

**Formation and Control
of
Combustion Pollutants
from
Gasoline-Fueled Spark-Ignition
Motor Vehicle Engines**

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Notice

The purpose of this document is to provide simple explanations regarding the formation and control of combustion pollutants from gasoline-fueled spark-ignition motor vehicle engines. Formation phenomena are explained on the basis of well-known cause and effect relationships. Control techniques are explained on the basis of the operating characteristics of systems which are already in widespread use. Consequently, this document takes the form of a synopsis of information that is available in other formats in the applicable reference literature.

Credits

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Contents

Acknowledgments.....	iii
Introduction.....	1
Chapter 1. Gasoline-fueled Spark-ignition Engines.....	5
Chapter 2. Pollutant Formation—General Effects.....	11
2.1. Fuel Complexity.....	11
2.2. Combustion Complexity.....	15
Chapter 3. Pollutant Formation—Specific Effects.....	20
3.1. Effect of Flame Quenching.....	21
3.2. Effect of Oxygen Content on CO Formation.....	22
3.3. Effect of Temperature on NO Formation.....	22
Chapter 4. Pollutant Control Approaches.....	24
4.1. Preventive Techniques.....	24
4.1.1. Combustion Chamber Redesign for HC Minimization.....	24
4.1.2. Fuel Control for CO Minimization.....	25
4.1.3. Temperature Control for NO Minimization.....	25
4.2. Remedial Techniques.....	27
4.2.1. Supplementary Air Oxidation.....	27
4.2.2. Catalytic Conversion.....	30
4.3. Interaction Complications.....	37
Appendix.....	39
Appendix 1. Comparison of Four-stroke Spark-ignition and Compression-ignition Engines.....	41
Speed and Power Output Control.....	41
Fuel Properties.....	42
Fuel Introduction.....	42
Combustion Initiation.....	43
Pollutant Formation.....	43
Appendix 2. Hydrocarbon Classes.....	47
Paraffin (Alkane) Hydrocarbons.....	48
Isoparaffin (Alkane) Hydrocarbons.....	48
Cycloparaffin (Alkane) Hydrocarbons.....	49
Olefin (Alkene) Hydrocarbons.....	49
Hydrocarbons with Six Carbon Atoms.....	50
Oxygenated Organic Compounds.....	51

Figures

Figure 1.	Engine Block and Head (cross-section).....	5
Figure 2.	Engine Block and Manifolds.....	6
Figure 3.	Spark-ignition Phases.....	7
Figure 4.	Molecular Structure of Selected Hydrocarbons.....	11
Figure 5.	Flame Quenching.....	21
Figure 6.	Surface/Volume Ratio Changes.....	25
Figure 7.	Internal Exhaust Gas Recirculation (Valve Overlap).....	27
Figure 8.	External Exhaust Gas Recirculation.....	28
Figure 9.	Aspirated Air Injection.....	29
Figure 10.	Forced Air Injection.....	30
Figure 11.	Exhaust Composition.....	35
Figure 12.	Closed Loop Fuel Flow Control System.....	36

Tables

Table 1.	Relationship of Combustion Phase and Piston Stroke.....	6
Table 2.	Hydrocarbon Compounds and Properties.....	13
Table 3.	Exhaust Pollutants.....	20
Table 4.	O ₂ & CO Concentration by Air/Fuel Ratio.....	33

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Introduction

The pollutant formation and control information provided in this synopsis is specifically applicable to gasoline-powered, four-stroke, reciprocating piston, spark-ignition motor vehicle engines. This information is presented with the hopeful intention of providing the non-technical reader with a basis for understanding the applicable chemical and physical phenomena. Consequently, the discussion of these phenomena emphasizes cause and effect relationships which may not be obvious to a reader who does not have an engineering background and, hence, might be overlooked by such a reader if such highlighting was not attempted.

For example, the discussion of spark-ignition engine construction and operation in Chapter 1 calls attention to the correspondence between

- the four strokes of the cycle and the four phases of the associated combustion process and
- the effects of the cycle and the process on the related pollutant formation mechanisms.

Chapter 2 discusses pollutant formation on an overall basis by relating two factors, fuel complexity and combustion complexity, to the generalized effects on the energy generation process and on the pollution formation mechanisms. Fuel complexity is discussed by relating the many different kinds of hydrocarbon compounds present in gasoline to the effects of the physical properties of the compounds on the combustion process. Combustion complexity is discussed in Chapter 2 in terms of the variations in the structure and operation of the engine. These variations affect the combustion of the fuel by limiting the use of the chemical energy in the fuel for developing mechanical energy needed for operating the vehicle.

This chapter also provides an understanding of how one set of complexities affects the other. The relationship between fuel complexity and combustion complexity is shown by pointing out that—

- using a complex fuel (with different types of hydrocarbons), instead of a simple fuel (with one type of hydrocarbon), complicates the combustion process and
- using a complex combustion process (involving the discontinuous burning of combustible air/fuel mixtures in an enclosed chamber),

instead of a simple process (involving the continuous open-flame burning), complicates the effective utilization of the fuel.

The emphasis on relationships is continued in Chapter 3 which discusses pollutant formation in detail by highlighting the differences between the various cause and effect events accounting for the presence of hydrocarbons (HC), carbon monoxide (CO), and nitric oxide (NO) in the exhaust. This discussion stresses the following:

- During the combustion process, most of the hydrogen and carbon atoms in the fuel hydrocarbon molecules are separated from each other and oxidized to water vapor (H_2O) and carbon dioxide (CO_2), respectively.
- A small fraction of the fuel molecules undergo less complete reactions which result in the carbon atoms being partially oxidized to carbon monoxide and the hydrogen atoms associating with each other to form diatomic hydrogen molecules.
- Another small fraction of the fuel molecules are more or less excluded from the combustion process, primarily as a result of flame quenching. These molecules pass through the combustion chamber either completely unaltered, restructured in some way, or converted into various forms of oxygenated organic compounds.
- NO molecules in the exhaust are not directly products of the combustion process but, rather, are products of a high temperature side reaction which involves the disassociation of some of the atmospheric nitrogen molecules, the oxidation of the liberated nitrogen atoms to NO, and the subsequent conversion of the NO to other nitrogen oxides, such as nitrogen dioxide (NO_2), when the exhaust gases are released to the atmosphere.

In a comparable way, Chapter 4 discusses pollution control by associating several techniques presently used with the two possible control approaches, preventive and remedial. Each technique is related to the pollutant formation phenomena discussed in Chapter 3.

Engine combustion chamber redesign is discussed as an HC *preventive* technique which reduces flame quenching and, hence, minimizes the number of fuel molecules that are isolated from the combustion process. Fuel flow control is discussed as a CO *preventive* technique which controls fuel input to ensure that the oxygen available in the ingested air is adequate to maximize the oxidation of the fuel HC molecules. Exhaust gas recirculation is discussed as an NO *preventive* technique which limits the

combustion chamber temperature to minimize the oxidation of atmospheric nitrogen.

Supplementary air injection is discussed as a *remedial* technique which adds air to the hot exhaust gases so that the additional oxygen can react with the HC and CO molecules that exit the combustion chamber. Catalytic conversion is discussed as a *remedial* technique which oxidizes HC and CO molecules and reduces NO molecules. This discussion is focused on closed loop fuel control systems which use three-way catalysts, lambda sensors, and electronic control units to maintain proportions of air and fuel close to the chemically correct, "stoichiometric," ratio.

The final relationships highlighted in Chapter 4 are the possible interactions between the various control techniques. This discussion illustrates the fact that a technique which is implemented to control one pollutant can have various undesirable side effects, such as promoting the formation of another pollutant, degrading engine or vehicle performance, or causing a decrease in the effectiveness of a remedial technique that is used to eliminate a different pollutant.

Two appendixes are included. In Appendix 1, the spark-ignition engine characteristics are briefly contrasted with those of compression-ignition engines. The differences discussed include the various operational parameters, such as the means used to control speed and power output, the physical properties of the fuels used, the means used to introduce the fuel into the combustion chambers, the means used to initiate the combustion process, and the phenomena which result in the emission of combustion pollutants.

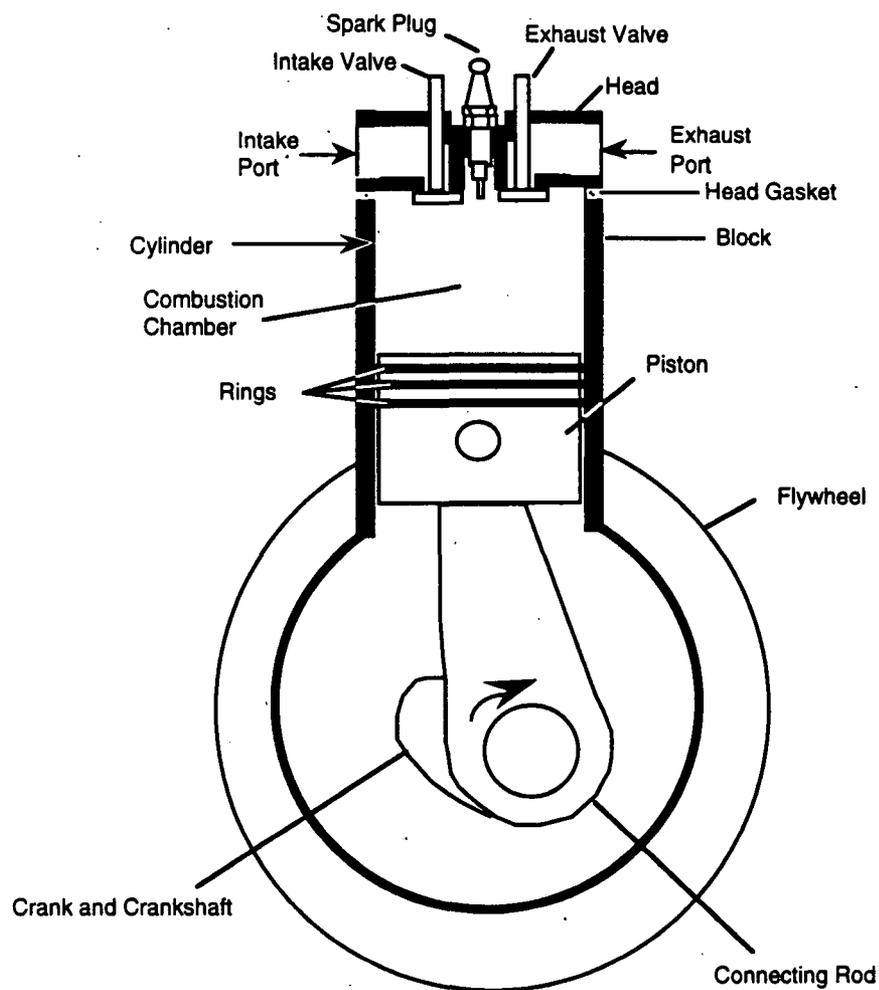
Appendix 2 presents additional information regarding hydrocarbon molecular structure. The discussion details the hydrocarbons present in gasoline fuels and the reconfigured and partially oxidized organic compounds produced when some fuel molecules pass through the combustion chamber of a spark-ignition engine without the complete liberation of the molecular carbon atoms.

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Chapter 1. Gasoline-Fueled Spark-ignition Engines

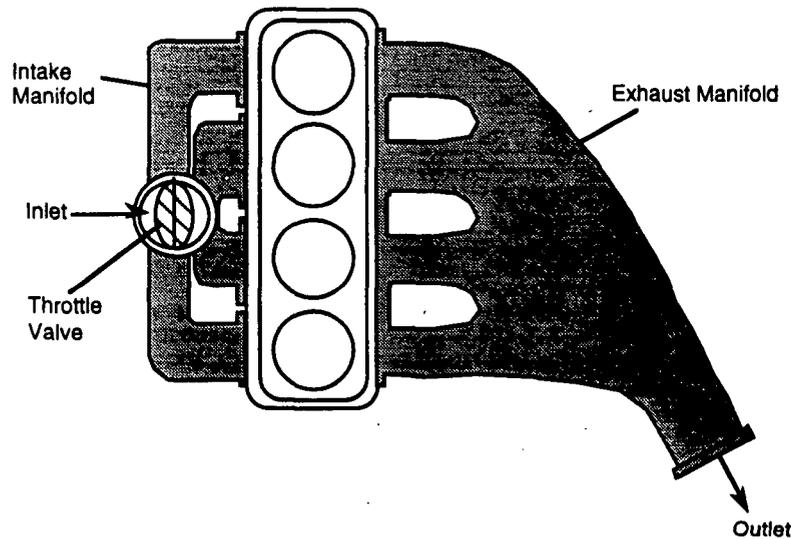
This synopsis focuses specifically on gasoline-powered, spark-ignition engines. Such engines utilize a throttled, spark-initiated, internal combustion process to convert the chemical energy in the fuel into the mechanical energy required for the operation of the motor vehicle. This conversion process takes place within several internal combustion chambers similar to the one shown in Figure 1. The radial boundary of the chamber is determined by the cylindrical cavity in the engine block. The engine head provides the fixed end to the chamber. The top of the reciprocating piston provides the opposite movable end. The combustible mixture of air and fuel enters the combustion chamber via the inlet port and one or more intake valves. The combustion gases exit the combustion chamber via one or more exhaust valves and the exhaust port.

Figure 1. Engine Block and Head (cross-section)



As shown in Figure 2, the several inlet ports of the head are connected to a common inlet by means of an intake manifold. A throttle valve regulates the ingestion of air or an air/fuel mixture, depending on the design of the engine. The exhaust ports are connected to a common exhaust outlet by means of an exhaust manifold.

Figure 2. Engine Block and Manifolds.

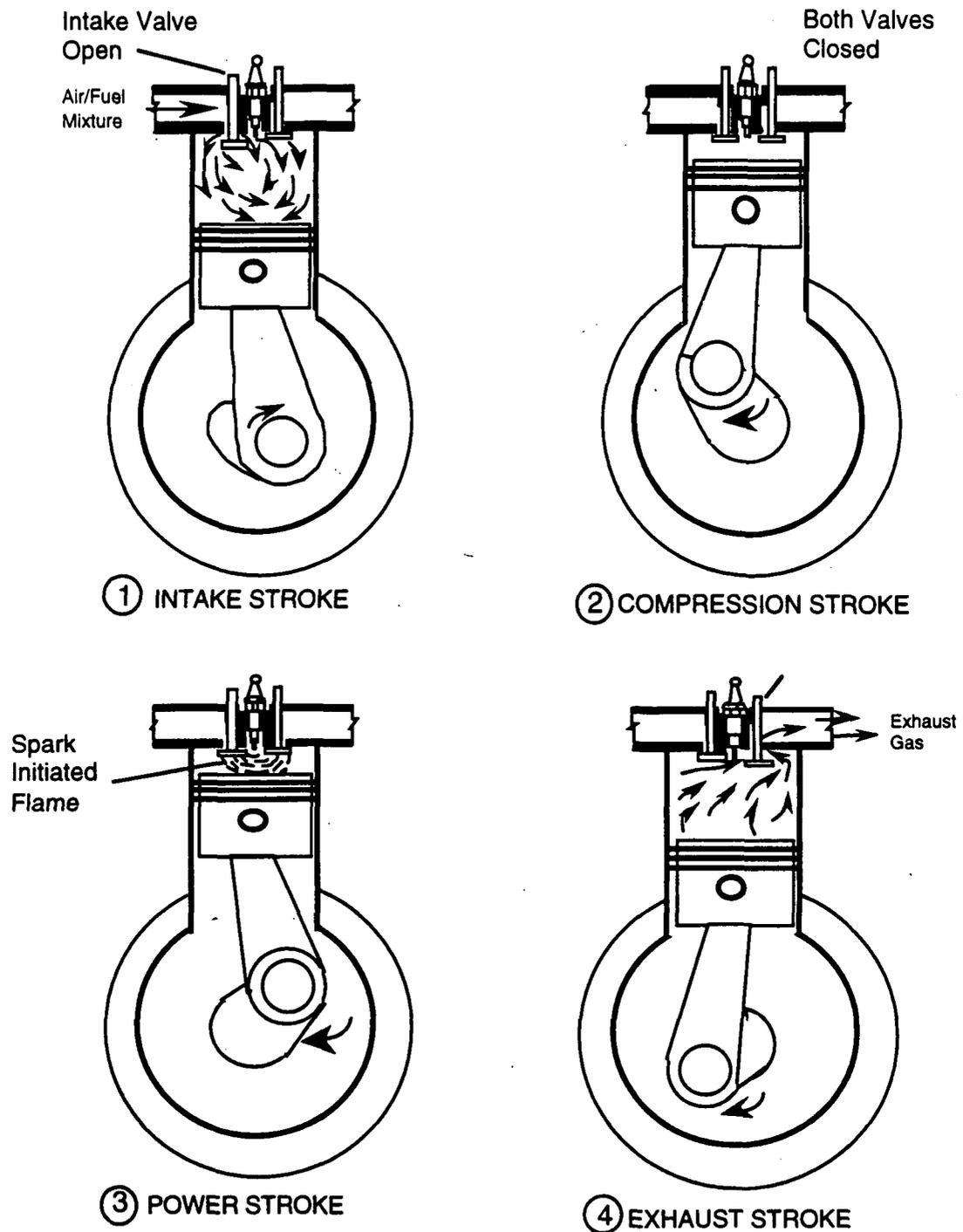


The four-stroke combustion cycle, which was first put to practical use by Nicolaus A. Otto in 1876, is shown in Table 1 and Figure 3. As Figure 3 illustrates, the four combustion phases do not start and stop at precise positions of the piston, although they are affected by, or have an effect on, the four up-and-down strokes of the piston.

Table 1. Relationship of Combustion Phase and Piston Stroke.

<i>Combustion Phase</i>	<i>Piston Stroke</i>
Air/fuel mixture is ingested	Intake
Mixture is compressed	Compression
Mixture is burned	Power
Combustion products are expelled	Exhaust

This "Otto cycle" or spark-ignition process is both similar and different from that of a compression-ignition process. Appendix 1 provides a brief contrast of the two types of engines and the resulting pollutants. This synopsis focuses on pollutants formed by the combustion process in a gasoline-powered, fuel-injected, four-stroke, spark-ignited motor vehicle engine.

Figure 3. Spark-ignition Phases.

When a naturally aspirated (unturbocharged or unsupercharged) spark-ignition engine is in operation, the movement of each piston away from the cylinder head during the intake stroke increases the available space in the cylinder. The increase in volume results in a decrease in pressure. The

accumulative effect of the successive intake strokes of the several pistons is the reduction of the intake manifold pressure to a negative (subatmospheric) value. The extent to which the intake system pressure is reduced depends on the speed of the engine and the position of the intake manifold throttle valve. The speed of the engine in revolutions per minute determines the total number of intake strokes per minute. The position of the throttle valve determines how much obstruction is offered to the inflow of ambient air. The absolute pressure in the intake manifold is the lowest (less than $\frac{1}{2}$ atmospheric pressure) at idle and highest (close to atmospheric pressure) at wide open throttle.

The subatmospheric pressure in the intake manifold facilitates the ingestion of ambient air via the air cleaner and the flow of the air to the intake ports of the several cylinders via the individual passageways or "runners" in the intake manifold. At some time prior to the arrival of the air at each cylinder inlet port, "atomized" fuel in the form of very fine droplets is added to the air. The fuel flow control system is designed to add the fuel at a rate which will result in the desired proportions of fuel and air.

At each cylinder inlet port, the subatmospheric pressure in the combustion chamber (which is lower than the subatmospheric pressure in the intake manifold) facilitates the entrance of the air/fuel mixture. This occurs when an intake valve opens as the piston moves away from the cylinder head. This is the first, or intake, stroke of the combustion cycle (see Figure 3).

The valve then closes and the piston moves toward the cylinder head during the second, or compression, stroke. This movement compresses the contained mixture and, as a consequence, heats it. An electric spark ignites the compressed and heated air/fuel mixture sometime during the time interval when the piston is advancing toward and then retreating from "top dead center" (the position where piston is at its closest point to the cylinder head).

The high pressure developed as a result of this combustion process forces the piston away from the cylinder head during the third (power) stroke of the operating cycle. The exhaust valve opens when the piston is again

moving toward the cylinder head so that the combustion gases can be expelled. This is the fourth and final (exhaust) stroke of the cycle.

This sequence of events is repeated over and over in each cylinder of the engine and the combustion gases flow into the exhaust manifold and escape into the atmosphere via the vehicle tailpipe(s). At any particular moment, the position of the air inlet throttle valve determines the speed of the engine and the power it is developing. When the valve is in its "closed" position, only enough air is ingested to allow engine operation at the desired idle speed without the generation of any power for vehicle operation. The small amount of fuel added allows the generation of enough power to keep the engine running smoothly at the idle speed. When the throttle valve is wide open and fuel is added at the appropriate rate, the engine is able to develop its maximum power output. Then its speed is determined by the load requirements placed on it by the operation of the vehicle.

If a hydrocarbon fuel containing no impurities could be burned under perfect conditions, the exhaust gases exiting the individual combustion chambers would contain only:

- molecules of carbon dioxide (CO₂) (containing the carbon atoms previously contained in the fuel molecules).
- molecules of water vapor (H₂O) (containing the hydrogen atoms previously contained in the fuel molecules).
- molecules of nitrogen (N₂) (originally in the ingested air and not involved in the combustion process).

This can be represented by the following equation:

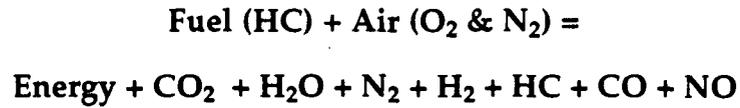


However, since most fuels contain some impurities and perfect combustion conditions can not be realized in actual practice, the exhaust gases may also contain varying percentages of:

- molecules of hydrogen (H₂) which result when fuel hydrogen atoms are not oxidized and associate to form diatomic molecules.
- fuel hydrocarbon (HC) molecules which were completely unchanged, or only partially changed, during their passage through the combustion chambers of the engine.
- molecules of carbon monoxide (CO) which are the result of the incomplete oxidation of the fuel carbon atoms.

- molecules of nitric oxide (NO) which were formed when the atmospheric nitrogen was subjected to the unique conditions existing in the engine's combustion chambers.
- molecules of inorganic compounds, such as sulfur oxides, which result from reactions involving fuel or lubricating oil impurities.

This can be represented by the following equation:



The formation and control of the pollutants resulting from these imperfect combustion conditions are discussed in the following chapters of this synopsis.

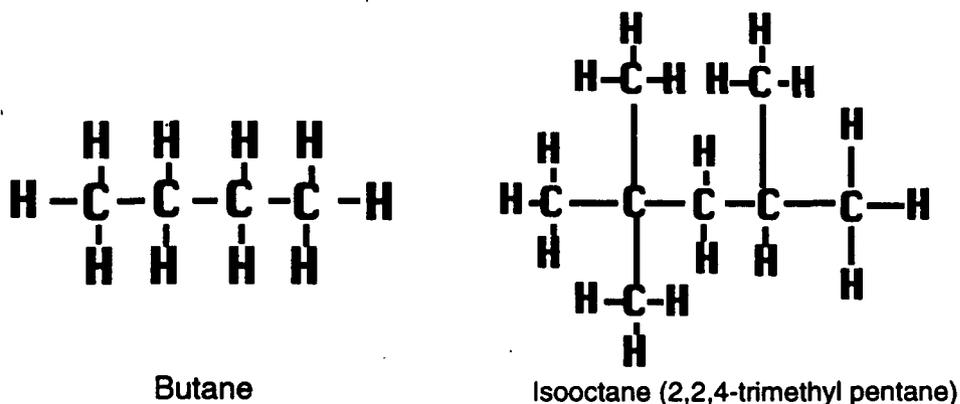
Chapter 2. Pollutant Formation—General Effects

Two factors, fuel complexity and combustion complexity, have a general effect on pollutant formation in that they preclude the complete oxidation of the fuel. Fuel complexity results from the many different kinds of hydrocarbon compounds present in gasoline. Combustion complexity results from the various structural and operational parameters of the engine which affect the oxidation of these various compounds.

2.1. Fuel Complexity

The term "gasoline" is used to describe the portion, or fraction, of petroleum distillate which has a boiling point range of about 75 to 415°F. This portion is a complex mixture of a wide variety of hydrocarbon compounds. The molecules of all of these compounds are comprised of only two kinds of atoms, carbon and hydrogen. However, the four attachment points at each carbon atom allow an almost limitless variety of molecular configurations. Some examples of these molecular structures are shown in Figure 4 and more appear in Appendix Two.

Figure 4. Molecular Structure of Selected Hydrocarbons.



Gasoline hydrocarbons can be classified into three main types: paraffins, olefins, and aromatics. The paraffin hydrocarbons are "saturated" in that each molecule contains the maximum possible number of hydrocarbon atoms. The olefin hydrocarbons are "unsaturated" or deficient in hydrogen atoms as a result of double bonding between adjacent carbon atoms in the chains. The aromatic hydrocarbons contain a unique structure, known as a benzene ring, consisting of six carbon atoms in a closed chain or

ring with single and double bonds alternating between the adjacent carbon atoms. Each hydrocarbon class can be found in gasoline and in exhaust emissions. The actual percentage of each type of hydrocarbon depends on the type of gasoline.

The addition of oxygen atoms to hydrocarbon molecules further increases the number of possible molecular configurations. In the case of the alcohols, a hydrogen atom is replaced with a oxygen/hydrogen hydroxyl (-OH) functional group. The two simplest alcohols, methanol (CH_3OH) and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), can be used alone as engine fuels or mixed with gasoline to form oxygenated fuels. When aldehydes and ketones are formed during the combustion of the fuel compound, a carbon atom is double bonded to one oxygen atom in lieu of being single bonded to two hydrogen atoms.

The physical properties of a hydrocarbon compound are affected by the number of carbon atoms in the molecule and the configuration of these atoms within the molecular structure. The effect of these details on physical properties is illustrated by Table 2.

The first twelve compounds in Table 2 illustrate how an increase in the number of molecular carbon atoms results in an increase in boiling point and a decrease in autoignition temperature. The decrease in the auto ignition temperature results from the increase in the susceptibility to thermal breakdown which accompanies the increase in the length of the molecule.

The last two compounds in the table illustrate how the configuration of molecular carbon atoms affects the boiling point and auto ignition temperature. The rearrangement of the six straight-chain carbon atoms in the paraffinic hexane molecule into the aromatic benzene configuration results in about a 14% increase in boiling point and about a 50% increase in auto ignition temperature. The rearrangement of the eight straight-chain carbon atoms in the paraffinic octane molecule into the branched-chain isooctane configuration (see Figure 4) results in about a 18% decrease in boiling point, but about a 53% increase in auto ignition temperature.

Auto ignition temperature is one of the most important physical properties of a gasoline hydrocarbon because it is an indication of detonation tendency. Detonation occurs when a portion of the air/fuel mixture in the combustion chamber spontaneously ignites before the arrival of the spark-

induced flame front. Such detonation results in the generation of a second very rapidly moving flame front. The resultant rapid increase in pressure in the combustion chamber produces the characteristic "knocking" sound.

Table 2. Hydrocarbon Compounds and Properties.

<i>Compound</i>	<i>Carbon Atoms</i>	<i>Physical State</i>	<i>Boiling Point (°F)</i>	<i>Auto ignition Temperature (°F)</i>	<i>Research Octane Number</i>
Methane	1	Gas	-259	1,346	110 ¹
Ethane	2	"	-127	1,050	104 ¹
Propane	3	"	-44	995	100
Butane	4	"	31	961	92
Pentane	5	Liquid	97	933	61
Hexane	6	"	155	909	25
Heptane	7	"	209	893	0
Octane	8	"	258	880	-17
Nonane	9	"	303	871	-45
Decane	10	"	345	866	—
Undecane	11	"	384	—	—
Dodecane	12	Solid	421 ²	—	—
Benzene	6	Liquid	177	1,363	110
Isooctane ³	8	"	211	1,350	100

¹ Estimated

² Melting point is 14°F

³ 2,2,4-trimethyl pentane

The octane number of a compound is an indication of its knocking tendency, as can be seen in the preceding table. The use of such numbers provides a means for rating the knocking, or detonation, tendencies of gasoline samples. This rating system is based on the knocking characteristics of normal heptane (0 octane) and isooctane (2,2,4-trimethyl pentane) (100 octane) when a mixture of these hydrocarbons is burned in a Cooperative Fuel Research single cylinder engine.

The octane number of a gasoline sample indicates the relative amounts (by volume) of isooctane and heptane in a mixture which exhibits a knocking tendency comparable to that of the gasoline sample. For example, a gasoline sample which has an octane rating of 80 has the same knocking tendency of a mixture of 80% isooctane and 20% heptane. Fuel samples with a lower detonation tendency than isooctane are rated with a different rating scale. This scale involves the supercharging of the test engine to increase the inlet air pressure when isooctane is used as the fuel.

By varying the operating conditions of the test engine, two different values, the research octane number (RON) and the motor octane number (MON), are obtained. The RON value, the lower of the two, is obtained by the use of more severe test engine operating conditions, such as a higher speed, a more advanced ignition timing, and a higher intake mixture temperature in the intake manifold. The difference between the MON and RON values is called the sensitivity of the sample. This value is used to indicate the tendency of a fuel to preignite and produce knock when the conditions under which a vehicle engine is operating becomes more demanding. The octane value shown on the service station dispensing pump is the average of the MON and RON values $\left(\frac{\text{MON} + \text{RON}}{2}\right)$.

A typical gasoline sample will contain different types of hydrocarbons with molecular carbon atoms predominately in the C₆ to C₁₂ range. The carbon atoms in these hydrocarbons can be arranged in different configurations. (The tables in the appendix show a few hydrocarbon molecular configurations in their simplest forms.) A specific gasoline sample can also contain some hydrocarbons with fewer than six carbon atoms. For example, some butane may be present, even though in the pure state this hydrocarbon is a gas at standard temperature and pressure conditions. A gasoline sample may also contain hydrocarbon molecules with more than 12 molecular carbon atoms, as well as configurations involving various degrees of unsaturation and different combinations of straight and branched chains and closed or aromatic rings.

Since the composition of "gasoline" fuels can vary over such a wide range, the combustion characteristics of a particular gasoline sample is dependent on the nature of the contained mixture of hydrocarbon compounds. For this reason, EPA regulations specify that emission testing must be performed with gasoline which has properties that fall within specified limits. Furthermore, the test fuels must be either

- kept in sealed containers to prevent the preferential evaporation and escape of the hydrocarbons with the lowest boiling points, or
- analyzed frequently enough to ensure that such preferential evaporation or "weathering" does not result in changes which cause physical properties, such as octane rating or vapor pressure, to exceed the specified tolerances.

2.2. Combustion Complexity

The conditions and consequences of combusting or burning gas in the open are different from those when gasoline is burned in the cylinders of a spark-ignition motor vehicle engine.

Burning in the open is a continuous process. The surface of the liquid fuel is exposed to atmospheric oxygen. When a flame is initiated, it is maintained by

1. the continuous escape of hydrocarbon molecules from the liquid surface.
2. the heating of these molecules to their kindling temperature.
3. the reaction of these molecules with oxygen (oxidation).

Burning in an engine cylinder is an intermittent or batch combustion process which differs from an open burning process in that:

1. oxidation occurs with a specific quantity of fuel and air. Air is mixed with "atomized" fuel. This mixture is not perfectly homogenous in that the size and distribution of the liquid droplets is not completely uniform.
2. the air/fuel mixture is introduced into sealed combustion chambers which have complicated internal surfaces. The mixture is then compressed and heated before it is ignited.
3. the combustion process in each separate combustion chamber is affected by numerous variables, such as:
 - (a) the amount of change in air/fuel mixture uniformity, such as stratification which causes "top to bottom" variations in the distribution of the fuel droplets.
 - (b) the amount of compression and, hence, the amount of heating the charge experiences prior to ignition.
 - (c) the manner in which the spark-initiated flame front expands with the combustion chamber.
 - (d) the degree to which the flame is extinguished as it approaches the relatively cool walls of the combustion chamber.
 - (e) the amount of temperature and pressure rise that occurs during the combustion process.
 - (f) the degree to which the limited time available for combustion affects the completion of the process.

An essential first step in the oxidation of the gasoline hydrocarbon compounds in the combustion chamber is the introduction of the air and fuel

in the proper proportions. The appropriate ratio of air to fuel is determined by:

- the number of carbon atoms in the average fuel molecule, and
- the ratio of hydrogen to carbon atoms in the average fuel molecule.

If a fuel which has an average carbon atom chain length of six and the average hydrogen atom/carbon atom ratio of 1.86 is used, the chemically correct or "stoichiometric" air/fuel ratio is 14.5 pounds of air to 1 pound of fuel. Under perfect combustion conditions, the following results would be obtained:

$$\begin{array}{rcl}
 14.5 \text{ lb air} & = & 1.07 \text{ lb O}_2 + 2.33 \text{ lb O}_2 + 11.1 \text{ lb N}_2 \\
 \underline{1.0 \text{ lb fuel}} & = & \underline{0.13 \text{ lb H}_2} + \underline{0.87 \text{ lb C}} \\
 15.5 \text{ lb exhaust} & = & 1.20 \text{ lb H}_2\text{O} + 3.20 \text{ lb CO}_2 + 11.1 \text{ lb N}_2
 \end{array}$$

However, even when the fuel is supplied at a rate that will theoretically result in chemically correct proportions of air and fuel, optimum engine operation may not be realized. The desired results can be precluded by a number of inhibiting factors inherent in the combustion process. One of these factors is the change in the initial air/fuel ratio which occurs before the mixture is actually introduced into the combustion chamber. The composition of this final mixture depends on a number of details; such as, how well the fuel is "atomized," how well the fuel and air are mixed, and how much exhaust remains in the combustion chamber to mix with the incoming air and fuel.

A second limitation is the incomplete utilization of the fuel that does get into the combustion chamber. As a consequence of these limitations, engine operation for maximum power output may require richer (less than stoichiometric) ratios whereas operation for maximum fuel economy may require leaner (greater than stoichiometric) ratios.

A number of factors can adversely affect the combustion process even when the proportion of air to fuel is chemically correct. One of the most important of these factors is the manner in which the air and fuel are introduced into the combustion chambers. A perfect induction system would:

- combine the fuel and air in a manner resulting in a perfectly homogeneous mixture of individual hydrocarbon, oxygen, and nitrogen molecules, and
- deliver the mixture in a manner resulting in a perfect distribution between the individual combustion chambers.

Such perfection is impossible, but an actual induction system should minimize fuel droplet size, maximize the mixing of the droplets in the air, and minimize adverse effects when the mixture is distributed between the combustion chambers. Carburetor-based fuel systems present limitations to achieving this goal.

When a carburetor-based system is naturally aspirated, subatmospheric pressure is used in two different ways. The downward movement of the piston during the intake stroke results in a pressure drop in the intake system. The decrease in pressure allows atmospheric pressure to force air into the intake system via the air cleaner and the associated runner of the intake manifold. The flow of the incoming air through one or more venturi in the carburetor results in another pressure drop which allows atmospheric pressure to force fuel into the air stream in the form of fine droplets. Such use of atmospheric pressure for fuel induction places severe limitations on the reduction of fuel droplet size and on the thorough mixing of these droplets with the incoming air.

These particular limitations can be largely overcome by the use of an injector which operates at a pressure in excess of atmospheric pressure and sprays the fuel into the air stream. However, the use of such a "throttle body" injection system does not eliminate adverse distribution effects. These adverse effects can be caused by differences between the intake manifold's individual runners or branches in regard to parameters such as temperature, total length, and aerodynamic flow resistance. Such differences can result in the individual combustion chambers receiving air and fuel in somewhat different proportions. Such unequal distribution effects can be minimized by the use of a multipoint system in which a separate fuel injector is located in the intake port of each combustion chamber.

In such multipoint systems, only the incoming air flows through the throttle body and the intake manifold runners. Each individual injector is operated by an electronic control unit in a manner which tends to result in

the correct amount of fuel being delivered to the intake port of the associated engine cylinder. Some cylinder-to-cylinder differences in the air/fuel ratios can result from distribution problems which can affect the flow of the air through the runners of the intake manifold. Nevertheless, multipoint injection systems largely eliminate the distribution problems that are associated with single point injection systems and carburetted systems.

A number of engine configuration and timing details can affect the combustion process. In regard to configuration details, some of the more important factors are the locations of the spark plugs and the valves in the chamber and the locations of the rings on the piston. In regard to timing details, some of the most significant parameters are the opening and closing of the intake and exhaust valves and the firing of the spark plugs. The movement of the intake and exhaust valves relative to the movement of the piston determines the movement of the air/fuel mixture and the exhaust gas, including the reverse flow of some of the exhaust gas when an "overlap" condition results in the intake and exhaust valves being open at the same time. The timing of the spark generation determines when the ignition of the air/fuel mixture is initiated and, hence, how much time is available for the completion of the combustion process. The ignition timing therefore has an effect on a number of variables such as the maximum pressure, the mean effective pressure, and the thermal efficiency.

As a result of the unique conditions under which combustion occurs in an internal combustion engine, fuel hydrocarbon molecules which are not completely changed by the oxidation process are partially altered in various ways. Long chains can be severed and some of the resultant fragments can be rejoined to form new molecular structures. The new structures may have a greater or lesser degree of unsaturation or ring formation than the original compounds in the fuel. In addition, new compounds, such as aldehydes (see Appendix 2), can be formed. Consequently, the proportion of a particular class of hydrocarbons in the exhaust will be quite different to the proportion in the original gasoline fuel. As a result of the reactions which occur in the combustion chamber, the relative proportion of paraffinic and aromatic compounds is reduced, the relative proportion of olefinic compounds is increased, and new oxygenated organic compounds are formed.

The use of a pure hydrocarbon compound, such as isooctane, as a fuel in lieu of gasoline will reveal the effectiveness of the combustion process in promoting complex chemical reactions. When the exhaust of an engine using such a pure fuel is analyzed, hundreds of different hydrocarbon molecules can be identified. This complex variety reveals how extensively the original isooctane molecules were chemically altered during their passage through the combustion chamber.

Chapter 3. Pollutant Formation—Specific Effects

In general, concern regarding the emission of combustion pollutants is concentrated on three specific pollutants; i.e., hydrocarbons (HC), carbon monoxide (CO), and nitric oxide (NO). These three kinds of pollutants differ in regard to the cause and effect phenomena which result in their presence in the exhaust (see Table 3).

Table 3. Exhaust Pollutants.

<i>Pollutant Type</i>	<i>Cause</i>	<i>Effect</i>
HC	Flame Quenching	Absence of fuel combustion
CO	Inadequate oxygen	Incomplete fuel oxidation
NO	Excessive temperature	Nitrogen "fixation"

As Table 3 indicates, HC emissions result from portions of the air/fuel mixture being partially or completely excluded from the combustion process. The hydrocarbons in the exhaust are the residual fuel hydrocarbons which passed through the combustion chamber without the oxidation of the molecules. Some of these fuel hydrocarbons remain in their original form. Some have their molecular structures changed as a result of the replacement of hydrogen atoms by oxygen atoms or as a result of changes in the carbon chain configuration. In all cases, the carbon and hydrogen atoms remain bound in some hydrocarbon or oxygenated organic molecular structure and are not fully oxidized to carbon dioxide (CO₂) and water (H₂O).

When fuel hydrocarbon molecules completely react with the oxygen molecules during the combustion process, the carbon atoms are oxidized to carbon dioxide (CO₂) and the hydrocarbon atoms are oxidized to water vapor. However, a small fraction of the fuel molecules undergo less complete conversions and different results are obtained. The carbon atoms are only partially oxidized to carbon monoxide (CO). Instead of hydrogen atoms being oxidized, they associate with each other to form diatomic hydrogen molecules.

NO emissions are unique relative to CO and HC emissions in that NO formation is not directly related to the combustion process. The oxidation or "fixation" of the atmospheric nitrogen would occur without the presence of any hydrocarbon fuel. At the high temperatures which occur in the combustion chamber, a fraction of the atmospheric nitrogen and oxygen

molecules react to form NO molecules which are subsequently converted to other nitrogen oxides, such as nitrogen dioxide (NO₂).

Details regarding the three phenomena causing each of these conditions are presented in the following sections.

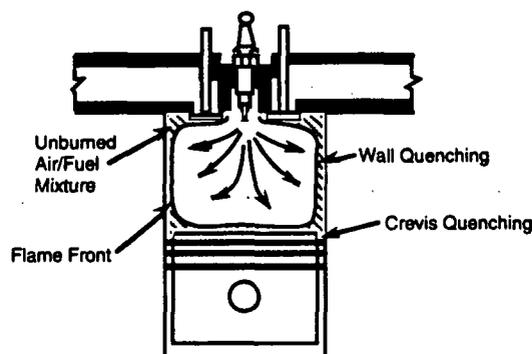
3.1. Effect of Flame Quenching on HC Emissions

When a gasoline-fueled spark-ignition engine operates under favorable conditions; i.e., close to a stoichiometric air/fuel ratio and with an absence of malfunctions such as ignition misfire, the primary source of hydrocarbons in the exhaust is the fuel molecules which were not adequately involved in the combustion process. Some of these molecules may have undergone some structural changes, such as a reduction in carbon-chain length or a replacement of some of the hydrogen atoms by oxygen atoms. The remainder of the uninvolved molecules will have passed unchanged through the combustion chamber as a consequence of being isolated from the combustion process as a result of "flame quenching."

When a flame in the combustion chamber is initiated at the spark plug, it expands very rapidly in all directions. However, quenching, or extinction, due to heat transfer can occur at the boundaries of the expanding "ball" of flame.

Wall quenching occurs when the flame front approaches the physical boundaries of the combustion chamber where a sharp drop in temperature occurs (see Figure 5). The fuel in close contact with these boundaries has a lower temperature as a result of its proximity to the cooler metal surfaces. When the temperature is too low to support combustion, the flame is quenched.

Figure 5. Flame Quenching.



Restriction, or crevice, quenching occurs when the flame front reaches a restriction which impedes further propagation. Typically, the flame encounters such a restriction when it reaches any very small volume in the combustion chamber. One such flame quenching volume is the cavity that is formed by (a) the upper surface of the topmost piston ring, (b) the outside diameter of the piston, and (c) the inside diameter of the cylinder (see Figure 5).

Regardless of the cause, when the flame is quenched, the fuel in the volume beyond the boundary where quenching occurs is more or less isolated from the combustion process. One fraction of this isolated fuel leaves the combustion chamber essentially in its original unaltered state. Another fraction leaves in an altered state, as a result of low temperature preflame reactions in the quenched zones. These altered molecules appear in the exhaust in form of aldehydes and other partially oxidized compounds (see Appendix 2. Oxygenated Organic Compounds.).

3.2. Effect of Oxygen Content on CO Formation

As was previously mentioned, some fuel hydrocarbon molecules do not completely react with oxygen molecules during the combustion process and the carbon atoms are only partially oxidized to carbon monoxide. The likelihood of such results occurring decreases as the availability of oxygen increases. However, even when relative proportions of oxygen and fuel molecules are considerably in excess of the stoichiometric, or "chemically correct" proportion, a very small fraction of the fuel carbon atoms are still only partially oxidized to carbon monoxide molecules.

3.3. Effect of Temperature on NO Formation

Unlike HC and CO emissions, NO emissions do not arise as a consequence of the incomplete oxidation of the fuel. NO emissions result from a side reaction that occurs under the unique conditions produced in the combustion chamber when the fuel is oxidized. These conditions are quite different than those that prevail when gasoline is burned in the open.

During open burning conditions, the nitrogen molecules in the air are not affected by the combustion process and atmospheric nitrogen acts as a non-reactive diluent. However, when gasoline is burned in the cylinders of an internal combustion engine, the high temperatures and pressures that are

produced cause some "fixing" of atmospheric nitrogen. A small percentage of the nitrogen molecules are "fixed" when they combine with oxygen in the combustion chamber. The primary immediate reaction product is nitric oxide (NO) which can undergo conversion into other oxides, such as nitrogen dioxide (NO₂), during transit through the exhaust system or during subsequent dispersion into the atmosphere.

Chapter 4. Pollutant Control Approaches

Two general approaches for minimizing the emission of pollutants from the tailpipe of a motor vehicle may be taken:

- the *preventive* approach which involves the modification of the combustion conditions to minimize the formation of pollutants in the combustion chamber, and
- the *remedial* approach which involves the treatment of the exhaust gas to minimize the concentrations of the pollutants which exit the combustion chamber.

Each approach uses a variety of techniques. This chapter discusses each of these techniques and the possible interactions and complications of these techniques.

4.1. Preventive Techniques

The three specific preventive techniques are

- changes in engine design (combustion chamber redesign),
- changes in engine operation (fuel flow controls), and
- changes in combustion conditions (temperature reduction).

These techniques will affect hydrocarbon, carbon monoxide, and nitric oxide emissions, respectively.

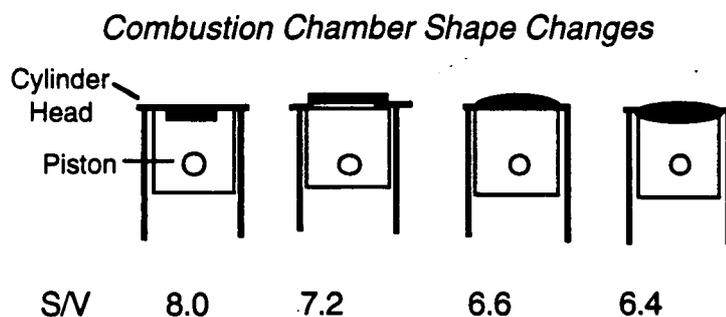
4.1.1. Combustion Chamber Redesign for HC Minimization

Flame quenching results in some fuel hydrocarbon molecules exiting unaltered, or partially altered, from the combustion chamber (see Chapter 3). Combustion chamber redesigns can minimize the effects of this phenomenon. Quenching due to wall effects can be reduced by design changes that reduce the surface area of the combustion chamber relative to the clearance volume (piston is at top dead center). Combustion chamber design changes that can be implemented to accomplish the desired decrease in the surface to volume (s/v) ratio include:

- reducing depressions and protrusions in the chamber.
- changing the nature of the surfaces that provide the clearance volume (see Figure 6).
- making the cylinder geometry more favorable.

Restriction quenching can be reduced by any chamber redesign which eliminates or reduces any small volume that impedes the propagation of the flame front. For example, if the topmost piston ring is moved up toward the end of the piston (see Figure 1), a volume reduction is realized in the annular cavity which is formed around the top of the piston. Consequently, the amount of fuel which is isolated from the oxidation process is reduced.

Figure 6. Surface/Volume Ratio Changes.



4.1.2. Fuel Control for CO Minimization

As was mentioned in section "3.2. Effect of Oxygen Content on CO Formation," an increase in the availability of oxygen tends to decrease the number of fuel carbon atoms that are only partially oxidized to carbon monoxide. Such increase in oxygen availability can be accomplished by reducing fuel input to increase the air-fuel ratio beyond the stoichiometric ratio so that combustion occurs under lean conditions.

However, such a lean approach to minimization of carbon monoxide formation is limited by several possible undesirable side effects, such as rough engine operation, increased nitrogen oxide formation, and adverse effects on downstream exhaust aftertreatment devices. Moreover, beyond a specific ultimate limit in lean operation, the proportion of fuel molecules to oxygen molecules becomes too low for efficient combustion. At that point, the mixture of air and fuel fails to ignite and "lean misfire" occurs.

4.1.3. Temperature Control for NO Minimization (Exhaust Gas Recirculation)

Fixing atmospheric nitrogen within the combustion chamber can be inhibited by any mechanism that reduces the maximum temperature developed during the combustion process. As was previously mentioned, one means for accomplishing the necessary temperature reduction is

retarding the spark. This change reduces the maximum temperature by shortening the time available for the completion of the combustion process. However, retarding ignition has disadvantages, such as the loss of power output that results from the reduction in the maximum pressure in the cylinder.

A more satisfactory means of lowering the maximum combustion temperature is to increase the heat capacity of the gases in the combustion chamber by diluting the new charge of air/fuel mixture with a gas that does not take part in the combustion process. The exhaust gas is ideally suited for this purpose because:

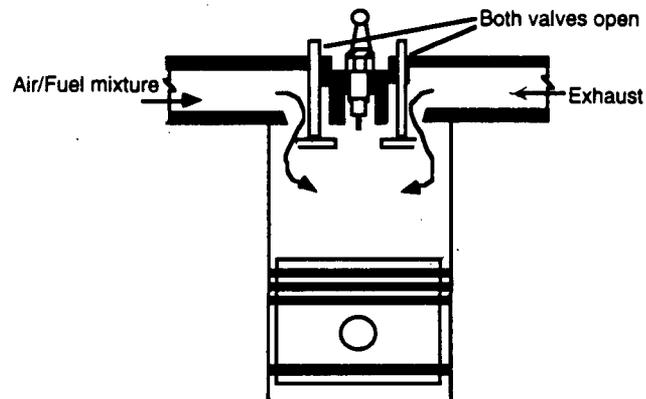
- it is readily available and can be easily recirculated back into the combustion chamber.
- it has a high concentration of carbon dioxide and water molecules which have higher heat absorption capacities than the molecules of a diatomic gas, such as atmospheric nitrogen.

Some dilution of the new mixture charge by exhaust gas is inherent in the four-stroke combustion cycle. At the completion of the exhaust stroke, some of the exhaust gas, which is at a pressure in excess of atmospheric pressure, is left behind in the clearance volume which remains when the piston is top dead center. When the intake valve opens at the start of the intake stroke and exposes the cylinder to the subatmospheric pressure in the intake system, pressure equalization occurs. As a result, a fraction of the residual exhaust backflows through the open intake valve and mixes with, and dilutes, the entering new charge of air/fuel mixture. Further dilution of the mixture is caused by the fraction of the exhaust which did not back flow out through the intake valve and remained in the cylinder.

Such inherent dilution is considerably enhanced when there is a "valve overlap" condition in which the exhaust valve is still open when the intake valve opens (see Figure 7). The reduction in cylinder pressure which results from the downward movement of the piston during the intake stroke results in a fraction of the exhaust gas which was forced out of the combustion chamber into the exhaust port during the exhaust stroke reentering the cylinder via the open exhaust valve. The primary purpose of such valve overlap is to produce the desired engine performance characteristics. Nevertheless, the resultant recirculation of exhaust gas results

in some reduction in the maximum combustion temperature and, hence, some reduction in NO formation.

Figure 7. Internal Exhaust Gas Recirculation (Valve Overlap).



When such inherent exhaust gas recirculation does not provide the desired reduction in NO formation, additional exhaust gas flow must be provided by means of some routing external to the combustion chamber. Such an "add-on" exhaust gas recirculation (EGR) emission control system can consist of (a) a connecting passageway between the intake and exhaust manifolds of the engine and (b) a valve which controls the flow of exhaust gas through the passageway (see Figure 8). The EGR system control mechanism is designed to open and close the valve as needed to minimize the formation of NO while also minimizing any undesirable effects on performance characteristics, such as a poor idle quality or reduced performance during wide open throttle acceleration.

4.2. Remedial Techniques

Two techniques are used remedially to remove pollutants which exit the combustion chamber:

- thermal oxidation in the exhaust manifold
- catalytic conversion in the exhaust stream

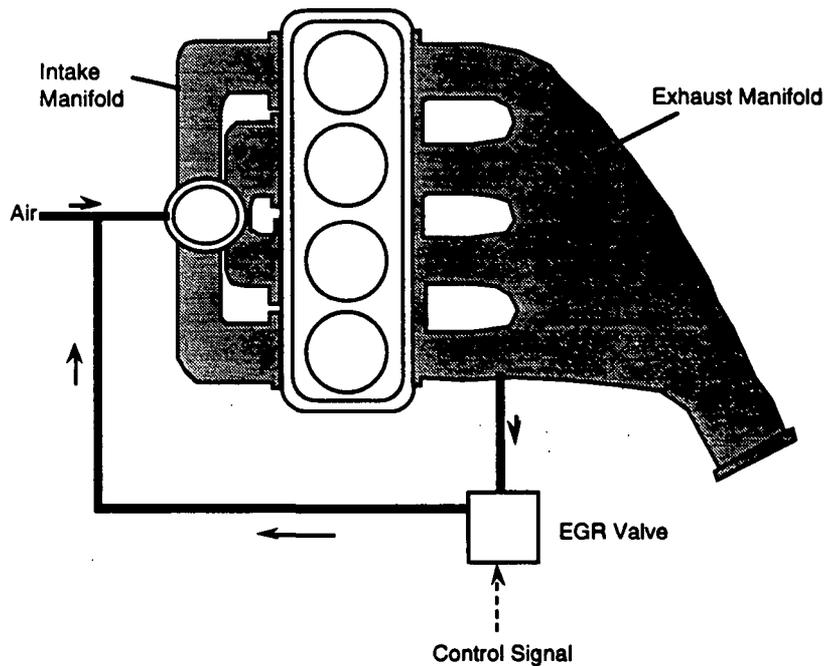
The first of these techniques uses supplemental air to oxidize HC and CO pollutants. The second oxidizes HC and CO and reduces NO pollutants.

4.2.1. Supplementary Air Oxidation

As discussed previously under preventive techniques, operating an engine under very lean conditions can reduce CO but a number of factors

preclude such operation. However, atmospheric oxygen can be added to the exhaust stream after the exhaust gases leave the combustion chamber. Such oxygen enrichment facilitates the continuation of the oxidation reactions that were initiated in the combustion chamber. The secondary air is injected directly into the exhaust ports of the cylinders. The carbon monoxide and hydrocarbons in the very hot exhaust gases are thermally oxidized without the production of a visible flame. One side benefit of such secondary air injection during cold starting is that the increase in exhaust gas temperature occurring as a result of the oxidation reactions reduces the time required for the downstream catalytic converter to reach the temperature necessary for efficient oxidation conversion.

Figure 8. External Exhaust Gas Recirculation.

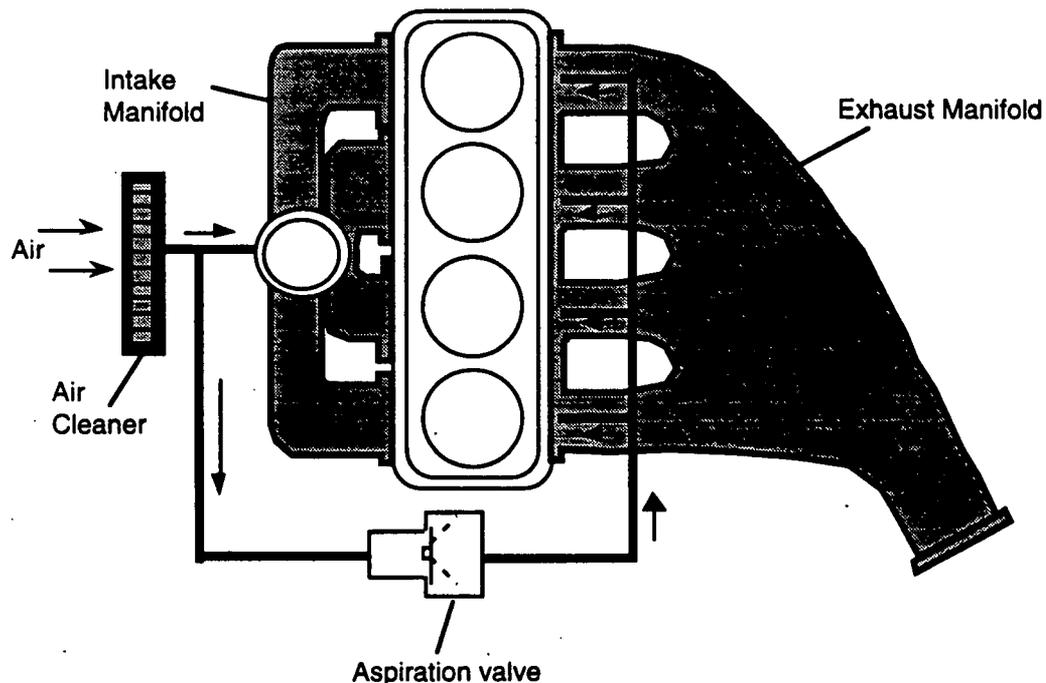


Depending on the purpose for the introduction of additional air into the system, negative or positive pressures (below or above atmospheric pressure) can be used to provide the necessary differential pressure. For example, a negative pressure system can be used when the purpose of secondary air introduction is to reduce emissions during idle operation, particularly when a cold engine is started and is warming up. During such engine operation, the concentration of oxygen in the exhaust manifold is too low to effectively oxidize the CO and HC in the exhaust gas. The necessary additional oxygen can be introduced by means of a simple aspiration system

which takes advantage of the negative pressure pulses in the exhaust manifold.

In the simplest form of such a system, the necessary air flow control functions are performed by a one-way aspirator valve located in a line connecting the exhaust port air injection tubes with an inlet for atmospheric air, usually in the air cleaner (see Figure 9). The aspirator valve allows the entrance of atmospheric air, but prevents the escape of exhaust gas. When the engine is idling and a large negative (below atmospheric) pressure pulse is produced at an exhaust port as the result of the opening of the associated exhaust valve, the higher atmospheric pressure forces the aspirator valve open. Atmospheric air flows into the system and exits at the exhaust port via the air injection tube. As soon as the exhaust valve closes and the pressure at the exhaust port rises above atmospheric pressure, the higher pressure closes the aspirator valve and the escape of exhaust gases into the atmosphere is prevented.

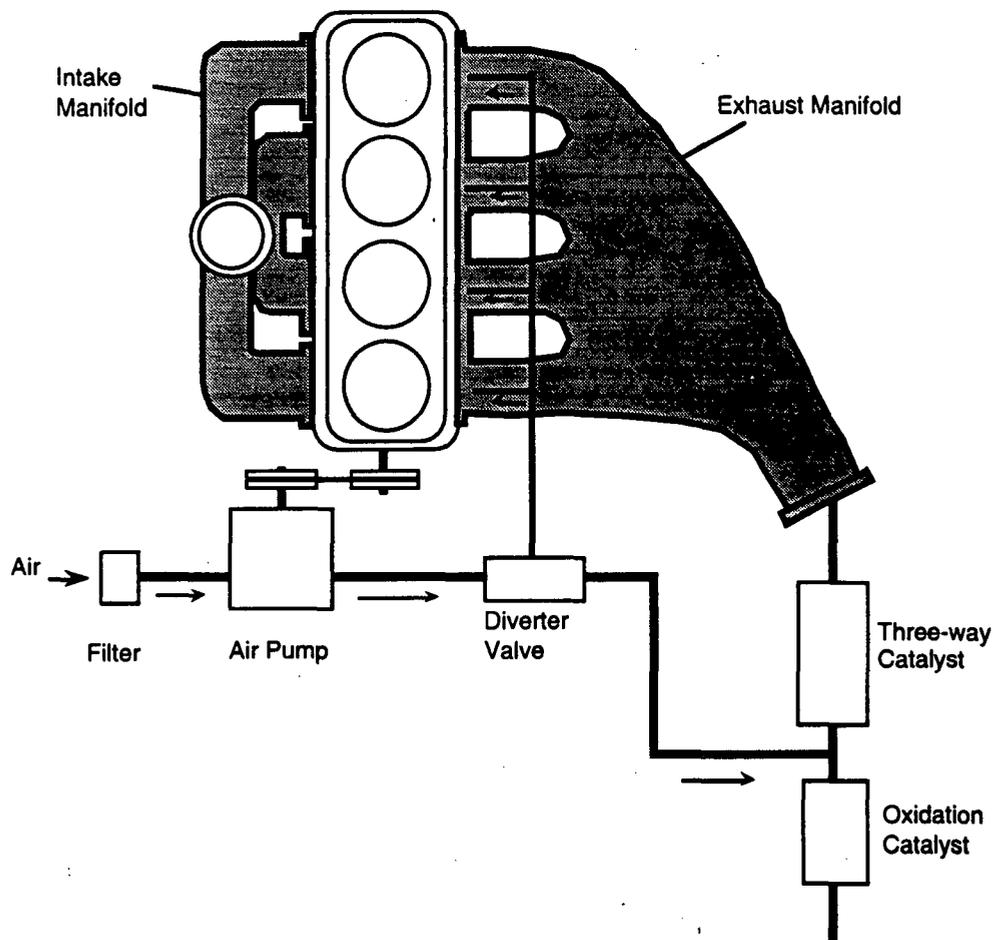
Figure 9. Aspirated Air Injection.



In some systems, secondary air is injected into the exhaust ports to promote thermal oxidation reactions and into the exhaust system, downstream of a three-way catalyst but upstream of an oxidation catalyst, to promote catalytic oxidation reactions. In such systems a positive pressure

system must be used. The required higher than atmospheric pressures are provided by an engine-driven mechanical air pump (see Figure 10). When the engine warmup process has been completed, the output of the pump is switched from the exhaust manifold to the injection point in the exhaust system upstream of the oxidation catalyst. The added air ensures that sufficient oxygen is in the converter for the required conversion efficiency.

Figure 10. Forced Air Injection.



4.2.2. Catalytic Conversion

Another aftertreatment of the exhaust gases, catalytic conversion, involves promoting chemical reactions which involve the CO, HC, and NO emissions. These polluting forms of carbon and nitrogen are then changed into non-polluting forms. The use of such exhaust aftertreatment as a remedial pollution control is made possible by catalytic converters which have the required performance characteristics. Such converters must be able to selectively promote the chemical reactions producing the desired results

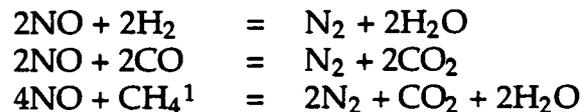
and to suppress other possible competitive reactions which either lower effectiveness or yield undesirable by-products.

Chemical Reactions—The carbon atoms in the combustion gases are in a polluting form when they exist in CO and HC molecules. If sufficient oxygen is present, passage through a "two-way" oxidation catalytic converter will result in a significant fraction of the CO molecules being oxidized to CO₂ molecules and the HC molecules being oxidized to CO₂ and water (H₂O) molecules .

The nitrogen atoms in the combustion gases are in a polluting form when they exist as nitric oxide (NO) molecules. When sufficient reducing agents are present, passage through a reducing catalyst will result in a significant fraction of the nitric oxide molecules being reduced to atmospheric diatomic nitrogen molecules (N₂).

The desired reactions, the oxidation of CO and HC and the reduction of NO, can occur more or less simultaneously when the exhaust gas is passed through a "three-way" oxidizing/reducing converter if the upstream composition of the exhaust is appropriately controlled. Such control of exhaust gas composition is necessary because the reduction of the NO to diatomic nitrogen (N₂) is somewhat more complex than the oxidation of CO and HC to CO₂ and H₂O.

In the oxidation conversions, new molecules are formed when their precursor "raw material" component parts combine with each other. However, the reverse does not occur in connection with the NO reduction. The process is not as simple as the breakup of the NO molecules with the release of both the nitrogen and oxygen atoms back to the atmosphere. The reduction of NO depends on the interaction of NO with other exhaust reducing components in various reactions, such as the following:



In connection with the above reactions, the following facts are worth noting:

¹ Where the methane molecule, CH₄, represents all possible HC molecules.

- all of the NO reduction conversions depend on the presence of reducing agents, such as H₂, CO, and HC.
- the last two reactions result in the elimination of all three pollutants, NO, CO, and HC.

System Requirements—The actual hardware that can be used to accomplish the desired conversion reactions depends on the requirements of a particular system. For example:

- if NO emissions are not a problem, a two-way oxidizing converter can be used to oxidize CO and HC,
- when NO emissions are a problem, a three-way catalyst can be used to simultaneously reduce NO and oxidize CO and HC, or
- if a three-way catalyst alone does not adequately lower the concentrations of CO and HC, a downstream oxidizing catalyst (see Figure 10) can be added to further lower the concentrations of these pollutants.²

The performance of catalytic converters is affected by the chemical composition of the exhaust. In the case of oxidizing converters, the relationship between composition and performance is fairly straight-forward. When the oxygen concentration falls to a level which inhibits the oxidation of CO and HC, performance is degraded.

In regard to three-way converter operation, the relationship between composition and performance is more complex. Such a converter will yield the desired results only when the concentrations of all of the several reactants remain within a limited range. For example, if the concentration of oxygen remains too low relative to the concentrations of CO and HC (as a result of continuous engine operation under rich conditions), adequate oxidation conversion of these pollutants will not be possible. Similarly, if the concentrations of reducing agents, such as CO and HC, remain too low relative to the concentration of NO (as a result of continuous engine operation under lean conditions), adequate reduction conversion of NO will not be possible. The solution to the problem which results from these conflicting requirements is to rapidly oscillate the exhaust composition between slightly

² The three-way catalyst and the oxidizing catalyst can be housed in one container or they can be housed in two separate containers. If necessary, air can be injected upstream of the oxidizing catalyst to ensure an adequate concentration of oxygen in the oxidizing catalyst.

lean (slight excess of oxygen) and slightly rich (slight excess of reducing agents) conditions.

Since exhaust composition depends on the composition of the ingested mixture or the air/fuel ratio, the possibility exists of using exhaust gas composition information to regulate fuel introduction. Regulating fuel introduction can then maintain the air/fuel ratio within the range that maximizes engine and converter performance. The operation of such a closed loop "feedback" fuel control system involves:

1. generating some output signal that is dependent on the exhaust gas composition.
2. detecting any change in that signal indicating that the air/fuel ratio needs to be adjusted.
3. adjusting the fuel flow rate to result in the desired air/fuel ratio.

The successful operation of such a system is dependent on its ability to make effective use of the small changes in exhaust composition which occur when air/fuel ratio deviations are held within the desirable narrow tolerance band.

The concentrations of all of the exhaust components, such as HC, CO, NO_x, and O₂, undergo very gradual changes when the air/fuel ratio varies over a very wide range. This effect is illustrated in the following table of typical oxygen (O₂) and carbon monoxide (CO) concentrations when the stoichiometric (chemically correct) ratio for a specific fuel is 14.7.

Table 4. O₂ & CO Concentration by Air/Fuel Ratio.

<i>Air/Fuel Ratio</i> <i>(Lbs. air/lb. fuel)</i>	<i>O₂</i> <i>(Volume %)</i>	<i>CO</i> <i>(Volume %)</i>
13.9 (very rich)	0.3	1.4
14.6 (rich)	0.5	0.4
14.7 (stoichiometric)	0.6	0.3
14.8 (lean)	0.7	0.2
15.3 (very lean)	1.2	0.1

As this table indicates:

- the changes in O₂ and CO concentrations are very gradual when the air/fuel ratio varies over a wide range from very rich (excess fuel) to very lean (excess air) or vice versa.
- the changes in O₂ and CO concentrations are very slight when the air/fuel ratio deviates slightly from the stoichiometric ratio.

- when the air/fuel ratio is very rich (13.9), the concentration of O₂ is still about one half of the O₂ concentration when the air/fuel ratio is stoichiometric.
- when the air/fuel ratio is very lean (15.3), the CO concentration is still about one third of the CO concentration when the air/fuel ratio is stoichiometric.

A fuel control system that is dependent on such small changes in the concentration of a particular exhaust gas component would have to meet or exceed very demanding performance criteria in regard to:

- the amount of air/fuel ratio deviation occurring before the need for a change in fuel flow rate is indicated, and
- the time delay between the fuel flow rate change and the elimination of the excessive air/fuel ratio deviation.

Such system requirements would be much more demanding under the non-steady state conditions that typify the operation of motor vehicle engines. During the operation of such engines, fuel flow requirements are greatly complicated by the numerous and rapid changes in engine speed and load that occur.

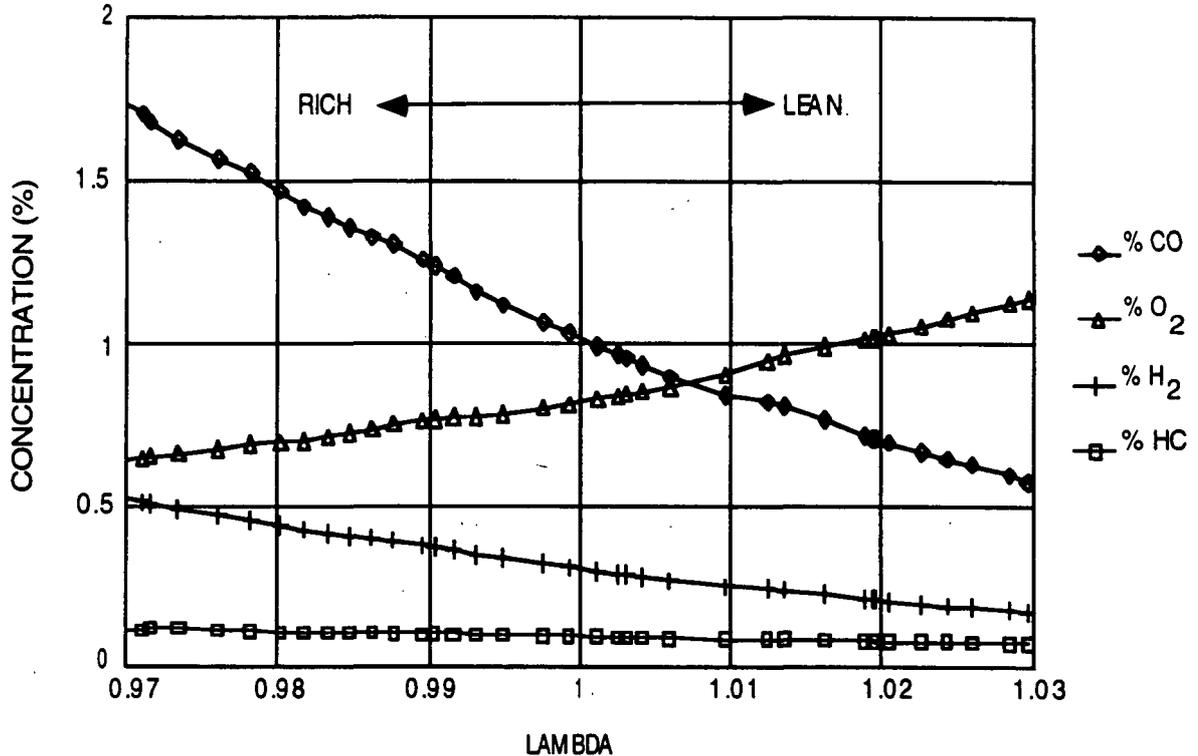
A more promising approach is to make use of the relative changes in the exhaust gas components. As Figure 11 shows, the concentration of oxygen decreases and the concentrations of reducing agents, such as hydrogen and CO, increase as the composition of the exhaust changes from slightly lean to slightly rich. The exhaust gas parameter which would have to be monitored would be the shift in the lambda of the exhaust, from rich ($\lambda < 1$) to lean ($\lambda > 1$), or vice versa, relative to the stoichiometric value.³

Closed Loop Fuel Control System—Such a "stoichiometric shift" approach to exhaust composition control is utilized in the closed loop fuel control system that is pictured in Figure 12. As is shown, the lambda sensor is installed upstream of the three-way catalyst to provide a signal which is used by the electronic control module (ECM). Depending on the "feedback" signal which is generated by the lambda sensor, the ECM makes the changes in the fuel flow

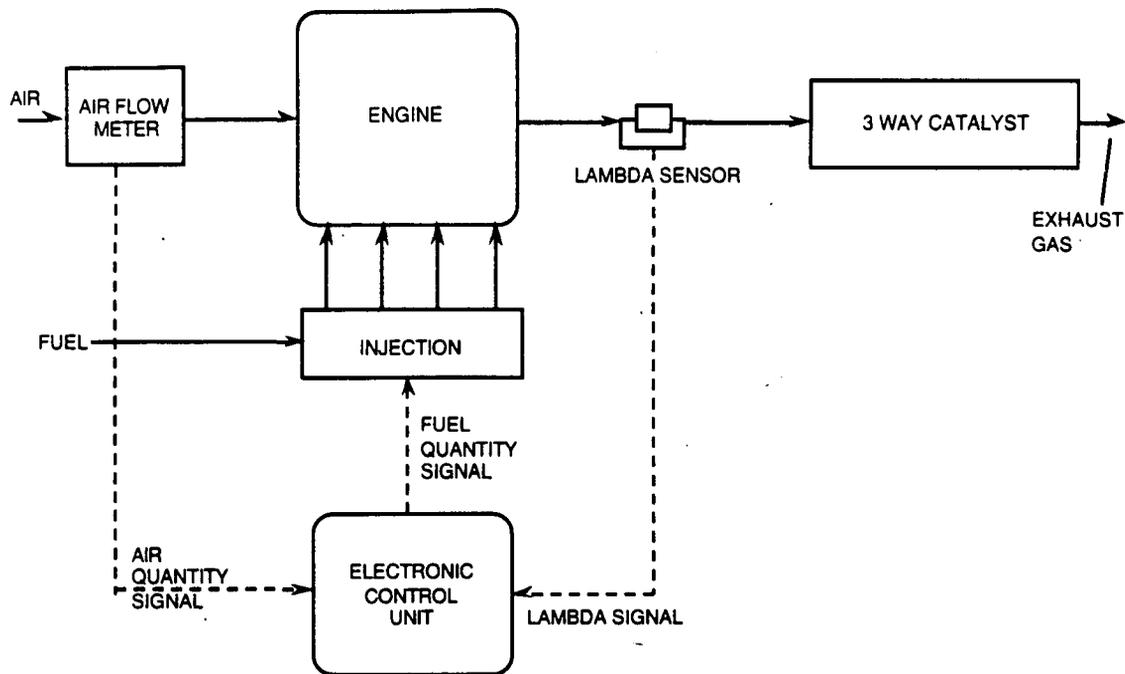
³ A "lambda" value indicates how the actual proportions of oxygen and reducing agents in an exhaust gas mixture compare with the chemically correct or stoichiometric proportions that would be necessary for the complete reaction of the oxygen with the reducing agents. Lambda is less than one when the exhaust composition is less than stoichiometric (rich conditions with excessive reducing agents) and more than one when the exhaust composition is greater than stoichiometric (lean conditions with excessive oxygen).

rate necessary to keep the exhaust composition close to stoichiometric. The control "loop" is "closed" when the sensor reacts to the change in exhaust gas composition resulting from the change in the fuel flow rate.

Figure 11. Exhaust Composition.



The detecting element of the lambda sensor is a tetravalent zirconium oxide (ZrO_4) ceramic thimble. This thimble is installed in the exhaust pipe so that the interior of the thimble is in contact with the outside atmosphere and the exterior is exposed to the exhaust gases. The zirconium oxide thimble is impermeable to atmospheric oxygen or any gas which is in atomic or molecular form. However, a very small amount of a lower valent oxide, such as the trivalent yttrium oxide (Y_2O_3), is dispersed in the zirconium oxide. The yttrium oxide provides anion vacancies which allow oxygen ions (with two negative charges) to diffuse through the walls of the thimble. Portions of the interior and exterior of the thimble are covered with porous platinum coatings which function as conductive electrodes and as catalyzing surfaces.

Figure 12. Closed Loop Fuel Flow Control System.

In this application, the lambda sensor functions as a voltaic cell which generates a signal voltage. This voltage is generated when the oxygen which migrates through the sensor thimble reacts with reducing agents, primarily hydrogen and carbon monoxide, in the exhaust. When the air/fuel mixture ingested by the engine is lean, the exhaust contains more oxygen than necessary for reaction with the reducing agents present. Under these conditions, very little opportunity exists for the reaction of the reducing agents with the oxygen migrating through the sensor thimble and the output voltage remains at about 0.1 volt.

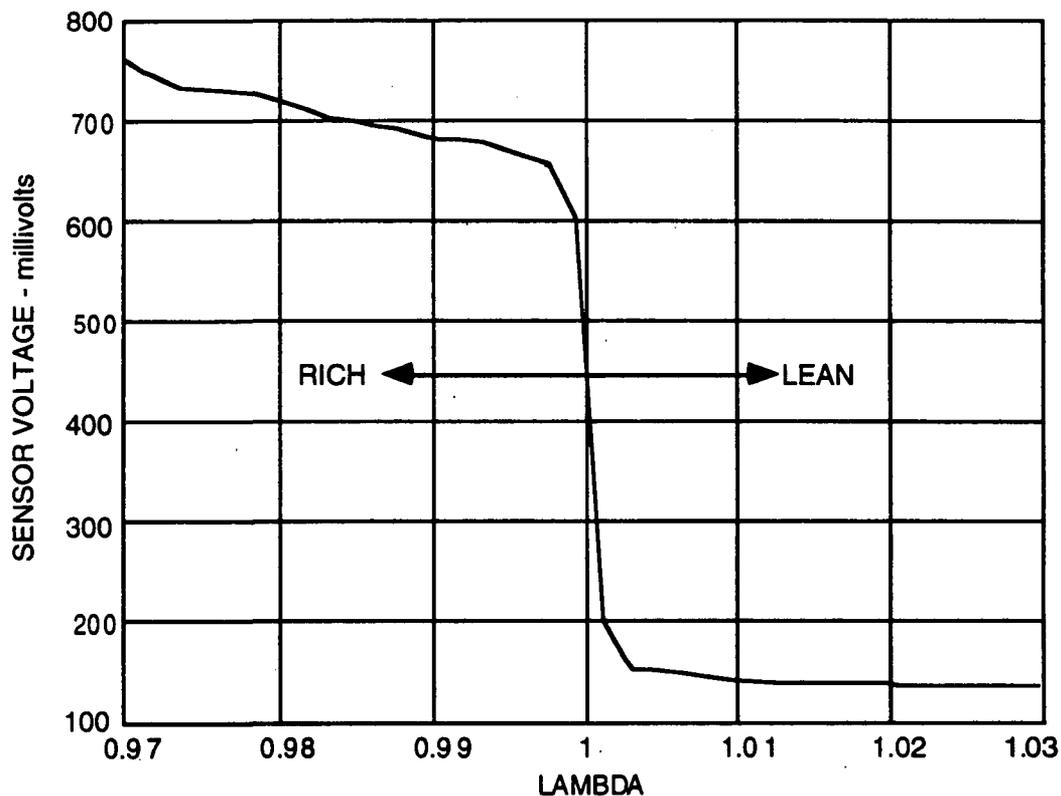
When the air/fuel mixture is rich, the exhaust contains less oxygen than needed for the reaction with the reducing agents. Under these conditions, the reducing agents can react with oxygen which migrates through the sensor thimble and a voltage potential of about 0.9 volts is developed. The switch-like operation of the lambda sensor is illustrated in Figure 13.

In the closed loop fuel flow control system shown in Figure 12, the air/fuel ratio continuously oscillates between conditions that are slightly rich or lean relative to the stoichiometric value. By optimizing the system, both the magnitude of the deviations of the air/fuel ratio from the stoichiometric

value and the duration of the deviations can be reduced. Such optimization reduces HC and CO tailpipe emissions by

- reducing the emission of the pollutants from the individual combustion chambers as a result of the operation of the engine with an air/fuel ratio close to stoichiometric, and
- reducing the concentrations of the pollutants in the exhaust stream as a result of the operation of the catalytic converter at the maximum effectiveness which results when the concentrations of oxygen and reducing agents in the exhaust are held close to their stoichiometric values.

Figure 13. Lambda Sensor Operation.



4.3. Interaction Complications

The application of the preceding control techniques is greatly complicated by the complex interactions that these techniques have on each other. The use of one technique to accomplish a specific change, such as the reduction of one type of pollutant, may result in another change which produces an undesirable effect. For example, a change in engine operating conditions which reduces the formation of one type of pollutant can increase

the formation of another type of pollutant. The change in engine operation may also have other undesirable affects, such a degradation of performance, an increase in fuel consumption, or an exhaust temperature decrease which may have an adverse effect on a downstream aftertreatment device.

This tendency of an engine operating change to simultaneously produce desirable and undesirable results is particularly troublesome in regard to the hydrocarbons and nitric oxides in the exhaust. This dilemma results from the fact that an increase in combustion efficiency tends to decrease exhaust hydrocarbons but increase exhaust nitric oxides. The increase in combustion efficiency results in a more complete oxidation of the fuel and, hence, a decrease in exhaust hydrocarbons. However, the increase in combustion efficiency results in an increase in the maximum temperature in the combustion chamber and, hence, an increase in exhaust nitric oxide as a consequence of the increase in the fixation of atmospheric nitrogen. Changes which decrease combustion efficiency and, hence, decrease nitric oxide formation, such as rich engine operation (excess fuel) and spark retardation, tend to increase the concentration of hydrocarbons in the exhaust and decrease engine efficiency and fuel economy. In these situations, a compromise is made to provide a balance between positive and negative effects.

Appendixes

Appendix 1.

Comparison of Four-Stroke

Spark-ignition and Compression-ignition Engines

Four-stroke spark-ignition and compression-ignition engines are similar in that they:

- use an intermittent internal combustion process in which the high pressure combustion gases are directly used as the working fluid. (External combustion engines, such as steam engines, use a continuous combustion process to heat a separate working fluid.),
- burn liquid hydrocarbon fuels,
- incorporate reciprocating pistons, and
- use four piston strokes to complete each combustion cycle.

However, these two types of engines differ in regard to:

- the means by which engine speed and power output are controlled,
- the physical properties and combustion characteristics of the required fuels,
- the manner in which the fuel is introduced into the combustion chamber,
- the technique which is used to initiate the combustion process, and
- the mechanisms which result in the formation of combustion pollutants.

The significance of these differences between the two types of engines are briefly discussed in the following paragraphs. This discussion excludes engines which use superchargers or turbochargers to blow air into the engine intake systems. Furthermore, the discussion excludes two-stroke cycle engines. At the present time, two-stroke, gasoline-fueled, spark-ignition engines are not used to power light-duty motor vehicles and only one engine manufacturer produces two-stroke, diesel-fueled, compression ignition engines for use in heavy-duty vehicles.

Speed and Power Output Control

In spark-ignition engines, *air flow* is the primary control parameter. The accelerator is connected to a throttle valve which regulates the rate at which atmospheric air enters the intake system. Prior to the flow of the air into each combustion chamber, fuel is added in an amount resulting in an

air/fuel mixture which will produce the desired engine speed and power output.

In compression-ignition engines, *fuel flow* is the primary control parameter. The accelerator is connected to fuel injectors which inject into each combustion chamber subsequent to the ingestion of the intake air, the amount of fuel needed for the desired engine speed and load. The entrance of atmospheric air into the engine intake system is uncontrolled. Consequently, when the engine is not operating at maximum speed and power output, the amount of air ingested is in excess of that needed for the complete combustion of the fuel.

Fuel Properties

In spark-ignition engines, the required gasoline fuels are comprised of complex mixtures of hydrocarbon compounds. These mixtures have distillation ranges of about 75 to 415°F. The majority of the hydrocarbon molecules in these mixtures have carbon atom numbers that range from six to twelve in number.

The preignition ("detonation") or knocking tendency of a gasoline fuel is indicated by an octane number. In this rating system, normal heptane (C₇) has an octane number of 0 and isooctane (C₈) (2,2,4-trimethyl pentane) has an octane number of 100. An octane number close to 90 is normally adequate for an engine which does not require a premium grade fuel.

In compression-ignition engines, the required diesel fuels are comprised of mixtures of hydrocarbons with distillation ranges of about 340 to about 660°F. The majority of the hydrocarbon molecules have carbon atom numbers that range from about C₁₄ to C₁₈.

The spontaneous ignition characteristic of a diesel fuel is indicated by its cetane number. In this rating system, heptane (C₇) has a cetane number of 57 and hexadecane, or "cetane" (C₁₆), has a cetane number of 100. A cetane number in the 40 to 50 range is usually adequate.

Fuel Introduction

In spark-ignition engines, "atomized" fuel in the form of minute droplets is added to the incoming air by means of a carburetor or one or more low pressure injectors. Atmospheric pressure forces the resulting mixture

into each combustion chamber during the intake stroke of the cycle. The *mixture* is subsequently compressed during the compression stroke.

In compression-ignition engines, fuel is injected into each combustion chamber (or prechamber) after the *air* has been ingested during the intake stroke of the cycle and then compressed during the compression stroke. The fuel is introduced into the chamber in the form of a spray of very small droplets. This spray results from the use of injectors, operating at pressures of several thousands of pounds per square inch, to force the fuel through very small openings in the injector tips.

Combustion Initiation

In spark-ignition engines, the ingested air/fuel mixture undergoes a compression of about 8 to 1 during the compression stroke of the cycle. As a consequence, pressures of 120 to 400 pounds per square inch and temperatures of around 900 °F are developed in the combustion chambers. The increase in temperature is not great enough to cause the spontaneous ignition of the fuel. Therefore, the combustion of the air/fuel mixture is initiated by means of an electric spark generated between the electrodes of one or more spark plugs. The flame then expands to fill the combustion chamber as the fuel in the mixture is progressively oxidized.

In compression-ignition engines, the ingested air undergoes a compression of about 15 to 1. As a consequence, the pressure of the air is increased to about 400 to 800 pounds per square inch and its temperature is increased to about 1400°F. At such elevated air temperatures, the fuel undergoes spontaneous ignition almost as soon as it emerges from the holes in the injector tips.

Pollutant Formation

In spark-ignition engines, pollutant formation problems include (a) the fuel wetting of the walls of the intake system, (b) the introduction of rich mixtures into the combustion chamber, and (c) the quenching of the flame after it is initiated. Two different phases of the combustion process can affect pollutant formation. The first phase is the premixing of the fuel and air prior to ingestion into the combustion chamber. The second phase is the burning of the mixture within this enclosed chamber.

The premixing phase can result in the subsequent formation of one or more pollutants as a consequence of: (a) the air/fuel ratio of the mixture entering the chamber deviates from the ratio needed for complete combustion, (b) a localized deviation occurs in part of the mixture, or (c) deviations occur between cylinders. These three phenomena are discussed further in the following paragraphs.

The air/fuel ratio of the mixture entering the engine may deviate from the ratio that is necessary for the maximum combustion of the fuel. In the most extreme case, combustion may not occur because the mixture is either too rich (excessive fuel) or too lean (excessive air) to burn, and raw fuel is emitted from the exhaust system. If the mixture is burnable but on the rich side, the combustion of the fuel will be decreased and CO emissions will be increased. If the mixture is burnable but on the lean side, NO emissions may be increased.

The mixture that actually enters the combustion chamber may not be homogeneous in that it varies in regard to the size and/or the distribution of the fuel droplets. Such a lack of homogeneity may result in localized rich or lean zones that have different combustion characteristics.

Some of the fuel droplets may separate out of the mixture as a result of being deposited on and "wetting" the interior surfaces of the intake system. In carburetted or single point injection systems, wetting can occur in the individual runners of the intake manifold. In multipoint injection systems, wetting can occur at the intake port of each cylinder. Such deposition of liquid fuel can result in mixtures with differing air/fuel ratios being delivered to the several cylinders in the engine. The extent of such wetting depends on a number of variables, one of the most important being the temperature of the intake system interior surfaces. When the amount of fuel being deposited is increasing, the mixture entering the combustion chamber will tend to be lean. When the amount of deposited fuel is decreasing, the mixture entering the combustion chamber will tend to be rich. These changes in composition will tend to lead to the formation of the emissions that are associated with each condition.

During the second phase, or burning of the mixture, undesirable quenching phenomena can result in the emission of unburned fuel. The

expanding ball of flame can be quenched, or extinguished, as a result of the approach of the flame front to the relatively cool walls of the combustion chamber or a restriction which impedes further propagation. In either case, the quenching of the flame results in the emission of unburned fuel from the combustion chamber.

In compression-ignition engines, the problems of the spark-ignition engine are avoided by the direct injection of the fuel into a volume of high temperature air and the resultant spontaneous ignition of the fuel. Consequently, compression-ignition engines are less subject to HC and CO emission formation than spark-ignition engines. However, the compression-ignition combustion process involves phenomena which can result in the formation of NO and/or smoke emissions.

In both spark-ignition and compression-ignition engines, NO formation is quite different than HC and CO formation in that NO is not a by-product of fuel combustion. In internal combustion engines, NO formation is a result of the "fixation" of atmospheric nitrogen. In open type burning atmospheric nitrogen acts as an unreactive diluent gas. However, the high temperatures and pressures that are developed in the cylinders of the spark-ignition, and to a greater degree in the cylinders of compression-ignition engines, result in the oxidation of the atmospheric nitrogen.

In compression-ignition engines, any incomplete oxidation of the carbon atoms in the fuel molecules tends to result in particulate emissions rather than HC and/or CO emissions as is the case with spark-ignition engines. In compression-ignition engines, the continuous spontaneous combustion of the fuel minimizes the possibility of fuel hydrocarbon molecules being completely excluded from the combustion process, as is the case with spark-ignition engines when flame quenching occurs. Furthermore, such continuous spontaneous combustion in cylinders of a compression-ignition engine which originally ingested fuel-free air, rather than an air/fuel mixture, eliminates CO formation occurring when a spark-ignition engine is operated under rich conditions (excess fuel). A number of factors unique to compression-ignition engines, such as the longer carbon chains in the fuel hydrocarbons, the higher initial temperatures and pressures in the combustion chambers, and the spontaneous ignition of fuel that is injected into a volume of hot air, result in compression-ignition engines

emitting fuel carbon in the form of elemental carbon particles, rather than in the form of unburned fuel or CO as is the case with spark-ignition engines. Under certain conditions, such as the severe overfueling of a heavy-duty compression-ignition engine, the emission of carbon particles becomes visibly evident as a plume of black smoke.

Appendix 2. Hydrocarbon Classes

Various distillation and extraction processes can be used to separate the hydrocarbons in raw petroleum into fractions with specific uses. All these hydrocarbon compounds are comprised of only two kinds of atoms, carbon and hydrogen. Each carbon atom has four positions for attachment of hydrogen atoms or other carbon atoms. As a consequence, the carbon atoms can be connected together in a great many ways.

The paraffin (alkane) hydrocarbons are saturated in that their molecules contain the maximum possible number of hydrogen atoms. The paraffin hydrocarbon atoms can be arranged in three ways. Normal paraffins have the carbon atoms connected to each other in straight chains (see figure). Isoparaffins have isomeric structures in which side chains of carbon atoms are attached to primary chains (see figure). Cycloparaffins have the carbon atoms arranged in closed chains or rings (see figure). The three types of paraffins comprise about 50% or more of the hydrocarbons in gasoline and about 35% of the hydrocarbons in exhaust gases.

The alkene or olefin hydrocarbons are unsaturated in that double bonds between two adjacent carbon atoms eliminate two sites for the attachment of hydrogen atoms (see figure). Like the paraffins, the olefins can have branched chain isomers. The olefins can also have the carbon atoms connected in closed rings. The olefins are rare in "straight run" gasoline which are produced by the simple distillation of raw petroleum. However, olefins are present in considerable quantity in highly "cracked" gasoline which are produced by refining processes that break or crack hydrocarbon molecules with long carbon chains. Olefins comprise as much as 10% of the hydrocarbons in gasoline and about 45% of the hydrocarbons in exhaust gases.

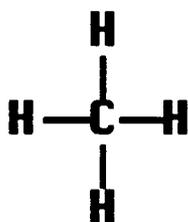
The aromatic hydrocarbons have one or more benzene rings in their molecular configuration. The unique benzene molecule is in the form of a closed ring in which six carbon atoms are connected by alternating single and double bonds. Aromatic hydrocarbons are found in crude petroleum and are the predominant hydrocarbon class in coal distillation products. Aromatic hydrocarbons comprise about 40% of the hydrocarbons in gasoline and 20% of the hydrocarbons in exhaust gases.

The oxygenated organic compounds have one or more oxygen atoms directly attached to the carbon atoms in their molecules (see figure). The various types of oxygenated organic compounds are alcohols, ethers, aldehydes, ketones, carboxylic acids, and esters.

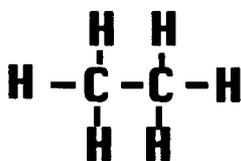
If the carbon atoms are connected together to form straight open chains, the general formula is C_nH_{2n+2} , where n is the number of carbon atoms in the chain. If carbon atoms in side chains are present, as in the paraffin isomers or isoparaffins, the same general formula is applicable. If the carbon atoms are arranged in closed chains or rings, as is the case with the cycloparaffins, the general formula is C_nH_{2n} . When there is only one double bond in the molecule, the general formula is C_nH_{2n} .

Paraffin (Alkane) Hydrocarbons (Saturated Straight Chain)

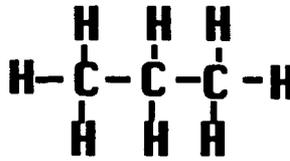
The first five hydrocarbons in the series are shown. Each terminal carbon atom has three attached hydrocarbon atoms and each interior carbon atom has two attached hydrocarbon atoms. In their pure isolated state, the first four members of the series; methane, ethane, propane, and butane, are in a gaseous state at standard temperature and pressure conditions.



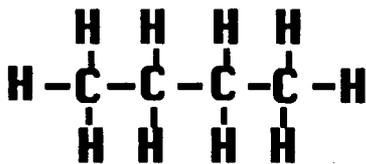
Methane



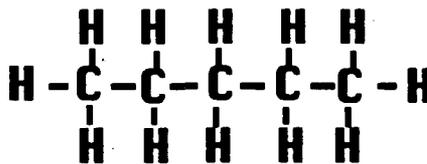
Ethane



Propane



Butane

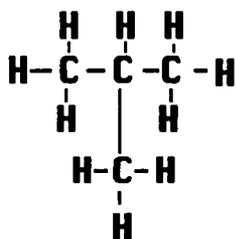


Pentane

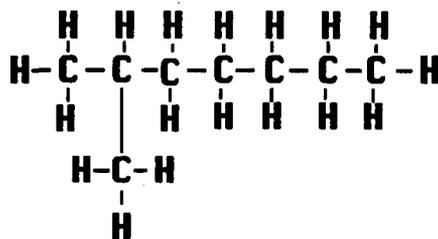
Isoparaffin (Alkane) Hydrocarbons (Saturated, Branched Chain)

Three different isomers are shown which have branched chains and at least one carbon atom in the molecule is attached to three other carbon atoms. Isobutane, the first member in the series, shows that a minimum of four

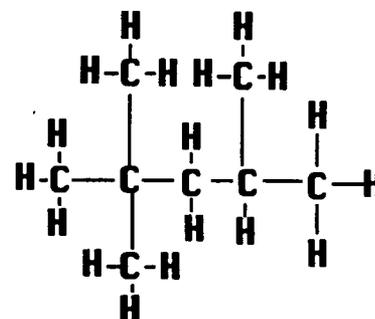
carbon atoms is necessary for chain branching. The two octane isomers show how configurations can vary when large molecules are involved.



Isobutane (2-methyl propane)



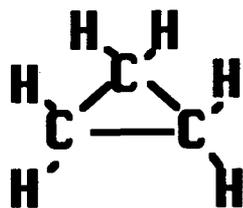
Isooctane (2-methyl heptane)



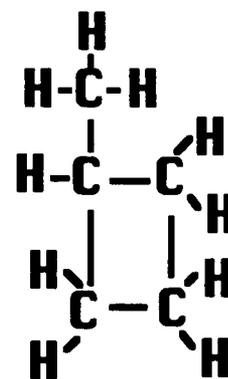
Isooctane (2,2,4-trimethyl pentane)

Cycloparaffin (Alkane) Hydrocarbons (Saturated, Closed Ring)

Two closed ring cyclohydrocarbon molecules are shown. The cyclopropane molecule shows that a minimum of three carbon atoms are necessary. The methylcyclobutane molecule shows how another structure, such as a straight chain, can be attached to a closed ring.



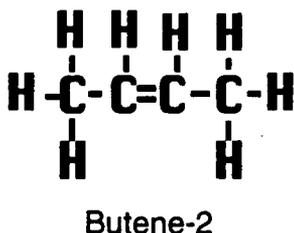
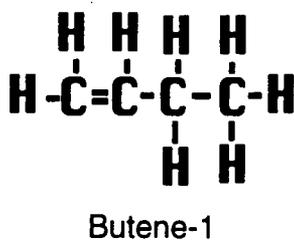
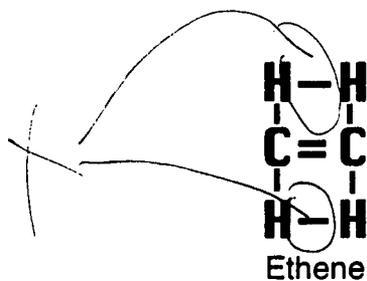
Cyclopropane



Methylcyclobutane

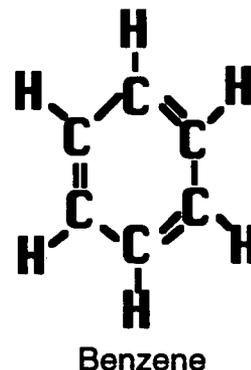
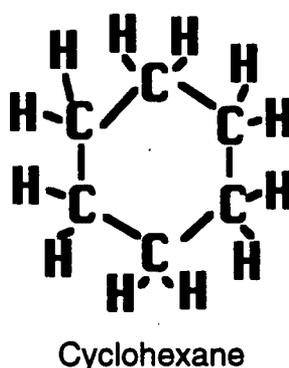
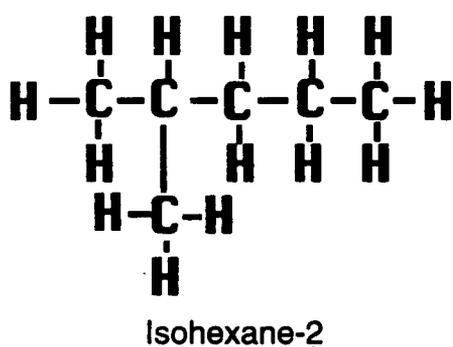
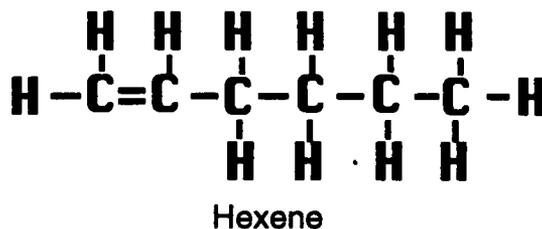
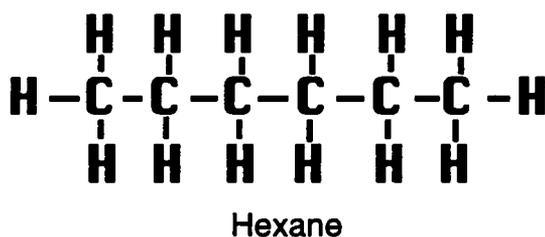
Olefin (Alkene) Hydrocarbons (Unsaturated)

Four alkene Hydrocarbon molecules which are "unsaturated" in that double bonding between two adjacent carbon atoms eliminates two hydrogen atoms from the molecule are shown. The two different butene molecules show how the location of the double bond can occupy different locations within a molecule. The butadiene molecule shows how a molecule can contain more than one double bond between carbon atoms.



Hydrocarbons with Six Carbon Atoms

Five of the ways are shown in which six carbon atoms can be arranged in isomeric molecular configurations. The benzene molecule, with its combination of single and double bonds, is a unique configuration. It has distinctive characteristics, such as an aromatic odor and a tendency to burn with a smoky flame.

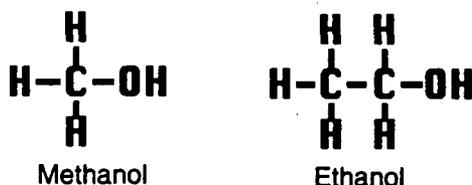


Oxygenated Organic Compounds

Two ways are shown in which oxygen atoms can be directly attached to the carbon atoms in a chain.

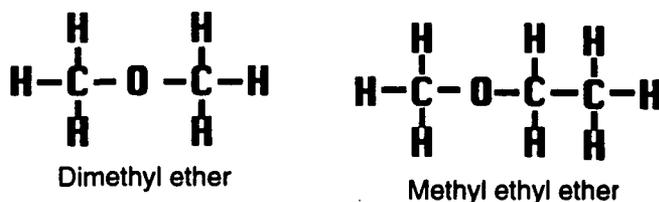
The alcohols have a hydroxyl (-OH) functional group attached to a terminal or intermediate carbon atom in the chain. The two simplest alcohols, methanol ("wood alcohol") and ethanol ("grain alcohol"), are shown in the figure.

Alcohols

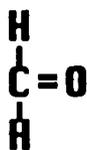


The ethers have an oxygen atom which serves as the connecting link between two carbon chains. The two simplest ethers, dimethyl ether and methyl ethyl ether are shown in the figure.

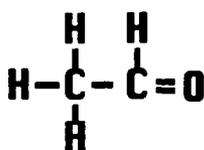
Ethers



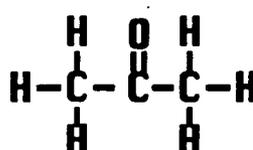
In some molecules, an oxygen atom replaces two hydrogen atoms by double bonding with a carbon atom to form a carbonyl (C=O) functional group. When the carbonyl group is attached to a terminal carbon atom at the end of a chain, the resulting compound is called an aldehyde. When the carbonyl group is attached to a carbon atom that is connected to two other carbon atoms, the resulting compound is called a ketone. The simplest forms of aldehydes and ketones are shown in the figure.

Aldehydes

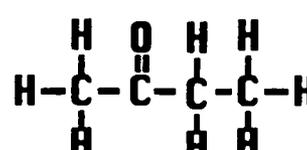
Formaldehyde



Acetaldehyde

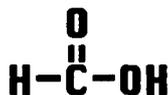


Acetone

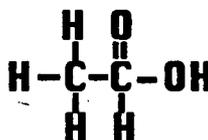
Ketones

Methy ethyl ketone

The carboxylic acids can be considered to be hybrids of alcohols and aldehydes in that a terminal carbon atom has a carbonyl group and a double bonded oxygen atom attached to it. The two simplest acids, formic acid and acetic acid, are shown in the figure.

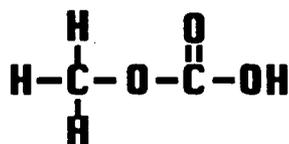
Carboxylic Acids

Formic Acid

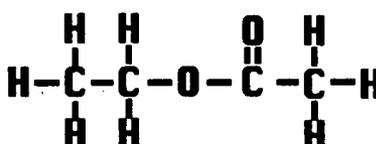


Acetic Acid

An ester has two carbon chains joined by a oxygen atom and one of the carbon atoms attached to the oxygen atom also has a double bonded oxygen attached to it. An ester can be synthesized by combining a molecule of an carboxylic acid and a molecule of an alcohol in a manner which results in the liberation of a molecule of water. In this respect, an ester can be considered to be the organic equivalent of an inorganic salt, such as sodium chloride (NaCl) which is formed when an acid, such as hydrochloric acid (HCl) reacts with a base, such as sodium hydroxide (NaOH). Consequently, the methyl formate molecule in the figure can be considered to be the end product when a methanol molecule and formic acid molecule combine. The ethyl acetate molecule in the figure can be considered to be the end product when an ethanol molecule and an acetic acid molecule combine.

Esters

Methyl Formate



Ethyl Acetate