CHAPTER II

THEORETICAL AND LITERATURE REVIEW

2.1 Fundamental principles of the four-stroke cycle engine.(2,3)

Reciprocating internal combustion engine operate on either the four stroke or 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 outboard marine engines.

The four-stroke cycle internal combustion engines utilizes 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 carburettor into the cylinder of the engine through an open intake valve by the down-stroke of a piston (Figure 2.1a)
- 2. A compression stroke to compress the air-fuel mixture by the upstroke of the piston. Both intake and exhaust valve are closed (Figure 2.1b)
- 3. Ignition and consequent burning of a homogenous 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 2.1c
- An exhaust stroke to sweep the cylinder free of burned gases,
 Figure 2.1d

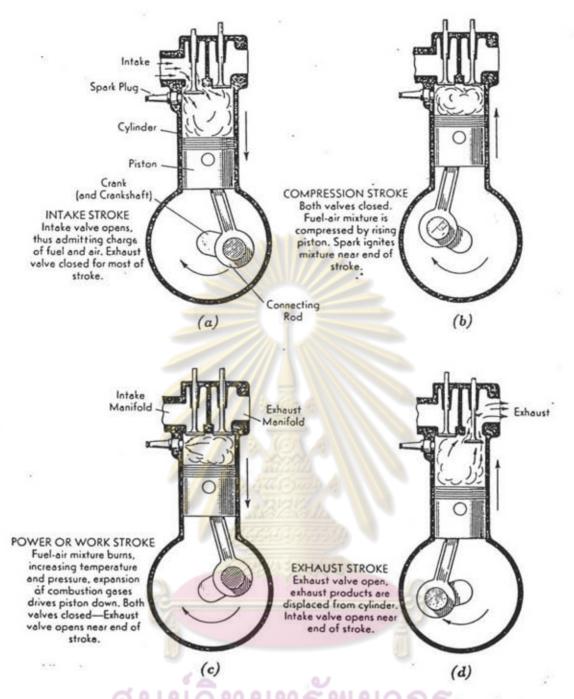


Figure 2.1 The four-stroke spark-ignition (SI) cycle.

2.2 Properties of gasoline (4)

In its simplest form, gasoline is a complex distillate of crude oil, comprising fractions that boil off over a range from about 25 °C to 220 °C for carburation, or ambient to 220 °C for gasoline injection since such system do not have float chambers from which the fuel can boil off when

หกลายคลาย ส**ล**ายน้ำแกรมักการ จุฬาสากรณ์มหาวิทยาลัก the engine is hot and perhaps flood the engine or cause vapor lock in fuel system. Evaporation from the surfaces of liquid occurs at temperatures a below their boiling points.

For use in motor vehicles, the gasoline must have certain chemical and physical properties, otherwise it will not pass satisfactorily up from the tank to carburetor or injectors, form suitable mixture with the air and burn efficiently in the cylinders to produce adequate power.

2.2.1 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 vapor 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.

2.2.2 Antiknock quality

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

2.2.3 Gum

Gasoline should be free of gum-forming materials in order to avoid clogging of engine fuel systems, carburetor malfunction and sticking of engine intake valves.

2.3 Gasoline Additive (5,7)

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 reformed, 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.

2.3.1. Antiknock compound

Oxygenated compounds that are widely used are methanol, ethanol, and MTBE. Methanol and ethanol gasoline blends have the most serious problem that when their water content exceeds a critical level, the blend separates into hydrocarbon and alcohol phases. Higher molecular weight alcohol such as TBA, IBA, or IPA can be used with methanol, increasing the gasoline solubility of the polar phase thus, increasing the equilibrium concentration of methanol in the gasoline phase. However, it has been found that methanol and formaldehyde in exhaust emission can cause slight air pollution. MTBE is more commonly used because it does not have the

problem mentioned above. The increasing demand for MTBE will lead to insufficient supply in future, therefore there are many research projects to discover other compounds that can work as efficiently as MTBE.

2.3.2. Dispersant

Dispersants are non-metallic or ashless cleaning agents. The structure of an ashless dispersants is similar to the structure of a detergent in that the dispersant has a hydrocarbon tail or oleophilic group which enables the dispersant to be fully soluble in the base fuel used. The dispersant also has a polar head. The polarity of a dispersant is derived from the inclusion of oxygen, phosphorus, or nitrogen atoms into the molecule. Figure 2.2 shows the stylized structure of an ashless dispersant.



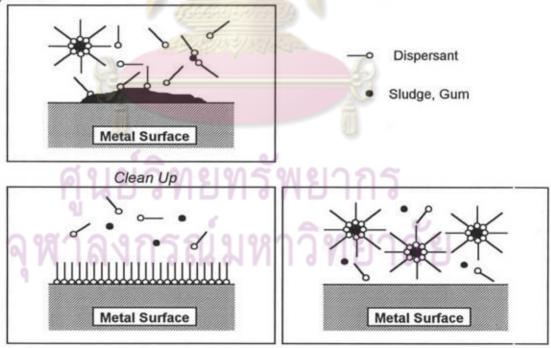
Figure 2.2 Stylised Dispersant (8)

Most dispersants currently in use are prepared from polyisobutylenes of 1,000 to 10,000 molecular weight. Their polar functionality arise from amino and/or hydroxyl (alcohol) groups. The connecting groups, in most cases, are either phenols or succinic acids. The products with succinic acid groups are called alkenyl succinimides and succinate esters. The products from phenols are alkyl hydroxybenzyl polyamines (also called Mannich

dispersants because of the name of the German chemist who discovered the method of preparation).

The dispersants are used in gasoline fuel to provide fuel inject or, carburettor, and valve cleanliness. Engine life is prolonged and undesirable engine exhaust emissions are reduced. The terms "detergents" and "dispersants" are often used interchangeably because both additive types keep insoluble combustion debris and fuel oxidation products dispersed with the fuel. Detergents are normally utilized to minimize high-temperature engine varnish and lacquer deposits while dispersants are used to control low-temperature engine sludge deposits. The harmful products of combustion and other contaminants are rendered harmless by the polar ends of dispersants. The hydrocarbon chain of dispersants helps to solubilize or suspend the debris.

The mechanism of dispersant in interaction with sludge is shown in Figure 2.3.



Keep Clean
Figure 2.3 Sludge Dispersion

CONVENTIONAL AMINE

Figure 2.4 The types of dispersant in gasoline fuel.

2.3.3. Deposit modifier additive.

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

2.3.4. Antioxidants

These are used wildely to inhibit oxidation reactions which form gums and there by 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 believe to act as chain-breakers in the various

oxidant and polymerization reactions. There are two major classes of antioxidant compounds, aromatic diamines and alkyl-substituted phenol, used in concentration of about 50 ppm

2.3.5. Metal deactivators.

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

2.3.6. Anti-rust agent.

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

Several types of hydrocarbon 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 carburettor icing and the build up of carburettor deposits.

2.3.7. Anti-icing agent.

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

Two general types of carburettor anti-icing additives: freezing-point depressants and surface-active agents. These are used in many gasolines to avoid the annoyance of cold weather stalls during engine warm up.

2.3.8. Carburetor detergent.

When an engine is idling, non-volatile full component, together with contents from exhaust emission and crankcase fumes down in though the air cleaner, tend to accumulate on the inside wall of carburettor just below the throttle blade.

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

^{2.3.9.}Dyes ย์วิทยทรัพยากร

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

2.3.10. Upper-cylinder lubricants.

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

2.4 Normal Combustion.(9,11)

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. Sulphur is also a constituent in oil. Low-sulphur oil is now in great demand as a fuel because the SO₂ emission is reduced. Low-sulphur 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 (C₈H₁₈). Gasoline is burned in the cylinders of an automobile engine which is expected to have the following reaction:

$$C_8H_{18} + xO_2 + x(3.76)N_2 \rightarrow aCO_2 + bH_2O + 3.76(x)N_2$$
 (2.1)
(Reactant) (Products)

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

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

If the reaction occurred in this manner it would be a stoichiometric combustion process, that is, all the oxygen atoms in the oxidiser react chemically to appear in the products. The nitrogen does not react.

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

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

AFR = 59.5 moles air/mole fuel

On a weight basis this becomes.

$$AFR = 59.5(28.95)/114 = unit air/unit fuel$$

(Air can be treated as mixture of 1 mole of O₂ to 3.76 mole of N₂)

This is a very typical AFR for hydrocarbons. Thus, the 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 produce in the combustion process. The real fact is that the combustion process is usually incomplete and therefor 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:

$$C_8H_{18} + xO_2 + yN_2 \rightarrow aCO + bH_2O + cO_2 + dH_2 + eCO + fH + gOH + iN_2 + jN + kNO+(2.3)$$

To investigate why combustion does not go to completion requires knowledge of both 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 automobile engine) will reach an equilibrium state which may include products of combustion other than just CO₂ and H₂O. High temperature combustion process 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 become kinetically limited. That is, it is limited not only by equilibrium considerations but also by the fact that reactions take to time proceed to completion, whether the completion state is one of stoichiometric combustion or not.

2.5 Chain reaction theory.(12)

The investigations into the actual mechanisms indicate that the reaction products which can be isolated and, in part, identified, such as aldehydes, ketones, 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 induction of 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 suggested the most wildly accepted explanation of gasphase oxidation of hydrocarbons. This mechanism proposed that, during reaction, products formed which reacted after a time (very long compared with the normal life of chain carrier), to initiate two new chains carriers, except at very high temperature, were taken to be free radicals or atoms. Thus the reaction may be represented by the following general scheme for

..(2.11)

the oxidation of alkane (where RH represents an alkane and X represents an initiating species):

Initiation RH + X°
$$\rightarrow$$
 R° + XH(2.4)

Propagation 2R° + 2O₂ \rightarrow 2RO₂°(2.5)

2RO₂° + RH \rightarrow RO₂H + R°(2.6)

RO₂H \rightarrow Products(2.7)

RO₂H \rightarrow RO° + °OH(2.8)

RO₂° \rightarrow RCHO + °OH(2.9)

RCHO + O₂ \rightarrow RCO° + HO₂°(2.10)

Surface

In this scheme, reaction (2.7) is the normal fate of, for example, the hydroperoxide formed during proportion. Occasionally, however, decomposition occurs which yields two chains centers (reaction 2.8) and brings about chain branching. Reaction (2.8) is not the only step by which branching occur, thus in reaction (2.9) an aldehyde is formed which reacts further to effect chain branching. The radical chains are terminated by surfaced destruction.

Termination (e.g.) 2RO₂

2.6 Formation of pollutants.(13,15)

2.6.1 Carbon monoxide.

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.

$$H_2O + CO \rightarrow H_2 + CO_2$$
(2.4)

At high flame temperature, this equilibrium yields significant quantities of carbon monoxide relative to carbon dioxide, even for fuel-lean mixture ratios. However, as the combustion gases cool from peak flame temperatures to the much lower temperature characteristic of exhaust products, this equilibrium shifts in a direction favouring oxidation of CO to CO₂. Consequently, for fuel-lean or chemically correct mixture ratios, relatively small quantities of carbon monoxide ultimately appear in exhaust combustion products. For fuel-rich mixture ratios, however, due to the simple insufficiency of oxygen, a significant concentration of carbon monoxide persist even in cool exhaust products.



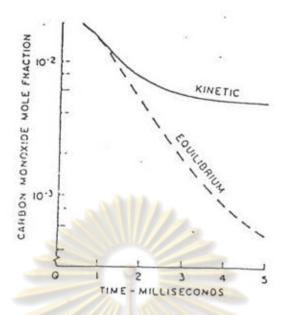


Figure 2.5 Carbon monoxide concentration as a function of time following combustion.

Figure 2.5 illustrates the behaviour of carbon monoxide in a spark ignition engine cycle. Here the variation of carbon monoxide concentration 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 portions of the combustion process, and as the products expand and cool, oxidation of CO to CO₂ occurs. The dashed line of Figure 2.5 represents CO concentrations that would result if chemical equilibrium prevailed throughout expansion. However, at the lower temperature during expansion, chemical reaction rates lag behind equilibrium leading to the solid curve of Figure 2.4 representing the actual situation.

The toxicity of carbon monoxide is well known. It occurs because the blood, which carries oxygen to the different parts of the body, has a higher affinity for carbon monoxide than oxygen. The effects are dependent upon both time and concentration, as shown in Table 2.1

Table 2.1 Effects of carbon monoxide in man.

Concentration (ppm)	Effects			
200	Possibly headache, mild frontal in 2 to 3 hours			
400	Headache, frontal, and nausea after 1 to 2 hours occipital after 2 to 3 hours			
800	Headache, dizziness and nausea in ¾ hours; collapse and possibly unconsciousness in 2 hours			
1600	Headache, dizziness and nausea in 20 minutes; collapse, unconsciousness, possibly death in 2 hour.			
3200	Headache and dizziness in 5 to 10 minutes; unconsciousness and danger of death in 30 minutes.			

2.6.2 Oxides of nitrogen.

The principal oxide of nitrogen formed in this combustion process is nitric oxide. Nitric oxide is a high- enthalpy species relative to N_2 to O_2 from the standpoint of basic thermodynamics. The emissions of nitric oxide, are governed by two parameters; the availability of for the reaction

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

and a high enough temperature to promote this reaction.

Like carbon monoxide, the oxides of nitrogen tend to bind to the haemoglobin in blood. However, probably the most undesirable toxic effect of oxides of nitrogen is there 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 smong.

2.6.3 Hydrocarbons

Unlike carbon monoxide and nitric oxide, hydrocarbons are not substances that one expects to find in high-temperature combustion gases. Chemical equilibrium calculations readily show that the quantities of hydrocarbon gases that exist in homogeneous high-temperature combustion products are immeasurable. Furthermore, the oxidation reactions for hydrocarbons under such conditions are among the most rapid observed. Thus, the appearance of unburned hydrocarbons in the exhaust of a combustion process must be associate with the existence of temperature or mixture heterogeneity at some point in the system.

The appearance of unburned hydrocarbons in combustion products implies that these particular hydrocarbons were never successfully ignited. Thus, the effect of heterogeneity resulting in unburned hydrocarbons can be viewed as one of ignition inhibition.

The simplest criterion that can be used to determine whether or not ignition of a parcel of reactants occurs is the internal heat generation or the rate of heat loss. These are:

- The local mixture composition may be so rich or lean that the oxidation reactions are very slow and ignition cannot occur because of heat losses.
- For small isolated elements of fuel-air mixture the element surface-to-volume ratio may become so large and heat losses consequently so great that ignition cannot occur.

 Hert losses from fuel-air mixture adjacent to a cool surface may be so great that ignition cannot occur.

One or more of these factors may play a role in each of the various types of combustion system presently in use. In the case of premixed flame, as employed in the spark-ignition engine, it is doubtful that item one or two above would be of major importance. Clearly, however, the presence of relatively cool combustion chamber walls can result in large heat losses from adjacent fuel-air mixture. As a consequence, a layer of unburned fuel-air mixture next to the walls will fail to ignite and 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 combustion reactions. It is generally considered that the thickness of this quench layer is a function of fuel-air ratio and pressure, among other things.

It is estimated that a significant portion of those hydrocarbons quenched by the cold combustion-chamber walls are burned during the expansion process, and it has been shown that under many typical operating conditions a fraction of these hydrocarbons surviving the expansion are burned in the exhaust system. For this reason both temperature and oxygen concentration in exhaust gases are important to the final concentrations of hydrocarbons emitted from the exhaust system. The importance of oxygen concentration is illustrated by Figure 2.5 showing the variation of hydrocarbon emission with air-fuel ratio.

The thickness of the quench zone is probably minimum slightly on the rich side. However, as the engine mixture is made leaner more oxygen is variable during the expansion and exhaust process to help destroy the increased hydrocarbons present because of the in creased quench thickness. Thus, for lean mixtures, even though the quench-zone thickness has increased, very few hydrocarbons survive the expansion and exhaust process until the mixture is so lean that erratic flame propagation occurs. High turbulence plus turbulent heated inlet manifolds will delay erratic flame propagation to very lean mixtures. 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 2.6

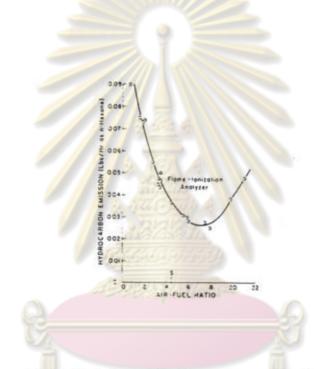


Figure 2.6 Variation of hydrocarbon with air-fuel ratio.

2.7 Effect of operating variables on engine exhaust emissions.(16,18)

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

2.7.1. Air-fuel ratio.

Both CO and HC emission can be reduced by increasing the air-fuel ratio. Figure 2.7. 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 remarkably 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 chancing the chamber to a more spherical shape, that is, short and fat.

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

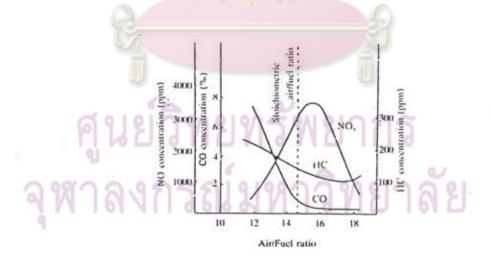


Figure 2.6 Typical concentrations of unburned hydrocarbons, carbon monoxide, and oxides of nitrogen as a function of air-fuel ratio at 60 mph

2.7.2. Engine speed

Emission 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 sequenced layer. In addition, increased exhaust port turbulence at higher speeds promotes exhaust system oxidation reactions through better mixing. Speed has no effect on concentration because oxidation of CO in exhaust is kinetically limited rather than mixing limited at normal exhaust temperatures. Figure 2.8 showns the effect of engine speed on hydrocarbon concentration in the rang between 1500 to 2500 rpm.

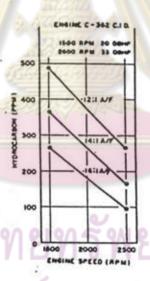


Figure 2.8 Effect of engine speed on exhaust gas hydrocarbon concentration at 12:1, 14:1, and 16:1 air-fuel ratio

Table 2.2 Relative emission rate for various engine-operating modes

Mode	Exhaust volume	Pollutant concentration		
		HC	СО	NO _X
Idle cruise	very low	high	high	very low
high speed	low	low	low	low
Accelerate	high	very low	very low	moderate
Moderate	high	low	low	high
Heavy	very high	moderate	high	moderate
Decelerate	very low	very high	high	very low

Table 2.2 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 carburettor vacuum signal, retards the ignition timing.

During acceleration and normal cruising speeds the increased carburettor 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 remain seated.

During deceleration, the per of highest CO and HC exhaust emission, carburettor 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 experted on the distributor vacuum advance unit pulling it into a position of maximum spark advance. As decelerator processes 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.

2.7.3 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 in Figure 2.8

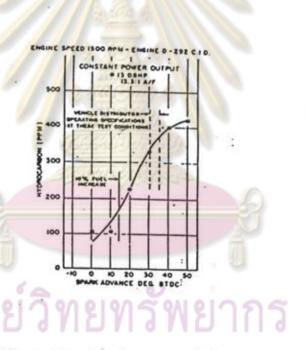


Figure 2.8 Effect of spark advance on exhaust gas hydrocarbon concentration at constant engine speed 1500 rpm

In a vehicle the emission reduction achieved by spark retard must be compromised by fuel economy loss considerations. Figure 2.10 shows the effect of spark ignition time at 30 mph on fuel economy.

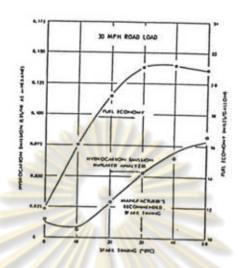


Figure 2.10 Effect of spark timing on exhaust hydrocarbon emissions andfuel economy in car at 30 mph road load

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 constants, 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 2.10. shows the CO emission for the engine as a function of spark timing constant power output.

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

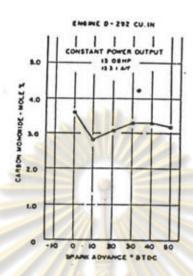


Figure 2.11 Effect of spark advance an exhaust gas carbon monoxide concentration for fixed throttle verus constant load at 1500 rpm

2.8 Literature review

Increasly stringent emission requirements for gasoline engines has heightened the importance of both engine design and fuel quality. Unlike the 1970s and early 1980s, the path is not being clouded with energy crises or lead additive phase-out issues. Oxygenate supplement, covering a range of alcohol and ether types have been recognised as range as mean of raising the octane of gasoline. Although fuel oxygenates first because 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 alcohol and ethers have high octane numbers, they are not as effective as lead for increasing the base fuel octane number

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 specification 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 increased demands of quality.

Koehl and co-workers studied emission effects of gasoline hydrocarbon components distilling above 300 °F to determine the effect of 90 % distillation temperature. Hydrocarbons and carbon monoxide were found to increase with addition of heavier components. The increases occurred with the fuels that had the highest concentrations of the heavier components. The NO_X decreased with addition of heavy components. Increasing fuel aromatic content increased benzene emissions.(19)

Adibis from its Copenhagen office, has performed a test program according to the quinoline of the Swedish EPA on one detergent additive and one valve seat protection additive in gasoline fuel. The test include CO, HC, NO_X and particulate. The results showed, that emission with and without additive reveals no sign of difference.(20)

Midpanon studied the effect of organotin compounds in gasoline on exhaust emissions from cars. She synthesized organotin compounds for blending with gasoline base. CO and HC were found to decrease with addition of organotin compounds.(21)