source such as a spark; above 600°C explosion occurs spontaneously at all pressures.†

The initiating steps proceed primarily through hydrogen peroxide (H_2O_2) to form the hydroxyl radical (OH) at lower temperatures, or through dissociation of H_2 at higher temperatures to form the hydrogen atom radical H. The basic radical-producing chain sequence is composed of three reactions:

$$\begin{aligned} &\text{(R1)} \quad H + O_2 = O + OH \\ &\text{(R2)} \quad O + H_2 = H + OH \\ &\text{(R3)} \quad H_2 + OH = H_2O + H \end{aligned} \tag{9.56}$$

The first two reactions are chain-branching; two radicals are produced for each one consumed. The third reaction is necessary to complete the chain sequence: starting with one hydrogen atom, the sequence R1 then R2 and R3 produces two H; starting with OH, the sequence R3, then R1, then R2 produces two OH. Since all three reactions are required, the multiplication factor is less than 2 but greater than 1. Repeating this sequence over and over again rapidly builds up high concentrations of radicals from low initial levels.

However, these three reactions do not correspond to the overall stoichiometry

$$H_2 + \tfrac{1}{2}O_2 = H_2O$$

and other reactions must become important. In flames, the chain-branching process ceases when the reverse of reactions R1–R3 become significant. A quasi equilibrium is established; while the overall process has proceeded a considerable way toward completion, a substantial amount of the available energy is still contained in the high radical concentrations. Over a longer time scale, this energy is released through three-body recombination reactions (the principal chain terminating reactions):

$$\begin{aligned} &\text{(R4)} \quad H + H + M = H_2 + M \\ &\text{(R5)} \quad O + O + M = O_2 + M \\ &\text{(R6)} \quad H + OH + M = H_2O + M \end{aligned} \tag{9.57}$$

M refers to any available third-body species, required in these recombination reactions to remove the excess energy.[92]

With this introductory background let us now turn to the autoignition of hydrocarbon-air mixtures. The process by which a hydrocarbon is oxidized can exhibit four different types of behavior, or a sequential combination of them, depending on the pressure and temperature of the mixture: slow reactions; single

† In between, three separate explosion limits—pressure-temperature boundaries for specific mixture ratios of fuel and oxidizer that separate regions of slow and fast reaction—exist; these are not, however, of interest to us here.

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or multiple cool flames (slightly exothermic reactions); two-stage ignition (cool flame followed by a hot flame); single-stage ignition (hot flame). Slow reactions are a low-pressure, low-temperature (<200°C) phenomenon not normally occurring in engines. At 300 to 400°C one or more combustion waves often appear, accompanied by faint blue light emission; the reaction is quenched, however, when only a small fraction of the reactants have reacted and the temperature rise is only tens of degrees. These are called *cool flames.* Depending on conditions and the fuel, a cool flame may be followed by a "hot flame" or high-temperature explosion where the reaction accelerates rapidly after ignition. This is termed *two-stage ignition.* As the temperature of the mixture increases, a transition from two-stage to single-stage ignition occurs. While all hydrocarbons exhibit induction intervals which are followed by a very rapid reaction rate, some hydrocarbon compounds do not exhibit the cool flame or two-stage ignition behavior.

Figure 9-66 shows these ignition limits for isooctane, methane, and benzene. For isooctane, ignition in the low-temperature regions is by a two-stage process: there is a first time interval before the cool flame appears and then a second time interval from the appearance of the cool flame to the hot flame combustion process. Ignition in the high-temperature region is by a continuous one-stage process. The cool flame phenomena vary enormously with hydrocarbon structure. Normal paraffins give strong cool flames, branched-chain paraffins are more resistant. Olefins give even lower luminosity cool flames with longer induction periods. Methane shows only the high-temperature ignition limit, as indicated in Fig. 9-66. Benzene, also, does not exhibit the cool flame phenomenon and other aromatics give hardly detectable luminosity.[75] It is thought that some com-

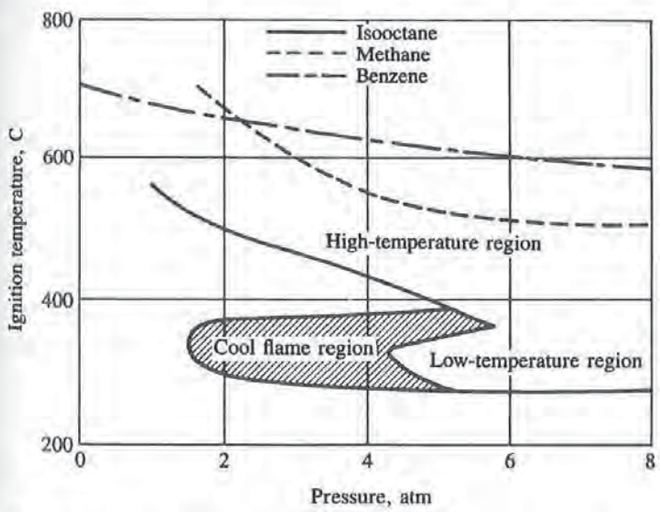


FIGURE 9-66
Ignition diagrams for isooctane, methane, and benzene. Two-stage ignition occurs in the low-temperature region; the first stage may be a cool flame. Single-stage ignition occurs in the high-temperature region.[94]

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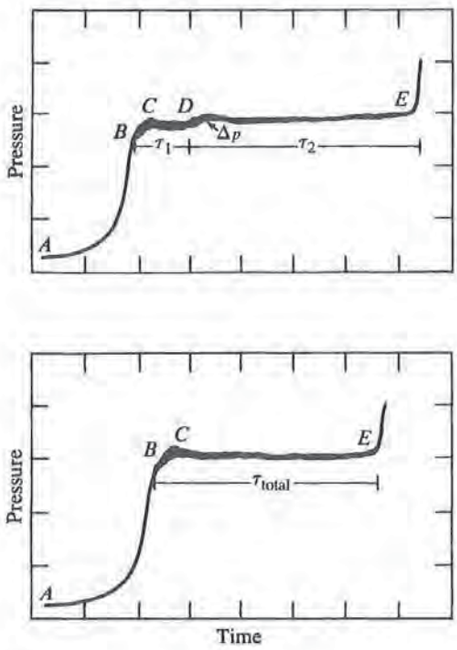


FIGURE 9-67
Pressure records of the autoignition of isooctane-air mixture ($\phi = 0.9$) in a rapid compression machine. $A \rightarrow B \rightarrow C$ is the compression process. Top: two-stage ignition (at D, then at E) at postcompression pressure of 1.86 MPa and temperature of 686 K. Bottom: single-stage ignition at E at post-compression conditions of 2.12 MPa and 787 K. Vertical scale: 690 kPa/division. Horizontal scale: 1 ms/division.[95]

pounds knock by a low-temperature two-stage ignition mechanism, some via a high-temperature single-stage ignition mechanism, and for some fuels both mechanisms may play a role.

Examples of these two mechanisms in rapid-compression machine experiments, where a homogeneous isooctane-air mixture was compressed to different final conditions in a piston-cylinder apparatus and allowed to autoignite, are shown in Fig. 9-67. $A \rightarrow B \rightarrow C$ is the piston-motion-produced compression. The top trace shows a well-defined cool flame at D, preceding hot ignition at E. The lower trace, at a higher temperature, shows a single-stage ignition process.[95]

Many of the above phenomena—long induction periods, initial slow increase in reaction rate, two-stage ignition process—cannot be explained with simple mechanisms like the hydrogen oxidation process reviewed above. Although chain-branching reactions are taking place, the radical generation process must be more complex. Explanations of the long induction periods are based on the formation of unstable but long-lived intermediates. These intermediates can then either react to form stable molecules or to form active radicals, the dominance and rate of either of these paths depending on the temperature: i.e.,[93]

$$\mathrm{A} \rightarrow \mathrm{M}^* \begin{cases} \mathrm{I} & \text{Stable molecules} \\ \mathrm{II} & \text{Radicals} \end{cases} \tag{9.58}$$

This is called a *degenerate-branching* mechanism. Hydroperoxides are an important metastable intermediate produced in the chain propagation process in the low-temperature ignition process. They have the form ROOH, where R is an

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organic radical (formed by abstracting a hydrogen atom from a fuel hydrocarbon molecule). However, at higher temperatures, ROOH is no longer the major product of the chain propagation process: instead, it is hydrogen peroxide, H_2O_2. While H_2O_2 is relatively stable at lower temperatures, above 500°C it decomposes into two OH radicals.

An outline of the basic hydrocarbon (RH) oxidation process due to Semenov is as follows:[93]

(R1)	$RH + O_2 \dashrightarrow \dot{R} + H\dot{O}_2$	}	Chain initiation
(R2)	$\dot{R} + O_2 \dashrightarrow R\dot{O}_2$	⎫	
(R3)	$\dot{R} + O_2 \dashrightarrow$ olefin $+ H\dot{O}_2$	⎪	
(R4)	$R\dot{O}_2 + RH \dashrightarrow ROOH + \dot{R}$	⎬	Chain propagation (9.59)
(R5)	$R\dot{O}_2 \dashrightarrow R'CHO + R''O$	⎪	
(R6)	$H\dot{O}_2 + RH \dashrightarrow H_2O_2 + \dot{R}$	⎭	
(R7)	$ROOH \dashrightarrow R\dot{O} + \dot{O}H$	⎫	Degenerate branching
(R8)	$R'CHO + O_2 \dashrightarrow R'\dot{C}O + H\dot{O}_2$	⎭	
(R9)	$R\dot{O}_2 \dashrightarrow$ destruction	}	Chain termination

The dot denotes an active radical; each dash denotes the number of free bonds on the organic radical R.

Reaction R1 is slow and explains the induction period in hydrocarbon combustion. R2 is fast and of near-zero activation energy. R3 leads to olefins known to occur in the oxidation of saturated hydrocarbons. R4 and R5 yield the main intermediates. The degenerate branching comes about from the delay in decomposition of the reactive species in R7 and R8. As one radical is used up to form the reactants in R7 and R8, the multiple radicals do not appear until these reactants decompose.[93] A more extensive discussion of hydrocarbon oxidation mechanisms can be found in Benson.[96]

The following evidence indicates the relevance of the above mechanism to knock in engines. End-gas sampling studies have identified products of slow combustion reactions of isooctane; these principally include olefins, cyclic ethers, aldehydes (R'CHO), and ketones (R''CO).[97] Such studies have shown increasing concentrations of peroxides (predominantly H_2O_2 with traces of organic peroxides) with isoparaffinic fuels which show two-stage ignition behavior. Higher temperature, single-stage ignition fuels such as benzene and toluene gave no detectable peroxide. Aldehydes and ketones have been measured in significant and increasing concentrations in motored engines where the peak cycle temperature was steadily increased. In motored engines, the occurrence of cool flames, the two-stage nature of the autoignition ignition process at intermediate compression temperatures, and the transition to a single-stage ignition process at very high compression ratios (i.e., motored-engine gas temperatures with a peak much higher than normal to simulate end-gas conditions in a firing engine) have also been demonstrated.[75, 94]

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Two types of models of this autoignition process have been developed and used: (1) empirical induction-time correlations; (2) chemical mechanisms which embody many or all of the features of the "full" hydrocarbon oxidation process given in Eq. (9.59).

Induction-time correlations are derived by matching an Arrhenius function to measured data on induction or autoignition times, for given fuel-air mixtures, over the relevant mixture pressure and temperature ranges. It is then assumed that autoignition occurs when

$$\int_{t=0}^{t_i} \frac{dt}{\tau} = 1 \tag{9.60}$$

where τ is the induction time at the instantaneous temperature and pressure for the mixture, t is the elapsed time from the start of the end-gas compression process ($t = 0$), and t_i is the time of autoignition. This equation can be derived by assuming that the overall rate of production of the critical species in the induction period chemistry, for a given mixture, depends only on the gas state and that the concentration of the critical species required to initiate autoignition is fixed (i.e., independent of the gas state).[98]

A number of empirical relations for induction time for individual hydrocarbons and blended fuels have been developed from fundamental or engine studies of autoignition (see Ref. 99). These relations have the form

$$\tau = Ap^{-n} \exp\left(\frac{B}{T}\right) \tag{9.61}$$

where A, n, and B are fitted parameters that depend on the fuel. The ability of these types of equations to predict the onset of knock with sufficient accuracy is unclear. The most extensively tested correlation is that proposed by Douaud and Eyzat:[100]

$$\tau = 17.68\left(\frac{\text{ON}}{100}\right)^{3.402} p^{-1.7} \exp\left(\frac{3800}{T}\right) \tag{9.62}$$

where τ is in milliseconds, p is absolute pressure in atmospheres, and T is in kelvin. ON is the appropriate octane number of the fuel (see Sec. 9.6.3). If the temperature and pressure time history of the end-gas during an individual cycle are known, Eqs. (9.60) and (9.62) together can be used to determine whether autoignition occurs before the normally propagating flame consumes the end-gas.

An important question with any model of the end-gas autoignition process is characterizing the end-gas temperature. During intake, the combustion chamber walls are hotter than the entering gases: thus, heat is transferred from the walls to the fresh mixture. During compression, the mixture temperature rises to levels substantially above the wall temperature. A thermal boundary layer will build up adjacent to the wall, as heat is now transferred to the wall. Unburned mixture away from the wall will be compressed essentially adiabatically (see Sec. 12.6.5). In addition, any unburned mixture which for some portion of time during intake and compression has been in close proximity to the exhaust valve and

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piston (which run at higher temperatures than the water-cooled wall regions) could be at higher temperatures than adiabatically compressed mixture, due to substantial heat transfer to the unburned mixture. Thus, the end-gas temperature is not uniform and the distribution of temperature is extremely complex. Often, the *mean* unburned mixture temperature is used to characterize its state. Alternatively, the *core* temperature corresponding to adiabatic compression of mixture from conditions at the start of compression is used. In the absence of substantial heating by the exhaust valve and piston, the core temperature is a better representation of the maximum unburned mixture at any point in the cycle.

While more complex and complete chemical models of the autoignition process are being developed for simple paraffinic hydrocarbon fuel compounds (e.g., Refs. 91 and 101), no detailed models are yet available for use with real blended fuels in engines. However, a generalized kinetic model for hydrocarbon oxidation based on a degenerate branched-chain mechanism, known as the Shell model, has been developed and tested with some success. The model uses generic chemical entities representative of a variety of individual species which undergo a set of generalized reactions. This is justified by the broadly similar (though complex) ignition behavior of a variety of different fuel molecules and the similar kinetics exhibited by the organic radicals of the same type in the hydrocarbon oxidation process [Eq. (9.59)].[95, 102]

The Shell model is based on a generic eight-step degenerate chain-branching reaction scheme. The scheme involves the fuel (RH), oxygen, radicals formed from the fuel (R), products (P), intermediate product (Q), and degenerate-branching agent (B). The rate constants are either fixed at values consistent with the literature or fitted so that measured induction times (such as those illustrated in Fig. 9-67) are adequately predicted.[102] An example of results obtained with this scheme is shown in Fig. 9-68. It shows the calculated pressure, temperature, and species concentrations in the end-gas region of an operating spark-ignition

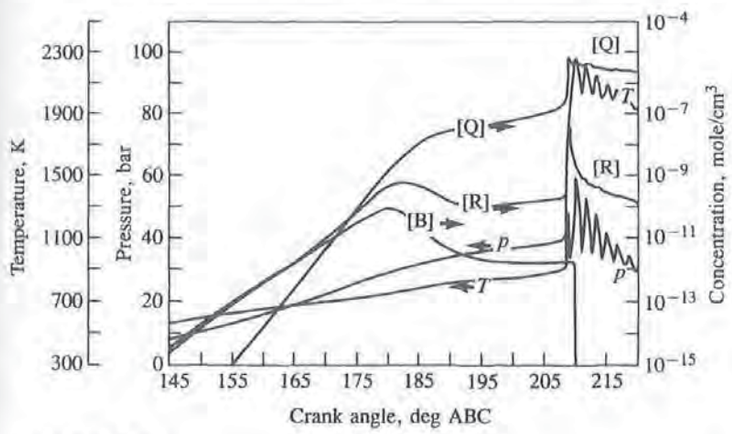


FIGURE 9-68
Pressure, temperature, and composition in the end-gas, before, during, and after autoignition, predicted by the Shell model in spark-ignition engine combustion process. B, Q, R defined in text.[103]

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engine, leading up to knock at 209° ABC. In this example, the autoignition model has been incorporated in a multidimensional model of the flow and flame propagation processes within the combustion chamber (see Sec. 14.5).[103]

9.6.3 Fuel Factors

The tendency to knock depends on engine design and operating variables which influence end-gas temperature, pressure, and the time spent at high values of these two properties before flame arrival. Thus, for example, the tendency to knock is decreased through reductions in the end-gas temperature that follow from decreasing the inlet air temperature and retarding the spark from MBT timing. However, knock is a phenomenon that is governed by both engine and fuel factors; its presence or absence in an engine depends primarily on the antiknock quality of the fuel.

Individual hydrocarbon compounds vary enormously in their ability to resist knock, depending on their molecular size and structure. Their tendency to knock has been measured by the *critical compression ratio* of an engine: i.e., the compression ratio at which, under specified operating conditions, the specific fuel compound will exhibit incipient knock. Knocking tendency is related to molecular structure† as follows:[105, 106]

Paraffins

1. Increasing the length of the carbon chain increases the knocking tendency.
2. Compacting the carbon atoms by incorporating side chains (thereby shortening the length of the basic chain) decreases the tendency to knock.
3. Adding methyl groups (CH_3) to the side of the basic carbon chain, in the second from the end or center position, decreases the knocking tendency.

Olefins

4. The introduction of one double bond has little antiknock effect; two or three double bonds generally result in appreciably less knocking tendency.
5. Exceptions to this rule are acetylene (C_2H_2), ethylene (C_2H_4), and propylene (C_3H_6), which knock much more readily than the corresponding saturated hydrocarbons.

Napthenes and aromatics

6. Napthenes have significantly greater knocking tendency than have the corresponding size aromatics.
7. Introducing one double bond has little antiknock effect; two and three double bonds generally reduce knocking tendency appreciably.

† See Sec. 3.3 for a review of hydrocarbon structure and its nomenclature. A more extensive discussion is given by Goodger.[104]

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8. Lengthening the side chain attached to the basic ring structure increases the knocking tendency in both groups of fuels, whereas branching of the side chain decreases the knocking tendency.

Figure 9-69 identifies the magnitude of these trends on a plot of the critical compression ratio against the number of carbon atoms in the molecule. The strong dependence of knocking tendency on fuel molecular size and structure is apparent.

Practical fuels are blends of a large number of individual hydrocarbon compounds from all the hydrocarbon series of classes: alkanes (paraffins), cyclanes (napthenes), alkenes (olefins), and aromatics (see Sec. 3.3). A practical measure of a fuel's resistance to knock is obviously required.[107, 108] This property is defined by the fuel's *octane number*. It determines whether or not a fuel will knock in a given engine under given operating conditions: the higher the octane number, the higher the resistance to knock. Octane number is not a single-valued quantity, and may vary considerably depending on engine design, operating conditions during test, ambient weather conditions during test, mechanical condition of engine, and type of oil and fuel used in past operation. The octane number (ON) scale is based on two hydrocarbons which define the ends of the scale. By definition, normal heptane (n-C_7H_{16}) has a value of zero and isooctane (C_8H_{18}: 2,2,4-trimethylpentane) has an octane number of 100. These hydrocarbons were chosen because of the great difference in their ability to resist knock and the fact that isooctane had a higher resistance to knock than any of the gasolines available at the time the scale was established. Blends of these two hydrocarbons define the knock resistance of intermediate octane numbers: e.g., a blend of 10 percent n-heptane and 90 percent isooctane has an octane number of 90. A fuel's octane number is determined by measuring what blend of these two hydrocarbons matches the fuel's knock resistance.

Several octane rating methods for fuels have been developed. Two of these—the research method (ASTM D-2699)† and the motor method (ASTM D-2700)—are carried out in a standardized single-cylinder engine. In the motor method, the engine operating conditions are more severe; i.e., the conditions are more likely to produce knock. In addition, road octane rating methods have been developed to define the antiknock quality of fuels in cars operated on the road or on chassis dynamometers. The engine used in the ASTM research and motor methods is the single-cylinder engine developed under the auspices of the Cooperative Fuel Research Committee in 1931—the CFR engine.‡ This test engine is a robust four-stroke overhead-valve engine with an 82.6-mm (3.25-in) bore and 114.3-mm (4.5-in) stroke. The compression ratio can be varied from 3 to 30 while

† ASTM denotes American Society for Testing and Materials; the letter and number defines the specific testing code.

‡ The Cooperative Fuel Research Committee is now the Coordinating Research Council, Inc.

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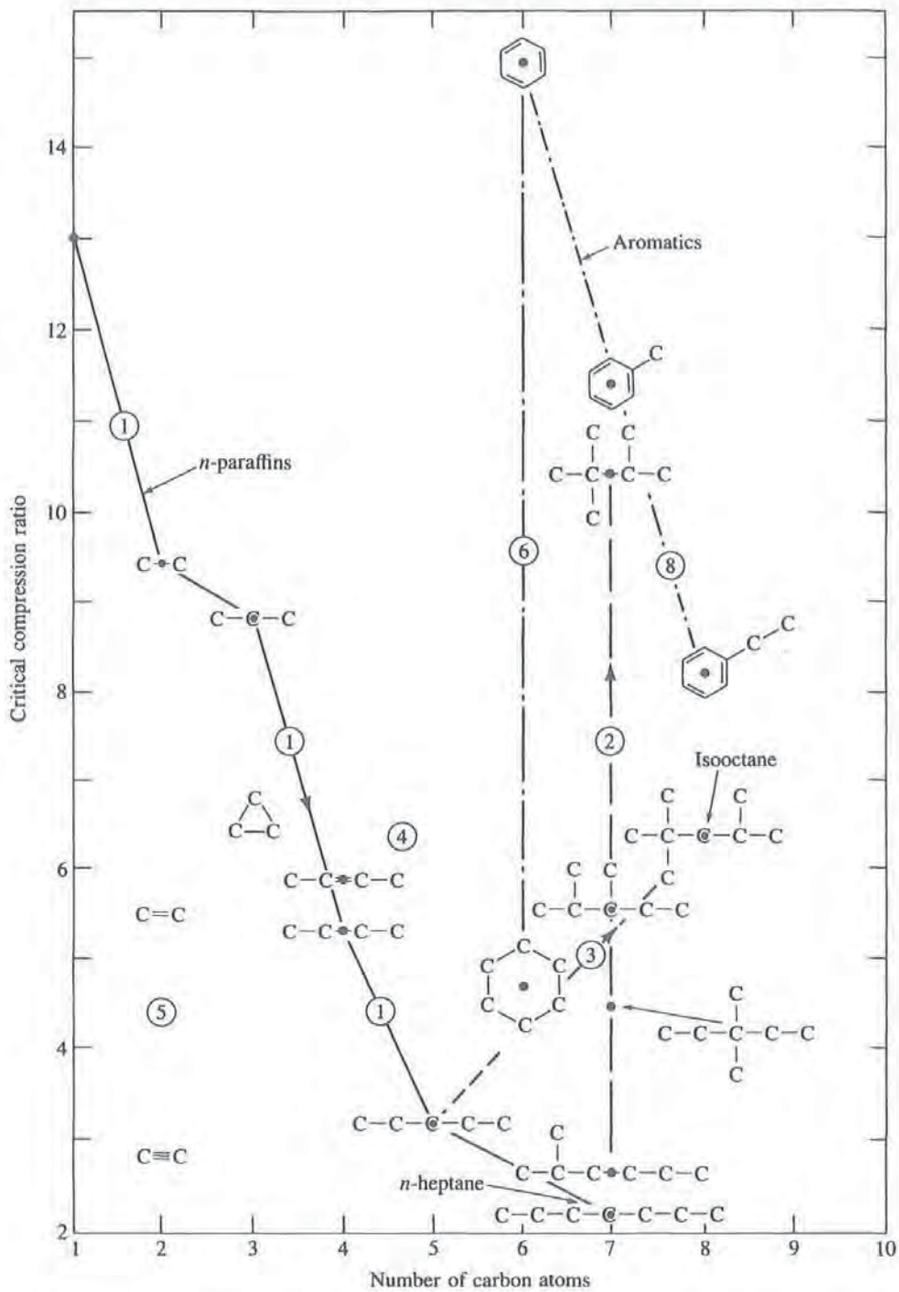


FIGURE 9-69
Critical compression ratio (for incipient knock at 600 rev/min and 450 K coolant temperature) as a function of number of carbon atoms in hydrocarbon molecule, illustrating the effects of changes in molecular structure. (*Developed from Lovell.*[105])

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TABLE 9.6
Operating conditions for research and motor methods

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

the engine is operating, with a mechanism which raises or lowers the cylinder and cylinder head assembly relative to the crankcase. A special valve mechanism maintains a constant tappet clearance with vertical adjustment of the head. The engine is equipped with multiple-bowl carburetors so two reference fuels (usually blends of *n*-heptane and isooctane) and the fuel being rated can be placed in separate bowls. By means of a selector valve, the engine can be operated on any of the three fuels. The engine operating conditions of the research and motor methods are summarized in Table 9.6. The test conditions are chosen to represent the engine operating range where knock is most severe. With the fuel under test, the fuel/air ratio is adjusted for maximum knock. The compression ratio is then adjusted to produce knock of a standardized intensity, as measured with a magnetostriction knock detector. The level of knock obtained with the test fuel is bracketed by two blends of the reference fuels not more than two octane numbers apart (with one knocking more and one less than the test fuel). The octane number of the gasoline is then obtained by interpolation between the knockmeter scale readings for the two reference fuels and their octane numbers. For fuels below 100 ON, the *primary reference fuels* are blends of isooctane and *n*-heptane; the percent by volume of isooctane in the blend is the octane number. For fuels above 100 ON, the antiknock quality of the fuel is determined in terms of isooctane plus milliliters of the antiknock additive, tetraethyl lead, per U.S. gallon.†

The octane ratings of several individual hydrocarbon compounds and common blended fuels are summarized in App. D, Table D.4. Practically all fuels exhibit a difference between their research and motor octane numbers. The motor method of determining ON uses more severe operating conditions than the

† The octane number of the fuel is calculated from $ON = 100 + 28.28T/[1.0 + 0.736T + (1.0 + 1.472T - 0.035216T^2)^{1/2}]$, where T is milliliters of tetraethyl lead per U.S. gallon. Tetraethyl lead, $(C_2H_5)_4Pb$, contains 64.06 weight percent lead; 1 ml of TEL contains 1.06 grams of lead.

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research method (higher inlet mixture temperature, more advanced timing). Thus, the motor octane number (MON) is usually lower than the research octane number (RON). The numerical difference between these octane numbers is called the *fuel sensitivity*:

$$\text{Fuel sensitivity} = \text{RON} - \text{MON} \tag{9.63}$$

Fuel sensitivity varies with the source of crude petroleum and refining processes used. The primary reference fuels themselves (mixtures of isooctane and *n*-heptane), by definition, have the same octane numbers by both the research and motor methods. Since the primary reference fuels are paraffins, we would expect other paraffins to have little or no sensitivity. In contrast, olefins and aromatics have high sensitivity. In general, therefore, straight-run gasolines containing high percentages of saturated hydrocarbons have low sensitivity, while cracked or reformed gasolines containing large percentages of unsaturated hydrocarbons have high sensitivity. Fuels having high sensitivity generally, but not always, have lower road octane ratings (i.e., octane ratings determined in cars in on-the-road use) than do low-sensitivity fuels of the same research octane number. Regular grade unleaded gasoline typically has a RON of at least 91 and a MON of about 83, giving a sensitivity of 8.

Research and motor octane number fuel ratings are made in a single-cylinder engine run at constant speed, wide-open throttle and fixed spark timing. These methods do not always predict how a fuel will behave in an automobile engine operated under a variety of speed, load, and weather conditions. Several methods of rating a gasoline in actual vehicles, either on the road or on chassis dynamometers which duplicate outdoor road conditions, have, therefore, been developed. These methods determine the fuel's *road octane number*.[107] The road ratings of current fuels usually lie between the motor and research ratings. Road octane number can be related to motor and research ratings with equations of the form

$$\text{Road ON} = a\,(\text{RON}) + b\,(\text{MON}) + c$$

where a, b, and c are experimentally derived constants. Recent studies show $a \approx b \approx 0.5$ gives good agreement. An *antiknock index* which is the mean of the research and motor octane numbers is now used in the United States to characterize antiknock quality:

$$\text{Antiknock index} = \frac{\text{RON} + \text{MON}}{2} \tag{9.64}$$

Refiners and automobile manufacturers are interested in the octane number requirement of engines or vehicles on the road. The *octane number requirement* (usually abbreviated to OR) of an engine or vehicle-engine combination is defined as the minimum fuel octane number that will resist knock throughout the engine's operating speed and load range. The octane number requirement of a single engine or vehicle does not usually provide adequate information for that particular model; every model has a range of requirements due to production tolerances and variations in engine and vehicle condition.

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Modern gasolines contain a number of chemical additives designed to improve fuel quality. These additives are used to raise the octane number of the fuel, control surface ignition, reduce spark plug fouling, resist gum formation, prevent rust, reduce carburetor icing, remove carburetor or injector deposits, minimize deposits in the intake system, and prevent valve sticking. The octane number of hydrocarbon fuels can be increased by antiknock agents. Their use generally allows an increase in antiknock quality to be achieved at less expense than modifying the fuel's hydrocarbon composition by refinery processing. The most effective antiknock agents are lead alkyls. Tetraethyl lead (TEL), $(C_2H_5)_4Pb$, was first introduced in 1923. Tetramethyl lead (TML), $(CH_3)_4Pb$, was introduced in 1960. Since TML boils in the mid-range of a gasoline (110°C), whereas TEL boils at the high end (200°C), the introduction of TML permitted better distribution of octane amongst the cylinders of an engine. In 1959 a manganese antiknock compound (methylcyclopentadienyl manganese tricarbonyl), now known as MMT, was introduced as a supplementary antiknock agent for TEL. It is also an antiknock agent in its own right.

About 1970, in the United States, low-lead and unleaded gasolines were introduced. Two factors influenced the reduction in the use of lead alkyls: concern about the toxicological aspects of lead in the urban environment and the use of catalytic devices for emission control that are poisoned by lead. Unleaded and reduced-lead-content gasolines are now required in the United States. Japan has almost completely converted to unleaded fuel. In Europe, requirements which reduce the lead content of gasolines and introduce unleaded fuel were implemented in the late 1980s. MMT is sometimes used as an antiknock additive in unleaded gasoline. However, its role as a deposit in plugging exhaust catalytic converters limits its use to low concentrations. The expanding use of unleaded fuels has increased interest in other methods of boosting the octane rating of gasolines. The use of oxygenates—alcohols and ethers—as gasoline extenders, which due to their excellent antiknock quality increase the fuel's octane rating, is becoming more common. A brief review of the mechanism by which these additives and compounds improve the knock resistance of gasolines follows.

Lead is the most effective antiknock element known. In the form of lead alkyls, it is stable and fuel-soluble. The precise mechanism by which lead alkyls control knock is not fully known. It is generally agreed that the alkyls decompose before they exert their antiknock action. The decomposed material—lead oxide, PbO—either as a vapor or as a fog (a dispersion of fine particles), inhibits the preflame chain-branching reaction which leads to autoignition of the fuel-air charge, thus slowing the reaction rate. However, lead has little effect on two-stage ignition until after the cool flame.[109] Commercially available tetraalkyl lead antiknock fluids are based on TEL, TML, physical mixtures of TEL and TML, and mixed ethyl-methyl compounds produced by reacting TML and TEL. This range of compounds offers volatilities between the extremes of TEL and TML. The individual alkyls vary in antiknock behavior as a function of fuel composition and combustion conditions. The average effect of various amounts of TEL in a large number of regular gasolines is summarized in Fig. 9-70: the effectiveness of

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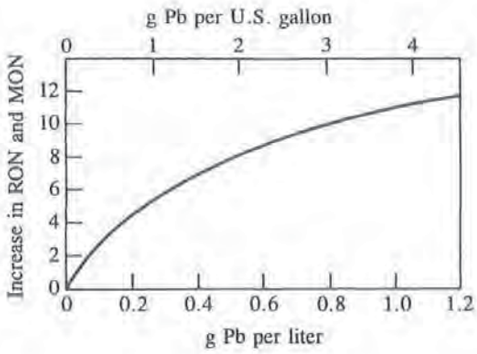


FIGURE 9-70
Gasoline octane number increase resulting from use of antiknock additive tetraethyl lead. Varies with fuel composition: average values shown.

each successive increment added steadily decreases. The addition of about 0.8 g lead per liter (3 g Pb per U.S. gallon, the maximum economic limit to lead concentration) provides an average gain of about 10 octane numbers in modern gasolines, though effectiveness varies with chemical composition of the fuel. TML offers a greater octane number gain than TEL in many gasolines, particularly in highly aromatic fuels with a low sulfur content. One of its major values, however, is in overcoming engine knock that results from fuel component segregation in the intake manifold; gasoline fractions of different volatility separate in the intake manifold of a multicylinder engine and the heavier fractions lag behind (see Sec. 7.6.3). When a gasoline containing a lead alkyl is burned in a spark-ignition engine, it produces nonvolatile combustion products. These deposit on the walls of the combustion chamber and on the spark plug, causing lead-fouling of the spark plug electrodes and tracking across the plug insulator, and hot corrosion of the exhaust valve. Commercial antiknock fluids, therefore, contain scavenging agents—combinations of ethylene dibromide and ethylene dichloride—which transfer the lead oxides which would otherwise deposit into volatile lead-bromine compounds which are largely exhausted with the combustion gases.

Low concentrations of methylcyclopentadienyl manganese tricarbonyl (MMT) act as an octane promoter; it is most effective in highly paraffinic gasolines. It is sometimes used as a supplement to TEL. MMT-TEL antiknock fluids are tailored to optimize octane cost effectiveness and the average fluid contains about 0.03 g Mn/g Pb. The octane gains vary significantly with fuel composition. In unleaded fuels MMT is sometimes used in low concentrations to provide from 0.5 to 1 octane number gain. On a weight of metal basis, MMT is about twice as effective as TEL in terms of research octane number gain and about equally effective in terms of motor octane number gain.[109]

The use of oxygenates (oxygen containing organic compounds) as extenders or substitutes for gasoline is increasing.[110] In some cases, this is because the oxygenate can be produced from nonpetroleum sources (e.g., biomass, coal) and thus may offer strategic or economic benefits. In other cases, the good antiknock blending characteristics of oxygenates can aid in meeting octane quality demands where increasingly stringent regulations limit lead alkyl use. Several oxygenates have been used as automotive fuels; those of major interest are methanol

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(CH_3OH), ethanol (C_2H_5OH), tertiary butyl alcohol (TBA) (C_4H_9OH), and methyl tertiary butyl ether (MTBE).

Table 9.7 lists the antiknock characteristics of these compounds and their physical and chemical characteristics relative to gasoline. The blending value of antiknock index [Eq. (9.64)] given in the table is not necessarily the same as the compound's antiknock index [$(R + M)/2$ from App. D, Table D.4] when used alone as a fuel, and depends on the gasoline composition with which the compound is blended. MTBE-gasoline blends have good water stability, and MTBE has little effect on vapor pressure and material compatibility. TBA is moderately susceptible to water extraction and loss. Ethanol is technically feasible as a high octane supplement or substitute for gasoline; economically it is less attractive than methanol.

Methanol, because it can be made from natural gas, coal, or cellulose materials, has near- and long-term potential. Its high octane quality (130 RON, 95 MON), when used in low-concentration ($\sim$5 percent) methanol-cosolvent-gasoline blends, can help offset the octane loss from lead alkyl phase-out. Problems with these blends include poor solubility in gasoline in the presence of water; toxicity; an energy content about half that of gasoline; high latent heat of vaporization and oxygen content which contribute to poor driveability; incompatibility with many commonly used metals and elastomers; blending effects on gasoline volatility which may force the displacement of large volumes of butane. Some of these problems can be partially reduced by using cosolvents such as TBA or isobutanol. Use of methanol as a neat fuel in specially designed engines permits advantage to be taken of its high octane rating via high compression ratios. Problems include its energy content of one-half that of gasoline; engine starting problems which require starting aids such as 5 to 10 percent isopentane at temperatures below 10°C or intake system heaters; toxicity; extensive engine modifications.[110]

The octane requirement of an engine-vehicle combination usually increases during use, primarily due to the buildup of combustion chamber deposits within the engine cylinder. While these deposits increase the engine's compression ratio modestly, their largest effect is to increase the temperature of the outer surface of

TABLE 9.7
Oxygenate properties[110]

	Methanol	Ethanol	TBA	MTBE	Gasoline
Typical $(R + M)/2$ blending value	112	110	98	105	87–93
Weight percent oxygen	50	35	22	18	0
Stoichiometric (A/F)	6.5	9.0	11.2	11.7	14.5
Specific gravity	0.796	0.794	0.791	0.746	0.74
Lower heating value, MJ/kg	20.0	26.8	32.5	35.2	44.0
Latent heat of vaporization, MJ/kg	1.16	0.84	0.57	0.34	0.35
Boiling temperature, °C	65	78	83	55	27–227

TBA, tertiary butyl alcohol; MTBE, methyl teriary butyl ether.

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the combustion chamber. This *increases* heat transfer *to* the fresh mixture during induction and *decreases* heat transfer from the unburned charge during compression. End-gas temperatures are therefore higher, thus increasing the likelihood of knock. As the combustion chamber deposits stabilize (over 15,000 to 25,000 km of driving), the engine's octane requirement typically increases by about 5 octane numbers; the increase can vary from between 1 to over 13 octane numbers.

Essentially all of the octane requirement increase results from the buildup of deposits on the combustion chamber walls: when the deposits are completely removed from the engine the octane requirement returns to close to its original value. The volume of deposits for leaded and unleaded fuels which build up inside the engine cylinder are similar in magnitude, and are in the range 0.3 to 1 cm^3 per cylinder. The compression ratio increase associated with this volume of deposits is small (0.1 compression ratio) and contributes therefore on the order of 10 percent of the octane requirement increase. The primary effect of the deposits is thought to be changes in heat transfer between the end-gas and the combustion chamber walls, as explained above. In an experiment where the deposits were removed from various regions of the combustion chamber in sequence and the octane requirement after each removal was determined, it was found that the deposits on the cylinder head around the end-gas region were the cause of about two-thirds of the total ORI observed. Though the volume of the deposits for leaded and unleaded fuels are comparable, the composition and density are substantially different. For unleaded fuels the major element is carbon (one-third to one-half by mass). The deposit density with leaded fuels is 2 to 5 g/cm^3; with unleaded fuels it is a factor of 5 lower.[111]

PROBLEMS

9.1. The table gives relevant properties of three different spark-ignition engine fuels. The design and operating parameters of a four-cylinder 1.6-liter displaced volume engine are to be optimized for each fuel over the engine's operating load and speed range. You may assume that for each engine-fuel combination, the gross indicated fuel conversion efficiency and imep at any operating condition are given by 0.8 times the fuel-air cycle efficiency at those conditions. Also, assume that for every five research octane number increase above 95 (the gasoline value) in fuel antiknock rating, the compression ratio can be increased by one unit. For gasoline, the engine compression ratio is 9, so if the octane number of the fuel is 100, a compression ratio of 10 can be used.

(*a*) At part-throttle operation—at an intake pressure of 0.5 atm and a speed of 2500 rev/min—estimate the gross indicated fuel conversion efficiency and specific fuel consumption for each engine-fuel combination. Each engine-fuel combination operates at the lean limit given.

(*b*) At the appropriate equivalence ratio for maximum power, with 1 atm inlet pressure at the same speed (2500 rev/min), the volumetric efficiencies are as shown. Explain these volumetric efficiency values. Each fuel is fully vaporized in the inlet manifold and the inlet mixture temperature is held constant for all fuels. Manifold and valve design remains the same.

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(*c*) Estimate the ratios of the maximum indicated mean effective pressure, at the same conditions as in (*b*), of the natural gas and methanol fueled engines to the maximum imep of the gasoline engine.

(*d*) If the methane engine burns 33 percent faster than the gasoline engine (i.e., its combustion event takes three-quarters of the time), sketch a *carefully drawn qualitative* cylinder pressure versus crank angle curve for the two engines, from halfway through the compression stroke to halfway through the expansion stroke. Put both curves on the same graph. Conditions are as in (*b*). Show the motored *and* firing pressure curves for each engine. The spark timing should be set for maximum brake torque for each engine. Show the location of spark timing, the location of maximum cylinder pressure, and the approximate location of the end of combustion.

Fuel properties

Fuel	Formula	Research octane number	ϕ at lean operating limit	Stoichiometric air/fuel ratio	Heating value, MJ/kg	η_u
Natural gas	CH_4	120	0.7	17.2	50	0.78
Methanol	CH_3OH	105	0.8	6.4	20	0.75
Gasoline	$(CH_2)_n$	95	0.9	14.9	44	0.85

ϕ = fuel/air equivalence ratio.

9.2. The figure shows the flame propagating radially outward from the center of a disc-shaped combustion chamber. Combustion in such a device has many features in common with spark-ignition engine combustion. The chamber diameter is 10 cm and the height is 1.5 cm. For this problem, the flame can be thought of as a thin cylindrical sheet. Its radius increases approximately linearly with time. The volume of the chamber is constant. The fuel is a typical hydrocarbon fuel; the mixture is stoichiometric; the initial temperature is room temperature.

(*a*) Sketch qualitative but *carefully proportioned* graphs of the following quantities versus time from the start of combustion to the end of combustion:
  (1) The ratio of actual pressure in the chamber to the initial pressure
  (2) The ratio of average density of the gas *ahead* of the flame to the initial density
  (3) The ratio of the average density of the gas *behind* the flame to the initial density

(*b*) On a qualitative but *carefully proportioned* graph of r/R_0 versus time show how the radial positions of gas elements, initially at $r/R_0 = 0$, 0.5, and 1.0 before combustion, change during the combustion process as the flame propagates radially outward from the center ($r = 0$) to the outer wall ($r = R_0$).

Note: Accurate numerical calculations are not required to answer this question. You will be graded on the amount of physical insight your diagrams and the supporting brief explanations of your logic communicate. You should write down any equations or approximate numerical values for relevant quantities that help explain your reasoning.

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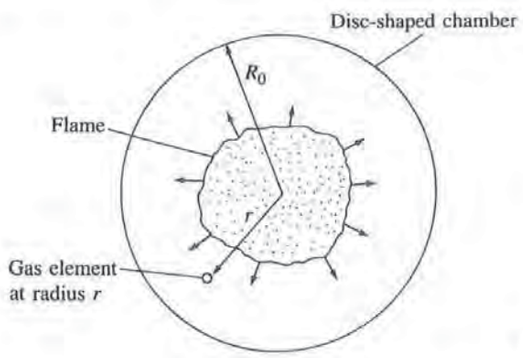


FIGURE P9-2

9.3. Highly compact bowl-in-piston or bowl-in-head combustion chambers permit SI engine operation at higher-than-normal compression ratios and with leaner mixtures. A vigorous swirling flow in the combustion chamber just prior to combustion is achieved by these chamber designs. The table compares the characteristics of a compact-chamber spark-ignition engine (Fig. P9-3) with a more conventional spark-ignition engine which has an open chamber (see Fig. 9-4).

	Compact chamber 1.5 liter	**Conventional 1.5 liter**
Compression ratio	14 : 1	9 : 1
Fuel octane requirement	97 RON	97 RON
Maximum bmep	980 kPa	965 kPa
Air/fuel ratio at WOT	17 : 1	13 : 1
MBT timing at 2000 rev/min and WOT	5° BTC	25° BTC
Air/fuel ratio at cruise conditions	22 : 1	16 : 1

For gasoline, the stoichiometric air/fuel ratio is 14.6. RON = research octane number, WOT = wide-open throttle, MBT = maximum brake torque.

Use the data provided, and any additional quantitative information you have or can generate easily, to answer the following questions:

(*a*) Explain whether the combustion process rate in the compact-chamber engine will be faster, slower, or about the same rate as the conventional engine combustion process.

(*b*) The compact-chamber engine has a higher compression ratio than the conventional engine, yet it has about the same maximum bmep at WOT in the mid-speed range. Explain quantitatively how the differences in compression ratio, air/fuel ratio, and MBT spark timing at WOT between the two engines influence maximum bmep and result in negligible total change.

(*c*) Both engines have been designed to have the same fuel octane requirement, yet the compact-chamber engine has a much higher compression ratio. Explain which features of the engine allow it to operate without knock at a 14 : 1 compression ratio while the conventional engine can only operate without knock at 9 : 1.

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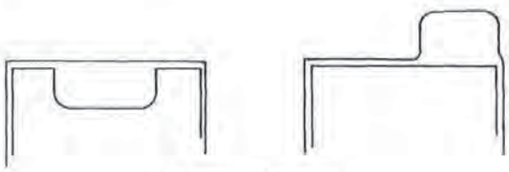


FIGURE P9-3

(*d*) The efficiency of the compact-chamber engine at part-throttle conditions is higher than that of the conventional engine. Briefly explain why this is the case and estimate approximately the ratio of the two engine efficiencies.

9.4. In a spark-ignition engine, a turbulent flame propagates through the uniform premixed fuel-air mixture within the cylinder and extinguishes at the combustion chamber walls.

(*a*) Draw a carefully proportioned qualitative graph of cylinder pressure p and mass fraction burned x_b as a function of crank angle θ for $-90° < \theta < 90°$ for a typical SI engine at wide-open throttle with the spark timing adjusted for maximum brake torque. Mark in the crank angles of spark discharge, and of the flame development period (0 to 10 percent burned) and end of combustion, on both p and x_b versus θ curves relative to the top-center crank position.

(*b*) Estimate approximately the fraction of the cylinder volume occupied by burned gases when the mass fraction burned is 0.5 (i.e., halfway through the burning process).

(*c*) A simple model for this turbulent flame is shown on the left in Fig. P9-4. The rate of burning of the charge dm_b/dt is given by

$$\frac{dm_b}{dt} = A_f \rho_u S_T$$

where A_f is the area of the flame front (which can be approximated by a portion of a cylinder whose axis is at the spark plug position), ρ_u is the unburned mixture

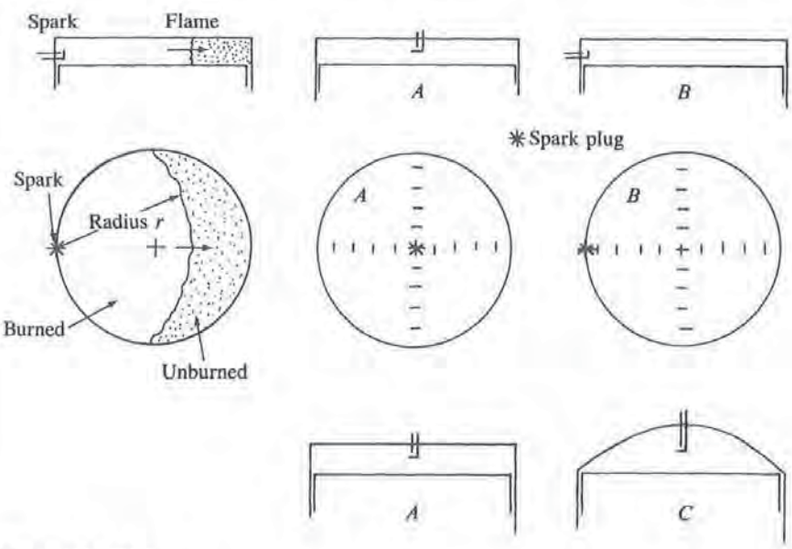


FIGURE P9-4

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density, and S_T is the turbulent flame speed (the speed at which the front moves relative to the unburned mixture ahead of it). The rate of mass burning is influenced therefore by combustion chamber geometry (through A_f) as well as those factors that influence S_T (turbulent intensity, fuel/air ratio, residual gas fraction, and EGR). Compare combustion chambers *A* and *B* shown in Fig. P9-4. Sketch the *approximate* location of the flame front when 50 percent of the mass has been burned. (A careful qualitative sketch is sufficient; however, provide a quantitative justification for your sketch.) Sketch the mass fraction burned versus crank angle curves for these two combustion chambers on the same graph, each with its spark timing set for maximum brake torque. You may assume the value of S_T is the same for *A* and *B*.

(*d*) Compare combustion chambers *A* and *C* in Fig. P9-4 which have the same flame travel distance but have different chamber shapes. Which chamber has
(1) the faster rate of mass burning during the first half of the combustion process;
(2) the faster rate of mass burning during the second half of the combustion process;
(3) the more advanced timing for maximum brake torque?
Explain your answers.

9.5. A new synthetic fuel with chemical formula $(CH_2O)_n$ is being developed from coal for automotive use. You are making an evaluation of what changes in the spark-ignition engines you produce might be required if gasoline is replaced by this fuel "X." First make the following calculations:

(*a*) What is the stoichiometric air/fuel ratio for "X"? How does this compare with the stoichiometric air/fuel ratio for gasoline?

(*b*) Given that in a constant-volume calorimeter experiment to determine the heating value of "X" the combustion of 50 g of fuel with excess air at standard conditions resulted in a temperature rise of 1.25°C of the water and calorimeter (of combined heat capacity 650 kJ/K), what is the heating value of a stoichiometric mixture of "X" and air, *per kilogram of mixture*? How does this value compare with a stoichiometric gasoline-air mixture?

Then,

(*c*) Compare *approximately* the specific fuel consumption of a spark-ignition engine operated on stoichiometric gasoline and "X" mixtures. What do you conclude about the relative size of the fuel systems required to provide equal power?

(*d*) "X"-air mixtures take twice as long to burn as gasoline-air mixtures (the crank angle between the spark and end of combustion is twice as large). Sketch carefully drawn pressure-time curves over the entire engine four-stroke cycle for the two mixtures, for the same displacement and compression ratio engines, for the same *imep* (for throttled engine operation) for stoichiometric mixtures, with optimum spark timing, indicating the relative crank angle location of spark, peak cylinder pressure, and end of combustion, and the relative values of intake pressure, peak cylinder pressure, and pressure at the exhaust valve opening, for the two mixtures at the same equivalence ratio. (You do not need to make calculations to sketch these graphs.)

(*e*) Though "X"-air mixtures are slower burning than gasoline-air mixtures, the engine compression ratio can be increased to 14 : 1 from the 8 : 1 values typical for gasoline. Using typical fuel-air cycle efficiencies and the relation between the fuel-air cycle and real cycle efficiency, determine whether the slower-burning

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higher-compression-ratio engine using "X" will be more efficient, have about the same efficiency, or be less efficient than the faster-burning lower-compression-ratio gasoline engine.

9.6. Knock in spark-ignition engines is an abnormal combustion condition. Almost everyone who rides a motorcycle or drives a car experiences this phenomenon at some time and usually changing into a lower gear will take the engine away from this condition. Use your experience of what changes in other variables do, and consult this and other textbooks to complete a table with the dependent variables shown at the top of the columns.

The independent variables are: speed, compression ratio, chamber surface/volume ratio, spark plug distance from cylinder axis, percent EGR, inlet mixture temperature, inlet mixture pressure, (F/A), wall temperature, air swirl, squish motion, fuel octane number. In these columns show the corresponding influence on the dependent variables by a "+" for an increase and a "−" for a decrease. Show the effect of increase in engine system independent variables on: cylinder pressure and temperature, flame speed, total burn time, autoignition induction period, tendency to knock. Provide in the extreme right-hand column brief comments to explain your answers.

Effect of increase in engine independent variable	Dependent variables						
	Cylinder		Flame speed	Total burn time	Induction period	Tendency to knock	Explanation
	Pressure	Temperature					
Speed, rev/min							
Etc.							

9.7. The attached graph gives the pressure–crank angle curve for a spark-ignition engine running at $\phi = 1.0$. The mass fraction burned x_b is also shown. Estimate the tem-

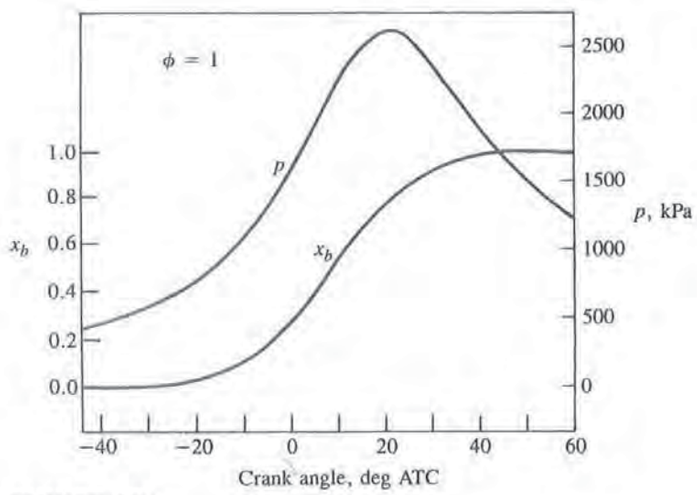


FIGURE P9-7

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perature of the reactants at a number of crank angles and plot a graph of T_u versus θ. Assume the reactants in the cylinder are at 333 K and 1 atm pressure at the start of compression. It is necessary to make simplifications in order to do this and you should explain clearly what other assumptions you make; they should be compatible with Prob. 9.8 below.

9.8. If the combustion takes place progressively through a large number of very small zones of gas and there is no mixing between the zones, determine:

(*a*) the temperature at $-30°$, just after combustion, of the zone which burns at $-30°$;

(*b*) the temperature at $0°$, just after combustion, of the zone which burns at $0°$;

(*c*) the temperature at $+30°$, just after combustion of the zone which burns at $+30°$;

(*d*) the temperature of the products in these three zones at $+30°$.

Plot your results versus crank angle to show whether there is a spatial distribution of temperature in the cylinder after combustion.

Note: Each small unburned gas element burns at essentially constant pressure and is subsequently compressed and/or expanded. Use charts (Chap. 4) or an equilibrium computer code. The unburned gas state is given by Prob. 9.7.

9.9. An approximate way to calculate the pressure in the end-gas just after knock occurs is to assume that all the end-gas (the unburned gas ahead of the flame) burns instantaneously at constant volume. We assume that the inertia of the burned gases prevents significant gas motion while the end-gas autoignites.

For the pressure data in Fig. P9-7, assume autoignition occurs at 10 crank angle degrees after the top-center position. Determine the maximum pressure reached in the end-gas after knock occurs. From the mass fraction burned and approximate average burned gas conditions at this time, estimate the volume occupied by the end-gas as a fraction of the cylinder volume just before autoignition occurs. Use the charts (Chap. 4) or an equilibrium computer code.

9.10. At spark timing (30° BTC) in an automobile spark-ignition engine (with bore = stroke = 85 mm and $r_c = 9$) at 2000 rev/min, operating on gasoline, the cylinder pressure is 7.5 atm and the mixture temperature is 650 K. The fuel-air mixture is stoichiometric with a residual gas fraction of 8 percent. The rapid burning angle $\Delta\theta_b$ (10 to 90 percent mass burned) is 35°. Estimate (*a*) the mean piston speed; (*b*) the average flame travel speed based on $\Delta\theta_b$ (the spark plug is located 15 mm from the cylinder axis); (*c*) the turbulence intensity at TC [see Eq. (8.23)]; (*d*) the laminar flame speed at spark; (*e*) the turbulent burning speed S_b at TC using Fig. 9-30 (appropriate firing and motored pressures are given in Fig. 9-2*a*); (*f*) the mean expansion speed of the burned gases u_b at TC. Discuss briefly the relative magnitudes of these velocities.

9.11. The following combustion chamber design changes increase the mass burning rate in a spark-ignition engine at fixed compression ratio, bore, speed, and inlet mixture conditions. Explain how each change affects the burning rate.

(*a*) Reducing the amount of EGR.

(*b*) Using two spark plugs per cylinder instead of one.

(*c*) Generating swirl within the cylinder using a mask on the cylinder head (see Fig. 8-14).

(*d*) Using a combustion chamber with higher clearance height near the spark plug and a more central plug location.

9.12. Explain why SI engine torque varies, at fixed speed and inlet mixture conditions, as

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the spark timing is varied from very advanced (e.g., 60° before TC) to close to TC. What is the "best" spark timing? Explain how it varies with engine speed and load.

9.13. (*a*) Explain the causes of the observed variation in cylinder pressure versus crank angle and imep in spark-ignition engines, cycle-by-cycle.
(*b*) What impacts do these cylinder pressure variations have on engine operation?

9.14. (*a*) Describe briefly what occurs when a spark-ignition engine "knocks."
(*b*) SI engine knock is primarily a problem at wide-open throttle and lower engine speeds. Explain why this is the case.
(*c*) With a knock sensor, the normal knock control strategy is to retard the spark timing when knock is detected, until knock no longer occurs. Explain why this strategy is effective and is preferred over other possible approaches (e.g., throttling the inlet, adding EGR).
(*d*) In a knocking engine, the crank angle at which autoignition occurs and the magnitude of the pressure oscillations which result vary substantially, cycle-by-cycle. Suggest reasons why this happens.

9.15. (*a*) The electrical energy stored in a typical ignition system coil is 50 mJ. Almost all this energy is transferred from the coil during the glow discharge phase. If the glow discharge lasts for 2 ms, use the data in Fig. 9-39 to estimate the glow discharge voltage and current.
(*b*) Only a fraction of this energy is transferred to the fuel-air mixture between the spark plug electrodes. Estimate the energy transferred during the breakdown and glow phases of the discharge, using the data in Fig. 9-40.
(*c*) Overall about one-tenth of the coil energy is transferred to the fuel-air mixture. What fraction of the cylinder contents' chemical energy ($m_f Q_{LHV}$) does this correspond to at a typical part-load condition ($p_i = 0.5$ atm, $\phi = 1.0$)? Assume 500 cm^3 per cylinder displaced volume. If the average burned gas temperature within the flame kernal just after spark is 3500 K and the cylinder pressure is 6 atm, what radius of kernal has fuel chemical energy equal to the electrical energy transferred to the kernal?

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CHAPTER 10

COMBUSTION IN COMPRESSION-IGNITION ENGINES

10.1 ESSENTIAL FEATURES OF PROCESS

The essential features of the compression-ignition or diesel engine combustion process can be summarized as follows. Fuel is injected by the fuel-injection system into the engine cylinder toward the end of the compression stroke, just before the desired start of combustion. Figures 1-17, 1-18, and 1-19 illustrate the major components of common diesel fuel-injection systems. The liquid fuel, usually injected at high velocity as one or more jets through small orifices or nozzles in the injector tip, atomizes into small drops and penetrates into the combustion chamber. The fuel vaporizes and mixes with the high-temperature high-pressure cylinder air. Since the air temperature and pressure are above the fuel's ignition point, spontaneous ignition of portions of the already-mixed fuel and air occurs after a delay period of a few crank angle degrees. The cylinder pressure increases as combustion of the fuel-air mixture occurs. The consequent compression of the unburned portion of the charge shortens the delay before ignition for the fuel and air which has mixed to within combustible limits, which then burns rapidly. It also reduces the evaporation time of the remaining liquid fuel. Injection continues until the desired amount of fuel has entered the cylinder. Atomization, vaporization, fuel-air mixing, and combustion continue until essentially all the fuel has passed through each process. In addition, mixing of the air remaining in the cylinder with burning and already burned gases continues throughout the combustion and expansion processes.

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It will be clear from this summary that the compression-ignition combustion process is extremely complex. The details of the process depend on the characteristics of the fuel, on the design of the engine's combustion chamber and fuel-injection system, and on the engine's operating conditions. It is an unsteady, heterogeneous, three-dimensional combustion process. While an adequate conceptual understanding of diesel engine combustion has been developed, to date an ability to describe many of the critical individual processes in a quantitative manner is lacking.

Some important consequences of this combustion process on engine operation are the following:

1. Since injection commences just before combustion starts, there is no knock limit as in the spark-ignition engine resulting from spontaneous ignition of the premixed fuel and air in the end-gas. Hence a higher engine compression ratio can be used in the compression-ignition engine, improving its fuel conversion efficiency relative to the SI engine.
2. Since injection timing is used to control combustion timing, the delay period between the start of injection and start of combustion must be kept short (and reproducible). A short delay is also needed to hold the maximum cylinder gas pressure below the maximum the engine can tolerate. Thus, the spontaneous ignition characteristics of the fuel-air mixture must be held within a specified range. This is done by requiring that diesel fuel have a cetane number (a measure of the ease of ignition of that fuel in a typical diesel environment; see Sec. 10.6.2) above a certain value.
3. Since engine torque is varied by varying the amount of fuel injected per cycle with the engine air flow essentially unchanged, the engine can be operated unthrottled. Thus, pumping work requirements are low, improving part-load mechanical efficiency relative to the SI engine.
4. As the amount of fuel injected per cycle is increased, problems with air utilization during combustion lead to the formation of excessive amounts of soot which cannot be burned up prior to exhaust. This excessive soot or black smoke in the exhaust constrains the fuel/air ratio at maximum engine power to values 20 percent (or more) lean of stoichiometric. Hence, the maximum indicated mean effective pressure (in a naturally aspirated engine) is lower than values for an equivalent spark-ignition engine.
5. Because the diesel always operates with lean fuel/air ratios (and at part load with very lean fuel/air ratios), the effective value of γ $(=c_p/c_v)$ over the expansion process is higher than in a spark-ignition engine. This gives a higher fuel conversion efficiency than the spark-ignition engine, for a given expansion ratio (see Sec. 5.5.3).

The major problem in diesel combustion chamber design is achieving sufficiently rapid mixing between the injected fuel and the air in the cylinder to complete combustion in the appropriate crank angle interval close to top-center. The

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foregoing discussion indicates (and more detailed analysis will confirm) that mixing rates control the fuel burning rate. Commercial diesel engines are made with a very large range of cylinder sizes, with cylinder bores varying from about 70 to 900 mm. The mean piston speed at maximum rated power is approximately constant over this size range (see Sec. 2.2), so the maximum rated *engine* speed will be inversely proportional to the stroke [see Eq. (2.9)]. For a fixed crank angle interval for combustion (of order 40 to 50° to maintain high fuel conversion efficiency), the time available for combustion will, therefore, scale with the stroke. Thus, at the small end of the diesel engine size range, the mixing between the injected fuel and the air must take place on a time scale some 10 times shorter than in engines at the large end of this range. It would be expected, therefore, that the design of the engine combustion chamber (including the inlet port and valve) and the fuel-injection system would have to change substantially over this size range to provide the fuel and air motion inside the cylinder required to achieve the desired fuel-air mixing rate. As engine size decreases, more vigorous air motion is required while less fuel jet penetration is necessary. It is this logic, primarily, that leads to the different diesel combustion chamber designs and fuel injection systems found in practice over the large size range of commercial diesel engines.

10.2 TYPES OF DIESEL COMBUSTION SYSTEMS

Diesel engines are divided into two basic categories according to their combustion chamber design: (1) *direct-injection (DI) engines*, which have a single open combustion chamber into which fuel is injected directly; (2) *indirect-injection (IDI) engines*, where the chamber is divided into two regions and the fuel is injected into the "prechamber" which is connected to the main chamber (situated above the piston crown) via a nozzle, or one or more orifices. IDI engine designs are only used in the smallest engine sizes. Within each category there are several different chamber geometry, air-flow, and fuel-injection arrangements.

10.2.1 Direct-Injection Systems

In the largest-size engines, where mixing rate requirements are least stringent, quiescent direct-injection systems of the type shown in Fig. 10-1a are used. The momentum and energy of the injected fuel jets are sufficient to achieve adequate fuel distribution and rates of mixing with the air. Additional organized air motion is not required. The combustion chamber shape is usually a shallow bowl in the crown of the piston, and a central multihole injector is used.

As engine size decreases, increasing amounts of air swirl are used to achieve faster fuel-air mixing rates. Air swirl is generated by suitable design of the inlet port (see Sec. 8.3); the swirl rate can be increased as the piston approaches TC by forcing the air toward the cylinder axis, into a bowl-in-piston type of combustion

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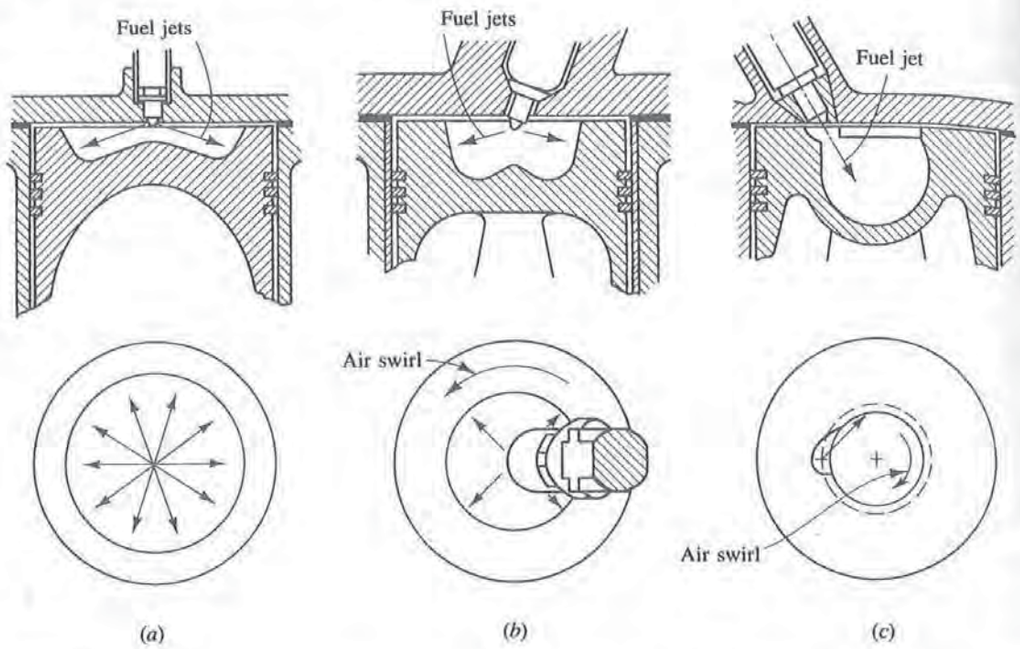


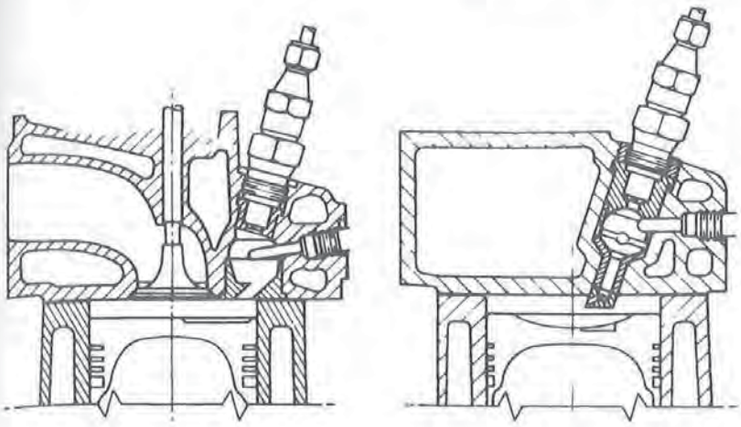
FIGURE 10-1
Common types of direct-injection compression-ignition or diesel engine combustion systems: (*a*) quiescent chamber with multihole nozzle typical of larger engines; (*b*) bowl-in-piston chamber with swirl and multihole nozzle; (*c*) bowl-in-piston chamber with swirl and single-hole nozzle. (*b*) and (*c*) used in medium to small DI engine size range.

chamber. Figure 10-1b and *c* shows the two types of DI engine with swirl in common use. Figure 10-1*b* shows a DI engine with swirl, with a centrally located multihole injector nozzle. Here the design goal is to hold the amount of liquid fuel which impinges on the piston cup walls to a minimum. Figure 10-1*c* shows the M.A.N. "M system" with its single-hole fuel-injection nozzle, oriented so that most of the fuel is deposited on the piston bowl walls. These two types of designs are used in medium-size (10- to 15-cm bore) diesels and, with increased swirl, in small-size (8- to 10-cm bore) diesels.

10.2.2 Indirect-Injection Systems

Inlet generated air swirl, despite amplification in the piston cup, has not provided sufficiently high fuel-air mixing rates for small high-speed diesels such as those used in automobiles. Indirect-injection or divided-chamber engine systems have been used instead, where the vigorous charge motion required during fuel injection is generated during the compression stroke. Two broad classes of IDI systems can be defined: (1) swirl chamber systems and (2) prechamber systems, as illustrated in Fig. 10-2*a* and *b*, respectively. During compression, air is forced from the main chamber above the piston into the auxiliary chamber, through the nozzle or orifice (or set of orifices). Thus, toward the end of compression, a vigorous flow in the auxiliary chamber is set up; in swirl chamber systems the connect-

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(*a*) (*b*)

FIGURE 10-2
Two common types of small indirect-injection diesel engine combustion system: (*a*) swirl prechamber; (*b*) turbulent prechamber.

ing passage and chamber are shaped so that this flow within the auxiliary chamber rotates rapidly.

Fuel is usually injected into the auxiliary chamber at lower injection-system pressure than is typical of DI systems through a pintle nozzle as a single spray, as shown in Fig. 1-18. Combustion starts in the auxiliary chamber; the pressure rise associated with combustion forces fluid back into the main chamber where the jet issuing from the nozzle entrains and mixes with the main chamber air. The glow plug shown on the right of the prechamber in Fig. 10-2 is a cold-starting aid. The plug is heated prior to starting the engine to ensure ignition of fuel early in the engine cranking process.

10.2.3 Comparison of Different Combustion Systems

The number of different combustion chamber types proposed and tried since the beginnings of diesel engine development is substantial. Over the years, however, through the process of evolution and the increased understanding of the physical and chemical processes involved, only a few designs based on a sound principle have survived. The important characteristics of those chambers now most commonly used are summarized in Table 10.1. The numbers for dimensions and operating characteristics are typical ranges for each different type of diesel engine and combustion system.

The largest, slowest speed, engines for power generation or marine applications use open quiescent chambers which are essentially disc shaped; the motion of the fuel jets is responsible for distributing and mixing the fuel. These are usually two-stroke cycle engines. In the next size range, in large truck and locomotive engines, a quiescent chamber consisting of a shallow dish or bowl in the

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TABLE 10.1
Characteristics of Common Diesel Combustion Systems

	Direct injection				Indirect injection	
System	**Quiescent**	**Medium swirl**	**High swirl "M"**	**High swirl multispray**	**Swirl chamber**	**Pre-chamber**
Size	Largest	Medium	Medium—smaller	Medium—small	Smallest	Smallest
Cycle	2-/4-stroke	4-stroke	4-stroke	4-stroke	4-stroke	4-stroke
Turbocharged/supercharged/naturally aspirated	TC/S	TC/NA	TC/NA	NA/TC	NA/TC	NA/TC
Maximum speed, rev/min	120–2100	1800–3500	2500–5000	3500–4300	3600–4800	4500
Bore, mm	900–150	150–100	130–80	100–80	95–70	95–70
Stroke/bore	3.5–1.2	1.3–1.0	1.2–0.9	1.1–0.9	1.1–0.9	1.1–0.9
Compression ratio	12–15	15–16	16–18	16–22	20–24	22–24
Chamber	Open or shallow dish	Bowl-in-piston	Deep bowl-in-piston	Deep bowl-in-piston	Swirl pre-chamber	Single/multi-orifice pre-chamber
Air-flow pattern	Quiescent	Medium swirl	High swirl	Highest swirl	Very high swirl in pre-chamber	Very turbulent in pre-chamber
Number of nozzle holes	Multi	Multi	Single	Multi	Single	Single
Injection pressure	Very high	High	Medium	High	Lowest	Lowest

piston crown is often used. The air utilization in these engines is low, but they are invariably supercharged or turbocharged to obtain high power density.

In the DI category, as engine size decreases and maximum speed rises, swirl is used increasingly to obtain high-enough fuel-air mixing rates. The swirl is generated by suitably shaped inlet ports, and is amplified during compression by forcing most of the air toward the cylinder axis into the deep bowl-in-piston combustion chamber. In about the same size range, an alternative system to the multihole nozzle swirl system is the M.A.N. "M" system (or wall-wetting system), where most of the fuel from the single-hole pintle nozzle is placed on the wall of the spherical bowl in the piston crown.

In the smallest engine sizes, the IDI engine has traditionally been used to obtain the vigorous air motion required for high fuel-air mixing rates. There are several different geometries in use. These either generate substantial swirl in the

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auxiliary chamber during the latter part of the compression stroke, using a nozzle or connecting passage that enters the auxiliary chamber tangentially, or they generate intense turbulence in the prechamber through use of several small orifices and obstructions to the flow within the prechamber. The most common design of swirl chamber is the Ricardo Comet design shown in Fig. 10-2*a*. An alternative IDI engine to the two types listed in Table 10-1 is the air cell system. In that system the fuel is injected into the main chamber and not the auxiliary "air cell." The auxiliary chamber acts as a turbulence generator as gas flows into and out of the cell.

10.3 PHENOMENOLOGICAL MODEL OF COMPRESSION-IGNITION ENGINE COMBUSTION

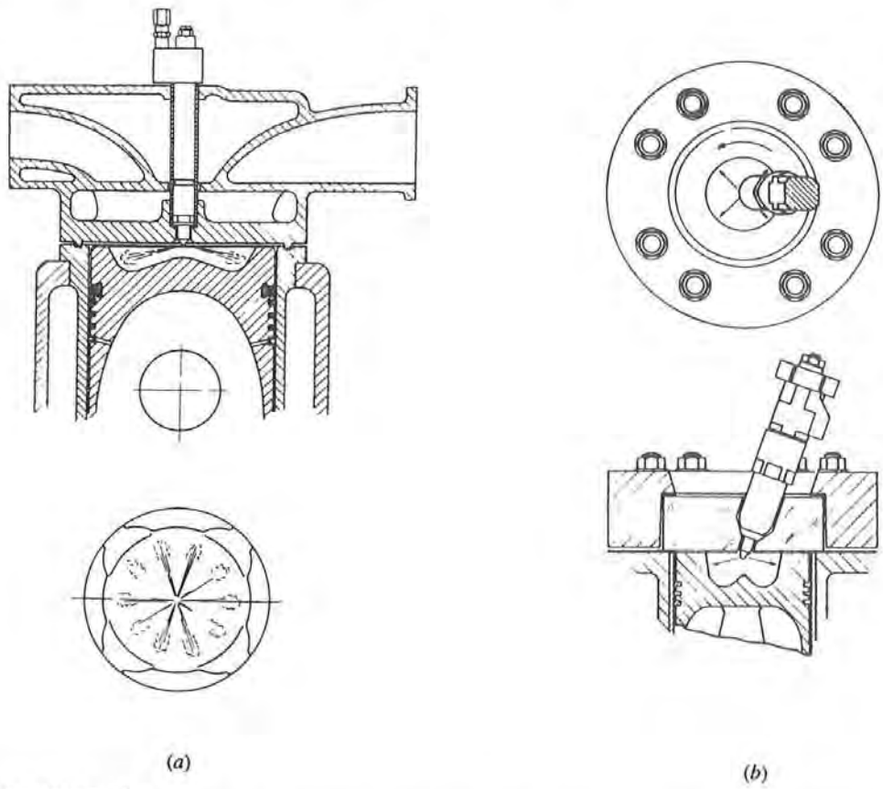
Studies of photographs of diesel engine combustion, combined with analyses of engine cylinder pressure data, have led to a widely accepted descriptive model of the compression-ignition engine combustion process. The concept of *heat-release rate* is important to understanding this model. It is defined as the rate at which the chemical energy of the fuel is released by the combustion process. It can be calculated from cylinder pressure versus crank angle data, as the energy release required to create the measured pressure, using the techniques described in Sec. 10.4. The combustion model defines four separate phases of diesel combustion, each phase being controlled by different physical or chemical processes. Although the relative importance of each phase does depend on the combustion system used, and engine operating conditions, these four phases are common to all diesel engines.

10.3.1 Photographic Studies of Engine Combustion

High-speed photography at several thousand frames per second has been used extensively to study diesel engine combustion. Some of these studies have been carried out in combustion chambers very close to those used in practice, under normal engine operating conditions (e.g., Refs. 1 and 2). Sequences of individual frames from movies provide valuable information on the nature of the combustion process in the different types of diesel engines. Figure 10-3 shows four combustion chamber geometries that have been studied photographically. These are: (*a*) a quiescent chamber typical of diesel engines in the 3 to 20 dm^3/cylinder displacement used for industrial, marine, and rail traction applications (only the burning of a single fuel spray of the multispray combustion system could be studied[2]); (*b*) a smaller high-speed DI engine with swirl and four fuel jets centrally injected; (*c*) an M.A.N. "M" DI system; and (*d*) a Ricardo Comet V swirl chamber IDI system.[1]

The combustion sequences were recorded on color film and show the following features:

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(*a*) (*b*)

FIGURE 10-3
Four diesel combustion chambers used to obtain photographs of the compression-ignition combustion process shown in Fig. 10-4 on color plate: (*a*) quiescent DI chamber; (*b*) multihole nozzle DI chamber with swirl: on p. 499; (*c*) M.A.N. "M" DI chamber; (*d*) Ricardo Comet IDI swirl chamber.[1,2]

Fuel spray(s). The fuel droplets reflect light from spot lamps and define the extent of the liquid fuel spray prior to complete vaporization.

Premixed flame. These regions are of too low a luminosity to be recorded with the exposure level used. The addition of a copper additive dope to the fuel gives these normally blue flames a green color bright enough to render them visible.

Diffusion flame. The burning high-temperature carbon particles in this flame provide more than adequate luminosity and appear as yellow-white. As the flame cools, the radiation from the particles changes color through orange to red.

Over-rich mixture. The appearance of a brown region, usually surrounded by a white diffusion flame, indicates an excessively rich mixture region where substantial soot particle production has occurred. Where this fuel-rich soot-laden cloud contacts unburned air there is a hot white diffusion flame.

Table 10.2 summarizes the characteristics of these different regions, discernable in the photographs shown in Fig. 10-4 on the color plate.

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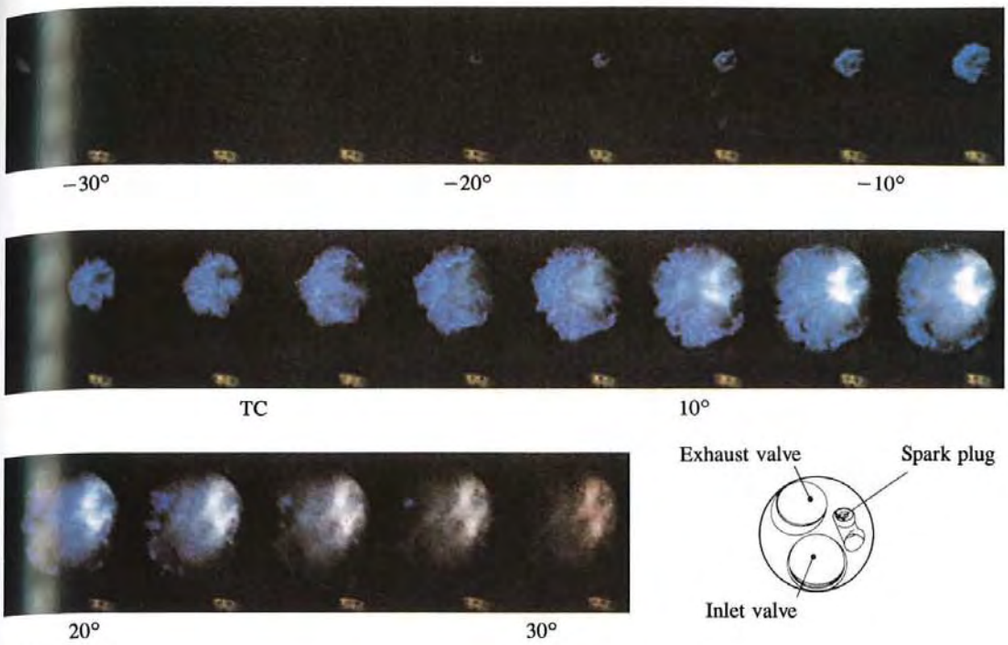


FIGURE 9-1

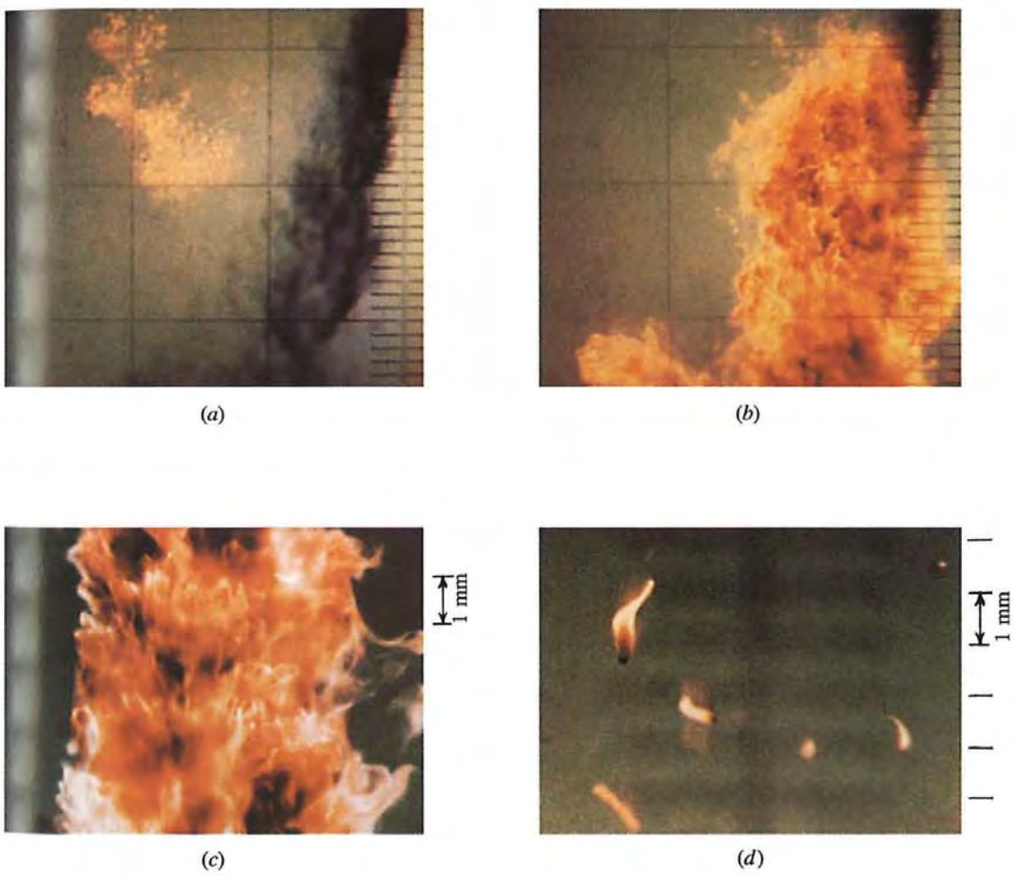


FIGURE 10-5

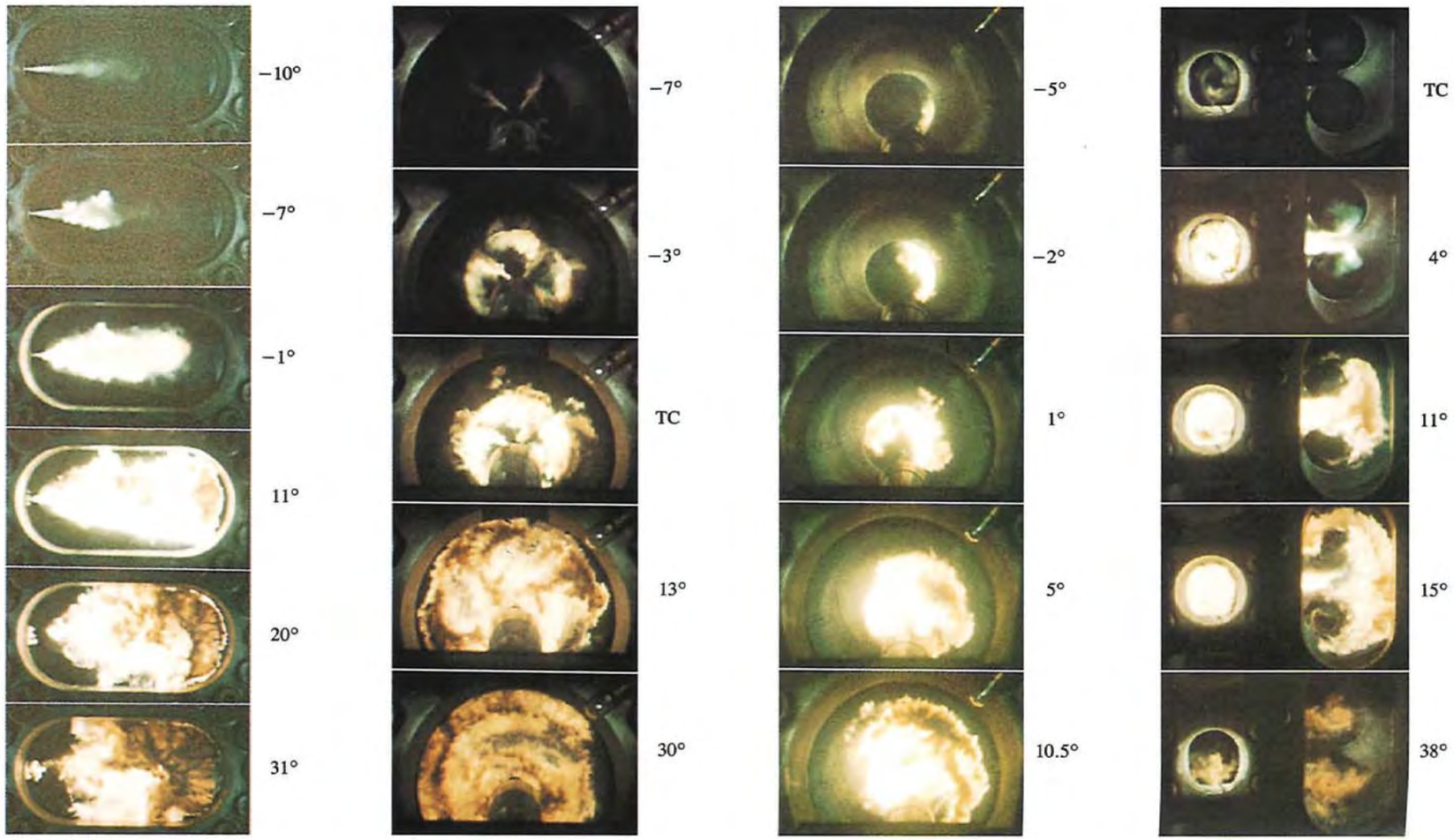
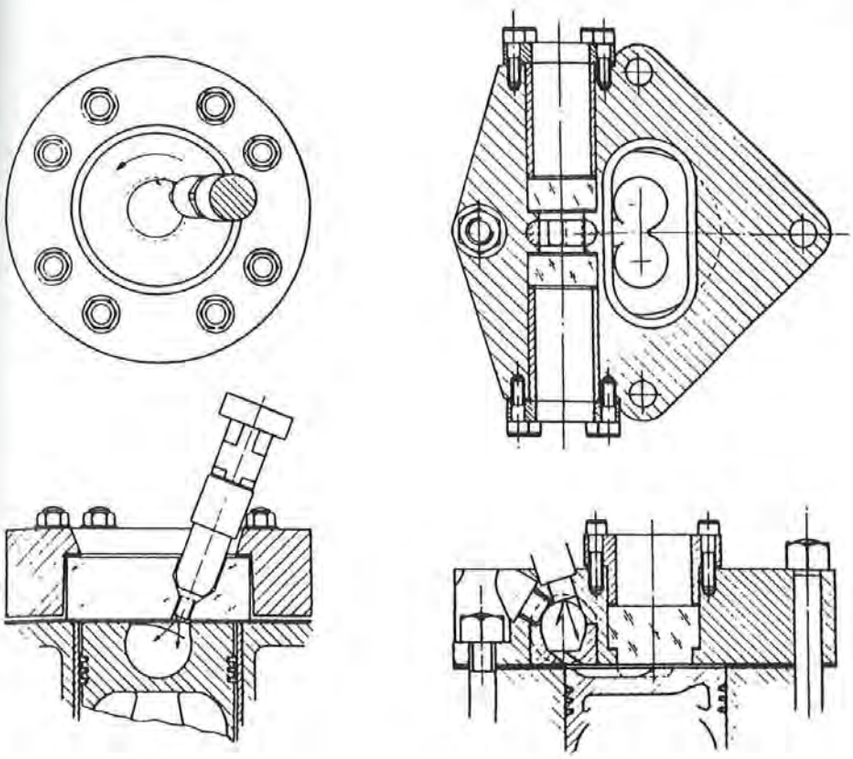


FIGURE 10-4

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(*c*) (*d*)

Figure 10-4*a* shows a sequence of photographs from one combustion event of the single spray, burning under conditions typical of a large quiescent DI engine. The fuel spray is shown penetrating into the chamber. Ignition occurs at $-8°$ in the fuel-air mixture left behind on the edge of the spray not far from the injector. The flame then spreads rapidly ($-7°$) along the outside of the spray to the spray tip. Here some of the fuel, which has had a long residence time in the chamber, burns with a blue-green low-luminosity flame (colored green by the copper fuel additive). The flame engulfing the remainder of the spray is brilliant white-yellow from the burning of the soot particles which have been formed in

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FIGURE 10-4 (On Color Plate, facing this page)
Sequence of photographs from high-speed movies taken in special visualization diesel engines shown in Fig. 10-3: (*a*) combustion of single spray burning under large DI engine conditions; (*b*) combustion of four sprays in DI engine with counterclockwise swirl; (*c*) combustion of single spray in M.A.N. "M" DI diesel; (*d*) combustion in prechamber (on left) and main chamber (on right) in Ricardo Comet IDI swirl chamber diesel. 1250 rev/min, imep = 827 kPa (120 lb/in^2)$^{1.2}$ (*Courtesy Ricardo Consulting Engineers.*)

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TABLE 10.2
Interpretation of diesel engine combustion color photographs[1]

Color	Interpretation
Grey	Background; the gas (air in early stages, combustion products later) is transparent and not glowing
Green	Early in combustion process; low luminosity "premixed"-type flame, rendered visible by copper added to fuel. Later; burned gas above about 1800°C
White, and yellow-white	Carbon particle burnup in diffusion flame, 2000–2500°C
Yellow, orange-red	Carbon burnup in diffusion flame at lower temperatures; last visible in film at 1000°C
Brown	Soot clouds from very fuel-rich mixture regions. Where these meet air (grey) there is always a white fringe of hot flame

the fuel-rich spray core. At this stage (−1°), about 60 percent of the fuel has been injected. The remainder is injected into this enflamed region, producing a very fuel-rich zone apparent as the dark brown cloud (11°). This soot cloud moves to the outer region of the chamber (11° to 20°); white-yellow flame activity continues near the injector, probably due to combustion of ligaments of fuel which issued from the injector nozzle as the injector needle was seating. Combustion continues well into the expansion stroke (31°C).

This sequence shows that fuel distribution is always highly nonuniform during the combustion process in this type of DI engine. Also the air which is between the individual fuel sprays of the quiescent open-chamber diesel mixes with each burning spray relatively slowly, contributing to the poor air utilization with this type of combustion chamber.

Figure 10-4*b* shows a combustion sequence from the DI engine with swirl (the chamber shown in Fig. 10-3*b*). The inner circle corresponds to the deep bowl in the piston crown, the outer circle to the cylinder liner. The fuel sprays (of which two are visible without obstruction from the injector) first appear at −13°. At −7° they have reached the wall of the bowl; the tips of the sprays have been deflected slightly by the anticlockwise swirl. The frame at −3° shows the first ignition. Bright luminous flame zones are visible, one on each spray. Out by the bowl walls, where fuel vapor has been blown around by the swirl, larger greenish burning regions indicating the presence of premixed flame can be seen. The fuel downstream of each spray is next to ignite, burning yellow-white due to the soot

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formed by the richer mixture. Flame propagation back to the injector follows extremely rapidly and at TC the bowl is filled with flame. At 5° ATC the flame spreads out over the piston crown toward the cylinder wall due to combustion-produced gas expansion and the reverse squish flow (see Sec. 8.4). The brown regions (13°) are soot-laden fuel-rich mixture originating from the fuel which impinges on the wall. The last frame (30° ATC) shows the gradual diminution of the soot-particle-laden regions as they mix with the excess air and burn up. The last dull-red flame visible on the film is at about 75° ATC, well into the expansion stroke.

Figure 10-4*c* shows the combustion sequence for the M.A.N. "M"-type DI engine. In the version of the system used for these experiments, the fuel was injected through a two-hole nozzle which produces a main jet directed tangentially onto the walls of the spherical cup in the piston crown, and an auxiliary spray which mixes a small fraction of the fuel directly with the swirling air flow. More recent "M" systems use a pintle nozzle with a single variable orifice.[3] At $-5°$ the fuel spray is about halfway round the bowl. Ignition has just occurred of fuel adjacent to the wall which has mixed sufficiently with air to burn. The flame spreads rapidly ($-2°$, 1°) to envelop the fuel spray, and is convected round the cup by the high swirl air flow. By shortly after TC the flame has filled the bowl and is spreading out over the piston crown. A soot cloud is seen near the top right of the picture at 5° ATC which spreads out around the circumference of the enflamed region. There is always a rim of flame between the soot cloud and the cylinder liner as excess air is mixed into the flame zone (10.5°). The flame is of the carbon-burning type throughout; little premixed green flame is seen even at the beginning of the combustion process.

Figure 10-4*d* shows the combustion sequence in a swirl chamber IDI engine of the Ricardo Comet V design. The swirl chamber (on the left) is seen in the view of the lower drawing of Fig. 10-3*d* (with the connecting passageway entering the swirl chamber tangentially at the bottom left to produce clockwise swirl). The main chamber is seen in the plan view of the upper drawing of Fig. 10-3*d*. Two sprays emerge from the Pintaux nozzle after the start of injection at $-11°$. The smaller auxiliary spray which is radial is sharply deflected by the high swirl. Frame 1 shows how the main spray follows the contour of the chamber; the auxiliary spray has evaporated and can no longer be seen. The first flame occurs at $-1°$ in the vaporized fuel from the auxiliary spray and is a green premixed flame. The flame then spreads to the main spray (TC), becoming a yellow-white carbon-particle-burning flame with a green fringe. At 4° ATC the swirl chamber appears full of carbon-burning flame, which is being blown down the throat and into the recesses in the piston crown by the combustion generated pressure rise in the prechamber. The flame jet impinges on the piston recesses entraining the air in the main chamber, leaving green patches where all carbon is burned out (4°, 11°, 15°). A brown soot cloud is emerging from the throat. By 15° ATC this soot cloud has spread around the cylinder, with a bright yellow-white flame at its periphery. This soot then finds excess air and burns up, while the yellow-white

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flame becomes yellow and then orange-red as the gases cool on expansion. By 38° ATC most of the flame is burnt out.

Magnified color photographs of the flame around a single fuel spray under conditions typical of a direct-injection diesel engine, shown in Fig. 10-5 on the color plate, provide additional insight into the compression-ignition and flame-development processes.[4] These photographs were obtained in a rapid compression machine: this device is a cylinder-piston apparatus in which air is rapidly compressed by moving the piston to temperatures and pressures similar to those in the diesel engine combustion chamber at the time of injection. A single fuel spray was then injected into the disc-shaped combustion chamber. The air flow prior to compression was forced to swirl around the cylinder axis and much of that swirl remains after compression.

Figure 10-5*a* shows a portion of the liquid fuel spray (which appears black due to back lighting) and the rapidly developing flame 0.4 ms after ignition occurs. Ignition commences in the *fuel vapor*–air mixture region, set up by the jet motion and swirling air flow, away from the liquid core of the spray. In this region the smaller fuel droplets have evaporated in the hot air atmosphere that surrounds them and mixed with sufficient air for combustion to occur. Notice that the fuel vapor concentration must be nonuniform; combustion apparently occurs around small "lumps" of mixture of the appropriate composition and temperature. Figure 10-5*b* shows the same flame at a later time, 3.2 ms after ignition. The flame now surrounds most of the liquid spray core. Its irregular boundary reflects the turbulent character of the fuel spray and its color variation indicates that the temperature and composition in the flame region are not uniform.

Figure 10-5*c* shows a portion of this main flame region enlarged to show its internal structure. A highly convoluted flame region is evident, which has a similar appearance to a gaseous turbulent diffusion flame. The major portion of the diesel engine flame has this character, indicative of the burning of fuel vapor–air pockets or lumps or eddies of the appropriate composition. Only at the end of the combustion process is there visible evidence of individual fuel droplets burning with an envelope flame. Figure 10-5*d* shows the same region of the combustion chamber as Fig. 10-5*c*, but at the end of the burning process well after injection has been completed. A few large droplets are seen burning with individual droplet flames. It is presumed that such large drops were formed at the end of the injection process as the injector nozzle was closing.

FIGURE 10-5 (On Color Plate, facing page 498)
Photographs from high-speed movie of single fuel spray injected into a swirling air flow in a rapid-compression machine. (*a*) Spray and flame 0.4 ms after ignition; scale on right in millimeters. (*b*) Flame surrounding spray 3.2 ms after ignition. (*c*) Magnified photograph of main portion of flame. (*d*) Individual droplet burning late in combustion process after injection completed. Air temperature ~500°C. 50 mg fuel injected.[4] (*Courtesy Professor M. Ogasawara, Osaka University.*)

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10.3.2 Combustion in Direct-Injection, Multispray Systems

Figure 10-6 shows typical data for cylinder pressure (p), fuel-injector needle-lift, and fuel pressure in the nozzle gallery through the compression and expansion strokes of a direct-injection diesel. The engine had central fuel injection through a four-hole nozzle into a disc-shaped bowl-in-piston combustion chamber. The rate of fuel injection can be obtained from the fuel-line pressure, cylinder pressure, nozzle geometry, and needle-lift profiles by considering the injector as one or more flow restrictions;[5] it is similar in phasing and comparable in shape to the needle-lift profile. There is a delay of 9° between the start of injection and start of combustion [identified by the change in slope of the $p(\theta)$ curve]. The pressure rises rapidly for a few crank angle degrees, then more slowly to a peak value about 5° after TC. Injection continues after the start of combustion. A rate-of-heat-release diagram† from the same study, corresponding to this rate of fuel injection and cylinder pressure data, is shown in Fig. 10-7. The general shape of the rate-of-heat-release curve is typical of this type of DI engine over its load and speed range. The heat-release-rate diagram shows negligible heat release until toward the end of compression when a slight loss of heat during the delay period (which is due to heat transfer to the walls and to fuel vaporization and heating) is

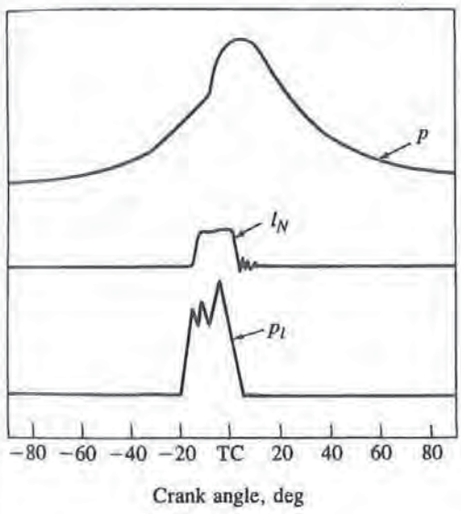


FIGURE 10-6
Cylinder pressure p, injector needle lift l_N, and injection-system fuel-line pressure p_l, as functions of crank angle for small DI diesel engine.[5]

† The heat-release rate plotted here is the net heat-release rate (see Sec. 10.4). It is the sum of the change of sensible internal energy of the cylinder gases and the work done on the piston. It differs from the rate of fuel energy released by combustion by the heat transferred to the combustion chamber walls. The heat loss to the walls is 10 to 25 percent of the fuel heating value in smaller engines; it is less in larger engine sizes. This net heat release can be used as an indicator of actual heat release when the heat loss is small.

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evident. During the combustion process the burning proceeds in three distinguishable stages. In the first stage, the rate of burning is generally very high and lasts for only a few crank angle degrees. It corresponds to the period of rapid cylinder pressure rise. The second stage corresponds to a period of gradually decreasing heat-release rate (though it initially may rise to a second, lower, peak as in Fig. 10-7). This is the main heat-release period and lasts about 40°. Normally about 80 percent of the total fuel energy is released in the first two periods. The third stage corresponds to the "tail" of the heat-release diagram in which a small but distinguishable rate of heat release persists throughout much of the expansion stroke. The heat release during this period usually amounts to about 20 percent of the total fuel energy.

From studies of rate-of-injection and heat-release diagrams such as those in Fig. 10-7, over a range of engine loads, speeds, and injection timings, Lyn[6] developed the following summary observations. First, the total burning period is much longer than the injection period. Second, the absolute burning rate increases proportionally with increasing engine speed; thus on a crank angle basis, the burning interval remains essentially constant. Third, the magnitude of the initial peak of the burning-rate diagram depends on the ignition delay period, being higher for longer delays. These considerations, coupled with engine combustion photographic studies, lead to the following model for diesel combustion.

Figure 10-8 shows schematically the rate-of-injection and rate-of-burning diagrams, where the injected fuel as it enters the combustion chamber has been divided into a number of elements. The first element which enters mixes with air and becomes "ready for burning" (i.e., mixes to within combustible limits), as shown conceptually by the lowest triangle along the abscissa in the rate-of-burning figure. While some of this fuel mixes rapidly with air, part of it will mix much more slowly. The second and subsequent elements will mix with air in a similar manner, and the total "ready-for-burning" diagram, enclosed by the dashed line, is obtained. The total area of this diagram is equal to that of the rate-of-injection diagram. Ignition does not occur until after the delay period is over, however. At the ignition point, some of the fuel already injected has mixed with enough air to be within the combustible limits. That "premixed" fuel-air

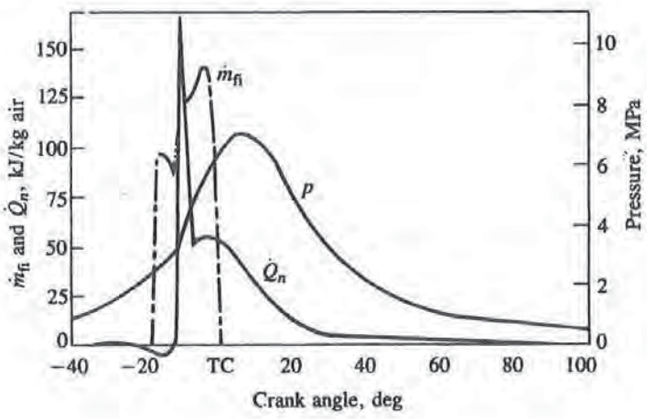


FIGURE 10-7
Cylinder pressure p, rate of fuel injection $\dot{m}_{fi}$, and net heat-release rate $\dot{Q}_n$ calculated from p for small DI diesel engine, 1000 rev/min, normal injection timing, bmep = 620 kPa.[5]

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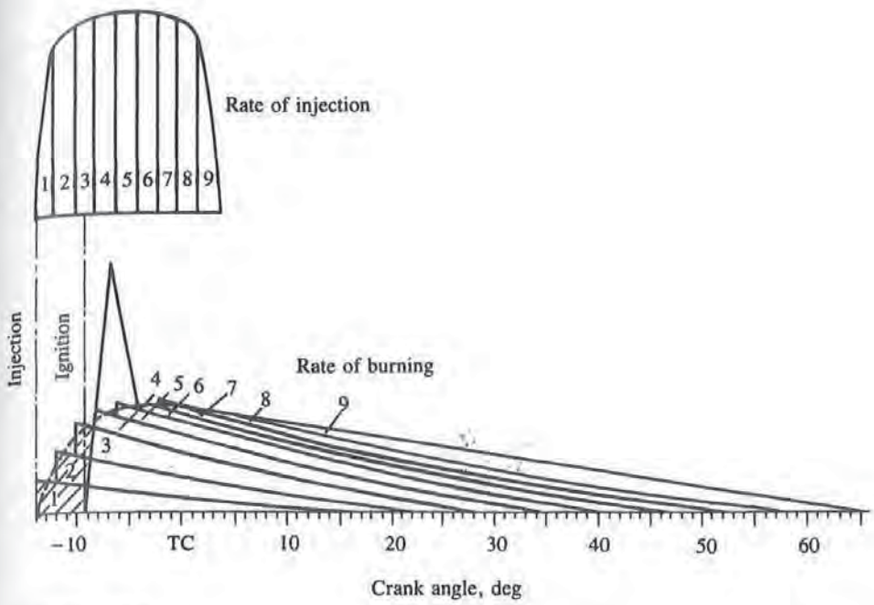


FIGURE 10-8
Schematic of relationship between rate of fuel injection and rate of fuel burning or energy release.[6]

mixture (the shaded region in Fig. 10-8) is then added to the mixture which becomes ready for burning after the end of the delay period, producing the high initial rate of burning as shown. Such a heat-release profile is generally observed with this type of naturally aspirated DI diesel engine. Photographs (such as those in Fig. 10-4*a* and *b*) show that up to the heat-release-rate peak, flame regions of low green luminosity are apparent because the burning is predominantly of the premixed part of the spray. After the peak, as the amount of premixed mixture available for burning decreases and the amount of fresh mixture mixed to be "ready for burning" increases, the spray burns essentially as a turbulent diffusion flame with high yellow-white or orange luminosity due to the presence of carbon particles.

To summarize, the following stages of the overall compression-ignition diesel combustion process can be defined. They are identified on the typical heat-release-rate diagram for a DI engine in Fig. 10-9.

Ignition delay (*ab*). The period between the start of fuel injection into the combustion chamber and the start of combustion [determined from the change in slope on the p-θ diagram, or from a heat-release analysis of the $p(\theta)$ data, or from a luminosity detector].

Premixed or rapid combustion phase (*bc*). In this phase, combustion of the fuel which has mixed with air to within the flammability limits during the ignition delay period occurs rapidly in a few crank angle degrees. When this burning mixture is added to the fuel which becomes ready for burning and burns during this phase, the high heat-release rates characteristic of this phase result.

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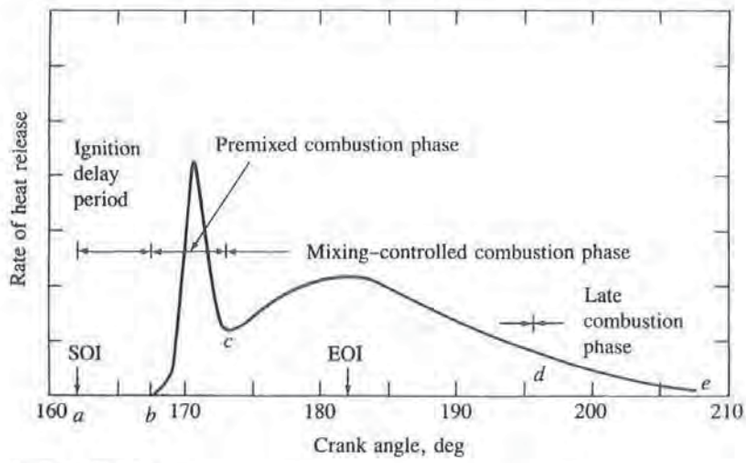


FIGURE 10-9
Typical DI engine heat-release-rate diagram identifying different diesel combustion phases.

Mixing-controlled combustion phase (*cd*). Once the fuel and air which premixed during the ignition delay have been consumed, the burning rate (or heat-release rate) is controlled by the rate at which mixture becomes available for burning. While several processes are involved—liquid fuel atomization, vaporization, mixing of fuel vapor with air, preflame chemical reactions—the rate of burning is controlled in this phase primarily by the fuel vapor–air mixing process. The heat-release rate may or may not reach a second (usually lower) peak in this phase; it decreases as this phase progresses.

Late combustion phase (*de*). Heat release continues at a lower rate well into the expansion stroke. There are several reasons for this. A small fraction of the fuel may not yet have burned. A fraction of the fuel energy is present in soot and fuel-rich combustion products and can still be released. The cylinder charge is nonuniform and mixing during this period promotes more complete combustion and less-dissociated product gases. The kinetics of the final burnout processes become slower as the temperature of the cylinder gases fall during expansion.

10.3.3 Application of Model to Other Combustion Systems

In the M.A.N. "M" DI engine system, and in IDI systems, the shapes of the heat-release-rate curve are different from those of the quiescent or moderate swirl DI shown in Figs. 10-7 and 10-9. With the "M" system, the initial heat-release "spike" is much less pronounced (in spite of the fact that a large fraction of the fuel is injected during the delay period) though the total burning period is about the same. Lyn[6] has suggested that the lower initial burning rate is due to the fact that the smaller number of nozzle holes (one or two instead of about four or more) and the directing of the main spray tangentially to the wall substantially reduce the free mixing surface area of the fuel jets. However, since the burning

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rates after ignition are relatively high, mixing must speed up. This occurs due to the centrifugal forces set up in the swirling flow. Initially, the fuel is placed near the wall, and mixing is inhibited by the effect of the high centrifugal forces on the fuel vapor which is of higher density than the air and so tends to remain near the wall. Once ignition occurs, the hot burning mixture expands, decreases in density, and is then moved rapidly toward the center of the chamber. This strong radial mixing is the rate-determining process. An additional delaying mechanism exists if significant fuel is deposited on the wall. At compression air temperatures, the heat transferred to the fuel film on the wall from the gases in the cylinder is too small to account for the observed burning rates. Only after combustion starts will the gas temperature and heat-transfer rates be high enough to evaporate the fuel off the wall at an adequate rate.

In the swirl chamber IDI engine, where the air in the main chamber is not immediately available for mixing, again the rate-determining processes are different.[6] There is no initial spike on the rate-of-heat-release curve as was the case with DI engines. The small size of the chamber, together with the high swirl rate generated just before injection, results in considerable fuel impingement on the walls. This and the fact that the ignition delay is usually shorter with the IDI engine due to the higher compression ratio used account for the low initial burning rate.

Based on the above discussion Lyn[6] proposed three basic injection, mixing, and burning patterns important in diesel engines:

A. Fuel injection across the chamber with substantial momentum. Mixing proceeds immediately as fuel enters the chamber and is little affected by combustion.
B. Fuel deposition on the combustion chamber walls. Negligible mixing during the delay period due to limited evaporation. After ignition, evaporation becomes rapid and its rate is controlled by access of hot gases to the surface, radial mixing being induced by differential centrifugal forces. Burning is therefore delayed by the ignition lag.
C. Fuel distributed near the wall: mixing proceeds during the delay, but at a rate smaller than in mechanism A. After ignition, mixing is accelerated by the same mechanism as in mechanism B.

Figure 10-10 shows, schematically, the construction of the burning-rate or heat-release-rate diagrams (from the same injection-rate diagram) for the DI diesel combustion system with a central multihole nozzle, for the "M"-type DI diesel, and for the swirl chamber IDI. For the DI engine with multihole nozzle, mechanism A is predominant. For the DI engine with fuel sprayed tangentially to the wall, mechanisms B and C prevail; the delayed mixing prevents excessively high initial burning rates. For the IDI swirl chamber engine, the shorter ignition delay together with mixing process C during the delay period produces a gradual increase in burning rate, as shown in Fig. 10-10*c*.

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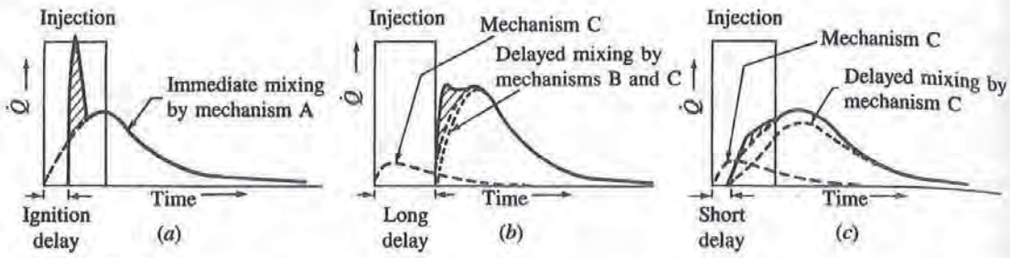


FIGURE 10-10
Schematic injection-rate and burning-rate diagrams in three different types of naturally aspirated diesel combustion system: (*a*) DI engine with central multihole nozzle; (*b*) DI "M"-type engine with fuel injected on wall; (*c*) IDI swirl chamber engine. Mechanisms A, B, and C defined in text.[6]

10.4 ANALYSIS OF CYLINDER PRESSURE DATA

Cylinder pressure versus crank angle data over the compression and expansion strokes of the engine operating cycle can be used to obtain quantitative information on the progress of combustion. Suitable methods of analysis which yield the rate of release of the fuel's chemical energy (often called heat release), or rate of fuel burning, through the diesel engine combustion process will now be described. The methods of analysis are similar to those described in Sec. 9.2.2 for spark-ignition engines and start with the first law of thermodynamics for an open system which is quasi static (i.e., uniform in pressure and temperature). The first law for such a system (see Fig. 9-11) is

$$\frac{dQ}{dt} - p\frac{dV}{dt} + \sum_i \dot{m}_i h_i = \frac{dU}{dt} \tag{10.1}$$

where dQ/dt is the heat-transfer rate across the system boundary into the system, $p(dV/dt)$ is the rate of work transfer done by the system due to system boundary displacement, $\dot{m}_i$ is the mass flow rate into the system across the system boundary at location i (flow out of the system would be negative), h_i is the enthalpy of flux i entering or leaving the system, and U is the energy of the material contained inside the system boundary.

The following problems make the application of this equation to diesel combustion difficult:

1. Fuel is injected into the cylinder. Liquid fuel is added to the cylinder which vaporizes and mixes with air to produce a fuel/air ratio distribution which is nonuniform and varies with time. The process is not quasi static.
2. The composition of the burned gases (also nonuniform) is not known.
3. The accuracy of available correlations for predicting heat transfer in diesel engines is not well defined (see Chap. 12).
4. Crevice regions (such as the volumes between the piston, rings, and cylinder wall) constitute a few percent of the clearance volume. The gas in these regions is cooled to close to the wall temperature, increasing its density and, therefore,

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the relative importance of these crevices. Thus crevices increase heat transfer and contain a nonnegligible fraction of the cylinder charge at conditions that are different from the rest of the combustion chamber.

Due to difficulties in dealing with these problems, both sophisticated methods of analysis and more simple methods give only approximate answers.

10.4.1 Combustion Efficiency

In both heat-release and fuel mass burned estimations, an important factor is the completeness of combustion. Air utilization in diesels is limited by the onset of black smoke in the exhaust. The smoke is soot particles which are mainly carbon. While smoke and other incomplete combustion products such as unburned hydrocarbons and carbon monoxide represent a combustion inefficiency, the magnitude of that inefficiency is small. At full load conditions, if only 0.5 percent of the fuel supplied is present in the exhaust as black smoke, the result would be unacceptable. Hydrocarbon emissions are the order of or less than 1 percent of the fuel. The fuel energy corresponding to the exhausted carbon monoxide is about 0.5 percent. Thus, the combustion inefficiency [Eq. (4.69)] is usually less than 2 percent; the combustion efficiency is usually greater than about 98 percent (see Fig. 3-9). While these emissions are important in terms of their air-pollution impact (see Chap. 11), from the point of view of energy conversion it is a good approximation to regard combustion and heat release as essentially complete.

10.4.2 Direct-Injection Engines

For this type of engine, the cylinder contents are a single open system. The only mass flows across the system boundary (while the intake and exhaust valves are closed) are the fuel and the crevice flow. An approach which incorporates the crevice flow has been described in Sec. 9.2.2; crevice flow effects will be omitted here. Equation (10.1) therefore becomes

$$\frac{dQ}{dt} - p\frac{dV}{dt} + \dot{m}_f h_f = \frac{dU}{dt} \tag{10.2}$$

Two common methods are used to obtain combustion information from pressure data using Eq. (10.2). In both approaches, the cylinder contents are assumed to be at a uniform temperature at each instant in time during the combustion process. One method yields fuel energy- or heat-release rate; the other method yields a fuel mass burning rate. The term *apparent* is often used to describe these quantities since both are approximations to the real quantities which cannot be determined exactly.

HEAT-RELEASE ANALYSIS. If U and h_f in Eq. (10.2) are taken to be the sensible internal energy of the cylinder contents and the sensible enthalpy of the injected

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fuel, respectively,† then dQ/dt becomes the difference between the chemical energy or heat released by combustion of the fuel (a positive quantity) and the heat transfer from the system (in engines, the heat transfer is from the system and by thermodynamic convention is a negative quantity). Since $h_{s,f} \approx 0$, Eq. (10.2) becomes

$$\frac{dQ_n}{dt} = \frac{dQ_{ch}}{dt} - \frac{dQ_{ht}}{dt} = p\frac{dV}{dt} + \frac{dU_s}{dt} \tag{10.3}$$

The apparent *net heat-release* rate, dQ_n/dt, which is the difference between the apparent *gross heat-release* rate dQ_{ch}/dt and the heat-transfer rate to the walls dQ_{ht}/dt, equals the rate at which work is done on the piston plus the rate of change of sensible internal energy of the cylinder contents.

If we further assume that the contents of the cylinder can be modeled as an ideal gas, then Eq. (10.3) becomes

$$\frac{dQ_n}{dt} = p\frac{dV}{dt} + mc_v\frac{dT}{dt} \tag{10.4}$$

From the ideal gas law, $pV = mRT$, with R assumed constant, it follows that

$$\frac{dp}{p} + \frac{dV}{V} = \frac{dT}{T} \tag{10.5}$$

Equation (10.5) can be used to eliminate T from Eq. (10.4) to give

$$\frac{dQ_n}{dt} = \left(1 + \frac{c_v}{R}\right)p\frac{dV}{dt} + \frac{c_v}{R}V\frac{dp}{dt}$$

or

$$\frac{dQ_n}{dt} = \frac{\gamma}{\gamma - 1}p\frac{dV}{dt} + \frac{1}{\gamma - 1}V\frac{dp}{dt} \tag{10.6}$$

Here γ is the ratio of specific heats, c_p/c_v. An appropriate range for γ for diesel heat-release analysis is 1.3 to 1.35; Eq. (10.6) is often used with a constant value of γ within this range. More specifically, we would expect γ for diesel engine heat-release analysis to have values appropriate to air at end-of-compression-stroke temperatures prior to combustion ($\approx$1.35) and to burned gases at the overall equivalence ratio following combustion ($\approx$1.26–1.3). The appropriate values for γ during combustion which will give most accurate heat-release information are not well defined.[7, 8]

More complete methods of heat-release analysis based on Eq. (10.2) have been proposed and used. These use more sophisticated models for the gas properties before, during, and after combustion, and for heat transfer and crevice effects.[8] However, it is also necessary to deal with the additional issues of: (1) mixture nonuniformity (fuel/air ratio nonuniformity *and* burned and unburned gas nonuniformities); (2) accuracy of any heat-transfer model used (see Chap. 12);

† That is, $U = U_s = U(T) - U(298\text{ K})$ and $h_f = h_{s,f} = h_f(T) - h_f(298\text{ K})$; see Sec. 5.5 for definition.

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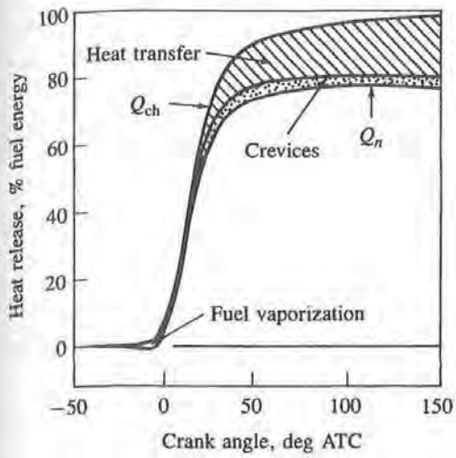


FIGURE 10-11
Gross and net heat-release profile during combustion, for a turbocharged DI diesel engine in mid-load, mid-speed range, showing relative magnitude of heat transfer, crevice, and fuel vaporization and heatup effects.

and (3) the effects of the crevice regions. These additional phenomena must be dealt with at an equivalent level of accuracy for more complex heat-release models to be worth while. For many engineering applications, Eq. (10.6) is adequate for diesel engine combustion analysis.

Additional insight can be obtained by incorporating a model for the largest of the effects omitted from Eq. (10.6), the heat transfer dQ_{ht}/dt (see Chap. 12); we thereby obtain a close approximation to the *gross* heat-release rate. The integral of the gross heat-release rate over the complete combustion process should then equal (to within a few percent only, since the analysis is not exact) the mass of fuel injected m_f times the fuel lower heating value Q_{LHV}: i.e.,

$$Q_{ch} = \int_{t_{start}}^{t_{end}} \frac{dQ_{ch}}{dt}\, dt = m_f Q_{LHV} \tag{10.7}$$

Of course, Eqs. (10.1) to (10.4), (10.6), and (10.7) also hold with crank angle θ as the independent variable instead of time t.

Figure 10-11 illustrates the relative magnitude of gross and net heat release, heat transfer, crevice effects, and heat of vaporization and heating up of the fuel for a turbocharged DI diesel engine operating in the mid-load, mid-speed range. The net heat release is the gross heat release due to combustion, less the heat transfer to the walls, crevice effects, and the effect of fuel vaporization and heatup (which was omitted above by neglecting the mass addition term in dU/dt). This last term is sufficiently small to be neglected. The enthalpy of vaporization of diesel fuel is less than 1 percent of its heating value; the energy change associated with heating up fuel vapor from injection temperature to typical compression air temperatures is about 3 percent of the fuel heating value. The heat transfer integrated over the duration of the combustion period is 10 to 25 percent of the total heat released.

FUEL MASS BURNING RATE ANALYSIS. If the internal energies of the fuel, air, and burned gases in Eq. (10.1) are evaluated relative to a consistent datum (such

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as that described in Sec. 4.5.2), then this equation can be used to obtain an apparent *fuel mass burning rate* from cylinder pressure versus crank angle data. (With such a species energy datum the "heat release" is properly accounted for in the internal energy and enthalpy terms.) Following Krieger and Borman,[9] Eq. (10.2) can be written as

$$\frac{d}{dt}(mu) = -p\frac{dV}{dt} + \frac{dQ}{dt} + h_f\frac{dm}{dt} \tag{10.8}$$

Here Q is the heat transfer to the gas within the combustion chamber (that is, $Q = -Q_{ht}$), m is the mass within the combustion chamber, and dm/dt has been substituted for $\dot{m}_f$.

Since the properties of the gases in the cylinder during combustion (assumed to be uniform and in chemical equilibrium at the pressure p and average temperature T) are in general a function of p, T, and the equivalence ratio ϕ,

$$u = u(T, p, \phi) \qquad \text{and} \qquad R = R(T, p, \phi)$$

Therefore

$$\frac{du}{dt} = \frac{\partial u}{\partial T}\frac{dT}{dt} + \frac{\partial u}{\partial p}\frac{dp}{dt} + \frac{\partial u}{\partial \phi}\frac{d\phi}{dt} \tag{10.9a}$$

$$\frac{dR}{dt} = \frac{\partial R}{\partial T}\frac{dT}{dt} + \frac{\partial R}{\partial p}\frac{dp}{dt} + \frac{\partial R}{\partial \phi}\frac{d\phi}{dt} \tag{10.9b}$$

Also,

$$\phi = \phi_0 + \left(\frac{m}{m_0} - 1\right)\frac{1 + (F/A)_0}{(F/A)_s} \tag{10.10}$$

and

$$\frac{d\phi}{dt} = \frac{1 + (F/A)_0}{(F/A)_s m_0}\frac{dm}{dt} \tag{10.11}$$

(F/A) is the fuel/air ratio; the subscript 0 denotes the initial value prior to fuel injection and the subscript s denotes the stoichiometric value. It then follows that

$$\frac{1}{m}\frac{dm}{dt} = \frac{-(RT/V)(dV/dt) - (\partial u/\partial p)(dp/dt) + (1/m)(dQ/dt) - CB}{u - h_f + D(\partial u/\partial \phi) - C[1 + (D/R)(\partial R/\partial \phi)]} \tag{10.12}$$

where

$$B = \frac{1}{p}\frac{dp}{dt} - \frac{1}{R}\frac{\partial R}{\partial p}\frac{dp}{dt} + \frac{1}{V}\frac{dV}{dt}$$

$$C = \frac{T(\partial u/\partial T)}{1 + (T/R)(\partial R/\partial T)}$$

$$D = \frac{[1 + (F/A)_0]m}{(F/A)_s m_0}$$

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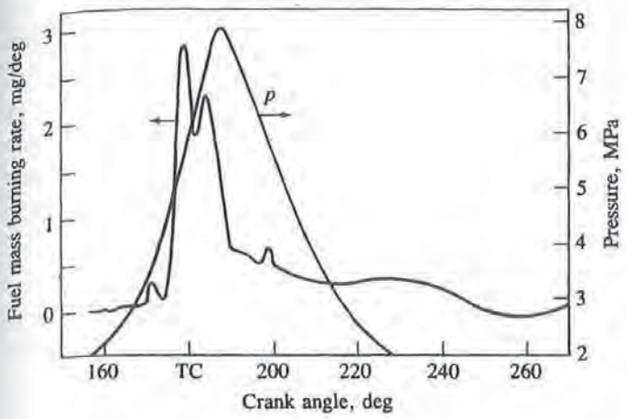


FIGURE 10-12
Cylinder pressure p and fuel mass burning rate calculated from p, as a function of crank angle, using the Krieger and Borman method[9] for DI diesel engine at 3200 rev/min and full load.

Equation (10.12) can be solved numerically for $m(t)$ given m_0, ϕ_0, $p(t)$, and appropriate models for the working fluid properties (see Sec. 4.7) and for the heat-transfer term dQ/dt (see Chap. 12).

Figure 10-12 shows cylinder pressure data for an open chamber DI diesel and fuel mass burning rate $dm/d\theta$ calculated from that data using the above method. The heat-transfer model of Annand was used (see Sec. 12.4.3). The result obtained is an *apparent* fuel mass burning rate. It is best interpreted, after multiplying by the heating value of the fuel, as the fuel chemical-energy or heat-release rate. The *actual* fuel burning rate is unknown because not all the fuel "burns" with sufficient air available locally to produce products of *complete* combustion. About 60 percent of the fuel has burned in the first one-third of the total combustion period. The integral of the fuel mass burning rate over the combustion process should equal the total fuel mass burned; in this case it is 3 percent less than the total fuel mass injected. Note that chemical energy continues to be released well into the expansion process. The accuracy of this type of calculation then decreases, however, since errors in estimating heat transfer significantly affect the apparent fuel burning rate.

Krieger and Borman also carried out sensitivity analyses for the critical assumptions and variables. They found that the effect of dissociation of the product gases was negligible. This permits a substantial simplification of Eq. (10.12). With no dissociation, $u = u(T, \phi)$, and $R = \tilde{R}/M$ can be taken as constant, since the molecular weight M changes little. Then

$$\frac{dm}{dt} = \frac{[1 + (c_v/R)]p(dV/dt) + (c_v/R)V(dp/dt) - (dQ/dt)}{h_f + (c_v/R)(pV/m) - u - D(\partial u/\partial \phi)} \tag{10.13}$$

where D, as before, is $[1 + (F/A)_0]m/[(F/A)_s m_0]$. Given the uncertainties inherent in the heat-transfer model and the neglect of nonuniformities and crevices, Eq. (10.13) represents an adequate level of sophistication.

The other sensitivity variations studied by Krieger and Borman were: shifting of the phasing of the pressure data 2° forward and 2° backward; translating the pressure data ± 34 kPa (5 lb/in^2); changing the heat transfer ± 50 percent;

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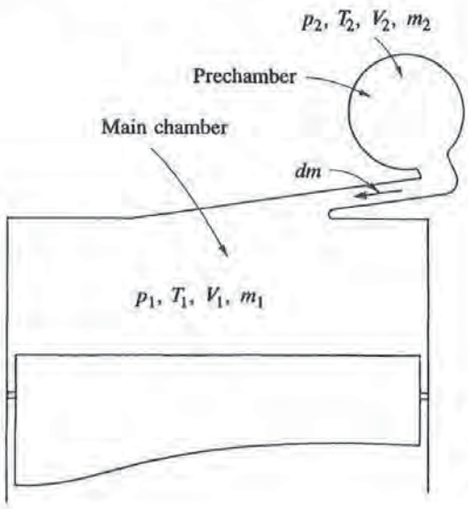


FIGURE 10-13
Schematic defining variables in main chamber (subscript 1) and prechamber (subscript 2) for IDI engine heat-release analysis.

increasing the initial mass 5 percent. The initial mass change had a negligible effect on the fuel burning rate calculations. The heat-transfer changes of ± 50 percent changed the mass of fuel burned by about ± 5 percent. The change in phasing of the pressure data was more significant. It needs to be stressed that *accurate* (in magnitude and phasing) pressure data are a most important requirement for useful heat-release or fuel mass burning rate analysis.

10.4.3 Indirect-Injection Engines

In IDI diesel engines, the pressures in each of the two chambers, main and auxiliary, are not the same during the combustion process. Since combustion starts in the auxiliary or prechamber, the fuel energy release in the prechamber causes the pressure there to rise above the main chamber pressure. Depending on combustion chamber design and operating conditions, the prechamber pressure rises to be 0.5 to 5 atm above that in the main chamber. This pressure difference causes a flow of fuel, air, and burning and burned gases into the main chamber, where additional energy release now occurs. The analysis of the DI diesel in the previous section was based on uniform pressure throughout the combustion chamber. For IDI engines the effect of the pressure difference between the chambers must usually be included.

Figure 10-13 shows an IDI combustion chamber divided at the nozzle into two open systems. Applying the first law [Eq. (10.1)] to the *main chamber* yields

$$\frac{dQ_1}{dt} - p_1 \frac{dV_1}{dt} + h_{2,1} \frac{dm}{dt} = \frac{dU_1}{dt} \tag{10.14}$$

and to the *auxiliary chamber* yields

$$\frac{dQ_2}{dt} - h_{2,1} \frac{dm}{dt} + h_f \frac{dm_f}{dt} = \frac{dU_2}{dt} \tag{10.15}$$

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Here dm/dt is the mass flow rate between the chambers with positive flow from the prechamber to the main chamber. If $dm/dt > 0$, $h_{2,1} = h_2$; if $dm/dt < 0$, $h_{2,1} = h_1$. If we define U_1 and U_2 as sensible internal energies and h_f as the sensible enthalpy of the fuel, then dQ_1/dt and dQ_2/dt represent the net heat-release rates—the difference between the combustion energy-release rates and the rates of heat transfer to the walls.

If we use an ideal gas model for the working fluid in each chamber, with c_v, c_p, and M constant, the relation $p_1 V_1 = m_1 R T_1$ and $p_2 V_2 = m_2 R T_2$ can be used to eliminate m and T from the dU/dt terms and, with the fact that $h_{s,f} = 0$, can be used to write Eqs. (10.14) and (10.15) as

$$\frac{dQ_1}{dt} = \frac{\gamma}{\gamma - 1} p_1 \frac{dV_1}{dt} + \frac{1}{\gamma - 1} V_1 \frac{dp_1}{dt} - c_p T_{2,1} \frac{dm}{dt} \tag{10.16}$$

$$\frac{dQ_2}{dt} = \frac{1}{\gamma - 1} V_2 \frac{dp_2}{dt} + c_p T_{2,1} \frac{dm}{dt} \tag{10.17}$$

When Eqs. (10.16) and (10.17) are added together, the term representing the enthalpy flux between the two chambers cancels out, and the following equation for *total* net heat-release results:

$$\frac{dQ}{dt} = \frac{dQ_1}{dt} + \frac{dQ_2}{dt} = \frac{\gamma}{\gamma - 1} p_1 \frac{dV_1}{dt} + \frac{1}{\gamma - 1}\left(V_1 \frac{dp_1}{dt} + V_2 \frac{dp_2}{dt}\right) \tag{10.18}$$

The comments made in the previous section regarding the interpretation of the net heat release (it is the gross heat release due to combustion less the heat transfer to the walls, and other smaller energy transfers due to crevices, fuel vaporization, and heatup) also hold here.

In practice, Eq. (10.18) is difficult to use since it requires experimental data for both the main and auxiliary chamber pressures throughout the combustion process. Access for two pressure transducers through the cylinder head is not often available; even when access can be achieved, the task of obtaining pressure data from two different transducers under the demanding thermal loading conditions found in IDI diesels, of sufficient accuracy such that the difference between the pressures (of order 0.5 to 5 atm) at pressure levels of 60 to 80 atm can be interpreted, requires extreme diligence in technique.[10, 11] Figure 10-14*a* and *b* shows apparent net heat-release rate profiles for an IDI diesel obtained using Eq. (10.18) with $\gamma = 1.35$.[11] Curves of dQ/dt and $dQ/d\theta$ are shown at three different speeds and essentially constant fuel mass injected per cycle. While the absolute heat-release rates increase with increasing speed, the relative rates are essentially independent of speed, indicating that combustion rates, which depend on fuel-air mixing rates, scale approximately with engine speed.

Equation (10.18) (or its equivalent) has been used assuming $p_2 = p_1$ and using either main chamber or auxiliary chamber pressure data alone. The error associated with this approximation can be estimated as follows. If we write $p_2 =$

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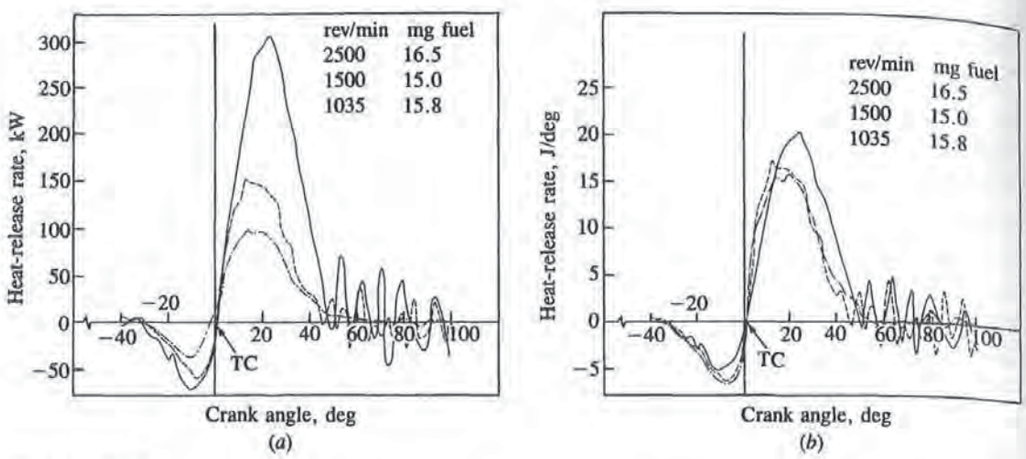


FIGURE 10-14
Calculated net heat-release-rate profiles for IDI diesel engine at constant load ($0.29 \leq \phi \leq 0.32$). (*a*) Heat-release rate in kilowatts. (*b*) Heat-release rate in joules per degree.[11]

$p_1 + \Delta p$ then Eq. (10.18) becomes

$$\frac{dQ}{dt} = \frac{\gamma}{\gamma - 1} p_1 \frac{dV_1}{dt} + \frac{V_1 + V_2}{\gamma - 1} \frac{dp_1}{dt} + \frac{V_2}{\gamma - 1} \frac{d(\Delta p)}{dt} \tag{10.19}$$

If the last term is omitted, Eq. (10.19) is identical to Eq. (10.6) derived for the DI diesel. Since the term $V(dp_1/dt)/(\gamma - 1)$ is much larger than the first term on the right-hand side of Eq. (10.19) during the early stages of the combustion process, the error involved in omitting the last term is given to a good approximation by $[V_2/(V_1 + V_2)]d(\Delta p)/dp_1$. In the initial stages of combustion this error can be quite large (of order 0.25 based on data in Ref. 10 close to TC). Later in the combustion process it becomes negligible (of order a few percent after 20° ATC).[10] Thus, neglecting Δp will lead to errors in predicting the initial heat-release *rate*. The magnitude of the error will depend on the design of the combustion chamber and on engine speed and load (with more restricted passageways, higher loads and speeds, giving higher values of Δp and, therefore, greater error). Later in the combustion process the error is much less, so *integrated* heat-release data derived ignoring Δp will show a smaller error.

A model analogous to the above, but using the approach of Krieger and Borman[9] (see Sec. 10.4.2), for the IDI diesel has been developed and used by Watson and Kamel.[10] The energy conservation equation for an *open* system developed in Sec. 14.2.2, with energy and enthalpy modeled using a consistent datum (see Sec. 4.5.2), with appropriate models for convective and radiation heat transfer and for gas properties, was applied to the main chamber and also to the prechamber. These equations were solved using accurately measured main chamber and prechamber pressure data to determine the apparent rate of heat release (here, the rate of fuel burning multiplied by the fuel heating value) in the main chamber and prechambers through the combustion process. The engine was a Ricardo Comet swirl chamber IDI design. Some results are shown in Fig.

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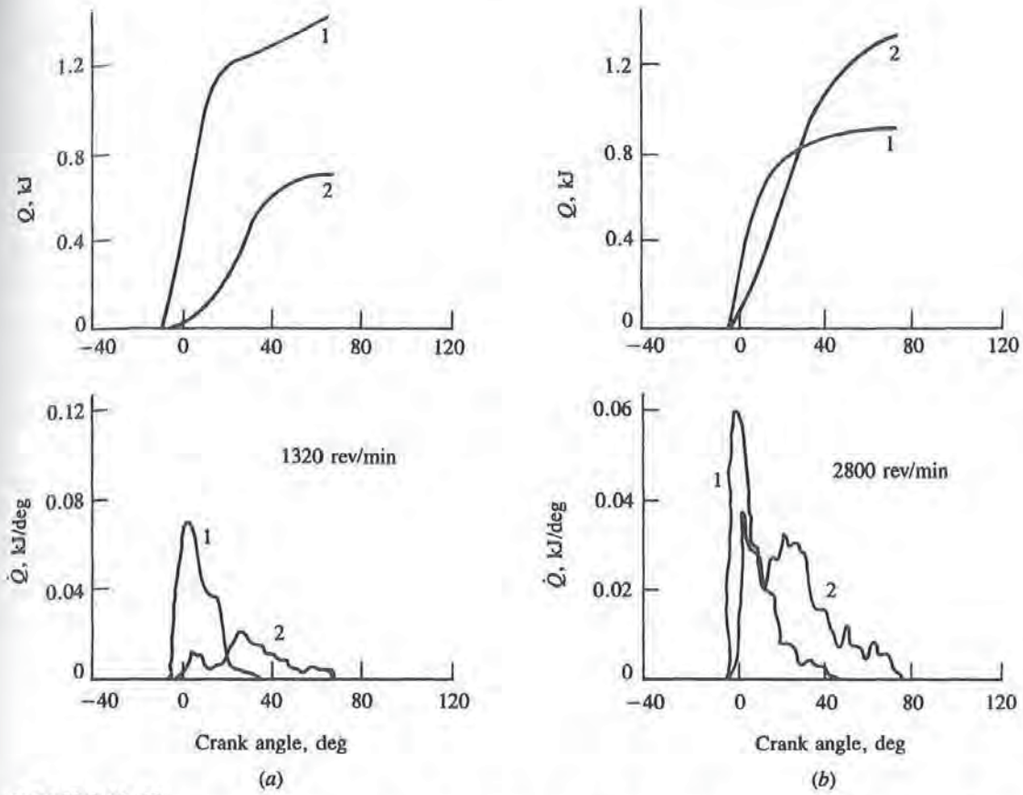


FIGURE 10-15
Calculated gross heat-release rates in IDI swirl-chamber diesel engine at full load. 1 Prechamber heat release. 2 Main chamber heat release. Top figures: integrated heat release. Bottom figures: heat-release rate. (*a*) 1320 rev/min; (*b*) 2800 rev/min.[10]

10-15. For this particular engine, at low engine speeds two-thirds of the heat release occurs in the prechamber; at higher engine speeds about two-thirds of the heat release occurs in the main chamber.

10.5 FUEL SPRAY BEHAVIOR

10.5.1 Fuel Injection

The fuel is introduced into the cylinder of a diesel engine through a nozzle with a large pressure differential across the nozzle orifice. The cylinder pressure at injection is typically in the range 50 to 100 atm. Fuel injection pressures in the range 200 to 1700 atm are used depending on the engine size and type of combustion system employed. These large pressure differences across the injector nozzle are required so that the injected liquid fuel jet will enter the chamber at sufficiently high velocity to (1) atomize into small-sized droplets to enable rapid evaporation and (2) traverse the combustion chamber in the time available and fully utilize the air charge.

Examples of common diesel fuel-injection systems were described briefly in Sec. 1.7 and illustrated in Figs. 1-17 to 1-19. (See also Refs. 12 and 13 for more

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extensive descriptions of diesel fuel-injection systems.) The task of the fuel-injection system is to meter the appropriate quantity of fuel for the given engine speed and load to each cylinder, each cycle, and inject that fuel at the appropriate time in the cycle at the desired rate with the spray configuration required for the particular combustion chamber employed. It is important that injection begin and end cleanly, and avoid any secondary injections.

To accomplish this task, fuel is usually drawn from the fuel tank by a supply pump, and forced through a filter to the injection pump. The injection pump sends fuel under pressure to the nozzle pipes which carry fuel to the injector nozzles located in each cylinder head. Excess fuel goes back to the fuel tank. Figures 1-17 and 1-19 show two common versions of fuel systems used with multicylinder engines in the 20 to 100 kW per cylinder brake power range which operate with injection pressures between about 300 and 1200 atm.

In-line injection pumps (Fig. 1-17) are used in engines in the 40 to 100 kW per cylinder maximum power range. They contain a plunger and barrel assembly for each engine cylinder. Each plunger is raised by a cam on the pump camshaft and is forced back by the plunger return spring. The plunger stroke is fixed. The plunger fits sufficiently accurately within the barrel to seal without additional sealing elements, even at high pressures and low speeds. The amount of fuel delivered is altered by varying the *effective* plunger stroke. This is achieved by means of a control rod or rack, which moves in the pump housing and rotates the plunger via a ring gear or linkage lever on the control sleeve. The plunger chamber above the plunger is always connected with the chamber below the plunger helix by a vertical groove or bore in the plunger. Delivery ceases when the plunger helix exposes the intake port (port opening), thus connecting the plunger chamber with the suction gallery. When this takes place depends on the rotational position of the plunger. In the case of a lower helix, delivery always starts (port closing) at the same time, but ends sooner or later depending on the rotational position of the plunger. With a plunger with an upper helix, port closing (start of delivery) not port opening is controlled by the helix and is varied by rotating the plunger. Figure 1-18 illustrates how the plunger helix controls fuel delivery.[14]

Distributor-type fuel-injection pumps (such as that illustrated in Fig. 1-19) are normally used in multicylinder engines with less than 30 kW per cylinder maximum power with injection pressures up to 750 atm. These pumps have only one plunger and barrel. The pump plunger is made to describe a combined rotary and stroke movement by the rotating cam plate. The fuel is accurately metered to each injection nozzle in turn by this plunger which simultaneously acts as the distributor. Such units are more compact and cheaper than in-line pumps but cannot achieve such high injection pressures. The distributor-type fuel-injection pump is combined with the automatic timing device, governor, and supply pump to form a single unit.

Single-barrel injection pumps are used on small one- and two-cylinder diesel engines, as well as large engines with outputs of more than 100 kW per cylinder. Figure 10-16 shows the layout of the injection system and a section

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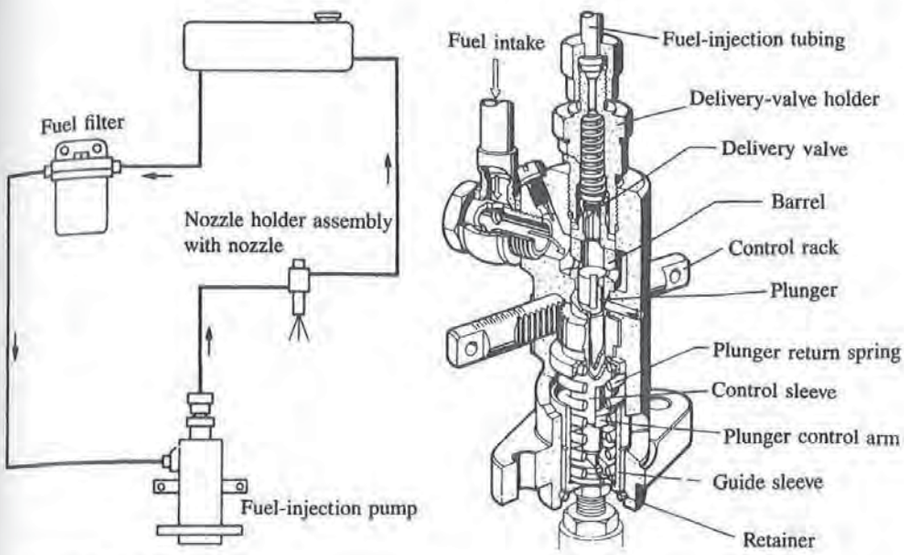


FIGURE 10-16
Fuel-injection system with single-barrel pump. Left: system layout. Right: section through fuel-injection pump. (*Courtesy Robert Bosch GmbH and SAE.*[14])

through the fuel-injection pump.[14] Such pumps are driven by an auxiliary cam on the engine camshaft. Also used extensively on larger engines are unit injectors where the pump and injector nozzle are combined into a single unit. An example of a unit injector and its driving mechanism used on a large two-stroke cycle diesel engine is shown in Fig. 10-17. Fuel, supplied to the injector through a fuel-distributing manifold, enters the cavity or plunger chamber ahead of the plunger through a metering orifice. When fuel is to be injected, the cam via the rocker arm pushes down the plunger, closing the metering orifice and compressing the fuel, causing it to flow through check valves and discharge into the cylinder through the injector nozzles or orifices. The amount of fuel injected is controlled by the rack, which controls the spill of fuel into the fuel drain manifold by rotating the plunger with its helical relief section via the gear.

The most important part of the injection system is the nozzle. Examples of different nozzle types and a nozzle holder assembly are shown in Fig. 1-18. The nozzles shown are fluid-controlled needle valves where the needle is forced against the valve seat by a spring. The pressure of the fuel in the pressure chamber above the nozzle aperture opens the nozzle by the axial force it exerts on the conical surface of the nozzle needle. Needle valves are used to prevent dribble from the nozzles when injection is not occurring. It is important to keep the volume of fuel left between the needle and nozzle orifices (the sac volume) as small as possible to prevent any fuel flowing into the cylinder after injection is over, to control hydrocarbon emissions (see Sec. 11.4.4). Multihole nozzles are used with most direct-injection systems; the M.A.N. "M" system uses a single-hole nozzle. Pintle nozzles, where the needle projects into and through the nozzle hole, are used in indirect-injection engine systems. The shape of the pin on the

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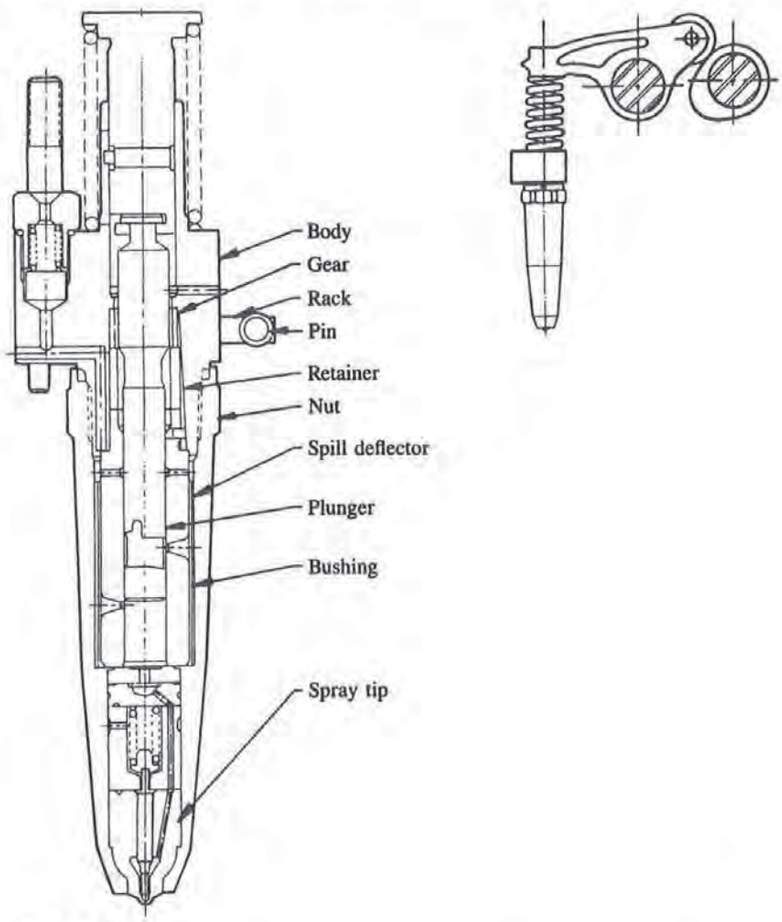


FIGURE 10-17
Unit fuel injector and its driving mechanism, typically used in large diesel engines.[15]

end of the nozzle needle controls the spray pattern and fuel-delivery characteristics. Auxiliary nozzle holes are sometimes used to produce an auxiliary smaller spray to aid ignition and starting. Open nozzle orifices, without a needle, are also used.

The technology for electronic control of injection is now available. In an electronic injector, such as that shown in Fig. 10-18, a solenoid operated control valve performs the injection timing and metering functions in a fashion analogous to the ports and helices of the mechanical injector. Solenoid valve closure initiates pressurization and injection, and opening causes injection pressure decay and end of injection. Duration of valve closure determines the quantity of fuel injected. The unit shown uses camshaft/rocker arm driven plungers to generate the injection pressure, and employs needle-valve nozzles of conventional design. Increased flexibility in fuel metering and timing and simpler injector mechanical design are important advantages.[16]

Accurate predictions of fuel behavior within the injection system require

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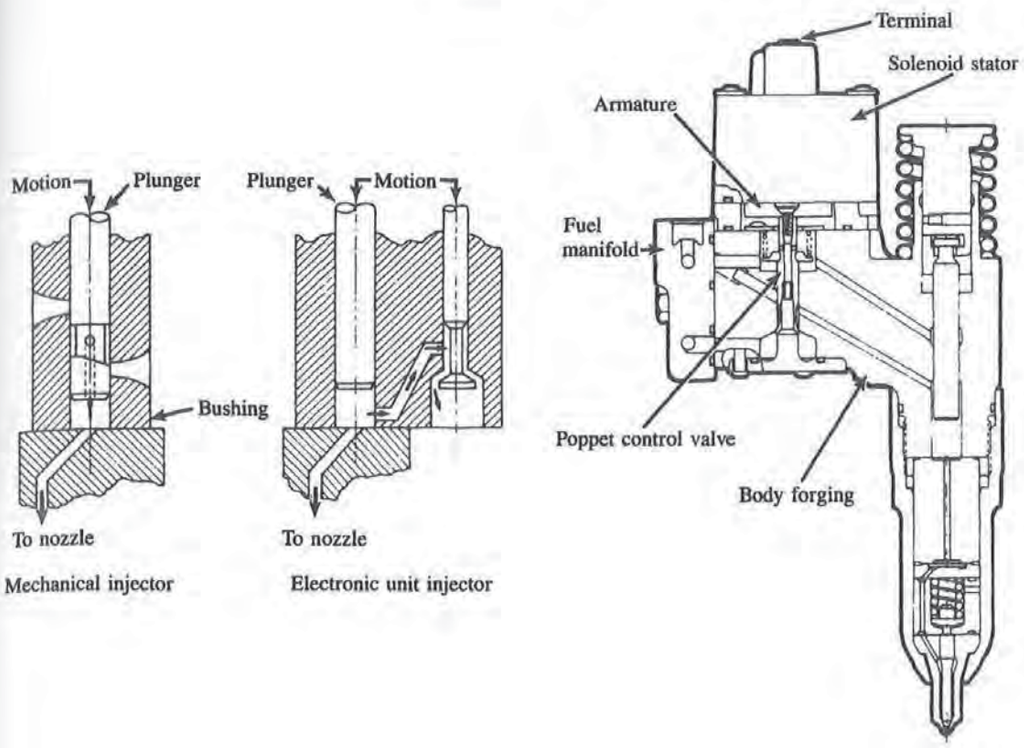


FIGURE 10-18
Electronically controlled unit fuel-injection system.[16]

sophisticated hydraulic models: Hiroyasu[17] provides an extensive reference list of such models. However, approximate estimates of the injection rate through the injector nozzles can be made as follows. If the pressure upstream of the injector nozzle(s) can be estimated or measured, and assuming the flow through each nozzle is quasi steady, incompressible, and one dimensional, the mass flow rate of fuel injected through the nozzle $\dot{m}_f$ is given by

$$\dot{m}_f = C_D A_n \sqrt{2\rho_f \Delta p} \tag{10.20}$$

where A_n is the nozzle minimum area, C_D the discharge coefficient, ρ_f the fuel density, and Δp the pressure drop across the nozzle. If the pressure drop across the nozzle and the nozzle open area are essentially constant during the injection period, the mass of fuel injected is then

$$m_f = C_D A_n \sqrt{2\rho_f \Delta p}\, \frac{\Delta\theta}{360N} \tag{10.21}$$

where $\Delta\theta$ is the nozzle open period in crank angle degrees and N is engine speed. Equations (10.20) and (10.21) illustrate the dependence of injected amounts of fuel on injection system and engine parameters.

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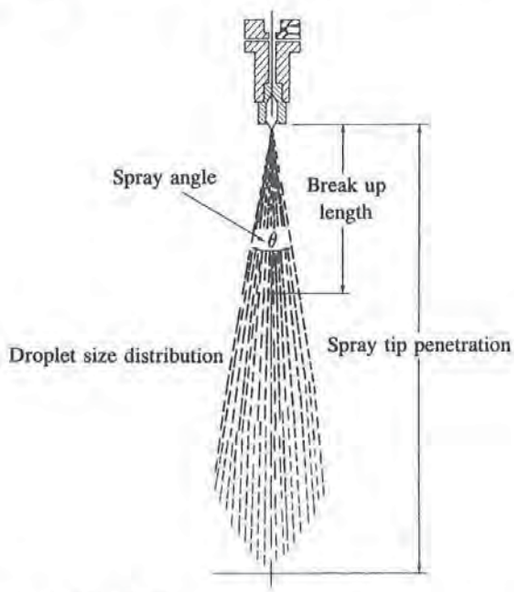


FIGURE 10-19
Schematic of diesel fuel spray defining its major parameters.[18]

10.5.2 Overall Spray Structure

The fuel is introduced into the combustion chamber of a diesel engine through one or more nozzles or orifices with a large pressure differential between the fuel supply line and the cylinder. Different designs of nozzle are used (e.g., single-orifice, multiorifice, throttle, or pintle; see Fig. 1-18), depending on the needs of the combustion system employed. Standard diesel injectors usually operate with fuel-injection pressures between 200 and 1700 atm. At time of injection, the air in the cylinder has a pressure of 50 to 100 atm, temperature about 1000 K, and density between 15 and 25 kg/m^3. Nozzle diameters cover the range 0.2 to 1 mm diameter, with length/diameter ratios from 2 to 8. Typical distillate diesel fuel properties are: relative specific gravity of 0.8, viscosity between 3 and 10 kg/m · s and surface tension about 3×10^{-2} N/m (at 300 K). Figure 10-19 illustrates the structure of a typical DI engine fuel spray. As the liquid jet leaves the nozzle it becomes turbulent and spreads out as it entrains and mixes with the surrounding air. The initial jet velocity is greater than 10^2 m/s. The outer surface of the jet breaks up into drops of order 10 μm diameter, close to the nozzle exit. The liquid column leaving the nozzle disintegrates within the cylinder over a finite length called the *breakup length* into drops of different sizes. As one moves away from the nozzle, the mass of air within the spray increases, the spray diverges, its width increases, and the velocity decreases. The fuel drops evaporate as this air-entrainment process proceeds. The tip of the spray penetrates further into the combustion chamber as injection proceeds, but at a decreasing rate. Figure 10-20 shows photographs of a diesel fuel spray injected into quiescent air in a rapid-compression machine which simulates diesel conditions.[19] Two different pho-

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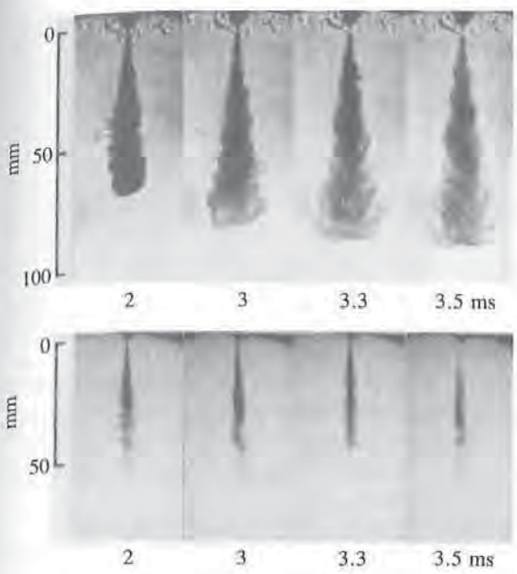


FIGURE 10-20
Shadowgraph and back-illuminated photographs of evaporating spray injected into nitrogen at 3.4 MPa and 670 K in rapid-compression machine. Times in milliseconds are after start of injection: injection duration 3.3 ms. Top (shadowgraph) photographs show full vapor and liquid region. Bottom (back-illuminated) photographs only show liquid-containing core.[19]

tographic techniques, back lighting and shadowgraph,† have been used to distinguish the liquid-containing core of the jet and the extent of the fuel vapor region of the spray which surrounds the liquid core. The region of the jet closest to the nozzle (until injection ceases at 3.3 ms) contains liquid drops and ligaments; the major region of the spray is a substantial vapor cloud around this narrow core which contains liquid fuel.

Different spray configurations are used in the different diesel combustion systems described earlier in this chapter. The simplest configuration involves multiple sprays injected into quiescent air in the largest-size diesels (Fig. 10-1*a*). Figures 10-19 and 10-20 illustrate the essential features of each spray under these circumstances until interactions with the wall occur. Each liquid fuel jet atomizes into drops and ligaments at the exit from the nozzle orifice (or shortly thereafter). The spray entrains air, spreads out, and slows down as the mass flow in the spray increases. The droplets on the outer edge of the spray evaporate first, creating a fuel vapor–air mixture sheath around the liquid-containing core. The highest velocities are on the jet axis. The equivalence ratio is highest on the centerline (and fuel-rich along most of the jet), decreasing to zero (unmixed air) at the spray boundary. Once the sprays have penetrated to the outer regions of the combustion chamber, they interact with the chamber walls. The spray is then forced to flow tangentially along the wall. Eventually the sprays from multihole nozzles

† The back lighting identifies regions where sufficient liquid fuel (as ligaments or drops) is present to attenuate the light. The shadowgraph technique responds to density gradients in the test section, so it identifies regions where fuel vapor exists.

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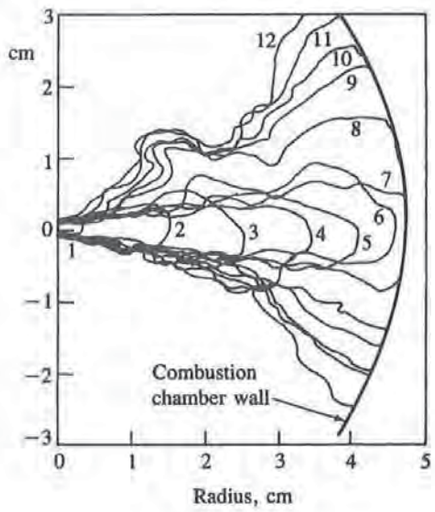


FIGURE 10-21
Sketches of outer vapor boundary of diesel fuel spray from 12 successive frames of rapid-compression-machine high-speed shadowgraph movie showing interaction of vaporizing spray with cylindrical wall of combustion chamber. Injection pressure 60 MPa. Time between frames 0.14 ms.[20]

interact with one another. Figure 10-21 shows diesel fuel sprays interacting with the cylindrical outer wall of a disc-shaped combustion chamber in a rapid-compression machine, under typical diesel-injection conditions. The cylinder wall causes the spray to split with about half flowing circumferentially in either direction. Adjacent sprays then interact forcing the flow radially inward toward the chamber axis.[20]

Most of the other combustion systems in Figs. 10-1 and 10-2 use air swirl to increase fuel-air mixing rates. A schematic of the spray pattern which results when a fuel jet is injected radially outward into a swirling flow is shown in Fig. 10-22. Because there is now relative motion in both radial and tangential directions between the initial jet and the air, the structure of the jet is more complex. As the spray entrains air and slows down it becomes increasingly bent toward the swirl direction; for the same injection conditions it will penetrate less with swirl than without swirl. An important feature of the spray is the large vapor-containing region downstream of the liquid-containing core. Figure 10-23 shows schlieren photographs of four fuel jets injected on the axis of an IDI diesel engine

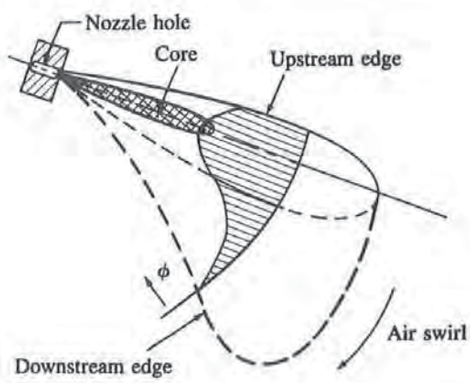


FIGURE 10-22
Schematic of fuel spray injected radially outward from the chamber axis into swirling air flow. Shape of equivalence ratio (ϕ) distribution within jet is indicated.

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FIGURE 10-23
Schlieren photographs of vaporizing sprays injected into swirling air flow in transparent prechamber of special IDI diesel.[21] Left: high sensitivity, showing boundaries of the vapor regions of spray. Right: low sensitivity, showing liquid-containing core (dark) in relation to vapor regions (mottled).

prechamber with high clockwise swirl. The photograph on the left, with high sensitivity, shows the outer boundary of the fuel vapor region of the spray; the low-sensitivity photograph on the right locates the liquid phase regions of the spray.[21] The interaction between the swirl and both liquid and vapor spray regions is evident, as is the spray interaction with the chamber wall.

Other spray flow patterns are used. The spray may enter the swirling air flow tangentially as in the M.A.N. "M" system shown in Fig. 10-1*c*. The spray then interacts immediately with the combustion chamber walls.

To couple the spray-development process with the ignition phase of the combustion, it is important to know which regions of the spray contain the fuel injected at the beginning of the injection process. These regions of the sprays are likely to autoignite first. Each spray develops as follows. At the start of injection the liquid fuel enters the quiescent air charge, atomizes, moves outward from the nozzle, and slows down rapidly as air is entrained into the spray and accelerated. This start-up process forms a vortex or "puff" at the head of the spray. The injected fuel which follows encounters less resistance; thus drops from that fuel overtake the drops from first-injected fuel, forcing them outward toward the periphery of the spray. At the tip of the unsteady spray the drops meet the highest aerodynamic resistance and slow down, but the spray continues to penetrate the air charge because droplets retarded at the tip are continually replaced by new higher-momentum later-injected drops.[22] Accordingly, droplets in the periphery of the spray and behind the tip of the spray come from the earliest injected fuel.[23] As Figs. 10-20 and 10-23 indicate, these drops evaporate quickly.

10.5.3 Atomization

Under diesel engine injection conditions, the fuel jet usually forms a cone-shaped spray at the nozzle exit. This type of behavior is classified as the atomization breakup regime, and it produces droplets with sizes very much less than the nozzle exit diameter. This behavior is different from other modes of liquid jet

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breakup. At low jet velocity, in the Rayleigh regime, breakup is due to the unstable growth of surface waves caused by surface tension and results in drops larger than the jet diameter. As jet velocity is increased, forces due to the relative motion of the jet and the surrounding air augment the surface tension force, and lead to drop sizes of the order of the jet diameter. This is called the first wind-induced breakup regime. A further increase in jet velocity results in breakup characterized by divergence of the jet spray after an intact or undisturbed length downstream of the nozzle. In this second wind-induced breakup regime, the unstable growth of short-wavelength waves induced by the relative motion between the liquid and surrounding air produces droplets whose average size is much less than the jet diameter. Further increases in jet velocity lead to breakup in the atomization regime, where the breakup of the outer surface of the jet occurs at, or before, the nozzle exit plane and results in droplets whose average diameter is much smaller than the nozzle diameter. Aerodynamic interactions at the liquid/gas interface appear to be one major component of the atomization mechanism in this regime.[22, 24]

A sequence of very short time exposure photographs of the emergence of a liquid jet from a nozzle of 0.34 mm diameter and $L_n/d_n = 4$ into high-pressure nitrogen at ambient temperature is shown in Fig. 10-24. The figure shows how the spray tip penetrates and the spray spreads during the early part of its travel.[25] Data such as these were used to examine the dependence of the spray development on gas and liquid density, liquid viscosity, and nozzle geometry.[24–26] The effects of the most significant variables, gas/liquid density ratio and nozzle geometry, on initial jet spreading angle are shown in Fig. 10-25. For a given geometry (cylindrical hole and length/diameter = 4), the initial jet spreading or spray angle increases with increasing gas/liquid density ratio as shown in Fig. 10-25*a*. Typical density ratios for diesel injection conditions are between 15×10^{-3} and 30×10^{-3}. Of several different nozzle geometry parameters examined, the length/diameter ratio proved to be the most significant (see Fig. 10-25*b*).

For jets in the atomization regime, the spray angle θ was found to follow the relationship

$$\tan \frac{\theta}{2} = \frac{1}{A} 4\pi \left(\frac{\rho_g}{\rho_l}\right)^{1/2} \frac{\sqrt{3}}{6} \tag{10.22}$$

where ρ_g and ρ_l are gas and liquid densities and A is a constant for a given nozzle geometry.† The data in Fig. 10-25*a* are fitted by $A = 4.9$. This behavior is in accord with the theory that aerodynamic interactions are largely responsible for jet breakup. Note that the data in Fig. 10-25*b* show a continuous trend as the jet breakup regime makes a transition from second wind-induced breakup (solid

† An empirical equation for A is $A = 3.0 + 0.28\ (L_n/d_n)$, where L_n/d_n is the length/diameter ratio of the nozzle.[25]

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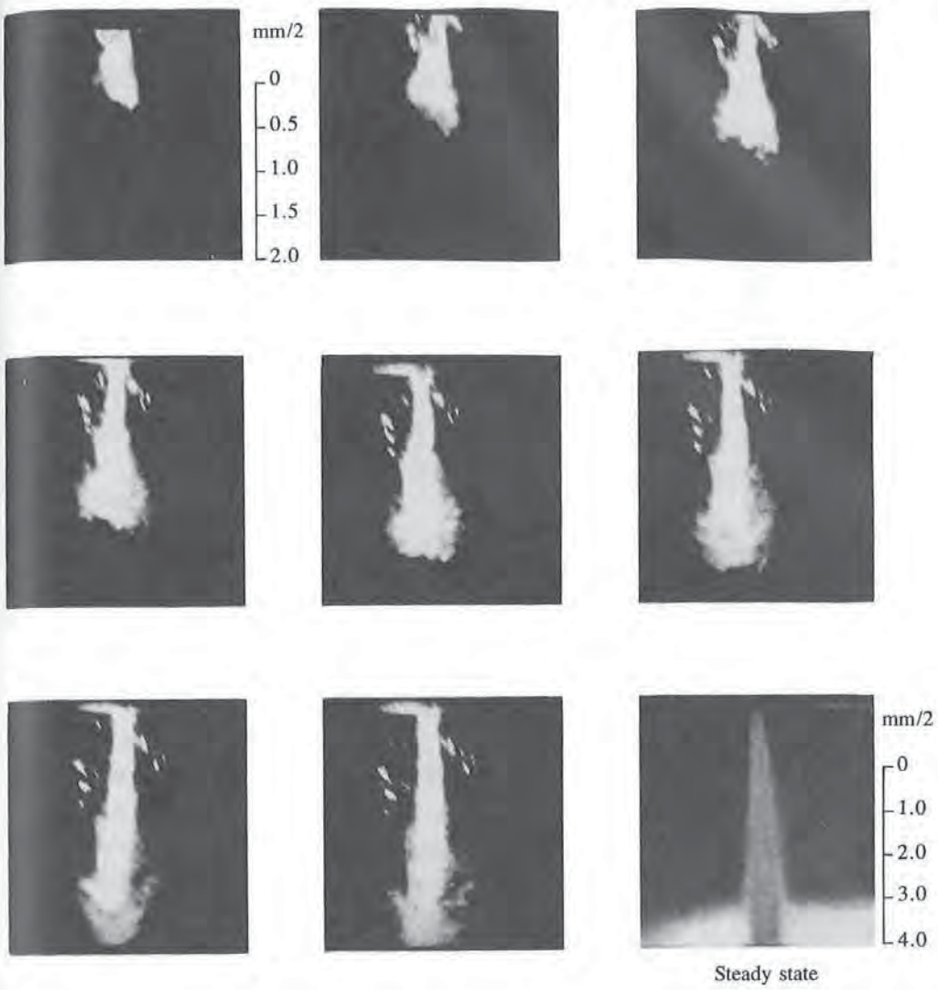
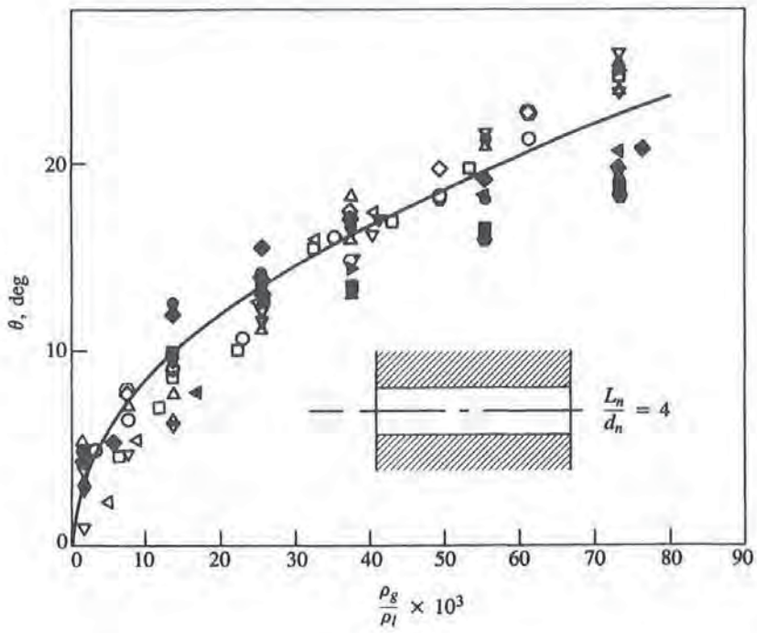


FIGURE 10-24
Photographs showing initial emergence and steady state (bottom right) of high-pressure liquid spray. Time between frames 2.1 μs. Liquid: water. Gas: nitrogen at 1380 kPa. Δp across nozzle 11 MPa. Nozzle diameter 0.34 mm.[25]

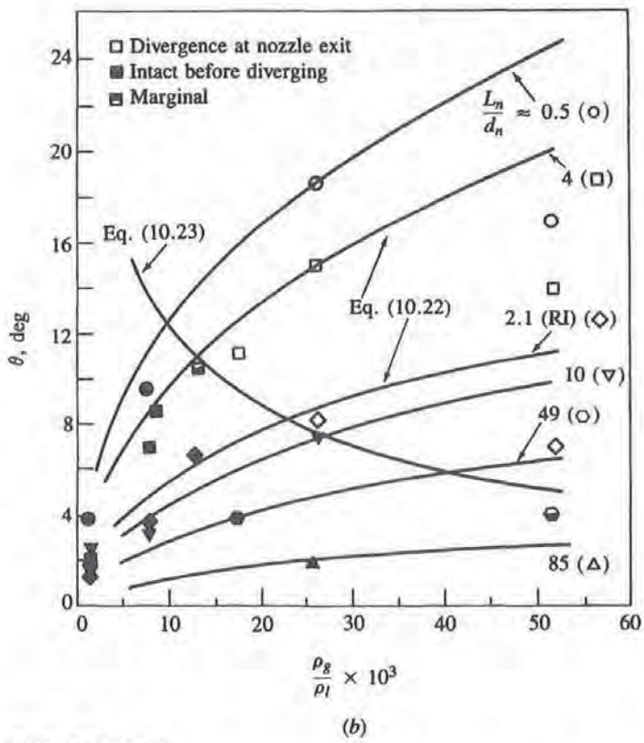
symbols) to atomization regime breakup (open symbols). The growth of aerodynamic surface waves is known to be responsible for jet breakup in the second wind-induced breakup regime. Such a mechanism can explain the observed data trends in the atomization regime, if an additional mechanism is invoked to explain nozzle geometry effects. One possible additional mechanism is liquid cavitation. A criterion for the onset of jet atomization at the nozzle exit plane was developed. For $(\rho_l/\rho_g)(\mathrm{Re}_l/\mathrm{We}_l)^2 > 1$ (which is true for distillate fuel injection applications) the design criterion is

$$\left(\frac{\rho_l}{\rho_g}\right)^{1/2} < k \tag{10.23}$$

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(*a*)



(*b*)

FIGURE 10-25

(*a*) Initial spray angle of atomizing jets versus density ratio (ρ_g/ρ_l = gas density/liquid density) for fixed nozzle geometry shown. Various fluids and gases at liquid pressures of 3.4–92 MPa. Nozzle diameters d_n = 0.254, 0.343, and 0.61 mm.[22] (*b*) Initial spray angle versus density ratio for a wide range of nozzle geometries. L_n/d_n = nozzle length/diameter ratio (RI = rounded inlet geometry). Solid symbols indicate jets which break up and diverge downstream of nozzle exit. Open symbols indicate jet breakup at nozzle exit.[25]

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where k is an empirical constant depending on nozzle geometry in the range 6 to 12 ($k = 18.3/\sqrt{A}$).

Jet breakup trends can be summarized as follows. The initial jet divergence angles increase with increasing gas density. Divergence begins progressively closer to the nozzle as gas density increases until it reaches the nozzle exit. Jet divergence angles increase with decreasing fuel viscosity; divergence begins at the nozzle exit once the liquid viscosity is below a certain level. Nozzle design affects the onset of the jet atomization regime. Jet divergence angles decrease with increasing nozzle length. For the same length, rounded inlet nozzles produce less divergent jets than sharp-edged inlet nozzles. The initial jet divergence angle and intact spray length are quasi steady with respect to changes in operating conditions which occur on time scales longer than about 20 μs.[25] Note that while all these results were obtained under conditions where evaporation was not occurring, the initial spray-development processes are not significantly affected by evaporation (see Sec. 10.5.6).

10.5.4 Spray Penetration

The speed and extent to which the fuel spray penetrates across the combustion chamber has an important influence on air utilization and fuel-air mixing rates. In some engine designs, where the walls are hot and high air swirl is present, fuel impingement on the walls is desired. However, in multispray DI diesel combustion systems, overpenetration gives impingement of liquid fuel on cool surfaces which, especially with little or no air swirl, lowers mixing rates and increases emissions of unburned and partially burned species. Yet underpenetration results in poor air utilization since the air on the periphery of the chamber does not then contact the fuel. Thus, the penetration of liquid fuel sprays under conditions typical of those found in diesel engines has been extensively studied.

Many correlations based on experimental data and turbulent gas jet theory have been proposed for fuel spray penetration.[17] These predict the penetration S of the fuel spray tip across the combustion chamber for injection into quiescent air, as occurs in larger DI engines, as a function of time. An evaluation of these correlations[27] indicated that the formula developed by Dent,[28] based on a gas jet mixing model for the spray, best predicts the data:†

$$S = 3.07\left(\frac{\Delta p}{\rho_g}\right)^{1/4}(td_n)^{1/2}\left(\frac{294}{T_g}\right)^{1/4} \tag{10.24}$$

where Δp is the pressure drop across the nozzle, t is time after the start of injection, and d_n is the nozzle diameter. All quantities are expressed in SI units: t in

† For nozzles where $2 \le L_n/d_n \le 4$, and for $t > 0.5$ ms. At exceptionally high chamber densities ($p > 100$ atm) Eq. (10.24) overpredicts penetration.

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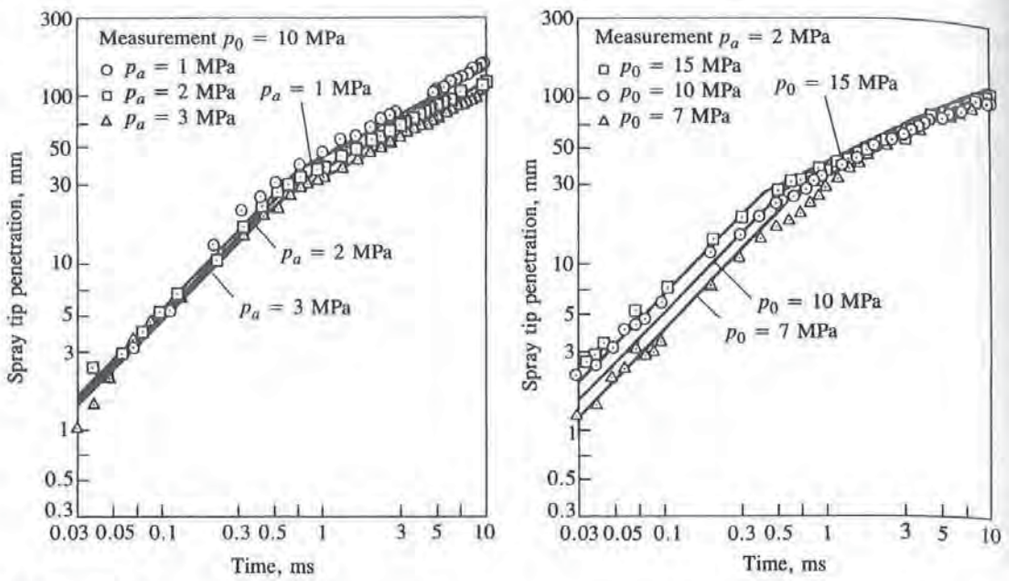


FIGURE 10-26
Spray tip penetration as function of time at various ambient pressures (p_a) and injection pressures (p_0). Fuel jets injected into quiescent air at room temperature.[29]

seconds, S and d_n in meters, Δp in pascals, ρ_g in kilograms per cubic meter, and T_g in kelvins.

More detailed studies have examined the spray tip location as a function of time, following start of a diesel injection process in high-pressure bombs. Data taken by Hiroyasu *et al.*,[29] shown in Fig. 10-26, illustrate the sensitivity of the spray tip position as a function of time to ambient gas state and injection pressure for fuel jets injected into quiescent air at room temperature. These data show that the initial spray tip penetration increases linearly with time t (i.e., the spray tip velocity is constant) and, following jet breakup, then increase as $\sqrt{t}$. Injection pressure has a more significant effect on the initial motion before breakup; ambient gas density has its major impact on the motion after breakup. Hiroyasu *et al.* correlated their data for spray tip penetration S(m) versus time as

$$t < t_{\text{break}}: \qquad S = 0.39\left(\frac{2\Delta p}{\rho_l}\right)^{1/2} t$$

$$t > t_{\text{break}}: \qquad S = 2.95\left(\frac{\Delta p}{\rho_g}\right)^{1/4} (d_n t)^{1/2} \tag{10.25}$$

where

$$t_{\text{break}} = \frac{29\rho_l d_n}{(\rho_g \Delta p)^{1/2}} \tag{10.26}$$

and Δp is the pressure drop across the nozzle (pascals), ρ_l and ρ_g are the liquid and gas densities, respectively (in kilograms per cubic meter), d_n is the nozzle

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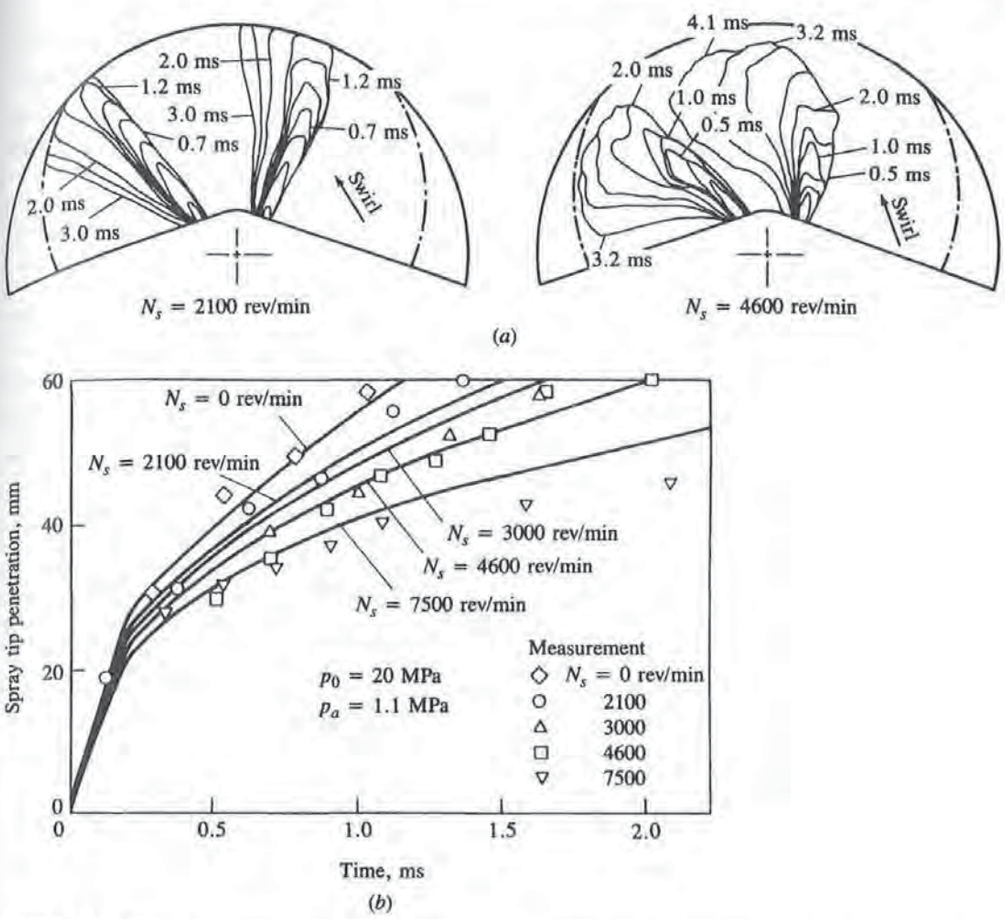


FIGURE 10-27
(*a*) Measured outer boundary of sprays injected into swirling air flow. (*b*) Spray tip penetration as a function of time for different swirl rates. Solid lines show Eq. (10.27).[29]

diameter (meters), and t is time (seconds). The results of Reitz and Bracco[25] indicate that the breakup or intact length depends on nozzle geometry details in addition to the diameter (see Fig. 10-25*b*). Note that under high injection pressures and nozzle geometries with short length/diameter ratios, the intact or breakup length becomes very short; breakup can occur at the nozzle exit plane.

The effect of combustion air swirl on spray penetration is shown in Fig. 10-27. Figure 10-27*a* shows how the spray shape and location changes as swirl is increased; Fig. 10-27*b* shows how spray tip penetration varies with time and swirl rate.[29] These authors related their data on spray tip penetration with swirl, S_s, through a correlation factor to the equivalent penetration, S, without swirl given by Eq. (10.25):

$$\frac{S_s}{S} = \left(1 + \frac{\pi R_s N S}{30 v_j}\right)^{-1} \tag{10.27}$$

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where R_s is the swirl ratio which equals the swirl rate in revolutions per minute divided by the engine speed N (revolutions per minute), and v_j is the initial fuel jet velocity (meters per second). The curves in Fig. 10-27*b* correspond to Eq. (10.27). Swirl both reduces the penetration of the spray and spreads out the spray more rapidly.

10.5.5 Droplet Size Distribution

Previous sections in Sec. 10.5 have discussed the overall characteristics of the diesel engine fuel spray—its spreading rate and penetration into the combustion chamber. While the distribution of fuel via the spray trajectory throughout the combustion chamber is important, atomization of the liquid fuel into a large number of small drops is also necessary to create a large surface area across which liquid fuel can evaporate. Here we review how the drop size distribution in the fuel spray depends on injection parameters and the air and fuel properties. Since the measurement of droplet characteristics in an operating diesel engine is extremely difficult, most results have come from studies of fuel injection into constant-volume chambers filled with high-pressure quiescent air at room temperature.

During the injection period, the injection conditions such as injection pressure, nozzle orifice area, and injection rate may vary. Consequently, the droplet size distribution at a given location in the spray may also change with time during the injection period. In addition, since the details of the atomization process are different in the spray core and at the spray edge, and the trajectories of individual drops depend on their size, initial velocity, and location within the spray, the drop size distribution will vary with position within the spray.[29] None of these variations has yet been adequately quantified.

The aerodynamic theory of jet breakup in the atomization regime summarized in Sec. 10.5.3 (which is based on work by G. I. Taylor) leads to the prediction that the initial average drop diameter D_d is proportional to the length of the most unstable surface waves:[22]

$$\bar{D}_d = C \frac{2\pi\sigma}{\rho_g v_r^2} \lambda^* \tag{10.28}$$

where σ is the liquid-fuel surface tension, ρ_g is the gas density, v_r is the relative velocity between the liquid and gas (taken as the mean injection velocity v_j), C is a constant of order unity, and λ^* is the dimensionless wavelength of the fastest growing wave. λ^* is a function of the dimensionless number $(\rho_l/\rho_g)(\mathrm{Re}_j/\mathrm{We}_j)^2$, where the jet Reynolds and Weber numbers are given by $\mathrm{Re}_j = \rho_l v_j d_n/\mu_l$ and $\mathrm{We}_j = \rho_l v_j^2 d_n/\sigma$ and d_n is the nozzle orifice diameter. λ^* goes to 3/2 as this number increases above unity. Near the edge of the spray close to the nozzle, this equation predicts observed drop size trends with respect to injection velocity, fuel properties, nozzle L/d, and nozzle diameter, though measured mean drop sizes are larger by factors of 2 to 3.[30] However, within the dense early region of the spray, secondary atomization phenomena—coalescence and breakup—occur

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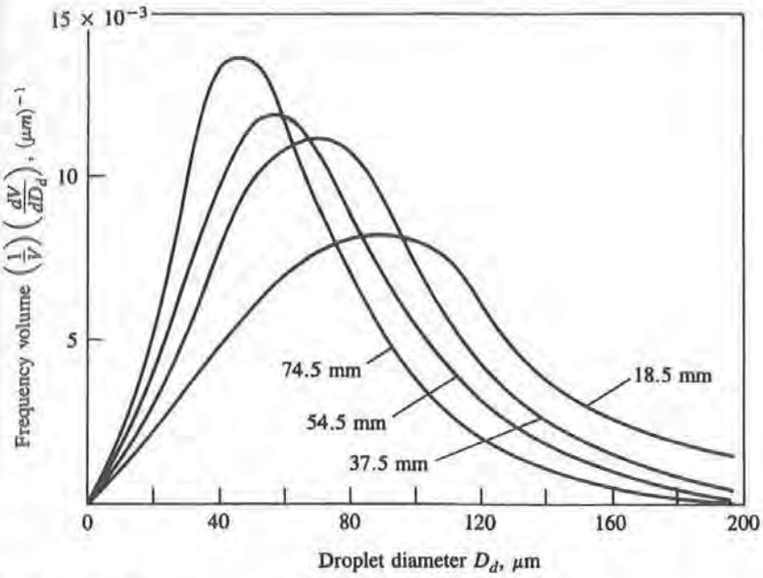


FIGURE 10-28
Droplet size distribution in diesel fuel spray injected through throttling pintle nozzle into quiescent room-temperature air at 11 atm. Nozzle opening pressure 9.9 MPa. Pump speed 500 rev/min. Droplets are sampled well downstream of injector at given radial distances from spray axis.[32]

which will change the droplet size distribution and mean diameter. The downstream drop size in the solid-cone sprays used in diesel-injection systems is markedly influenced by both drop coalescence and breakup. Eventually a balance is reached as coalescence decreases (due to the expansion of the spray) and breakup ceases (due to the reduced relative velocity between the drops and the entrained gas).[31]

Measurements of droplet size distributions within a simulated diesel spray indicate how size varies with location. Figure 10-28 shows the variation in drop size distribution with radial distance from the spray axis, at a fixed axial location. The drop sizes were measured with a liquid immersion technique where a sample of drops is collected in a small cell filled with an immiscible liquid. Size distributions can be expressed in terms of:

1. The incremental number of drops Δn within the size range $D_d - \Delta D_d/2 < D_d < D_d + \Delta D_d/2$
2. The incremental volume ΔV of drops in this size range
3. The cumulative number of drops n less than a given size D_d
4. The cumulative volume V of drops less than a given size D_d

Since the drops are spherical:

$$\frac{dn}{dD_d} = \frac{6}{\pi D_d^3}\frac{dV}{dD_d} \tag{10.29}$$

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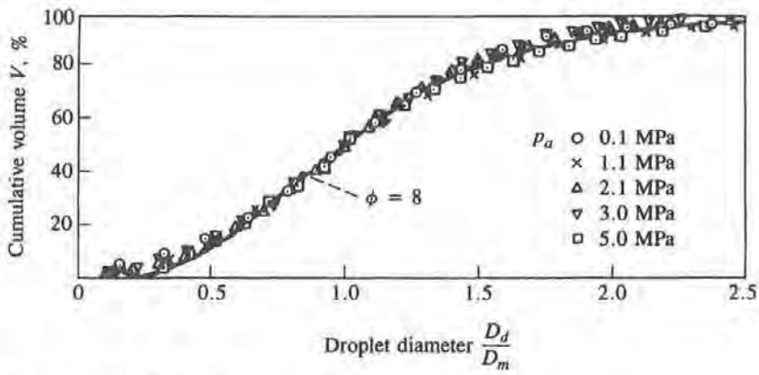


FIGURE 10-29
Normalized drop-size cumulative frequency distribution in spray injected into ambient-temperature air for air pressures from 0.1 to 5 MPa. Throttling pintle nozzle with nozzle opening pressure of 9.9 MPa. Median drop diameter $D_m = 1.224D_{SM}$.[32]

The distributions shown in the figure are frequency distributions of drop volume.[32] The peak in the distribution shifts to larger drop diameters as the radial position decreases: on average, the drops are smaller at the periphery of the spray.

To characterize the spray, expressions for drop size distribution and mean diameter are desirable. An appropriate and commonly used mean diameter is the *Sauter mean diameter:*

$$D_{SM} = \left(\int D_d^3\, dn\right) \Big/ \left(\int D_d^2\, dn\right) \tag{10.30}$$

where dn is the number of drops with diameter D_d in the range $D_d - dD_d/2 < D_d < D_d + dD_d/2$. The integration is usually carried out by summing over an appropriate number of drop size groups. The Sauter mean diameter is the diameter of the droplet that has the same surface/volume ratio as that of the total spray.

Various expressions for the distribution of drop sizes in liquid sprays have been proposed. One proposed by Hiroyasu and Kadota[32] based on the chi-square statistical distribution fits the available experimental data. Figure 10-29 shows how the chi-square distribution with a degree of freedom equal to 8 fits well to experimental measurements of the type shown in Fig. 10-28. Here D_m is the median drop diameter which for this chi-square curve is $1.224D_{SM}$. The nondimensional expression for drop size distribution in sprays injected through hole nozzles, pintle nozzles, and throttling pintle nozzles given by the chi-square distribution is

$$\frac{dV}{V} = 13.5\left(\frac{D_d}{D_{SM}}\right)^3 \exp\left[-3\left(\frac{D_d}{D_{SM}}\right)\right] d\left(\frac{D_d}{D_{SM}}\right) \tag{10.31}$$

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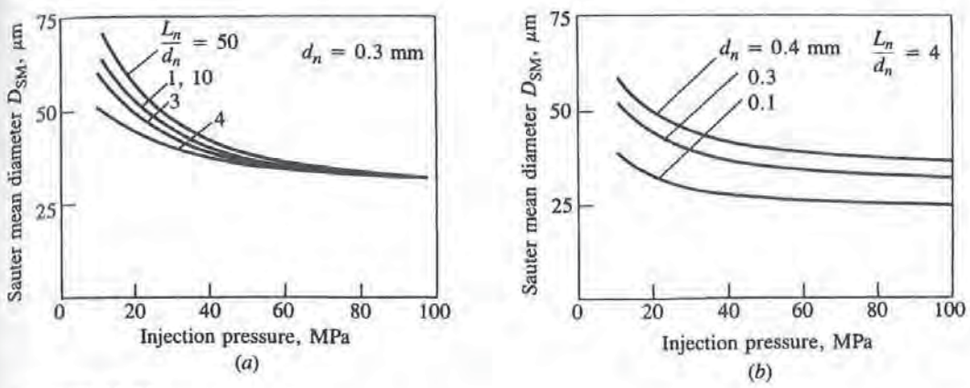


FIGURE 10-30
Effect of fuel-injection pressure and nozzle geometry and size on Sauter mean drop diameter. (*a*) Effect of nozzle length/diameter ratio L_n/d_n and injection pressure. (*b*) Effect of nozzle diameter d_n and injection pressure.[18]

An empirical expression for the Sauter mean diameter D_{SM} (in micrometers) for typical diesel fuel properties given by Hiroyasu and Kadota[32] is

$$D_{SM} = A(\Delta p)^{-0.135}\rho_a^{0.121}V_f^{0.131} \tag{10.32}$$

where Δp is the mean pressure drop across the nozzle in megapascals, ρ_a is the air density in kilograms per cubic meter, and V_f is the amount of fuel delivered per cycle per cylinder in cubic millimeters per stroke. A is a constant which equals 25.1 for pintle nozzles, 23.9 for hole nozzles, and 22.4 for throttling pintle nozzles. Other expressions for predicting D_{SM} can be found in Ref. 17.

The effects of injection pressure, nozzle geometry and size, air conditions, and fuel properties on Sauter mean diameter in sprays obtained with diesel fuel-injection nozzles have been extensively studied. Various immersion, photographic, and optical techniques for making such measurements have been used.[17] Some of the major effects are illustrated in Figs. 10-30 and 10-31 which show

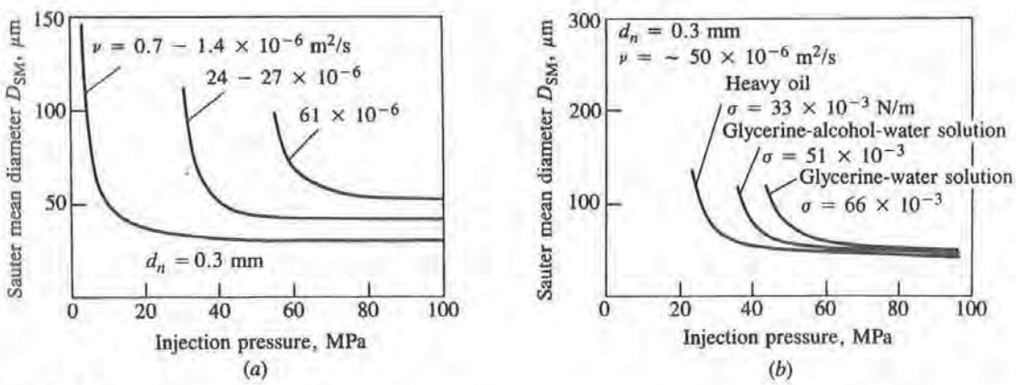


FIGURE 10-31
Effect of (*a*) liquid viscosity ν and (*b*) liquid surface tension σ on Sauter mean drop diameter as a function of injection pressure. Air conditions: 3 MPa and ambient temperature.[17]

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average Sauter mean diameters determined optically from studies of steady diesel fuel sprays in a pressurized vessel. Figure 10-30 shows that nozzle size affects the mean drop size in the expected direction. Nozzle length/diameter ratio is also shown to be important: an $L_n/d_n = 4$ gives the minimum mean drop size at low and intermediate injection pressures. This L_n/d_n also corresponds to the minimum value of spray breakup length and to the maximum spray cone angle. Fuel viscosity and surface tension also affect mean drop size as shown in Fig. 10-31, with the effects being most significant at lower injection pressures.

10.5.6 Spray Evaporation

The injected liquid fuel, atomized into small drops near the nozzle exit to form a spray, must evaporate before it can mix with air and burn. Figure 10-20 showed the basic structure of an evaporating diesel spray under conditions typical of a large direct-injection engine. Back illumination showed that a core exists along the axis of the spray where the liquid fuel ligaments or drops are sufficiently dense to attenuate the light beam. Once the start-up phase of the injection process is over, the length of this core remains essentially constant until injection ends. This core is surrounded by a much larger vapor-containing spray region which continues to penetrate deeper into the combustion chamber: the core extends only partway to the spray tip. Additional insight into the physical structure of evaporating sprays can be obtained from the schlieren photographs taken just after the end of injection in a prechamber engine with air swirl, shown in Fig. 10-32. The lowest magnification picture (A) shows the overall structure of the spray. The only liquid-containing region evident is that part of the core nearest the nozzle which shows black on the left of the photograph. The spreading vapor region of the spray, carried around the chamber by the swirling air flow, appears mottled due to local turbulent vapor concentration and temperature fluctuations. The dark region within the spray vapor region is due to soot formed where the fuel vapor concentration is sufficiently high. It is probable that, after the breakup length, the dense black liquid core of the spray is composed of individual droplets but the concentration is so high along the optical path that the light beam is fully extinguished. However, the last part of the core close to the nozzle tip (B) disperses sufficiently for individual features to be resolved. The small black dots are liquid fuel drops in the size range 20 to 100 μm. Fuel drop vapor trails can be observed in the highest magnification photo (C) corresponding to various stages of evaporation. These range from drops showing little surrounding vapor to vapor trails with little liquid remaining at the head. The vapor trails show random orientations relative to the spray axis, presumably due to local air turbulence. The process of droplet evaporation under normal engine operating conditions appears to be rapid relative to the total combustion period.[21]

Let us examine the drop evaporation process in more detail. Consider a liquid drop at close to ambient temperature injected into air at typical end-of-compression engine conditions. Three phenomena will determine the history of the drop under these conditions:

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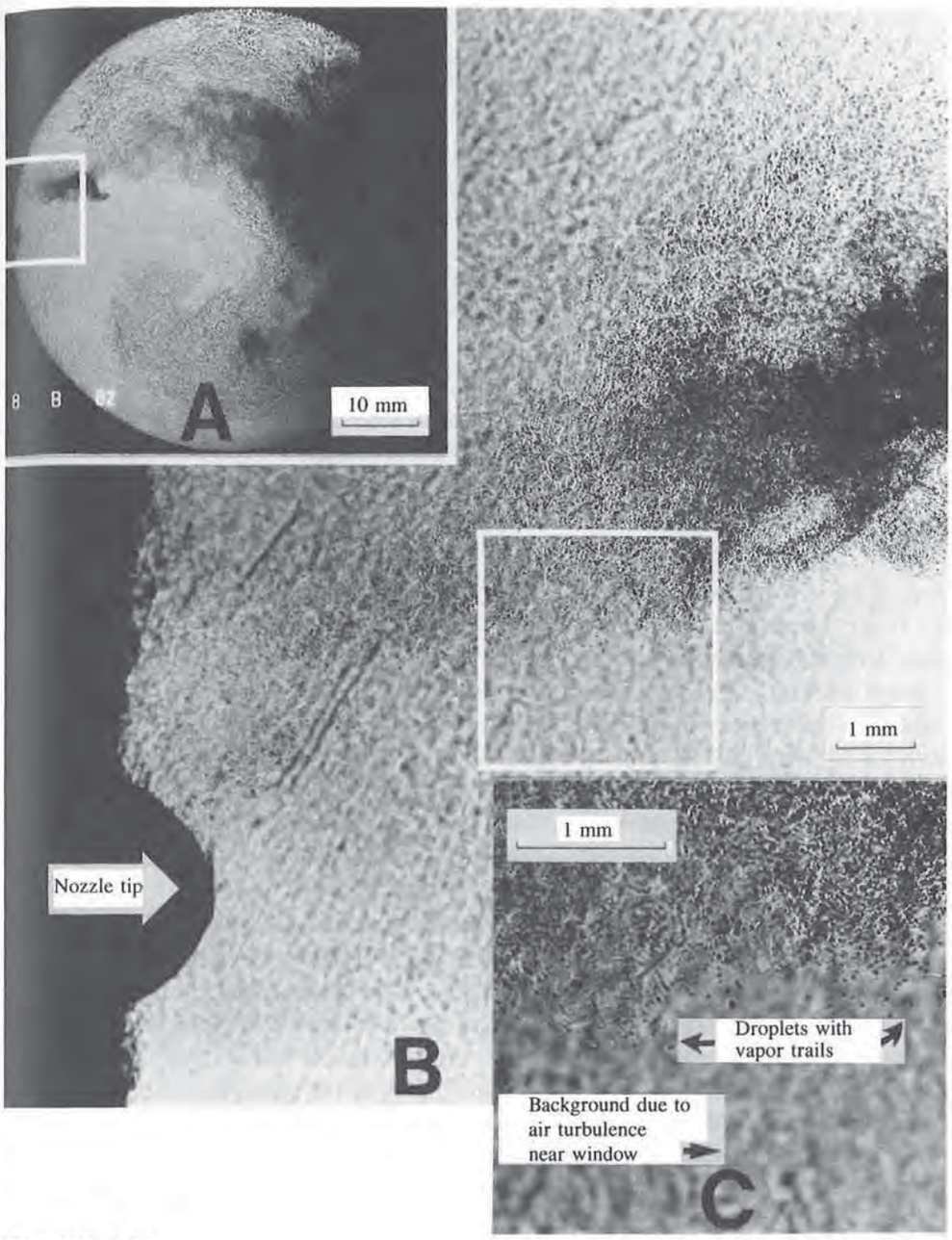


FIGURE 10-32
Shadowgraph photographs at three magnifications taken just after the end of injection of diesel-fuel spray into swirling air flow in prechamber of special diesel engine. Nozzle hole diameter = 0.25 mm.[21]

1. Deceleration of the drop due to aerodynamic drag
2. Heat transfer to the drop from the air
3. Mass transfer of vaporized fuel away from the drop

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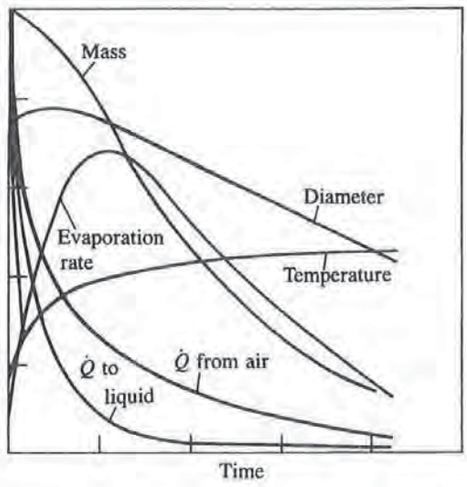


FIGURE 10-33
Schematic of variation of mass, diameter, temperature, evaporation rate, heat-transfer rate from air, and heat-transfer rate to liquid drop core as function of time during evaporation process of individual drop in diesel environment at the time of injection.

As the droplet temperature increases due to heat transfer, the fuel vapor pressure increases and the evaporation rate increases. As the mass transfer rate of vapor away from the drop increases, so the fraction of the heat transferred to the drop surface which is available to increase further the drop temperature decreases. As the drop velocity decreases, the convective heat-transfer coefficient between the air and the drop decreases. The combination of these factors gives the behavior shown in Fig. 10-33 where drop mass, temperature, velocity, vaporization rate, and heat-transfer rate from the air are shown schematically as a function of time following injection.[33] Analysis of individual fuel drops 25 μm in diameter, injected into air at typical diesel conditions, indicates that evaporation times are usually less than 1 ms.[34]

Such an analysis is relevant to drops that are widely separated (e.g., at the edge of the spray). In the spray core, where drop number densities are high, the evaporation process has a significant effect on the temperature and fuel-vapor concentration in the air within the spray. As fuel vaporizes, the local air temperature will decrease and the local fuel vapor pressure will increase. Eventually thermodynamic equilibrium would pertain: this is usually called adiabatic saturation.[33] Calculated thermodynamic equilibrium temperatures for diesel spray conditions are plotted in Fig. 10-34 as a function of the fuel/air mass ratio for *n*-dodecane and *n*-heptane. The initial liquid fuel temperature was 300 K. The ratio of fuel vapor to air mass at these equilibrium conditions is also shown. To the left of the peaks in the m_{fv}/m_a curves, only fuel vapor is present. To the right of these peaks, liquid fuel is also present because the vapor phase is saturated.[35] Liquid fuel vaporization causes substantial reductions in gas temperature. While this equilibrium situation may not be reached within the spray, these results are useful for understanding the temperature distribution within an evaporating spray.

To quantify accurately the fuel vaporization rate within a diesel fuel spray requires the solution of the coupled conservation equations for the liquid drop-

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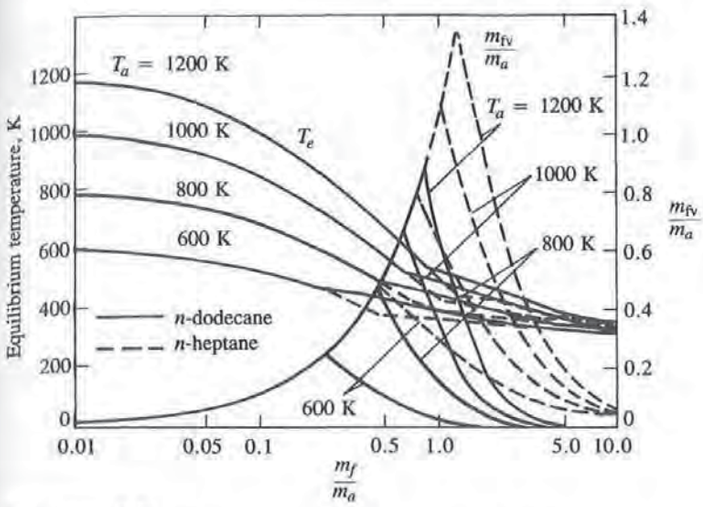


FIGURE 10-34
Adiabatic-saturation conditions for equilibrium mixtures formed by injecting *n*-dodecane and *n*-heptane, initially liquid at 300 K, into air at initial temperature T_a between 600 and 1200 K and initial density 6.5 kg/m^3. Equilibrium mixture temperature (T_e) and ratio of fuel vapor mass (m_{fv}) to air mass (m_a) shown as function of ratio of total fuel mass m_f to m_a. Fuel vapor only present to left of peaks in m_{fv}/m_a curves: liquid fuel also present to right of peaks.[35]

lets and the air within the combustion chamber. Various phenomenological models and computational fluid dynamic models have been developed for this purpose (see Secs. 14.4.3 and 14.5.5). In the most sophisticated of these, the spray is assumed to be composed of discrete computational particles each of which represents a group of droplets of similar size, temperature, etc. The distribution functions in droplet size, velocity, temperature, etc., produced by the fuel injector are statistically sampled and the resulting discrete particles are followed along lagrangian trajectories as they interact and exchange mass, momentum, and energy with the surrounding gas. Drops interact directly with each other via collisions and indirectly via evaporation by modifying the ambient vapor concentration and gas temperature. Studies with such models indicate that, under normal diesel engine conditions, 70 to 95 percent of the injected fuel is in the vapor phase at the start of combustion. Evaporation is more than 90 percent complete after 1 ms. However, only 10 to 35 percent of the vaporized fuel has mixed to within flammability limits in a typical medium-speed DI diesel engine. Thus combustion is largely mixing-limited, rather than evaporation-limited.[36] Of course, under cold-starting conditions, evaporation becomes a major constraint.

10.6 IGNITION DELAY

10.6.1 Definition and Discussion

The ignition delay in a diesel engine was defined as the time (or crank angle) interval between the start of injection and the start of combustion. The start of

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injection is usually taken as the time when the injector needle lifts off its seat (determined by a needle-lift indicator). The start of combustion is more difficult to determine precisely. It is best identified from the change in slope of the heat-release rate, determined from cylinder pressure data using the techniques described in Sec. 10.4, which occurs at ignition. Depending on the character of the combustion process, the pressure data alone may indicate when pressure change due to combustion first occurs; in DI engines under normal conditions ignition is well defined, but in IDI engines the ignition point is harder to identify. Flame luminosity detectors are also used to determine the first appearance of the flame. Experience has shown that under normal conditions, the point of appearance of the flame is later than the point of pressure rise and results in greater uncertainty or error in determining the ignition point.

Both physical and chemical processes must take place before a significant fraction of the chemical energy of the injected liquid fuel is released. The physical processes are: the atomization of the liquid fuel jet; the vaporization of the fuel droplets; the mixing of fuel vapor with air. The chemical processes are the precombustion reactions of the fuel, air, residual gas mixture which lead to autoignition. These processes are affected by engine design and operating variables, and fuel characteristics, as follows.

Good atomization requires high fuel-injection pressure, small injector hole diameter, optimum fuel viscosity, and high cylinder air pressure at the time of injection (see Sec. 10.5.3). The rate of vaporization of the fuel droplets depends on the size of the droplets, their distribution, and their velocity, the pressure and temperature inside the chamber, and the volatility of the fuel. The rate of fuel-air mixing is controlled largely by injector and combustion chamber design. Some combustion chamber and piston head shapes are designed to amplify swirl and create turbulence in the air charge during compression. Some engine designs use a prechamber or swirl chamber to create the vigorous air motion necessary for rapid fuel-air mixing (see Sec. 10.2). Also, injector design features such as the number and spatial arrangement of the injector holes determine the fuel spray pattern. The details of each nozzle hole affect the spray cone angle. The penetration of the spray depends on the size of the fuel droplets, the injection pressure, the air density, and the air-flow characteristics. The arrangement of the sprays, the spray cone angle, the extent of spray penetration, and the air flow all affect the rate of air entrainment into the spray. These physical aspects of fuel-injection and fuel-spray behavior are reviewed in Sec. 10.5.

The chemical component of the ignition delay is controlled by the precombustion reactions of the fuel. A fundamental discussion of autoignition or spontaneous hydrocarbon oxidation in premixed fuel-air mixtures is given in Sec. 9.6.2. Since the diesel engine combustion process is heterogeneous, its spontaneous ignition process is even more complex. Though ignition occurs in vapor phase regions, oxidation reactions can proceed in the liquid phase as well between the fuel molecules and the oxygen dissolved in the fuel droplets. Also, cracking of large hydrocarbon molecules to smaller molecules is occurring. These chemical processes depend on the composition of the fuel and the cylinder charge tem-

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perature and pressure, as well as the physical processes described above which govern the distribution of fuel throughout the air charge.

Since the ignition characteristics of the fuel affect the ignition delay, this property of a fuel is very important in determining diesel engine operating characteristics such as fuel conversion efficiency, smoothness of operation, misfire, smoke emissions, noise, and ease of starting. The ignition quality of a fuel is defined by its cetane number. Cetane number is determined by comparing the ignition delay of the fuel with that of primary reference fuel mixtures in a standardized engine test (see below). For low cetane fuels with too long an ignition delay, most of the fuel is injected before ignition occurs, which results in very rapid burning rates once combustion starts with high rates of pressure rise and high peak pressures. Under extreme conditions, when autoignition of most of the injected fuel occurs, this produces an audible knocking sound, often referred to as "diesel knock." For fuels with very low cetane numbers, with an exceptionally long delay, ignition may occur sufficiently late in the expansion process for the burning process to be quenched, resulting in incomplete combustion, reduced power output, and poor fuel conversion efficiency. For higher cetane number fuels, with shorter ignition delays, ignition occurs before most of the fuel is injected. The rates of heat release and pressure rise are then controlled primarily by the rate of injection and fuel-air mixing, and smoother engine operation results.

10.6.2 Fuel Ignition Quality

The ignition quality of a diesel fuel is defined by its *cetane number*. The method used to determine the ignition quality in terms of cetane number is analogous to that used for determining the antiknock quality of gasoline in terms of octane number. The cetane number scale is defined by blends of two pure hydrocarbon reference fuels. Cetane (*n*-hexadecane, $C_{16}H_{34}$), a hydrocarbon with high ignition quality, represents the top of the scale with a cetane number of 100. An isocetane, heptamethylnonane (HMN), which has a very low ignition quality, represents the bottom of the scale with a cetane number of 15.† Thus, cetane number (CN) is given by

$$\text{CN} = \text{percent } n\text{-cetane} + 0.15 \times \text{percent HMN} \tag{10.33}$$

The engine used in cetane number determination is a standardized single-cylinder, variable compression ratio engine with special loading and accessory equipment and instrumentation. The engine, the operating conditions, and the test procedure are specified by ASTM Method D613.[37] The operating requirements include: engine speed—900 rev/min; coolant temperature—100°C; intake air temperature—65.6°C (150°F); injection timing—13° BTC; injection

† In the original procedure α-methylnapthalene ($C_{11}H_{10}$) with a cetane number of zero represented the bottom of the scale. Heptamethylnonane, a more stable compound, has replaced it.

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pressure—10.3 MPa (1500 lb/in^2). With the engine operating under these conditions, on the fuel whose cetane number is to be determined, the compression ratio is varied until combustion starts at TC: i.e., an ignition delay period of 13° (2.4 ms at 900 rev/min) is produced. The above procedure is then repeated using reference fuel blends. Each time a reference fuel is tried, the compression ratio is adjusted to give the same 13° ignition delay. When the compression ratio required by the actual fuel is bracketed by the values required by two reference blends differing by less than five cetane numbers, the cetane number of the fuel is determined by interpolation between the compression ratios required by the two reference blends.

Because of the expense of the cetane number test, many correlations which predict ignition quality based on the physical properties of diesel fuels have been developed.[38, 39] A calculated *cetane index* (CCI) is often used to estimate ignition quality of diesel fuels (ASTM D976[40]). It is based on API gravity and the mid-boiling point (temperature 50 percent evaporated). It is applicable to straight-run fuels, catalytically cracked stocks, and blends of the two. Its use is suitable for most diesel fuels and gives numbers that correspond quite closely to cetane number. A *diesel index* is also used. It is based on the fact that ignition quality is linked to hydrocarbon composition: *n*-paraffins have high ignition quality, and aromatic and napthenic compounds have low ignition quality. The aniline point (ASTM D611[41]—the lowest temperature at which equal volumes of the fuel and aniline become just miscible) is used, together with the API gravity, to give the diesel index:

$$\text{Diesel index} = \text{aniline point (°F)} \times \frac{\text{API gravity}\dagger}{100} \tag{10.34}$$

The diesel index depends on the fact that aromatic hydrocarbons mix completely with aniline at comparatively low temperatures, whereas paraffins require considerably higher temperatures before they are completely miscible. Similarly, a high API gravity denotes low specific gravity and high paraffinicity, and, again, good ignition quality. The diesel index usually gives values slightly above the cetane number. It provides a reasonable indication of ignition quality in many (but not all) cases.

10.6.3 Autoignition Fundamentals

Basic studies in constant-volume bombs, in steady-flow reactors, and in rapid-compression machines have been used to study the autoignition characteristics of fuel-air mixtures under controlled conditions. In some of these studies the fuel and air were premixed; in some, fuel injection was used. Studies with fuel injec-

† API gravity is based on specific gravity and is calculated from: API gravity, deg = (141.5/specific gravity at 60°F) − 131.5.

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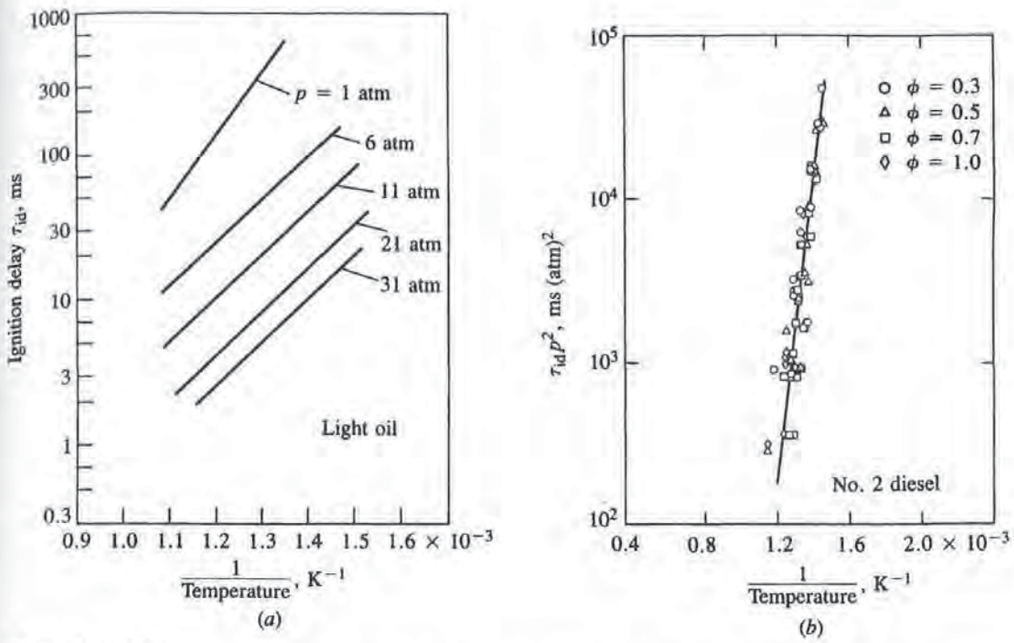


FIGURE 10-35
(*a*) Ignition delay as function of reciprocal air temperature for light oil spray injected into constant-volume combustion bomb. Injection pressure 9.8 MPa (100 atm). Air pressures indicated.[42] (*b*) Ignition delay × (pressure)^2 measured in steady-flow reactor for No. 2 diesel fuel as function of reciprocal temperature. Fuel/air equivalence ratio ϕ varied from 0.3 to 1.0.[43]

tion into constant-temperature and pressure environments have shown that the temperature and pressure of the air are the most important variables for a given fuel composition. Ignition delay data from these experiments have usually been correlated by equations of the form:

$$\tau_{id} = Ap^{-n} \exp\left(\frac{E_A}{\tilde{R}T}\right) \tag{10.35}$$

where τ_{id} is the ignition delay (the time between the start of injection and the start of detectable heat release), E_A is an apparent activation energy for the fuel autoignition process, $\tilde{R}$ is the universal gas constant, and A and n are constants dependent on the fuel (and, to some extent, the injection and air-flow characteristics).

Figure 10-35*a* shows ignition delay data obtained by injecting liquid fuel sprays into a high-pressure heated constant-volume bomb.[42] Figure 10-35*b* shows ignition delay data from a steady-flow high-pressure reactor where vaporized fuel was mixed rapidly with the heated air stream.[43] The match between the form of Eq. (10.35) and the data is clear. Figure 10-35*b* also shows an equivalence ratio dependence of the ignition delay. Representative values for A, n, and E_A for Eq. (10.35), taken from these and other studies, are given in Table 10.3. Ignition delay times calculated with these formulas for various diesel engines are given in

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TABLE 10.3
Constants for Arrhenius equation for ignition delay:[44]

$$\tau_{id}(\text{ms}) = Ap^{-n} \exp\left[E_A/(\bar{R}T)\right]$$

	Conditions				Parameters		
Investigator	Apparatus	Fuel	p, atm	T, K	n	A	$E_A/\bar{R}$, K
Spadaccini and TeVelde[43] No. 1	Steady flow	No. 2 diesel	10–30	650–900	2	2.43×10^{-9}	20,926
Spadaccini and TeVelde[43] No. 2	Steady flow	No. 2 diesel	10–30	650–900	1	4.00×10^{-10}	20,080
Stringer *et al.*[45]	Steady flow	Diesel 45–50 cetane number	30–60	770–980	0.757	0.0405	5,473
Wolfer[46]	Constant-volume bomb	Fuel with cetane number >50	8–48	590–782	1.19	0.44	4,650
Hiroyasu *et al.*[29]	Constant-volume bomb	Kerosene	1–30	673–973	1.23	0.0276	7,280

Table 10.4. Air pressures and temperatures at TC piston position were estimated from measured cylinder pressure data. Measured ignition delay times in these types of engines are: 0.6 to 3 ms for low-compression-ratio DI diesel engines over a wide range of operating conditions; 0.4 to 1 ms for high-compression-ratio and turbocharged DI diesel engines; 0.6 to 1.5 ms for IDI diesel engines.[44]

The variation in the calculated delay times can be attributed to several factors:

1. In some cases the correlations are being extrapolated outside their original range of operating conditions.
2. The methods used to detect the start of combustion, and hence the duration of the delay, are not identical.
3. The experimental apparatus and the method of fuel-air mixture preparation are different.

The third factor is probably the most significant. As has been explained, the phenomenon of autoignition of a fuel spray consists of sequences of physical and chemical processes of substantial complexity. The relative importance of each process depends on the ambient conditions, on fuel properties, and on how the fuel-air mixture is prepared. For example, fuel evaporation times are significant in cold engines, but not under fully warmed-up conditions. Thus, an equation of the simple form of Eq. (10.35) can only fit the data over a limited range of conditions. The correlations of Spadaccini and TeVelde[43] have much higher activation energies. Normally, lower values of $E_A/\bar{R}$ imply that physical processes such as vaporization and mixing are important and relevant to chemical processes. Thus, fuel preparation, mixture inhomogeneity, heat loss, and nonuniform flow patterns

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TABLE 10.4
Calculated ignition delay times[44]

Engine	Conditions			τ_{id}, ms				
				Spadaccini and TeVelde[43]				
	Speed, rev/min	p, atm	T, K	No. 1	No. 2	Stringer *et al.*[48]	Wolfer[46]	Hiroyasu *et al.*[29]
IDI Diesel								
1. Low swirl	600	45.6	690	17.3	38.2	6.26	3.94	9.60
	1200	49.3	747	1.47	3.83	3.22	2.15	3.90
	1800	52.5	758	0.86	2.44	2.76	1.82	3.13
2. High swirl	600	45.2	674	36.3	76.9	7.60	4.68	12.5
	1200	48.4	721	4.18	10.3	4.25	2.75	5.67
	1800	51.8	744	1.47	4.07	3.19	2.08	3.82
DI Diesel								
1. Low compression ratio		42.8	781	0.57	1.37	2.60	1.92	2.39
2. High compression ratio	1500	58.8	975	0.0015	0.0060	0.508	0.407	0.322

affect the ignition delay. While the work of Spadaccini and TeVelde probably describes the chemical ignition delay more accurately, since great care was taken to obtain a uniform mixture and flow, the experiments in constant-volume bombs with diesel-type fuel injectors are more relevant to the diesel engine compression-ignition combustion process because they include the appropriate physical and chemical processes. The available engine ignition delay data suggest that for delays less than about 1 ms, the rate of decrease in delay with increasing temperature becomes much less than that indicated by the data in Fig. 10-35. This is due to the increasing relative importance of physical processes relative to chemical processes during the delay period. Thus relations of the form of Eq. (10.35) should be used with caution.

In general, τ_{id} is a function of mixture temperature, pressure, equivalence ratio, and fuel properties (though no accepted form for the variation with equivalence ratio is yet established). In the above referenced studies, the fuel was injected into a uniform air environment where the pressure and temperature only changed due to the cooling effect of the fuel-vaporization and fuel-heating processes. In an engine, pressure and temperature change during the delay period due to the compression resulting from piston motion. To account for the effect of changing conditions on the delay the following empirical integral relation is usually used:

$$\int_{t_{si}}^{t_{si}+\tau_{id}} \left(\frac{1}{\tau}\right) dt = 1 \tag{10.36}$$

where t_{si} is the time of start of injection, τ_{id} is the ignition delay period, and τ is the ignition delay at the conditions pertaining at time t. Whether the variation in conditions is significant depends on the amount of injection advance before TC that is used and the length of the delay.

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10.6.4 Physical Factors Affecting Delay

The physical factors that affect the development of the fuel spray and the air charge state (its pressure, temperature, and velocity) will influence the ignition delay. These quantities depend on the design of the fuel-injection system and combustion chamber, and the engine operating conditions. The injection system variables affecting the fuel-spray development are injection timing, quantity, velocity, rate, drop size, and spray form or type. The relevant charge conditions depend on the combustion system employed, the details of the combustion chamber design, inlet air pressure and temperature, compression ratio, injection timing, the residual gas conditions, coolant and oil temperature, and engine speed. Data on these interactions are available for different types of diesel engines. The trends observed with the different diesel combustion systems are generally similar, though some of the details are different. In this section the ignition delay trends during normal (fully warmed-up) engine operation are considered. The dependence of the ignition delay on engine design and operating variables during engine starting and warm-up is also very important, and may be different from fully warmed-up behavior due to lower air temperature and pressure.

INJECTION TIMING. At normal engine conditions (low to medium speed, fully warmed engine) the minimum delay occurs with the start of injection at about 10 to 15° BTC.[47] The increase in the delay with earlier or later injection timing occurs because the air temperature and pressure change significantly close to TC. If injection starts earlier, the initial air temperature and pressure are lower so the delay will increase. If injection starts later (closer to TC) the temperature and pressure are initially slightly higher but then decrease as the delay proceeds. The most favorable conditions for ignition lie in between.

INJECTION QUANTITY OR LOAD. Figure 10-36 shows the effect of increasing injection quantity or engine load on ignition delay. The delay decreases approximately linearly with increasing load for this DI engine. As load is increased, the residual gas temperature and the wall temperature increase. This results in higher charge temperature (and also, to a lesser extent, charge pressure) at injection, thus shortening the ignition delay. When adjustment is made for this increasing temperature, it is found that increasing the quantity of fuel injected has no significant effect on the delay period under normal operating conditions. Under engine starting conditions, however, the delay increases due to the larger drop in mixture temperature associated with evaporating and heating the increased amount of fuel.[47] This latter result should be expected since it is the first part of the injected fuel which ignites first; subsequent injected fuel (above the minimum required to maintain the fuel-air mixture within the flammability limits during the delay) does not influence the delay.

DROP SIZE, INJECTION VELOCITY, AND RATE. These quantities are determined by injection pressure, injector nozzle hole size, nozzle type, and geometry.

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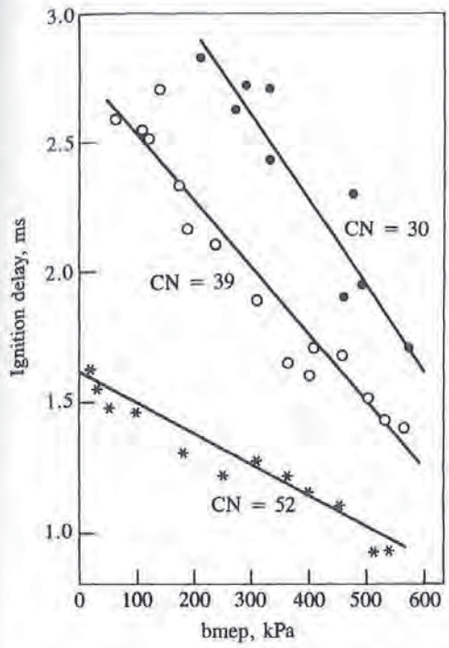


FIGURE 10-36
Ignition delays measured in a small four-stroke cycle DI diesel engine with $r_c = 16.5$ as a function of load at 1980 rev/min. Fuel cetane numbers 30, 39, and 52.[48]

Experiments by Lyn and Valdmanis[47] have shown that none of these factors has a significant effect on the delay. At normal operating conditions, increasing injection pressure produces only modest decreases in the delay. Doubling the nozzle hole diameter at constant injection pressure to increase the fuel flow rate (by a factor of about 4) and increase the drop size (by about 30 percent) had no significant effect on the delay. Studies of different nozzle hole geometries showed that the length/diameter ratio of the nozzle was not significant; nor did changes in nozzle type (multihole, pintle, pintaux) cause any substantial variation in delay at normal engine conditions.

INTAKE AIR TEMPERATURE AND PRESSURE. Figure 10-35 showed values of ignition delay for diesel fuels plotted against the reciprocal of charge temperature for several charge pressures at the time of injection. The intake air temperature and pressure will affect the delay via their effect on charge conditions during the delay period. Figure 10-37 shows the effects of inlet air pressure and temperature as a function of engine load. The fundamental ignition data available show a strong dependence of ignition delay on charge temperatures below about 1000 K at the time of injection. Above about 1000 K, the data suggest that the charge temperature is no longer so significant. Through this temperature range there is an effect of pressure at the time of injection on delay: the higher the pressure the shorter the delay, with the effect decreasing as charge temperatures increase and delay decreases. Since air temperature and pressure during the delay period are such important variables, other engine variables that affect the relation between the inlet air state and the charge state at the time of injection will influence the delay. Thus, an increase in the compression ratio will decrease the ignition delay,

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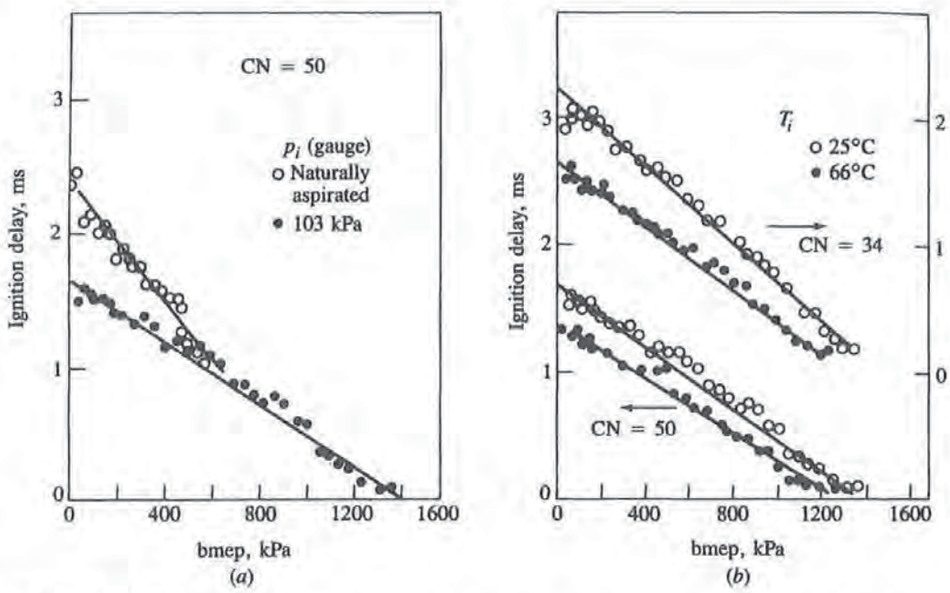


FIGURE 10-37
Effect of inlet air pressure and temperature on ignition delay over load range of small DI diesel at 1980 rev/min. (*a*) Engine naturally aspirated and with 1 atm boost; inlet air temperature $T_i = 25°C$; 50 cetane number fuel. (*b*) Engine naturally aspirated; $T_i = 25$ and 66°C; 34 and 50 cetane number fuel.[48]

and injection timing will affect the delay (as was discussed earlier), largely due to the changes in charge temperature and pressure at the time of injection.

ENGINE SPEED. Increases in engine speed at constant load result in a slight decrease in ignition delay when measured in milliseconds; in terms of crank angle degrees, the delay increases almost linearly.[48] A change in engine speed changes the temperature/time and pressure/time relationships. Also, as speed increases, injection pressure increases. The peak compression temperature increases with increasing speed due to smaller heat loss during the compression stroke.[47]

COMBUSTION CHAMBER WALL EFFECTS. The impingement of the spray on the combustion chamber wall obviously affects the fuel evaporation and mixing processes. Impingement of the fuel jet on the wall occurs, to some extent, in almost all of the smaller, higher speed engines. With the "M" system, this impingement is desired to obtain a smooth pressure rise. The ignition delay with the "M" system is longer than in conventional DI engine designs.[47] Engine and combustion bomb experiments have been carried out to examine the effect of wall impingement on the ignition delay. Figure 10-38 shows the effect of jet wall impingement on ignition delay measured in a constant-volume combustion bomb, for a range of air pressures and temperatures, and wall temperatures.[29] The wall was perpendicular to the spray and was placed 100 mm from the nozzle tip. The data shows that the presence of the wall reduces the delay at the lower

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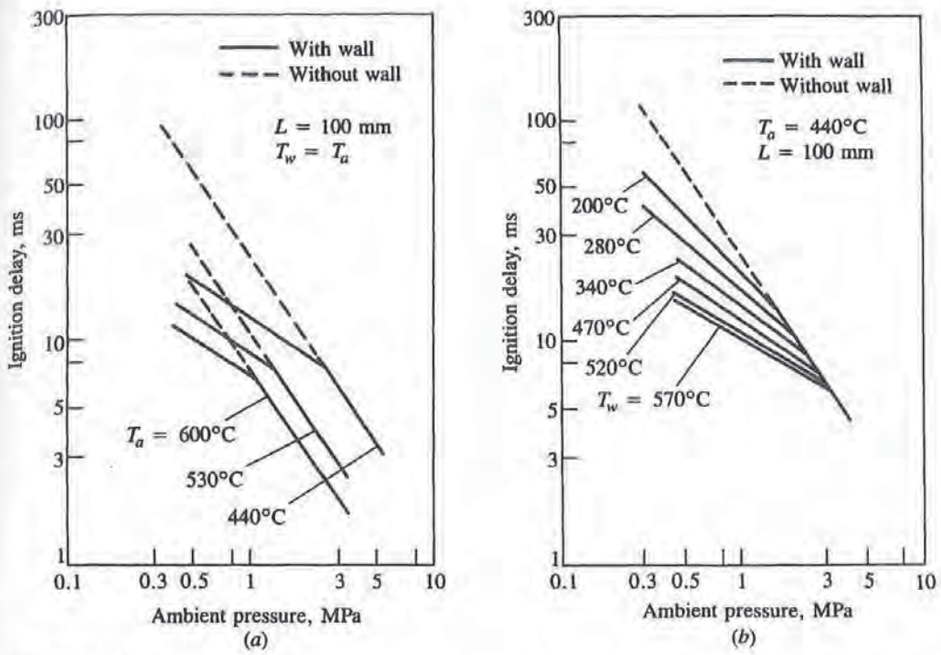


FIGURE 10-38
Effect of spray impingement on wall 100 mm from nozzle on ignition delay from combustion bomb studies. (*a*) Effect of air temperature as a function of air pressure; $T_w = T_{air}$. (*b*) Effect of wall temperature at 440°C air temperature.[29]

pressures and temperatures studied, but has no significant effect at the high pressures and temperatures more typical of normal diesel operation. Engine experiments where the delay was measured while the jet impingement process was varied showed analogous trends. The jet impingement angle (the angle between the fuel jet axis and the wall) was varied from almost zero (jet and wall close to parallel) to perpendicular. The delay showed a tendency to become longer as the impingement angle decreased. The most important result is not so much the modest change in delay but the difference in the initial rate of burning that results from the differences in fuel evaporation and fuel-air mixing rates.

SWIRL RATE. Changes in swirl rate change the fuel evaporation and fuel-air mixing processes. They also affect wall heat transfer during compression and, hence, the charge temperature at injection. Only limited engine studies of the effect of swirl rate variations on ignition delay have been made. At normal operating engine speeds, the effect of swirl rate changes on the delay are small. Under engine starting conditions (low engine speeds and compression temperatures) the effect is much more important,[47] due presumably to the higher rates of evaporation and mixing obtained with swirl.

OXYGEN CONCENTRATION. The oxygen concentration in the charge into which the fuel is injected would be expected to influence the delay. The oxygen concentration is changed, for example, when exhaust gas is recycled to the intake

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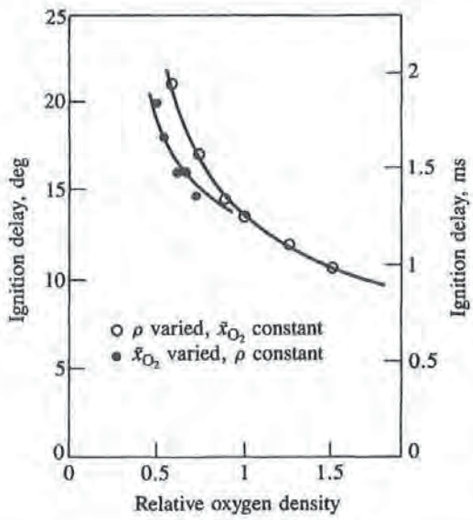


FIGURE 10-39
Effect of oxygen density in gas on ignition delay in single-cylinder DI engine of 1.3-dm^3 displacement with $r_c = 15$ at 1800 rev/min. Oxygen density changed by recycling exhaust gas at constant inlet density and by varying inlet pressure from 0.5 to 3 atm with air.[49]

for the control of oxides of nitrogen emissions (see Chap. 11). Results of a study carried out in a single-cylinder DI engine operated at a constant air/fuel ratio (30 : 1), manifold temperature, injection timing, and speed (1800 rev/min), where the oxygen concentration was varied by recirculating known amounts of cooled exhaust, are shown in Fig. 10-39.[49] Oxygen density is normalized by the naturally aspirated no-recirculation test value. As oxygen concentration is decreased, ignition delay increases.

10.6.5 Effect of Fuel Properties

Since both physical and chemical processes take place during the ignition delay, the effects of changes in the physical and chemical properties of fuels on the delay period have been studied. The chemical characteristics of the fuel are much the more important. The ignition quality of the fuel, defined by its cetane number, will obviously affect the delay. The dependence of cetane number on fuel molecular structure is as follows. Straight-chain paraffinic compounds (normal alkanes) have the highest ignition quality, which improves as the chain length increases. Aromatic compounds have poor ignition quality as do the alcohols (hence, the difficulties associated with using methanol and ethanol, possible alternative fuels, in compression-ignition engines). Figure 10-40 illustrates these effects. A base fuel was blended with pure paraffinic (normal, iso-, and cycloalkanes), aromatic, and olefinic hydrocarbons of various carbon numbers, by up to 20 percent by volume. The base fuel, a blend of 25 percent *n*-hexadecane and 75 percent isooctane, had a cetane number of 38.3. The figure shows that the resulting ignition delays correlate well as a function of cetane number at constant compression ratio and engine operating conditions. Addition of normal alkanes (excluding *n*-pentane and lower carbon number alkanes) improve the ignition quality. As the chain length of the added paraffin gets longer (higher carbon number) the cetane number improve-

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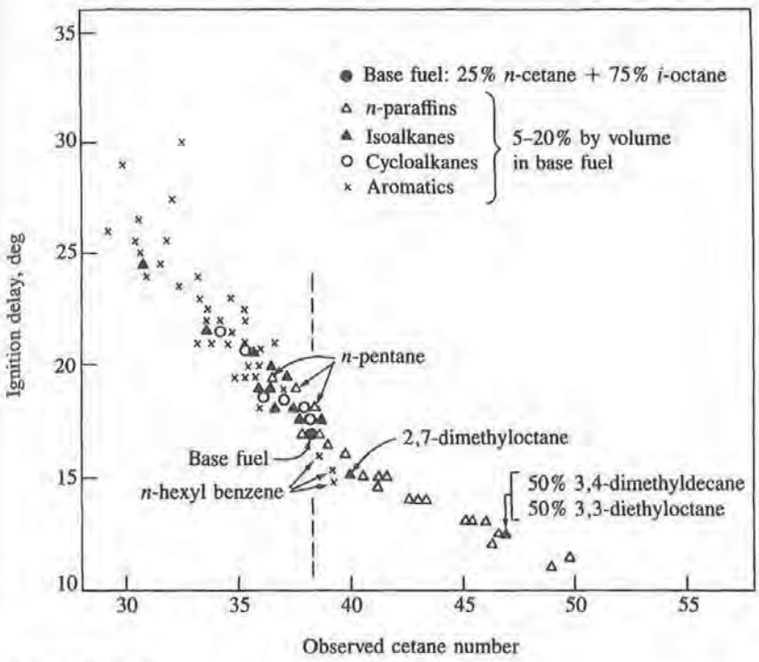


FIGURE 10-40
Effect of type of hydrocarbon structure on ignition quality of fuels in DI diesel combustion process at constant compression ratio and engine operating conditions.[50]

ment increases. Isoalkanes, depending on the degree of branching, degrade ignition quality (unless the branching is concentrated at one end of the molecule, when these types of isoalkanes improve ignition quality). Cycloalkanes and aromatics generally reduce the cetane number, unless they have a long *n*-alkane chain attached to the ring. The cetane number of a fuel (a measure of its ability to autoignite) generally varies inversely with its octane number (a measure of its ability to resist autoignition; see Fig. 9-69 for the effect of hydrocarbon structure on knock). The cetane number of commercial diesel fuel is normally in the range 40 to 55.

Engine ignition delay data with diesel fuels of different cetane number, at various constant loads and speeds, shown in Fig. 10-41, demonstrate similar trends. Within the normal diesel fuel cetane number range of 40 to 55, an approximately linear variation is evident. However, decreasing fuel cetane number below about 38 may result in a more rapid increase in ignition delay.

Cetane number is controlled by the source of crude oil, by the refining process, and by additives or ignition accelerators. Just as it is possible to reduce the tendency to knock or autoignite in spark-ignition engine fuels by adding antiknock agents, so there are additives that improve the ignition quality of compression-ignition engine fuels. Generally, substances that increase the tendency to knock enhance ignition, and vice versa. Ignition-accelerating additives include organic peroxides, nitrates, nitrites, and various sulfur compounds. The most important of these commercially are the alkyl nitrates (isopropyl nitrate,

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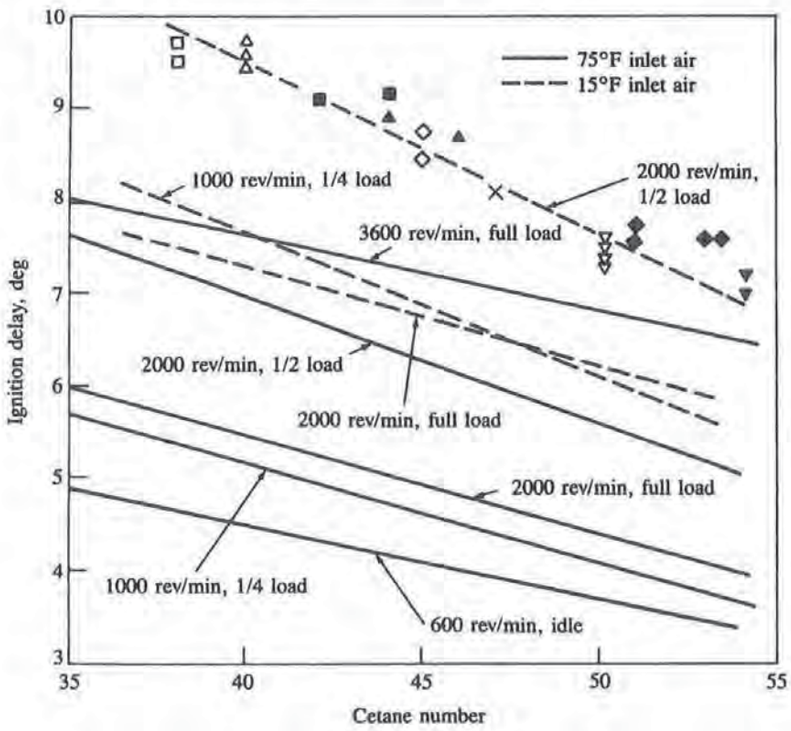


FIGURE 10-41
Effect of fuel cetane number on ignition delay over the load and speed range of 6.2-dm^3 eight-cylinder IDI swirl-chamber diesel engine. Top curve indicates typical fit between data and least-squares straight line over this cetane number range.[51]

primary amyl nitrates, primary hexyl nitrates, octyl nitrate).[52] Typically, about 0.5 percent of these additives by volume in a distillate fuel gives about a 10 cetane number increase in a fuel's ignition quality, though their effectiveness may depend on the composition of the base fuel. The incremental effect of increasing amounts of ignition-accelerating additives on cetane number decreases.[48] Usually, the ignition delay obtained with cetane improved blends are found to be equivalent to those obtained with natural diesel fuels of the same cetane number. Two potential practical uses for ignition accelerators are in upgrading the ignition characteristics of poorer quality diesel fuel and (in much larger amounts) making possible the use of alcohols in compression-ignition engines.

The physical characteristics of diesel fuel do not significantly affect the ignition delay in fully or partially warmed-up engines. Tests with fuels of different front-end volatility (over the cetane number range 38 to 53), and with substantially different front-end ignition quality for the same average cetane number, showed no discernible differences. Fuel viscosity variations over a factor of 2.5 were also tested and showed no significant effect.[48] Thus, in a warmed-up engine, variations in fuel atomization, spray penetration, and vaporization rate over reasonable ranges do not appear to influence the duration of the delay period significantly (see also Sec. 10.5.6 on fuel vaporization).

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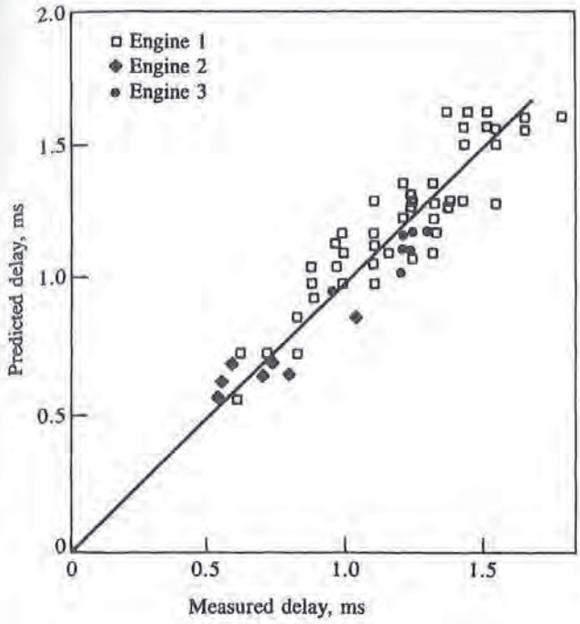


FIGURE 10-42
Comparison of engine ignition delays predicted with Eq. (10.37) with corresponding measured values.[54]

10.6.6 Correlations for Ignition Delay in Engines

Many correlations have been proposed for predicting ignition delay as a function of engine and air charge variables. These usually have the form of Eq. (10.35) and have been based on data from more fundamental experiments in combustion bombs and flow reactors. An important factor in assessing the appropriateness of any correlation is how it is to be used to predict the magnitude of the delay. If an equation for predicting the complete delay process (including all the physical and chemical processes from injection to combustion) is required, then the data show that such a simple form for the equation is unlikely to be adequate for the full range of engine conditions (see Table 10.4). However, if a model for the autoignition process of a premixed fuel-air mixture during the delay period is required, for use in conjunction with models for the physical processes of fuel evaporation and fuel-air mixing, then correlations such as those listed in Table 10.3 may be sufficiently accurate.

An empirical formula, developed by Hardenberg and Hase[53] for predicting the duration of the ignition delay period in DI engines, has been shown to give good agreement with experimental data over a wide range of engine conditions (see Fig. 10-42).[54] This formula gives the ignition delay (in crank angle degrees) in terms of charge temperature T (kelvins) and pressure p (bars) during the delay (taken as TC conditions) as

$$\tau_{id}(\text{CA}) = (0.36 + 0.22\bar{S}_p) \exp\left[E_A\left(\frac{1}{\bar{R}T} - \frac{1}{17{,}190}\right)\left(\frac{21.2}{p - 12.4}\right)^{0.63}\right] \quad (10.37)$$

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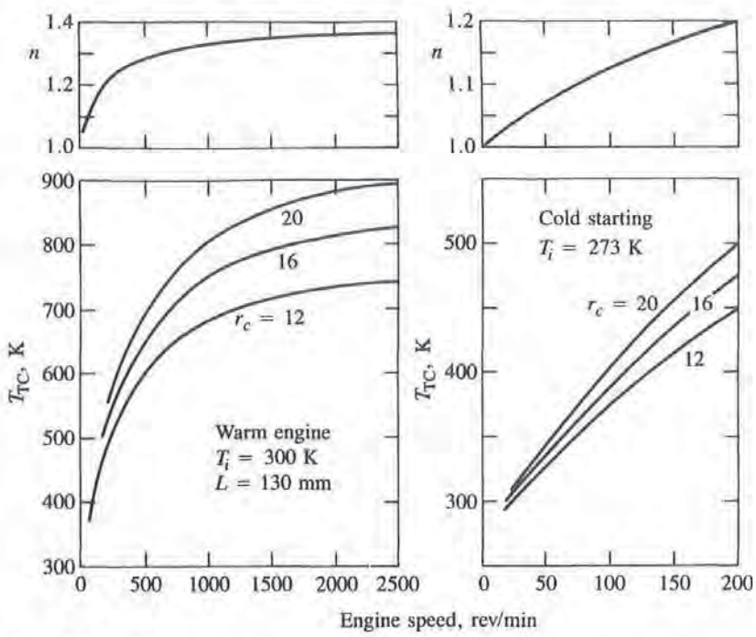


FIGURE 10-43
Exponent n for polytropic model of compression process in Eq. (10.39) and corresponding end-of-compression air temperature at TC. Warm and cold DI diesel engine with 130 mm stroke.[53]

where $\bar{S}_p$ is the mean piston speed (meters per second) and $\tilde{R}$ is the universal gas constant (8.3143 J/mol·K). E_A (joules per mole) is the apparent activation energy, and is given by

$$E_A = \frac{618{,}840}{\text{CN} + 25} \tag{10.38}$$

where CN is the fuel cetane number. The apparent activation energy decreases with increasing fuel cetane number. The delay in milliseconds is given by

$$\tau_{\text{id}}(\text{ms}) = \frac{\tau_{\text{id}}(\text{CA})}{0.006N}$$

where N, engine speed, is in revolutions per minute. Values for T and p can be estimated using a polytropic model for the compression process:

$$T_{\text{TC}} = T_i r_c^{n-1} \qquad p_{\text{TC}} = p_i r_c^n \tag{10.39a,b}$$

where n is the polytropic exponent (see Sec. 9.2.2), r_c is the compression ratio, and the subscript i denotes intake manifold conditions. Values of the polytropic exponent are given in Fig. 10-43 for a direct-injection diesel under warm and cold engine operating conditions.[49,53]

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10.7 MIXING-CONTROLLED COMBUSTION

10.7.1 Background

Earlier sections of this chapter have developed our current understanding of the individual processes which together make up the total injection-mixing-burning sequence—atomization, vaporization, fuel spray development, air entrainment, ignition, and combustion. While the phenomenological model developed by Lyn[6] provides satisfactory logical links between these processes, quantitative links are still lacking. Especially difficult to quantify are the relations between fuel spray behavior, flame structure, and fuel burning rate—the area of focus of this section. The color photographs of the compression-ignition combustion process in different types of diesel engines in Figs. 10-4 and 10-5 (see color plate between 498 and 499) show how the flame immediately following ignition spreads rapidly and envelops the spray. Depending on the spray configuration, the visible flame may then fill almost the entire combustion chamber. The flame and spray geometries are closely related. Mixing processes are also critical during the ignition delay period: while the duration of the delay period is not influenced in a major way by the rates of spray processes which together control "mixing," the amount of fuel mixed with air to within combustible limits during the delay (which affects the rate of pressure rise once ignition has occurred) obviously is directly related to mixing rates. Thus substantial observational evidence supports the mixing-controlled character of diesel engine combustion.

However, while it is well accepted that diesel combustion is normally controlled by the fuel-air mixing rate, fundamentally based quantitatively accurate models for this coupled mixing and combustion process are not yet available. The difficulties are twofold. First, the spray geometry in real diesel combustion systems is extremely complex. Second, the phenomena which must be described (and especially the unsteady turbulent diffusion diesel engine flame) are inadequately understood. Current capabilities for modeling these phenomena are reviewed in Chap. 14. Thermodynamic-based models of the diesel combustion process with atomization, vaporization, and spray development described by empirical or turbulent-jet-based submodels have been developed and used to predict burning rates. These are described in Secs. 14.4.3 and 14.4.4, and show reasonable but not precise agreement with data. Fluid-mechanic-based models of air flow, fuel spray behavior, and combustion are under active development (see Sec. 14.5). While realistic air-flow predictions are now feasible, predictions of spray behavior are less well developed and combustion-rate predictions are still exploratory.

In the following sections, the evidence linking spray characteristics to flame structure and burning rates is summarized.

10.7.2 Spray and Flame Structure

The structure of each fuel spray is that of a narrow liquid-containing core (densely filled with drops of order 20 μm in diameter) surrounded by a much

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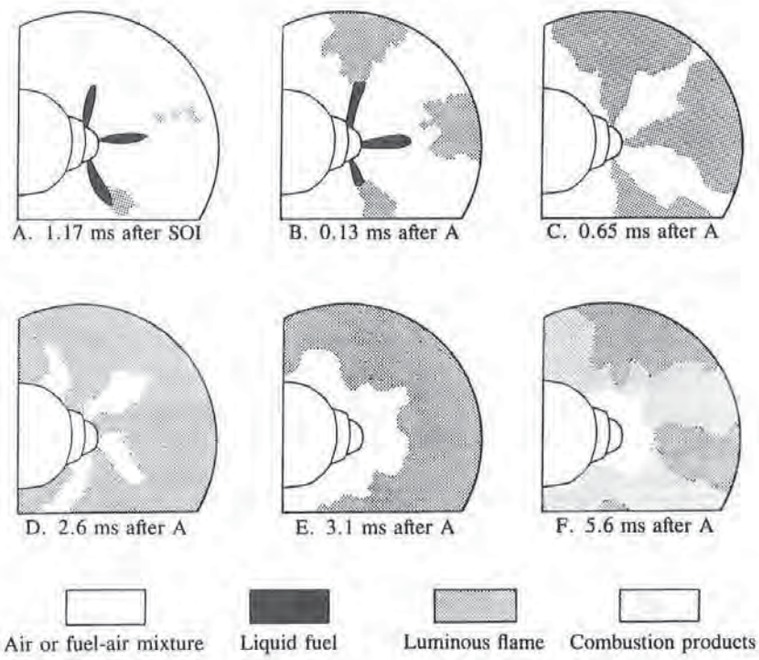
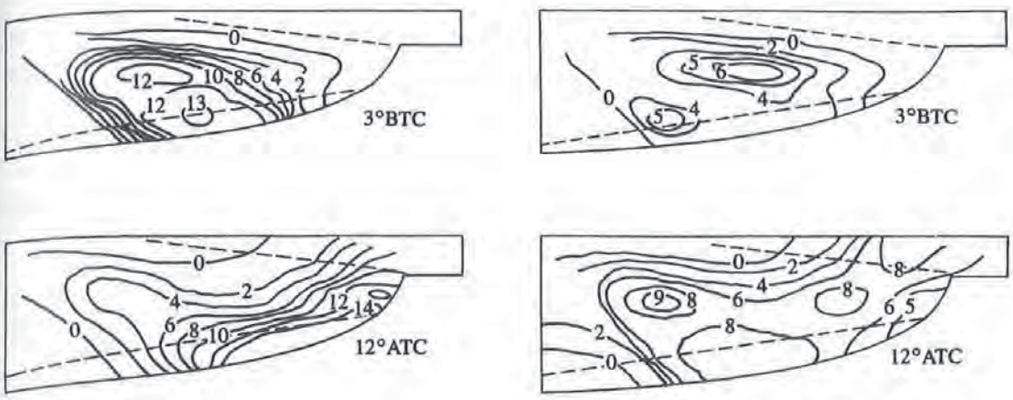


FIGURE 10-44
Tracings of outer boundary of liquid fuel spray and flame from high-speed movies of diesel combustion taken in a rapid-compression machine, looking down on piston through transparent head. First occurrence of luminous flame at A, 1.17 ms after start of injection. End of injection at D.[57]

larger gaseous-jet region containing fuel vapor (see Fig. 10-20). The fuel concentration in the core is extremely high: local fuel/air equivalence ratios near the nozzle of order 10 have been measured during the injection period. Fuel concentrations within the spray decrease with increasing radial and axial position at any given time, and with time at a fixed location once injection has ended.[55] The fuel distribution within the spray is controlled largely by turbulent-jet mixing processes. Fuel vapor concentration contours determined from interferometric studies of unsteady vaporizing diesel-like sprays, presented by Lakshminarayan and Dent,[56] confirm this gaseous turbulent-jet-like structure of the spray, with its central liquid-containing core which evaporates relatively quickly once fuel injection ends.

The location of the autoignition sites and subsequent spreading of the enflamed region in relation to the fuel distribution in the spray provides further evidence of the mixing-controlled character of combustion. Figure 10-44 shows how this process occurs under conditions typical of direct-injection quiescent-chamber diesel engines. It shows tracings of the liquid fuel spray and flame boundaries taken from high-speed movies of the injection and combustion processes with central injection of five fuel jets into a disc-shaped chamber in a rapid-compression machine.[57] These and other similar studies show that autoignition first occurs toward the edge of the spray, between the spray tip (which may by then have interacted with the combustion chamber walls, and which contains

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(*a*) CO (*b*) CO_2

FIGURE 10-45
Contours of constant CO and CO_2 concentration in a plane along the spray axis calculated from gas composition data obtained with a rapid-acting sampling valve in a large 30.5-cm bore DI quiescent-chamber diesel engine with $r_c = 12.85$ operated at 500 rev/min. Injection starts 17° BTC, ignition occurs 8° BTC, injection ends 5° ATC.[60]

later-injected fuel as explained in Sec. 10.5.2) and the injector nozzle. Experiments where air/fuel ratio contours for a gaseous fuel jet injected into a swirling air flow in a rig simulated the fuel-air mixing process in open-chamber diesels,[58] under conditions chosen to match a set of diesel combustion rapid-compression-machine experiments where the autoignition sites and subsequent flame development were recorded on movies,[59] showed that autoignition occurred in a concentration band between the equivalence ratios of 1 and 1.5. Subsequent flame development, along mixture contours close to stoichiometric, occurs rapidly, as indicated in Fig. 10-44. Initially, this is thought to be due to spontaneous ignition of regions close to the first ignition site due to the temperature rise associated with the strong pressure wave which emanates from each ignition site due to local rapid chemical energy release. Also, spontaneous ignition at additional sites on the same spray, well separated from the original ignition location, can occur. Turbulent mixing provides another flame-spreading mechanism. From this point flame development is rapid, and the gas expansion which occurs on burning deforms the original spray form. These processes take place in each fuel spray in a closely comparable though not necessarily identical manner. Combustion movies such as those in Figs. 10-4 and 10-44 show that flame rapidly envelops each spray once spontaneous ignition occurs.

Gas-sampling data indicate that the burned gases within the flame-enveloped spray are only partially reacted and may be fuel-rich. Figure 10-45 shows CO and CO_2 concentration contours determined from rapid-acting sample valve measurements from the combustion chamber of a large quiescent-chamber two-stroke cycle diesel engine.[60] The contour maps shown correspond to the centerline of one of the five injected fuel sprays. Injection commenced at

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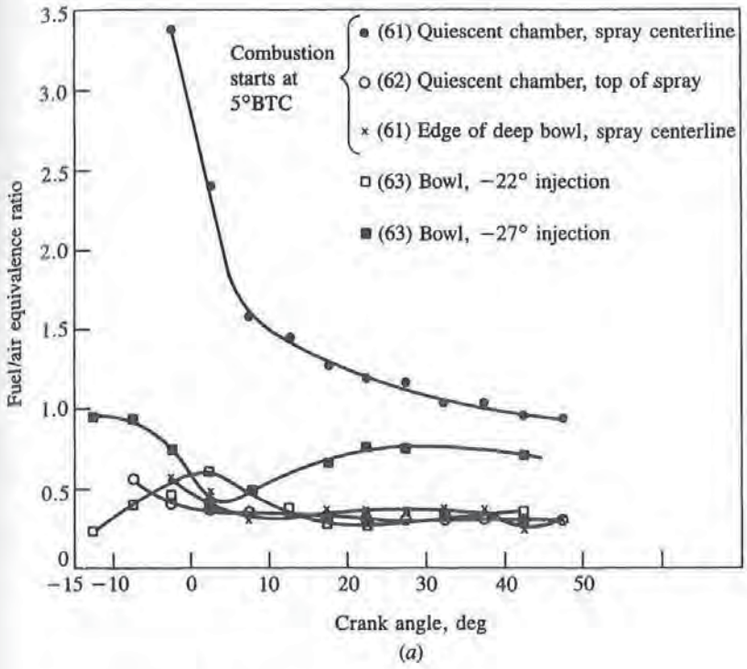
17° BTC and ended about 5° ATC; ignition occurred at 8° BTC. The contours at 3° BTC show high CO concentrations in the burned gases which now occupy most of the spray region, indicating locally very fuel-rich conditions. Later, at 12° ATC, fuel injection has ceased, this rich core has moved outward to the piston-bowl wall, and combustion within the expanded spray region is much more complete. This oxidation of CO, as air is entrained into the spray region, mixes, and burns, releases substantial additional chemical energy.

The role of air swirl in promoting much more rapid fuel-air mixing in medium-size and smaller diesel engines is evident from similar gas-sampling studies in engines with these different combustion systems. The variation of gas species and unburned hydrocarbon concentrations within critical regions of the combustion chamber have been mapped out by a number of investigators.[61–63] These data show that during the early stages of injection and combustion, the boundaries of the individual sprays can be identified as they are convected around the combustion chamber bowl by the swirl. The fuel distribution within the combustion chamber is highly nonuniform. However, within each spray, sufficient air has mixed into the spray to bring the peak fuel/air equivalence ratios within the spray, in the outer regions of the chamber, to close to stoichiometric values.[63] This substantially different character of the spray with swirl is clear from the data in Fig. 10-46. Figure 10-46*a* shows equivalence ratio values determined from gas sampling, versus crank angle, from several studies with different designs of combustion chamber. While the local values obviously depend on the relation of the sample valve location to spray position at any given crank angle, the much lower values of equivalence ratio with swirl relative to quiescent chambers, during injection and the early stages of combustion, clearly indicate that swirl enhances mixing rates substantially. As combustion ends, these data indicate relatively uniform fuel distribution within the combustion chamber, at least on a gross geometric scale. However, early in the combustion process the high CO levels, found in all these combustion systems as shown in Fig. 10-46*b*, indicate that the burned gases are only partially reacted. With quiescent chambers this is largely due to lack of oxygen. With swirl, however, substantial oxygen is present. Whether the high CO with swirl is due to kinetic limitations or to smaller-scale mixture nonhomogeneities is unclear.

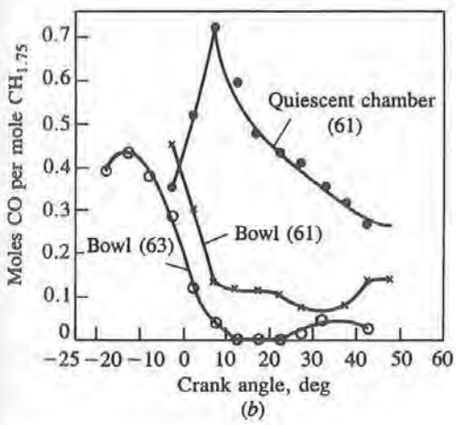
10.7.3 Fuel-Air Mixing and Burning Rates

The model of diesel combustion obtained from heat-release analyses of cylinder pressure data identifies two main stages of combustion (see Fig. 10-9). The first is the premixed-combustion phase, when the fuel which has mixed sufficiently with air to form an ignitable mixture during the delay period is consumed. The second is the mixing-controlled combustion phase, where rates of burning (at least in naturally aspirated engines) are lower. Experimental evidence from heat-release analysis indicates that the majority of the fuel (usually more than 75 percent) burns during the second mixing-controlled phase. Such evidence forms the basis for the heat-release models used in diesel engine cycle simulations. For example,

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(*a*)



(*b*)

FIGURE 10-46
Time and space-resolved gas-composition data obtained from rapid-acting sampling valves from within the combustion chambers of quiescent and high-swirl bowl-in-piston DI diesel engines. (*a*) Local fuel/air equivalence ratios on spray centerline and periphery with quiescent chamber, edge of deep bowl with swirl, and within a shallow bowl with swirl, three-quarters of the way out to the bowl wall, for two injection timings (−22° and −27°). (*b*) CO concentration on spray centerline with quiescent chamber, edge of deep bowl, and within shallow bowl with swirl.[61–63]

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the fraction of the fuel β which burns in the premixed phase has been correlated by Watson *et al.* (see Sec. 14.4.3) by the relation

$$\beta = 1 - \frac{a\phi^b}{\tau_{id}^c} \tag{10.40}$$

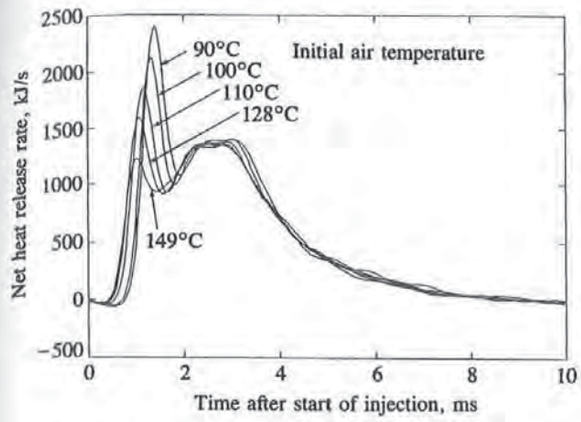
where ϕ is the fuel/air equivalence ratio, τ_{id} the ignition delay (in milliseconds), and $a \approx 0.9$, $b \approx 0.35$, and $c \approx 0.4$ are constants depending on engine design. Equation (10.40) shows the expected trends for the premixed fraction, with changes in the overall equivalence ratio ϕ (increasing injection duration as load is increased) and changes in the ignition delay.

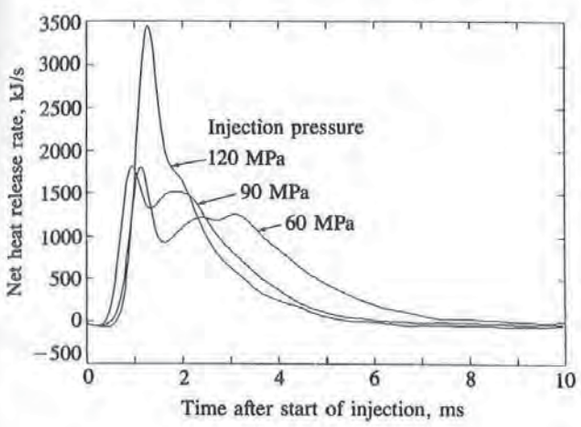
That the fuel-burning or heat-release rate is predominantly mixing controlled is supported by the following types of evidence. Estimates of the rate at which fuel-air mixture with composition within the combustible limits is produced in diesel sprays under typical engine conditions, based on a variety of turbulent-jet models of the spray (e.g., see Refs. 29, 36, and 59 and also Sec. 14.4.3), show that mixing rates and burning rates are comparable in magnitude. Estimates of characteristic times for the turbulent-jet mixing processes in diesel combustion chambers show these to be comparable to the duration of the heat-release process, and much longer than characteristic times for evaporation and the combustion chemical kinetics.[36, 44]

Then, measured diesel-combustion heat-release profiles show trends with engine design and operating parameter changes that correspond to fuel-air mixing being the primary controlling factor. Examples of heat-release profiles measured in rapid-compression-machine studies of diesel combustion, shown in Fig. 10-47, illustrate this clearly. The rapid-compression machine had a disc-shaped chamber of 10 cm diameter with a 3.1 cm clearance height at the end of a compression process through a volume ratio of 15.4; a five-hole centrally located fuel-injector nozzle was used. Figure 10-47*a* shows the heat-release profiles for different initial air temperatures which produce different ignition delays. Longer delays allow more fuel to mix to within combustible limits during the delay, so the peak premixed heat-release rate increases. However, the mixing-controlled-phase heat-release-rate magnitudes are essentially the same because the spray-mixing processes are little affected by these changes in air temperature. Figure 10-47*b* and *c* shows that heat-release rates throughout the combustion process are increased by increased fuel-injection rate (achieved by increasing the fuel-injection pressure) and by swirl. Both these changes increase the fuel-air mixing rates within the fuel spray and therefore increase the heat-release rate during the mixing-controlled combustion phase.

Diesel engine heat-release rate trends, as design and operating variables are changed, can be related to mixing rates in analogous fashion. Table 10.5 summarizes the trends that have been investigated. The directional effects of changes in engine parameters on the ignition delay period and the fuel-air mixing rate are all consistent with the measured changes in premixed and mixing-controlled heat-release rates. The controlling role of fuel-air mixing in the diesel engine fuel spray on combustion is clear.

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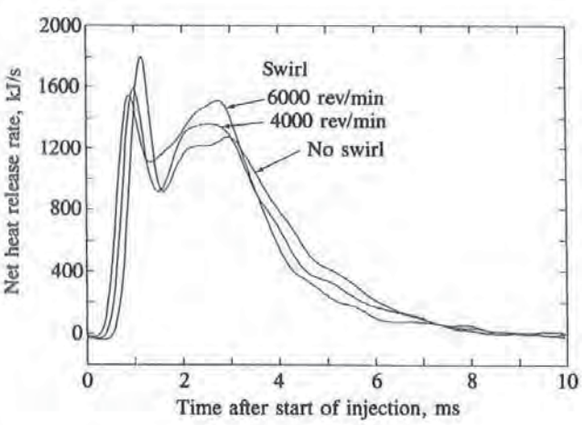


FIGURE 10-47
Net heat-release rates, as a function of time after start of injection, calculated from cylinder pressure data from rapid-compression-machine studies of DI diesel combustion. (*a*) Effect of varying initial air temperature: 4000 rev/min swirl, injection pressure 60 MPa. (*b*) Effect of varying injection pressure: no swirl. (*c*) Effect of varying swirl: injection pressure 60 MPa.[20]

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TABLE 10.5
Effects of engine design and operating variables on heat-release rates

		Effect on			
Reference	**Parameter varied**	τ_{id}	$\dot{m}_m$	$\dot{Q}_p$	$\dot{Q}_m$
5, 64	Injection rate ↑	*	↑	↑	↑
65	Turbocharger boost ↑	↓	*	↓	*
66	Compression ratio ↓	↑	*	↑	*
66	Number of injector holes ↑	*	↑	↑	↑
67, 68	Injection advance ↑	↑	*	↑	*
67, 68	Swirl ↑	*	↑	↑	↑
67	Intake-air temperature ↓	↑	*	↑	*
68, 69	Injection pressure ↑	*	↑	↑	↑
11, 69	Speed ↑	*	↑	↑	↑

τ_{id}, ignition delay; $\dot{m}_m = (dm/dt)_m$, fuel-air mixing rate; $\dot{Q}_p = (dQ/dt)_p$, heat-release rate during premixed-combustion phase; $\dot{Q}_m = (dQ/dt)_m$, heat-release rate during mixing-controlled-combustion phase. ↑ increase; ↓ decrease; * minor effect.
Source: From Plee and Ahmad.[44]

PROBLEMS

10.1. Describe the sequence of processes which must occur before the liquid fuel in the injection system in a direct-injection compression-ignition engine is fully burned.

10.2. Small high-swirl direct-injection CI engines have fuel conversion efficiencies which are about 10 percent higher than values typical of equivalent indirect-injection engines. (IDI engines are used because they achieve higher bmep.) What combustion-system-related differences contribute to this higher efficiency?

10.3. In a diesel engine, because the fuel distribution is nonuniform the burned gas temperature is nonuniform. Consider small fuel-air mixture elements initially at 1000 K and 6.5 MPa at top-center with a range of equivalence ratios. Each element burns at essentially constant pressure. Calculate (using the charts in Chap. 4, or an appropriate chemical equilibrium thermodynamic computer code) the burned gas temperature for mixture equivalence ratios of 0.4, 0.6, 0.8, 1.0, 1.2. Assume the fuel is isooctane.

10.4. The levels of combustible species in the exhaust of a direct-injection diesel engine are: HC, 0.8 g/kW · h; CO, 3 g/kW · h; particulates, 0.7 g/kW · h. If the specific fuel consumption is 210 g/kW · h calculate the combustion efficiency.

10.5. Consider the naturally aspirated direct-injection diesel engine in Fig. 1-23 operating at 2300 rev/min and an equivalence ratio of 0.7. Estimate the following:
(*a*) Mass of air in each cylinder per cycle, mass, and volume (as liquid) of diesel fuel injected per cylinder per cycle.
(*b*) Estimate the average drop size [e.g., use Eq. (10.32)]. The cylinder pressure at time of injection (close to TC) is 50 atm; the fuel injection pressure is 500 atm.
(*c*) Assuming all fuel droplets are the same size as the average drop, how many drops are produced per injection? If these drops are uniformly distributed throughout the air charge at TC, what is the approximate distance between drops? (Neither of these assumptions is correct; however, the calculations illustrate the difficulty of the fuel-air mixing process.)

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10.6. Estimate the following quantities for a typical direct-injection diesel fuel spray. The injection pressure is 500 atm; the cylinder pressure during injection is 50 atm.
(*a*) Assuming that the flow through the nozzle orifice is incompressible and quasi steady, estimate the liquid fuel velocity at the orifice exit. At this velocity, how long would the fuel take to reach the cylinder wall? The bore is 125 mm.
(*b*) Each nozzle orifice diameter d_n is 0.34 mm and $L_n/d_n = 4$. Determine the spray angle and plot spray tip penetration versus time.
(*c*) Use Eq. (10.32) to estimate the initial average drop size assuming that the injection process in (*a*) above continues for 1 millisecond and the injector nozzle has four orifices.

10.7. Diesel fuel is injected as a liquid at room temperature into air at 50 atm and 800 K, close to TC at the end of compression. If the overall equivalence ratio is 0.7, estimate the reduction in average air temperature which would occur when the fuel is fully vaporized and uniformly mixed. Assume such mixing takes place at constant volume prior to any combustion.

10.8. Using Eq. (10.37) estimate the ignition delay in milliseconds and crank angle degrees for these operating conditions in Table 10.4: low swirl IDI diesel 600 and 1800 rev/min; high swirl IDI diesel 1800 rev/min; DI diesel low and high compression ratio. The fuel cetane number is 45; stroke = 0.1 m. Discuss whether the predicted trends with speed, swirl, and compression ratio are consistent with Sec. 10.6.4.

10.9. The compression ratio of truck diesel engines must be set at about 18 so that the engine will start when cold. Using Eqs. (10.37) to (10.39) develop a graph of τ_{id} (in degrees) as a function of compression ratio for $r_c = 12$ to 20. Assume $p_i = 1$ atm, $T_i = 255$ K, $n = 1.13$, speed = 100 rev/min, bore = stroke = 120 mm, fuel cetane number = 45. If the ignition delay must be less than 20° CA for satisfactory starting, what compression ratio is required?

10.10. Equation (10.40) predicts the fraction β of the fuel injected into a direct-injection diesel engine which burns in the premixed phase. Plot β as a function of τ_{id} for $\phi = 0.4$. Show that for turbocharged DI diesel engines where τ_{id} is 0.4 to 1 ms, the premixed combustion phase is much less important than it normally is for naturally aspirated engines where τ_{id} is between 0.7 and 3 ms.

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CHAPTER 11

POLLUTANT FORMATION AND CONTROL

11.1 NATURE AND EXTENT OF PROBLEM

Spark-ignition and diesel engines are a major source of urban air pollution. The spark-ignition engine exhaust gases contain oxides of nitrogen (nitric oxide, NO, and small amounts of nitrogen dioxide, NO_2—collectively known as NO_x), carbon monoxide (CO), and organic compounds which are unburned or partially burned hydrocarbons (HC). The relative amounts depend on engine design and operating conditions but are of order: NO_x, 500 to 1000 ppm or 20 g/kg fuel; CO, 1 to 2 percent or 200 g/kg fuel; and HC, 3000 ppm (as C_1) or 25 g/kg fuel. Piston blowby gases, and fuel evaporation and release to the atmosphere through vents in the fuel tank and carburetor after engine shut-down, are also sources of unburned hydrocarbons. However, in most modern engines these nonexhaust sources are effectively controlled by returning the blowby gases from the crankcase to the engine intake system and by venting the fuel tank and carburetor float bowl through a vapor-absorbing carbon cannister which is purged by some of the engine intake air during normal engine operation. In diesel engine exhaust, concentrations of NO_x are comparable to those from SI engines. Diesel hydrocarbon emissions are significant though exhaust concentrations are lower by about a factor of 5 than typical SI engine levels. The hydrocarbons in the exhaust may also condense to form white smoke during engine starting and warm-up.

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Specific hydrocarbon compounds in the exhaust gases are the source of diesel odor. Diesel engines are an important source of particulate emissions; between about 0.2 and 0.5 percent of the fuel mass is emitted as small ($\sim$0.1 μm diameter) particles which consist primarily of soot with some additional absorbed hydrocarbon material. Diesel engines are not a significant source of carbon monoxide.

Use of alcohol fuels in either of these engines substantially increases aldehyde emissions. While these are not yet subject to regulation, aldehydes would be a significant pollutant if these fuels were to be used in quantities comparable to gasoline and diesel. Currently used fuels, gasoline and diesel, contain sulfur: gasoline in small amounts ($\leq$600 ppm by weight S), diesel fuel in larger amounts ($\leq$0.5 percent). The sulphur is oxidized (or burned) to produce sulfur dioxide, SO_2, of which a fraction can be oxidized to sulfur trioxide, SO_3, which combines with water to form a sulfuric acid aerosol.

In general, the concentrations of these pollutants in internal combustion engine exhaust differ from values calculated assuming chemical equilibrium. Thus the detailed chemical mechanisms by which these pollutants form and the kinetics of these processes are important in determining emission levels. For some pollutant species, e.g., carbon monoxide, organic compounds, and particulates, the formation and destruction reactions are intimately coupled with the primary fuel combustion process. Thus an understanding of the formation of these species requires knowledge of the combustion chemistry. For nitrogen oxides and sulfur oxides, the formation and destruction processes are not part of the fuel combustion process. However, the reactions which produce these species take place in an environment created by the combustion reactions, so the two processes are still intimately linked. A summary of the mechanisms by which these pollutants form in internal combustion engines provides an introduction to this chapter. In subsequent sections, the details of the basic formation mechanisms of each pollutant and the application of these mechanisms to the combustion process in both spark-ignition and compression-ignition engines will be developed.

The processes by which pollutants form within the cylinder of a conventional spark-ignition engine are illustrated qualitatively in Fig. 11-1. The schematic shows the combustion chamber during four different phases of the engine operating cycle: compression, combustion, expansion, and exhaust. Nitric oxide (NO) forms throughout the high-temperature burned gases behind the flame through chemical reactions involving nitrogen and oxygen atoms and molecules, which do not attain chemical equilibrium. The higher the burned gas temperature, the higher the rate of formation of NO. As the burned gases cool during the expansion stroke the reactions involving NO freeze, and leave NO concentrations far in excess of levels corresponding to equilibrium at exhaust conditions. Carbon monoxide also forms during the combustion process. With rich fuel-air mixtures, there is insufficient oxygen to burn fully all the carbon in the fuel to CO_2; also, in the high-temperature products, even with lean mixtures, dissociation ensures there are significant CO levels. Later, in the expansion stroke, the CO oxidation process also freezes as the burned gas temperature falls.

The unburned hydrocarbon emissions have several different sources.

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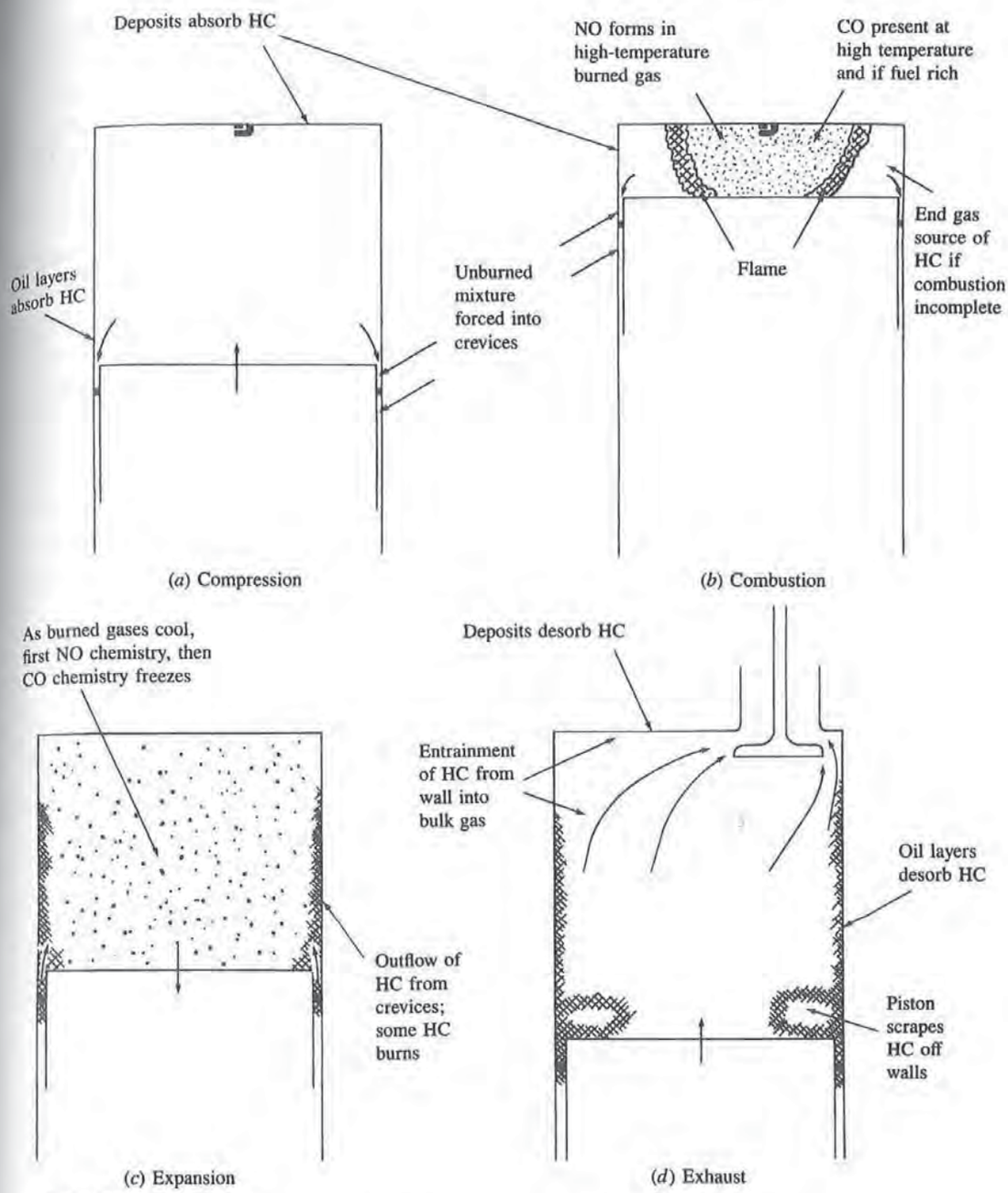


FIGURE 11-1
Summary of HC, CO, and NO pollutant formation mechanisms in a spark-ignition engine.

During compression and combustion, the increasing cylinder pressure forces some of the gas in the cylinder into crevices, or narrow volumes, connected to the combustion chamber: the volumes between the piston, rings, and cylinder wall are the largest of these. Most of this gas is unburned fuel-air mixture; much of it

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escapes the primary combustion process because the entrance to these crevices is too narrow for the flame to enter. This gas, which leaves these crevices later in the expansion and exhaust processes, is one source of unburned hydrocarbon emissions. Another possible source is the combustion chamber walls. A quench layer containing unburned and partially burned fuel-air mixture is left at the wall when the flame is extinguished as it approaches the wall. While it has been shown that the unburned HC in these thin (≤ 0.1 mm) layers burn up rapidly when the combustion chamber walls are clean, it has also been shown that the porous deposits on the walls of engines in actual operation do increase engine HC emissions. A third source of unburned hydrocarbons is believed to be any engine oil left in a thin film on the cylinder wall, piston and perhaps on the cylinder head. These oil layers can absorb and desorb fuel hydrocarbon components, before and after combustion, respectively, thus permitting a fraction of the fuel to escape the primary combustion process unburned. A final source of HC in engines is incomplete combustion due to bulk quenching of the flame in that fraction of the engine cycles where combustion is especially slow (see Sec. 9.4.3). Such conditions are most likely to occur during transient engine operation when the air/fuel ratio, spark timing, and the fraction of the exhaust recycled for emission control may not be properly matched.

The unburned hydrocarbons exit the cylinder by being entrained in the bulk-gas flow during blowdown and at the end of the exhaust stroke as the piston pushes gas scraped off the wall out of the exhaust valve. Substantial oxidation of the hydrocarbons which escape the primary combustion process by any of the above processes can occur during expansion and exhaust. The amount of oxidation depends on the temperature and oxygen concentration time histories of these HC as they mix with the bulk gases.

One of the most important variables in determining spark-ignition engine emissions is the fuel/air equivalence ratio, ϕ. Figure 11-2 shows qualitatively how NO, CO, and HC exhaust emissions vary with this parameter. The spark-ignition engine has normally been operated close to stoichiometric, or slightly fuel-rich, to ensure smooth and reliable operation. Figure 11-2 shows that leaner mixtures give lower emissions until the combustion quality becomes poor (and eventually misfire occurs), when HC emissions rise sharply and engine operation becomes erratic. The shapes of these curves indicate the complexities of emission control. In a cold engine, when fuel vaporization is slow, the fuel flow is increased to provide an easily combustible fuel-rich mixture in the cylinder. Thus, until the engine warms up and this enrichment is removed, CO and HC emissions are high. At part-load conditions, lean mixtures could be used which would produce lower HC and CO emissions (at least until the combustion quality deteriorates) and moderate NO emissions. Use of recycled exhaust to dilute the engine intake mixture lowers the NO levels, but also deteriorates combustion quality. Exhaust gas recirculation (EGR) is used with stoichiometric mixtures in many engine control systems. Note that the highest power levels are obtained from the engine with slightly rich-of-stoichiometric mixtures and no recycled exhaust to dilute the incoming charge. As we will see, several emission control techniques are required

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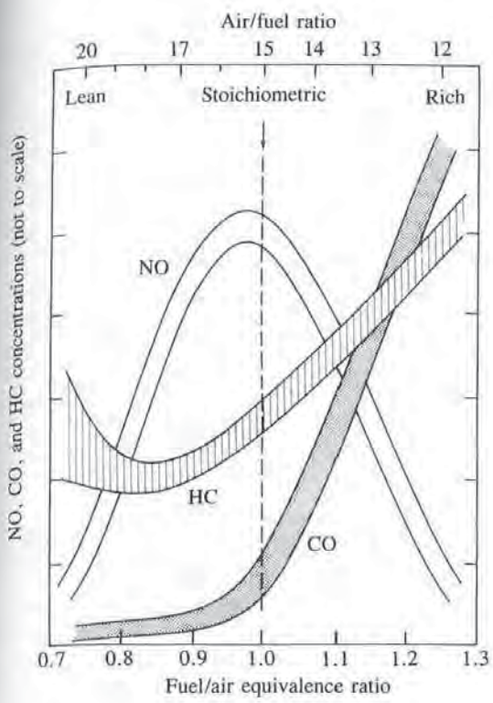


FIGURE 11-2
Variation of HC, CO, and NO concentration in the exhaust of a conventional spark-ignition engine with fuel/air equivalence ratio.

to reduce emissions of all three pollutants, over all engine operating modes, and achieve acceptable average levels.

In the diesel engine, the fuel is injected into the cylinder just before combustion starts, so throughout most of the critical parts of the cycle the fuel distribution is nonuniform. The pollutant formation processes are strongly dependent on the fuel distribution and how that distribution changes with time due to mixing. Figure 11-3 illustrates how various parts of the fuel jet and the flame affect the formation of NO, unburned HC, and soot (or particulates) during the "premixed" and "mixing-controlled" phases of diesel combustion in a direct-injection engine with swirl. Nitric oxide forms in the high-temperature burned gas regions as before, but temperature and fuel/air ratio distributions within the burned gases are now nonuniform and formation rates are highest in the close-to-stoichiometric regions. Soot forms in the rich unburned-fuel-containing core of the fuel sprays, within the flame region, where the fuel vapor is heated by mixing with hot burned gases. Soot then oxidizes in the flame zone when it contacts unburned oxygen, giving rise to the yellow luminous character of the flame. Hydrocarbons and aldehydes originate in regions where the flame quenches both on the walls and where excessive dilution with air prevents the combustion process from either starting or going to completion. Fuel that vaporizes from the nozzle sac volume during the later stages of combustion is also a source of HC. Combustion generated noise is controlled by the early part of the combustion process, the initial rapid heat release immediately following the ignition-delay period.

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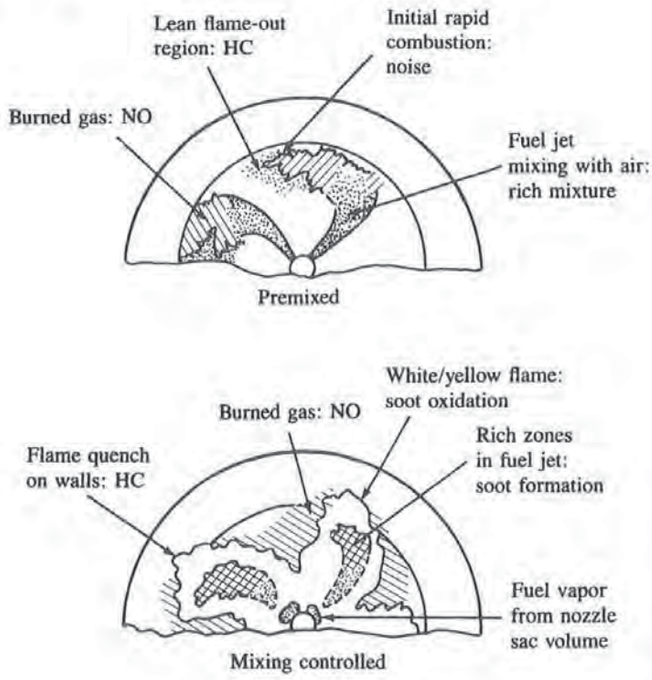


FIGURE 11-3
Summary of pollutant formation mechanisms in a direct-injection compression-ignition engine during "premixed" and "mixing-controlled" combustion phases.

11.2 NITROGEN OXIDES

11.2.1 Kinetics of NO Formation

While nitric oxide (NO) and nitrogen dioxide (NO_2) are usually grouped together as NO_x emissions, nitric oxide is the predominant oxide of nitrogen produced inside the engine cylinder. The principal source of NO is the oxidation of atmospheric (molecular) nitrogen. However, if the fuel contains significant nitrogen, the oxidation of the fuel nitrogen-containing compounds is an additional source of NO. Gasolines contain negligible amounts of nitrogen; although diesel fuels contain more nitrogen, current levels are not significant.

The mechanism of NO formation from atmospheric nitrogen has been studied extensively.[1] It is generally accepted that in combustion of near-stoichiometric fuel-air mixtures the principal reactions governing the formation of NO from molecular nitrogen (and its destruction) are†

$$O + N_2 = NO + N \tag{11.1}$$

$$N + O_2 = NO + O \tag{11.2}$$

$$N + OH = NO + H \tag{11.3}$$

† This is often called the extended Zeldovich mechanism. Zeldovich[1] was the first to suggest the importance of reactions (11.1) and (11.2). Lavoie *et al.*[2] added reaction (11.3) to the mechanism; it does contribute significantly.

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TABLE 11.1
Rate constants for NO formation mechanism[1]

Reaction	Rate constant, $cm^3/mol \cdot s$	Temperature range, K	Uncertainty, factor of or %
(1) $O + N_2 \rightarrow NO + N$	$7.6 \times 10^{13} \exp[-38{,}000/T]$	2000–5000	2
(−1) $N + NO \rightarrow N_2 + O$	1.6×10^{13}	300–5000	±20% at 300 K 2 at 2000–5000 K
(2) $N + O_2 \rightarrow NO + O$	$6.4 \times 10^{9}\ T \exp[-3150/T]$	300–3000	±30% 300–1500 K 2 at 3000 K
(−2) $O + NO \rightarrow O_2 + N$	$1.5 \times 10^{9}\ T \exp[-19{,}500/T]$	1000–3000	±30% at 1000 K 2 at 3000 K
(3) $N + OH \rightarrow NO + H$	4.1×10^{13}	300–2500	±80%
(−3) $H + NO \rightarrow OH + N$	$2.0 \times 10^{14} \exp[-23{,}650/T]$	2200–4500	2

The forward and reverse rate constants (k_i^+ and k_i^-, respectively) for these reactions have been measured in numerous experimental studies. Recommended values for these rate constants taken from a critical review of this published data are given in Table 11.1. Note that the equilibrium constant for each reaction, $K_{c,i}$ (see Sec. 3.7.2), is related to the forward and reverse rate constants by $K_{c,i} = k_i^+/k_i^-$. The rate of formation of NO via reactions (11.1) to (11.3) is given by [see Eqs. (3.55) and (3.58)]

$$\frac{d[NO]}{dt} = k_1^+[O][N_2] + k_2^+[N][O_2] + k_3^+[N][OH] - k_1^-[NO][N] - k_2^-[NO][O] - k_3^-[NO][H] \quad (11.4)$$

where [ ] denote species concentrations in moles per cubic centimeter when k_i have the values given in Table 11.1. The forward rate constant for reaction (11.1) and the reverse rate constants for reactions (11.2) and (11.3) have large activation energies which results in a strong temperature dependence of NO formation rates.

A similiar relation to (11.4) can be written for $d[N]/dt$:

$$\frac{d[N]}{dt} = k_1^+[O][N_2] - k_2^+[N][O_2] - k_3^+[N][OH] - k_1^-[NO][N] + k_2^-[NO][O] + k_3^-[NO][H] \quad (11.5)$$

Since [N] is much less than the concentrations of other species of interest ($\sim 10^{-8}$ mole fraction), the steady-state approximation is appropriate: $d[N]/dt$ is set equal to zero and Eq. (11.5) used to eliminate [N]. The NO formation rate then becomes

$$\frac{d[NO]}{dt} = 2k_1^+[O][N_2]\,\frac{1 - [NO]^2/(K[O_2][N_2])}{1 + k_1^-[NO]/(k_2^+[O_2] + k_3^+[OH])} \quad (11.6)$$

where $K = (k_1^+/k_1^-)(k_2^+/k_2^-)$.

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TABLE 11.2
Typical values of R_1, R_1/R_2, and $R_1/(R_2 + R_3)$†

Equivalence ratio	R_1‡	R_1/R_2	$R_1/(R_2 + R_3)$
0.8	5.8×10^{-5}	1.2	0.33
1.0	2.8×10^{-5}	2.5	0.26
1.2	7.6×10^{-6}	9.1	0.14

† At 10 atm pressure and 2600 K.
‡ Units gmol/cm^3 · s.

NO forms in both the flame front and the postflame gases. In engines, however, combustion occurs at high pressure so the flame reaction zone is extremely thin ($\sim$0.1 mm) and residence time within this zone is short. Also, the cylinder pressure rises during most of the combustion process, so burned gases produced early in the combustion process are compressed to a higher temperature than they reached immediately after combustion. Thus, NO formation in the postflame gases almost always dominates any flame-front–produced NO. It is, therefore, appropriate to assume that the combustion and NO formation processes are decoupled and to approximate the concentrations of O, O_2, OH, H, and N_2 by their equilibrium values at the local pressure and equilibrium temperature.

To introduce this equilibrium assumption it is convenient to use the notation $R_1 = k_1^+[O]_e[N_2]_e = k_1^-[NO]_e[N]_e$, where $[\ ]_e$ denotes equilibrium concentration, for the one-way equilibrium rate for reaction (11.1), with similiar definitions for $R_2 = k_2^+[N]_e[O_2]_e = k_2^-[NO]_e[O]_e$ and $R_3 = k_3^+[N]_e[OH]_e = k_3^-[NO]_e[H]_e$. Substituting $[O]_e$, $[O_2]_e$, $[OH]_e$, $[H]_e$, and $[N_2]_e$ for [O], $[O_2]$, [OH], [H], and $[N_2]$ in Eq. (11.6) yields

$$\frac{d[NO]}{dt} = \frac{2R_1\{1 - ([NO]/[NO]_e)^2\}}{1 + ([NO]/[NO]_e)R_1/(R_2 + R_3)} \tag{11.7}$$

Typical values of R_1, R_1/R_2 and $R_1/(R_2 + R_3)$ are given in Table 11.2. The difference between R_1/R_2 and $R_1/(R_2 + R_3)$ indicates the relative importance of adding reaction (11.3) to the mechanism.

The strong temperature dependence of the NO formation rate can be demonstrated by considering the initial value of $d[NO]/dt$ when $[NO]/[NO]_e \ll 1$. Then, from Eq. (11.7),

$$\frac{d[NO]}{dt} = 2R_1 = 2k_1^+[O]_e[N_2]_e \tag{11.8}$$

The equilibrium oxygen atom concentration is given by

$$[O]_e = \frac{K_{p(O)}[O_2]_e^{1/2}}{(\tilde{R}T)^{1/2}} \tag{11.9}$$

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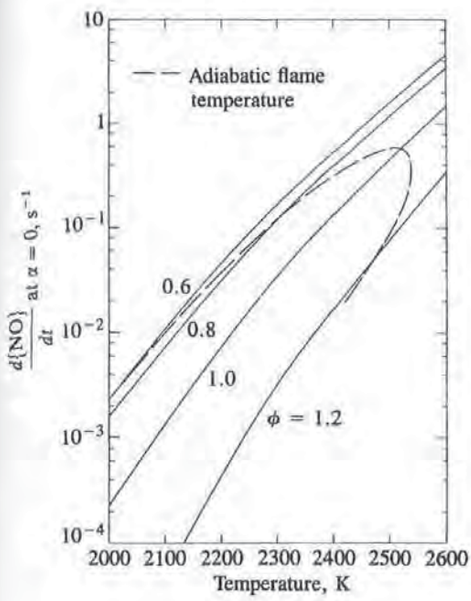


FIGURE 11-4
Initial NO formation rate, mass fraction per second (for $[NO]/[NO]_e \ll 1$), as a function of temperature for different equivalence ratios (ϕ) and 15 atm pressure. Dashed line shows adiabatic flame temperature for kerosene combustion with 700 K, 15 atm air.[3]

where $K_{p(O)}$ is the equilibrium constant for the reaction

$$\tfrac{1}{2}O_2 = O$$

and is given by

$$K_{p(O)} = 3.6 \times 10^3 \exp\left(\frac{-31{,}090}{T}\right) \quad \text{atm}^{1/2} \tag{11.10}$$

The initial NO formation rate may then be written [combining Eqs. (11.8), (11.9), and (11.10) with k_1^+ from Table 11.1] as

$$\frac{d[NO]}{dt} = \frac{6 \times 10^{16}}{T^{1/2}} \exp\left(\frac{-69{,}090}{T}\right)[O_2]_e^{1/2}[N_2]_e \quad \text{mol/cm}^3 \cdot \text{s} \tag{11.11}$$

The strong dependence of $d[NO]/dt$ on temperature in the exponential term is evident. High temperatures and high oxygen concentrations result in high NO formation rates. Figure 11-4 shows the NO formation rate as a function of gas temperature and fuel/air equivalence ratio in postflame gases. Also shown is the adiabatic flame temperature attained by a fuel-air mixture initially at 700 K at a constant pressure of 15 atm. For adiabatic constant-pressure combustion (an appropriate model for each element of fuel that burns in an engine), this initial NO formation rate peaks at the stoichiometric composition, and decreases rapidly as the mixture becomes leaner or richer.

A characteristic time for the NO formation process, τ_{NO}, can be defined by

$$\tau_{NO}^{-1} = \frac{1}{[NO]_e}\frac{d[NO]}{dt} \tag{11.12}$$

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$[NO]_e$ can be obtained from the equilibrium constant

$$K_{NO} = 20.3 \times \exp(-21{,}650/T)$$

for the reaction

$$O_2 + N_2 = 2NO$$

as $[NO]_e = (K_{NO}[O_2]_e[N_2]_e)^{1/2}$. Equations (11.11) and (11.12) can be combined to give

$$\tau_{NO} = \frac{8 \times 10^{-16} T \exp(58{,}300/T)}{p^{1/2}} \tag{11.13}$$

where τ_{NO} is in seconds, T in kelvins, and p in atmospheres. Use has been made of the fact that $\tilde{x}_{N_2} \approx 0.71$. For engine combustion conditions, τ_{NO} is usually comparable to or longer than the times characteristic of changes in engine conditions so the formation process is kinetically controlled. However, for close-to-stoichiometric conditions at the maximum pressures and burned gas temperatures, τ_{NO} is of the same order as typical combustion times (1 ms) and equilibrium NO concentrations may be attained.

Evidence that this formation model is valid under conditions typical of those found in engines is provided by high-pressure combustion bomb studies. Newhall and Shahed[4] have measured the NO production, using the q-band absorption technique, behind hydrogen-air and propane-air planar flames propagating axially in a cylindrical bomb. Some results are compared with predictions made with this kinetic scheme (coupled with an "unmixed" combustion calculation to determine local pressure and temperature; see Sec. 9.2.1) in Fig. 11-5. The agreement is excellent. Note that the NO concentration rises smoothly from

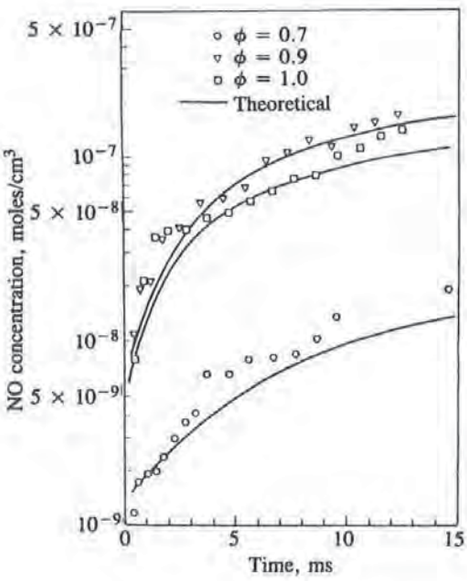


FIGURE 11-5
Measured and calculated rate-limited NO concentrations behind flame in high-pressure cylindrical bomb experiments with H_2-air mixture. ϕ = equivalence ratio.[4]

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TABLE 11.3
Typical nitrogen content of distillate fuels[1]

Fraction	Average nitrogen, wt %	Range, wt %
Crude	0.65	—
Heavy distillates	1.40	0.60–2.15
Light distillates	0.07	0–0.60

close to zero, indicating that at these high pressures there is negligible NO production within the flame front itself.

Fuel nitrogen is also a source of NO via a different and yet to be fully explained mechanism. Table 11.3 shows the typical nitrogen content of petroleum-derived fuels. During distillation, the fuel nitrogen is concentrated in the higher boiling fractions. In distillate fuels, the nitrogen can exist as amines and ring compounds (e.g., pyridine, quinoline, and carbazoles). During combustion these compounds are likely to undergo some thermal decomposition prior to entering the combustion zone. The precursors to NO formation will therefore be low molecular weight nitrogen-containing compounds such as NH_3, HCN, and CN. The detailed information on the kinetics of NO formation from these compounds is limited. Oxidation to NO is usually rapid, occurring on a time scale comparable to that of the combustion reactions. The NO yield (amount of fuel nitrogen converted to NO) is sensitive to the fuel/air equivalence ratio. Relatively high NO yields (approaching 100 percent) are obtained for lean and stoichiometric mixtures; relatively low yields are found for rich mixtures. NO yields are only weakly dependent on temperature, in contrast to the strong temperature dependence of NO formed from atmospheric nitrogen.[1]

11.2.2 Formation of NO_2

Chemical equilibrium considerations indicate that for burned gases at typical flame temperatures, NO_2/NO ratios should be negligibly small. While experimental data show this is true for spark-ignition engines, in diesels NO_2 can be 10 to 30 percent of the total exhaust oxides of nitrogen emissions.[5] A plausible mechanism for the persistence of NO_2 is the following.[6] NO formed in the flame zone can be rapidly converted to NO_2 via reactions such as

$$NO + HO_2 \rightarrow NO_2 + OH \tag{11.14}$$

Subsequently, conversion of this NO_2 to NO occurs via

$$NO_2 + O \rightarrow NO + O_2 \tag{11.15}$$

unless the NO_2 formed in the flame is quenched by mixing with cooler fluid. This explanation is consistent with the highest NO_2/NO ratio occurring at light load in diesels, when cooler regions which could quench the conversion back to NO are widespread.[5]

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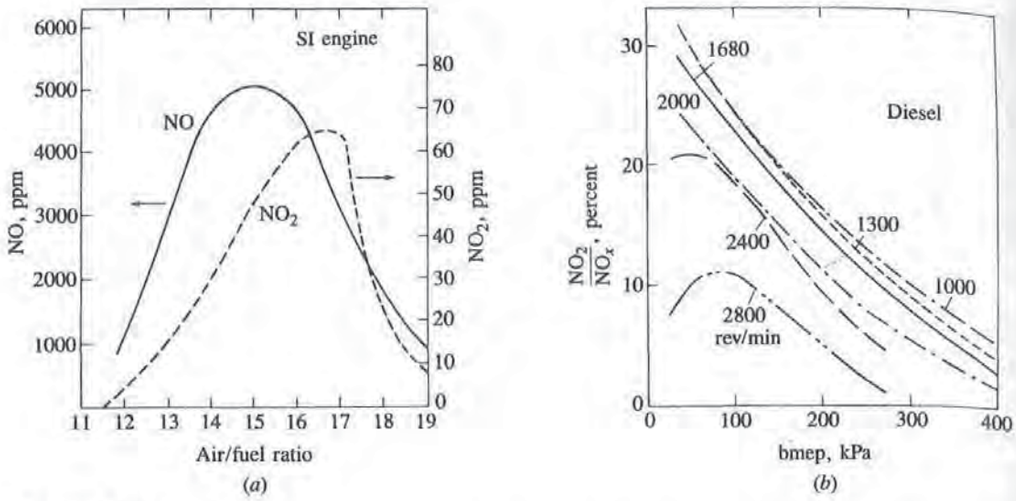


FIGURE 11-6
(*a*) NO and NO_2 concentrations in SI engine exhaust as function of air/fuel ratio, 1500 rev/min, wide-open throttle; (*b*) NO_2 as percent of total NO_x in diesel exhaust as function of load and speed.[5]

Figure 11-6 shows examples of NO and NO_2 emissions data from a spark-ignition and a diesel engine. The maximum value for the ratio (NO_2/NO) for the SI engine is 2 percent, at an equivalence ratio of about 0.85. For the diesel this ratio is higher, and is highest at light load and depends on engine speed.

It is customary to measure total oxides of nitrogen emissions, NO plus NO_2, with a chemiluminescence analyzer and call the combination NO_x. It is always important to check carefully whether specific emissions data for NO_x are given in terms of mass of NO or mass of NO_2, which have molecular weights of 30 and 46, respectively.

11.2.3 NO Formation in Spark-Ignition Engines

In conventional spark-ignition engines the fuel and air (and any recycled exhaust) are mixed together in the engine intake system, and vigorous mixing with the residual gas within the cylinder occurs during the intake process. Thus the fuel/air ratio and the amount of diluent (residual gas plus any recycled exhaust) is approximately uniform throughout the charge within the cylinder during combustion.† Since the composition is essentially uniform, the nature of the NO formation process within the cylinder can be understood by coupling the kinetic mechanism developed in Sec. 11.2.1 with the burned gas temperature distribution and pressure in the cylinder during the combustion and expansion processes. The

† It is well known that the mixture composition within the cylinder is not completely uniform and varies from one cycle to the next. Both these factors contribute to cycle-by-cycle combustion variations. For the present discussion, the assumption of mixture uniformity is adequate.

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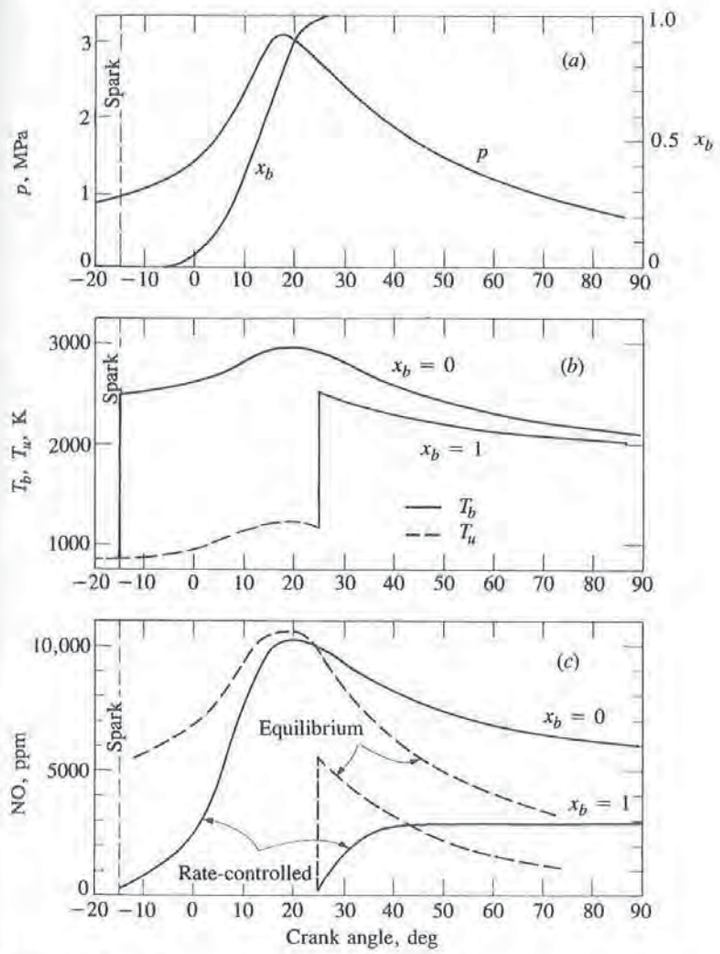


FIGURE 11-7
Illustration of SI engine NO formation model: (*a*) measured cylinder pressure p and calculated mass fraction burned x_b; (*b*) calculated temperature of unburned gas T_u and burned gas T_b in early- and late-burning elements; (*c*) calculated NO concentrations in early- and late-burning elements for rate-controlled model and at equilibrium.[7]

temperature distribution which develops in the burned gases due to the passage of the flame across the combustion chamber has been discussed in Sec. 9.2.1. Mixture which burns early is compressed to higher temperatures after combustion, as the cylinder pressure continues to rise; mixture which burns later is compressed primarily as unburned mixture and ends up after combustion at a lower burned gas temperature. Figure 11-7*a* and *b* shows measured cylinder pressure data from an operating engine, with estimates of the mass fraction burned (x_b) and the temperatures of a gas element which burned just after spark discharge and a gas element which burned at the end of the burning process. The model used to estimate these temperatures assumed no mixing between mixture elements which burn at different times. This assumption is more realistic than the

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alternative idealization that the burned gases mix rapidly and are thus uniform (see Sec. 9.2.1). If the NO formation kinetic model [Eq. (11.7)] is used to calculate NO concentrations in these burned gas elements, using the equilibrium concentrations of the species O, O_2, N_2, OH, and H corresponding to the average fuel/air equivalence ratio and burned gas fraction of the mixture and these pressure and temperature profiles, the rate-limited concentration profiles in Fig. 11-7*c* are obtained. Also shown are the NO concentrations that would correspond to chemical equilibrium at these conditions. The rate-controlled concentrations rise from the residual gas NO concentration, lagging the equilibrium levels, then cross the equilibrium levels and "freeze" well above the equilibrium values corresponding to exhaust conditions. Depending on details of engine operating conditions, the rate-limited concentrations may or may not come close to equilibrium levels at peak cylinder pressure and gas temperature. Also, the amount of decomposition from peak NO levels which occurs during expansion depends on engine conditions as well as whether the mixture element burned early or late.[7]

Once the NO chemistry has frozen during the early part of the expansion stroke, integration over all elements will give the final average NO concentration in the cylinder which equals the exhaust concentration. Thus, if $\{NO\}$ is the local mass fraction of NO, then the average exhaust NO mass fraction is given by

$$\{\overline{NO}\} = \int_0^1 \{NO\}_f \, dx_b \tag{11.16}$$

where $\{NO\}_f$ is the final frozen NO mass fraction in the element of charge which burned when the mass fraction burned was x_b. Note that $\{NO\} = [NO]M_{NO}/\rho$, where $M_{NO} = 30$, the molecular weight of NO. The average exhaust concentration of NO as a mole fraction is given by

$$\tilde{x}_{NOav} = \{\overline{NO}\} \frac{M_{exh}}{M_{NO}} \tag{11.17}$$

and the exhaust concentration in ppm is $\tilde{x}_{NOav} \times 10^6$. The earlier burning fractions of the charge contribute much more to the exhausted NO than do later burning fractions of the charge: frozen NO concentrations in these early-burning elements can be an order of magnitude higher than concentrations in late-burning elements. In the absence of vigorous bulk gas motion, the highest NO concentrations occur nearest the spark plug.

Substantial experimental evidence supports this description of NO formation in spark-ignition engines. The NO concentration gradient across the burned gas in the engine cylinder, due to the temperature gradient, has been demonstrated using gas sampling techniques[8, 9] and using measurements of the chemiluminescent radiation from the reaction $NO + O \rightarrow NO_2 + h\nu$ to determine the local NO concentration. Figure 11-8 shows NO concentration data as a function of crank angle, taken by Lavoie[10] through two different windows in the cylinder head of a specially constructed L-head engine where each window was a different distance from the spark plug. The stars indicate the estimated initial NO concentration that results from mixing of the residual gas with the fresh charge, at the

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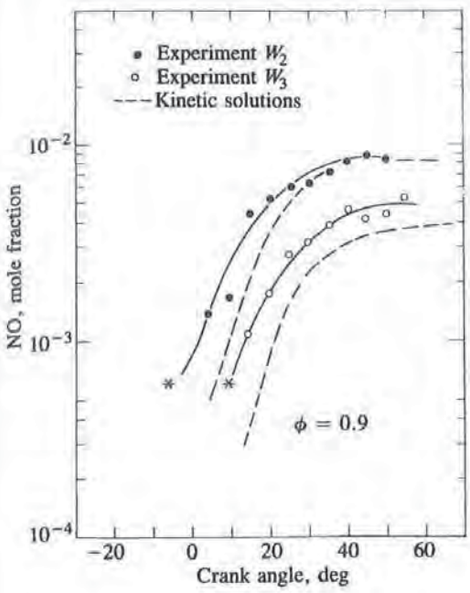


FIGURE 11-8
Spectroscopically measured NO concentrations through two windows W_3 and W_2 in special L-head SI engine (W_2 is closer to spark than W_3). The asterisks mark estimated initial conditions and flame arrival times. The dashed lines are calculated rate-limited concentrations for parts of charge burning at these flame arrival times with zero initial NO concentration.[10]

time of arrival of the flame at each window. The observed NO mole fractions rise smoothly from these initial values and then freeze about one-third of the way through the expansion process. NO levels observed at window W_2, closest to the spark plug, were substantially higher than those observed at window W_3. The dashed lines show calculated NO concentrations obtained using the NO formation kinetic model with an "unmixed" thermodynamic analysis for elements that burned at the time of flame arrival at each window. Since the calculated values started from zero NO concentration at the flame front (and not the diluted residual gas NO level indicated by the star), the calculations initially fall below the data. However, the difference between the two measurement locations and the frozen levels are predicted with reasonable accuracy. Thus, the rate-limited formation process, freezing of NO chemistry during expansion, and the existence of NO concentration gradients across the combustion chamber have all been observed.

The most important engine variables that affect NO emissions are the fuel/air equivalence ratio, the burned gas fraction of the *in-cylinder* unburned mixture, and spark timing. The burned gas fraction depends on the amount of diluent such as recycled exhaust gas (EGR) used for NO_x emissions control, as well as the residual gas fraction. Fuel properties will affect burned gas conditions; the effect of normal variations in gasoline properties is modest, however. The effect of variations in these parameters can be explained with the NO formation mechanism described above: changes in the time history of temperature and oxygen concentration in the burned gases during the combustion process and early part of the expansion stroke are the important factors.[11]

EQUIVALENCE RATIO. Figure 11-9 shows the effect of variations in the fuel/air equivalence ratio on NO emissions. Maximum burned gas temperatures occur at

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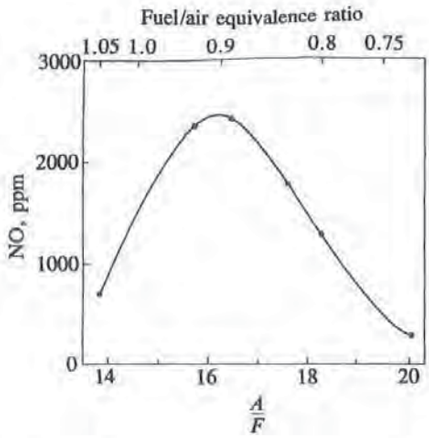


FIGURE 11-9
Variation of exhaust NO concentration with A/F and fuel/air equivalence ratio. Spark-ignition engine, 1600 rev/min, $\eta_v = 50$ percent, MBT timing.[12]

$\phi \approx 1.1$; however, at this equivalence ratio oxygen concentrations are low. As the mixture is enriched, burned gas temperatures fall. As the mixture is leaned out, increasing oxygen concentration initially offsets the falling gas temperatures and NO emissions peak at $\phi \approx 0.9$. Detailed predictions of NO concentrations in the burned gases suggest that the concentration versus time histories under fuel-lean conditions are different in character from those for fuel-rich conditions. In lean mixtures NO concentrations freeze early in the expansion process and little NO decomposition occurs. In rich mixtures, substantial NO decomposition occurs from the peak concentrations present when the cylinder pressure is a maximum. Thus in lean mixtures, gas conditions at the time of peak pressure are especially significant.[7]

BURNED GAS FRACTION. The unburned mixture in the cylinder contains fuel vapor, air, and burned gases. The burned gases are residual gas from the previous cycle and any exhaust gas recycled to the intake for NO_x emissions control. The residual gas fraction is influenced by load, valve timing (especially the extent of valve overlap), and, to a lesser degree, by speed, air/fuel ratio, and compression ratio as described in Sec. 6.4. The burned gases act as a diluent in the unburned mixture; the absolute temperature reached after combustion varies inversely with the burned gas mass fraction. Hence increasing the burned gas fraction reduces NO emissions levels. However, it also reduces the combustion rate and, therefore, makes stable combustion more difficult to achieve (see Secs. 9.3 and 9.4).

Figure 11-10 shows the effect of increasing the burned gas fraction by recycling exhaust gases to the intake system just below the throttle plate. Substantial reductions in NO concentrations are achieved with 15 to 25 percent EGR, which is about the maximum amount of EGR the engine will tolerate under normal part-throttle conditions. Of course, increasing the EGR at fixed engine load and speed increases the inlet manifold pressure, while fuel flow and air flow remain approximately constant.

The primary effect of the burned gas diluent in the unburned mixture on the NO formation process is that it reduces flame temperatures by increasing the

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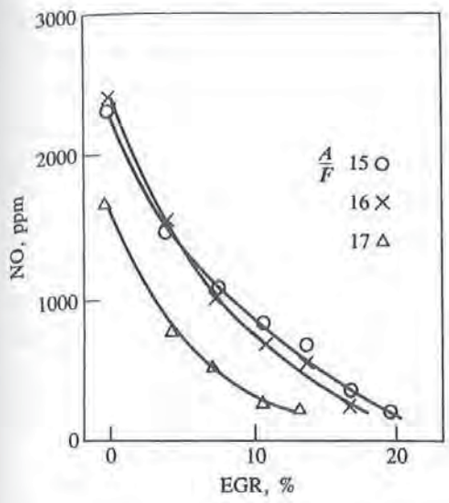


FIGURE 11-10
Variation of exhaust NO concentration with percent recycled exhaust gas (EGR). Spark-ignition engine, 1600 rev/min, $\eta_v = 50$ percent, MBT timing.[12]

heat capacity of the cylinder charge, per unit mass of fuel. Figure 11-11 shows the effect of different diluent gases added to the engine intake flow, in a single-cylinder engine operated at constant speed, fuel flow, and air flow.[13] The data in Fig. 11-11*a* show that equal volume percentages of the different diluents produce different reductions in NO emissions. The same data when plotted against diluent heat capacity (diluent mass flow rate × specific heat, c_p) collapse to a single

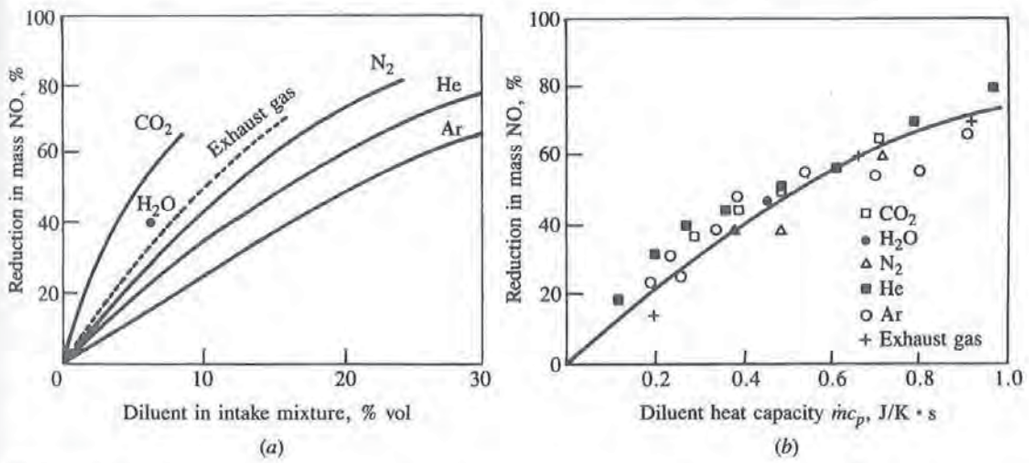


FIGURE 11-11
(*a*) Percentage reduction in mass NO emissions with various diluents. (*b*) Correlation of NO reduction with diluent heat capacity. Spark-ignition engine operated at 1600 rev/min, constant brake load (intake pressure ~0.5 atm), with MBT spark timing.[13]

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curve.† A similiar study where the burned gas fraction in the unburned charge was varied by changing the valve overlap, compression ratio, and EGR, separately, showed that, under more realistic engine operating conditions, it is the heat capacity of the total diluent mass in the in-cylinder mixture that is important. Whether the diluent mass is changed by varying the valve overlap, EGR, or even the compression ratio is not important.[14]

EXCESS AIR AND EGR. Because of the above, it is possible to correlate the influence of engine operating variables (such as air/fuel ratio, engine speed, and load) and design variables (such as valve timing and compression ratio) on NO emissions with two parameters which define the in-cylinder mixture composition: the fuel/air equivalence ratio (often the air/fuel ratio is used instead) and the gas/fuel ratio. The gas/fuel ratio (G/F) is given by

$$\frac{G}{F} = \frac{\text{total mass in cylinder}}{\text{fuel mass in cylinder}} = \frac{A}{F}\left(1 + \frac{x_b}{1 - x_b}\right) \tag{11.18}$$

where x_b is the burned gas fraction [Eq. (4.3)]. These together define the relative proportions of fuel, air, and burned gases in the in-cylinder mixture, and hence

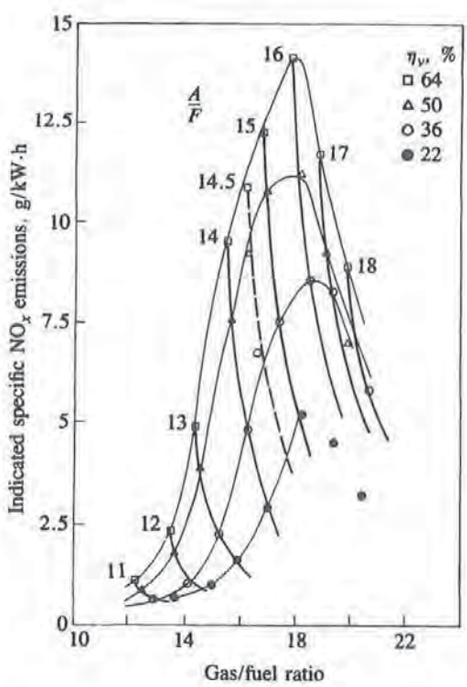


FIGURE 11-12
Correlation between gas/fuel ratio (G/F) and indicated specific NO_x emissions at various air/fuel ratios (A/F) and volumetric efficiencies (η_v). Spark-ignition engine operated at 1400 rev/min with spark timing retarded to give 0.95 of maximum brake torque.[15]

† Some of the scatter in Fig. 11-11 is due to the fact that the residual gas fraction is slightly different for each diluent.

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will correlate NO emissions.† Figure 11-12 shows the correlation of specific NO emissions, from a four-cylinder engine, over a wide range of engine operating conditions with the air/fuel ratio and gas/fuel ratio. Lines of constant air/fuel ratio and volumetric efficiency are shown; the direction of increasing dilution with residual gas and EGR at constant air/fuel ratio is to the right. Excessive dilution results in poor combustion quality, partial burning, and, eventually, misfire (see Sec. 9.4.3). Lowest NO emissions consistent with good fuel consumption (avoiding the use of rich mixtures) are obtained with a stoichiometric mixture, with as much dilution as the engine will tolerate without excessive deterioration in combustion quality.[15]

Comparisons between predictions made with the NO formation model (described at the beginning of this section) and experimental data show good agreement with normal amounts of dilution.[16] With extreme dilution, at NO levels of about 100 ppm or less, the NO formed within the flame reaction zone cannot, apparently, be neglected. Within the flame, the concentrations of radicals such as O, OH, and H can be substantially in excess of equilibrium levels, resulting in much higher formation rates within the flame than in the postflame gases. It is believed that the mechanism [reactions (11.1) to (11.3)] and the formation rate equation (11.6) are valid. However, neglecting flame-front-formed NO is no longer an appropriate assumption.[17]

SPARK TIMING. Spark timing significantly affects NO emission levels. Advancing the timing so that combustion occurs earlier in the cycle increases the peak cylinder pressure (because more fuel is burned before TC and the peak pressure moves closer to TC where the cylinder volume is smaller); retarding the timing decreases the peak cylinder pressure (because more of the fuel burns after TC). Higher peak cylinder pressures result in higher peak burned gas temperatures, and hence higher NO formation rates. For lower peak cylinder pressures, lower NO formation rates result. Figure 11-13 shows typical NO emission data for a spark-ignition engine as a function of spark timing. NO emission levels steadily decrease as spark timing is retarded from MBT timing and moved closer to TC. Since exact determination of MBT timing is difficult (and not critical for fuel consumption and power where the variation with timing around MBT is modest), there is always considerable uncertainty in NO emissions at MBT timing. Often, therefore, an alternative reference timing is used, where spark is retarded from MBT timing to the point where torque is decreased by 1 or 2 percent from the maximum value. Great care with spark timing is necessary to obtain accurate NO emissions measurements under MBT-timing operating conditions.

† Spark timing also affects NO emissions, as discussed next. The above discussion relates to engines run with timing at MBT or with torque at a fixed percentage of (and close to) the maximum.

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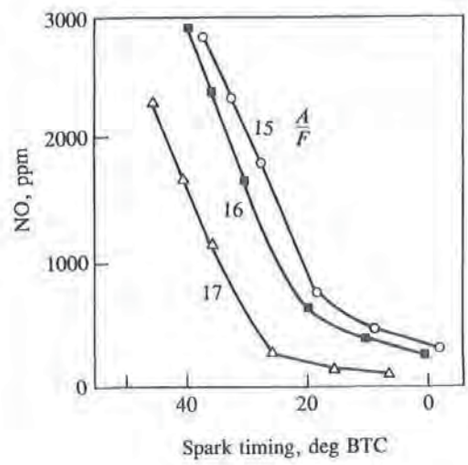


FIGURE 11-13
Variation of exhaust NO concentration with spark retard. 1600 rev/min, $\eta_v = 50$ percent; left-hand end of curve corresponds to MBT timing for each A/F.[12]

11.2.4 NO_x Formation in Compression-Ignition Engines

The kinetic mechanisms for NO and NO_2 formation described in Secs. 11.2.1 and 11.2.2 and the assumptions made regarding equilibration of species in the C—O—H system apply to diesels as well as to spark-ignition engines. The critical difference, of course, is that injection of fuel into the cylinder occurs just before combustion starts, and that nonuniform burned gas temperature and composition result from this nonuniform fuel distribution during combustion. The fuel-air mixing and combustion processes are extremely complex. During the "premixed" or uncontrolled diesel combustion phase immediately following the ignition delay, fuel-air mixture with a spread in composition about stoichiometric burns due to spontaneous ignition and flame propagation. During the mixing controlled combustion phase, the burning mixture is likely to be closer to stoichiometric (the flame structure is that of a turbulent, though unsteady, diffusion flame). However, throughout the combustion process mixing between already burned gases, air, and lean and rich unburned fuel vapor–air mixture occurs, changing the composition of any gas elements that burned at a particular equivalence ratio. In addition to these composition (and hence temperature) changes due to mixing, temperature changes due to compression and expansion occur as the cylinder pressure rises and falls.

The discussion in Sec. 11.2.1 showed that the critical equivalence ratio for NO formation in high-temperature high-pressure burned gases typical of engines is close to stoichiometric. Figure 11-4 is relevant here: it shows the initial NO formation rate in combustion products formed by burning a mixture of a typical hydrocarbon fuel with air (initially at 700 K, at a constant pressure of 15 atm). NO formation rates are within a factor of 2 of the maximum value for $0.85 \lesssim \phi \lesssim 1.1$.

The critical time period is when burned gas temperatures are at a maximum: i.e., between the start of combustion and shortly after the occurrence of peak cylinder pressure. Mixture which burns early in the combustion process

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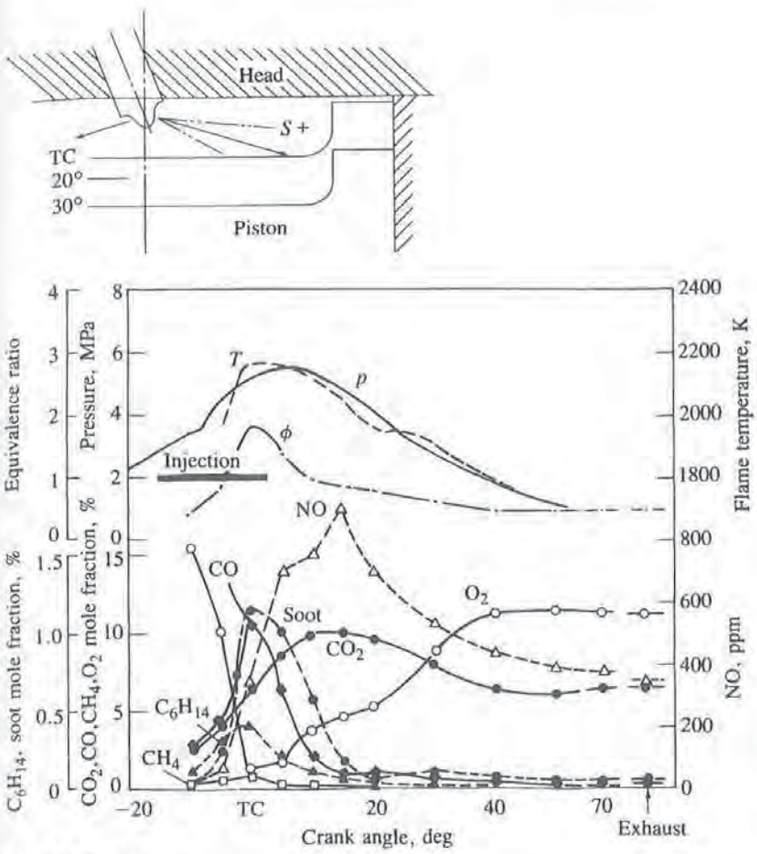


FIGURE 11-14
Concentrations of soot, NO, and other combustion product species measured at outer edge of bowl-in-piston combustion chamber (location *S*) of quiescent DI diesel with rapid sampling valve. Cylinder gas pressure p, mean temperature T, and local equivalence ratio ϕ shown. Bore = 95 mm, stroke = 110 mm, r_c = 14.6. Four-hole nozzle with hole diameter = 0.2 mm.[18]

is especially important since it is compressed to a higher temperature, increasing the NO formation rate, as combustion proceeds and cylinder pressure increases. After the time of peak pressure, burned gas temperatures decrease as the cylinder gases expand. The decreasing temperature due to expansion *and* due to mixing of high-temperature gas with air or cooler burned gas freezes the NO chemistry. This second effect (which occurs only in the diesel) means that freezing occurs more rapidly in the diesel than in the spark-ignition engine, and much less decomposition of the NO occurs.

The above description is supported by the NO concentration data obtained from experiments where gas was sampled from within the cylinder of normally operating diesel engines with special gas-sampling valves and analyzed. Figure 11-14 shows time histories of major species concentrations, through the combustion process, determined with a rapid-acting sampling valve (1 ms open time) in a quiescent *direct-injection diesel* engine. Concentrations at different positions in the combustion chamber were obtained; the sample valve location for the Fig.

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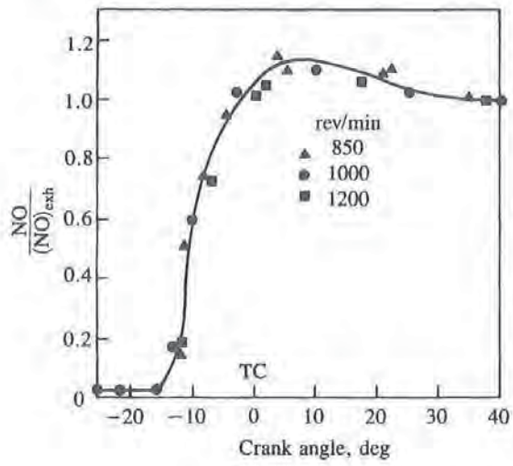


FIGURE 11-15
Ratio of cylinder-average NO concentration at given crank angle (determined from cylinder-dumping experiments) to exhaust NO concentration. DI diesel, equivalence ratio = 0.6, injection timing at 27° BTC.[19]

11-14 data is shown. Local NO concentrations rise from the residual gas value following the start of combustion, to a peak at the point where the local burned gas equivalence ratio changes from rich to lean (where the CO_2 concentration has its maximum value). As the local burned gas equivalence ratio becomes leaner due to mixing with excess air, NO concentrations decrease since formation becomes much slower as dilution occurs. At the time of peak NO concentrations within the bowl (15° ATC), most of the bowl region was filled with flame. The total amount of NO within the cylinder of this type of direct-injection diesel during the NO formation process has also been measured.[19] At a predetermined time in one cycle, once steady-state warmed-up engine operation had been achieved, the contents of the cylinder were dumped into an evacuated tank by rapidly cutting open a diaphragm which had previously sealed off the tank system. Figure 11-15 shows how the ratio of the average cylinder NO concentration divided by the exhaust concentration varies during the combustion process. NO concentrations reach a maximum shortly after the time of peak pressure. There is a modest amount of NO decomposition. Variations in engine speed have little effect on the shape of this curve. The 20 crank angle degrees after the start of combustion is the critical time period.

Results from similar cylinder-dumping experiments where injection timing and load (defined by the overall equivalence ratio) were varied also showed that almost all of the NO forms within the 20° following the start of combustion. As injection timing is retarded, so the combustion process is retarded; NO formation occurs later, and concentrations are lower since peak temperatures are lower. The effect of the overall equivalence ratio on NO_x concentrations is shown in Fig. 11-16. At high load, with higher peak pressures, and hence temperatures, and larger regions of close-to-stoichiometric burned gas, NO levels increase. Both NO and NO_x concentrations were measured; NO_2 is 10 to 20 percent of total NO_x. Though NO levels decrease with a decreasing overall equivalence ratio, they do so much less rapidly than do spark-ignition engine NO emissions (see Fig. 11-9) due to the nonuniform fuel distribution in the diesel. Though the

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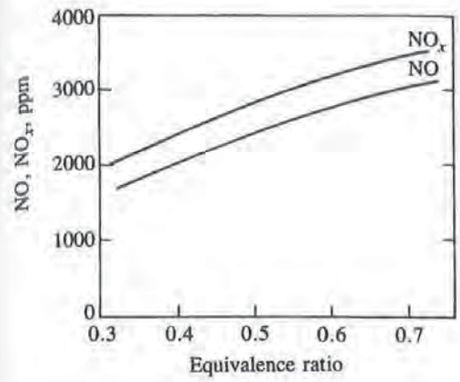


FIGURE 11-16
Exhaust NO_x and NO concentrations as a function of overall equivalence ratio or engine load. DI diesel, 1000 rev/min, injection timing at 27° BTC.[19]

amount of fuel injected decreases proportionally as the overall equivalence ratio is decreased, much of the fuel still burns close to stoichiometric. Thus NO emissions should be roughly proportional to the mass of fuel injected (provided burned gas pressures and temperatures do not change greatly).

Similar gas-sampling studies have been done with *indirect-injection* diesel engines. Modeling studies suggest that most of the NO forms within the prechamber and is then transported into the main chamber where the reactions freeze as rapid mixing with air occurs. However, the prechamber, except at light load, operates rich overall so some additional NO can form as the rich combustion products are diluted through the stoichiometric composition.[20] Figure 11-17 shows local NO concentrations and equivalence ratios as a function of crank angle determined with a rapid-acting sampling valve at different locations

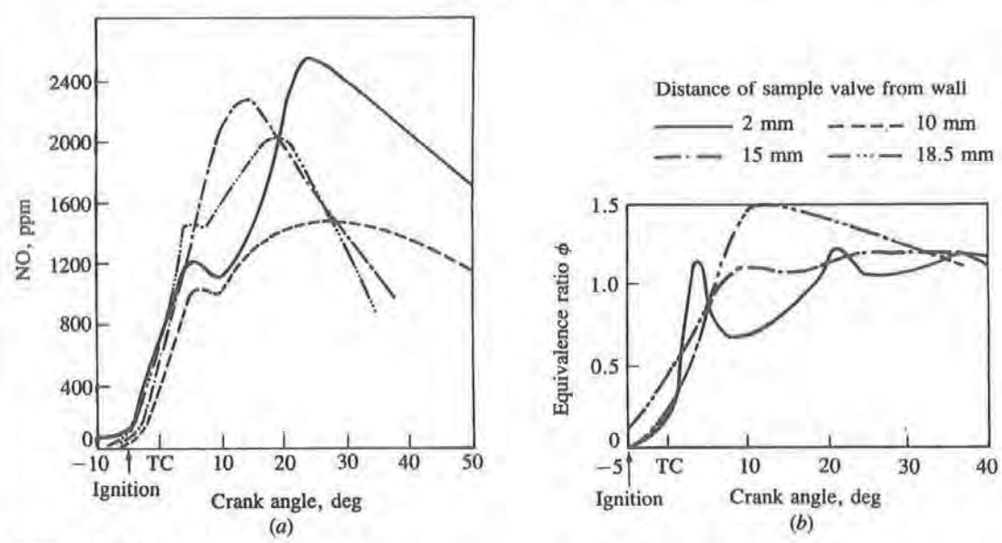


FIGURE 11-17
(*a*) NO concentrations measured with rapid sampling valve and (*b*) calculated equivalence ratios at different distances from the wall in swirl chamber of IDI diesel engine, as function of crank angle. Engine speed = 1000 rev/min, injection at 13° BTC, ignition at 5° BTC.[21]

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within the prechamber of a Comet swirl chamber IDI engine.[21] The gas mixture rapidly becomes stoichiometric or fuel-rich. Composition nonuniformities across the prechamber are substantial. Peak NO concentrations, as expected, correspond approximately to locally stoichiometric regions. Because the mixture remains fuel-rich in the prechamber as the burned gases expand (after the time of peak pressure which occurs between 6 and 10° ATC), substantial NO decomposition within the prechamber can occur. However, by this time much of the gas (and NO) in the prechamber has been transferred to the main chamber where freezing of the NO chemistry will occur. Cylinder-gas dumping experiments, where both main chamber and prechamber gases were dumped and quenched, confirm this description. Cylinder average NO concentrations, determined by rapidly opening a diaphram which separated the engine cylinder from an evacuated tank at predetermined points in the cycle of an otherwise normally operated IDI engine, rise rapidly once combustion starts, until the NO chemistry is effectively frozen at about 15° ATC. Little net NO decomposition occurs.[22] Heat-release-rate diagrams obtained from pressure data analysis for the same IDI engine indicate that combustion is only about one-half complete at the time the NO formation process ceases.

Diluents added to the intake air (such as recycled exhaust) are effective at reducing the NO formation rate, and therefore NO_x exhaust emissions. As with spark-ignition engines, the effect is primarily one of reducing the burned gas temperature for a given mass of fuel and oxygen burned. Figure 11-18 shows the effect of dilution of the intake air with N_2, CO_2, and exhaust gas on NO_x exhaust levels.[23] The heat capacity of CO_2 (per mole) at the temperatures relevant to diesel combustion is about twice that of N_2. That of exhaust gas is slightly higher than that of N_2. Therefore these data show that the effect is primarily one of reduced burned gas temperatures. Note that the composition of the exhaust gas of a diesel varies with load. At idle, there is little CO_2 and H_2O, and the composition does not differ much from that of air. At high load the heat

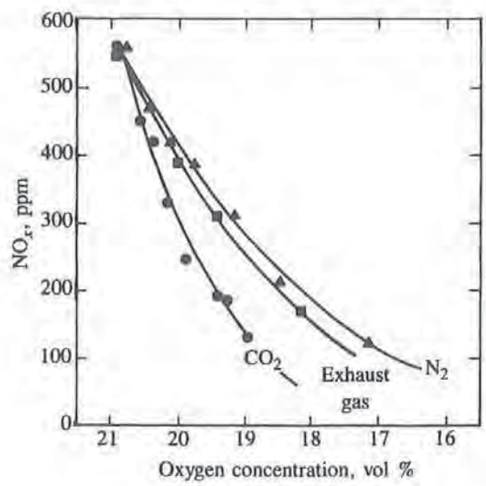


FIGURE 11-18
Effect of reduction in oxygen concentration by different diluents (exhaust gas, CO_2, N_2) on NO_x emissions in DI diesel. Bore = 140 mm, stroke = 152 mm, r_c = 14.3. Speed = 1300 rev/min, fuel rate = 142 mm^3/stroke, injection timing at 4° BTC.[23]

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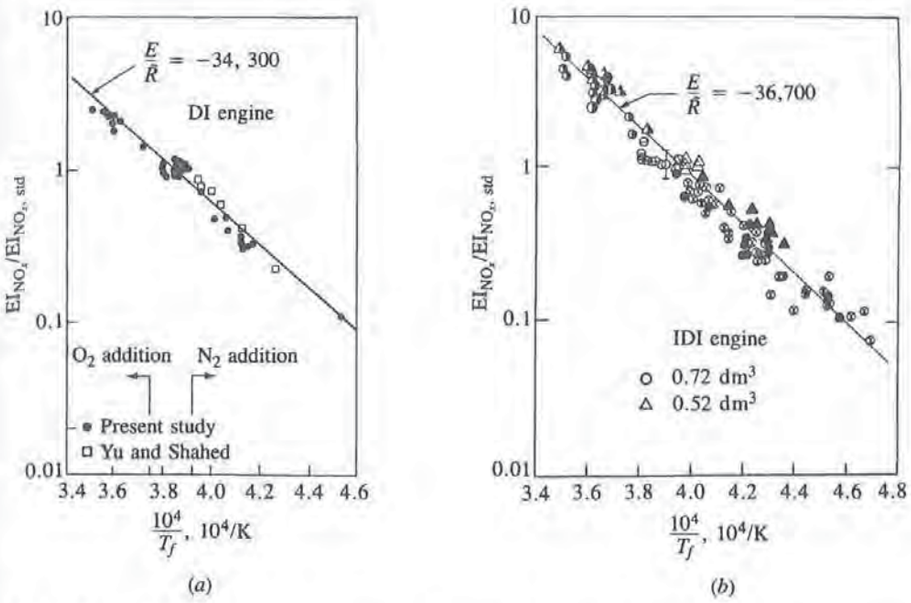


FIGURE 11-19
Correlation of NO_x emissions index EI_{NO_x} for a wide range of operating conditions with reciprocal of stoichiometric mixture flame temperature for: (*a*) DI engines; (*b*) IDI engines. Flame temperatures varied by addition of different diluents and oxygen.[25,26] Values of EI_{NO_x} normalized with value at standard conditions.

capacity increases as the concentrations of CO_2 and H_2O are substantially higher. Similar studies in an *indirect-injection* engine show comparable trends. Addition of diluents [exhaust gas (EGR) and nitrogen] reduce peak flame temperatures and NO_x emissions; also, addition of oxygen (which corresponds to a *reduction* in diluent fraction) increases flame temperatures and therefore increases NO_x emissions.[24]

Confirmation that NO forms in the close-to-stoichiometric burned gas regions and the magnitude of the stoichiometric burned gas temperature controls NO_x emissions is given by the following. Plee *et al.*[25,26] have shown that the effects of changes in intake gas composition (with EGR, nitrogen, argon, and oxygen addition) and temperature on NO_x emissions can be correlated by

$$EI_{NO_x} = \text{constant} \times \exp\left(\frac{E}{\tilde{R}T_f}\right) \tag{11.19}$$

T_f(kelvin) is the stoichiometric adiabatic flame temperature (evaluated at a suitable reference point: fuel-air mixture at top-center pressure and air temperature) and E is an overall activation energy. Figure 11-19 shows EI_{NO_x} for a range of intake air compositions and temperatures, and two DI and two IDI engines for several loads and speeds, normalized by the engine NO_x level obtained for standard air, plotted on a log scale against the reciprocal of the stoichiometric adiabatic flame at TC conditions. A single value of $E/\tilde{R}$ correlates the data over two

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orders of magnitude. There is, of course, some scatter since the model used is overly simple, and load, speed, and other engine design and operating parameters affect the process. The overriding importance of the burned gas temperature of close-to-stoichiometric mixture is clear, however.

11.3 CARBON MONOXIDE

Carbon monoxide (CO) emissions from internal combustion engines are controlled primarily by the fuel/air equivalence ratio. Figure 11-20 shows CO levels in the exhaust of a conventional spark-ignition engine for several different fuel compositions.[27] When the data are plotted against the relative air/fuel ratio or the equivalence ratio, they are correlated by a single curve. For fuel-rich mixtures CO concentrations in the exhaust increase steadily with increasing equivalence ratio, as the amount of excess fuel increases. For fuel-lean mixtures, CO concentrations in the exhaust vary little with equivalence ratio and are of order 10^{-3} mole fraction.

Since spark-ignition engines often operate close to stoichiometric at part load and fuel rich at full load (see Sec. 7.1), CO emissions are significant and must be controlled. Diesels, however, always operate well on the lean side of stoichiometric; CO emissions from diesels are low enough to be unimportant, therefore, and will not be discussed further.

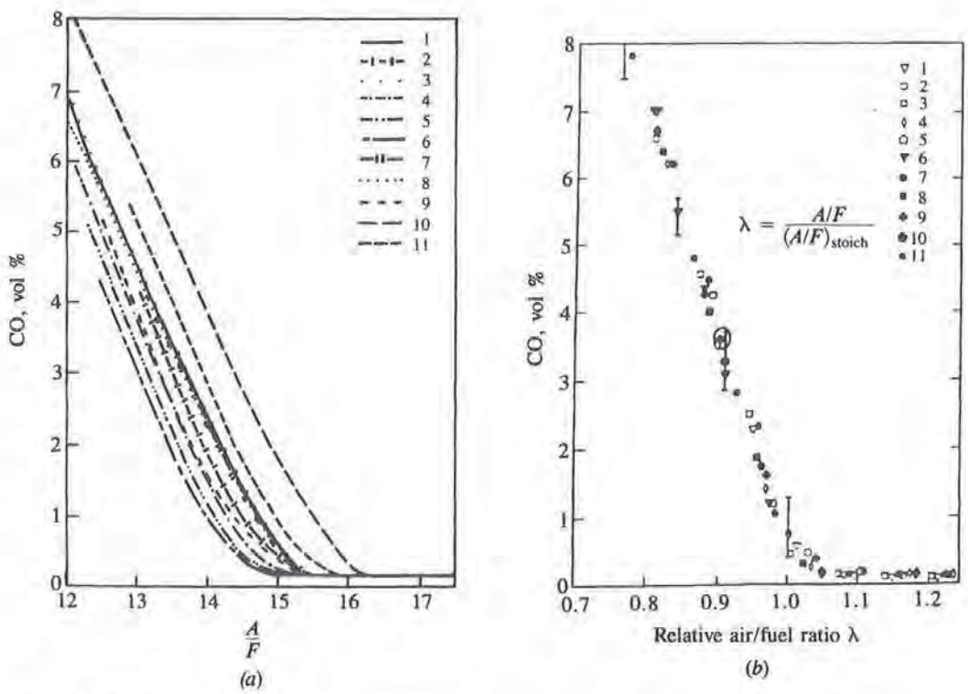


FIGURE 11-20
Variation of SI engine CO emissions with eleven fuels of different H/C ratio: (*a*) with air/fuel ratio; (*b*) with relative air/fuel ratio λ.[27]

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The levels of CO observed in spark-ignition engine exhaust gases are lower than the maximum values measured within the combustion chamber, but are significantly higher than equilibrium values for the exhaust conditions. Thus the processes which govern CO exhaust levels are kinetically controlled. In premixed hydrocarbon-air flames, the CO concentration increases rapidly in the flame zone to a maximum value, which is larger than the equilibrium value for adiabatic combustion of the fuel-air mixture. CO formation is one of the principal reaction steps in the hydrocarbon combustion mechanism, which may be summarized by[1]

$$RH \rightarrow R \rightarrow RO_2 \rightarrow RCHO \rightarrow RCO \rightarrow CO \tag{11.20}$$

where R stands for the hydrocarbon radical. The CO formed in the combustion process via this path is then oxidized to CO_2 at a slower rate. The principal CO oxidation reaction in hydrocarbon-air flames is

$$CO + OH = CO_2 + H \tag{11.21}$$

The rate constant for this reaction is[1]

$$k_{CO}^{+} = 6.76 \times 10^{10} \exp\left(\frac{T}{1102}\right) \quad \text{cm}^3/\text{gmol} \tag{11.22}$$

It is generally assumed that in the postflame combustion products in a spark-ignition engine, at conditions close to peak cycle temperatures (2800 K) and pressures (15 to 40 atm), the carbon-oxygen-hydrogen system is equilibrated. Thus CO concentrations in the immediate postflame burned gases are close to equilibrium. However, as the burned gases cool during the expansion and exhaust strokes, depending on the temperature and cooling rate, the CO oxidation process [reaction (11.21)] may not remain locally equilibrated.

Newhall carried out a series of kinetic calculations for an engine expansion stroke assuming the burned gas at the time of peak cylinder pressure was uniform and in equilibrium.[28] Of the reactions important to CO chemistry, only three-body radical-recombination reactions such as

$$H + H + M = H_2 + M \tag{11.23}$$

$$H + OH + M = H_2O + M \tag{11.24}$$

$$H + O_2 + M = HO_2 + M \tag{11.25}$$

were found to be rate controlling. The bimolecular exchange reactions and the CO oxidation reaction (11.21) were sufficiently fast to be continuously equilibrated. Only during the later stages of the expansion stroke was the CO concentration predicted to depart from equilibrium, as shown in Fig. 11-21. Using this technique to predict average CO levels at the end of expansion over a range of equivalence ratios (rich to lean), Newhall obtained a good match to experimental data (see Fig. 11-22). The kinetically controlled aspects of the CO emissions mechanism have thus been confirmed.

These calculations showed that a partial equilibrium amongst the bimolecular exchange reactions occurred *a posteriori*. Analyses based explicitly on this partial equilibrium assumption (which are considerably simpler) have been

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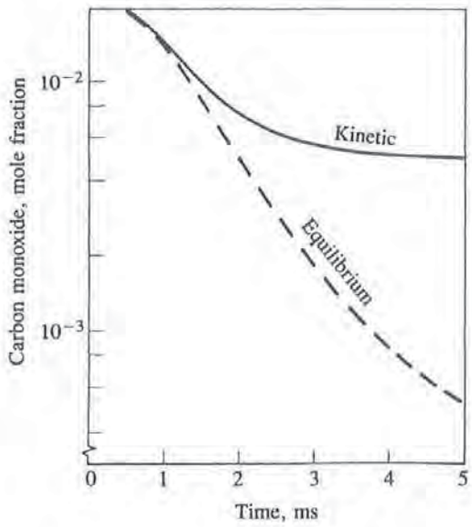


FIGURE 11-21
Results of kinetic calculations of CO concentrations during expansion stroke following TC combustion in SI engine; stoichiometric mixture.[28]

carried out.[29, 30] The appropriate three-body atom and radical recombination reactions [e.g., (11.23) to (11.25)] were treated as the rate-limiting constraint on the total number of particles or moles per unit volume of burnt gases, i.e.,

$$\left(\frac{1}{V}\right)\frac{dn}{dt} = \sum_{i=1}^{k}(R_i^- - R_i^+) \tag{11.26}$$

V is the volume of the elemental system considered, n is the total number of moles, R_i^+ and R_i^- are the forward and backward rates for reaction i, and k represents the number of three-body recombination reactions included. All other

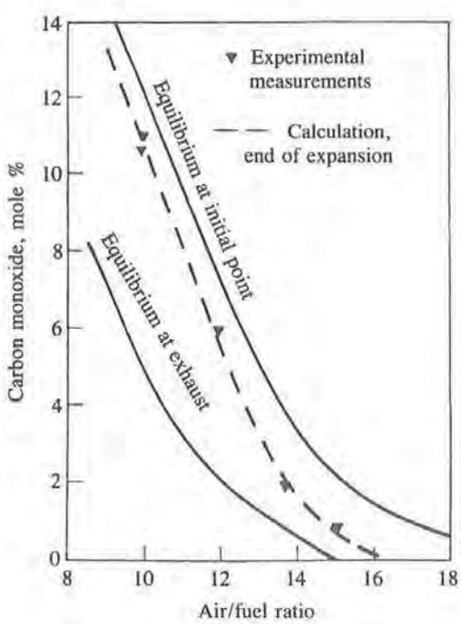


FIGURE 11-22
Predicted CO concentration at end of expansion stroke, compared with measured exhaust concentrations, as function of air/fuel ratio. Equilibrium levels at TC combustion and exhaust conditions also shown.[28]

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reactions were assumed to be equilibrated. The studies using this simplified kinetic model have confirmed that at peak cylinder pressures and temperatures, equilibration times for CO are faster than times characteristic of changes in burnt gas conditions due to compression or expansion. Thus the CO concentration rapidly equilibrates in the burnt gases just downstream of the reaction zone following combustion of the hydrocarbon fuel. However, it has already been pointed out in Sec. 9.2.1 that the burnt gases are not uniform in temperature. Also, the blowdown of cylinder pressure to the exhaust manifold level during the exhaust process and the decrease in gas temperature that accompanies it occupies a substantial portion of the cycle—about 60 crank angle degrees. Thus, the temperature- and pressure-time profiles of parts of the charge at different locations throughout the cylinder differ, depending on when these parts of the charge burn and when they exit the cylinder through the exhaust valve and enter the exhaust manifold.

The results of an idealized calculation which illustrate these effects are shown in Fig. 11-23. The CO mole fractions in different elements or parts of the burnt gas mixture are plotted versus crank angle; x_b is the fraction of the total charge which had burned when each element shown burned; z is the mass fraction which had left the cylinder at the time each element left the cylinder. The partial equilibrium calculations show the burned gases are close to equilibrium until about 60 crank angle degrees after top-center. During the exhaust blowdown process after the exhaust valve opens, gas which leaves the cylinder early

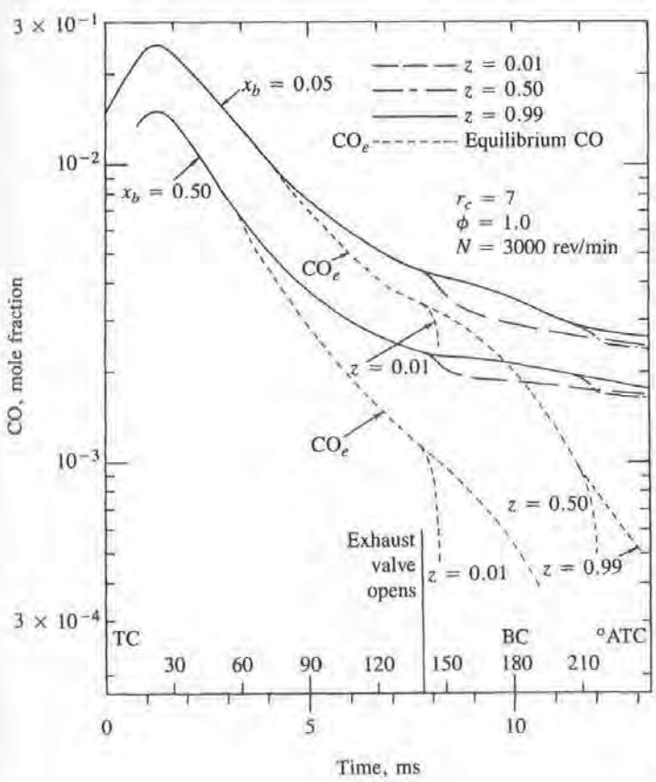


FIGURE 11-23
CO concentrations in selected elements of SI engine cylinder charge, which burn at different times and which exit the cylinder at different times. x_b is mass fraction burned when element burned. z is fraction of gas which has already left cylinder during exhaust process prior to element leaving cylinder. Speed = 3000 rev/min, $r_c = 7$, equivalence ratio = 1.0.[30]

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($z \ll 1$) cools more rapidly than gas which leaves late ($z \approx 1$). In these calculations, mixing between gas elements which burn at different times was neglected. It can be seen that a CO gradient exists across the burned gases and that the CO concentration in the exhaust gases is unlikely to be uniform. Experiments with single-cylinder engines support these conclusions that CO is in equilibrium during the combustion process but deviates from equilibrium late in the expansion stroke (e.g., see Refs. 10 and 31).

Conclusions from these detailed studies are as follows. The measured average exhaust CO concentrations for fuel-rich mixtures are close to equilibrium concentrations in the burned gases during the expansion process. For close-to-stoichiometric mixtures, the partial equilibrium CO predictions are in agreement with measurements and are orders of magnitude above CO equilibrium concentrations corresponding to exhaust conditions. For fuel-lean mixtures, measured CO emissions are substantially higher than predictions from any of the models based on kinetically controlled bulk gas phenomena. One possible explanation of this lean-mixture discrepancy is that only partial oxidation to CO may occur of some of the unburned hydrocarbons emerging during expansion and exhaust from crevices in the combustion chamber and from any oil layers or deposits on the chamber walls.

While many questions about details of the CO oxidation mechanisms remain, as a practical matter exhaust emissions are determined by the fuel/air equivalence ratio. The degree of control achieved within the engine to date has come from improving mixture uniformity and leaning-out the intake mixture. In multicylinder engines, because CO increases rapidly as the inlet mixture becomes richer than stoichiometric, cylinder-to-cylinder variations in equivalence ratio about the mean value are important; nonuniform distribution can significantly increase average emissions. Thus improved cylinder-to-cylinder fuel/air ratio distribution has become essential. Also, because it is necessary to enrich the fuel-air mixture when the engine is cold, CO emissions during engine warm-up are much higher than emissions in the fully warmed-up state. Further, in transient engine operation during acceleration and deceleration, control of fuel metering has had to be improved. Additional reductions in CO beyond what can be achieved in the engine are possible with exhaust treatment devices, which are reviewed in Sec. 11.6. Oxidation of CO in the exhaust system without use of special exhaust treatment devices does not occur to any significant degree because the exhaust gas temperature is too low (Fig. 11-23 shows that the CO oxidation reactions effectively freeze as the gas passes through the exhaust valve).

11.4 UNBURNED HYDROCARBON EMISSIONS

11.4.1 Background

Hydrocarbons, or more appropriately organic emissions, are the consequence of incomplete combustion of the hydrocarbon fuel. The level of unburned hydrocarbons (HC) in the exhaust gases is generally specified in terms of the total hydro-

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TABLE 11.4
Hydrocarbon composition of spark-ignition engine exhaust (by class)[33]

	Carbon, percent of total HC			
	Paraffins	**Olefins**	**Acetylene**	**Aromatics**
Without catalyst	33	27	8	32
With catalyst	57	15	2	26

carbon concentration expressed in parts per million carbon atoms (C_1).† While total hydrocarbon emission is a useful measure of combustion inefficiency, it is not necessarily a significant index of pollutant emissions. Engine exhaust gases contain a wide variety of hydrocarbon compounds. Table 11.4 shows the average breakdown by class of the hydrocarbons in spark-ignition engine exhaust gases, both with and without a catalytic converter, with gasoline fuel. Some of these hydrocarbons are nearly inert physiologically and are virtually unreactive from the standpoint of photochemical smog. Others are highly reactive in the smog-producing chemistry. (Some hydrocarbons are known carcinogens; see Sec. 11.5.2). Based on their potential for oxidant formation in the photochemical smog chemistry, hydrocarbon compounds are divided into nonreactive and reactive categories. Table 11.5 shows one reactivity scale which has been used to estimate the overall reactivity of exhaust gas hydrocarbon mixtures. Other scales are used for the same purpose.[34] Scales that assign high values for reactivity to the olefins (like Table 11.5), which react most rapidly in the photochemical smog reaction, probably best approximate smog-formation potential near the sources of hydrocarbon pollution. The simplest scale, which divides the HC into two classes—methane and nonmethane hydrocarbons—probably best approximates the end result for all HC emissions. All hydrocarbons except methane react, given enough time. More detailed breakdowns of the composition of spark-ignition and diesel engine exhaust HC are available in the literature.[33, 35]

Fuel composition can significantly influence the composition and magnitude of the organic emissions. Fuels containing high proportions of aromatics and olefins produce relatively higher concentrations of reactive hydrocarbons. However, many of the organic compounds found in the exhaust are not present

† This is because the standard detection instrument, a flame ionization detector (FID), is effectively a carbon atom counter: e.g., one propane molecule generates three times the response generated by one methane molecule. Some data in the literature are presented as ppm propane (C_3), or ppm hexane (C_6); to convert to ppm C_1 multiply by 3 or by 6, respectively. Older measurements of hydrocarbon emissions were made with nondispersive infrared (NDIR) detectors which had different sensitivities for the different hydrocarbon compounds. For gasoline-fueled engines, HC emissions determined by FID analyzers are about twice the levels determined by NDIR analyzers,[32] though this scaling is not exact.

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TABLE 11.5
Reactivity of classes of hydrocarbons

Hydrocarbons	Relative reactivity†
C_1–C_4 paraffins Acetylene Benzene	0
C_4 and higher molecular weight paraffins Monoalkyl benzenes *Ortho*- and *para*-dialkyl benzenes Cyclic paraffins	2
Ethylene *Meta*-dialkyl benzenes Aldehydes	5
1-Olefins (except ethylene) Diolefins Tri- and tetraalkyl benzenes	10
Internally bonded olefins	30
Internally bonded olefins with substitution at the double bond Cycloolefins	100

† General Motors Reactivity Scale (0–100). Based on the NO_2 formation rate for the hydrocarbon relative to the NO_2 formation rate for 2,3-dimethyl-2-benzene.[34]

in the fuel, indicating that significant pyrolysis and synthesis occur during the combustion process.

Oxygenates are present in engine exhaust, and are known to participate in the formation of photochemical smog. Some oxygenates are also irritants and odorants. The oxygenates are generally categorized as carbonyls, phenols, and other noncarbonyls. The carbonyls of interest are low molecular weight aldehydes and aliphatic ketones. The volatile aldehydes are eye and respiratory tract irritants. Formaldehyde is a major component ($\lesssim$20 percent of total carbonyls). Carbonyls account for about 10 percent of the HC emissions from diesel passenger car engines, but only a few percent of spark-ignition engine HC emissions. Phenols are odorants and irritants: levels are much lower than aldehyde levels. Other noncarbonyls include methanol, ethanol, nitromethane, methyl formate. Whether these are significant with conventional hydrocarbon fuels is unclear.[35] Use of alcohol fuels increases oxygenate emissions. Both methanol and aldehyde emissions increase substantially above gasoline-fueled levels with methanol-fueled spark-ignition engines.

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11.4.2 Flame Quenching and Oxidation Fundamentals

Flame quenching or extinction occurs at the walls of engine combustion chambers. The cool walls of the chamber act as a sink for heat and the active radical species generated within the flame. Quenching of the flame occurs under several different geometrical configurations: the flame may be propagating normal to, parallel to, or at an angle to the wall; the flame may quench at the entrance to a crevice—a thin volume with a narrow entrance to the combustion chamber such as the region between the piston crown and the cylinder wall. When the flame quenches, it leaves a layer or volume of unburned mixture ahead of the flame. (Whether this results in unburned hydrocarbon emissions depends on the extent to which these quench region hydrocarbons can subsequently be oxidized.)

Flame-quenching processes are analyzed by relating the heat release within the flame to the heat loss to the walls under conditions where quenching just occurs. This ratio, a Peclet number (Pe), is approximately constant for any given geometrical configuration. The simplest configuration for study is the two-plate quench process, where the minimum spacing between two parallel plates through which a flame will propagate is determined. The Peclet number for this two-plate configuration is given by:

$$\mathrm{Pe}_2 = \frac{\rho_u S_L c_{p,f}(T_f - T_u)}{k_f(T_f - T_u)/d_{q2}} = \frac{\rho_u S_L c_{p,f} d_{q2}}{k_f} \tag{11.27}$$

which is approximately constant over a wide range of conditions. ρ, S_L, c_p, T, and k are the density, laminar flame speed, specific heat at constant pressure, gas temperature, and thermal conductivity, respectively, with the subscripts u and f referring to unburned and flame conditions. d_{q2} is the two-plate quench distance. The wall temperature and unburned gas temperature are assumed to be equal; this assumption is also appropriate in the engine context since there is ample time during the compression stroke for a thermal boundary layer to build up to a thickness of at least the quench distance.

Lavoie[36] has developed empirical correlations for two-plate quench-distance data for propane-air mixtures: only limited data for liquid hydrocarbon fuels such as isooctane are available. The data in the pressure range 3 to 40 atm are well fitted by

$$\mathrm{Pe}_2 = \frac{9.5}{\phi}\left(\frac{p}{3}\right)^{0.26 \min(1,\, 1/\phi^2)} \tag{11.28}$$

where p is the pressure in atmospheres and ϕ is the fuel/air equivalence ratio. The two-plate quench distance d_{q2} is then obtained from Eq. (11.27) and Prandtl number and viscosity relations for the flame conditions (see Sec. 4.8 or Ref. 36). Thus the minimum size crevice region into which a flame will propagate can be determined.

For the process of a flame front quenching on a single wall, there are many possible geometries. The simplest is where the flame front is parallel to the wall

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and approaches it head on. The one-wall quench distance d_{q1}, defined as the position of closest approach of the reaction zone to the wall, scales with flame properties in a similar way to the two-plate quench distance. Thus, a one-wall Peclet number relation can be formed:

$$\mathrm{Pe}_1 = \frac{\rho_u S_L c_{p,u} d_{q1}}{k_u} \approx 8 \tag{11.29}$$

where the subscript u denotes properties evaluated at unburned gas conditions.

Using the wall temperature as representative of the unburned gas temperature (because the thermal boundary-layer thickness is greater than typical quench distances), Lavoie showed that

$$\frac{d_{q1}}{d_{q2}} = \frac{\mathrm{Pe}_1}{\mathrm{Pe}_2} = 0.2 \tag{11.30}$$

is a reasonable fit to the single-wall quench data. Typical two-wall quench distances for spark-ignition engine conditions are 0.2 to 1 mm; these distances represent the minimum crevice size the flame will enter. Single-wall quench distances are, therefore, in the range 0.04 to 0.2 mm.

While a fraction of the fuel hydrocarbons can escape the primary combustion process unburned or only partially reacted, oxidation of some of these hydrocarbons can occur during the expansion and exhaust processes. Hydrocarbon oxidation rates have been determined in a number of different studies and several different empirical correlations of the data in the form of overall reaction rate equations have been proposed. A reasonable fit to the experimental data on unburned HC burnup is the rate expression:[36]

$$\frac{d[\mathrm{HC}]}{dt} = -6.7 \times 10^{15} \exp\left(\frac{-18{,}735}{T}\right) \tilde{x}_{\mathrm{HC}} \tilde{x}_{\mathrm{O_2}} \left(\frac{p}{RT}\right)^2 \tag{11.31}$$

where [ ] denotes concentration in moles per cubic centimeter, $\tilde{x}_{\mathrm{HC}}$ and $\tilde{x}_{\mathrm{O_2}}$ are the mole fractions of HC and O_2, respectively, t is in seconds, T in kelvins, and the density term (p/RT) has units of moles per cubic centimeter. The spread in the data about this equation is substantial, however.

Studies of combustion of premixed fuel-air mixtures at high pressure in closed vessels or bombs have been useful in identifying the mechanisms by which hydrocarbons escape complete combustion. The residual unburned hydrocarbons left in the bomb following a combustion experiment have been shown to come primarily from crevices in the bomb walls. Unburned HC levels were proportional to total crevice volume, and decreased to very low values ($\sim$10 ppm C) as all the crevices were filled with solid material. Thus wall quench hydrocarbons apparently diffuse into the burned gases and oxidize following the quenching event.[37] Analytical studies of the flame quenching process, and postquench diffusion and oxidation with kinetic models of the hydrocarbon oxidation process, are in agreement with these bomb data.[38] Flame quenching can be thought of as a two-stage process. The first step is the extinction of the flame at a short distance from the cold wall, determined by a balance between thermal conduction of heat

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from the hot reaction zone to the wall and heat released in the reaction zone by the flame reactions. The second step is the postquench diffusion and oxidation occurring on a time scale of one or a few milliseconds after quenching. The diffusion and oxidation process ultimately reduces the mass of wall quench hydrocarbons to several orders of magnitude below its value at the time of quenching.

Closed-vessel combustion experiments have also been used to show that oil layers on the walls of the bomb cause an increase in residual unburned HC levels after combustion is complete. The additional HC that result in experiments with oil films present are primarily (>95 percent) fuel molecules, and are directly proportional to the amount of oil placed on the walls of the reactor and the solubility of the specific fuel in the oil. These results show that absorption of fuel in the oil occurs prior to ignition. This dissolved fuel is then desorbed into the burned gases well after combustion is complete. Thus fuel absorption into and desorption from any oil layers is a potentially important engine HC mechanism.[39]

11.4.3 HC Emissions from Spark-Ignition Engines

Unburned hydrocarbon levels in the exhaust of a spark-ignition engine under normal operating conditions are typically in the range 1000 to 3000 ppm C_1. This corresponds to between about 1 and $2\frac{1}{2}$ percent of the fuel flow into the engine; the engine combustion efficiency is high. As indicated in Fig. 11-2, HC emissions rise rapidly as the mixture becomes substantially richer than stoichiometric. When combustion quality deteriorates, e.g., with very lean mixtures, HC emissions can rise rapidly due to incomplete combustion or misfire in a fraction of the engine's operating cycles. As outlined in Sec. 11.1, there are several mechanisms that contribute to total HC emissions. Also, any HC escaping the primary combustion process may oxidize in the expansion and exhaust processes. While a complete description of the HC emissions process cannot yet be given, there are sufficient fundamental data available to indicate which mechanisms are likely to be most important, and thus how major engine variables influence HC emission levels.

Four possible HC emissions formation mechanisms for spark-ignition engines (where the fuel-air mixture is essentially premixed) have been proposed: (1) flame quenching at the combustion chamber walls, leaving a layer of unburned fuel-air mixture adjacent to the wall; (2) the filling of crevice volumes with unburned mixture which, since the flame quenches at the crevice entrance, escapes the primary combustion process; (3) absorption of fuel vapor into oil layers on the cylinder wall during intake and compression, followed by desorption of fuel vapor into the cylinder during expansion and exhaust; (4) incomplete combustion in a fraction of the engine's operating cycles (either partial burning or complete misfire), occurring when combustion quality is poor (e.g., during engine transients when A/F, EGR, and spark timing may not be adequately controlled). In addition, as deposits build up on the combustion chamber walls,

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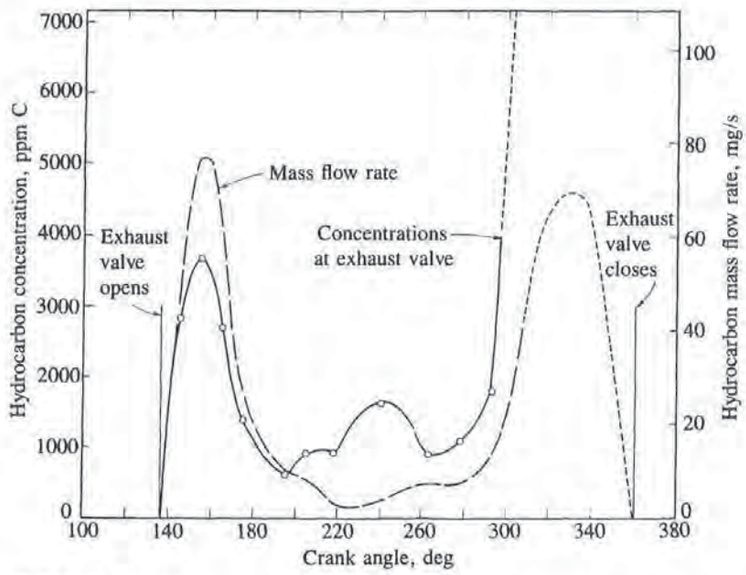


FIGURE 11-24
Variation in HC concentration and HC mass flow rate at the exhaust valve during the exhaust process. SI engine operating at 1200 rev/min and $\phi = 1.2$, unthrottled.[40]

HC emissions increase. Whether the deposits constitute an additional mechanism or merely modify one of the above mechanisms is unclear.

All these processes (except misfire) result in unburned hydrocarbons close to the combustion chamber walls, and not in the bulk of the cylinder gases. Thus, the distribution of HC in the exhaust gases would not be expected to be uniform. Experiments have been done to determine the unburned HC concentration distribution in the exhaust port during the exhaust process to provide insight into the details of the formation mechanisms. Gas concentrations were measured with a rapid-acting sampling valve placed at the exhaust port exit. Figure 11-24 shows results from these time-resolved HC concentration measurements. HC concentrations vary significantly during the exhaust process. Gas which remains in the exhaust port between exhaust pulses has a high HC concentration, so purging techniques where air or nitrogen was bled into the exhaust port were used to displace this high HC gas while the exhaust valve was closed. The high HC concentration in the blowdown exhaust gases is clearly discernible, as is the rapid rise in HC concentration toward the end of the exhaust stroke. The cylinder-exit HC concentrations were then multiplied by the instantaneous exhaust gas mass flow rate to obtain the instantaneous HC mass emission rate from the cylinder throughout the exhaust process, also shown in Fig. 11-24. The unburned HC are exhausted in two peaks of approximately equal mass: the first of these coincides with the exhaust blowdown mass flow pulse (which removes the majority of the *mass* from the cylinder); the second occurs toward the end of the exhaust stroke where HC concentrations are very high and the mass flow rate is relatively low.[40] Other experiments have confirmed these observations.[41] Clearly, mixing of

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unburned HC with the bulk cylinder gases occurs during expansion and/or the exhaust blowdown process. Then, the final stages of piston motion during the exhaust stroke push most of the remaining fraction of the cylinder mass with its high HC concentration into the exhaust. This would be expected to leave a high concentration of HC in the residual gas in the cylinder. Experiments conducted in which the valve mechanism of a single-cylinder engine was arranged to disengage during operation and trap residual gases in the cylinder confirm this. For one set of typical engine operating conditions, approximately one-third of the hydrocarbons left unburned in an engine combustion event was retained in the cylinder and recycled.[42]

FLAME QUENCHING AT THE WALLS. The existence of quench layers on the cold combustion chamber walls of a spark-ignition engine was shown photographically by Daniel.[43] Photographs of the flame region immediately after flame arrival at the wall through a window in the cylinder head showed a thin nonradiating layer adjacent to the wall. The quench layer thicknesses measured were in the range 0.05 to 0.4 mm (thinnest at high load), in rough agreement with predictions based on experiments in combustion bombs. However, more recent work in bombs and engines indicates that diffusion of hydrocarbons from the quench layer into the burned gases and its subsequent oxidation occur on a time scale of a few milliseconds, at least with smooth clean combustion chamber walls. The constant-volume combustion bomb data which suggested this conclusion and the kinetic calculations which support this explanation of why quench layers are not significant with smooth clean walls have already been described in Sec. 11.4.2. The following evidence shows these conclusions are also valid in an engine.

A special rapid-acting poppet valve was used in a single-cylinder engine to sample the gases from a torus-shaped region, of height of order 0.25 mm and diameter about 6 mm, adjacent to the wall over a 1-ms period. Sampling was repeated every cycle to provide a steady stream of sampled gases for analysis. Figure 11-25 shows the variation in concentrations of HC species through the combustion, expansion, and exhaust processes. The fuel was propane (C_3H_8). The fuel concentration drops rapidly to a low value when the flame arrives at the valve; at the same time, intermediate hydrocarbon product concentrations rise and then fall sharply to values below 1 ppm. Beginning at 60° ATC, all HC concentrations rise and vary somewhat during the remainder of the cycle in a way that depends strongly on engine operating conditions. The observed rapid rise in partial oxidation products immediately after flame arrival is consistent with the flame quenching short of the wall. The presence of CH_2O and CH_3CHO in significant quantities indicates that low-temperature oxidation processes are occurring. However, since all HC product concentrations fall rapidly within 2 ms of flame arrival to very low values, the unburned HC in the quench layer diffuse into the bulk burned gases and oxidize. The increase in HC concentrations later in the cycle results from the sampling of hydrocarbons from sources other than quench layers.[44]

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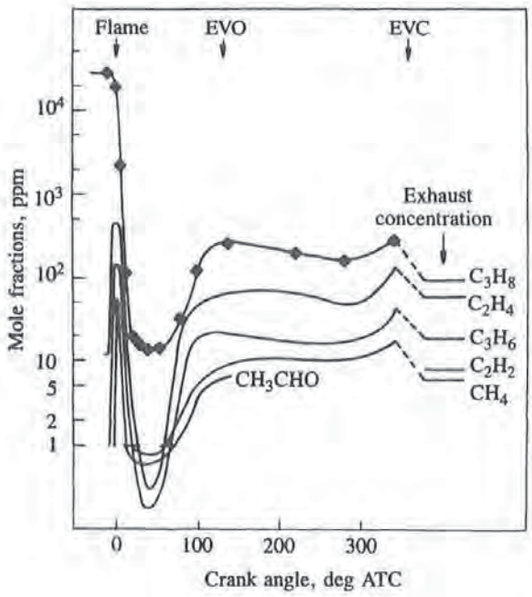


FIGURE 11-25
Concentrations (mole fractions) of selected hydrocarbons adjacent to combustion chamber wall, as a function of crank angle during combustion, expansion, and exhaust processes. Mass sampled with rapid-acting valve held constant at 7.6×10^{-6} g per pulse. Total exhaust HC = 400 ppm C. Engine speed = 1250 rev/min, imep = 380 kPa, equivalence ratio = 0.9, MBT spark timing, no EGR.[44]

Though quench layers on clean smooth combustion chamber walls are not a significant source of unburned hydrocarbons, it has been shown that wall surface finish does affect exhaust HC levels. Comparisons have been made between the standard "rough" as-cast cylinder head surfaces and the same cylinder heads when smoothed. The average exhaust HC concentration decreased by 103 ppm C, or 14 percent; the smoothed surface area was 32 percent of the total combustion chamber surface area.[45] Buildup of deposits on the combustion chamber surfaces also affect HC emission levels, as will be discussed later.

CREVICE HC MECHANISM. The crevices in the combustion chamber walls—small volumes with narrow entrances—into which the flame is unable to penetrate have been shown to be a major source of unburned HC. The largest of these crevice regions is the volumes between the piston, piston rings, and cylinder wall. Other crevice volumes in production engines are the threads around the spark plug, the space around the plug center electrode, crevices around the intake and exhaust valve heads, and the head gasket crevice. Table 8.1 shows the size and relative importance of these crevice regions in one cylinder of a production V-6 engine determined from measurements of cold-engine components. Total crevice volume is a few percent of the clearance volume and the piston and ring pack crevices are the dominant contributor.

The important crevice processes occurring during the engine cycle are the following. As the cylinder pressure rises during compression, unburned mixture is forced into the crevice regions. Since these volumes are thin they have a large surface/volume ratio; the gas flowing into each crevice cools by heat transfer to close to the wall temperature. During combustion, while the pressure continues to rise, unburned mixture continues to flow into the crevice volumes. When the

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flame arrives at each crevice, it can either propagate into the crevice and fully or partially burn the fuel and air within the crevice or it can quench at the crevice entrance. Whether the flame quenches depends on crevice entrance geometry, the composition of the unburned mixture, and its thermodynamic state as described in Sec. 11.4.2. After flame arrival and quenching, burned gases will flow into each crevice until the cylinder pressure starts to decrease. Once the crevice gas pressure is higher than the cylinder pressure, gas flows back from each crevice into the cylinder.

The most important of these crevices, the volumes between the piston, piston rings, and cylinder wall, is shown schematically in Fig. 8-27. This crevice consists of a series of volumes, connected by flow restrictions such as the ring side clearance and ring gap whose geometry changes as the ring moves up and down in the ring groove sealing either at the top or bottom ring surface. The gas flow, pressure distribution, and ring motion are therefore coupled, and their behavior during the compression and expansion strokes has already been discussed in Sec. 8.6. During compression and combustion, mass flows *into* the volumes in this total crevice region. Once the cylinder pressure starts to decrease (after about 15° ATC) gas flows out of the top of these crevice regions in Fig. 8-27 into the cylinder at low velocity adjacent to the cylinder wall. The important result is that the fraction of the total cylinder charge (5 to 10 percent) trapped in these regions at the time of peak cylinder pressure escapes the primary combustion process. Most of this gas flows back into the cylinder during the expansion process. Depending on spark plug location in relation to the position of the top ring gap, well above 50 percent of this gas can be unburned fuel-air mixture. Its potential contribution to unburned HC emissions is obvious.

There is substantial evidence to support the above description of crevice HC phenomena and the piston ring crevice region in particular. Visualization studies in a special engine have identified the spark plug crevice outflow, low-velocity gas expansion out of the volume above the first ring after the time of peak pressure, and the jet-like flows through the top ring gap later in the expansion process when the pressure difference across the ring changes sign.[46] Gas sampling from the volume above the top ring, using a rapid-acting sample valve mounted in the piston crown, has shown that the gas composition in this region corresponds to unburned fuel-air mixture until flame arrival at the crevice entrance closest to the sampling valve location. Next, product gases enter the crevice as the cylinder pressure continues to rise. Then, during expansion as gas flows out of this region, the composition of the gas sampled reverts back toward that of the unburned mixture which enters the crevice region earlier.[47]

Direct evidence that the piston and ring crevice regions are a major contributor to exhaust HC emissions comes from experiments where the volume of this crevice region was substantially changed. Wentworth[48] almost completely eliminated this crevice by moving the top piston ring as close to the crown of the piston as possible, and sealing this ring at top and bottom in its groove with O rings. Tests of this sealed ring-orifice design in a production engine showed reductions of between 47 and 74 percent from baseline HC levels over a range of

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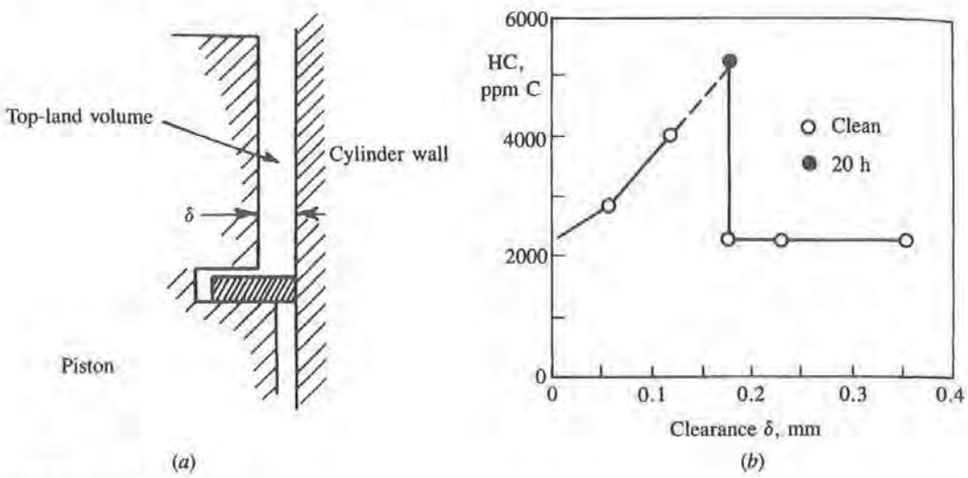


FIGURE 11-26
(*a*) Piston top-land crevice volume. (*b*) Effect of increasing top-land clearance on exhaust hydrocarbon emissions. Unthrottled spark-ignition engine, $r_c = 6$, 885 rev/min, $A/F = 13$, MBT timing.[49]

speeds and loads. Haskell and Legate,[49] in experiments in a single-cylinder CFR engine, steadily increased the piston top-land clearance (see Fig. 11-26*a*) and measured the effect on exhaust HC emissions. Figure 11-26*b* shows the results: HC emissions increase as the top-land clearance increases until the clearance equals about 0.18 mm, when emissions drop to the zero clearance level. This clearance (0.18 mm) is close to the two-plate quench distance estimated from Eq. (11.27). For piston top-land clearances above this value, the flame can enter the crevice and burn up much of the crevice HC.

The relative importance of the different crevices in the combustion chamber walls has been examined by using the cylinder head and piston of a four-cylinder production engine to form two constant-volume reactors or combustion bombs.[50] The cylinder head was sealed with a steel plate across the head gasket plane to make one reactor; the piston and ring pack and cylinder wall, again sealed with a plate at the head gasket plane, formed the second reactor. Each reactor was filled with a propane-air mixture and combustion initiated with a spark discharge across a spark plug; following combustion the burned gases were exhausted, sampled, and analyzed. The crevices were sequentially filled with epoxy or viton rubber, and after filling each crevice, the exhaust HC emission level determined. It was found that the ring pack crevices produced approximately 80 percent of the total scaled HC emissions, the head gasket crevice about 13 percent, and the spark plug threads 5 percent. All other HC sources in these reactors produced less than 2 percent of the total HC. While these numbers cannot be applied directly to an operating engine (the crevice filling and emptying rates in the bomb experiments are substantially different from these rates in an engine), they do underline the importance of the ring pack crevice region.

Blowby is the gas that flows from the combustion chamber, past the piston and into the crankcase. It is forced through any leakage paths afforded by the

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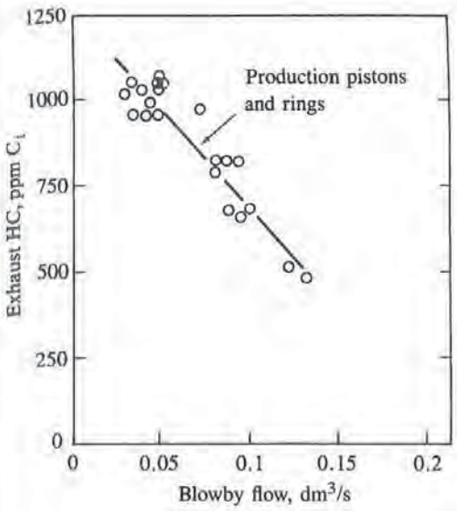


FIGURE 11-27
Effect of increasing crankcase blowby on exhaust hydrocarbon emissions. Production pistons and rings. SI engine at 1200 rev/min, intake manifold pressure 0.6 atm, $A/F = 14.2$.[51]

piston-bore-ring assembly in response to combustion chamber pressure. Blowby of gases from the cylinder to the crankcase removes gas from this crevice region and thereby prevents some of the crevice gases from returning to the cylinder. Crankcase blowby gases used to be vented directly to the atmosphere and constituted a significant source of HC emissions. The crankcase is now vented to the engine intake system, the blowby gases are recycled, and this source of HC emissions is now fully controlled. Blowby at a given speed and load is controlled primarily by the greatest flow resistance in the flow path between the cylinder and the crankcase. This is the smallest of the compression ring ring-gap areas. Figure 8-30 shows how blowby increases linearly with the smallest gap area. Figure 11-27 shows how exhaust HC levels decrease as blowby increases and more crevice HC flows to the crankcase. Crankcase blowby gases represent a direct performance loss. They are a smaller efficiency loss because crankcase gases are now recycled to the engine intake system.

The location of the ring gap in relation to the spark plug also affects HC emission levels. Experiments have shown that HC emissions are highest when the top ring gap is farthest from the spark plug; the gas flowing into the crevice directly above the gap is then unburned mixture for the longest possible time. With the top ring gap closest to the spark plug, HC exhaust levels are lowest because burned gas reaches the gap location at the earliest time in the combustion process. The difference, highest to lowest, was between 9 and 42 percent of the average level for any set of operating conditions, and in most cases was above 20 percent.[51]

The fate of these crevice HC when they flow back into the cylinder during expansion and exhaust is not well understood. Both jet-like flows (e.g., that from the ring gap) and low-velocity creeping flows (e.g., that from the piston top-land crevice) have been observed (see Fig. 8-29). While the former could mix rapidly with the high-temperature bulk burned gases, the latter will enter the cool gases

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TABLE 11.6
Amount of gas flowing into and out of crevice regions†

	% mass	ppm C
Total gas in all crevice regions	8.2	
Total gas back to combustion chamber	7.0	
Unburned back to combustion chamber	3.7–7.0‡	5000–9400
Unburned to blowby	0.5–1.2‡	
Total unburned escaping primary combustion	4.2–8.2‡	

† For V-6 engine operating at 2000 rev/min and wide-open throttle.
‡ Depends on spark plug and ring gap location.

in the cylinder wall boundary layer and mix and (probably) burn much more slowly. Hydrocarbon transport and oxidation processes are discussed more fully below.

Table 11.6 presents a summary of estimates of the total mass of gas and mass of unburned mixture in the piston, ring, and cylinder wall crevice region for a typical spark-ignition engine.[46] When compared to exhaust HC levels, it is clear that these crevices are a major source of unburned hydrocarbons.

ABSORPTION AND DESORPTION IN ENGINE OIL. The presence of lubricating oil in the fuel or on the walls of the combustion chamber is known to result in an increase in exhaust hydrocarbon levels. In experiments where exhaust HC concentrations rose irregularly with time, with engine operating conditions nominally constant, it was shown that oil was present on the piston top during these high emission periods. When engine oil was added to the fuel, HC emissions increased, the amount of additional HC in the exhaust increasing with the increasing amount of oil added. The increase in exhaust HC was primarily unreacted fuel (isooctane) and not oil or oil-derived compounds.[51] The increase in HC can be substantial: exhaust HC levels from a clean engine can double or triple when operated on a fuel containing 5 percent lubricating oil over a period of order 10 minutes. (With deposits from leaded-fuel operation present on the combustion chamber walls, however, a much smaller increase in exhaust HC was observed.) It has been proposed that fuel vapor absorption into and desorption from oil layers on the walls of the combustion chamber could explain these phenomena.[49]

The absorption and desorption mechanism would work as follows. The fuel vapor concentration within the cylinder is close to the inlet manifold concentration during intake and compression. Thus, for about one crankshaft revolution, any oil film on the walls will absorb fuel vapor. During the latter part of compression, the fuel vapor pressure is increasing so, by Henry's law, absorption will continue even if the oil was saturated during intake. During combustion the fuel vapor concentration in the bulk gases goes essentially to zero so the absorbed fuel vapor will desorb from the liquid oil film into the gaseous combustion products. Desorption could continue throughout the expansion and exhaust strokes.

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Some of the desorbed fuel vapor will mix with the high-temperature combustion products and oxidize. However, desorbed vapor that remains in the cool boundary layer or mixes with the cooler bulk gases late in the cycle may escape full oxidation and contribute to unburned HC emissions.

Experiments, where measured amounts of oil were placed on the piston crown, confirm that oil layers on the combustion chamber surface increase exhaust HC emissions. The exhaust HC levels increased in proportion to the amount of oil added when the engine was fueled with isooctane. Addition of 0.6 cm^3 of oil produced an increase of 1000 ppm C in exhaust HC concentration. Fuel and fuel oxidation species, not oil oxidation products, were responsible for most of this increase. Similar experiments performed with propane fuel showed no increase in exhaust HC emissions when oil was added to the cylinder. The increase in exhaust HC is proportional to the solubility of the fuel in the oil. The exhaust HC levels decreased steadily back to the normal engine HC level before oil addition, over a period of several minutes. At higher coolant temperatures, the increase in HC on oil addition is less, and HC concentrations decreased back to the normal level more quickly. Increasing oil temperature would decrease viscosity, increasing the rate of drainage into the sump. It also changes the solubility and diffusion rate of the fuel in the oil.[52]

At the outer surface of the oil layer, the concentration of fuel vapor dissolved in the oil is given by Henry's law for dilute solutions in equilibrium:

$$\tilde{x}_f = \frac{p_f}{H} \tag{11.32}$$

where $\tilde{x}_f$ is the mole fraction of fuel vapor in the oil, p_f is the partial pressure of fuel vapor in the gas, and H is Henry's constant. If the oil layer is sufficiently thin, and hence diffusion sufficiently rapid, Eq. (11.32) can be used to estimate the mole fraction of the fuel dissolved in the oil. Since $p_f = n_{f,c}\tilde{R}T/V$ (where $n_{f,c}$ is the number of moles of fuel in the cylinder, T is the temperature, and V the cylinder volume) and $x_f = n_{f,o}/(n_{f,o} + n_o) = n_{f,o}/n_o$ for $n_o \gg n_{f,o}$ (where $n_{f,o}$ is the number of moles of fuel dissolved in the oil and n_o is the number of moles of oil),[53] then

$$\frac{n_{f,o}}{n_{f,c}} = \frac{n_o \tilde{R}T}{HV} \tag{11.33}$$

Diffusion is sufficiently rapid for Eq. (11.33) to be valid if the diffusion time constant τ_d is much less than characteristic engine times: i.e.,

$$\tau_d \approx \frac{\delta^2}{D} \ll N^{-1}$$

where δ is the oil layer thickness, D is the diffusion coefficient for fuel vapor in the oil, and N is engine speed. D for a hydrocarbon through a motor oil is of order 10^{-6} cm^2/s at 300 K and of order 10^{-5} cm^2/s at 400 K. Oil film thicknesses on the cylinder wall vary during the operating cycle between about 1 and 10 μm.[54, 55] Thus diffusion times for engine conditions are 10^{-1} to 10^{-3} s; for the thinnest oil layers approximate equilibration would be achieved. A theoretical

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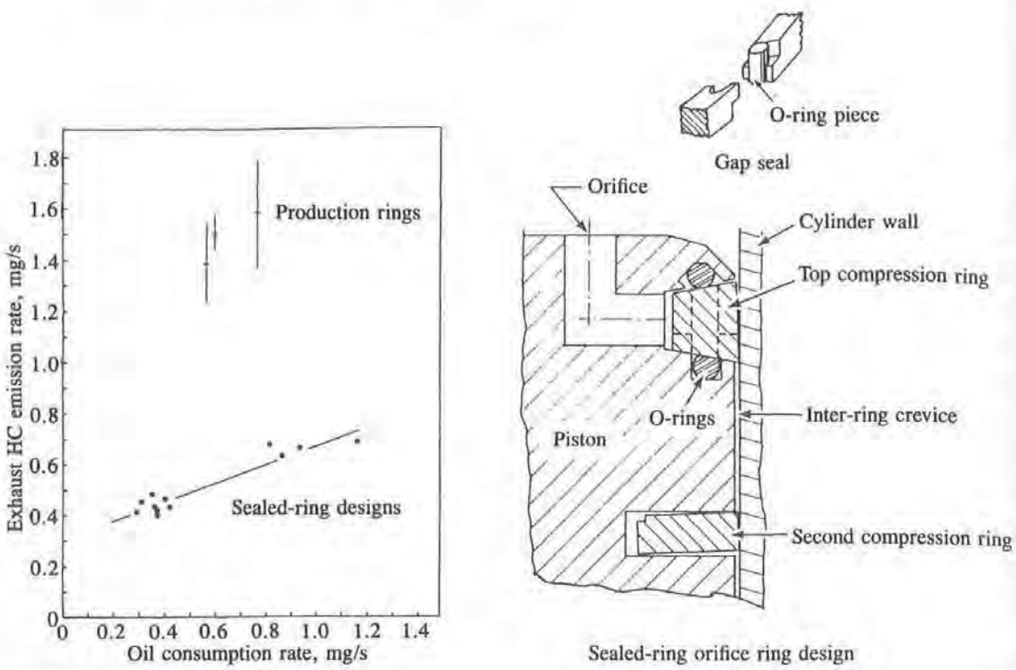


FIGURE 11-28
Correlation between exhaust hydrocarbon emissions and oil consumption rate. Production piston rings and sealed ring–orifice ring designs. SI engine at 1600 rev/min, imep = 422 kPa, equivalence ratio = 0.9, r_c = 8.0, intake pressure = 54 kPa, MBT spark timing.[57]

study of this problem—the one-dimensional cyclic absorption and desorption of a dilute amount of gas in a thin (constant thickness) isothermal liquid layer where diffusion effects are important—has been carried out. It suggests that oil layers on the cylinder wall could be a significant contributor to HC emission levels.[56]

Correlations between engine oil consumption and exhaust HC emissions provide a perspective on the relative importance of oil absorption/desorption and crevice mechanisms. Wentworth measured oil consumption and HC emissions in a spark-ignition engine for a range of piston ring designs.[57] Some of these designs were of the sealed ring–orifice type which effectively eliminates all the crevices between the piston, piston rings, and cylinder, and prevents any significant gas flow into or out of the ring region. HC emissions increase with increasing oil consumption for both production ring designs and the sealed ring–orifice designs, as shown in Fig. 11-28. Extrapolation to zero oil consumption from normal consumption levels shows a reduction in exhaust HC levels, but this decrease is significantly less than the difference in emission levels between the production and the sealed ring–orifice designs which effectively remove the major crevice region. The production piston used had a chamfered top land. The HC emissions for a normal piston top-land design would probably be higher.

POOR COMBUSTION QUALITY. Flame extinction in the bulk gas, before all of the flame front reaches the wall, is a source of HC emissions under certain engine

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operating conditions. As the cylinder pressure falls during the expansion stroke, the temperature of the unburned mixture ahead of the flame decreases. This slows the burning rate [the laminar flame speed decreases so the burning rate in Eq. (9.52) decreases]. If the pressure and temperature fall too rapidly, the flame can be extinguished. This type of bulk quench has been observed in spark-ignition engines; it results in very high HC concentrations for that particular cycle. Engine conditions where bulk quenching is most likely to occur are at idle and light load where engine speed is low and the residual gas fraction is high, with high dilution with excessive EGR or overly lean mixtures, and with substantially retarded combustion. Even if steady-state engine calibrations of A/F, EGR, and spark-timing are such that bulk quenching does not occur, under transient engine operation these variables may not be appropriately set to avoid bulk quenching in some engine cycles due to the different dynamic characteristics of the engine subsystems which control these variables.

The existence of zones of stable and unstable engine operation with lean or dilute mixtures has already been discussed (see Sec. 9.4.3). Detailed engine combustion studies have shown that, as mixture composition becomes more dilute (e.g., by increasing EGR) and unburned gas temperature and pressure during combustion become lower, combustion quality (or variability) and engine stability deteriorate. The standard deviation in a parameter such as indicated mean effective pressure (which depends for its magnitude on the proper timing of the start of combustion and on the duration of the combustion process) increases due first to an increase in the number of slower burning cycles, then as conditions worsen to the occurrence of partial burning cycles, and finally to some misfiring cycles. Figure 9-36 showed how unburned hydrocarbon emissions from a spark-ignition engine rise as the EGR rate is increased at constant load and speed, and combustion quality (defined by the ratio of standard deviation in imep to the average imep) deteriorates. Initially the increase in HC is modest and is caused by changes in the other HC emission mechanisms described above. However, when partial burning cycles are detected, HC emissions rise more rapidly due to incomplete combustion of the fuel in the cylinder in these cycles. When misfiring cycles—no combustion—occur the rise in HC becomes more rapid still.

The relative importance of bulk gas quenching in a fraction of the engine's operating cycles due to inadequate combustion quality as a source of HC, compared with the other sources described in this section, has yet to be established. However, one obvious technique for reducing its importance, burning the mixture faster so that combustion is completed before conditions conducive to slow and partial burning exist in the cylinder, does reduce engine exhaust HC emissions. Figure 11-29 shows a comparison of HC emissions from a moderate burn rate engine with HC emissions with a faster burn rate [i.e., with improved combustion quality—lower coefficient of variation in imep, COV_{imep}, Eq. (9.50)], achieved by the use of two spark plugs instead of one.[58] The exhaust measurements show lower HC emissions when significant amounts of EGR are used for NO_x control for the faster, and hence less variable, combustion process. Such evidence suggests that occasional partial burning cycles may occur, even under

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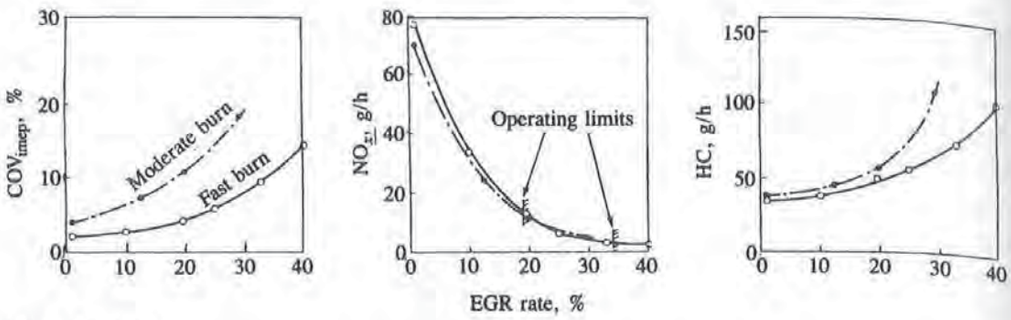


FIGURE 11-29
Effect of increasing burn rate on tolerance to recycled exhaust gas (EGR) and HC and NO_x emissions levels. COV_{imep} defined by Eq. (9.50). SI engine at 1400 rev/min, 324 kPa imep, equivalence ratio = 1.0, MBT timing.[58]

conditions where combustion appears to be "normal," and that this mechanism is important in practice.

EFFECT OF DEPOSITS. Deposit buildup on the combustion chamber walls (which occurs in vehicles over several thousands of miles) is known to increase unburned HC emissions. With leaded gasoline operation, the increase in HC emissions varies between about 7 and 20 percent. The removal of the deposits results typically in a reduction in HC emissions to close to clean engine levels. With unleaded gasoline, while the deposit composition is completely different (carbonaceous rather than lead oxide), the increase in HC emissions with accumulated mileage is comparable. Soft sooty deposits, such as those which accumulate after running the engine on a rich mixture, also cause an increase in HC emissions. Again, when the deposits were removed the emission rate fell about 25 percent to the original level.[59] Studies with simulated deposits (pieces of metal-foam sheet 0.6 mm thick) attached to the cylinder head and piston also showed increases in HC emissions. The increase varied between about 10 and 100 ppm C/cm^2 of simulated deposit area. The effect for a given area of deposit varied with deposit location. Locations close to the exhaust valve, where the flow direction during the exhaust process would be expected to be directly into the exhaust port, showed the highest increase in emissions.[45]

It is believed that absorption and desorption of hydrocarbons by these surface deposits is the mechanism that leads to an increase in emissions. Deposits can also build up in the piston ring crevice regions. A reduction in volume of these crevice regions would decrease HC emissions (and such a decrease has been observed). However, changes in piston–cylinder wall clearance due to deposits can affect the flame-quenching process and could increase emissions.[49]

HYDROCARBON TRANSPORT MECHANISMS. All of the above mechanisms (except misfire) result in high hydrocarbon concentrations adjacent to the combustion chamber walls. While any jet-type flows out of crevices during the expan-

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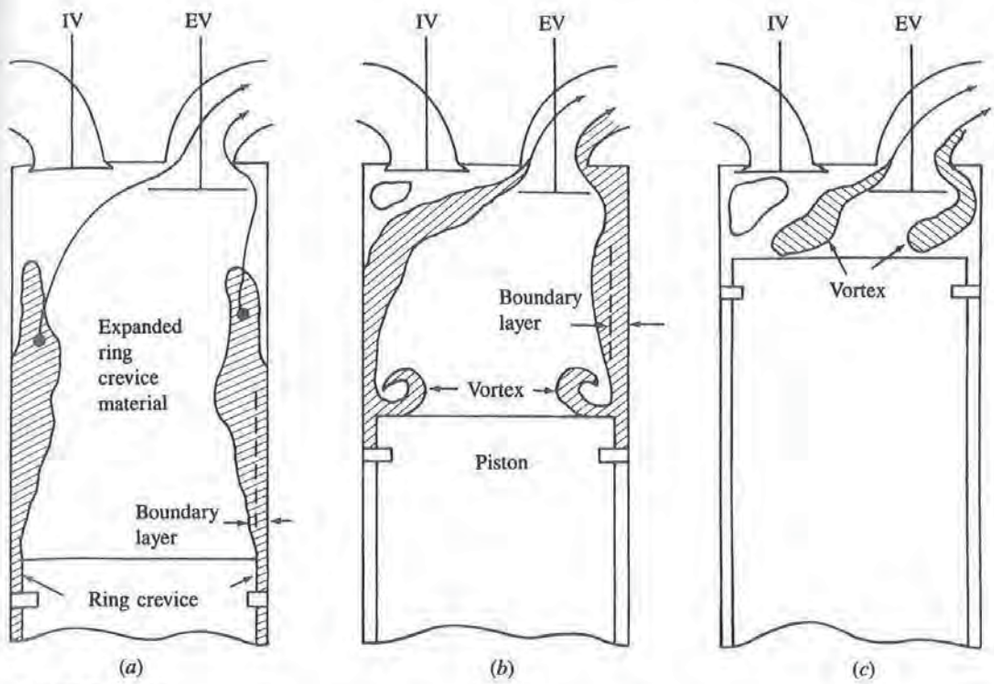


FIGURE 11-30
Schematic of flow processes by which ring crevice HC and HC desorbed from cylinder wall oil film exit the cylinder: (*a*) exhaust blowdown process; (*b*) during exhaust stroke; (*c*) end of exhaust stroke.[60]

sion and exhaust strokes can transport unburned HC into the bulk gases, most of the HC will remain near the wall. Two mechanisms by which gas near the cylinder wall exits the cylinder have been demonstrated. One is entrainment in the vigorous gas flow out of the cylinder which occurs during the exhaust blowdown process. The other is the vortex generated in the piston crown–cylinder wall corner during the exhaust stroke.

Figure 11-30 illustrates these flow processes. In Fig. 11-30*a* the engine cylinder is shown as the exhaust valve opens during the blowdown process. At this time the unburned HC from the ring crevice regions, laid along the wall during expansion (and possibly HC from the oil film on the cylinder wall), is expanding into the cylinder as the cylinder pressure falls. Some of this material will be entrained by the bulk gases in the rapid motion which occurs during exhaust blowdown (see Sec. 6.5). The rapid thinning of the thermal boundary-layer regions on the combustion chamber walls during blowdown, which would result from entrainment of the denser hydrocarbon-containing gas adjacent to the wall, has been observed in schlieren movies taken in a transparent engine.[46] This process, plus entrainment of any HC from the spark plug and head gasket crevices, would contribute to unburned HC in the blowdown gases which contain about half the total HC emissions (see Fig. 11-24). During the exhaust stroke this bulk gas entrainment process will continue, exhausting additional unburned HC, as shown in Fig. 11-30*b*.

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The second mechanism starts at the beginning of the exhaust stroke in the piston crown–cylinder wall corner. The piston motion during the exhaust stroke scrapes the boundary-layer gases off the cylinder wall (which contain the remainder of the piston and ring crevice hydrocarbons), rolls them up into a vortex, and pushes them toward the top of the cylinder. This piston crown–cylinder wall corner flow is discussed in Sec. 8.7, and has been observed in transparent engines as well as in water-flow engine analog studies. At the end of the exhaust stroke, the height of this vortex is comparable to the engine clearance height. As shown in Fig. 11-30*c*, a recirculation flow is likely to build up in the upper corner of the cylinder away from the exhaust valve, causing the vortex to detach from the wall and partly sweep out of the cylinder. In the corner nearest the valve, the flow is deflected around the valve, also tending to pull part of the vortex out of the chamber. In this way it is possible for a large part of the vortex, which now contains a substantial fraction of the unburned HC originally located adjacent to the cylinder wall, to leave the cylinder at the end of the exhaust stroke. This vortex flow is thought to be the mechanism that leads to the high HC concentrations measured at the end of the exhaust process, which contributes the other half of the exhausted HC mass (see Fig. 11-24), and to be responsible for the HC concentrations measured in the residual gases being much higher than average exhaust HC levels.[42] This study showed that at close to wide-open-throttle conditions, only about two-thirds of the HC which fail to oxidize inside the cylinder were exhausted, though 95 percent of the gas within the cylinder flows out through the exhaust valve. The residual gas HC concentration was about 11 times the average exhaust level. At part-throttle conditions, where the residual gas fraction is higher, it has been estimated that only about half of the unreacted HC in the cylinder will enter the exhaust.[61]

HYDROCARBON OXIDATION. Unburned hydrocarbons which escape the primary engine combustion process by the mechanisms described above must then survive the expansion and exhaust process without oxidizing if they are to appear in the exhaust. Since the formation mechanisms produce unburned HC at temperatures close to the wall temperature, mixing with bulk burned gas must take place first to raise the HC temperature to the point where reaction can occur. The sequence of processes which links the source mechanisms to hydrocarbons at the exhaust exit is illustrated in Fig. 11-31; it involves mixing and oxidation in both the cylinder and the exhaust system.

There is considerable evidence that substantial oxidation does occur. The oxidation of unburned HC in the quench layers formed on the combustion chamber walls on a time scale of order 1 ms after the flame is extinguished has already been discussed. Because the quench layers are thin, diffusion of HC into the bulk burned gas is rapid. Because the burned gases are still at a high temperature, oxidation then occurs quickly. Measurements of in-cylinder HC concentrations by gas sampling prior to exhaust valve opening show levels about 1.5 to 2 times the average exhaust level.[44, 63] The exhaust unburned HC are a mixture of fuel hydrocarbon compounds and pyrolysis and partial oxidation pro-

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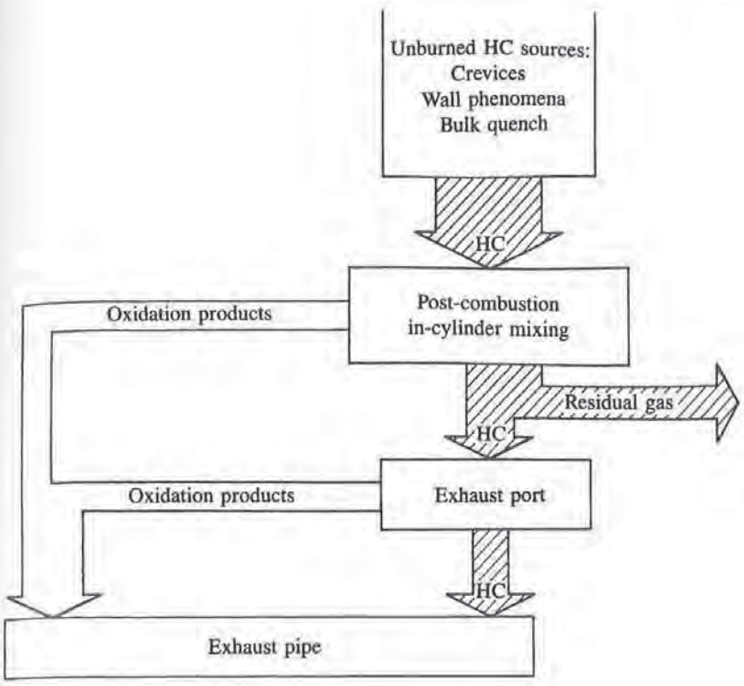


FIGURE 11-31
Schematic of complete SI engine HC formation and oxidation mechanism within the cylinder and exhaust system.[62]

ducts. While the relative proportion of fuel compared to reaction product hydrocarbon compounds varies substantially with engine operating conditions, an average value for passenger car vehicle exhausts is that fuel compounds comprise 40 percent of the total HC. Though partially reacted HC are produced in the flame-quenching process, these are closest to the high-temperature burned gases and are likely to mix and burn rapidly. That such a large fraction of the exhaust HC are reaction products indicates that substantial postformation HC reactions are occurring. There is direct evidence that HC oxidation in the exhaust system occurs.[64] Since in-cylinder gas temperatures are higher, it is likely that mixing of unburned HC with the bulk cylinder gases limits the amount of oxidation rather than the reaction kinetics directly.

Overall empirically based expressions for the rate of oxidation of hydrocarbons of the form of Eq. (11.31) have been developed and used to examine in-cylinder and exhaust burnup. A characteristic time τ_{HC} for this burnup process can be defined:

$$\frac{1}{\tau_{HC}} = \frac{1}{[HC]} \frac{d[HC]}{dt} \tag{11.34}$$

Using an expression similar to Eq. (11.31) for $d[HC]/dt$, Weiss and Keck[63] have shown that any HC mixing with the burned gases in the cylinder prior to exhaust

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blowdown will oxidize. The in-cylinder gas temperature prior to blowdown generally exceeds 1250 K; the characteristic reaction time τ_{HC} is then less than 1 ms. During blowdown the temperature falls rapidly to values typically less than 1000 K; τ_{HC} is then greater than about 50 ms. An experimental study of HC exiting from a simulated crevice volume has shown that complete HC oxidation only occurs when the cylinder gas temperature is above 1400 K.[65] Thus a large fraction of the HC leaving crevice regions or oil layers during the exhaust process can be expected to survive with little further oxidation. Gas-sampling data show little decrease in in-cylinder HC concentrations during the exhaust stroke, thus supporting this conclusion.[44, 63] Overall, probably about half of the unburned HC formed by the source mechanisms described above will oxidize within the engine cylinder (the exact amount cannot yet be predicted with any accuracy; it is likely to depend on engine design and operating conditions[61]).

As shown schematically in Fig. 11-31, oxidation of HC in the exhaust system can occur. Often this is enhanced by air addition into the port region to ensure that adequate oxygen for burnup is available. However, since the gas temperature steadily decreases as the exhaust gases flow through the exhaust port and manifold, the potential for HC burnup rapidly diminishes. To oxidize the hydrocarbons in the gas phase, a residence time of order 50 ms or longer at temperatures in excess of 600°C are required. To oxidize carbon monoxide temperatures in excess of 700°C are required. Average exhaust gas temperatures at the cylinder exit (at the exhaust valve plane) are about 800°C; average gas temperatures at the exhaust port exit are about 600°C.† Figure 6-21 shows an example of the measured cylinder pressure, measured gas temperature at the exhaust port exit, and estimated mass flow rate into the port and gas temperature in the cylinder, during the exhaust process at a part-throttle operating condition. Port residence time and gas temperatures vary significantly through the process. Precise values of these variables obviously depend on engine operating conditions. It is apparent that only in the exhaust port and upstream end of the manifold can any significant gas-phase HC oxidation occur.

The importance of exhaust gas temperature to exhaust system emissions burnup is illustrated by the results shown in Fig. 11-32.[66] The exhaust system of a four-cylinder engine was modified by installing a section of heated and insulated pipe to maintain the exhaust gas temperature constant in the absence of any HC or CO burnup. The exhaust temperature entering this test section was varied by adjusting the engine operating conditions. The figure shows CO and HC concentrations as functions of residence time in the exhaust test section (or effectively as a function of distance from the engine). T_e is the entering gas temperature. The exhaust composition was fuel lean with 3 percent O_2 in the burned

† Note that there is a significant variation in the temperature of the exhaust gases throughout the exhaust process. The gas exhausted first is about 100 K hotter than the gas exhausted at the end of the process (see Sec. 6.5).

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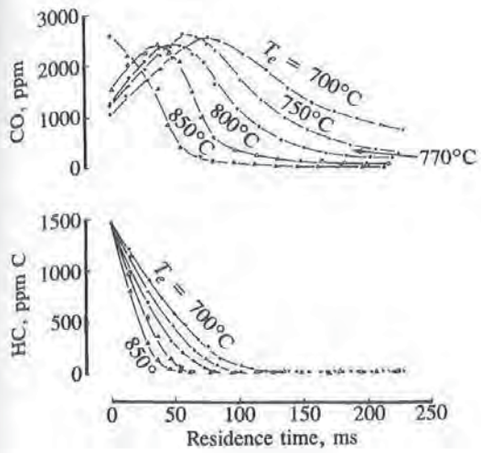


FIGURE 11-32
Effect of exhaust gas temperature on HC and CO burnup in the exhaust. SI engine at 1600 rev/min, engine air flow = 7.7 dm^3/s, lean mixture with 3% O_2 and 13% ($CO + CO_2$) in exhaust.[66]

gas stream. HC oxidation starts immediately (for $T \gtrsim 600°C$), the rate of oxidation increasing rapidly with increasing temperature. Under fuel-lean conditions, incomplete HC oxidation can result in an increase in CO levels. CO oxidation commences later, when the gas temperature rises above the entering value due to heat released by the already occurring HC oxidation. The further heat released by CO oxidation accelerates the CO burnup process. These data underline the importance of the exhaust port heat-transfer and mixing processes. Both mixing between the hotter blowdown gases (with their lower HC concentration) and the cooler end-of-exhaust gases (with their higher HC concentration) and mixing between burned exhaust gas and secondary air are important.

Engine experiments where the exhaust gas reactions were quenched by timed injection of cold carbon dioxide at selected locations within the exhaust port have shown that significant reductions in HC concentration in the port can occur. Parallel modeling studies of the HC burnup process (based on instantaneous mass flow rate, estimated exhaust gas temperature, and an overall hydrocarbon reaction-rate expression), which predicted closely comparable magnitudes and trends, indicated that gas temperature and port residence time are the critical variables. The percent of unburned HC exiting the cylinder which reacted in the exhaust system (with most of the reaction occurring in the port) varied between a few and 40 percent. Engine operating conditions that gave highest exhaust temperatures (stoichiometric operation, higher speeds, retarded spark timing, lower compression ratio) and longest residence times (lighter load) gave relatively higher percent reductions. Air injection at the exhaust valve-stem base, phased to coincide with the exhaust process, showed that for stoichiometric and slightly rich conditions secondary air flow rates up to 30 percent of the exhaust flow substantially increased the degree of burnup. The timing of the secondary air flow relative to the exhaust flow and the location of the air injection point in the port are known to be critical.[64]

Reductions in exhaust port heat losses through the use of larger port cross-sectional areas (to reduce flow velocity and surface area per unit volume), inser-

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tion of port liners to provide higher port wall temperatures, and attention to port design details to minimize hot exhaust gas impingement on the walls are known to increase the degree of reaction occurring in the port.

SUMMARY. It will be apparent from the above that the HC emissions formation process in spark-ignition engines is extremely complex and that there are several paths by which a small but important amount of the fuel escapes combustion. It is appropriate here to summarize the overall structure of the spark-ignition engine hydrocarbon emission problem and identify the key factors and engine variables that influence the different parts of that problem. Table 11.7 provides such a summary. The total process is divided into four sequential steps: (1) the formation of unburned hydrocarbon emissions; (2) the oxidation of a fraction of these HC emissions within the cylinder, following mixing with the bulk gases; (3) the flow of a fraction of the unoxidized HC from the cylinder into the exhaust; (4) the oxidation in the exhaust system of a fraction of the HC that exit the cylinder. The detailed processes and the design and operating variables that influence each of these steps in a significant way are listed.

The four separate formation mechanisms identified in step 1 have substantial, though as yet incomplete, evidence behind them. They are listed in the most likely order of importance. Each has been extensively described in this section. It is through each of these mechanisms that fuel or fuel-air mixture escapes the primary combustion process. That fuel must then survive the expansion and exhaust processes and pass through the exhaust system without oxidation if it is to end up in the atmosphere as HC emissions. The rate of mixing of these unburned HC with the hot bulk cylinder gases, the temperature and composition of the gases with which these HC mix, and the subsequent temperature-time and composition-time histories of the mixture will govern the amount of in-cylinder oxidation that occurs. The distribution of these HC around the combustion chamber is nonuniform (and changes with time); they are concentrated close to the walls of the chamber. The fraction of these HC that will exit the chamber during the exhaust process will depend on the details of the in-cylinder flow patterns that take them through the exhaust valve. Overall, the magnitude of the residual fraction will be one major factor; the residual gas is known to be much richer in HC than the average exhaust. In particular, the flow patterns in the cylinder toward the end of the exhaust stroke as the gas scraped off the cylinder wall by the piston moves toward the exhaust valve will be important. Finally, a fraction of the unburned HC which leave the cylinder through the exhaust valve will burn up within the exhaust system. Gas-phase oxidation in the exhaust ports and hotter parts of the exhaust manifold is significant. The amount depends on the gas temperature, composition, and residence time. If catalysts or a thermal reactor are included in the exhaust system, very substantial additional reduction in HC emission levels can occur. These devices and their operating characteristics are described in Sec. 11.6.

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TABLE 11.7
Critical factors and engine variables in HC emissions mechanisms

1. *Formation of HC*
   - (*a*) Crevices
     - (1) Crevice volume
     - (2) Crevice location (relative to spark plug)
     - (3) Load
     - (4) Crevice wall temperature
     - (5) Mixture composition†
   - (*b*) Oil layers
     - (1) Oil consumption
     - (2) Wall temperature
     - (3) Speed
   - (*c*) Incomplete combustion
     - (1) Burn rate and variability
     - (2) Mixture composition†
     - (3) Load
     - (4) Spark timing‡
   - (*d*) Combustion chamber walls
     - (1) Deposits
     - (2) Wall roughness
2. *In-cylinder mixing and oxidation*
   - (*a*) Mixing rate with bulk gas
     - (1) Speed
     - (2) Swirl ratio
     - (3) Combustion chamber shape
   - (*b*) Bulk gas temperature during expansion and exhaust
     - (1) Speed
     - (2) Spark timing‡
     - (3) Mixture composition†
     - (4) Compression ratio
     - (5) Heat losses to walls
   - (*c*) Bulk gas oxygen concentration
     - (1) Equivalence ratio
   - (*d*) Wall temperature
     - (1) Important if HC source near wall
     - (2) For crevices: importance depends on geometry
3. *Fraction HC flowing out of cylinder*
   - (*a*) Residual fraction
     - (1) Load
     - (2) Exhaust pressure
     - (3) Valve overlap
     - (4) Compression ratio
     - (5) Speed
   - (*b*) In-cylinder flow during exhaust stroke
     - (1) Valve overlap
     - (2) Exhaust valve size and location
     - (3) Combustion chamber shape
     - (4) Compression ratio
     - (5) Speed
4. *Oxidation in exhaust system*
   - (*a*) Exhaust gas temperature
     - (1) Speed
     - (2) Spark timing‡
     - (3) Mixture composition†
     - (4) Compression ratio
     - (5) Secondary air flow
     - (6) Heat losses in cylinder and exhaust
   - (*b*) Oxygen concentration
     - (1) Equivalence ratio
     - (2) Secondary air flow and addition point
   - (*c*) Residence time
     - (1) Speed
     - (2) Load
     - (3) Volume of critical exhaust system component
   - (*d*) Exhaust reactor§
     - (1) Oxidation catalyst
     - (2) Three-way catalyst
     - (3) Thermal reactor

† Fuel/air equivalence ratio and burned gas fraction (residual plus recycled exhaust gas).
‡ Relative to MBT timing.
§ Of at least as great an importance as engine details if present in total emission control system. See Sec. 11.6.

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11.4.4 Hydrocarbon Emission Mechanisms in Diesel Engines

BACKGROUND. Diesel fuel contains hydrocarbon compounds with higher boiling points, and hence higher molecular weights, than gasoline. Also, substantial pyrolysis of fuel compounds occurs within the fuel sprays during the diesel combustion process. Thus, the composition of the unburned and partially oxidized hydrocarbons in the diesel exhaust is much more complex than in the spark-ignition engine and extends over a larger molecular size range. Gaseous hydrocarbon emissions from diesels are measured using a hot particulate filter (at 190°C) and a heated flame ionization detector. Thus the HC constituents vary from methane to the heaviest hydrocarbons which remain in the vapor phase in the heated sampling line (which is also maintained at about 190°C). Any hydrocarbons heavier than this are therefore condensed and, with the solid-phase soot, are filtered from the exhaust gas stream upstream of the detector. The particulate emission measurement procedure measures a portion of total engine hydrocarbon emissions also. Particulates are collected by filtering from a diluted exhaust gas stream at a temperature of 52°C or less. Those hydrocarbons that condense at or below this temperature are absorbed onto the soot. They are the extractable fraction of the particulate: i.e., that fraction which can be removed by a powerful solvent, typically between about 15 and 45 percent of the total particulate mass. This section discusses gaseous hydrocarbon emissions; particulate emissions—soot and extractable material—are discussed in Sec. 11.5.

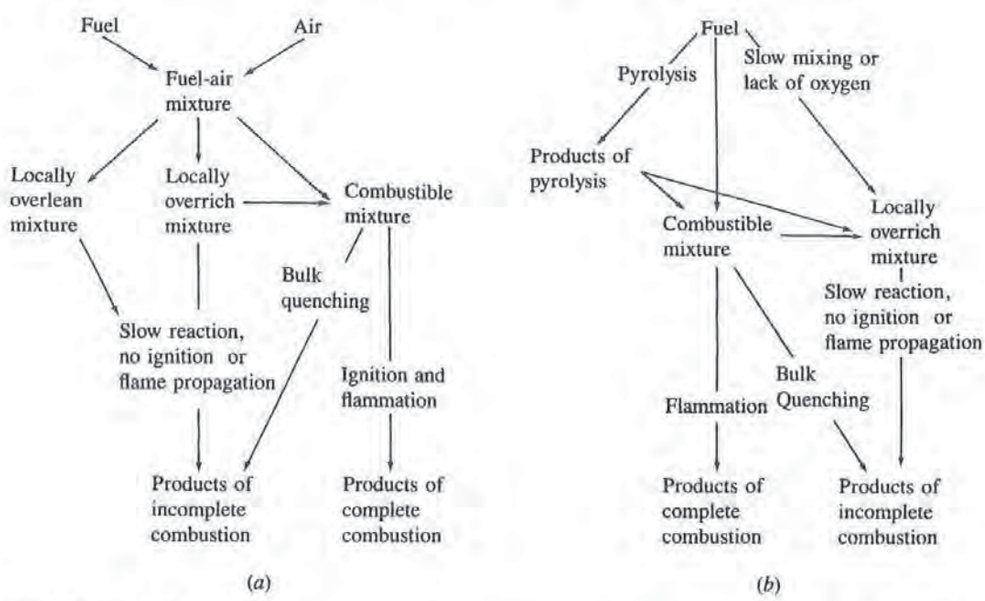


FIGURE 11-33
Schematic representation of diesel hydrocarbon formation mechanisms: (*a*) for fuel injected during delay period; (*b*) for fuel injected while combustion is occurring.[23]

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The complex heterogeneous nature of diesel combustion, where fuel evaporation, fuel-air and burned-unburned gas mixing, and combustion can occur simultaneously, has been discussed extensively in Chap. 10. As a result of this complexity, there are many processes that could contribute to diesel engine hydrocarbon emissions. In Chap. 10 the diesel's compression-ignition combustion process was divided into four stages: (1) the ignition delay which is the time between the start of injection and ignition; (2) the premixed or rapid combustion phase, during which the fuel that has mixed to within combustible limits during the delay period burns; (3) the mixing controlled combustion phase, during which the rate of burning depends on the rate of fuel-air mixing to within the combustible limits; (4) the late combustion phase where heat release continues at a low rate governed by the mixing of residual combustibles with excess oxygen and the kinetics of the oxidation process. There are two primary paths by which fuel can escape this normal combustion process unburned: the fuel-air mixture can become too lean to autoignite or to support a propagating flame at the conditions prevailing inside the combustion chamber, or, during the primary combustion process, the fuel-air mixture may be too rich to ignite or support a flame. This fuel can then be consumed only by slower thermal oxidation reactions later in the expansion process after mixing with additional air. Thus, hydrocarbons remain unconsumed due to incomplete mixing or to quenching of the oxidation process.†

Figure 11-33 shows schematically how these processes can produce incomplete combustion products. Fuel injected during the ignition delay (Fig. 11-33*a*) will mix with air to produce a wide range of equivalence ratios. Some of this fuel will have mixed rapidly to equivalence ratios lower than the lean limit of combustion (locally overlean mixture), some will be within the combustible range, and some will have mixed more slowly and be too rich to burn (locally overrich mixture). The overlean mixture will not autoignite or support a propagating flame at conditions prevailing inside the combustion chamber (though some of this mixture may burn later if it mixes with high-temperature burned products early in the expansion stroke). In the "premixed" combustible mixture, ignition occurs where the local conditions are most favorable for autoignition. Unless quenched by thermal boundary layers or rapid mixing with air, subsequent autoignition or flame fronts propagating from the ignition sites consume the combustible mixture. Complete combustion of overrich mixture depends on further mixing with air or lean already-burned gases within the time available before rapid expansion and cooling occurs. Of all these possible mechanisms, the overlean mixture path is believed to be the most important.[23]

For the fuel injected after the ignition delay period is over (Fig. 11-33*b*), rapid oxidation of fuel or the products of fuel pyrolysis, as these mix with air,

† Note that under normal engine operating conditions, the combustion inefficiency is less than 2 percent; see Sec. 4.9.4 and Fig. 3-9.

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results in complete combustion. Slow mixing of fuel and pyrolysis products with air, resulting in overrich mixture or quenching of the combustion reactions, can result in incomplete combustion products, pyrolysis products, and unburned fuel being present in the exhaust.[23]

Hydrocarbon emission levels from diesels vary widely with operating conditions, and different HC formation mechanisms are likely to be most important at different operating modes. Engine idling and light-load operation produce significantly higher hydrocarbon emissions than full-load operation. However, when the engine is overfueled, HC emissions increase very substantially. As will be explained more fully below, overmixing (overleaning) is an important source of HC, especially under light-load operation. Undermixing, resulting in overrich mixture during the combustion period, is the mechanism by which some of the fuel remaining in the injector nozzle sac volume escapes combustion, and is also the cause of very high HC emissions during overfueling. Wall temperatures affect HC emissions, suggesting that wall quenching is important, and under especially adverse conditions very high cyclic variability in the combustion process can cause an increase in HC due to partial burning and misfiring cycles.

OVERLEANING. As soon as fuel injection into the cylinder commences, a distribution in the fuel/air equivalence ratio across the fuel sprays develops. The amount of fuel that is mixed leaner than the lean combustion limit ($\phi_L \sim 0.3$) increases rapidly with time.[23] Figure 11-34 illustrates this equivalence ratio distribution in the fuel spray at the time of ignition. In a swirling flow, ignition occurs in the slightly lean-of-stoichiometric region downstream of the spray core

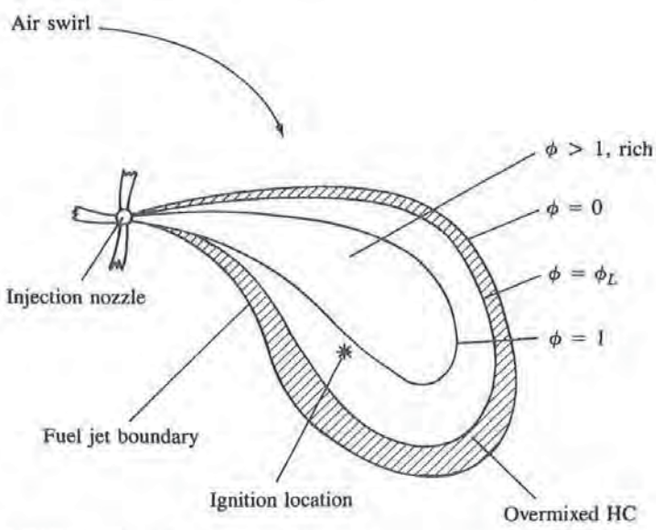


FIGURE 11-34
Schematic of diesel engine fuel spray showing equivalence ratio (ϕ) contours at time of ignition. ϕ_L = equivalence ratio at lean combustion limit (≈ 0.3). Shaded region contains fuel mixed leaner than ϕ_L.[67]

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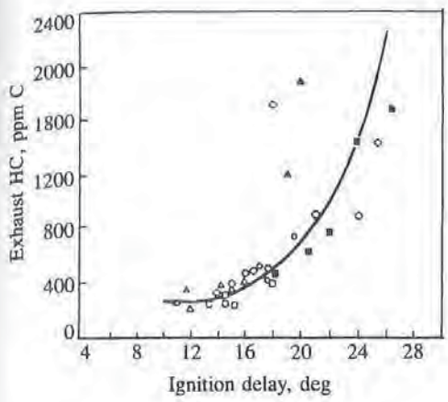


FIGURE 11-35
Correlation of exhaust HC concentration with duration of ignition delay for DI diesel engine. Various fuels, engine loads, injection timings, boost pressures, at 2800 rev/min.[67]

where the fuel which has spent most time within the combustible limits is located. However, the fuel close to the spray boundary has already mixed beyond the lean limit of combustion and will not autoignite or sustain a fast reaction front. This mixture can only oxidize by relatively slow thermal-oxidation reactions which will be incomplete. Within this region, unburned fuel, fuel decomposition products, and partial oxidation products (aldehydes and other oxygenates) will exist; some of these will escape the cylinder without being burned. The magnitude of the unburned HC from these overlean regions will depend on the amount of fuel injected during the ignition delay, the mixing rate with air during this period, and the extent to which prevailing cylinder conditions are conducive to autoignition. A correlation of unburned HC emissions with the length of the ignition delay would be expected. The data in Fig. 11-35 from a direct-injection naturally aspirated engine show that a good correlation between these variables exists. As the delay period increases beyond its minimum value (due to changes in engine operating conditions), HC emissions increase at an increasing rate.[67] Thus, overleaning of fuel injected during the ignition delay period is a significant source of hydrocarbon emissions, especially under conditions where the ignition delay is long.

UNDERMIXING. Two sources of fuel which enter the cylinder during combustion and which result in HC emissions due to slow or under mixing with air have been identified. One is fuel that leaves the injector nozzle at low velocity, often late in the combustion process. The most important source here is the nozzle sac volume, though secondary injections can increase HC emissions if the problem is severe. The second source is the excess fuel that enters the cylinder under overfueling conditions.

At the end of the fuel-injection process, the injector sac volume (the small volume left in the tip of the injector after the needle seats) is left filled with fuel. As the combustion and expansion processes proceed, this fuel is heated and vaporizes, and enters the cylinder at low velocity through the nozzle holes. This fuel vapor (and perhaps large drops of fuel also) will mix relatively slowly with air

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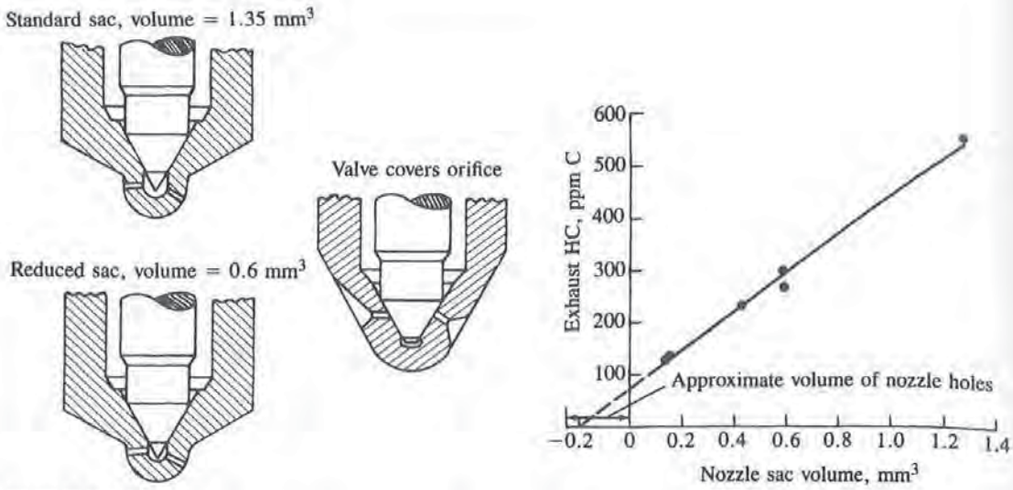


FIGURE 11-36
Effect of nozzle sac volume on exhaust HC concentration, DI diesel engine, at minimum ignition delay. $V_d = 1$ dm³/cylinder, 1700–2800 rev/min.[67]

and may escape the primary combustion process. Figure 11-36 shows HC emissions at the minimum ignition delay for a direct-injection diesel engine as a function of sac volume, along with drawings of some of the injector nozzles used. The correlation between HC emissions (under conditions when the overleaning mechanism is least significant) and sac volume is striking. The extrapolation to zero HC emissions suggests that the fuel in the nozzle holes also contributes. Not all the fuel in the sac volume is exhausted as unburned hydrocarbons. For example, in Fig. 11-36 a volume of 1 mm³ gives 350 ppm C_1 while 1 mm³ of fuel would give 1660 ppm C_1. The sac volume may not be fully filled with fuel. Also, the higher-boiling-point fractions of the fuel may remain in the nozzle. Significant oxidation may also occur. In indirect-injection engines, similar trends have been observed, but the HC emission levels at short ignition delay conditions are substantially lower. The sac volume in current production nozzles helps to equalize the fuel pressures immediately upstream of the nozzle orifices. A small sac volume makes this equalization less complete and exhaust smoke deteriorates. The contribution of sac and hole volumes to exhaust HC can be reduced to below 0.75 g/kW · h for a 1 dm³ per cylinder displacement DI engine.[67]

In DI engines, exhaust smoke limits the full-load equivalence ratio to about 0.7. Under transient conditions as the engine goes through an acceleration process, overfueling can occur. Even though the overall equivalence ratio may remain lean, locally overrich conditions may exist through the expansion stroke and into the exhaust process. Figure 11-37 shows the effect of increasing the amount of fuel injected at constant speed, with the injection timing adjusted to keep the ignition delay at its minimum value (when HC emissions from overleaning are lowest). HC emissions are unaffected by an increasing equivalence ratio until a critical value of about 0.9 is reached when levels increase dramatically. A

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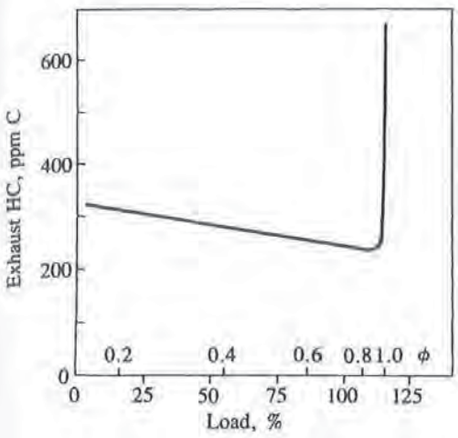


FIGURE 11-37
Effect of overfueling on exhaust HC concentration. DI diesel engine, speed = 1700 rev/min, injection timing at full-load 15° BTC.[67]

similar trend exists for IDI engines.[67] This mechanism is not significant under normal operating conditions, but can contribute HC emissions under acceleration conditions if overfueling occurs. However, it produces less HC than does overleaning at light load and idle.[23]

QUENCHING AND MISFIRE. Hydrocarbon emissions have been shown to be sensitive to oil and coolant temperature: when these temperatures were increased from 40 to 90°C in a DI diesel, HC emissions decreased by 30 percent. Since ignition delay was maintained constant, overmixing phenomena should remain approximately constant. Thus, wall quenching of the flame may also be a significant source of HC, depending on the degree of spray impingement on the combustion chamber walls.

While cycle-by-cycle variation in the combustion process in diesel engines is generally much less than in spark-ignition engines, it can become significant under adverse conditions such as low compression temperatures and pressures and retarded injection timings. Substantial variations, cycle-by-cycle, in HC emissions are thought to result. In the limit, if misfire (no combustion) occurs in a fraction of the operating cycles, then engine HC emissions rise as the percentage of misfires increases. However, complete misfires in a well-designed and adequately controlled engine are unlikely to occur over the normal operating range.[23]

SUMMARY. There are two major causes of HC emissions in diesel engines under normal operating conditions: (1) fuel mixed to leaner than the lean combustion limit during the delay period; (2) undermixing of fuel which leaves the fuel injector nozzle at low velocity, late in the combustion process. At light load and idle, overmixing is especially important, particularly in engines of relatively small cylinder size at high speed. In IDI engines, the contribution from fuel in the nozzle sac volume is less important than with DI engines. However, other sources of low velocity and late fuel injection such as secondary injection can be significant.

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11.5 PARTICULATE EMISSIONS

11.5.1 Spark-Ignition Engine Particulates

There are three classes of spark-ignition engine particulate emissions: lead, organic particulates (including soot), and sulfates.

Significant sulfate emissions can occur with oxidation-catalyst equipped engines. Unleaded gasoline contains 150 to 600 ppm by weight sulfur, which is oxidized within the engine cylinder to sulfur dioxide, SO_2. This SO_2 can be oxidized by the exhaust catalyst to SO_3 which combines with water at ambient temperatures to form a sulfuric acid aerosol. Levels of sulfate emissions depend on the fuel sulfur content, the operating conditions of the engine, and the details of the catalyst system used. Typical average automobile sulfate emission rates are 20 mg/km or less.[68]

For automobile engines operated with regular and premium leaded gasolines (which contain about 0.15 g Pb/liter or dm^3) the particulate emission rates are typically 100 to 150 mg/km. This particulate is dominated by lead compounds: 25 to 60 percent of the emitted mass is lead.[69] The particulate emission rates are considerably higher when the engine is cold, following start-up. The exhaust temperature has a significant effect on emission levels. The particle size distribution with leaded fuel is about 80 percent by mass below 2 μm diameter and about 40 percent below 0.2 μm diameter. Most of these particles are presumed to form and grow in the exhaust system due to vapor phase condensation enhanced by coagulation. Some of the particles are emitted directly, without settling. Some of the particles either form or are deposited on the walls where agglomeration may occur. Many of these are removed when the exhaust flow rate is suddenly increased, and these particles together with rust and scale account for the increase in mass and size of particles emitted during acceleration. Only a fraction (between 10 and 50 percent) of the lead consumed in the fuel is exhausted, the remainder being deposited within the engine and exhaust system.

Use of unleaded gasoline reduces particulate emissions to about 20 mg/km in automobiles without catalysts. This particulate is primarily soluble (condensed) organic material. Soot emissions (black smoke) can result from combustion of overly rich mixtures. In properly adjusted spark-ignition engines, soot in the exhaust is not a significant problem.

11.5.2 Characteristics of Diesel Particulates

MEASUREMENT TECHNIQUES. Diesel particulates consist principally of combustion generated carbonaceous material (soot) on which some organic compounds have become absorbed. Most particulate material results from incomplete combustion of fuel hydrocarbons; some is contributed by the lubricating oil. The emission rates are typically 0.2 to 0.6 g/km for light-duty diesels in an automobile. In larger direct-injection engines, particulate emission rates are 0.5 to 1.5 g/brake kW · h. The composition of the particulate material depends on the conditions in the engine exhaust and particulate collection system. At tem-

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peratures above 500°C, the individual particles are principally clusters of many small spheres or spherules of carbon (with a small amount of hydrogen) with individual spherule diameters of about 15 to 30 nm. As temperatures decrease below 500°C, the particles become coated with adsorbed and condensed high molecular weight organic compounds which include: unburned hydrocarbons, oxygenated hydrocarbons (ketones, esters, ethers, organic acids), and polynuclear aromatic hydrocarbons. The condensed material also includes inorganic species such as sulfur dioxide, nitrogen dioxide, and sulfuric acid (sulfates).

The objective of most particulate measurement techniques is to determine the amount of particulate being emitted to the atmosphere. Techniques for particulate measurement and characterization range from simple smoke meter opacity readings to analyses using dilution tunnels. Most techniques require lengthy sample-collection periods because the emission rate of individual species is usually low. The physical conditions under which particulate measurements are made are critical because the emitted species are unstable and may be altered through loss to surfaces, change in size distribution (through collisions), and chemical interactions among other species in the exhaust at any time during the measurement process (including sampling, storage, or examination). The most basic information is normally obtained on a mass basis: for example, grams per kilometer for a vehicle, grams per kilowatt-hour for an engine, grams per kilogram of fuel or milligrams per cubic meter of exhaust (at standard conditions). Smoke meters measure the relative quantity of light that passes through the exhaust or the relative reflectance of particulate collected on filter paper. They do not measure mass directly. They are used to determine visible smoke emissions and provide an approximate indication of mass emission levels. Visible smoke from heavy-duty diesels at high load is regulated. In the standard mass emission measurement procedure, dilution tunnels are used to simulate the physical and chemical processes the particulate emissions undergo in the atmosphere. In the dilution tunnel, the raw exhaust gases are diluted with ambient air to a temperature of 52°C or less, and a sample stream from the diluted exhaust is filtered to remove the particulate material.

PARTICULATE COMPOSITION AND STRUCTURE. The structure of diesel particulate material is apparent from the photomicrographs shown in Fig. 11-38 of particulates collected from the exhaust of an IDI diesel engine. The samples are seen to consist of collections of primary particles (spherules) agglomerated into aggregates (hereafter called particles). Individual particles range in appearance from clusters of spherules to chains of spherules. Clusters may contain as many as 4000 spherules. Occasional liquid hydrocarbon and sulfate droplets have been identified. The spherules are combustion generated soot particles which vary in diameter between 10 and 80 nm, although most are in the 15 to 30 nm range. Figure 11-39 shows a typical distribution of spherule size (solid line) determined by sizing and counting images in the photomicrographs. The number-mean diameter ($=\sum N_i d_i/N$) is 28 nm. The volume contribution of these

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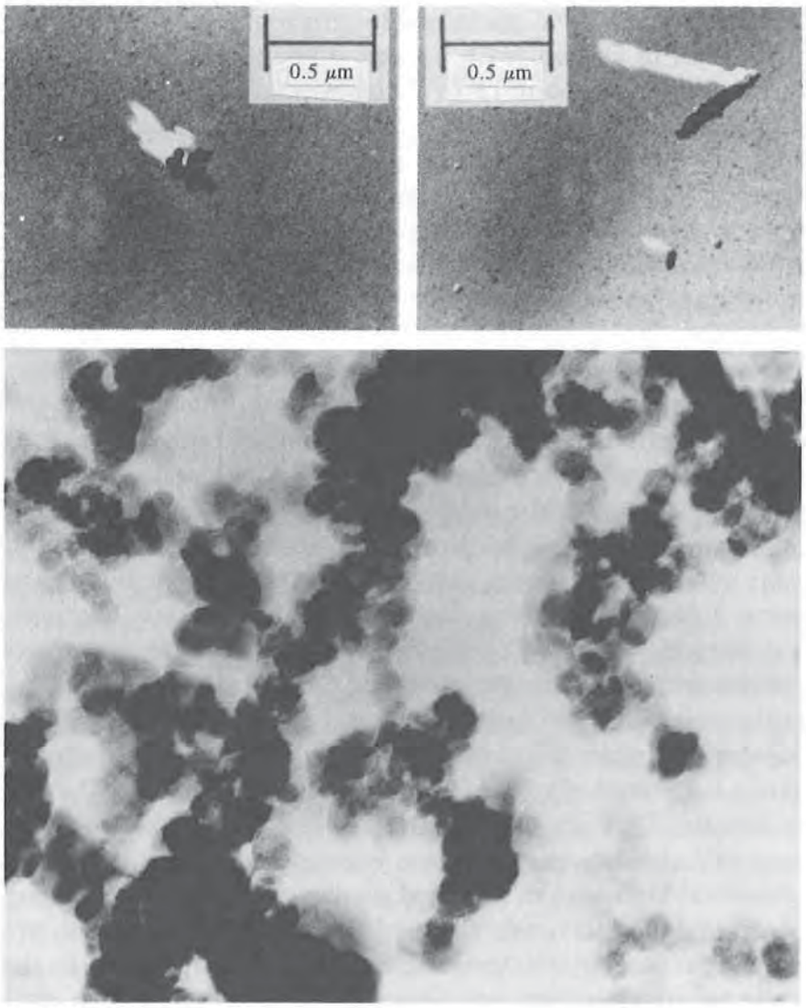


FIGURE 11-38
Photomicrographs of diesel particulates: cluster (upper left), chain (upper right), and collection from filter (bottom).[70]

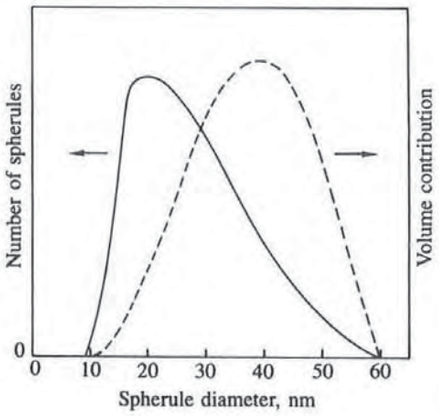


FIGURE 11-39
Typical distributions of spherule diameter and volume.[70]

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TABLE 11.8
Chemical composition of particular matter[70]

	Idle	48 km/h
Extractable composition	$C_{23}H_{29}O_{4.7}N_{0.21}$	$C_{24}H_{30}O_{2.6}N_{0.18}$
H/C	1.26	1.63
Dry soot composition	$CH_{0.27}O_{0.22}N_{0.01}$	$CH_{0.21}O_{0.15}N_{0.01}$
H/C	0.27	0.21

spherules is shown as the dashed curve in Fig. 11-39. The volume-mean diameter, $(\sum N_i d_i^3/N)^{1/3}$, is 31 nm.

Determination of the *particle* size distribution with a similar technique involves assigning a single dimension to a complex and irregular aggregate, and introduces uncertainties arising from only having two-dimensional images of particles available. Other approaches based on inertial impactors and electrical aerosol analysers have been used. Some of the data suggest that the particle size distribution is bimodal. The smaller-size range is thought to be liquid hydrocarbon drops and/or individual spherules characterized by number-mean diameters of 10 to 20 nm; the larger-size range is thought to be the particles of agglomerated spherules characterized by number-mean diameters of 100 to 150 nm. However, other particulate samples have not shown a bimodal distribution: volume-mean diameters ranged from 50 to 220 nm with no notable trend with either speed or load.[70]

The exhaust particulate is usually partitioned with an extraction solvent into a soluble fraction and a dry-soot fraction. Two commonly used solvents are dichloromethane and a benzene-ethanol mixture. Typically 15 to 30 mass percent is extractable, though the range of observations is much larger ($\sim$10 to 90 percent). Thermogravimetric analysis (weighing the sample as it is heated) produces comparable results. Typical average chemical compositions of the two particulate fractions are given in Table 11.8. Dry soot has a much lower H/C ratio than the extractable material. Although most of the particulate emissions are formed through incomplete combustion of fuel hydrocarbons, engine oil may also contribute significantly. The number-average molecular weight of the extractable material shown in Table 11.8 ranged from about 360 to 400 for a variety of engine conditions. This fell between the average molecular weight of the fuel (199) and that of the lubricating oil (443 when fresh and 489 when aged).[70] Radioactive tracer studies in a light-duty IDI diesel have shown that the oil was the origin of between 2 to 25 percent by mass of the total particulate and 16 to 80 percent of the extractable organic portion, the greatest percentages being measured at the highest engine speed studied (3000 rev/min). All of the oil contribution appeared in the extractable material. The contributions from the different individual compounds in the fuel have also been studied. All the compounds tested—paraffins,

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FIGURE 11-40
Lattice-imaging micrograph of a diesel particulate.[72]

olefins, and aromatics—contributed to the particulate emissions; as a group, aromatics were the greatest contributors. Eighty percent of the carbon-14 used to tag individual fuel compounds was found in the *insoluble* fraction and 20 percent in the *soluble* particulate fraction.[71]

In addition to the elements listed in Table 11.8, trace amounts of sulfur, zinc, phosphorus, calcium, iron, silicon, and chromium have been found in particulates. Sulfur and traces of calcium, iron, silicon, and chromium are found in diesel fuel; zinc, phosphorus, and calcium compounds are frequently used in lubricating oil additives.[70]

A lattice image of a diesel particle is shown in Fig. 11-40; it suggests a concentric lamellate structure arranged around the center of each spherule. This arrangement of concentric lamellas is similar to the structure of carbon black. This is not surprising; the environment in which diesel soot is produced is similar to that in which oil furnace blacks are made. The carbon atoms are bonded together in hexagonal face-centered arrays in planes, commonly referred to as platelets. As illustrated in Fig. 11-41, the mean layer spacing is 0.355 nm (only slightly larger than graphite). Platelets are arranged in layers to form crystallites. Typically, there are 2 to 5 platelets per crystallite, and on the order of 10^3 crys-

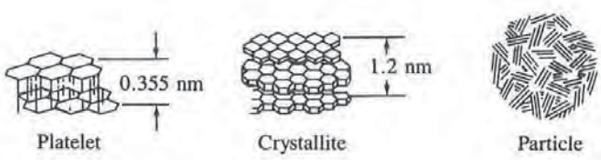


FIGURE 11-41
Substructure of carbon particle.[73]

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tallites per spherule. The crystallites are arranged with their planes more or less parallel to the particle surface. This structure of unordered layers is called turbostatic. The spherules, 10 to 50 nm in diameter, are fused together to form particles as shown in Fig. 11-40. A single spherule contains 10^5 to 10^6 carbon atoms.[70, 73]

A surface area of about 200 m^2/g has been measured for diesel soot. A smooth-surfaced 30-nm diameter sphere with a density of 2 g/cm^3 would have a surface/mass ratio of 100 m^2/g, so the measured value is about twice the superficial area. Approximating a particle of agglomerated spherules by a single sphere of 200 nm diameter gives a surface/mass ratio of 15 m^2/g.[70] These data and estimates of superficial area per unit mass indicate that diesel soot has low porosity.

SOLUBLE FRACTION COMPONENTS. The extractable organic fraction of diesel particulate emissions includes compounds that may cause health and environmental hazards. Thus chemical and biological characterization of the soluble organic fraction are important. Both soxhlet and sonification methods are used to extract the organic fraction from particulate samples. Because the particulates are mixtures of polar and nonpolar components, full extraction requires different solvents; any one solvent is a compromise. Methylene chloride is the most commonly used extractant, however. Since a complex mixture of organic compounds is associated with diesel particulates, a preliminary fractionation scheme is used to group similar types of compounds before final separation and identification. The scheme most frequently used results in seven fractions generally labeled as: basics, acidics, paraffins, aromatics, transitionals, oxygenates, and ether insolubles. Table 11.9 indicates the types of components in each fraction and the approximate proportions. The biological activity of the soluble organic fraction and its subfractions is most commonly assessed with the Ames *Salmonella*/microsomal test. With this test, a quantitative dose-response curve showing the mutagenicity of a sample compound is obtained. The Ames test uses a mutant strain of *Salmonella typhimurium* that is incapable of producing histidine. Mutagenicity is defined as the ability of a tested compound to revert—back-mutate—this bacterium to its wild state, where it regains its ability to produce histidine.[35]

11.5.3 Particulate Distribution within the Cylinder

Measurements have been made of the particulate distribution within the combustion chamber of operating diesel engines. The results provide valuable information on the particulate formation and oxidation processes and how these relate to the fuel distribution and heat-release development within the combustion chamber. Techniques used to obtain particulate concentration data include: use of rapid-acting poppet or needle valves which draw a small gas sample from the cylinder at a specific location and time for analysis (e.g., Refs. 21

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TABLE 11-9
Components of the soluble organic fraction[35]

Fraction	Components of fraction	Percent of total
Acidic	Aromatic or aliphatic Acidic functional groups Phenolic and carboxylic acids	3–15
Basic	Aromatic or aliphatic Basic functional groups Amines	<1–2
Paraffin	Aliphatics, normal and branched Numerous isomers From unburned fuel and/or lubricant	34–65
Aromatic	From unburned fuel, partial combustion, and recombination of combustion products; from lubricants Single ring compounds Polynuclear aromatics	3–14
Oxygenated	Polar functional groups but not acidic or basic Aldehydes, ketones, or alcohols Aromatic phenols and quinones	7–15
Transitional	Aliphatic and aromatic Carbonyl functional groups Ketones, aldehydes, esters, ethers	1–6
Insoluble	Aliphatic and aromatic Hydroxyl and carbonyl groups High molecular weight organic species Inorganic compounds Glass fibers from filters	6–25

and 74), optical absorption techniques (e.g., Refs. 75 and 76), and cylinder dumping where the cylinder contents are rapidly emptied into an evacuated tank at a preset time in the cycle (e.g., Ref. 77). Both DI and IDI engines have been studied. Of course, concentration data taken at specific locations in the cylinder during the engine cycle are not necessarily representative of the cylinder contents in general; nor do they represent the time history of a given mass of gas. The fuel distribution, mixing, and heat-release patterns in the cylinder are highly nonuniform during the soot-formation process, and the details of gas motion in the vicinity of the sampling location as the piston changes position are usually unknown.

In direct-injection diesel engines, the highest particulate concentrations are found in the core region of each fuel spray where local average equivalence ratios are very rich (see Secs. 10.5.6 and 10.7.2). Soot concentrations rise rapidly soon after combustion starts. Figure 11-42 shows a set of sample-valve soot-concentration data from a large (30.5-cm bore, 38.1-cm stroke), quiescent, direct-

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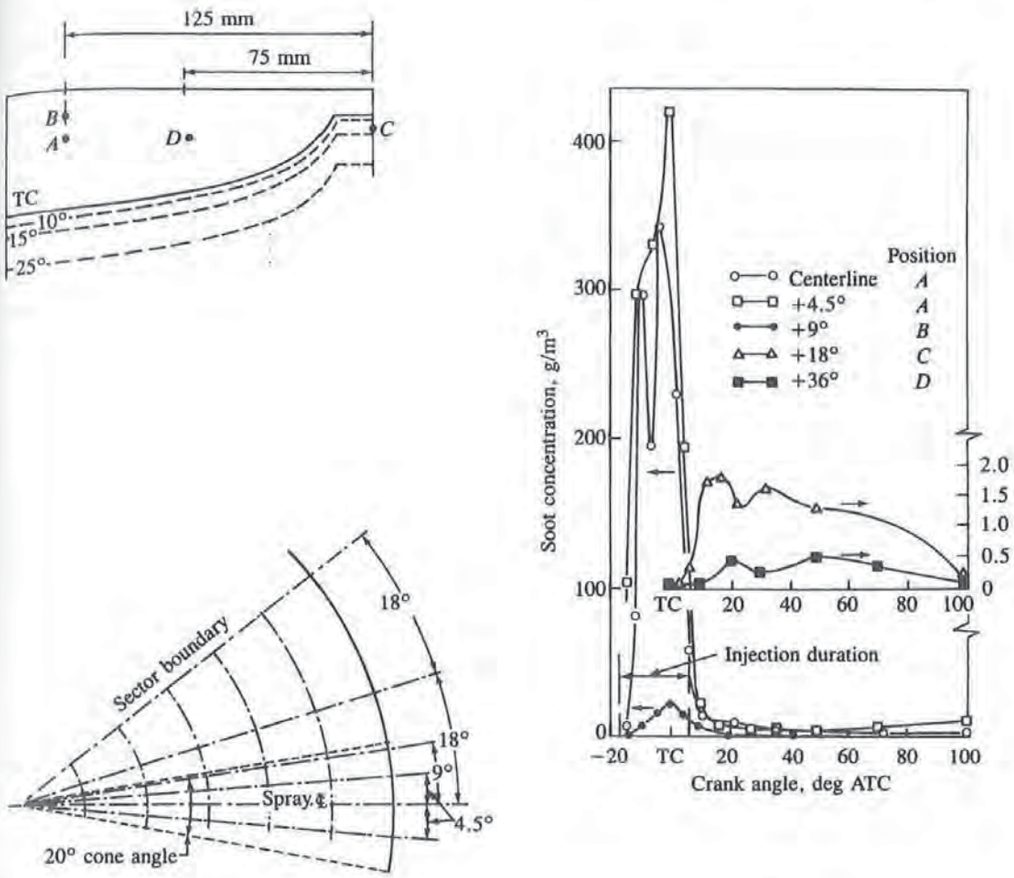


FIGURE 11-42
Particulate concentrations, in g/m³ at standard temperature and pressure, in various regions of the fuel spray as a function of crank angle in quiescent DI diesel engine, measured with rapid sampling valve. Different sample valve locations in combustion chamber and spray indicated on left. Cylinder bore = 30.5 cm, stroke = 38.1 cm, r_c = 12.9, engine speed = 500 rev/min, bmep = 827 kPa.[74]

injection diesel engine which illustrates these points.[74] The particulate concentrations on the fuel spray axis close to the injector orifice are remarkably high (~200 to 400 g/m³ at standard temperature and pressure). This corresponds to a large fraction of the fuel carbon in the extremely rich fuel vapor core being sampled as particulate (as soot and condensed HC species). Such high particulate fractions of the local fuel carbon (~50 percent) have also been found in the very fuel rich cores of high-pressure liquid-fueled turbulent diffusion flames. Pyrolysis of the fuel is therefore an important source of soot. These very high local soot concentrations decrease rapidly once fuel injection ceases and the rich core mixes to leaner equivalence ratios. Soot concentrations in the spray close to the piston bowl outer radius and at the cylinder wall rise later, are an order of magnitude less, and decay more slowly. Away from the fuel spray core, soot concentrations

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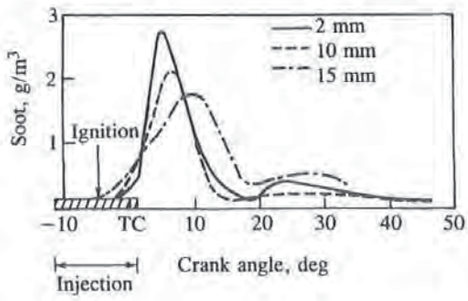


FIGURE 11-43
Particulate concentrations at various distances from wall of prechamber in swirl-chamber IDI diesel engine, measured with rapid sampling valve. Engine speed = 1000 rev/min, injection at 12° BTC, ignition at 5° BTC.[21]

decrease rapidly with increasing distance from the centerline. A useful comparison with these soot concentrations is the fuel concentration in a *stoichiometric* mixture, about 75 g fuel/m^3. Approximate estimates of the mean soot concentration inside the cylinder through the combustion process suggests that almost all (over 90 percent) of the soot formed is oxidized prior to exhaust. Similar results have been obtained in a small direct-injection engine with swirl.[78, 79] Peak soot concentrations in the outer regions of the fuel spray were comparable ($\sim$10 g/m^3). Measurements were not made in the spray core near the injector orifice; however, based on the equivalence ratio results in Fig. 10-46, soot concentrations would be expected to be lower due to the more rapid mixing with air that occurs with swirl.

Similar data are available from sampling in the prechamber of an IDI swirl chamber engine.[21] Figure 11-43 shows soot concentrations 2, 10, and 15 mm from the wall of the prechamber. Equivalence ratio distributions from this study have already been shown in Fig. 11-17. Concentrations peak 5 to 10° ATC at levels $\sim$2 g/m^3; these are substantially lower than DI engine peak soot concentrations (presumably due to the more rapid mixing of fuel and air in the IDI engine). Concentrations in the prechamber at these locations then decrease substantially.

A better indication of average concentrations within the cylinder is given by total cylinder sampling experiments. Measurements of the total number of soot particles and soot volume fraction through the combustion process have been made in an IDI passenger car diesel. The contents of the engine cylinder, at a preselected point in the cycle, were rapidly expelled through a blowdown port, diluted, and collected in a sample bag. Figure 11-44 shows one set of results. Particles first appear shortly after the start of combustion (4 to 5° ATC). The number density rises to a maximum at 20° ATC and then falls rapidly as a result of particle coagulation and, possibly, oxidation. The exhaust particulate number density is less than one-tenth of the peak value. The volume fraction soot data (soot mass concentration is proportional to volume fraction) show a much flatter maximum earlier in the combustion process and a decrease (due to oxidation) from 20 to 40° ATC to about one-third of the peak value. Oxidation apparently ceases at about 40° ATC at these conditions.

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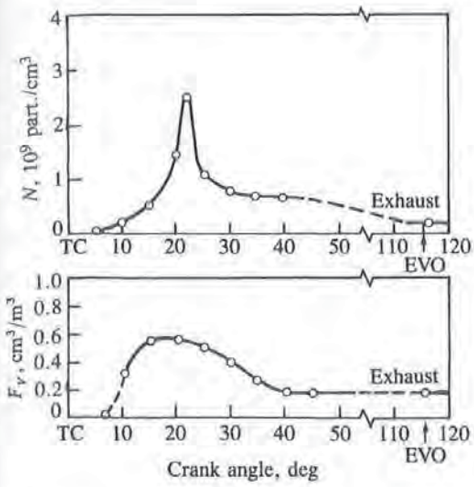


FIGURE 11-44
Cylinder-average particle-number density N and particle-volume fraction F_V, as a function of crank angle in IDI diesel engine determined from cylinder-dumping experiments. 1000 rev/min, $\phi = 0.32$, injection starts at 3.5° BTC. Gas volumes at standard temperature and pressure.[77]

11.5.4 Soot Formation Fundamentals

The soot particles, whose characteristics have been described in the above two sections, form primarily from the carbon in the diesel fuel. Thus, the formation process starts with a fuel molecule containing 12 to 22 carbon atoms and an H/C ratio of about 2, and ends up with particles typically a few hundred nanometers in diameter, composed of spherules 20 to 30 nm in diameter each containing some 10^5 carbon atoms and having an H/C ratio of about 0.1. Most of the information available on the fundamentals of soot formation in combustion comes from studies in simple premixed and diffusion flames, stirred reactors, shock tubes, and constant-volume combustion bombs. A recent review[80] summarizes the extensive literature available from such studies. Also, the production of carbon black requires a high yield of soot from pyrolysis of a hydrocarbon feedstock, and the literature from that field has much to contribute (see Ref. 81). However, the characteristics of diesel combustion which make it unsuitable for more fundamental studies—the high gas temperatures and pressures, complex fuel composition, dominance of turbulent mixing, the unsteady nature of the process, and the three-dimensional geometry—also make it difficult to interpret fundamental ideas regarding soot formation in the diesel context. There is much about the soot formation process in diesel engines, therefore, that is poorly and incompletely understood.

Soot formation takes place in the diesel combustion environment at temperatures between about 1000 and 2800 K, at pressures of 50 to 100 atm, and with sufficient air *overall* to burn fully all the fuel. The time available for the formation of solid soot particles from a fraction of the fuel is in the order of milliseconds. The resulting aerosol—dispersed solid-phase particles in a gas—can be characterized by the total amount of condensed phase (often expressed as the soot volume fraction, F_V, the volume of soot/total volume), the number of soot particles per unit volume (N), and the size of the particles (e.g., average diameter d). F_V, N, and d are mutually dependent [e.g., for spherical particles $F_V =$

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$(\pi/6)Nd^3$], and any two of these variables characterize the system. It is most convenient to consider N and F_V as the independent variables since they each relate to the "almost-separate" stages of soot particle generation (the source of N) and soot particle growth (the source of F_V).

These stages can be summarized as follows:[80]

1. Particle formation, where the first condensed phase material arises from the fuel molecules via their oxidation and/or pyrolysis products. These products typically include various unsaturated hydrocarbons, particularly acetylene and its higher analogues ($C_{2n}H_2$), and polycyclic aromatic hydrocarbons (PAH). These two types of molecules are considered the most likely precursors of soot in flames. The condensation reactions of gas-phase species such as these lead to the appearance of the first recognizable soot particles (often called nuclei). These first particles are very small ($d < 2$ nm) and the formation of large numbers of them involve negligible soot loading in the region of their formation.
2. Particle growth, which includes both surface growth, coagulation, and aggregation. Surface growth, by which the bulk of the solid-phase material is generated, involves the attachment of gas-phase species to the surface of particles and their incorporation into the particulate phase. Figure 11-45, where the log of the molecular weight of a species is plotted against its hydrogen mole fraction $\tilde{x}_H$, illustrates some important points about this process. Starting with a fuel molecule of $\tilde{x}_H \gtrsim 0.5$ it is apparent that neither purely polyacetylene chain

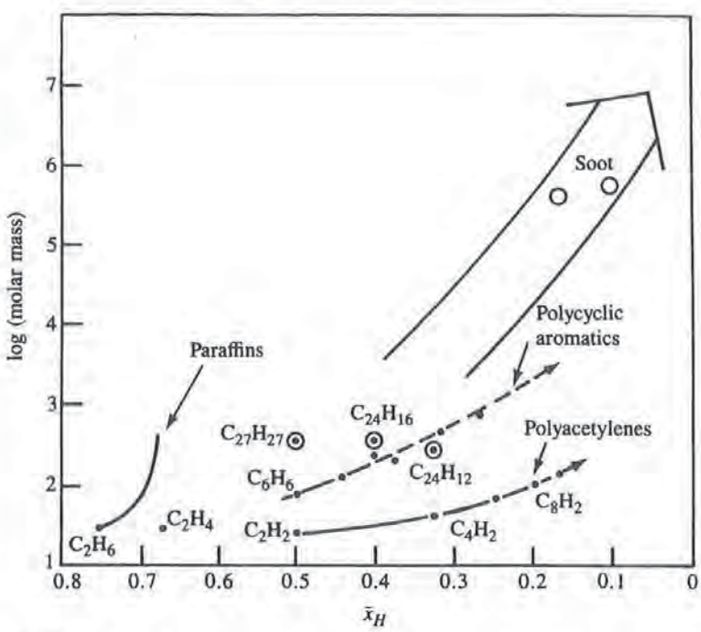


FIGURE 11-45
Paths to soot formation on plot of species molecular weight M versus hydrogen mole fraction $\tilde{x}_H$.[80]

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growth nor purely PAH growth would lead to soot particles which have $\tilde{x}_H$ in the range 0.1 to 0.2. What is required is condensation of species with the right hydrogen content, or condensation of species with higher hydrogen content followed by dehydrogenation, or a combination of both these processes. Obviously some polyacetylenes and some PAH can satisfy these requirements, as can saturated platelets (e.g., $C_{27}H_{27}$; see Sec. 11.5.2). Surface growth reactions lead to an increase in the amount of soot (F_V) but the number of particles (N) remains unchanged. The opposite is true for growth by coagulation, where the particles collide and coalesce, which decreases N with F_V constant. Once surface growth stops, continued aggregation of particles into chains and clusters can occur.

These stages of particle generation and growth constitute the soot formation process. At each stage in the process oxidation can occur where soot or soot precursors are burned in the presence of oxidizing species to form gaseous products such as CO and CO_2. The eventual emission of soot from the engine will depend on the balance between these processes of formation and burnout. The emitted soot is then subject to a further mass addition process as the exhaust gases cool and are diluted with air. Adsorption into the soot particle surface and condensation to form new particles of hydrocarbon species in the exhaust gases occurs in the exhaust system and in the dilution tunnel which simulates what happens in the atmosphere. Figure 11-46 illustrates the relationship between these processes.[70] Although they are illustrated as discrete processes, there is some overlap, and they may occur concurrently in a given elemental mixture region within the diesel combustion chamber. Of course, due also to the nonhomogeneous nature of the mixture and the duration of fuel injection and its overlap with combustion, at any given time different processes are in progress in different regions or packets of fluid. The fundamentals of each of these processes will now be reviewed.

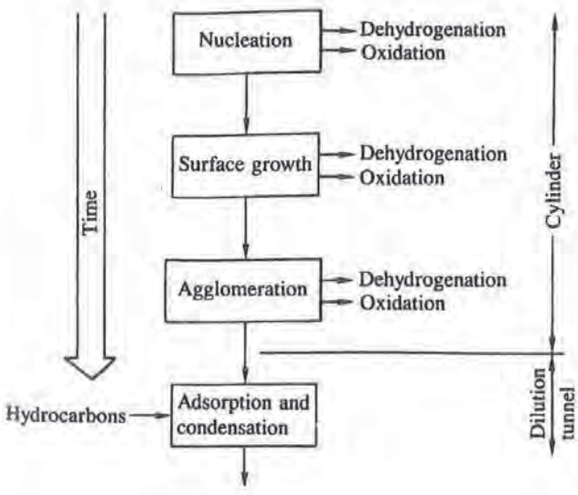


FIGURE 11-46
Processes leading to net production of diesel particulates.[70]

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SOOT PARTICLE FORMATION. Empirically, it has been found useful to define the composition of the fuel-oxidizer mixture at the onset of soot formation in flames by the carbon/oxygen ratio. Equilibrium considerations indicate that soot formation should occur when, in

$$C_m H_n + yO_2 \rightarrow 2_y CO + \frac{n}{2} H_2 + (m - 2y)C_s \tag{11.35}$$

m becomes larger than $2y$: i.e., the C/O ratio exceeds unity. The corresponding fuel/air equivalence ratio is given by

$$\phi = 2\left(\frac{C}{O}\right)(1 + \delta) \tag{11.36}$$

where $\delta = n/(4m)$; ϕ is 3 for (C/O) = 1, with $n/m = 2$. The experimentally observed critical C/O ratios are less than unity, however, varying with fuel composition and details of the experimental setup from about 0.5 to 0.8. The critical C/O ratio for soot formation increases with increasing temperature but is only weakly dependent on pressure. Beyond the carbon formation limit, the yield of soot increases rapidly with increasing C/O ratio and is strongly enhanced by increasing pressure.[80]

It is obvious that soot formation is a nonequilibrium process. Yet despite decades of study, the precise details of the chemistry leading to the establishment of soot nuclei still elude investigators. Several different theories have been advanced to explain the pyrolysis process—the extensive decomposition and atomic rearrangement of the fuel molecules—that culminates in nucleation. Reviews of these theories can be found in Refs. 73, 80, and 81. Often-cited mechanisms are thermal cracking that results in fragmentation of fuel molecules into smaller ones, condensation reactions and polymerization that result in larger molecules, and dehydrogenation that lowers the H/C ratio of the hydrocarbons destined to become soot. Three different paths to the production of soot appear to exist, depending on the formation temperature. At the lowest temperatures ($\lesssim$1700 K) only aromatics or highly unsaturated aliphatic compounds of high molecular weight are very effective in forming solid carbon through pyrolysis. At intermediate temperatures typical of diffusion flames ($\gtrsim$1800 K), all normally used hydrocarbon fuels produce soot if burned at sufficiently rich stoichiometry, but appear to do so by following a different path. At very high temperatures, above the range of interest for diesel combustion, a third nucleation process seems likely that involves carbon vapor.[70]

A simple mechanistic model for nucleation in the low and intermediate temperature ranges which has considerable experimental support for its basic features has been advanced by Graham et al.[82] It is illustrated in Fig. 11-47. At low temperatures, an aromatic hydrocarbon can produce soot via a relatively fast direct route that involves condensation of the aromatic rings into a graphitelike structure. Above about 1800 K, however, a slower, less-direct route is favored that entails ring breakup into smaller hydrocarbon fragments. These fragments then polymerize to form larger unsaturated molecules that ultimately produce

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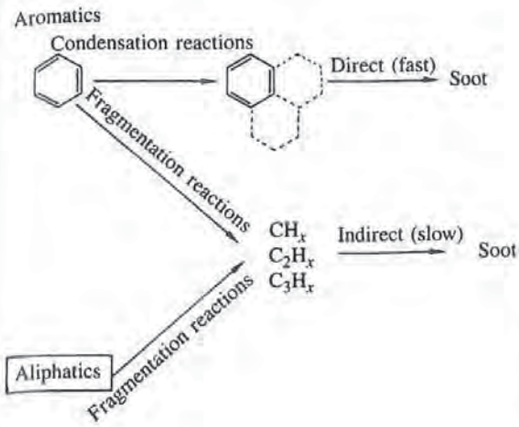


FIGURE 11-47
Mechanistic model for formation of soot from aromatic and aliphatic hydrocarbon compounds.[70]

soot nuclei. Aliphatic molecules can only follow this latter less-direct route. Experimental measurements in flames suggest that polyunsaturated hydrocarbon compounds are involved in nucleation, and acetylenes and polyacetylenes have been detected that decrease in concentration as the mass of carbon formed increases. Such observations fit the indirect path in Fig. 11-47. Results of studies of pyrolysis of benzene between 1300 and 1700 K support a physical condensation mechanism for the low-temperature path. This mechanism begins with the transformation of the initial hydrocarbon into macromolecules by a gas-phase reaction. The partial pressure of these macromolecules grows until supersaturation becomes sufficient to force their condensation into liquid microdroplets. These become nuclei, and subsequently formed gaseous macromolecules then contribute to nuclei growth.[70]

SOOT PARTICLE GROWTH. Nucleation produces a large number of very small particles with an insignificant soot loading. The bulk of the solid-phase material is generated by surface growth, which involves the gas-phase deposition of hydrocarbon intermediates on the surfaces of the spherules that develop from the nuclei. A qualitative description of the changes that occur as a function of time in a premixed flame during nucleation and surface growth is shown in Fig. 11-48. The soot fraction F_V, in units of soot volume per unit volume of gas, is related to the number density N and the volume-mean diameter of the soot particles by

$$F_V = \frac{\pi}{6} N d^3 \tag{11.37}$$

d is the actual diameter of the spherules, or the diameter of a sphere of equivalent volume to an agglomerated particle. The rate of change of particle number density with time t can be written

$$\frac{dN}{dt} = \dot{N}_n - \dot{N}_a \tag{11.38}$$

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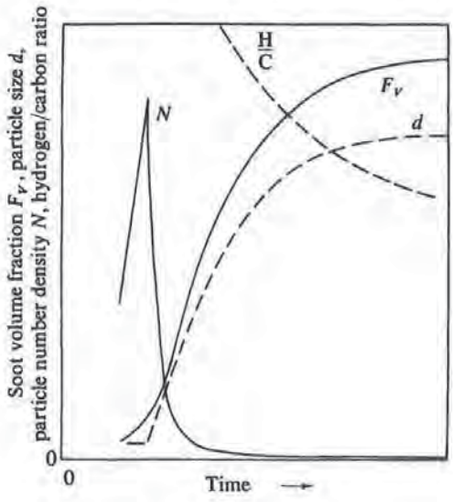


FIGURE 11-48
Variation in soot volume fraction F_V, particle number density N, particle size d, and soot hydrogen/carbon ratio with time in a flame.[70]

where $\dot{N}_n$ is the rate at which fresh nuclei appear and $\dot{N}_a$ is the rate of agglomeration of spherules or particles that collide and stick. At the peak of the N curve, $\dot{N}_n = \dot{N}_a$. To the left of the peak, $\dot{N}_n > \dot{N}_a$, the particle diameter remains essentially constant at the minimum detectable diameter and the (small) rise in soot volume is dominated by nucleation. To the right of the peak in the N curve, $\dot{N}_a > \dot{N}_n$. The number of agglomerating collisions is high because of the high number density; at the same time nucleation ends because there is enough dispersed surface area for gaseous deposition of hydrocarbon intermediates so the probability of generating new nuclei falls to zero. With nucleation halted slightly to the right of the N curve peak, all the subsequent increase in soot volume fraction (the majority) stems from surface growth. To the right of the N curve peak, the number density falls in the case illustrated by three orders of magnitude. This is the result of agglomeration, which is responsible for a portion of the increase in particle diameter. Agglomeration does not contribute to the rise in soot volume fraction, F_V. Surface growth that takes place on nuclei and on spherules is responsible for forming the concentric shells (somewhat distorted and warped) that constitute the outer portions of spherules and which are distinct from the less-organized spherule center (see Figs. 11-40 and 11-41). Surface growth on agglomerated particles may partly fill in the crevices at the junctures of adjoining spherules to provide the nodular structure evident in Fig. 11-40.[70]

Once particles have formed, interparticle collisions can lead to agglomeration, thereby decreasing the number of particles and increasing their size. Three types of agglomeration have been identified in soot formation. During the early stages of particle growth, collision of two spherical particles may result in their *coagulation* into a single spheroid. This is easy to visualize in hydrocarbon pyrolysis where the beginnings of a soot particle may have the viscosity of a tarry liquid.[70] Also, when the individual particles are small, rapid surface growth will quickly restore the original spherical shape.[73] This process occurs up to diameters of about 10 nm. On the other hand, if spherules have solidified before colli-

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sion and surface growth rates have diminished, the resulting particles resemble a cluster in which the original spherules retain much of their individual identity. After surface growth essentially ceases, continued coalescence of the soot particles results in the formation of chainlike structures of discrete spherules. This suggests electrostatic forces are significant. Positive charge measured on these particle chains is claimed to be the cause of their chainlike structure.[70, 73] This latter coalescence once surface growth ceases is termed *aggregation.*

It has been shown experimentally that during coagulation the rate of decrease of particle number density was proportional to the product of a coagulation coefficient and the square of the number density:

$$-\frac{dN}{dt} = KN^2 \tag{11.39}$$

This is the Smoluchowski equation for coagulation of a liquid colloid. Based on brownian motion, this equation is applicable when the Knudsen number (ratio of mean free path to particle diameter) exceeds 10. K depends on such factors as particle size and shape, size distribution, and the temperature, pressure, and density of the gas. Equation (11.39) has been used to predict coagulation rates in low-pressure sooting flames.[73, 80] It has also been modified so that it applies where the particle size and mean free path are comparable by using a more complex expression for K (see Ref. 83). These studies show that under conditions approximating those in engine flames, the fraction of the initial number density N_0 remaining at time t is given approximately by

$$\frac{N}{N_0} \approx (KN_0 t)^{-1} \tag{11.40}$$

Thus as t increases, N/N_0 decreases rapidly. Although these coagulation calculations are simplistic (in that many of the assumptions made are not strictly valid since soot particles are not initially distributed homogeneously in the combustion space, they are not monodisperse, and surface growth and oxidation may be taking place during agglomeration), an overall conclusion is that the rate of coagulation of spherules and particles to larger particles is very sensitive to number density. Thus the number of particles decreases rapidly with advancing crank angle in the diesel engine during the early part of the expansion process (see Fig. 11-44) and agglomeration is essentially complete well before the exhaust valve opens.

Throughout the soot formation process in a flame, the H/C ratio of the hydrocarbons formed in the pyrolysis and nucleation process and of the soot particles continually decreases. The H/C ratio decreases from a value of about 2, typical of common fuels, to of order 1 in the youngest soot particles that can be sampled, and then to 0.2 to 0.3 once surface growth has ceased in the fully agglomerated soot.[80] The latter stages of this process are indicated in Fig. 11-48. The addition of mass to the soot particles occurs by reaction with gas-phase molecules. The reacting gas-phase hydrocarbons appear to be principally acetylenes, with larger polymers adding faster than the smaller. Small polyacetylenes

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undergo further polymerization in the gas phase, presumably by the same mechanism leading to nucleation. As a result of preferential addition of the larger polymers, the H/C ratio of the particles decreases toward its steady-state value. Thus most of the polyacetylenes added must be of very high molecular weight or dehydrogenation must also take place.[73, 80]

11.5.5 Soot Oxidation

In the overall soot formation process, shown schematically in Fig. 11-46, oxidation of soot at the precursor, nuclei, and particle stages can occur. The engine cylinder soot-concentration data reviewed in Sec. 11.5.3 indicate that a large fraction of the soot formed is oxidized within the cylinder before the exhaust process commences. In the discussion of diesel combustion movies in Sec. 10.3.1, dark brown regions were observed in the color photographs (see color plate, Fig. 10-4); these were interpreted as soot particle clouds, and were seen to be surrounded by a diffusion flame which appeared white from the luminosity of the high-temperature soot particles consumed in this flame. As air mixed with this soot-rich region, the white flame eradicated the dark soot clouds as the particles were burned up.

In general, the rate of heterogeneous reactions such as the oxidation of soot depends on the diffusion of reactants to and products from the surface as well as the kinetics of the reaction. For particles less than about 1 μm diameter, diffusional resistance is minimal. The soot oxidation process in the diesel cylinder is kinetically controlled, therefore, since particle sizes are smaller than this limit. There are many species in or near the flame that could oxidize soot: examples are O_2, O, OH, CO_2, and H_2O. Recent reviews of soot formation[70, 73, 80] have concluded that at high oxygen partial pressures, soot oxidation can be correlated with a semiempirical formula based on pyrographite oxidation studies. For fuel-rich and close-to-stoichiometric combustion products, however, oxidation by OH has been shown to be more important than O_2 attack, at least at atmospheric pressure.

It is argued on the basis of structural similarities that the rates of oxidation of soot and of pyrographites should be the same. This is a significant simplification. It has proved difficult to follow the oxidation of soot aerosols in flames, and if care is taken to avoid diffusional resistance, studies of bulk samples of pyrographite can then be used as a basis for understanding soot oxidation. The semiempirical formula of Nagle and Strickland-Constable has been shown[84] to correlate pyrographite oxidation for oxygen partial pressures $p_{O_2} < 1$ atm and temperatures between 1100 and 2500 K. This formula is based on the concept that there are two types of sites on the carbon surface available for O_2 attack. For the more reactive type A sites, the oxidation rate is controlled by the fraction of sites not covered by surface oxides (and therefore is of mixed order, between 0 and 1 in p_{O_2}). Type B sites are less reactive, and react at a rate which is first order in p_{O_2}. A thermal rearrangement of A sites into B sites is also allowed (with rate constant k_T). A steady-state analysis of this mechanism gives a surface mass oxi-

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TABLE 11.10
Rate constants for Nagle and Strickland-Constable soot oxidation mechanism[84]

Rate constant	Units
$k_A = 20 \exp(-15{,}100/T)$	$g/cm^2 \cdot s \cdot atm$
$k_B = 4.46 \times 10^{-3} \exp(-7640/T)$	$g/cm^2 \cdot s \cdot atm$
$k_T = 1.51 \times 10^5 \exp(-48{,}800/T)$	$g/cm^2 \cdot s$
$k_Z = 21.3 \exp(2060/T)$	atm^{-1}

dation rate w (g C/cm$^2 \cdot$ s):

$$\frac{w}{12} = \left(\frac{k_A p_{O_2}}{1 + k_Z p_{O_2}}\right) x + k_B p_{O_2}(1 - x) \tag{11.41}$$

where x is the fraction of the surface occupied by type A sites and is given by

$$x = \left(1 + \frac{k_T}{p_{O_2} k_B}\right)^{-1} \tag{11.42}$$

The empirical rate constants determined by Nagle and Strickland-Constable for this model are listed in Table 11.10. According to this mechanism, the reaction is first order at low oxygen partial pressures, but approaches zero order at higher pressures. At a given oxygen pressure, the rate initially increases exponentially with temperature (equivalent activation energy is k_A/k_Z or 34,100 cal/mol). Beyond a certain temperature the rate decreases as the thermal rearrangement favors formation of less reactive B sites. When, at sufficiently high temperature, the surface is completely covered with B sites, the rate is first order in oxygen partial pressure and increases again with temperature.[80]

Park and Appleton[84] have compared this formula with oxidation rate data obtained from pyrographite samples, carbon black particles, and with the available flame soot oxidation data. Figure 11-49 shows both the soot oxidation rate predicted by Eqs. (11.41) and (11.42) as a function of temperature and oxygen partial pressure, and the above-mentioned data. The formula correlates the data shown to within a factor of 2. Under diesel engine conditions, the O_2 partial pressure can be high ($\sim$several atmospheres), as can the temperatures of close-to-stoichiometric mixtures ($\lesssim$2800 K).

Equations (11.41) and (11.42) have been used to estimate the amount of soot that can be oxidized in a typical IDI diesel engine. It was assumed that soot was present in stoichiometric combustion products at selected times in the cycle and that mixing with air leaned out the burned gas mixture at different rates until the overall fuel/air equivalence ratio was reached. The surface recession rate during this process was computed. Figure 11-50 shows sample results at an engine speed of 1600 rev/min and an overall cylinder equivalence ratio of 0.58. Fast, intermediate, and slow mixing occurred in 30, 70, and 140°, respectively. The surface recession rate rises to a maximum as p_{O_2} increases and then decreases as the

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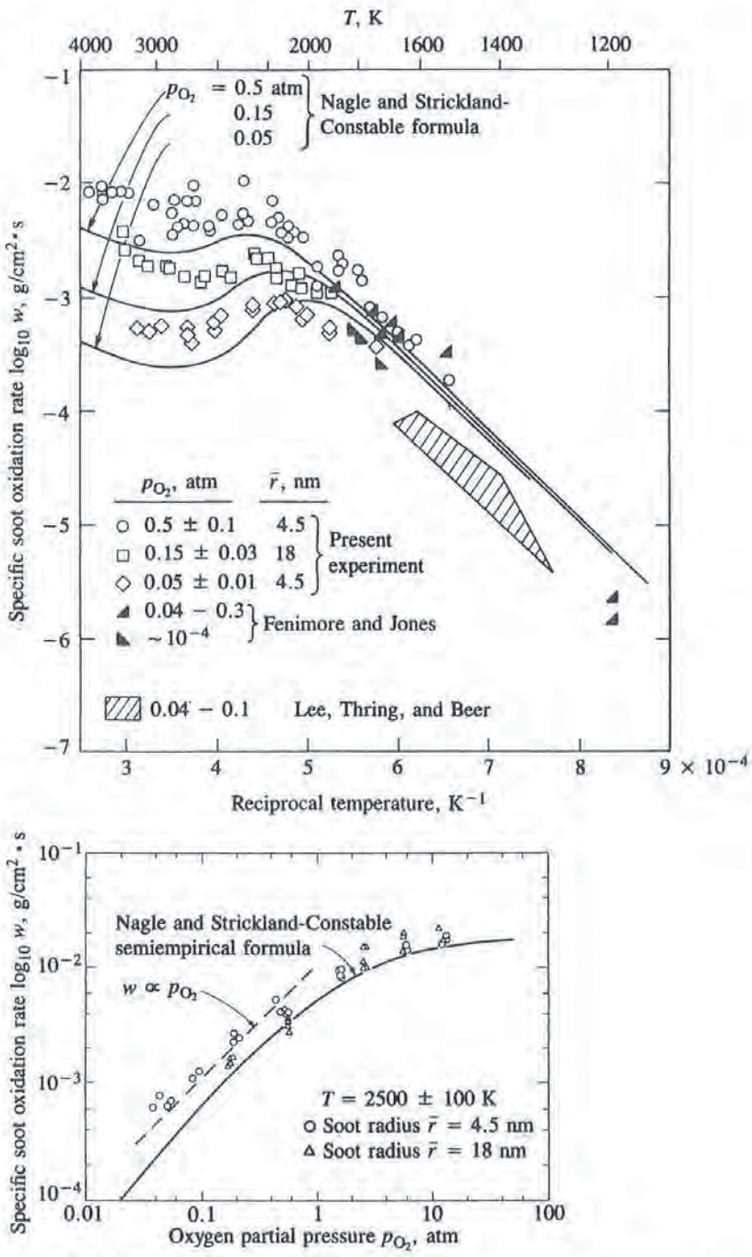


FIGURE 11-49
Specific soot oxidation rate measurements and predictions as a function of temperature and oxygen partial pressure.[84]

falling gas temperature more than offsets the increasing oxygen concentration. While the shape of the recession rate versus time curves depends on the mixing rate, the total amount of carbon burned (the area under each curve in Fig. 11-50*b*) is about the same (0.1 μg/mm^2). However, the point in the cycle at which the soot-containing burned gas mixture passes through stoichiometric is much

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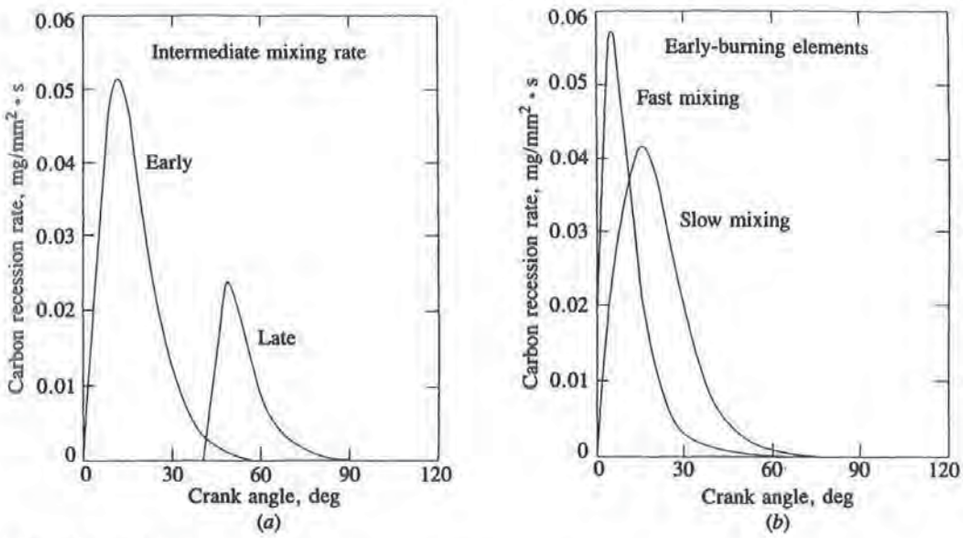


FIGURE 11-50
Soot particle burnup rate in diesel combustion environment: (*a*) in early- and late-burned fuel-air elements with intermediate mixing rate; (*b*) for fast and slow mixing for early-burning elements.[83]

more important. For the late mixing element shown (mixing lean of stoichiometric at 40° ATC), the total carbon mass oxidized is only 40 percent of that for the early mixing calculation. This is due primarily to the decreasing gas temperatures as the expansion stroke proceeds, and not the longer time available for burnup.[83]

For a spherical particle, the mass burning rate w (g/cm^2 · s) can be converted to a surface recession rate using

$$\frac{dr}{dt} = \frac{-w}{\rho}$$

where ρ is the density (≈ 2 g/cm^3). The integrated values of $w(t)$ when divided by ρ then give the maximum radius of a soot particle that can be burned up. Integrated values of 0.1 μg/mm^2 (estimated for TC start of burnup) correspond to a radius of about 50 nm or diameter of 100 nm. Individual spherule diameters are about 30 nm, so soot which mixes with air early in the expansion stroke is likely to be fully burned. Thus the soot present in the exhaust would be expected to come from regions which mix with air too late for the oxidation rate to be sufficient for particle burnup.

Agglomeration will have an indirect influence on the amount of soot oxidized through its effect on surface area. In the limiting case of a spherical cluster, n monodisperse spherules ($10 \lesssim n \lesssim 100$) can be imagined as compacted into a single solid sphere of equal volume. Alternatively, the same n spherules can be imagined compacted into a cylinder of diameter equal to that of the original spherules. Since oxidative attack is essentially an exterior surface phenomenon, the surface/volume ratio is the appropriate measure of the effect of particle shape on soot mass burnup rate. It can be shown that the surface/volume ratios for the

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single sphere, cylinder, and individual spherule are in the ratio $n^{-1/3}$, $\frac{2}{3}$, and 1, respectively. Thus agglomeration will decrease the relative oxidation rate. In the limit spherical clusters are less desirable than a chain; the larger the cluster the bigger the relative reduction in surface area. However, the densely packed spherule limit does not appear to be approached in practice. A specific surface area, of about 200 m^2/g for diesel soot, has been measured.[85] A smooth-surfaced 30-nm diameter spherule with a 2-g/cm^3 density has a surface/mass ratio of 100 m^2/g; the measured value is about twice this value, indicating low porosity and an agglomerate structure which is loosely rather than densely packed.[83]

Equation (11.41) shows a maximum recession rate in combustion products corresponding to a fuel/air equivalence ratio of about 0.9. Recent evidence shows that in an atmospheric pressure environment with rich and close-to-stoichiometric combustion products where O_2 mole fractions are low, oxidation by OH radical attack is much more significant than oxidation by O or O_2. The OH radical may be important in oxidizing soot in the flame zone under close-to-stoichiometric conditions.

11.5.6 Adsorption and Condensation

The final process in the particulate formation sequence illustrated in Fig. 11-46 is adsorption and condensation of hydrocarbons. This occurs primarily after the cylinder gases have been exhausted from the engine, as these exhaust gases are diluted with air. In the standard particulate mass emission measurement process this occurs in a dilution tunnel which simulates approximately the actual atmospheric dilution process. A diluted exhaust gas sample is filtered to remove the particulate. After equilibrating the collection filter at controlled conditions to remove water vapor, the particulate mass is obtained by weighing. In the prescribed EPA procedure, the filter temperature must not exceed 52°C. For a given exhaust gas temperature, the filter (and sample) temperature depends on the dilution ratio, as shown in Fig. 11-51.

The effect of the dilution ratio (and the dependent sample temperature) on collected particulate mass is shown in Fig. 11-52 for a standard dilution tunnel,

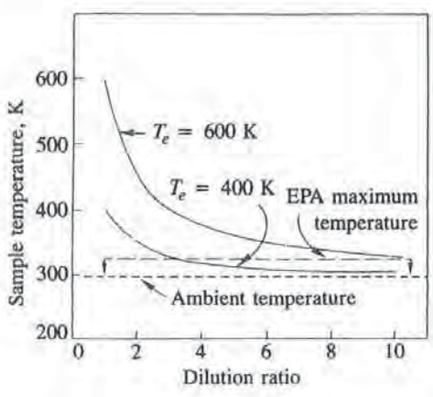


FIGURE 11-51
Effect of exhaust gas dilution ratio on the temperature of the collected particulate sample as a function of engine exhaust temperature T_e.[70]

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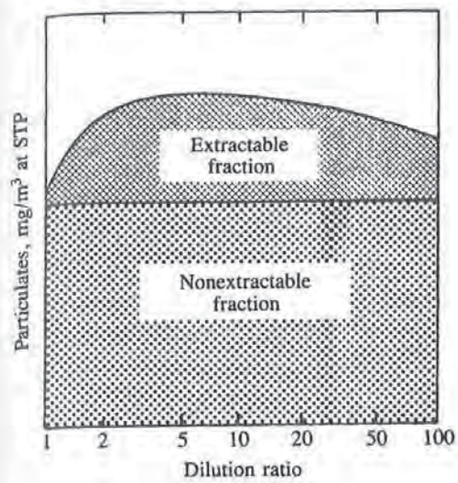


FIGURE 11-52
Typical effect of dilution ratio on particulate mass emission and its partitioning between extractable and nonextractable fractions.[70]

where the total sample is partitioned into extractable and nonextractable fractions. The nonextractable fraction is the carbonaceous soot generated during combustion and is not affected by the dilution process. With no dilution (dilution ratio of unity) the difference between the total and nonextractable mass is small; the bulk of the extractable fraction is acquired after the exhaust gas is mixed with dilution air. Extensive studies of this dilution process have shown that both adsorption and condensation occur. Adsorption involves the adherence of molecules of unburned hydrocarbons to the surfaces of the soot particles by chemical or physical (van der Waals) forces. This depends on the fraction of the available particle surface area occupied by hydrocarbons and on the partial pressure of the gaseous hydrocarbons that drives the adsorption process. As the dilution ratio increases from unity, the effect of decreasing temperature on the number of active sites dominates and, as shown in Fig. 11-52, the extractable fraction increases. At high dilution ratios, the sample temperature becomes insensitive to the dilution ratio (see Fig. 11-51) but the decreasing hydrocarbon partial pressure causes the extractable mass to fall again. Condensation will occur whenever the vapor pressure of the gaseous hydrocarbon exceeds its saturated vapor pressure. Increasing dilution decreases hydrocarbon concentrations and hence vapor pressure. However, the associated reduction in temperature does reduce the saturation pressure. High exhaust concentrations of hydrocarbons are the conditions where condensation is likely to be most significant, and the hydrocarbons most likely to condense are those of low volatility. Sources of low-volatility hydrocarbons are the high-boiling-point end of the fuel, unburned hydrocarbons that have been pyrolyzed but not consumed in the combustion process, and the lubricating oil.[70]

Experiments with a passenger car IDI diesel, where the oil was tagged with a radioactive tracer, have shown that the oil can contribute from 2 to 25 percent of the total particulate mass, with the greatest contribution occurring at high speed. On average, over half of the extractable mass was traceable to the oil. All the material traceable to the oil was found in the extractable fraction, indicating that the oil did not participate in the combustion process. However, the oil is not

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always a significant contributer: in another engine, fuel was the dominant source of extractable material.[70, 71]

11.6 EXHAUST GAS TREATMENT

11.6.1 Available Options

Our discussion so far has focused on *engine* emissions. Further reductions in emissions can be obtained by removing pollutants from the exhaust gases in the engine exhaust system. Devices developed to achieve this result include catalytic converters (oxidizing catalysts for HC and CO, reducing catalysts for NO_x, and three-way catalysts for all three pollutants), thermal reactors (for HC and CO), and traps or filters for particulates.

The temperature of exhaust gas in a spark-ignition engine can vary from 300 to 400°C during idle to about 900°C at high-power operation. The most common range is 400 to 600°C. Spark-ignition engines usually operate at fuel/air equivalence ratios between about 0.9 and 1.2 (see Sec. 7.1). The exhaust gas may therefore contain modest amounts of oxygen (when lean) or more substantial amounts of CO (when rich). In contrast, diesel engines, where load is controlled by the amount of fuel injected, always operate lean. The exhaust gas therefore contains substantial oxygen and is at a lower temperature (200 to 500°C). Removal of gaseous pollutants from the exhaust gases after they leave the engine cylinder can be either thermal or catalytic. In order to oxidize the hydrocarbons in the gas phase without a catalyst, a residence time of order or greater than 50 ms and temperatures in excess of 600°C are required. To oxidize CO, temperatures in excess of 700°C are required. Temperatures high enough for some homogeneous thermal oxidation can be obtained by spark retard (with some loss in efficiency) and insulation of the exhaust ports and manifold. The residence time can be increased by increasing the exhaust manifold volume to form a *thermal reactor* (see Sec. 11.6.3). However, this approach has limited application.

Catalytic oxidation of CO and hydrocarbons in the exhaust can be achieved at temperatures as low as 250°C. Thus effective removal of these pollutants occurs over a much wider range of exhaust temperatures than can be achieved with thermal oxidation. The only satisfactory method known for the removal of NO from exhaust gas involves catalytic processes. Removal of NO by catalytic oxidation to NO_2 requires temperatures <400°C (from equilibrium considerations) and subsequent removal of the NO_2 produced. Catalytic reaction of NO with added ammonia NH_3 is not practical because of the transient variations in NO produced in the engine. Reduction of NO by CO, hydrocarbons, or H_2 in the exhaust to produce N_2 is the preferred catalytic process. It is only feasible in spark-ignition engine exhausts. Use of catalysts in spark-ignition engines for CO, HC, and NO removal has become widespread. Catalysts are discussed in Sec. 11.6.2.

Particulates in the exhaust gas stream can be removed by a trap. Due to the small particle size involved, some type of filter is the most effective trapping

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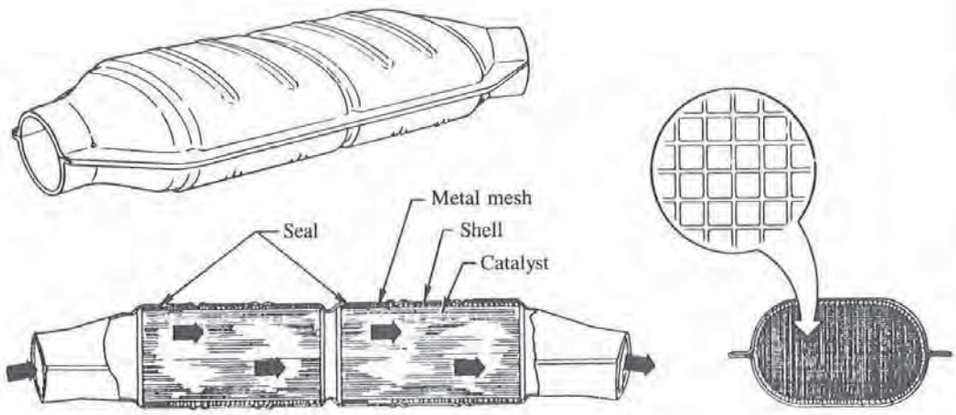
method. The accumulation of mass within the trap and the increase in exhaust manifold pressure during trap operation are major development problems. Diesel particulates, once trapped, can be burned up either by initiating oxidation within the trap with an external heat source or by using a trap which contains catalytically active material. The operation of particulate traps is reviewed briefly in Sec. 11.6.4.

11.6.2 Catalytic Converters

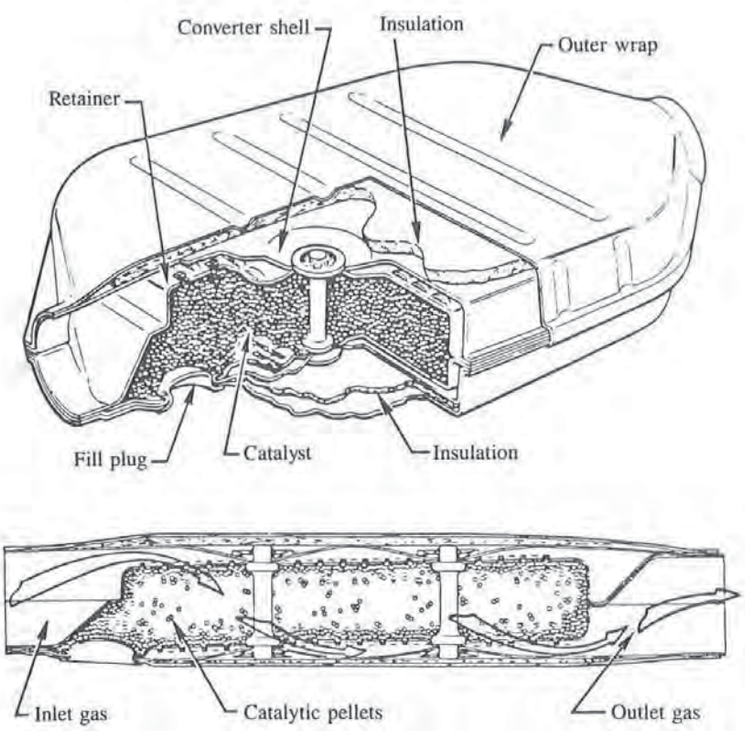
The catalytic converters used in spark-ignition engines consist of an active catalytic material in a specially designed metal casing which directs the exhaust gas flow through the catalyst bed. The active material employed for CO and HC oxidation or NO reduction (normally noble metals, though base metals oxides can be used) must be distributed over a large surface area so that the mass-transfer characteristics between the gas phase and the active catalyst surface are sufficient to allow close to 100 percent conversion with high catalytic activity. The two configurations commonly used are shown in Fig. 11-53. One system employs a ceramic honeycomb structure or monolith held in a metal can in the exhaust stream. The active (noble metal) catalyst material is impregnated into a highly porous alumina washcoat about 20 μm thick that is applied to the passageway walls. The typical monolith has square-cross-section passageways with inside dimensions of $\sim$1 mm separated by thin (0.15 to 0.3 mm) porous walls. The number of passageways per square centimeter varies between about 30 and 60. The washcoat, 5 to 15 percent of the weight of the monolith, has a surface area of 100 to 200 m^2/g. The other converter design uses a bed of spherical ceramic pellets to provide a large surface area in contact with the flow. With pellet catalysts, the noble metal catalyst is impregnated into the highly porous surface of the spherical alumina pellets (typically 3 mm diameter) to a depth of about 250 μm. The pellet material is chosen to have good crush and abrasion resistance after exposure to temperatures of order 1000°C. The gas flow is directed down through the bed as shown to provide a large flow area and low pressure drop. The gas flow is turbulent which results in high mass-transfer rates; in the monolith catalyst passageways, it is laminar.

OXIDATION CATALYSTS. The function of an oxidation catalyst is to oxidize CO and hydrocarbons to CO_2 and water in an exhaust gas stream which typically contains $\sim$12 percent CO_2 and H_2O, 100 to 2000 ppm NO, $\sim$20 ppm SO_2, 1 to 5 percent O_2, 0.2 to 5 percent CO, and 1000 to 6000 ppm C_1 HC, often with small amounts of lead and phosphorus. About half the hydrocarbons emitted by the SI engine are unburned fuel compounds. The saturated hydrocarbons (which comprise some 20 to 30 percent) are the most difficult to oxidize. The ease of oxidation increases with increasing molecular weight. Sufficient oxygen must be present to oxidize the CO and HC. This may be supplied by the engine itself

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(*a*)



(*b*)

FIGURE 11-53
Catalytic converters for spark-ignition engine emission control: (*a*) monolith design; (*b*) pelletized design.[62]

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running lean of stoichiometric or with a pump that introduces air into the exhaust ports just downstream of the valve. Venturi air addition into the exhaust port using the pressure pulsations generated by the exhaust process can also be used to add the required air.

Because of their high intrinsic activity, noble metals are most suitable as the catalytic material. They show higher specific activity for HC oxidation, are more thermally resistant to loss of low-temperature activity, and are much less deactivated by the sulfur in the fuel than base metal oxides. A mixture of platinum (Pt) and palladium (Pd) is most commonly used. For the oxidation of CO, olefins, and methane, the specific activity of Pd is higher than that of Pt. For the oxidation of aromatic compounds, Pt and Pd have similar activity. For oxidation of paraffin hydrocarbons (with molecular size greater than C_3), Pt is more active than Pd. Pure noble metals sinter rapidly in the 500 to 900°C temperature range experienced by exhaust catalysts. Since catalytic behavior is manifested exclusively by surface atoms, the noble metals are dispersed as finely as possible on an inert support such as γ-A_2O_3 which prevents particle-to-particle metal contact and suppresses sintering. The particle size of the noble metal particles in a fresh catalyst is less than 50 nm. This can increase to $\sim$100 nm when the catalyst is exposed to the high temperatures of the exhaust in vehicle operation. Typical noble metal concentrations in a commercial honeycomb catalyst are between 1 and 2 g/dm^3 of honeycomb volume, with Pt/Pd = 2 on a weight basis. As a rough rule of thumb, the ceramic honeycomb volume required is about half the engine displaced volume. This gives a space velocity through the converter (volume flow rate of exhaust divided by converter volume) over the normal engine operating range of 5 to 30 per second.[68]

The *conversion efficiency* of a catalyst is the ratio of the rate of mass removal in the catalyst of the particular constituent of interest to the mass flow rate of that constituent into the catalyst: e.g., for HC,

$$\eta_{cat} = \frac{\dot{m}_{HC,\,in} - \dot{m}_{HC,\,out}}{\dot{m}_{HC,\,in}} = 1 - \frac{\dot{m}_{HC,\,out}}{\dot{m}_{HC,\,in}} \tag{11.43}$$

The variation of conversion efficiency of a typical oxidizing catalytic converter with temperature is shown in Fig. 11-54. At high enough temperatures, the steady-state conversion efficiencies of a new oxidation catalyst are typically 98 to 99 percent for CO and 95 percent or above for HC. However, the catalyst is ineffective until its temperature has risen above 250 to 300°C. The term *light-off temperature* is often used to describe the temperature at which the catalyst becomes more than 50 percent effective.

The above numbers apply to fresh noble metal oxidation catalysts; as catalysts spend time in service their effectiveness deteriorates. Catalysis involves the adsorption of the reactants onto surface sites of high activity, followed by chemical reaction, then desorption of the products. Catalyst degradation involves both the deactivation of these sites by catalyst poisons and a reduction in the effective area of these sites through sintering. Poisoning affects both the warm-up and

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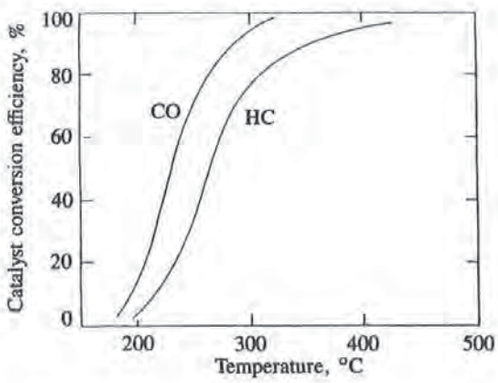


FIGURE 11-54
Conversion efficiency for CO and HC as a function of temperature for typical oxidizing catalytic converter.[62]

steady-state performance of the catalyst. When poisoning occurs, catalytic activity is impeded through prolonged contact with interfering elements that either physically block the active sites or interact chemically with the active material. The lead in fuel antiknock agents and the phosphorus in oil additives are the most important poisons. Though lead antiknock agents are not added to the gasoline used with catalyst-equipped vehicles, this "unleaded" fuel can be contaminated with small amounts ($\sim$10 mg Pb/dm^3) from the fuel distribution system. Between 10 and 30 percent of the lead in the fuel ends up on the catalyst. Its effect on catalyst conversion efficiency depends on the amount of lead on the catalyst, as shown in Fig. 11-55. Lead depresses the catalytic oxidation of HC to a greater extent than oxidation of CO. The oxidation activity of saturated hydrocarbons is particularly depressed. The extent of the poisoning that results from traces of critical elements in the fuel and oil depends on which elements are present and the amounts absorbed, as well as the composition of the catalyst and its operating conditions (especially its temperature).[68] Sintering is promoted by exposure of the catalyst to high operating temperatures. It involves the migration and agglomeration of sites, thus decreasing their active surface area. Sintering slows warm-up but has minimal effect on the steady-state conversion efficiency.

The oxidation kinetics of CO over Pt and Pd noble metal catalysts can be described by

$$\frac{d[\mathrm{CO}]}{dt} = \frac{K_1 p_{\mathrm{CO}} p_{\mathrm{O_2}}}{(1 + K_2 p_{\mathrm{CO}} + K_3 p_{\mathrm{HC}})^2 (1 + K_4 p_{\mathrm{NO}}^n)} \tag{11.44}$$

where K_1 to K_4 and n are constants at any given temperature, and p_{CO}, $p_{\mathrm{O_2}}$, p_{HC}, and p_{NO} are the partial pressures of carbon monoxide, oxygen, hydrocarbons, and nitric oxide, respectively. A similar relationship can be written for the olefinic and aromatic HC oxidation rate (these being the most reactive hydrocarbons). These relationships incorporate the fact that the rates of CO and HC oxidation are inhibited by high CO and reactive HC concentrations, and that NO concentrations in the range 0 to 1000 ppm strongly inhibit oxidation also. The oxidation rate of paraffin hydrocarbons varies with the first power of the HC partial pres-

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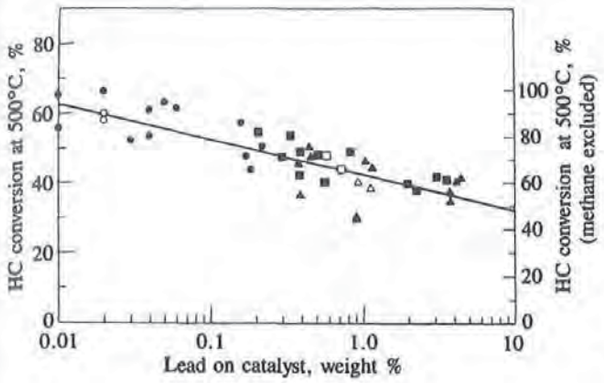


FIGURE 11-55
HC conversion efficiency as a function of lead concentration on catalyst. Total HC conversion on left; nonmethane HC conversion on right. 0.001–0.013 g Pb/dm^3 in fuel.[68]

sure, is inhibited by CO, olefins, and NO, and increases as the O_2 partial pressure is decreased to near-stoichiometric values.[68]

It will be apparent from the above that two extremely important considerations for successful use of catalysts for automotive applications are the test procedure that is used to measure emissions and the methods used to determine if the catalyst has the required durability. The U.S. Federal Test Procedure requires that the vehicle under test be at a temperature of 16 to 30°C for 12 hours prior to the test and that emissions are measured from the time the ignition key is turned on until the test has ended. In spark-ignition engines the mixture fed into the engine during start-up is enriched substantially (carburetors have a choke to accomplish this; additional fuel is injected with port or manifold fuel injection). The rationale is that if sufficient fuel is added to the inlet air, enough will evaporate to start the engine. However, until the rest of the fuel is consumed, the engine then runs rich and emits high concentrations of CO and HC. The catalyst is cold at this time, and until it warms up, these emissions will pass through without reaction. It is important that the catalyst be brought to its light-off temperature as quickly as possible (preferably in less than 60 s) and that mixture enrichment during start-up be held to a minimum. Thus catalysts should have low thermal inertia for rapid warm-up and low light-off temperatures for CO and HC, so they become effective quickly. The closer they are placed to the engine the faster they will reach light-off. However, they will then experience higher temperatures when fully warmed up and so be more susceptible to thermal degradation. While it is not too difficult to prepare catalysts that are highly effective when fresh, it is much more difficult to maintain effectiveness over extended mileage (50,000 miles) in which the catalyst is exposed to high temperatures and catalyst poisons. These can degrade both cold-start and warmed-up performance. Also, catalyst durability is affected by engine durability. Any engine malfunction that will expose the catalyst to excessive amounts of unburned fuel (such as ignition failure, misfire with too lean a mixture, or excessively rich operation) will severely overheat the catalyst.

Oxidation-catalyst-equipped vehicles may emit sulfuric acid aerosol. Unleaded gasoline contains 150 to 600 ppm by weight of S, which leaves the

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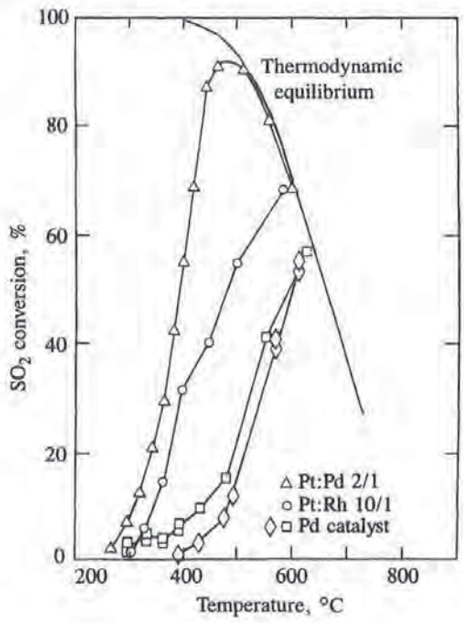


FIGURE 11-56
SO_2 conversion to SO_3 as a function of temperature with 5% O_2 concentration and no reducing gases present. Space velocity (volume flow per unit volume) ~ 10 s^{-1}. Results for Pt–Pd, Pt–Rh, and Pd catalysts.[68]

combustion chamber as SO_2. This SO_2 can be oxidized by the catalyst to SO_3 which combines with water at ambient conditions to form an H_2SO_4 aerosol. The SO_3 can be chemisorbed on the alumina catalyst surface; when large pellet beds are used, considerable storage of SO_3 at temperatures $<500°C$ can occur. At higher catalyst temperatures, this stored SO_3 is emitted as an SO_3–SO_2 mixture. SO_3 production can be controlled by lowering or raising the catalyst temperature. Figure 11-56 shows that at low temperatures SO_3 production is kinetically limited; at high temperatures SO_3 production is thermodynamically limited. Palladium and rhodium produce less SO_3 than Pt and have comparable HC and CO catalytic activity. By decreasing oxygen concentrations leaving the catalyst to ~1 percent, SO_3 production can be substantially reduced.[68]

NO CATALYSIS. NO is removed by reduction using the CO, hydrocarbons, and H_2 in the exhaust. The reactions are shown in Table 11.11. No catalyst is available for the decomposition of NO to O_2 and N_2 (thermodynamically favored at exhaust temperatures) which is sufficiently active for use in engine exhausts. NO reduction can be carried out under rich conditions where there is an excess of reducing species over oxidizing species. The catalyst used under these conditions is referred to as an *NO reduction catalyst*. Such a system requires a follow-up oxidation catalyst, together with addition of air from an air pump before the oxidation catalyst, to remove the remaining CO and hydrocarbons. Such a two-bed system can remove all three pollutants (NO, CO, and HC) from the exhaust. However, the rich operation necessary for NO reduction results in a fuel consumption penalty and constrains the performance of the NO catalyst since a fraction of the NO removed is converted to ammonia NH_3 rather than N_2. NH_3

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TABLE 11.11
Possible NO reactions under reducing conditions[68]

1. $NO + CO \rightarrow \frac{1}{2}N_2 + CO_2$
2. $2NO + 5CO + 3H_2O \rightarrow 2NH_3 + 5CO_2$
3. $2NO + CO \rightarrow N_2O + CO_2$
4. $NO + H_2 \rightarrow \frac{1}{2}N_2 + H_2O$
5. $2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O$
6. $2NO + H_2 \rightarrow N_2O + H_2O$

Reactions 3 and 6 occur at 200°C, which is below that usually found in auto exhausts.

formation under rich operation in the first bed must be small in this two-bed system because the second (oxidation) catalyst readily oxidizes NH_3 back to NO. Reduction of NO by CO or H_2 can be accomplished by base metal catalysts (e.g., CuO, NiO) in the temperature range 350 to 600°C. However, these catalyst materials are deactivated by sulfur and have shown limited thermal stability when used in vehicle exhausts. Alumina-supported noble metal catalysts reduce NO with CO–H_2 mixtures. Their NO-reduction activity is in the order Ru > Rh > Pd > Pt. Ruthenium (Ru) and rhodium (Rh) produce considerably less NH_3 than Pd or Pt under slightly rich conditions. While these properties make ruthenium a desirable NO catalyst, it forms volatile oxides under oxidizing conditions which results in loss of ruthenium from the alumina support.[68]

THREE-WAY CATALYSTS. If an engine is operated at all times with an air/fuel ratio at or close to stoichiometric, then both NO reduction and CO and HC oxidation can be done in a single catalyst bed. The catalyst effectively brings the exhaust gas composition to a near-equilibrium state at these exhaust conditions; i.e., a composition of CO_2, H_2O, and N_2. Enough reducing gases will be present to reduce NO and enough O_2 to oxidize the CO and hydrocarbons. Such a catalyst is called a *three-way catalyst* since it removes all three pollutants simultaneously. Figure 11-57 shows the conversion efficiency for NO, CO, and HC as a function of the air/fuel ratio. There is a narrow range of air/fuel ratios near stoichiometric in which high conversion efficiencies for all three pollutants are achieved. The width of this window is narrow, about 0.1 air/fuel ratios (7×10^{-3} in equivalence ratio units) for catalyst with high mileage use, and depends on catalyst formulation and engine operating conditions.

This window is sufficiently narrow to be beyond the control capabilities of an ordinary carburetor, though it can sometimes be achieved with sophisticated carburetors and fuel-injection systems. Thus closed-loop control of equivalence ratio has been introduced. An oxygen sensor in the exhaust is used to indicate whether the engine is operating on the rich or lean side of stoichiometric, and provide a signal for adjusting the fuel system to achieve the desired air-fuel mixture (see Sec. 7.4). Holding the equivalence ratio precisely on the chosen near-

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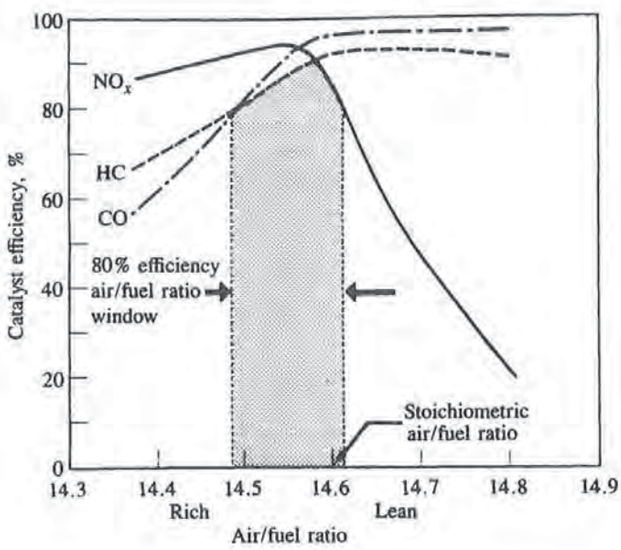


FIGURE 11-57
Conversion efficiency for NO, CO, and HC for a three-way catalyst as a function of exhaust gas air/fuel ratio.[68]

stoichiometric value is not a practical expectation of such a feedback system, and the equivalence ratio oscillates around the set point in an approximately periodic manner as the fuel flow is varied. Experimental data show that there is a considerable widening of the air/fuel ratio window where all three pollutants are effectively removed, with cyclic variation of the fuel flow. The maximum conversion in the middle of the window is reduced, however, from its value when there are no fluctuations. The effect of fluctuations depends on the frequency; frequencies of about 0.5 to 1 hertz are most effective and the usable window (at lower conversion efficiencies) can be broadened to about 1 air/fuel ratio. Some of the benefits of fluctuations in equivalence or air/fuel ratios are available even without any deliberate attempt to produce such variations with closed-loop feedback. Open-loop systems exhibit variations in the air/fuel ratio during normal vehicle operation.

Because of these cyclic variations in exhaust gas composition about a set point close to stoichiometric, it is desirable that the catalyst be able to reduce NO when a slight excess of oxygen is present (on the lean side) and remove CO and HC when there is a slight deficiency of oxygen (on the rich side). Rhodium is the principal ingredient used in commercial catalysts to remove NO. It is very active for NO reduction, is much less inhibited by CO and sulfur compounds, and produces less NH_3 than Pt. To remove NO under slightly lean-of-stoichiometric conditions, the catalyst must react the CO, H_2, or HC with NO rather than with O_2, as the exhaust gas passes through the catalyst bed. Rhodium shows some NO reduction activity slightly lean of stoichiometric. On the rich side, the three-way catalyst window is determined by hydrocarbon and CO removal. Platinum is most commonly used for HC and CO oxidation; it has good activity under stoichiometric and slightly lean conditions. When sufficient rhodium is present, the participation of Pt in NO removal is minimal. In the rich

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regime, the three-way catalyst consumes all the oxygen that is present in the exhaust, and as a consequence removes an equivalent amount of CO, H_2, and hydrocarbons; it is thought that the H_2 is removed first. In addition, the water-gas shift reaction

$$CO + H_2O = H_2 + CO_2$$

and the steam-reforming reaction

$$\text{Hydrocarbon} + H_2O \rightarrow CO, CO_2, H_2$$

can consume CO and HC. The exhaust contains an H_2/CO ratio of about $\frac{1}{3}$ (see Sec. 4.9.1), where the equilibrium ratio at 500°C is about 4. Considerable CO removal can be expected if the water-gas shift equilibrium is approached. Platinum is active in promoting this equilibrium. For large molecular weight paraffin hydrocarbons, and for olefins and aromatic hydrocarbons, the equilibrium for the steam-reforming reactions lies to the right. This reaction can therefore lead to considerable hydrocarbon removal. Rhodium is particularly active in the steam-reforming reaction; platinum is also active.[68]

The conversions of NO, CO, and hydrocarbons in a three-way catalyst operated with cyclical variations in equivalence ratio are larger than estimates based on summation of steady-state values during the cycle. At least part of the improved performance is thought to be due to the ability of the catalyst to undergo reduction-oxidation reactions. Such a catalyst component is usually referred to as an oxygen-storage component. In its oxidized state it can provide oxygen for CO and hydrocarbon oxidation in a rich exhaust gas environment, and in the process be reduced. When the exhaust cycles to lean conditions, this reduced component can react with O_2 or NO (which removes NO directly or indirectly by reducing the O_2 concentration). The oxidized component can then oxidize CO and HC in the next rich cycle, etc. Components such as ReO_2 or CeO_2 which exhibit this "redox" behavior can be included in three-way catalyst formulations. Commercial three-way catalysts contain platinum and rhodium (the ratio Pt/Rh varying substantially in the range 2 to 17) with some A_2O_3, NiO, and CeO_2. Alumina is the preferred support material.[68]

11.6.3 Thermal Reactors

In Secs. 11.3 and 11.4.2 it was explained that oxidation of CO and HC occurred during the expansion and exhaust processes in the cylinder of a conventional spark-ignition engine and, under certain circumstances, in the exhaust system. Oxidation after passage through the exhaust port can be enhanced with a *thermal reactor*—an enlarged exhaust manifold that bolts directly onto the cylinder head. Its function is to promote rapid mixing of the hot exhaust gases with any secondary air injected into the exhaust port (required with fuel-rich engine operation to produce a net oxidizing atmosphere), to remove nonuniformities in temperature and composition in the exhaust gases, and to retain the gases at a high enough

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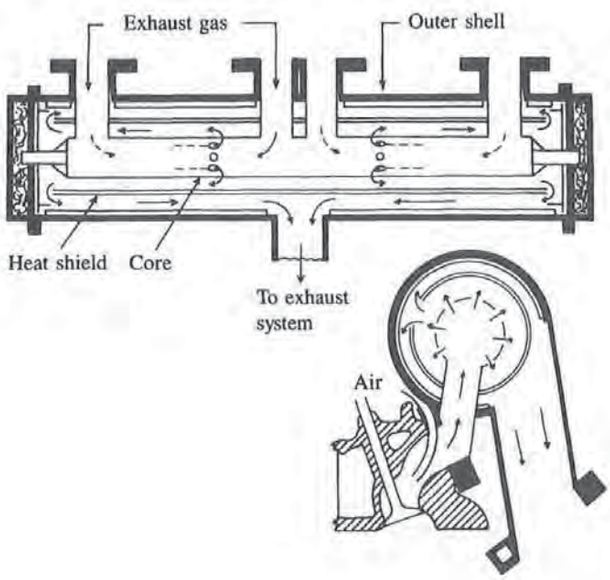


FIGURE 11-58
Schematic of exhaust thermal reactor for HC and CO oxidation.

temperature for sufficient time to oxidize much of the HC and CO which exits the cylinder. An example of a thermal reactor design is shown in Fig. 11-58.

The temperature levels typically required for bulk gas oxidation of HC and CO in a reactor are about 600 and 700°C, respectively. Note that they are considerably higher than those required for equivalent conversion in a catalytic converter and that higher temperatures are required for CO oxidation than for HC oxidation. The exhaust gas temperature in the manifold of a conventional engine is not sufficient to achieve any substantial reduction in engine exhaust port emissions. To achieve greater reductions, the reactor must be designed to reduce heat losses and increase residence time. In addition, to achieve rapid warm-up after engine start, a low thermal inertia reactor is desirable. Typically, a thin steel liner acts as the core of the reactor inside a cast-iron outer casing; with suitably arranged flow paths, this construction holds heat losses to a minimum by thermally isolating the core.

The effectiveness of the reactor depends on its operating temperature, the availability of excess oxygen mixed throughout the reacting gases, and the reactor volume. The operating temperature depends on the reactor inlet gas temperature, heat losses, and the amount of HC, CO, and H_2 burned up in the reactor. This latter factor is important: 1.5 percent CO removal results in a 220 K temperature rise. As a consequence, reactors with fuel-rich cylinder exhaust gas and secondary air give greater fractional reductions in HC and CO emissions than reactors with fuel-lean cylinder exhaust (which do not require any secondary air). As has already been explained, a higher core gas temperature is required to burn up the same fraction of CO which enters the reactor as of HC which enters. For lean engine exhaust gas, where the reactor core gas temperatures are a hundred degrees K lower than under fuel-rich operation, substan-

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tial reductions in CO emissions are difficult to achieve. For very lean operation, HC burnup becomes marginal.

A practical limitation to reactor effectiveness with fuel-rich engine operation is mixing of secondary air and engine exhaust gases in the exhaust port and the reactor core. The secondary air flow with a conventional air pump is effectively shut off by the exhaust blowdown process, and virtually no oxidation occurs in the exhaust port because the air and exhaust gases are segregated. Mixing in the reactor itself is promoted by suitably arranging the reactor inlet and exit ports and by using baffles. In systems with conventional secondary air pumps, maximum reductions in CO and HC occur with 10 to 20 percent excess air in the mixture. However, even with very high reactor core gas temperatures, 100 percent HC and CO oxidation is not achieved due to incomplete mixing. Improved control of secondary air flow has been shown to increase significantly CO emissions burnup.

11.6.4 Particulate Traps

An exhaust treatment technology that substantially reduces diesel engine particulate emissions is the trap oxidizer. A temperature-tolerant filter or trap removes the particulate material from the exhaust gas; the filter is then "cleaned off" by oxidizing the accumulated particulates. This technology is difficult to implement because: (1) the filter, even when clean, increases the pressure in the exhaust system; (2) this pressure increase steadily rises as the filter collects particulate matter; (3) under normal diesel engine operating conditions the collected particulate matter will not ignite and oxidize; (4) once ignition of the particulate occurs, the burnup process must be carefully controlled to prevent excessively high temperatures and trap damage or destruction. Trap oxidizers have been put into production for light-duty automobile diesel engines. Their use with heavy-duty diesel engines poses more difficult problems due to higher particulate loading and lower exhaust temperatures.

Types of particulate filters include: ceramic monoliths, alumina-coated wire mesh, ceramic foam, ceramic fiber mat, woven silica-fiber rope wound on a porous tube. Each of these has different inherent pressure loss and filtering efficiency. Regeneration of the trap by burning up the filtered particulate material can be accomplished by raising its temperature to the ignition point while providing oxygen-containing exhaust gas to support combustion and carry away the heat released. Diesel particulate matter ignites at about 500 to 600°C. This is above the normal temperature of diesel exhaust so either the exhaust gas flowing through the trap during regeneration must be heated (positive regeneration) or ignition must be made to occur at a lower temperature with catalytic materials on the trap or added to the fuel (catalytic regeneration). Catalytic coatings on the trap reduce the ignition temperature by up to 200°C.

Figure 11-59 shows a ceramic-coated trap oxidizer mounted on the exhaust system of a turbocharged IDI diesel engine. The trap is a ceramic honeycomb with half the cells closed at the inlet end and the other half of the cells closed at

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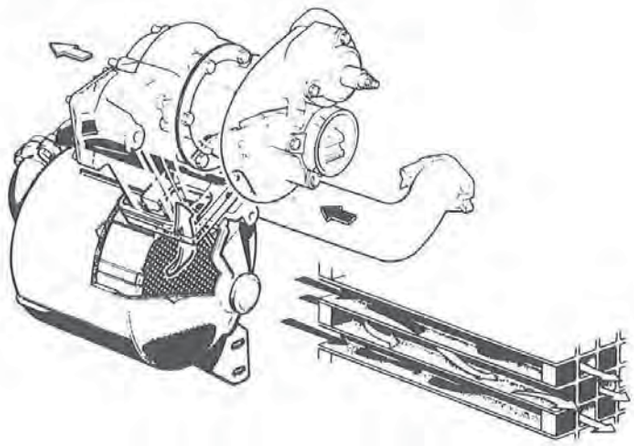


FIGURE 11-59
Catalytic ceramic-monolith particulate trap oxidizer mounted on exhaust of turbocharged automobile diesel engine.[86]

the exit end. Thus the particulate laden exhaust is forced to flow through the porous ceramic cell walls. The outside of the honeycomb is insulated and the trap is mounted close to the engine to maintain as high a trap temperature as possible. The pressure drop across the unloaded trap increases from 0.02 atm at 1000 rev/min to 0.15 atm at the maximum engine speed of 4500 rev/min. As the trap loads up, the pressure drop increases, requiring more fuel to be injected to compensate for the loss in power. This leads to higher exhaust temperature which eventually results in catalytic ignition of the particulate. The particulate oxidation rate depends on the trap temperature. With suitable trap location and design, the regeneration process is largely self-regulating. The particulate emissions from the engine are reduced by 70 percent or more.[86]

PROBLEMS

11.1. Figure 11-2 shows concentrations of NO, CO, and HC in a spark-ignition engine exhaust as a function of fuel/air equivalence ratio. Assume the concentration scale is parts per million. Explain the trends shown as the mixture is first made richer and then leaner than stoichiometric.

11.2. Figure 11-2 is for a spark-ignition engine. Construct a similar qualitative graph of NO, CO, and HC concentrations versus equivalence ratio for a direct-injection four-stroke cycle diesel engine.

11.3. A spark-ignition engine driving a car uses, on average, 120 grams of gasoline per mile traveled. The average emissions from the engine (upstream of the catalyst) are 1.5, 2, and 20 grams per mile of NO_x (as NO_2), HC, and CO, respectively. The engine operates with a stoichiometric gasoline-air mixture. Find the average concentrations in parts per million of NO_x, HC (as ppm C_1), and CO in the engine exhaust.

11.4. Calculate the average combustion inefficiency corresponding to the spark-ignition engine emissions levels given in Prob. 11.3. Include any hydrogen you estimate would be present in the exhaust stream.

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11.5. A three-way catalytic converter is used with the spark-ignition engine in Prob. 11.3. For 10 percent of the driving time, the catalyst is cold and ineffective, and does not reduce the engine's emissions. For 90 percent of the time, the catalyst is hot and has conversion efficiencies as given in Fig. 11-57. Estimate the average *vehicle* emissions of NO_x, HC, and CO in grams per mile.

11.6. Figure 15-11 shows the variation in NO and HC emissions as concentrations (ppm) in the exhaust of a spark-ignition engine as a function of speed and load. Convert these data to graphs of indicated specific NO and HC emissions (g/kW · h) versus speed and imep. Assume η_v (based on atmospheric air density) = imep (kPa) $\times 10^{-3}$.

11.7. Use the data in Fig. 11-44 to estimate:

(*a*) The exhaust particulate emissions as a fraction of the maximum particulate loading during the cycle.

(*b*) The maximum measured soot loading and the exhaust soot loading as fractions of the fuel carbon.

(*c*) The equivalent sphere size of each soot particle at the number density peak (22° ATC) and in the exhaust.

Assume a particulate density of 2 g/cm^3. Note that the gas volumes in Fig. 11-44 are determined at standard temperature and pressure.

11.8. Explain the following emissions trends. Highest marks will be given for succinct summaries of the *important* technical issues.

(*a*) Nitric oxide (NO) emissions from diesels and spark-ignition engines as the equivalence ratio is varied show significantly different behavior (see Figs. 11-9 and 11-16). Redraw these graphs on the same plot and explain the different trends for these two types of engines as ϕ decreases on the lean side of stoichiometric.

(*b*) Recirculation of a fraction of the exhaust gases to the intake is used to control engine nitric oxide emissions at part load. Exhaust gas recycle is usually more effective with spark-ignition engines than with diesels, as shown in Fig. P11-8. Explain why these trends are different.

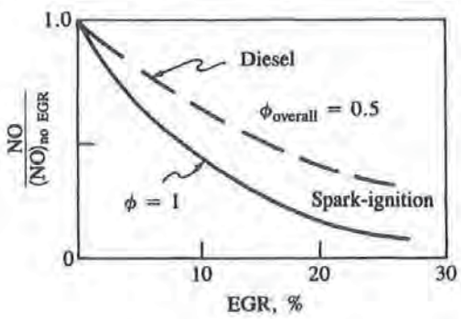


FIGURE P11-8

(*c*) Brake specific particulate emissions from diesels are a major problem. Particulate emissions from conventional spark-ignition engines are negligible. Briefly explain why the particulate emission levels from these two types of engines are so different in magnitude.

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(*d*) Diesels have low carbon monoxide (CO) emissions. Spark-ignition engine CO emissions when *averaged* over a typical urban automobile trip (cold engine start, warm-up, cruise, idle, acceleration, etc.) are substantial and require a catalyst for effective control. Explain this difference in average CO emissions (upstream of any catalyst) from these two types of engines.

11.9. The following questions refer to an engine with these geometric and operating characteristics (see Fig. 11-26*a*): $\phi = 1.0$; compression ratio = 8 : 1; bore = 100 mm; stroke = 100 mm; piston diameter above top ring = 99.4 mm; distance from piston crown top to top ring = 9.52 mm; volumetric efficiency = 0.8; temperature in cylinder at the start of compression = 333 K; pressure in cylinder at start of compression = 1 atm; mixture temperature before entering cylinder = 30°C; brake specific fuel consumption = 300 g/kW · h.

A substantial fraction of spark-ignition engine hydrocarbon emissions comes from the crevice between the piston crown and cylinder wall. Gas is forced into this crevice as the cylinder pressure increases and flows out of this crevice as the cylinder pressure decreases. The gas in the crevice can be assumed to be at the wall temperature, 400 K. The gas pushed into the crevice ahead of the flame is unburned mixture; the gas pushed in behind the flame is burned mixture. About two-thirds of the crevice gas is unburned. The maximum cylinder pressure is 3 MPa.

(*a*) Calculate the mass fraction of the cylinder gas which is in the crevice between the piston and cylinder wall and above the first piston ring, at the time of peak pressure.

(*b*) Assuming that half of the unburned fuel in this region is oxidized within the cylinder and a further one-third is oxidized in the exhaust port, calculate the engine HC emissions from this source in parts per million (ppm C_1) by volume.

(*c*) Calculate the ratio of brake specific hydrocarbon emissions to brake specific fuel consumption.

(*d*) Calculate the brake specific hydrocarbon emissions in grams of HC per kilowatt-hour.

11.10. Nitric oxide, NO, forms via reactions (11.1) to (11.3). Reaction (11.1) is "slow" and reactions (11.2) and (11.3) are "fast," so the initial rate of formation of NO is given by Eq. (11.8):

$$\frac{d[\mathrm{NO}]}{dt} = 2k_1^+[\mathrm{N_2}]_e[\mathrm{O}]_e$$

where [ ] denote concentrations in gram-moles per cubic centimeter, k_1^+ is the rate constant for reaction (11.1), and the factor of 2 enters because the N atom formed in (11.1) immediately reacts via (11.2) or (11.3) to give an additional NO molecule:

$$k_1^+ = 7.6 \times 10^{13} \exp\left(\frac{-38{,}000}{T}\right) \qquad \mathrm{cm^3/gmol \cdot s}$$

where T is in kelvin.

Using the equilibrium composition data provided for mole fraction atomic oxygen (O), molecular nitrogen (N_2), and nitric oxide (NO):

(*a*) Plot the formation rate of NO as a function of the equivalence ratio at 3000 K and 5.5 MPa, and as a function of temperature for a stoichiometric mixture at 5.5 MPa.

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(*b*) Estimate approximately the time taken to reach equilibrium NO levels at $\phi = 1$, 2750 K and 3000 K, 5.5 MPa.

(*c*) If the stoichiometric mixture inducted into the engine reaches 3000 K and 5.5 MPa after combustion, in the absence of any exhaust gas recirculation, calculate the percentage of the exhaust that must be recycled to the intake (at the initial intake temperature) to reduce the NO formation rate by a factor of 4 (assume the final pressure 5.5 MPa stays the same; of course, the final temperature decreases as the exhaust gas is recycled).

$p = 5.5$ MPa

		Mole fraction	
ϕ	T(K)	O	N_2
0.9	3000	2.1×10^{-3}	0.73
1.0	3000	1.5×10^{-3}	0.73
1.1	3000	1×10^{-3}	0.73

$\phi = 1.0$, $p = 5.5$ MPa

	Mole fraction		
T(K)	O	N_2	NO
2500	6×10^{-5}	0.73	—
2750	5×10^{-4}	0.73	4×10^{-3}
3000	1.5×10^{-3}	0.73	8×10^{-3}

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CHAPTER 12

ENGINE HEAT TRANSFER

12.1 IMPORTANCE OF HEAT TRANSFER

The peak burned gas temperature in the cylinder of an internal combustion engine is of order 2500 K. Maximum metal temperatures for the inside of the combustion chamber space are limited to much lower values by a number of considerations, and cooling for the cylinder head, cylinder, and piston must therefore be provided. These conditions lead to heat fluxes to the chamber walls that can reach as high as 10 MW/m^2 during the combustion period. However, during other parts of the operating cycle, the heat flux is essentially zero. The flux varies substantially with location: regions of the chamber that are contacted by rapidly moving high-temperature burned gases generally experience the highest fluxes. In regions of high heat flux, thermal stresses must be kept below levels that would cause fatigue cracking (so temperatures must be less than about 400°C for cast iron and 300°C for aluminum alloys). The gas-side surface of the cylinder wall must be kept below about 180°C to prevent deterioration of the lubricating oil film. Spark plug and valves must be kept cool to avoid knock and preignition problems which result from overheated spark plug electrodes or exhaust valves. Solving these engine heat-transfer problems is obviously a major design task.

Heat transfer affects engine performance, efficiency, and emissions. For a given mass of fuel within the cylinder, higher heat transfer to the combustion chamber walls will lower the average combustion gas temperature and pressure,

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and reduce the work per cycle transferred to the piston. Thus specific power and efficiency are affected by the magnitude of engine heat transfer. Heat transfer between the unburned charge and the chamber walls in spark-ignition engines affects the onset of knock which, by limiting the compression ratio, also influences power and efficiency. Most critical is heat transfer from the hot exhaust valve and piston to mixture in the end-gas region. Changes in gas temperature due to the heat-transfer impact on emission formation processes, both within the engine's cylinder and in the exhaust system where afterburning of CO and HC occurs. The exhaust temperature also governs the power that can be obtained from exhaust energy recovery devices such as a turbocharger turbine. Friction is both affected by engine heat transfer and contributes to the coolant load. The cylinder liner temperature governs the piston and ring lubricating oil film temperature, and hence its viscosity. Piston and liner distortion due to temperature nonuniformities have a significant impact on the piston component of engine friction. Some of the mechanical energy dissipated due to friction must be rejected to the atmosphere by the cooling system. The fan and water pump power requirements are determined by the magnitude of the heat rejected. The importance of engine heat transfer is clear.

To examine heat transfer more fully, it is helpful to divide the engine into its subsystems. The intake system consists of intake manifold and inlet ports and valves. Heat transfer to the inflowing charge reduces volumetric efficiency (see Sec. 6.2.1). However, in spark-ignition engines, the intake mixture is heated, with carbureted and single-point injected engines, to aid in vaporizing the fuel (see Sec. 7.6.3). Within the engine cylinder, the temperature of the charge relative to the wall temperature and the flow field vary enormously throughout the cycle. Both of these variables have a major influence on heat transfer. During the intake process, the incoming charge is usually cooler than the walls and the flow velocities are high. During compression the charge temperature rises above the wall temperature, and gas velocities decrease (see Sec. 8.2.2). Heat transfer is now from the cylinder gases to the chamber walls. During combustion gas temperatures increase substantially and the gas expansion which occurs on combustion produces increased gas motion. This is the period when heat-transfer rates to the walls are highest. Also, as the cylinder pressure rises, a small fraction of the cylinder charge is forced into crevice regions, resulting in additional heat transfer (see Sec. 8.6). During expansion, gas temperatures decrease so heat-transfer rates decrease. When the exhaust valve opens, however, the blowdown process (Sec. 6.5) produces high velocities within the cylinder, and past the exhaust valve and in the exhaust port. Substantial heat transfer from the exhausting gases to the valve, port, and (to a lesser extent) manifold occurs during the exhaust process. An example of how the heat-transfer rate to the total combustion chamber walls varies throughout the four-stroke operating cycle of a spark-ignition engine is shown in Fig. 14-9. The heat-transfer rate was estimated from the cylinder pressure, unburned and burned gas temperatures, combustion chamber surface area, and wall temperature, assuming gas velocities scaled with mean piston speed. An ability to predict the magnitude of the heat transfer between the working fluid,

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the walls of the intake system, combustion chamber, and exhaust system, and to the coolant is of obvious importance to the engine designer.

12.2 MODES OF HEAT TRANSFER

The following modes of heat transfer are important.

12.2.1 Conduction

Heat is transferred by molecular motion, through solids and through fluids at rest, due to a temperature gradient. The heat transfer by conduction, per unit area per unit time, $\dot{\mathbf{q}}$, in a steady situation is given by Fourier's law:

$$\dot{\mathbf{q}} = -k\nabla T \tag{12.1}$$

where k is the thermal conductivity. For a steady one-dimensional temperature variation

$$\dot{q}_x = \frac{\dot{Q}}{A} = -k\frac{dT}{dx}$$

Heat is transferred by conduction through the cylinder head, cylinder walls, and piston; through the piston rings to the cylinder wall; through the engine block and manifolds.

12.2.2 Convection

Heat is transferred through fluids in motion and between a fluid and solid surface in relative motion. When the motion is produced by forces other than gravity, the term *forced convection* is used. In engines the fluid motions are turbulent (see Chap. 8).

Heat is transferred by forced convection between the in-cylinder gases and the cylinder head, valves, cylinder walls, and piston during induction, compression, expansion, and exhaust processes. Heat is transferred by forced convection from the cylinder walls and head to the coolant (which may be liquid or gas), and from the piston to the lubricant or other piston coolant. Substantial convective heat transfer occurs to the exhaust valve, exhaust port, and exhaust manifold during the exhaust process. Heat transfer by convection in the inlet system is used to raise the temperature of the incoming charge. Heat is also transferred from the engine to the environment by convection.

In steady-flow forced-convection heat-transfer problems, the heat flux $\dot{q}$ transferred to a solid surface at temperature T_w from a flowing fluid stream at temperature T is determined from the relation

$$\dot{q} = h_c(T - T_w) \tag{12.2}$$

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where h_c is called the heat-transfer coefficient. For many flow geometries (such as flow through pipes or over a plate), h_c is given by relations of the form

$$\left(\frac{h_c L}{k}\right) = \text{constant} \times \left(\frac{\rho v L}{\mu}\right)^m \left(\frac{c_p \mu}{k}\right)^n \tag{12.3}$$

where L and v are a characteristic length and velocity. The terms in brackets from left to right are the Nusselt, Reynolds, and Prandtl dimensionless numbers, respectively. For gases, the Prandtl number ($c_p \mu/k$) varies little and is about 0.7 (see Sec. 4.8).

When boiling occurs at the surface (i.e., vapor is formed in the liquid), as may be the case in high heat flux areas on the coolant side in water-cooled engines, then different relationships for h_c must be used.

12.2.3 Radiation

Heat exchange by radiation occurs through the emission and absorption of electromagnetic waves. The wavelengths at which energy is transformed into thermal energy are the visible range (0.4 to 0.7 μm) and the infrared (0.7 to 40 μm). Heat transfer by radiation occurs from the high-temperature combustion gases and the flame region to the combustion chamber walls (although the magnitude of this radiation heat transfer relative to convective heat transfer is only significant in diesel engines). Heat transfer by radiation to the environment occurs from all the hot external surfaces of the engine.

The theory of radiant heat transfer starts from the concept of a "black body," i.e., a body that has a surface that emits or absorbs equally well radiation of all wavelengths and that reflects none of the radiation falling on it. The heat flux from one plane black body at temperature T_1 to another at temperature T_2 parallel to it across a space containing no absorbing material is given by

$$\dot{q} = \sigma(T_1^4 - T_2^4) \tag{12.4}$$

where σ is the Stefan-Boltzmann constant 5.67×10^{-8} W/m$^2 \cdot$K^4. Real surfaces are not "black" but reflect radiation to an extent which depends on wavelength. Gases are far from this black-body idealization. They absorb and emit radiation almost exclusively within certain wavelength bands characteristic of each species. These departures from black-body behavior are usually dealt with by applying a multiplying factor (an emissivity, ε) to Eq. (12.4). Similarly, a "shape factor" is applied to account for the fact that the angle of incidence of the radiation usually varies over any actual surface. These factors can be calculated for simple cases.

12.2.4 Overall Heat-Transfer Process

Figure 12-1 shows, schematically, the overall heat-transfer process from the gases within the cylinder through the combustion chamber wall to the coolant flow. The heat flux into the wall has in general both a convective and a radiation component. The heat flux is conducted through the wall and then convected from

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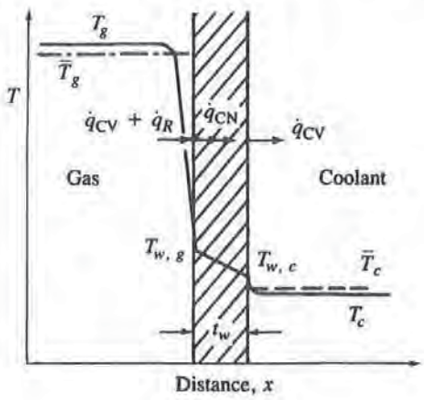


FIGURE 12-1
Schematic of temperature distribution and heat flow across the combustion chamber wall.

the wall to the coolant. A schematic temperature profile, and mean gas and coolant temperatures, $\bar{T}_g$ and $\bar{T}_c$, are shown.

In internal combustion engines, throughout each engine operating cycle, the heat transfer takes place under conditions of varying gas pressure and temperature, and with local velocities which vary more or less rapidly depending on intake port and combustion chamber configuration (see Chap. 8). In addition, the surface area of the combustion chamber varies through the cycle. The heat flux into the containing walls changes continuously from a small negative value during the intake process to a positive value of order several megawatts per square meter early in the expansion process. The flux variation lags behind the change in gas temperature. This lag between heat flux and driving temperature difference is clearly perceptible[1] but the precision of measurements to date suffice only for a rough estimate of its magnitude. Generally, investigators have concluded that the assumption that the heat-transfer process is *quasi steady* is sufficiently accurate for most calculation purposes. However, gas temperature and gas velocities vary significantly across the combustion chamber. The heat flux distribution over the combustion chamber walls is, therefore, nonuniform.

For a steady one-dimensional heat flow through a wall as indicated in Fig. 12-1, the following equations relate the heat flux $\dot{q} = \dot{Q}/A$ and the temperatures indicated:

Gas side:
$$\dot{q} = \dot{q}_{CV} + \dot{q}_R = h_{c,g}(\bar{T}_g - T_{w,g}) + \sigma\varepsilon(\bar{T}_g^4 - T_{w,g}^4) \tag{12.5}$$

where ε is the emissivity. The radiation term is generally negligible for SI engines.

Wall:
$$\dot{q} = \dot{q}_{CN} = \frac{k(T_{w,g} - T_{w,c})}{t_w} \tag{12.6}$$

Coolant side:
$$\dot{q} = \dot{q}_{CV} = h_{c,c}(T_{w,c} - \bar{T}_c) \tag{12.7}$$

If $h_{c,g}$ and $h_{c,c}$ are known, the temperatures $\bar{T}_g$, $T_{w,g}$, $T_{w,c}$, and $\bar{T}_c$ can be related to each other.

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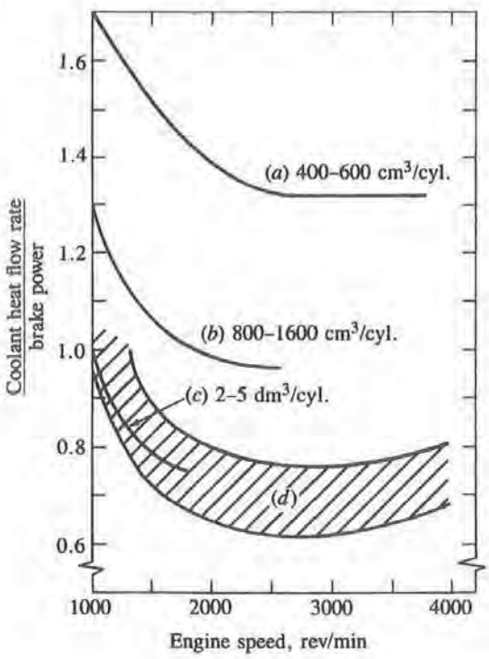


FIGURE 12-2
Ratio of coolant heat flow rate to brake power as a function of engine speed. Different size and types of engines: (*a*) small automotive diesels; (*b*) larger automotive diesels; (*c*) various diesels; (*d*) spark-ignition engines. (*Developed from Howarth.*[2])

12.3 HEAT TRANSFER AND ENGINE ENERGY BALANCE

Figure 12-2 shows the magnitude of the heat-rejection rate to the coolant relative to the brake power for a range of engine types and sizes at maximum power. This ratio decreases with increasing engine speed and with increasing engine size. The smaller diesel engine designs use higher gas velocities to achieve the desired fuel-air mixing rates and have less favorable surface/volume ratios (see Sec. 10.2).

An overall first law energy balance for an engine provides useful information on the disposition of the initial fuel energy. For a control volume which surrounds the engine (see Fig. 3-8), the steady-flow energy-conservation equation is

$$\dot{m}_f h_f + \dot{m}_a h_a = P_b + \dot{Q}_{\text{cool}} + \dot{Q}_{\text{misc}} + (\dot{m}_f + \dot{m}_a)h_e \tag{12.8}$$

where P_b is the brake power, $\dot{Q}_{\text{cool}}$ is the heat-transfer rate to the cooling medium, $\dot{Q}_{\text{misc}}$ is the heat rejected to the oil (if separately cooled) plus convection and radiation from the engine's external surface. It proves convenient to divide the exhaust enthalpy h_e into a sensible part $h_{e,s} = h_e(T) - h_e(298\ \text{K})$, plus the exhaust reference state enthalpy (see Sec. 4.5). Then Eq. (12.8) can be written:

$$P_b + \dot{Q}_{\text{cool}} + \dot{Q}_{\text{misc}} + \dot{H}_{e,\text{ic}} + \dot{m}h_{e,s} = \dot{m}_f Q_{\text{LHV}} \tag{12.9}$$

where $\dot{H}_{e,\text{ic}}$ represents the exhaust enthalpy loss due to incomplete combustion. Typical values of each of these terms relative to the fuel flow × heating value are given in Table 12.1.

The energy balance within an engine is more complicated and is illustrated

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TABLE 12.1
Energy balance for automotive engines at maximum power

	P_b	$\dot{Q}_{cool}$	$\dot{Q}_{misc}$	$\dot{H}_{e,ic}$	$\dot{m}h_{e,s}$
	(percentage of fuel heating value)				
SI engine	25–28	17–26	3–10	2–5	34–45
Diesel	34–38	16–35	2–6	1–2	22–35

Sources: From Khovakh,[3] Sitkei,[4] and Burke *et al.*[5]

in the energy flow diagram in Fig. 12-3. The indicated power is the sum of the brake power and the friction power. A substantial part of the friction power (about half) is dissipated between the piston and piston rings and cylinder wall and is transferred as thermal energy to the cooling medium. The remainder of the friction power is dissipated in the bearings, valve mechanism, or drives auxiliary devices, and is transferred as thermal energy to the oil or surrounding environment (in $\dot{Q}_{misc}$). The enthalpy initially in the exhaust gases can be subdivided into the following components: a sensible enthalpy (60 percent), an exhaust kinetic energy (7 percent), an incomplete combustion term (20 percent), and a heat transfer to the exhaust system (12 percent) (part of which is radiated

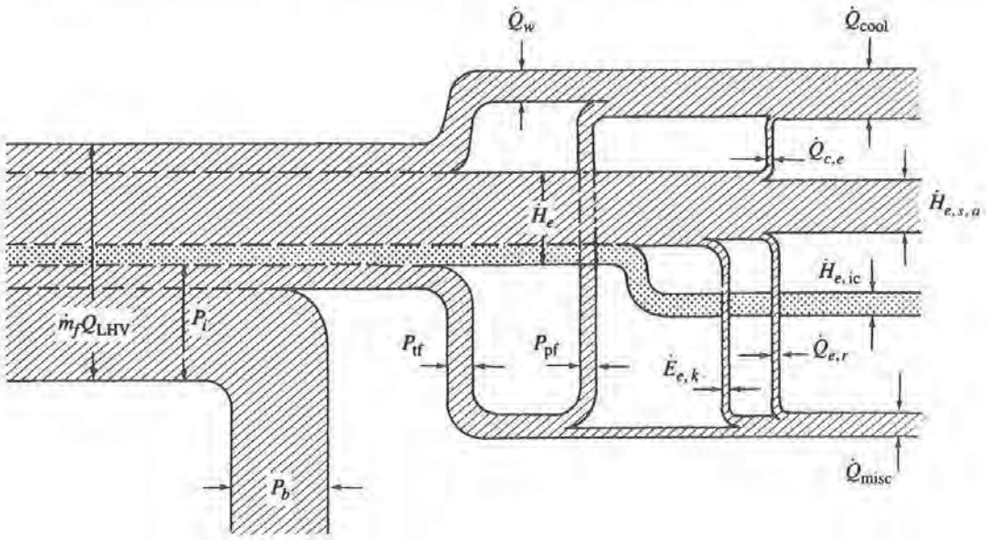


FIGURE 12-3
Energy flow diagram for IC engine. ($\dot{m}_f Q_{LHV}$) = fuel flow rate × lower heating value, $\dot{Q}_w$ = heat-transfer rate to combustion chamber wall, $\dot{H}_e$ = exhaust gas enthalpy flux, P_b = brake power, P_{tf} = total friction power, P_i = indicated power, P_{pf} = piston friction power, $\dot{Q}_{cool}$ = heat-rejection rate to coolant, $\dot{Q}_{c,e}$ = heat-transfer rate to coolant in exhaust ports, $\dot{H}_{e,s,a}$ = exhaust sensible enthalpy flux entering atmosphere, $\dot{H}_{e,ic}$ = exhaust chemical enthalpy flux due to incomplete combustion, $\dot{Q}_{e,r}$ = heat flux radiated from exhaust system, $\dot{E}_{e,k}$ = exhaust kinetic energy flux, $\dot{Q}_{misc}$ = sum of remaining energy fluxes and transfers.

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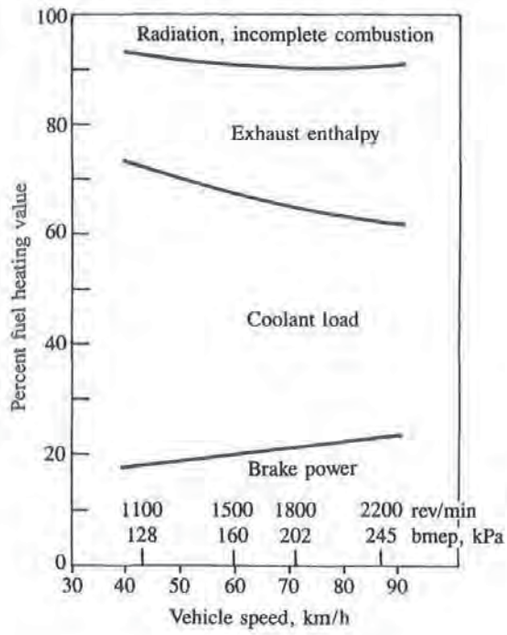


FIGURE 12-4
Brake power, coolant load, sensible exhaust enthalpy, and miscellaneous energy transfers as percent of fuel flow × heating value for spark-ignition engine at road-load operating conditions.[6]

to the environment and the remainder ends up in the cooling medium).† Thus the heat carried away by the coolant medium consists of heat transferred to the combustion chamber walls from the gases in the cylinder, heat transferred to the exhaust valve and port in the exhaust process, and a substantial fraction of the friction work.

At part-load, a greater fraction of the fuel heating value is absorbed into the coolant. Figure 12-4 shows data for a six-cylinder SI engine operated at road-load over a range of vehicle speeds. At low speeds and loads, the coolant heat-transfer rate is 2 to 3 times the brake power.

Although the heat losses are such a substantial part of the fuel energy input, elimination of heat losses would only allow a fraction of the heat transferred to the combustion chamber walls to be converted to useful work. The remainder would leave the engine as sensible exhaust enthalpy. Consider this example for an automotive high-speed naturally aspirated CI engine with a compression ratio of 15. The indicated efficiency is 45 percent, and 25 percent of the fuel energy is carried away by the cooling water. Of this 25 percent, about 2 percent is due to friction. Of the remaining 23 percent, about 8 percent is heat loss during combustion, 6 percent heat loss during expansion, and 9 percent heat loss during exhaust. Of the 8 percent lost during combustion about half (or 4 percent of the fuel energy) could be converted into useful work on the piston (see Fig. 5-9). Of the 6 percent heat loss during expansion, about one-third (or 2 percent) could

† The percentages are approximate.

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have been utilized. Thus, of the 25 percent lost to the cooling system, only about 6 percent could have been converted to useful work on the piston, which would increase the indicated efficiency of the engine from 45 to 51 percent.

For a spark-ignition engine, the conversion to useful work will be lower, because the compression ratio is lower. However, as shown in Fig. 12-4, the heat losses at part-load (an important operating regime for automobile use) are a substantially larger fraction of the fuel heating value. Studies with computer simulations of the SI engine operating cycle indicate that at typical part-load conditions a proportional reduction in combustion-chamber-wall heat losses of 10 percent results in a proportional increase (improvement) in brake fuel conversion efficiency of about 3 percent.[7]

12.4 CONVECTIVE HEAT TRANSFER

12.4.1 Dimensional Analysis

While the overall time-averaged heat transfer to the coolant medium is adequate for some design purposes, the instantaneous heat flux during the engine cycle is a necessary input for realistic cycle calculations (see Sec. 14.4) and provides the fundamental input for obtaining the heat flux distribution to various parts of an operating engine. Equations (12.5), (12.6), and (12.7) provide the framework for calculating the heat flux $\dot{q}$, based on the assumption that at each point in the cycle the heat-transfer process is quasi steady. For example, neglecting radiation, if $\bar{T}_g$, $\bar{T}_{w,g}$, and $h_{c,g}$ can be calculated at each point in the cycle, $q(\theta)$ is obtained. Alternatively, if $\bar{T}_c$, $h_{c,c}$, $\bar{T}_g$, and $h_{c,g}$ are known, $\dot{q}$, $T_{w,g}$, and $T_{w,c}$ can be computed.

Dimensional analysis can be used to develop the functional form of relationships which govern the gas-side heat-transfer coefficient.[8] The engine convective heat-transfer process can be characterized geometrically by a length dimension—say the bore B—and a number of length ratios y_1, y_2, y_3, etc. (of which one will be the axial cylinder length z divided by the bore z/B), which define the cylinder and combustion chamber geometry. The flow pattern, similarly, may be characterized by one chosen velocity v and a set of velocity ratios u_1, u_2, u_3, etc. The gas properties of importance are the thermal conductivity k, the dynamic viscosity μ, the specific heat c_p, and the density ρ. If there is combustion, then the chemical energy release rate per unit volume $\dot{q}_{ch}$ may be important. The engine speed N and relative position in the cycle denoted by crank angle θ introduce the cyclical nature of the process. Thus

$$f(h_c, B, z, y_1, y_2, \ldots, y_m, v, u_1, u_2, \ldots, u_n, k, \mu, c_p, \rho, \dot{q}_{ch}, N, \theta) = 0$$

Applying dimensional analysis, with mass, length, time, and temperature as the independent dimensions, reduces the variables to four-fewer nondimensional groups:

$$F\left(\frac{h_c B}{k}, \frac{\rho v B}{\mu}, \frac{c_p \mu}{k}, \frac{c_p T}{v^2}, \frac{NB}{v}, \frac{\dot{q}_{ch}}{\rho c_p N T}, \frac{z}{B}, y_1, \ldots, y_m, u_1, \ldots, u_n, \theta\right) = 0$$

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The first three groups are the familiar Nusselt, Reynolds, and Prandtl numbers, respectively. The next has the nature of a Mach number since $c_p T$ is proportional to the square of the sound speed. For Mach numbers much less than 1, the Mach number dependence is known to be small and can be omitted. It is usual to take for v the mean piston speed $\bar{S}_p = 2LN$. Then, by introducing the bore/stroke ratio B/L, the term NB/v is eliminated. z/B is a function of the compression ratio r_c, the ratio of connecting rod to crank radius $R = l/a$, and θ. Thus

$$F\left(\frac{h_c B}{k}, \frac{\rho \bar{S}_p B}{\mu}, \frac{c_p \mu}{k}, \frac{B}{L}, \frac{\dot{q}_{ch}}{\rho c_p N T}, r_c, R, y_1, \ldots, y_m, \theta, u_1, \ldots, u_n\right) = 0 \quad (12.10)$$

The dimensionless groups may be varied (but not reduced in number) by combination. While Eq. (12.10) reveals nothing about the functional form of the relationship between the groups, it does provide a basis for evaluating the correlations which have been proposed.

Many formulas for calculating instantaneous engine heat-transfer coefficients have been proposed (see Ref. 9 for a review). Only those with a functional form which fits Eq. (12.10) will be summarized here. The basis of these correlations is the assumption that the Nusselt, Reynolds, and Prandtl number relationship follows that found for turbulent flow in pipes or over flat plates:

$$\mathrm{Nu} = a\ \mathrm{Re}^m\ \mathrm{Pr}^n \quad (12.11)$$

Distinctions should be made between correlations intended to predict the *time-averaged* heat flux to the combustion chamber walls, the *instantaneous spatially averaged* heat flux to the chamber walls (which is required for engine performance analysis), and the *instantaneous local* heat fluxes (which are not uniform over the combustion chamber and may be required for thermal stress calculations). In using these heat-transfer correlations, the critical choices to be made are (1) the velocity to be used in the Reynolds number; (2) the gas temperature at which the gas properties in Eq. (12.11) are evaluated; and (3) the gas temperature used in the convective heat-transfer equation (12.2).

The most widely used correlations and the basis of their derivation will now be summarized. Because the experimental data for evaluating these correlations in CI engines includes both convective and radiative heat fluxes, comparison of these correlations with data is deferred to Sec. 12.6.

12.4.2 Correlations for Time-Averaged Heat Flux

Taylor and Toong[10] have correlated overall heat-transfer data from 19 different engines. It was assumed that coolant and wall temperatures varied little between designs and that the effects of geometrical differences were small. Thus, at a given fuel/air ratio, the convective part of the heat flux should correlate with Reynolds number. To allow for variations in fuel/air ratio, Taylor and Toong defined an

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average effective gas temperature $T_{g,a}$ such that

$$\int Ah_c(T - T_{g,a})d\theta = 0$$

over the engine cycle. $T_{g,a}$ is the temperature at which the wall would stabilize if no heat was removed from outside. $T_{g,a}$ was obtained by extrapolating average heat-transfer data plotted versus gas-side combustion chamber surface temperature back to the zero heat-transfer axis. The Nusselt number, defined as

$$\text{Nu} = \frac{\bar{Q}B}{(\pi B^2/4)(T_{g,a} - T_c)k_g} = \frac{4\bar{Q}}{\pi B k_g(T_{g,a} - T_c)} \tag{12.12}$$

plotted against Reynolds number, defined as

$$\text{Re} = \frac{\dot{m}B}{\mu_g(\pi B^2/4)} = \frac{4\dot{m}}{\pi\mu_g B} \tag{12.13}$$

where $\dot{m}$ is the charge mass flow rate, is shown in Fig. 12-5. Taylor and Toong proposed a power law of 0.75. Annand[8] suggests three separate lines for the three different types of engines covered, with slope 0.7. The diesel line is about 25 percent higher than the spark-ignition engine line (which corresponds in part to the radiative heat flux component present in diesels). The air-cooled engine line is lower than the liquid-cooled line, presumably because surface temperatures are higher. The average gas temperature values developed by Taylor and Toong are shown in the insert in Fig. 12-5.

12.4.3 Correlations for Instantaneous Spatial Average Coefficients

Annand[8] developed the following convective heat-transfer correlation to match previously published experimental data on instantaneous heat fluxes to selected cylinder head locations:

$$\left(\frac{h_c B}{k}\right) = a\left(\frac{\rho \bar{S}_p B}{\mu}\right)^b \tag{12.14}$$

The value of a varied with intensity of charge motion and engine design. With normal combustion, $0.35 \leq a \leq 0.8$ with $b = 0.7$, and a increases with increasing intensity of charge motion. Gas properties are evaluated at the cylinder-average charge temperature $\bar{T}_g$:

$$\bar{T}_g = \frac{pVM}{m\bar{R}} \tag{12.15}$$

The same temperature is used in Eq. (12.2) to obtain the convective heat flux.

Note that in developing this correlation, the effects of differences in geometry and flow pattern between engines [the ratios $y_1, \ldots, y_m$ and $u_1, \ldots, u_n$ in Eq. (12.10)] have been incorporated in the proportionality constant a, and the

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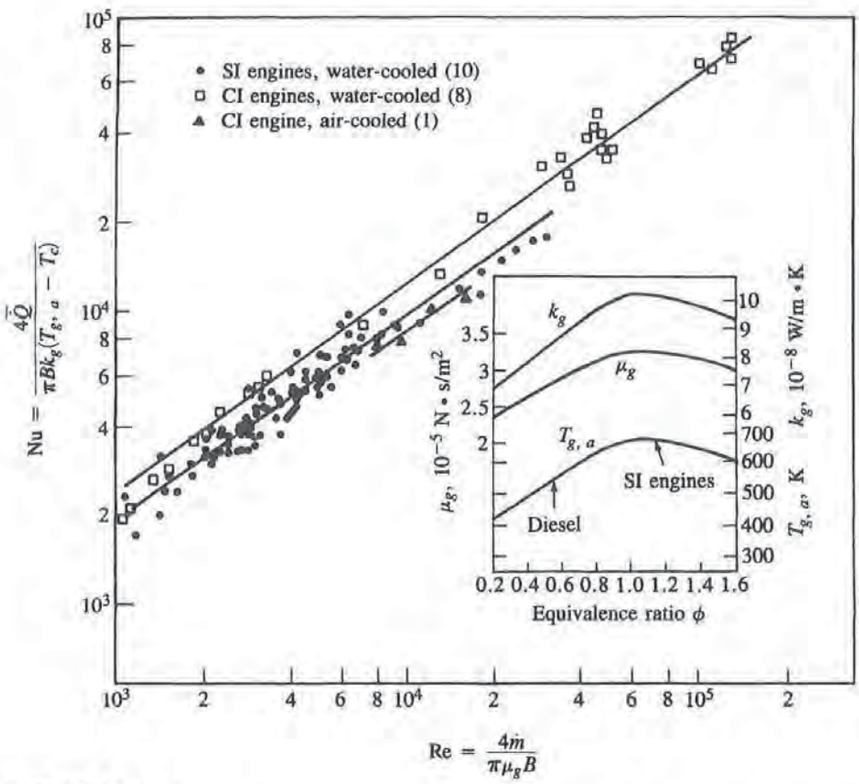


FIGURE 12-5
Overall engine heat-transfer correlation: gas-side Nusselt number versus Reynolds number for different types of IC engines. See text for definition of symbols. Insert gives effective gas temperature (wall temperature for adiabatic operation), gas viscosity μ_g and thermal conductivity k_g. Lines have slope 0.7.[8, 10]

effect of chemical energy release is omitted. While only data from cylinder head thermocouple locations were used as a basis for this correlation, it has often been used to estimate instantaneous spatial average heat fluxes for the entire combustion chamber.

Woschni[11] assumed a correlation of the form

$$\mathrm{Nu} = 0.035\ \mathrm{Re}^m \tag{12.16}$$

With the cylinder bore B taken as the characteristic length, with w as a local average gas velocity in the cylinder, and assuming $k \propto T^{0.75}$, $\mu \propto T^{0.62}$, and $p = \rho RT$, the above correlation can be written

$$h_c = CB^{m-1} p^m w^m T^{0.75-1.62m} \tag{12.17}$$

During intake, compression, and exhaust, Woschni argued that the average gas velocity should be proportional to the mean piston speed. During combustion and expansion, he attempted to account directly for the gas velocities induced by the change in density that results from combustion ($\sim$10 m/s), which are comparable to mean piston speeds. Thus a term proportional to the pressure

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rise due to combustion ($p - p_m$) was added (p_m is the motored cylinder pressure). The coefficients relating the local average gas velocity w to the mean piston speed and ($p - p_m$) were determined by fitting the correlation, integrated over the engine cycle, to time-averaged measurements of heat transfer to the coolant for a wide range of engine operating conditions for a direct-injection four-valve diesel without swirl. T in Eq. (12.17) is the mean cylinder gas temperature defined by Eq. (12.15); the same temperature is used to obtain the heat flux from the heat-transfer coefficient h_c. Thus this correlation represents *spatially averaged* combustion chamber heat fluxes.

The average cylinder gas velocity w (meters per second) determined for a four-stroke, water-cooled, four-valve direct-injection CI engine without swirl was expressed as follows:

$$w = \left[C_1 \bar{S}_p + C_2 \frac{V_d T_r}{p_r V_r} (p - p_m) \right] \tag{12.18}$$

where V_d is the displaced volume, p is the instantaneous cylinder pressure, p_r, V_r, T_r are the working-fluid pressure, volume, and temperature at some reference state (say inlet valve closing or start of combustion), and p_m is the motored cylinder pressure at the same crank angle as p.

For the gas exchange period: $C_1 = 6.18, \quad C_2 = 0$
For the compression period: $C_1 = 2.28, \quad C_2 = 0$
For the combustion and expansion period: $C_1 = 2.28, \quad C_2 = 3.24 \times 10^{-3}$

Subsequent studies in higher-speed engines with swirl indicated higher heat transfer than these velocities predicted. For engines with swirl, cylinder averaged gas velocities were given by Eq. (12.18) with:

For the gas exchange period: $C_1 = 6.18 + 0.417 \frac{v_s}{\bar{S}_p}$

For the rest of cycle: $C_1 = 2.28 + 0.308 \frac{v_s}{\bar{S}_p}$

where $v_s = B\omega_p/2$ and ω_p is the rotation speed of the paddle wheel used to measure the swirl velocity (see Sec. 8.3.1).[12] Spark-ignition engine tests showed that the above velocities gave acceptable predictions for this type of engine also.[13]

Woschni's correlation, with the exponent in Eq. (12.17) equal to 0.8, can be summarized as:

$$h_c(\mathrm{W/m^2 \cdot K}) = 3.26 B(\mathrm{m})^{-0.2} p(\mathrm{kPa})^{0.8} T(\mathrm{K})^{-0.55} w(\mathrm{m/s})^{0.8} \tag{12.19}$$

with w defined above.

Hohenberg[14] examined Woschni's formula and made changes to give better predictions of time-averaged heat fluxes measured with probes in a direct-injection diesel engine with swirl. The modifications include use of a length based on instantaneous cylinder volume instead of bore, changes in the effective gas velocity, and in the exponent of the temperature term.

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12.4.4 Correlations for Instantaneous Local Coefficients

LeFeuvre *et al.*[15] and Dent and Sulaiman[16] have proposed the use of the flat-plate forced convection heat-transfer correlation formula

$$\left(\frac{h_c l}{k}\right) = 0.036\left(\frac{\rho v l}{\mu}\right)^{0.8}\left(\frac{\mu c_p}{k}\right)^{0.333} \tag{12.20}$$

where l is the length of the plate and v the flow velocity over the plate. This formula has been applied to DI diesel engines with swirl, with l and v evaluated at a radius r as

$$l = 2\pi r \qquad v = r\omega$$

ω being the solid-body angular velocity of the charge. The heat flux at any radius r (with Pr = 0.73) is then given by

$$\dot{q}(r) = 0.023\,\frac{k}{r}\left(\frac{\omega r^2}{\nu}\right)^{0.8}[\bar{T}_g(r) - T_w(r)] \tag{12.21}$$

This equation can be used if the swirl variation with crank angle is known (see Sec. 8.3) and an appropriate local gas temperature can be determined. It would not be consistent to use the cylinder average gas temperature given by Eq. (12.15) because during combustion substantial temperature nonuniformities exist between burned gases and air or mixture which has yet to burn or mix with already burned gas.

An alternative approach is zonal modeling, where the combustion chamber is divided into a relatively small number of zones each with its own temperature, heat-transfer coefficient, and heat-transfer surface area history. This approach has been applied to spark-ignition engines (e.g., Ref. 17), where the division of the in-cylinder gases during combustion into a higher-temperature burned gas region behind the flame and lower-temperature unburned gas region ahead of the flame is clear (see Fig. 9-4). The heat transfer to the combustion chamber surfaces in contact with the unburned and burned gas zones [analagous to Eq. (12.2)] is given by

$$\dot{Q}_u = A_{u,w}\,h_{c,u}(T_u - T_w) \qquad \dot{Q}_b = A_{b,w}\,h_{c,b}(T_b - T_w) \tag{12.21a,b}$$

respectively. Since h_c depends on local gas properties and velocities, $h_{c,u}$ and $h_{c,b}$ are not necessarily the same. Examples of how the burned gas wetted areas on the piston, cylinder head, and liner vary during the combustion process are given in Fig. 14-8. Since the burned gas temperature T_b is much larger than the unburned gas temperature, the heat flux from the burned gas zone dominates.

One useful development of this two-zone approach is the division of the burned gas zone into an adiabatic core and a thermal boundary layer. The advantages are: (1) this corresponds more closely to the actual temperature distribution (see Sec. 12.6.5); (2) a model for the boundary-layer flow provides a more fundamental basis for evaluating the heat-transfer coefficient. The local heat

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flux is then given by[18]

$$\dot{q} = \frac{k_e(T_{ac} - T_w)}{\delta} \tag{12.22}$$

where k_e is the effective thermal conductivity in the boundary layer, T_{ac} is the adiabatic core temperature, and δ the boundary-layer thickness. In the laminar regime δ would grow as $t^{1/2}$; in the turbulent regime δ would grow as $t^{0.8}$. Both growth regimes are observed.

Zonal models have also been used to describe DI diesel engine heat transfer.[19] A bowl-in-piston chamber was divided into three flow regions and two gas-temperature zones during combustion. An effective velocity

$$w = (U_x^2 + U_y^2 + 2k)^{1/2}$$

was used to obtain the heat-transfer coefficient, where U_x and U_y are the two velocity components parallel to the surface outside the boundary layer and k is the turbulent kinetic energy. Zonal models would be expected to be more accurate than global models. However, only limited validation has been carried out.

12.4.5 Intake and Exhaust System Heat Transfer

Convective heat transfer in the intake and exhaust systems is driven by much higher flow velocities than in-cylinder heat transfer. Intake system heat transfer is usually described by steady, turbulent pipe flow correlations.[9] With liquid fuel present in the intake, the heat-transfer phenomena become especially complicated (see Sec. 7.6). Exhaust flow heat-transfer rates are the largest in the entire cycle due to the very high gas velocities developed during the exhaust blowdown process and the high gas temperature (see Sec. 6.5). Exhaust system heat transfer is important since it affects emissions burnup in the exhaust system, catalyst, or particulate trap, it influences turbocharger performance, and it contributes significantly to the engine cooling requirements.

The highest heat-transfer rates occur during blowdown, to the exhaust valve and port. Detailed exhaust port convective heat-transfer correlations have been developed and tested. These are based on Nusselt-Reynolds number correlations. For the valve open period, relations of the form

$$\mathrm{Nu} = K\ \mathrm{Re}_j^n \tag{12.23}$$

have been proposed and evaluated.[20] For $L_v/D_v \lesssim 0.2$, the flow exits the valve as a jet, and $\mathrm{Re}_j = v_j D_v/\nu$, where D_v is the valve diameter, v_j the velocity of the exhaust gases through the valve opening, and ν the kinematic velocity. For $L_v/D_v \gtrsim 0.2$, the port is the limiting area and a pipe flow model with $\mathrm{Re} = v_p D_p/\nu$ is more appropriate. v_p is the velocity in the port and D_p is the port diameter. For the valve closed period, the correlation

$$\mathrm{Nu} = 0.022\ \overline{\mathrm{Re}}_D^{0.8} \tag{12.24}$$

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was developed. Here $\overline{\mathrm{Re}}_D = \bar{v}_p D_p/\nu$, where $\bar{v}_p$ is the time-averaged exhaust port gas velocity and D_p is the port diameter. For straight sections of exhaust pipe downstream of the port, an empirical correlation based on measurements of average heat-transfer rates to the pipe has been derived:[21]

$$\mathrm{Nu} = 0.0483\ \mathrm{Re}^{0.783} \tag{12.25}$$

The Reynolds number is based on pipe diameter and velocity. Heat-transfer correlations for steady developing turbulent flow in pipes predict values about half that given by Eq. (12.25).

12.5 RADIATIVE HEAT TRANSFER

There are two sources of radiative heat transfer within the cylinder: the high-temperature burned gases and the soot particles in the diesel engine flame. In a spark-ignition engine, the flame propagates across the combustion chamber from the point of ignition through previously mixed fuel and air. Although the flame front is slightly luminous (see color plate, Fig. 9-1), all the chemical intermediaries in the reaction process are gaseous. Combustion is essentially complete early in the expansion stroke. In the compression-ignition engine (and in fuel-injected stratified-charge engines), most of the fuel burns in a turbulent diffusion flame as fuel and air mix together. There can be many ignition locations, and the flame conforms to the shape of the fuel spray until dispersed by air motion (see color plate, Figs. 10-4 and 10-5). The flame is highly luminous, and soot particles (which are mostly carbon) are formed at an intermediate step in the combustion process.

The radiation from soot particles in the diesel engine flame is about five times the radiation from the gaseous combustion products. Radiative heat transfer in conventional spark-ignition engines is small in comparison with convective heat transfer. However, radiative heat transfer in diesel engines is not negligible; it contributes 20 to 35 percent of the total heat transfer and a higher fraction of the maximum heat-transfer rate.

12.5.1 Radiation from Gases

Gases absorb and emit radiation in narrow wavelength bands rather than in a continuous spectrum as do solid surfaces. The simpler gas molecules such as H_2, O_2, and N_2 are essentially transparent to radiation. Of the gases important in combustion, CO, CO_2, and H_2O emit sufficient energy to warrant consideration. In gases, emission and absorption will occur throughout the gas volume. These processes will be governed by the number of molecules along the radiation path. For each species, this will be proportional to the product of the species partial pressure p_i and the path length l. In addition the radiative capacity depends on gas temperature T_g. Thus the emissivity of the gas ε_g can be expressed as

$$\varepsilon_g = f(T_g, p_1 l, \ldots, p_n l) \tag{12.26}$$

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The mean path length for a volume V with surface area A is given with sufficient accuracy by

$$l = 0.9 \times \frac{4V}{A} \tag{12.27}$$

$4V/A$ is the mean path length for a hemispherical enclosure.

Standard methods have been developed for estimating ε_g for mixtures of CO_2 and H_2O by Hottel and others (see Ref. 22). Charts based on experimental data give ε_{CO_2} and ε_{H_2O} as functions of $p_i l$ and T_g. Correction factors are applied for total pressures above one atmosphere and for the overlapping of spectral bands of CO_2 and H_2O. Estimates for engine combustion gases at peak conditions give $\varepsilon_g \approx 0.1$ and peak heat fluxes due to gas radiation of order 0.2 MW/m^2. This amounts to ~ 5 percent of the peak convective heat transfer. Since gas radiation is proportional to T_g^4, this radiative flux falls off more rapidly from peak values than convective heat flux and, when integrated over the cycle, can be neglected.

12.5.2 Flame Radiation

Flame radiation is a much more complex process because the detailed geometry and chemical composition of the radiating region are not well known. Since the radiation from the optically transparent or nonluminous flames of spark-ignition engines is small, we will deal only with luminous nontransparent flames where the radiation comes from incandescent soot particles and has a continuous spectrum. Because the particle size distribution, number density and temperature, and flame geometry in a diesel engine are not well defined, flame emissivities cannot be calculated from first principles. Direct measurements of flame emissivities are required. A number of measurements of the magnitude and spectral distribution of radiation from a diesel engine combustion chamber have been made (see Ref. 9 for a summary). The most extensive of these by Flynn *et al.*[23] in a direct-injection engine used a monochromator to measure intensity of radiation at seven wavelengths. The viewing path cut through the piston crown into the central region of the bowl-in-piston combustion chamber. Fuel was injected through a five-hole nozzle and some air swirl was provided. At any given crank angle, the distribution of energy over the seven wavelengths was used to reconstruct the complete energy spectrum and to calculate the apparent radiation temperature and optical thickness.

The energy distribution was skewed from that of a grey-body model (for which emissivity is independent of wavelength), and the monochromatic emissivity was well fitted by the equation

$$\varepsilon_\lambda = 1 - \exp\left(\frac{-kl}{\lambda^{0.95}}\right) \tag{12.28}$$

used to describe the emissivity variation from clouds of small particles. Figure 12-6 shows sample results for the monochromatic emissive power and monochro-

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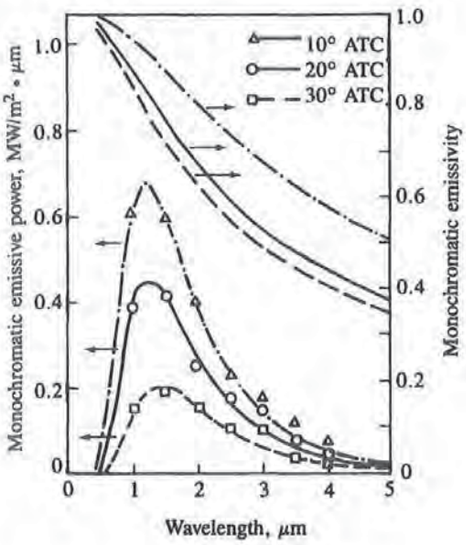


FIGURE 12-6
Variation in monochromatic emissive power and emissivity, with wavelength, at three different crank angles. DI diesel engine with 114 mm bore, 1995 rev/min, overall equivalence ratio 0.46. Radiation from piston bowl measured through cutout in piston crown.[23]

matic emissivity. Equation (12.28), combined with Planck's equation for blackbody monochromatic emissive power

$$e_{b,\lambda} = \frac{2\pi K_1}{\lambda^5 (e^{K_2/\lambda T_R} - 1)} \tag{12.29}$$

where $K_1 = 0.59548 \times 10^{-16}$ W · m² and $K_2 = 1.43879$ cm · K, defined an apparent radiation temperature T_R and optical thickness kl for the radiating medium. An apparent grey-body emissivity ε_a was also calculated from the standard equation

$$\varepsilon_a = \frac{\int \varepsilon_\lambda e_{b,\lambda}\, d\lambda}{\int e_{b,\lambda}\, d\lambda}$$

Figure 12-7 shows sample results for four equivalence ratios at an engine speed of 2000 rev/min. The radiation flux has approximately the same shape and time span as the net heat-release rate curve (which was determined from the cylinder pressure curve). During the period of maximum radiation, the apparent emissivity is 0.8 to 0.9; it then decreases as the expansion process proceeds.[23] In previous experiments on the same engine, instantaneous total heat fluxes had been measured at various locations on the cylinder head.[24] A comparison of radiant and total heat fluxes (both peak and average) showed that the radiation heat flux can be a substantial fraction of the peak heat flux. The average radiant flux is about 20 percent of the average total flux: the percentage varies significantly with load. These conclusions are supported by other experimental data summarized in the next section.

The radiation or apparent flame temperatures measured in diesels by several investigators show consistent results (see Fig. 12-8). Also included in the figure during the combustion and expansion process are typical values of: (1) the

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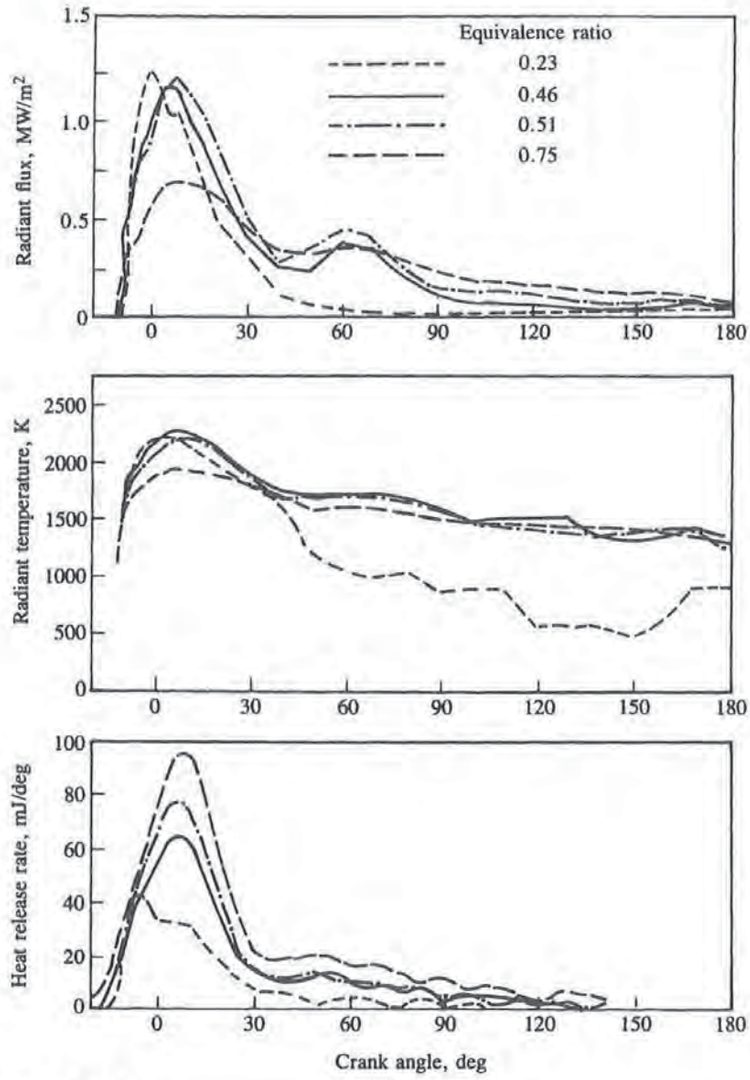


FIGURE 12-7
Radiant heat flux, apparent radiant temperature and net heat-release rate as function of crank angle for DI diesel engine at four different loads. Engine and measurement details as in Fig. 12-6; 2000 rev/min.[23]

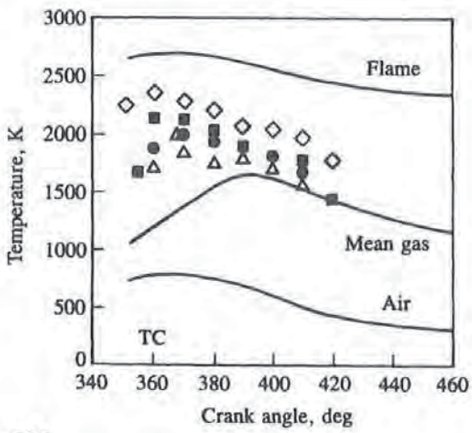


FIGURE 12-8
Apparent radiation temperatures measured in diesel engines, compared to calculated maximum adiabatic flame, cylinder-mean and air temperatures, during the combustion period. Adiabatic flame temperature is temperature attained by burning air at air temperature with fuel for equivalence ratio of 1.1. (*Data from Dent and Sulaiman,*[16] *Flynn* et al.,[23] *Lyn,*[25] *Kamimoto* et al.;[26] *calculated curves from Assanis and Heywood.*[27])

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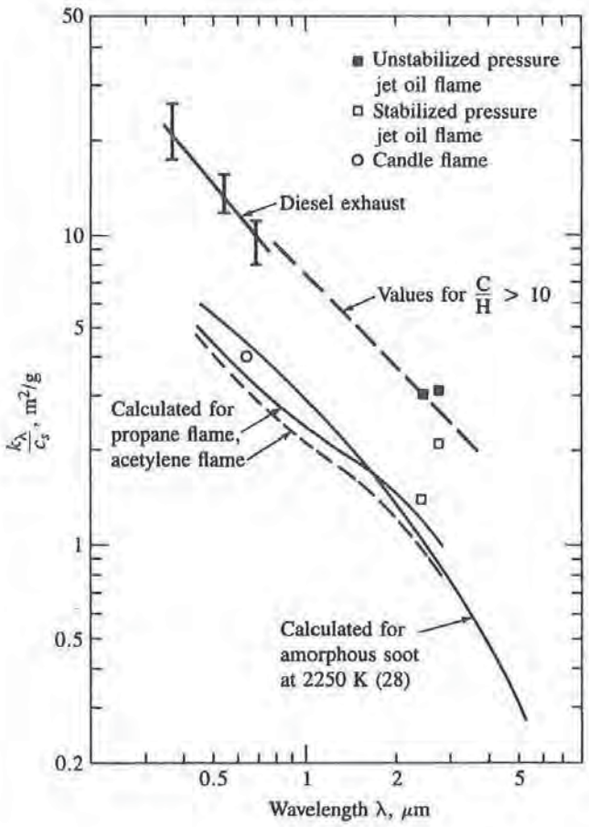


FIGURE 12-9
Measured and calculated values of k_λ/c_s as a function of wavelength λ. k_λ is monochromatic absorption coefficient, c_s is the soot concentration. (*From Field* et al.[28] *and Greeves and Meehan.*[29])

temperature of any air not yet mixed with fuel or burned gases; (2) the average temperature of the cylinder contents; and (3) the maximum possible flame temperature [corresponding to combustion of a slightly rich mixture ($\phi = 1.1$) with air at the temperature shown]. The measured radiation temperatures fall between the maximum flame temperatures and the bulk temperature. Such a model has been proposed, fits the available data, and has been used.[27] Zonal models have been proposed (e.g., the burned gas region is stoichiometric[16, 19]) to define an appropriate flame temperature.

The emissivity of an incandescent soot-burning flame can be calculated from a knowledge of the monochromatic absorption coefficient, which is given by

$$k_\lambda = 36\pi \frac{c_s}{\rho_s} \frac{n^2\kappa}{\lambda[(n^2 + n^2\kappa^2)^2 + 4(n^2 - n^2\kappa^2 + 1)]} = 36\pi \frac{c_s}{\rho_s} f(\lambda, T) \quad (12.30)$$

where n is the refractive index, κ is the absorption term in the complex refractive index, c_s is the soot concentration in kilograms per cubic meter, and ρ_s is the density of the soot particles (≈ 2 g/m^3).[28] The absorption coefficient depends on wavelength and temperature, is independent of particle size, and depends only on the soot mass loading. Figure 12-9 shows several estimates of k_λ/c_s as a function of λ. The strong dependence on λ shows that clouds of soot particles are markedly not grey. There is a considerable spread in the different estimates shown.

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This could be the result of different soot compositions (the C/H ratio affects the optical properties) and temperatures. To find a mean value for the absorption coefficient of a wide spectrum of radiation, the expression

$$k_a = \frac{\int k_\lambda e_{b,\lambda}\, d\lambda}{\int e_{b,\lambda}\, d\lambda}$$

must be evaluated. For example, for radiation from a black body at temperature 1800 K, the mean absorption coefficient is $\approx 1300 c_s$ per meter, where c_s is in kilograms per cubic meter. At higher black-body temperatures, the value of k_a would be higher.

Annand[30] has applied this approach to a diesel engine. The apparent flame emissivity was related to the apparent mean absorptivity by

$$\varepsilon_a = 1 - \exp(-k_a l) \tag{12.31}$$

For Flynn's data, the peak emissivity is 0.8 which gives $k_a l = 1.6$. Since $l \approx 0.07$ m, this gives $k_a \approx 22\ \text{m}^{-1}$ and $c_s \approx 16\ \text{g/m}^3$ ($\approx 1\ \text{g/m}^3$ at NTP), which is a soot loading comparable with values measured in diesel engines during combustion (see Figs. 11-42 to 11-44).

12.5.3 Prediction Formulas

Well-accepted prediction formulas for radiant heat flux in an engine are not available. Annand has proposed a radiation term of the form

$$\dot{q}_R = \beta\sigma(\bar{T}_g^4 - T_w^4) \tag{12.32}$$

where σ is the Stefan-Boltzmann constant, $\bar{T}_g$ is the mean gas temperature, and T_w is the wall temperature. This term was coupled with a convective heat flux term to give a correlation for predicting total heat flux. In a first evaluation, when coupled with Eq. (12.14), $\beta = 0.6$ was proposed.[8] In a later study with a modified convective heat-transfer correlation,[31] $\beta \approx 1.6$ was proposed. (Note that since the temperature used is the average gas temperature and not the apparent flame temperature, β is not an emissivity.) The limited evaluation of this approach shows that $\beta = 0.6$ gave approximately correct magnitude for $\dot{q}_R$ for one engine and was too low for another.[32] $\beta = 1.6$ gave radiant heat fluxes higher than experimental data.[33]

Flynn *et al.*[23] developed an empirical expression for instantaneous radiant heat flux to fit their data, of the form

$$\dot{q}_R = 2\bar{\dot{q}}_R\, b(a+1)\left(\frac{\theta - \theta_s}{360}\right)^a \exp\left[\frac{(\theta - \theta_s)^{a+1}}{360}\right] \tag{12.33}$$

where θ_s is the crank angle at the start of the radiation pulse. Correlations for $\bar{\dot{q}}_R$, a, b, and θ_s in terms of engine speed, manifold pressure, crank angle at the start of fuel injection, and the equivalence ratio were obtained and presented. This corre-

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lation gave a reasonable match to Flynn's data, an example of which was shown in Fig. 12-7.

It has been proposed that the apparent absorptivity should be proportional to pressure.[4, 33] The assumption is then made that the proportionality constant would be a unique function of the equivalence ratio and crank angle. Although k_a is dependent on p for gas radiation, it is not clear that the same proportionality should apply to soot radiation.

12.6 MEASUREMENTS OF INSTANTANEOUS HEAT-TRANSFER RATES

12.6.1 Measurement Methods

Values of instantaneous heat flux into the combustion chamber walls have been obtained from measurements of the instantaneous surface temperature. The temperature variation at the wall is a result of the time-varying boundary condition at the gas/wall interface. It is damped out within a small distance (~ 1 mm) from the wall surface, so measurements must be made at the surface. Various types of thermocouple or thermistor have been used.[9] One-dimensional unsteady heat conduction into the wall is then assumed:

$$\frac{\partial T}{\partial t} = \frac{1}{\rho c}\frac{\partial}{\partial x}\left(k\frac{\partial T}{\partial x}\right) \tag{12.34}$$

A sinusoidal variation with time of heat flux into a semi-infinite solid can be shown to produce a sinusoidal variation of surface temperature of the same frequency displaced in phase by 90°. The surface temperature T_w is expressed as a Fourier series:

$$T_w = T_m + \sum_{n=1}^{N} [A_n \cos(n\omega t) + B_n \sin(n\omega t)] \tag{12.35}$$

where T_m is the time-averaged value of T_w, A_n and B_n are Fourier coefficients, n is a harmonic number, and ω is the angular frequency (radians per second). The boundary conditions are $T = T_w(t)$ at $x = 0$ and $T = T_l$ (constant) at $x = l$. The solution of Eq. (12.35) is[1]

$$T(x, t) = T_m - (T_m - T_l)\frac{x}{l} + \sum_{n=1}^{N} \exp(-\phi_n x) F_n(x, t) \tag{12.36}$$

where

$$F_n = A_n \cos(n\omega t - \phi_n x) + B_n \sin(n\omega t - \phi_n x)$$

and $\phi_n = (n\omega/2\alpha)^{1/2}$, where α is the thermal diffusivity of the wall material $k/(\rho c)$.

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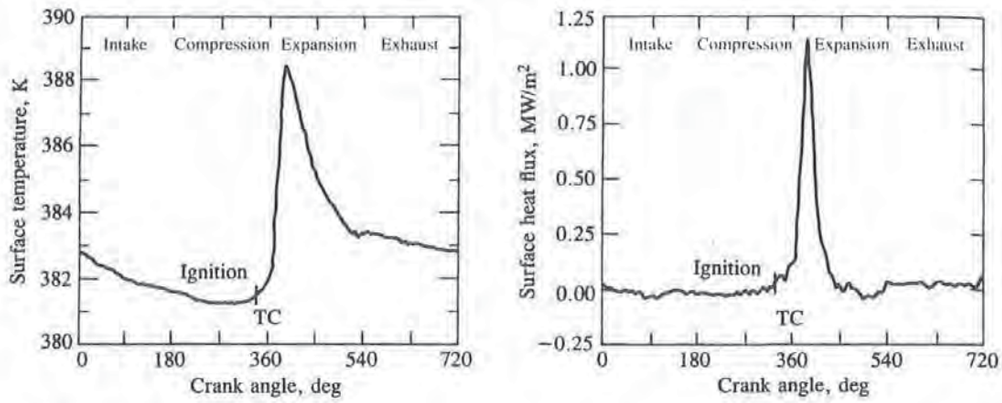


FIGURE 12-10
Surface temperature measured with thermocouple in cylinder head, and surface heat flux calculated from surface temperature, as a function of crank angle. Spark-ignition engine operated at part-load.[34]

The heat flux components at each frequency that caused that variation can be calculated via Fourier's law [Eq. (12.1)], and summed to give the total fluctuation of heat flux with time:

$$\dot{q}_w = \frac{k}{l}(T_m - T_l) + k\sum_{n=1}^{N} \phi_n[(A_n + B_n)\cos(n\omega t) - (A_n - B_n)\sin(n\omega t)] \quad (12.37)$$

Alternative approaches for solving Eq. (12.34) are through use of an electrical analogy to heat flow and by numerical methods. The latter become necessary if wall material properties depend significantly on temperature, as do combustion chamber deposits and some insulating ceramic materials. Several measurements of this type in spark-ignition and diesel engines have been made. A summary of these measurements can be found in Ref. 9.

Radiant heat fluxes are determined by a variety of techniques: e.g., photodetector and infrared monochromator; thermocouple shielded by a sapphire window; pyroelectric thermal detector.

12.6.2 Spark-Ignition Engine Measurements

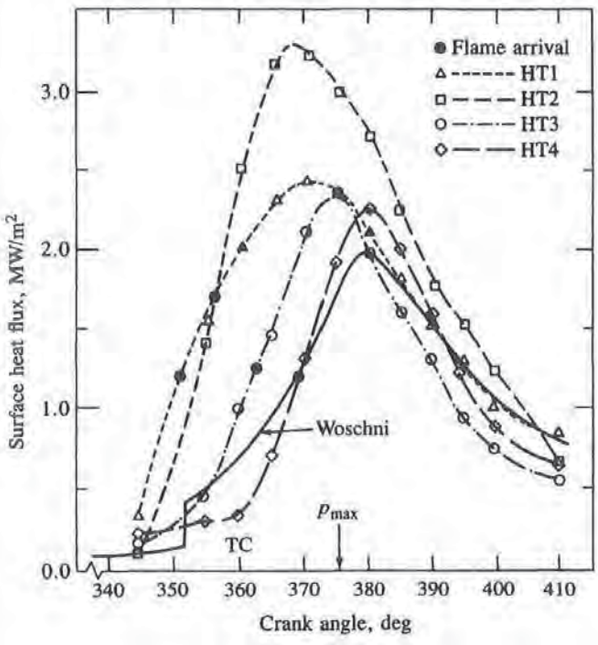
Figure 12-10 shows the surface temperature variation with crank angle, and the heat flux variation calculated from it, on the cylinder head of a spark-ignition engine at a part-load low-speed operating condition. The swing in surface temperature at this point (about halfway from the on-the-cylinder-axis spark plug to the cylinder wall) is 7 K. The heat flux rises rapidly when the flame arrives at the measurement location, has its maximum at about the time of peak cylinder pressure when gas temperatures peak (see Section 9.2.1), and then decays to relatively low levels by 60° ATC as expansion cools the burned gases. Peak heat fluxes on the cylinder head of 1.5 to 3 MW/m^2 were measured over the normal engine speed and load range.[34, 35]

The heat flux profile varies significantly with location and from one cycle to the next. Figure 12-11 illustrates both these effects. When the rapid rise in heat

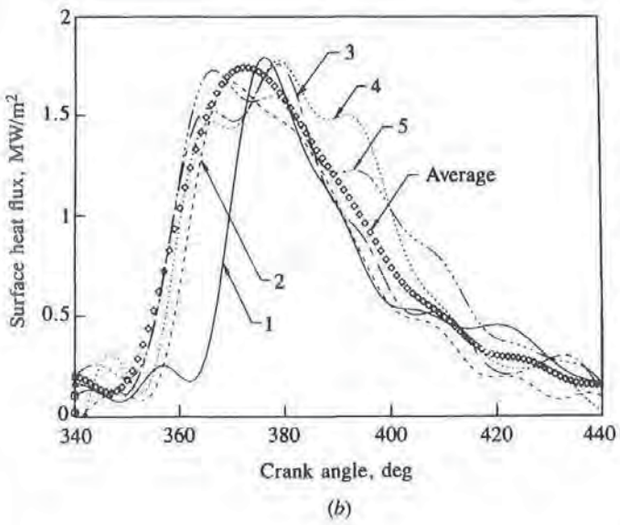
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flux occurs depends on the flame arrival time at the measurement location. Thus the heat fluxes determined from surface temperature data averaged over many cycles show their rapid rise later, the further the distance from the spark plug location (Fig. 12-11*a*). The individual cycle data in Fig. 12-11*b* show how variations in the flame arrival time from one cycle to the next essentially shift the rising portion of the heat flux profile in time. Note that due to this cyclic variation, the average profile shows a less rapid rise in heat flux than do individual cycles.

Such measurements show that increasing engine speed and increasing engine load increase the surface heat flux. Retarding timing delays the rise in heat



(*a*)



(*b*)

FIGURE 12-11
(*a*) Variation of surface heat flux with crank angle at four temperature measurement locations in the cylinder head of a spark-ignition engine. Each curve is an average over many cycles. Distances from on-axis spark plug are: HT1, 18.7 mm; HT2, 27.5 mm; HT3, 37.3 mm; HT4, 46.3 mm. Bore = 104.7 mm, 2000 rev/min, part-load $\eta_v = 40$ percent, $A/F = 18$, MBT timing. Solid curve shows heat flux predicted by Woschni's correlation.[34] (*b*) Heat flux histories for five consecutive individual cycles and 198-cycle average at location HT1. 1500 rev/min, $A/F = 18$, $\eta_v = 40$ percent, MBT timing.[35]

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flux and reduces the peak value. Maximum heat fluxes occur with close-to-stoichiometric mixtures.[34, 35] All these trends would be expected from the variations in burned gas temperature that result from these changes in engine operation.

12.6.3 Diesel Engine Measurements

Measurements of instantaneous heat fluxes in diesel engines show similar features. The heat flux distribution is usually highly nonuniform. There may also be significant variations between the heat flux profiles from individual cycles. Figure 12-12 shows surface heat fluxes at two locations in a medium-swirl DI diesel, one over the piston bowl (higher heat flux) and the other over the piston squish area, in relation to the heat-release profile. The heat flux increases rapidly once combustion starts, reaches a maximum at close to the time of maximum cylinder pressure, and decreases to a low value by 40 to 60° ATC. Peak heat fluxes to the primary combustion chamber surfaces (the piston bowl and head directly above the bowl) are of order 10 MW/m^2.

In smaller diesel engines with swirl, the mean heat flux to the piston within the piston bowl is usually higher than the mean heat fluxes to the cylinder head and the annular squish portion of the piston crown (by about a factor of two).[16, 31] This would be expected since the piston bowl is the zone where most of the combustion takes place and gas velocities are highest. There are, in addition, substantial variations in heat flux at different locations within the piston bowl, on the head, and on the annular region of the piston crown.

In contrast to the above results obtained on smaller high-speed (~10-cm bore) diesels with swirl with deep bowl-in-piston combustion chambers of diameter about half the piston diameter, results from tests on a medium-speed 30-cm bore quiescent shallow-bowl piston direct-injection supercharged diesel showed a much more uniform heat flux distribution over the combustion chamber walls.[37]

Heat fluxes to the cylinder liner are much lower still (an order of magnitude less than the peak flux to the combustion chamber surface) and are also nonuniform. Figure 12-13 compares heat fluxes to the cylinder head with three locations along the liner. Even at the top of the liner, the peak heat flux is only 15 to 20

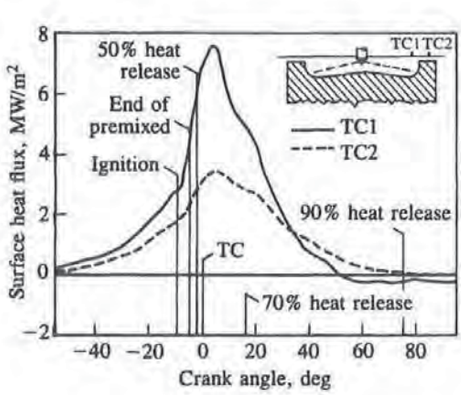


FIGURE 12-12
Measured surface heat flux at two locations in the cylinder head of a medium-swirl DI diesel engine. TC1 above the piston bowl, TC2 above the piston squish area as shown. Percentages of heat release are indicated. Bore = stroke = 114 mm, $r_c = 16$, 2000 rev/min, overall equivalence ratio = 0.5, intake pressure = 1.5 atm.[36]

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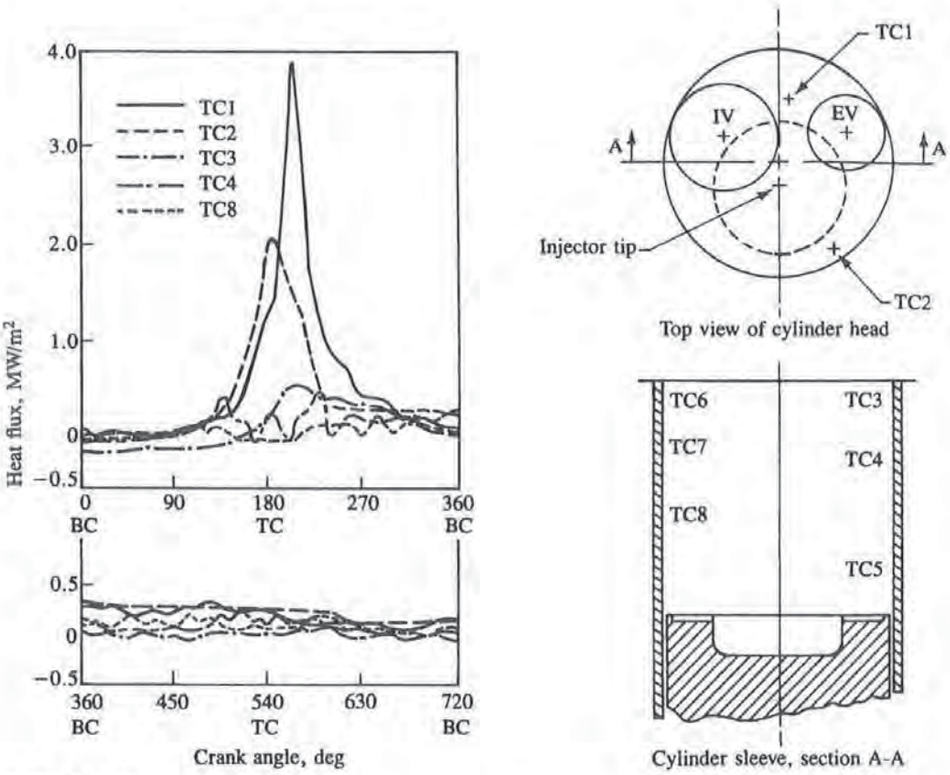


FIGURE 12-13
Measured surface heat fluxes at different locations in cylinder head and liner of naturally aspirated four-stroke cycle DI diesel engine. Bore = stroke = 114 mm, 2000 rev/min, overall equivalence ratio = 0.45.[15]

percent of the flux to the primary combustion chamber surfaces. Again this would be expected, since the combustion gases do not contact the lower parts of the cylinder wall until later in the expansion stroke when their temperature is much below the peak value.

Figure 12-14 shows examples of radiant heat flux measured above the piston bowl of a medium-swirl DI diesel engine as a function of engine speed and load.[16] The limited radiant heat flux data available exhibit the following trends. The rapid increase in radiant heat flux following combustion is delayed relative to the start of pressure rise due to combustion (by about 5°); this delay increases with increasing speed. The peak radiant flux remains approximately constant with increasing equivalence ratios up to $\phi \approx 0.5$. Further increases in the equivalence ratio produce a drop in level of radiant flux. The time-averaged radiant heat flux increased approximately linearly with increasing manifold pressure; however, peak radiative flux levels remained essentially unchanged. Peak and time-averaged values of the radiant heat flux decreased as injection timing was retarded.

In diesel engines, the relative importance of radiant heat transfer (as a percentage of the total heat flux) depends on the location on the combustion

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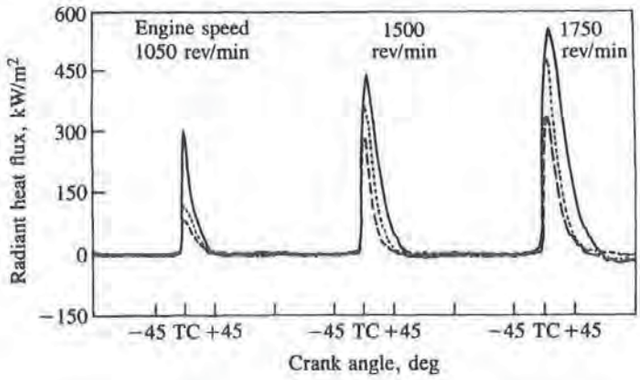


FIGURE 12-14
Measured radiant heat flux to cylinder head above the piston bowl in a high-swirl DI diesel engine when load and speed are varied. Solid curve: 80 percent load. Dotted curve: 40 percent load. Dashed curve: no load.[16]

chamber surface, crank angle, engine load, engine size, and engine design. The time-averaged radiant heat transfer increases as a proportion of the total heat transfer, with increasing load, as indicated in Fig. 12-15.[9] At high load, the total radiant heat flux is between 25 and 40 percent of the total time-averaged heat flux.

12.6.4 Evaluation of Heat-Transfer Correlations

The convective (or combined convective plus radiative) heat flux correlations have been compared with instantaneous engine heat-transfer measurements. One difficulty in this evaluation is the determination of spatially averaged combustion-chamber heat fluxes from the experimental data for comparison with correlations intended to predict the mean chamber heat flux as a function of crank angle. The area-averaged instantaneous heat flux prediction using Woschni's equation (12.19) for the spark-ignition engine conditions shown in Fig. 12-11*a* is comparable in magnitude to, though lower than, the measured heat fluxes to the cylinder head.

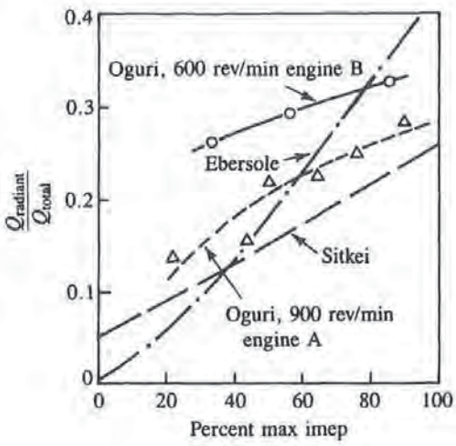


FIGURE 12-15
Radiant heat flux as fraction of total heat flux over the load range of several different diesel engines.[9]

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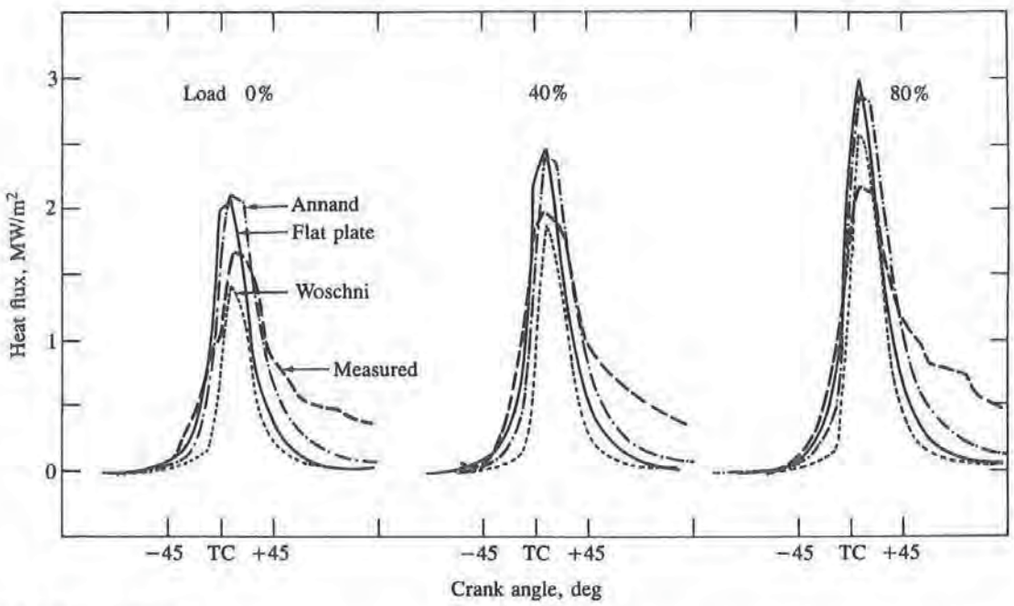


FIGURE 12-16
Comparison of measured mean heat fluxes on the cylinder head at 1050 rev/min in a fired high-swirl DI diesel engine with various prediction equations. Annand, Eq. (12.14), Woschni, Eq. (12.19), flat plate, Eq. (12.20) using measured gas motion.[16]

More extensive comparisons have been made of predictions with data for diesel engines. Annand's correlations, Eqs. (12.14) and (12.32) with $a = 0.06$, $b = 0.85$, and β (for the combustion phase only) $= 0.57$, gave reasonable agreement with instantaneous cylinder head heat fluxes, and overall time-averaged heat fluxes for a medium-speed quiescent DI engine design.[37] In a small high-speed diesel with swirl, values of $a = 0.13$, $b = 0.7$, and $\beta = 1.6$ gave an approximate fit to estimates of the instantaneous area-mean heat flux[31] and time-averaged heat flux to the piston.[38] Comparisons of the Annand and Woschni correlations generally show that the Annand correlation predicts higher heat fluxes at the same crank angle.[11, 24] The most careful comparison of all three correlations summarized in Secs. 12.4.3 and 12.4.4 with experimental data has been made by Dent and Sulaiman in a small high-speed diesel engine with swirl.[16] The mean experimental heat flux was estimated from a number of thermocouple measurements located at different points around the combustion chamber surface. Figure 12-16 shows the comparison. The Woschni correlation falls below the others at light load because the combustion-induced velocity term is smaller. Expansion stroke heat fluxes are underpredicted by all three correlations. Given the uncertainty in converting the measurements to an average heat flux value, the agreement is reasonably good.

Dent examined additional modifications to the flat plate formula [Eq. (12.20)], which was based on a cylinder-mean gas temperature. During combustion a two-zone model is more appropriate. Assuming an equivalence ratio

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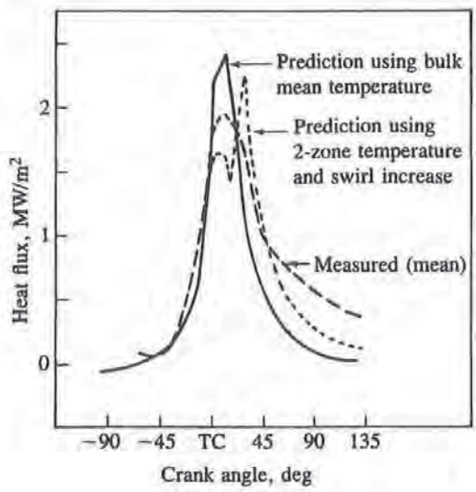


FIGURE 12-17
Measured heat fluxes on cylinder head in fired high-swirl DI diesel engine at 1050 rev/min and 40 percent load compared with predictions based on bulk mean gas temperature and using temperatures based on two-zone (air and burned gas) model.[16]

for the burned gas (Dent assumed stoichiometric), a combustion zone temperature can be determined from the relation

$$\bar{T}_b = \frac{m\bar{T}_g - m_a T_a}{m_b}$$

where m_a is the mass of air, T_a is the air temperature, and m_b is the burned gas mass, $m_b = m - m_a$. In addition, the observed swirl enhancement which occurs due to the combustion was included by multiplying the swirl velocity used in the heat-transfer correlation by the square root of the ratio (density of air in the motored case)/(density of burned gas in fired case). The combination of both effects (see Fig. 12-17) improves the shape of the predictions by broadening and lowering the peak.

Each of the convective-heat-transfer correlations described has limited experimental support. However, under engine design and operating conditions different from those under which they were derived, the predictions should be viewed with caution. Woschni's correlation is the correlation used most extensively for predicting spatially averaged instantaneous convective heat fluxes. However, the empirical constants which relate the mean piston speed and combustion-induced motion to the velocity used in the Reynolds number, determined by Woschni, will not necessarily apply to all the different types of engine. If local velocities are known, the flat-plate-based correlations provide the best available approach. Annand's correlation has the advantage of being the simplest correlation to use. Since the radiation component in diesel engine heat transfer is normally 20 to 40 percent of the total an approximate estimate of its value may suffice.

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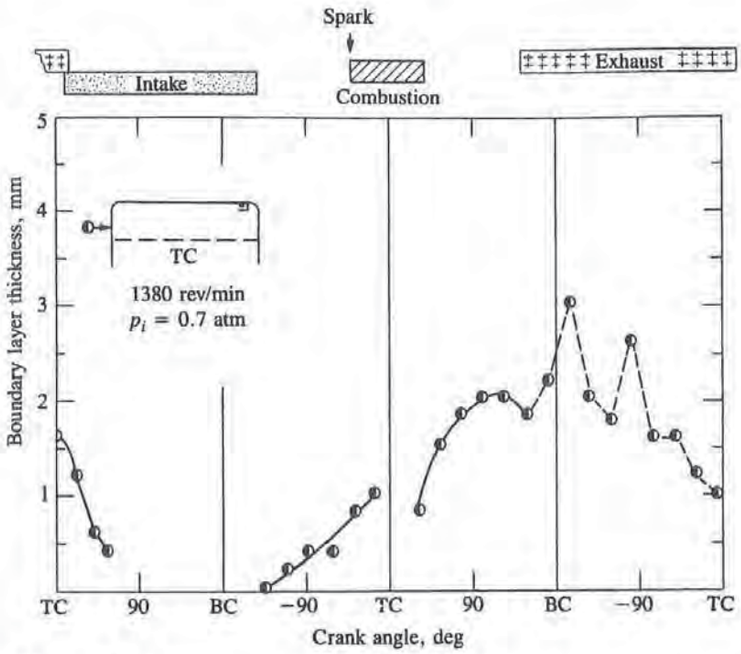


FIGURE 12-18
Thermal boundary-layer thickness, at the top of the cylinder wall in the clearance volume, determined from schlieren photographic measurements in a special visualization square-piston spark-ignition engine.[39]

12.6.5 Boundary-Layer Behavior

Measurements of thermal boundary-layer thickness in an operating spark-ignition engine have been made using schlieren photography in a special flow-visualization engine. Figure 12-18 shows one set of measurements on the cylinder wall in the clearance volume opposite the spark plug. The boundary-layer thickness decreases during intake and increases steadily during compression and expansion to about 2 mm. It stops growing and becomes unstable during the exhaust process, separating from the cylinder wall and becoming entrained into the bulk gas leaving the cylinder. The thickness of the thermal boundary layer varies substantially at different locations throughout the chamber. While the trends with crank angle were similar, the layers on the cylinder head and piston crown were substantially (up to 2 to 3 times) thicker during compression and expansion in the simple disc-shaped chamber studied.[39] This different behavior probably results because there is no bulk flow adjacent to the head and piston crown.

Estimates of thermal boundary-layer thickness in spark-ignition engines, based on convective-heat-transfer correlations and thermal energy conservation for the growing layer give thicknesses comparable to these measurements. Note that a substantial fraction of the cylinder mass is contained within the thermal

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boundary layer. For example, for an average thickness of 3 mm at 90° ATC during expansion, the volume of the boundary layer is 20 percent of the combustion chamber volume for typical engine dimensions. Since the average density in the boundary layer is about twice that in the bulk gases, some 30 to 40 percent of the cylinder mass would be contained within this boundary layer.

12.7 THERMAL LOADING AND COMPONENT TEMPERATURES

The heat flux to the combustion chamber walls varies with engine design and operating conditions. Also, the heat flux to the various parts of the combustion chamber is not the same. As a result of this nonuniform heat flux and the different thermal impedances between locations on the combustion chamber surface and the cooling fluid, the temperature distribution within engine components is nonuniform. This section reviews the variation in temperature and heat flux in the components that comprise the combustion chamber.

12.7.1 Component Temperature Distributions

Figures 12-19 to 12-22 show illustrative examples of measured temperature distributions in various engine components. Normally, the heat flux is highest in the center of the cylinder head, in the exhaust valve seat region, and to the center of the piston. It is lowest to the cylinder walls. Cast-iron pistons run about 40 to 80°C hotter than aluminum pistons. With flat-topped pistons (typical of spark-ignition engines) the center of the crown is hottest and the outer edge cooler by 20 to 50°C. Diesel engine piston crown surface temperatures are about 50°C higher than SI engine equivalent temperatures. As shown in Fig. 12-19, the maximum piston temperatures with DI diesel engine pistons are at the lip of the

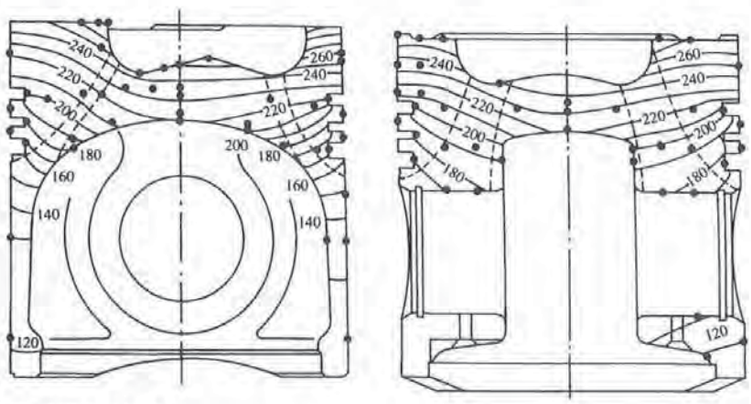


FIGURE 12-19
Isothermal contours (solid lines) and heat flow paths (dashed lines) determined from measured temperature distribution in piston of high-speed DI diesel engine. Bore 125 mm, stroke 110 mm, $r_c = 17$, 3000 rev/min, and full load.[40]

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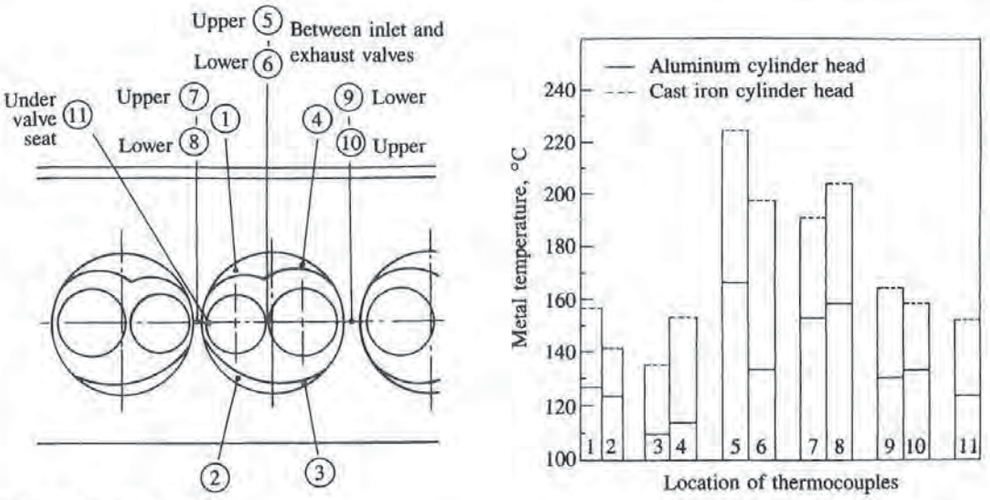


FIGURE 12-20
Variation of cylinder head temperature with measurement location in spark-ignition engine operating at 2000 rev/min, wide-open throttle with coolant water at 95°C and 2 atm.[41]

bowl. In IDI diesel engines, maximum piston temperatures occur where the prechamber jet impinges on the piston crown.

Figure 12-20 shows the temperatures at various locations on a four-cylinder SI engine cylinder head. The maximum temperatures occur where the heat flux is high and access for cooling is difficult. Such locations are the bridge between the valves and the region between the exhaust valves of adjacent cylinders. Figure 12-21 shows how the average heat flux and temperature vary along the length of a DI diesel engine liner. Because the lower regions of the liner are only exposed to combustion products for part of the cycle after significant gas expansion has occurred, the heat flux and temperature decrease significantly with distance from

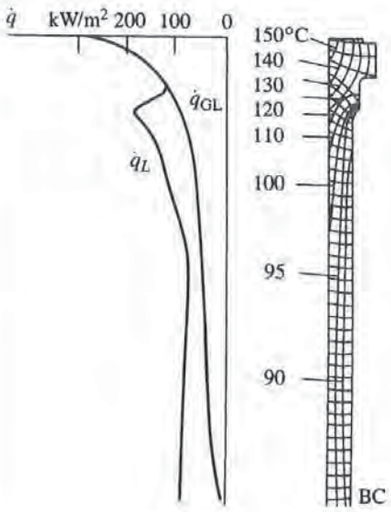


FIGURE 12-21
Temperature and heat flux distribution in the cylinder liner of a high-speed DI diesel engine at 1500 rev/min and bmep = 11 bar. $\dot{q}_L$ is heat flux into the liner; $\dot{q}_{GL}$ is heat flux from the gas to the liner. Difference is friction-generated heat flux.[42]

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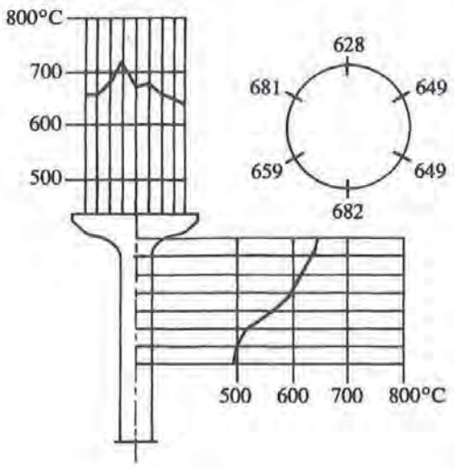


FIGURE 12-22
Temperature distribution in one of the four exhaust valves of a two-stroke-cycle uniflow DDA 4-53 DI diesel engine. Bore = 98 mm, stroke = 114 mm.[43]

the cylinder head. Note that the heat generated by friction between the piston and the liner, the difference between $\dot{q}_{GL}$ (the gas to liner heat flux) and $\dot{q}_L$ (the total heat flux into the liner), is a significant fraction of the liner thermal loading.

The exhaust valve is cooled through the stem and the guide, and the valve seat. In small-size valves the greater part of the heat transfer occurs through the stem; with large-size valves, the valve seat carries the higher thermal load.

Temperature distributions in engine components can be calculated from a knowledge of the heat fluxes across the component surface using finite element analysis techniques. For steady-state engine operation, the depth within a component to which the unsteady temperature fluctuations (caused by the variations in heat flux during the cycle) penetrate is small, so a quasi-steady solution is satisfactory. Results from such calculations for a spark-ignition engine piston illustrate the method.[44] A mean heat-transfer coefficient from the combustion chamber gases to the piston crown and a mean chamber gas temperature were defined (using the input from a cycle simulation of the type described in Sec.

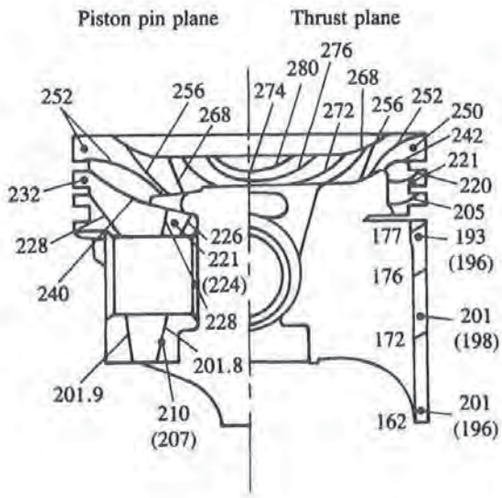


FIGURE 12-23
Measured (dots) and calculated temperature (°C) distributions in piston pin and thrust planes of the piston of a four-cylinder 2.5-dm^3 spark-ignition engine at 4600 rev/min and wide-open throttle.[44]

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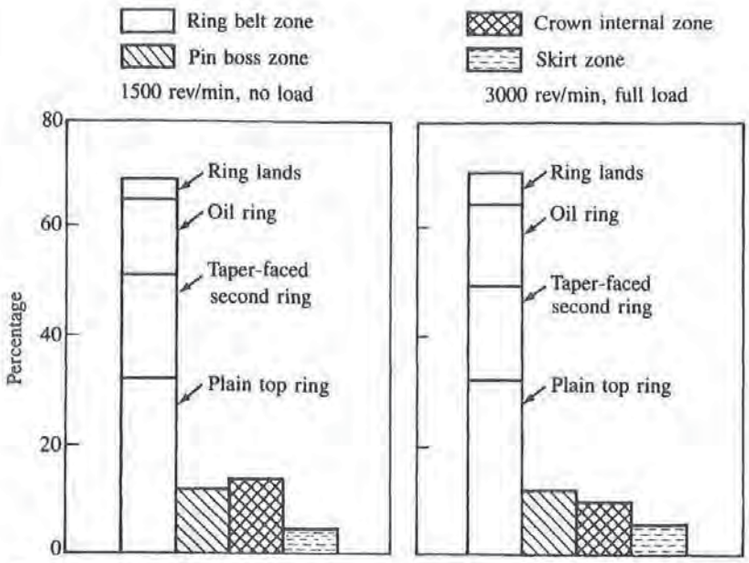


FIGURE 12-24
Heat outflow from various zones of piston as percentage of heat flow in from combustion chamber. High-speed DI diesel engine, 125 mm bore, 110 stroke, $r_c = 17$.[40]

14.4). These define the time-averaged heat flux into the piston. Heat-transfer coefficients for the different surfaces of the piston (underside of dome, ring-land areas, ring regions, skirt outer and inner surfaces, wrist pin bearings, etc.) were estimated. The actual piston shape was approximated with a three-dimensional grid for one quadrant of the piston. A standard finite element analysis of the heat flow through the piston yields the temperature distribution within the piston. The thermal stresses can therefore be calculated and added to the mechanical stress field to determine the total stress distribution. This can be used to define the potential fatigue regions in the actual piston design. Figure 12-23 shows the temperature distribution calculated with this approach, compared with measurements (indicated by dots). The agreement is acceptable, except in the piston skirt where the heat-transfer rate between the skirt and cylinder liner has been overestimated.

Detailed measurements of the temperature distribution in the piston allow the relative amounts of heat which flow out of the different piston surfaces to be estimated. Figure 12-24 shows examples of such estimates for a DI diesel engine at no-load and full-load. About 70 percent of the heat flows out through the ring zone, and much smaller amounts through the pin boss zone, underside of the crown and skirt. In larger diesel engines and highly loaded diesel engines, one or more cooling channels are incorporated into the piston crown. This reduces the heat flow out through the ring area significantly.[45]

12.7.2 Effect of Engine Variables

The following variables affect the magnitude of the heat flux to the different surfaces of the engine combustion chamber and the temperature distribution in the

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components that comprise the chamber: engine speed; engine load; overall equivalence ratio; compression ratio; spark or injection timing; swirl and squish motion; mixture inlet temperature; coolant temperature and composition; wall material; wall deposits. Of these variables, speed and load have the greatest effect. Equation (12.19), derived from the Nusselt-Reynolds number relation

$$h_c = \text{constant} \times B^{-0.2} p^{0.8} T^{-0.55} w^{0.8}$$

and the relation for heat-transfer rate per unit area [Eq. (12.2)]

$$\dot{q} = h_c(T - T_w)$$

are useful for predicting trends as engine operating and design variables change.

The effect of the above variables on engine and component heat flux will now be summarized. The comments which follow apply primarily to spark-ignition engines. In compression-ignition engines, the distribution of heat flux and temperature varies greatly with the size of cylinder and form of the combustion chamber.

SPEED, LOAD, AND EQUIVALENCE RATIO. Predictions of spark-ignition engine heat transfer as a function of speed and load are shown in Fig. 12-25. The cycle heat transfer is expressed as a percent of the fuel's chemical energy (mass of fuel × Q_{LHV}). The heat transfer to the total combustion chamber surface (excluding the exhaust port) was calculated using a thermodynamic-based cycle simulation (see Sec. 14.4). The relative importance of heat losses *per cycle* decreases as speed and load increase: the *average* heat transfer *per unit time*, however, increases as speed and load increase.

Since speed and load affect p, T, and w in Eq. (12.19), simpler correlations have been developed to predict component heat fluxes from experimental data. Time-averaged heat fluxes at several combustion chamber locations, determined from measurements of the temperature gradient in the chamber walls, have been fitted with the empirical expression

$$\dot{q} = \text{constant} \times \left(\frac{\dot{m}_f}{A_p}\right)^n \tag{12.38}$$

with n between 0.5 and 0.75 (the value of n depending on engine type and location within the combustion chamber). Results for a modern four-cylinder SI

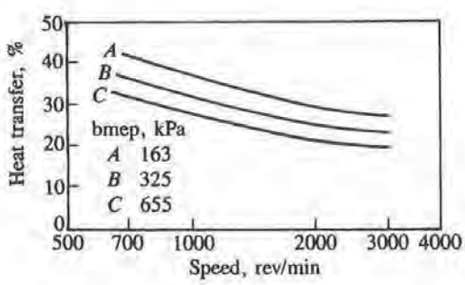


FIGURE 12-25
Predicted average heat-transfer rate (as percent of fuel flow rate × Q_{LHV}) to combustion chamber walls of an eight-cylinder 5.7-dm³ spark-ignition engine as a function of speed and load. Stoichiometric operation; MBT timing.[46]

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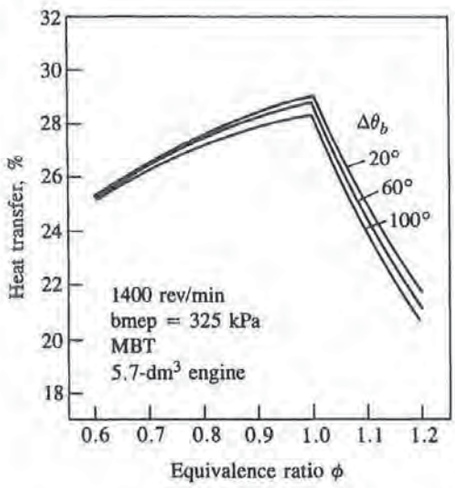


FIGURE 12-26
Predicted average heat-transfer rate (as percent of fuel flow rate × Q_{LHV}) to combustion chamber walls of an eight-cylinder 5.7-dm³ spark-ignition engine as a function of equivalence ratio and burn rate ($\Delta\theta_b$ = combustion duration).[46]

engine and several diesel engine designs, with appropriate values of n, can be found in Refs. 47 to 49. While this correlation is not dimensionless and does not satisfy Eq. (12.19), it provides a convenient method for reducing the experimental data. The heat flux to the cylinder head and liner for a spark-ignition engine were well correlated by Eq. (12.38) with $n = 0.6$. The flux distribution over the cylinder head at a fuel flow rate per unit piston area of 0.195 kg/s · m² for several different DI diesel engines were comparable in magnitude. The effect of speed at wide-open throttle on component temperatures for a spark-ignition engine can be found in Ref. 47. Exhaust valve, piston crown and top ring groove, and nozzle throat temperatures for a Comet prechamber diesel as a function of fuel flow rate can be found in Ref. 49.

The peak heat flux in an SI engine occurs at the mixture equivalence ratio for maximum power $\phi \approx 1.1$, and decreases as ϕ is leaned out or enriched from this value.[50] The major effect is through the gas temperature in Eqs. (12.2) and (12.19). However, as a fraction of the fuel's chemical energy, the heat transfer per cycle is a maximum at $\phi = 1.0$ and decreases for richer and leaner mixtures, as shown by the thermodynamic-based cycle-simulation predictions in Fig. 12-26. In CI engines, the air/fuel ratio variation is incorporated directly in the load variation effects.

COMPRESSION RATIO. Increasing the compression ratio in an SI engine decreases the total heat flux to the coolant until $r_c \approx 10$; thereafter heat flux increases slightly as r_c increases.[50] The magnitude of the change is modest; e.g., a 10 percent decrease in the maximum heat flux (at the valve bridge) occurs for an increase in r_c from 7.1 to 9.4.[47] Several gas properties change with increasing compression ratio (at fixed throttle setting): cylinder gas pressures and peak burned gas temperatures increase; gas motion increases; combustion is faster; the surface/volume ratio close to TC increases; the gas temperature late in the expansion stroke and during the exhaust stroke is reduced. Measured mean exhaust temperatures confirm the last point, which probably dominates the trend at lower

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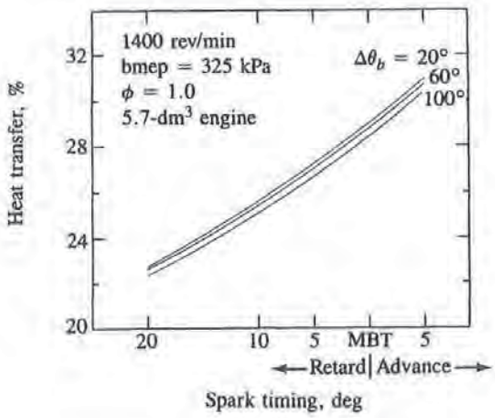


FIGURE 12-27
Predicted average heat-transfer rate (as percentage of fuel flow rate × Q_{LHV}) to combustion chamber walls of an eight-cylinder 5.7-dm^3 spark-ignition engine as a function of spark timing and burn rate ($\Delta\theta_b$ = combustion duration).[46]

compression ratios. As the compression ratio increases further, the other factors (which all increase heat transfer) become important.

The effect of changes in compression ratio on component temperatures depends on location. Generally, head and exhaust valve temperatures decrease with increasing compression ratio, due to lower expansion and exhaust stroke temperatures. The piston and spark plug electrode temperatures increase, at constant throttle setting, due to the higher peak combustion temperatures at higher compression ratios. If knock occurs (see Sec. 9.6), increases in heat flux and component temperatures result; see below.

SPARK TIMING. Retarding the spark timing in an SI engine decreases the heat flux as shown in Fig. 12-27. A similar trend in CI engines with retarding injection timing would be expected. The burned gas temperatures are decreased as timing is retarded because combustion occurs later when the cylinder volume is larger. Temperature trends vary with component. Piston and spark plug electrode temperatures change most with timing variations; exhaust valve temperature increases as timing is retarded due to higher exhausting gas temperatures.[47]

SWIRL AND SQUISH. Increased gas velocities, due to swirl or squish motion, will result in higher heat fluxes. Equation (12.19) indicates that the effect on local heat flux, relative to quiescent engine designs, should be proportional to (local gas velocity)$^{0.8}$. There is no direct evidence to support this correlation but there is evidence that use of a shrouded value to increase gas velocities within the cylinder increases the total heat transfer.[50]

INLET TEMPERATURE. The heat flux increases linearly with increasing inlet temperature; the gas temperatures throughout the cycle are increased. An increase of 100 K gives a 13 percent increase in heat flux.[51]

COOLANT TEMPERATURE AND COMPOSITION. Increasing liquid coolant temperature increases the temperature of components directly cooled by the liquid coolant. Figure 12-28 shows the result of a 50-K rise in coolant tem-

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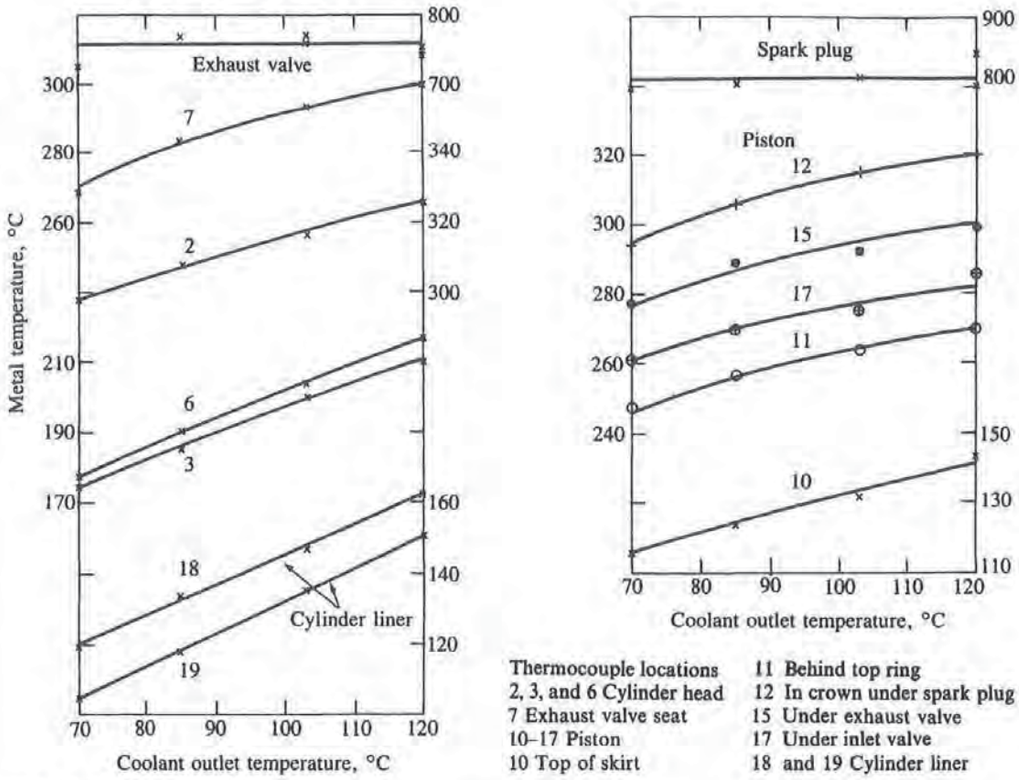


FIGURE 12-28
Effect of coolant temperature on cylinder head, liner, exhaust valve, valve seat, piston, and spark plug metal temperatures. Spark-ignition engine at 5520 rev/min and wide-open throttle. $r_c = 8.5$.[47]

perature in a spark-ignition engine. The exhaust valve and spark plug temperatures are unchanged. The smaller response of the metal temperatures to coolant temperature change occurs at higher heat flux locations (such as the valve bridge), and indicates that heat transfer to the coolant has entered the nucleate-boiling regime in that region. The response is greater where heat fluxes are lower (e.g., the cylinder liner), indicating that there heat transfer to the coolant is largely by forced convection. When nucleate boiling occurs (i.e., when steam bubbles are formed in the liquid at the metal surface, although the bulk temperature of the coolant is below the saturation temperature), the metal temperature is almost independent of coolant temperature and velocity. Addition of antifreeze (ethylene glycol) to coolant water changes the thermodynamic properties of the coolant.

WALL MATERIAL. While the common metallic component materials of cast iron and aluminum have substantially different thermal properties, they both operate with combustion chamber surface temperatures (200 to 400°C) that are low relative to burned gas temperatures. There is substantial interest in using materials that could operate at much higher temperatures so that the heat losses from the working fluid would be reduced. Ceramic materials, such as silicon nitride and

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TABLE 12.2
Thermal properties of wall materials

Material	Thermal conductivity k, W/m·K	Density ρ, kg/m^3	Specific heat c, J/kg·K	Thermal diffusivity α, m^2/s	$k\rho c$	Skin depth δ, mm	Peak temperature swing, K
Cast iron	54	7.2×10^3	480	1.57×10^{-5}	1.8×10^8	2.8	18
Aluminum	155	2.75×10^3	915	6.2×10^{-5}	3.9×10^8	5.4	12
Reaction-bonded silicon nitride	5–10	2.5×10^3	710	2.8×10^{-6}	1.3×10^7	1.2	70
Sprayed zirconia	1.2	5.2×10^3	732	3.2×10^{-7}	4.6×10^6	0.39	95

zirconia, have lower thermal conductivity than cast iron, would operate at higher temperatures, and thereby insulate the engine. The thermal properties of some of these materials are listed in Table 12.2. With these thermally insulating materials it is possible to reduce the heat transfer through the wall by a substantial amount.

This approach is most feasible for diesel engines where there is the possibility of eliminating the conventional engine coolant system and improving engine efficiency. Since the coolant-side heat transfer is essentially steady during each cycle, a high enough thermal resistance in the wall material can bring the net heat transfer close to zero. However, there is still substantial heat transfer between the working fluid in the cylinder and the combustion chamber walls. Figure 12-29 illustrates these heat-transfer processes by comparing the mean gas temperature to the piston surface temperature for metal and ceramic combustion chamber wall materials. The results come from a thermodynamic simulation of a turbocompounded diesel engine system operating cycle. From Eq. (12.2) the heat transfer is *from* the gas when $T_g > T_w$ and *to* the gas when $T_g < T_w$. With the ceramic material at about 800 K surface temperature, the *net* heat transfer is much reduced compared with the metal case. However, there is substantial heat transfer to the gas from the ceramic walls during intake (which reduces volumetric efficiency) and compression (which increases compression stroke work), and still substantial heat transfer from the gas during combustion and expansion.

The heat transfer from the hot walls to the incoming charge makes thermally insulating materials unattractive for spark-ignition engines. Such heat transfer would increase the unburned mixture temperature leading to earlier onset of knock (see Sec. 9.6).

The variation in ceramic surface temperature in Fig. 12-29 indicates the inherently unsteady nature of the heat-transfer interaction with the wall. During combustion and expansion, the thermal energy transferred from the gas to the wall is stored in a thin layer of wall material adjacent to the surface. While some

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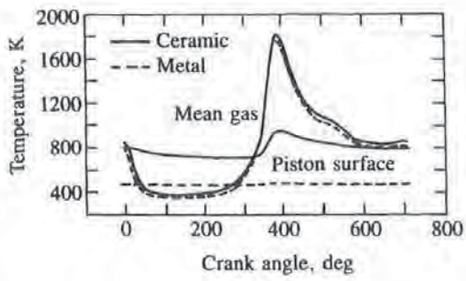


FIGURE 12-29
Mean gas temperature and piston surface temperature profiles predicted by turbocompounded DI diesel engine simulation for water-cooled metal combustion chamber walls and for partly insulated engine with ceramic walls.[27]

of this thermal energy diffuses through the wall, during intake and compression much of it is transferred back to the now low-temperature cylinder contents. The depth of penetration of the thermal wave into the material, the skin depth δ, is proportional to $\sqrt{\alpha/\omega}$, where $\alpha = k/(\rho c)$ is the thermal diffusivity and ω the frequency of the wave (proportional to engine speed). Values of α and δ are given in Table 12.2 for an engine speed of 1900 rev/min: $\sqrt{\alpha}/\delta = 1.4$, a constant. The magnitude of the temperature fluctuation (important because it is a source of fluctuating thermal stress) is proportional to $(\delta\rho c)^{-1}$: this varies as $(k\rho c)^{-1/2}$. Estimated peak temperature swings for the materials in Table 12.2 are tabulated.

KNOCK. Knock in an SI engine is the spontaneous ignition of the unburned "end-gas" ahead of the flame as the flame propagates across the combustion chamber. It results in an increase in gas pressure and temperature above the normal combustion levels (see Sec. 9.6). Knock results in increased local heat fluxes to regions of the piston, the cylinder head, and liner in contact with the end-gas. Increases to between twice and three times the normal heat flux in the end-gas region have been measured.[13, 52] It is thought that the primary knock damage to the piston crown in this region is due to the combination of extremely high local pressures and higher material temperatures.

PROBLEMS

12.1. If radiation in the combustion chamber is negligible, Eqs. (12.5), (12.6), and (12.7) can be combined into the following overall equation approximating the time-averaged heat transfer from the engine:

$$\dot{q} = h_{c,a}(\bar{T}_g - \bar{T}_c)$$

Derive the expression for $h_{c,a}$.

12.2. Given that the average heat flux through a particular zone in a cast iron liner 1 cm thick is 0.2 MW/m^2, the coolant temperature is 85°C, and the coolant side heat-transfer coefficient is 7500 W/m$^2 \cdot$K, find the average surface temperature on the combustion chamber and coolant sides of the liner at that zone.

12.3. Figure 12-1 gives a schematic of the temperature profile from the gas inside the combustion chamber out to the coolant. Draw an equivalent figure showing schematically the temperature profiles at the following points in the engine cycle: (*a*) intake; (*b*) just prior to combustion; (*c*) just after combustion; (*d*) during the exhaust stroke. Your sketch should be carefully proportioned.

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12.4. Using dimensional analysis, compare the relative heat losses of two geometrically similar SI engines (same bore/stroke ratio, same connecting rod/stroke ratio) operating at the same imep and power. Engine A has twice the displacement per cylinder of engine B. Assume that the wall temperature and the gas temperature for both engines are the same.

12.5. (*a*) Using Woschni's correlation, evaluate the percentage increase in heat transfer expected from an engine with a mean piston speed of 10 m/s when the swirl ratio is raised from 0 to 5. Do your comparison for the intake process only. The engine bore is 0.15 m and the engine speed is 2000 rev/min.

(*b*) Explain how both the generation of swirl and the change in heat transfer that results affect the volumetric efficiency of an engine.

12.6. (*a*) Explain how you would estimate the thermal boundary-layer thickness on the combustion chamber wall of an internal combustion engine.

(*b*) Using representative data, make a rough estimate of the thickness of the thermal boundary layer in the combustion chamber of an SI engine just after the completion of combustion and the fraction of the cylinder mass contained within the boundary layer. $B \approx 100$ mm. Transport properties given in Sec. 4.8.

12.7. (*a*) Using the analysis found in Sec. 12.6.1, calculate the depth below the surface where the amplitude of the temperature oscillations has attenuated to 1 percent of the amplitude at the surface. The wall material is aluminum and the four-stroke cycle engine is operating at 2500 rev/min. For this estimate, consider only the temperature oscillations which have a frequency equal to the engine firing frequency ($\omega = 2\pi N/n_R$).

(*b*) Repeat the calculation for the engine operating at 5000 rev/min.

(*c*) What is the dependence of the penetration depth on the amplitude of surface temperature fluctuations?

12.8. The instantaneous heat-transfer rate $\dot{Q}$ from the cylinder gases to the combustion chamber walls in a spark-ignition engine may be estimated approximately from the equation

$$\dot{Q} = h_c A(\bar{T}_g - \bar{T}_w)$$

where h_c is the heat-transfer coefficient, A is the surface area, $\bar{T}_g$ is the average temperature of the gas in the cylinder, and $\bar{T}_w$ is the average wall temperature. The heat-transfer coefficient can be obtained from the Nusselt, Reynolds, and Prandtl number relationship:

$$\mathrm{Nu} = C(\mathrm{Re})^m(\mathrm{Pr})^n$$

where $C = 0.4$, $m = 0.75$, $n = 0.4$. The characteristic velocity and length scale used in this relation are the mean piston speed and the cylinder bore.

Assuming appropriate values for the engine geometry and operating conditions at wide-open throttle with the wall temperature at 400 K, at an engine speed of 2500 rev/min, and using the cylinder pressure versus crank angle curve of Fig. 14-9, calculate the following:

(*a*) The *average* temperature of the gas in the cylinder at $\theta = -180°$, $-90°$, $0°$, $20°$, $40°$, $90°$, $150°$.

(*b*) The instantaneous heat-transfer coefficient h_c and heat-transfer rate $\dot{Q}$ from the gas to the combustion chamber walls of one cylinder at these crank angles. Plot these results versus θ.

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(*c*) Estimate the fraction of the fuel energy that is transferred to the cylinder walls during compression and expansion.

Assume for the gas that the viscosity $\mu = 7 \times 10^{-5}$ kg/m · s, the thermal conductivity $k = 1.5 \times 10^{-1}$ J/m · s · K, the molecular weight = 28, and the Prandtl number is 0.8. Assume that the combustion chamber is disc-shaped with $B = 102$ mm, $L = 88$ mm, and $r_c = 9$. (The calculations required for this problem are straightforward; do not attempt anything elaborate.)

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