Compound

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 gallon which is equivalent to 0.08 percent by volume of the fuel into which it is blended.

When gasoline containing TEL alone is burned in a spark-ignition engine, it produces nonvolatile combustion products. Therefore, commercial antiknock fluids contain a scavenging agent, ethylene dibromide and/or ethylene dichloride, which transform the combustion products of the antiknock into forms which are vaporized readily from hot engine surfaces.

TEL has certain well recognized disadvantages such as tending to increase deposits in the combustion chamber, tending to plus, 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, this results in a decrease in the extraction rate of useful product from the petroleum. These disadvantages have been minimized through improved gasolines, and the use of other additives. The use of oxygenates in motor fuels has been recognized as a way of boosting octane and has also been credited with giving a "smoother burning" gasoline.

3.2 Deposit Modifier Additive

Phosphorus compounds are widely used as deposit modifiers. These additives suppress surface ignition by raising the temperature required to initiate glowing of deposits and by reducing the rate of heat release from oxidation of the deposits.

3.3 Antioxidants

These are used widely to inhibit oxidation reactions which form gums and thereby tend to improve the stability of gasoline in use or in storage. Thus, antioxidants retard the oxidation and polymerization of unstable hydrocarbons. Although the mechanism of this action is not well defined, antioxidants are believed to act as "chain-breakers" in the various oxidation and polymerization reactions. There are two major classes of antioxidant compounds, aromatic diamines and alkyl-substituted phenol, used in concentrations of about 50 ppm.

3.4 Metal Deactivators

Trace levels of soluble metal compounds, particularly copper, catalyze the oxidation of hydrocarbons and can lead to the very rapid formation of high levels of gum. Metal deactivators overcome this problem by chelating the metal, rendering it inactive.

3.5 Anti-rust Agent

These additives are added to gasoline at the refinery to protect storage tanks, fuel lines, and the fuel systems of engines from the corrosive conditions caused by the small amounts of water usually present in gasoline.

Several types of hydrocarbons soluble compounds are used as rust inhibitors. These include various fatty acid amines, sulfonates, alkyl phosphates, and amine phosphates. Most of them act by coating metal surfaces with a very thin protective film which keeps water from contacting the surfaces. This "surface-active" property can also help to prevent carburetor icing and the build-up of carburetor deposits.

3.6 Anti-icing Agent

Ice can interfere with engine operation either by plugging fuel line or upsetting carburetor through ice formation in the air or fuel passages. Plugging of fuel lines stems from water present in the fuel.

Two general type of carburetor anti-icing additives-freezing-point depressants and surface-active agent-are used in many gasolines to avoid the annoyance of cold weather stalls during engine warm up.

3.7 Carburetor Detergent

When an engine is idling, nonvolatile fuel components, together with contains from exhaust and crankcase fumes drawn in though the air cleaner, tend to accumulate on the inside walls of the carburetor just below the throttle blade.

Detergent additive are used to prevent deposit build up in carburetors and to remove deposits already formed. The effectiveness of these detergents, which include amides and alkyl phosphates, stems from their surface-active properties.

3.8 Dyes

Dyes are added to gasoline to identity various makes or grades of gasoline. Dyes are hydrocarbon-soluble organic compounds. Dye concentration depends on the intensity of color desired by the refiner to meet a color standard.

3.9 Upper-Cylinder Lubricants

Many refiners incorporate from 0.2 to 0.5 percent of light lubricating oil or similar material into their gasolines to provide extra lubrication for 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.

Combustion and Theory of Knock (20, 22-23)

1. Normal Combustion

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.

A flame created at the spark plug advances into the unburned mixture so that the 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 coolant and in the exhaust gases.

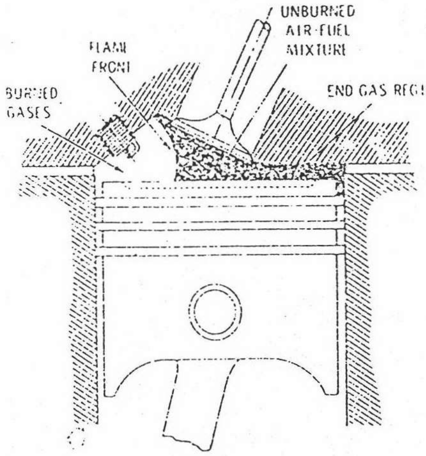


Figure 2.19 Schematic of normal combustion process (20)

2. Abnormal Combustion

Abnormal combustion in a spark-ignition engine can be described as any chemical reaction of the 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. These self-ignition processes encompass a general category which can describe such phenomena as (Figure 2.19):

1) knock: an end gas explosion.
2) run on: a compression ignition at idle, sometimes refereed 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 cycle/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.

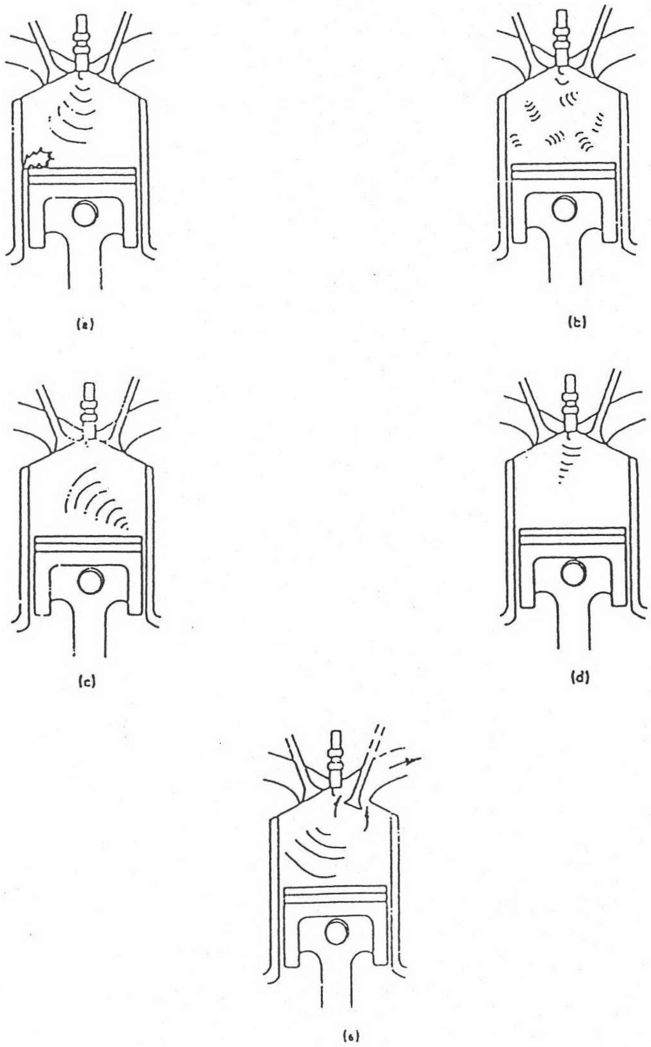


Figure 2.20 Abnormal combustion characteristics (8)

(a) Knock (an end-gas explosion)

(b) Run on (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)

Several engine design and operating variables affect knock. In general, the tendency to knock usually changes with changes in the variables listed in Table 2.4.

Table 2.4 Engine vailables which affect knock (20)

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. high engine speed
4. increased barometric pressure	4. high humidity
5. higher coolant temperature	5. increased change dilution (i.e. exhaust gas recirculation)
6. increased load (throttle opening)	6. A/F richer or leaner than shoichiometric

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

3. Characteristics of Knock (24-27)

Combustion of fuel is practically complete within the narrow flame front, yielding carbon monoxide, carbon dioxide, hydrocarbons, oxides of nitrogen, and water. When the gases behind the flame front begin to cool down, readjustments occur in the equilibria:

$$2CO + O_2 \longrightarrow 2CO_2 \qquad (2.5)$$

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad (2.6)$$

$$\text{and} \quad H_2 + 2OH \longrightarrow 2H_2O \qquad (2.7)$$

The spectrum of the flame front in an engine is 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; 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; the so-called "end gas".

In nonknock operation no indication is found of any extensive chemical change in the end gas. When the fuel or 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 1918 Richard stated that knock resulted from a simultaneous and spontaneous ignition of the last part of the charge to burn. Elbe and Lewis 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 unburned charge ahead of the flame.

The series of facts brought out by 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 provide a reasonable basis for the explanation of the phenomena observed. Detailed discussions of chain-reaction theory are available. In general, it appears that the oxidizability of fuel is the basic factor in determining its knocking tendency.

The Use of Oxygenated Compounds in Motor Gasolines (28-30)

Unlike the 1970s and early 1980s, the path is not being clouded with energy crises or lead additives phase out issues. Oxygenated supplements, covering a range of alcohol and ether types have been recognized as a means of raising the octane of gasolines. Although fuel oxygenates first became popular as an octane replacement for lead in gasoline, they are now making gasoline a cleaner burning fuel that will reduce the emission of pollutants from the automobile. 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. Thus they cannot be regarded as a means of total lead replacement. 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 a means of fulfilling three basic needs: extending the gasoline pool; improving octane values; and providing the refiner with additional blending flexibility to meet ever-increasing demands on quality.

This is especially true in the USA, where methanol and ethanol-containing fuels have been cited as a cause of poor vehicle driveability. Sometimes complaints arising through oxygenate misuse during blending and distribution can be justified, but the root cause can often be traced back to a lack of knowledge on the part of the fuel blender rather than of oxygenates themselves. Water tolerance and hence phase separation can be particularly difficult in this respect. This may be one of the reasons why a high growth rate in the use of MTBE. U.S oxygenate supply and demand were predicted in Tables 2.5, and Figure 2.20.

Table 2.5 Oxygenate supply/demand balance (30)

	1991	1992	1993	1994	1995
U.S					
MTBE	94	133	201	278	334
TAME	1	2	18	29	30
Ethanol	99	113	129	133	133
Net foreign					
MTBE	16	20	43	123	145
Total	210	286	391	563	637
Annualized surplus/(shortfall)		(14)	(11)	159	(24)

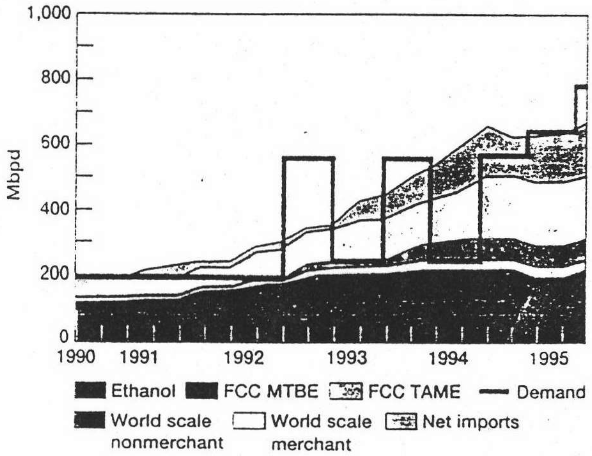


Figure 2.21 US oxygenate supply/demand MTBE equivalents (30)

1. Manufacture of Oxygenates

1.1 Methanol

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

$$2H_2O + 2C + CH_4 + CO \xrightarrow{O_2} 2CO + 4H_2 \longrightarrow 2CH_3OH \qquad (2.8)$$

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

$$CO + 2H_2 \longrightarrow CH_3OH \qquad (2.9)$$

1.2 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:

$$C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2 \qquad (2.10)$$

"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.:

$$C_2H_4 + H_2O \longrightarrow C_2H_5OH \qquad (2.11)$$

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

1.3 Tertiary Butyl Alcohol

Tertiary butyl alcohol (TBA), the most commonly used of the methanol co-sovents, 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 reactions are shown as follows:

$$\underset{\text{Isobutane}}{4(CH_3)_2CHCH_3} + \underset{\text{Oxygen}}{3O_2} \longrightarrow \underset{\text{TBA}}{2(CH_3)_3COH} + \underset{\text{TBHA}}{2(CH_3)_3COOH} \qquad (2.12)$$

$$\underset{\text{TBHA}}{(CH_3)_3COOH} + \underset{\text{Propylene}}{CH_3CHCH_2} \longrightarrow \underset{\text{TBA}}{(CH_3)_3COH} + \underset{\text{PO}}{CH_3CHOCH_2} \qquad (2.13)$$

The GTBA tends to be rather impure, (ca 95%volome and contain up to 0.81%volome water). However, this product is satisfactory for motor gasoline blending.

1.4 Mixed Alcohol

A number of commercial processes produce mixtures of alcohols that are suitable as motor gasoline supplements; e.g. Snamprogetti's MAS (mixture of alcohols superior) and the Union Carbide product 'Ucarnol", both of which are mixtures of methanol with higher alcohols acting as co-sovents for the methanol.

1.5 Methyl tertiary Butyl Ether (MTBE) (31)

Licensed etherification processes available today differ in technological details, but all are based on the same chemistry. The synthesis of MTBE from isobutylene and methanol proceeds according to the following reaction in the presence of a strongly acidic ion exchange resin catalyst. The reaction is reversible and exothermic:

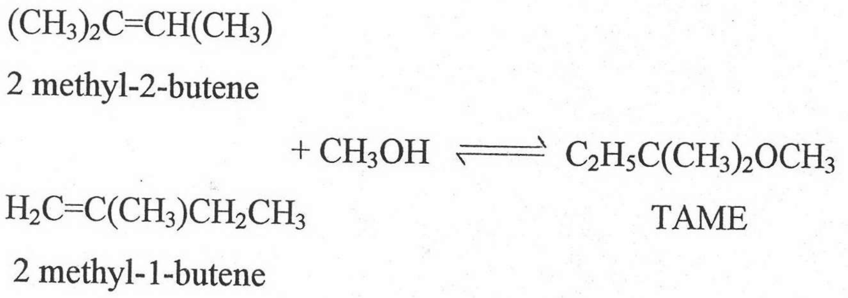
$$\underset{\text{Isobutylene}}{(CH_3)_2C{=}CH_2} + \underset{\text{Methanol}}{CH_3OH} \longrightarrow \underset{\text{MTBE}}{(CH_3)_3COCH_3} \qquad (2.14)$$

The MTBE formation reaction is equilibrium limited. Higher temperature increases 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 licensers are found in the reaction section. The reaction sections are designed to effectively control the exothermic heat of reaction.

1.6 Tertiary Amyl Methyl Ether

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



$$\left.\begin{array}{l}\underset{\text{2 methyl-2-butene}}{(CH_3)_2C{=}CH(CH_3)}\\[2ex] \underset{\text{2 methyl-1-butene}}{H_2C{=}C(CH_3)CH_2CH_3}\end{array}\right. + CH_3OH \rightleftharpoons \underset{\text{TAME}}{C_2H_5C(CH_3)_2OCH_3} \qquad (2.15)$$

Commercially, the feed for this process is either the C_5 fraction of a light catalytically cracked gasoline stream or a partially hydrogenated light steam-cracked gasoline stream.

1.7 Mixed Ether (32)

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 give a product known as "etherified spirits".

The isobutanol is advantageously not separated from the other higher alcohols but rather the whole higher alcohols 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 tert-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.

UK Patent Application GB 2123411A provided a process for the manufacture of a mixture of ethers useful as gasoline additive comprising:

i) synthesizing, from synthesis gas comprising hydrogen, carbon monoxide, and optionally, carbon dioxide, a mixture of alcohol 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 ether resulting from dehydration of methanol and optionally ethanol, including at least part of methanol, and optionally ethanol in alcohol mixture.

2. Materials Compatibility

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

Methanol > ethanol > TBA > MTBE

However, increasing oxygenate content, temperature and, in the corrosion test, water content increased the magnitude of the attack.

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 grater 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 higher water tolerances and, when added to methanol/hydrocarbon blends, increase the water tolerance of the methanol. Hence high 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 blend, the oxygenate concentration and/or the bulk temperature of the product. It is essential 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.

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

4.1 Exhaust Emissions (33-40)

Oxygenated supplements in gasoline can affect the level of exhaust emissions 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.With general trends in engine tune with mileage, etc., the mixture enrichment that would ensue 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 to lower CO and HC emissions, refinery blending of high octane oxygenates such as alcohols and ethers are expected to have a much greater overall emissions reduction benefit than just splash blending of oxygenates.

Blending oxygenates into gasoline can produce a significant reduction in unburned hydrocarbons and carbon monoxide in exhaust emissions. the maximum reduction in exhaust hydrocarbons (approximately 10%) occurred with the lower oxygen level fuel, which averaged about 2% in this data base (Figure2.21).

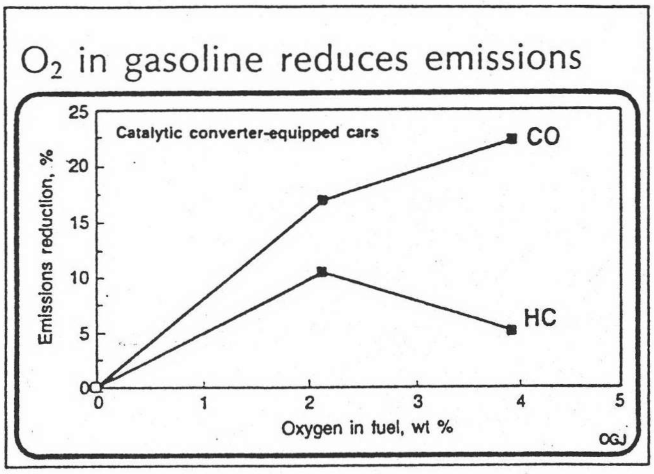


Figure 2.22 Oxygen in gasoline reduces emissions (29)

In the case of alcohols, the alcohols in fuel blends significantly reduced the concentration of carbon monoxide in the exhaust emissions (up to 40-50 percent compared to pure gasoline only), with methanol slightly more effective than ethanol. Hydrocarbon emissions were also decreased by increasing the alcohol content of the fuel, with minimum hydrocarbon production occurring at percent alcohol-gasoline blends in conjunction with near-stoichiometric air-fuel ratios. However, aldehyde emissions were found to be markedly higher with alcohol-gasoline blends. The 10 percent alcohol-gasoline blend were found to produce about 50 percent more aldehyde emissions than pure gasoline.

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

4.2 Fuel Economy

Figures 2.22 and 2.23 show that the fuel economy of commercial oxygenated gasolines is essentially unchanged by increasing amounts of oxygenates. Indeed, Figure 2.23 show that there could be marginal benefits in terms of reduced energy consumption with increased fuel oxygen content.

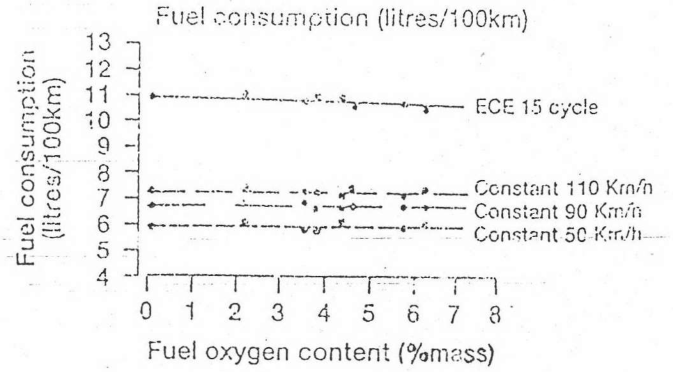


Figure 2.22 Volumetric fuel consumption (average of five vehicles) (28)

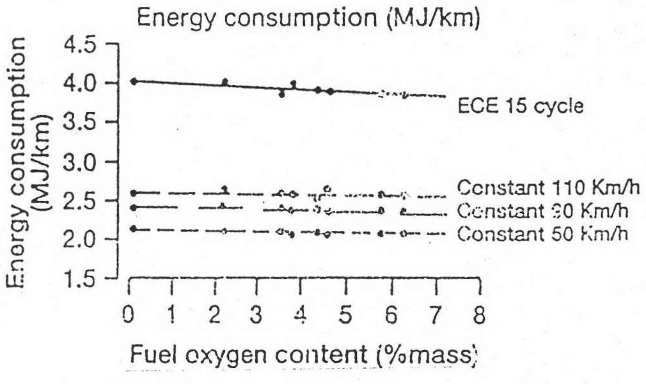
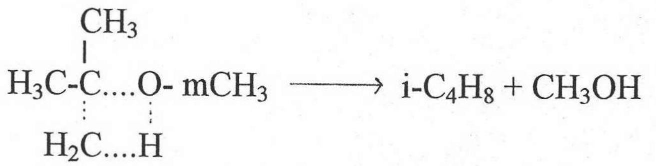


Figure 2.23 Fuel energy consumption (average of five vehicles) (28)

5 Oxidation of Metyl tertiary-Butyl Ether (41-47)

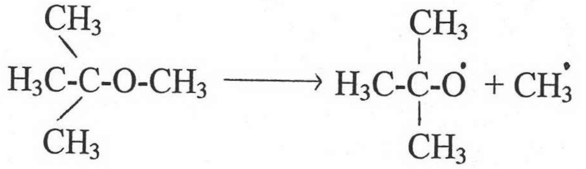
The oxidation of MTBE has been studied in the Princeton atmospheric pressure flow reactor at initial temperatures of 1028K and 1119K, and equivalence ratios near one. The reaction is primarily governed by the formation of a four centered complex which decomposes to form isobutene and methanol, as previously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



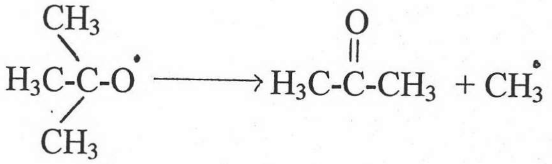
$$\underset{H_2C....H}{H_3C\text{-}\overset{CH_3}{C}....O\text{- }mCH_3} \longrightarrow i\text{-}C_4H_8 + CH_3OH \qquad (2.16)$$

The existence of alternative unimolecular 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.), and the resulting radical can then undergo β-scission to form acetone and another methyl radical:

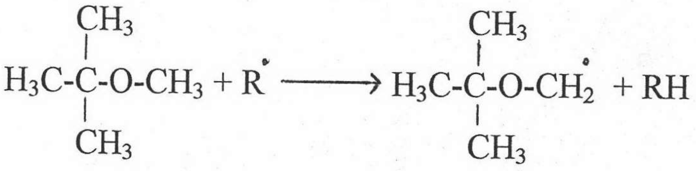


$$\mathrm{H_3C\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}O\text{-}CH_3 \longrightarrow H_3C\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}\dot{O} + \dot{CH_3}} \tag{2.17}$$

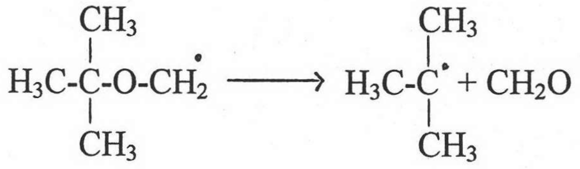


$$\mathrm{H_3C\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}\dot{O} \longrightarrow H_3C\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 + \dot{CH_3}} \tag{2.18}$$

The C-H bond strengths of the methyl-ether group on MTBE are approximately 93 kcal/mol, 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:



$$\mathrm{H_3C\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}O\text{-}CH_3 + \dot{R} \longrightarrow H_3C\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}O\text{-}\dot{CH_2} + RH} \tag{2.19}$$



$$H_3C\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}\text{-}O\text{-}\dot{C}H_2 \longrightarrow H_3C\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C^{\bullet}}}}} + CH_2O \qquad (2.20)$$

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 if only reaction (2.16) were present. This is due to the production of formaldehyde, an extremely reactive compound, via reaction (2.20). 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.

Tin Chemicals (48-49)

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, and 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 compound known as organotins has increased dramatically.

Tin chemicals have 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 favorable environmental aspects that often give a decisive advantage over alternative materials. Inorganic tin compounds in particular are regarded as not presenting any health or environmental problems because, at physiological pH, the metal dose not react and the oxides are insoluble.

Tin (IV) Chloride $SnCl_4$

Tin (IV) chloride is a coolroes liquid which freezes at -30.2°C and boils at 114°C. It reacts vigorously wit water, and hence fumes in moist air due to hydrolysis. By adding the anhydrous liquid to water under carefully controlled conditions, while solid crystals of the pentahydrate, $SnCl_4.5H_2O$, 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.

2. Tin (IV) Oxide SnO_2

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 oxidize systems which find extensive use as heterogeneous catalysts in industry. The ability of SnO_2 to oxides 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.

3. 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 devised into four classes: the mono-, di-, and tetra-organotins. 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 temperature. 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.

4. Tetraorganotin Compounds R_4Sn

Tetraorganotins are the first organotin products formed by the Wurtz, aluminum 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. Tetrametyltin, $(CH_3)_4Sn$, is another precursor used to produce conductive tin (IV) oxide films on glass.

Basic Methods of Preparation of Organotin Compounds (50-52)

The three principal ways in which the carbon-tin bond can be formed involve the reaction between an organometallic compound and a tin derivative (eq. 2.21), or between a tin-metal compound and an alkyl halide (eq. 2.22), or between a tin hydride and an alkene (eq. 2.23). The acidolysis reaction (eq. 2.24) is of more limited scope.

$$\mathrm{RM} + \equiv\mathrm{SnX} \longrightarrow \equiv\mathrm{SnR} + \mathrm{MX} \qquad (2.21)$$

$$\mathrm{RX} + \equiv\mathrm{SnM} \longrightarrow \equiv\mathrm{SnR} + \mathrm{MX} \qquad (2.22)$$

$$\mathrm{C{=}C} + \equiv\mathrm{SnH} \longrightarrow \equiv\mathrm{SnCCH} \qquad (2.23)$$

$$\mathrm{RH} + \equiv\mathrm{SnNR'_2} \longrightarrow \equiv\mathrm{SnR} + \mathrm{HNR'_2} \qquad (2.24)$$

Organotin compounds (R_4Sn, R_3SnX, R_2SnX_2, and R_3SnX_3) are prepared by various kinds of synthetic methods such as the Grignard reaction, Wurtz reaction, reactions with organoaluminums, and direct reactions. The Grignard reaction, Wurtz reaction and reactions with organoaluminums are generally suitable for the preparation of R_4Sn, and, on the other hand, direct reactions are suitable for the preparation of R_2SnX_2.

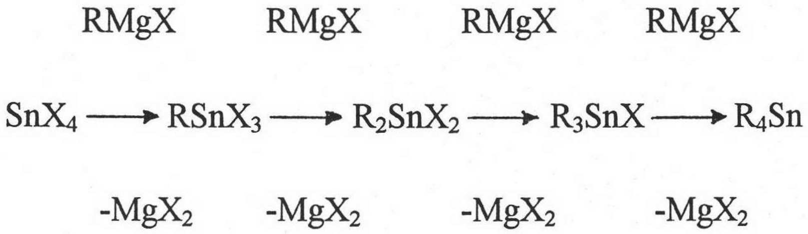
1. Grignard Reaction

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.

$$4RMgX + SnX_4 \longrightarrow R_4Sn + 4MgX_2 \qquad (2.25)$$

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. 2.22), and the stannic halides are alkylated stepwise as shown in (eq. 2.23). 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.



$$SnX_4 \xrightarrow[-MgX_2]{RMgX} RSnX_3 \xrightarrow[-MgX_2]{RMgX} R_2SnX_2 \xrightarrow[-MgX_2]{RMgX} R_3SnX \xrightarrow[-MgX_2]{RMgX} R_4Sn \qquad (2.26)$$

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. Phennyltin 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. 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.

$$SnX_4 + 4RX + 8Na \longrightarrow R_4Sn + 8NaX \qquad (2.27)$$

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.

$$SnX_4 \xrightarrow[-2NaX]{RX + 2Na} RSnX_3 \xrightarrow[-2NaX]{RX + 2Na} R_2SnX_2 \xrightarrow[-2NaX]{RX + 2Na} R_3SnX \xrightarrow[-2NaX]{RX + 2Na} R_4Sn \qquad (2.28)$$

Various kinds of side reactions also proceed.

$$R_2SnX_2 + 2Na \longrightarrow R_2Sn + 2NaX \qquad (2.29)$$

$$2R_3SnX + 2Na \longrightarrow R_3SnSnR_3 + 2NaX \qquad (2.30)$$

$$2RX + 2Na \longrightarrow R\text{-}R + 2NaX \qquad (2.31)$$

$$SnX_4 + 2Na \longrightarrow SnX_2 + 2NaX \qquad (2.32)$$

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 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 temperature.

3 Organoaluminums

Organotin compounds are prepared by reaction of organoaluminums with stannic halides as shown in (eq. 2.33).

$$4R_3Al + 3SnX_4 \longrightarrow 3R_4Sn + 4AlX_3 \qquad (2.33)$$

This reaction is also always accompanied by the formation of R_3SnX, R_2SnX_2 and $RSnX_3$. Koster reported that the AlX_3,. formed by alkylation of the organoaluminum compound as shown in (eq. 2.33), 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. 2-26 and 2.28).

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 compounds has the advantage that it can be carried out in the absence of solvent.

4. Direct Reaction

The organotin halide may be synthesized directly from tin metal

$$2RX + Sn \longrightarrow R_2SnX_2 \qquad (2.34)$$

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

4.1 Rochow Method

The direct reaction of organosilicon compounds, discovered by Rochow in 1944, was applied to the preparation of methyltin (eq. 2.35) and phenyltin compounds in 1953.

$$Sn + CH_3Cl \xrightarrow{300\text{-}330°C,\ Cu} (CH_3)_3SnCl \qquad (2.35)$$

4.2 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 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 compound; 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 temperature of the diorganotin compounds in water gives the triorganotin compounds.

$$2PhCH_2Cl + Sn \xrightarrow[\text{in toluene}]{110^\circ C,\ 88\%} (PhCH_2)_2SnCl_2 \qquad (2.36)$$

$$3PhCH_2Cl + 2Sn \xrightarrow[\text{in water}]{100^\circ C,\ 94\%} (PhCH_2)_3 + SnCl + SnCl_2 \qquad (2.37)$$

4.3 Matsuda-Matsuda Method

Sumio Matsuda and Haruo Matsuda extensively studied the direct reaction of alkyl 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.

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.

$$3R_4Sn + SnCl_4 \longrightarrow 4R_3SnCl \qquad (2.38)$$

$$R_4Sn + SnCl_4 \longrightarrow 2R_2SnCl_2 \qquad (2.39)$$

$$R_4Sn + 3SnCl_4 \longrightarrow 4RSnCl_3 \qquad (2.40)$$

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