COMBUSTION

Combustion is a chemical reaction in which certain element of the fuel combine with oxygen and releasing a large quantity of energy causing an increase in temperature of gases. There are many thousands of different hydrocarbon fuel components, which consist mainly of hydrogen and carbon but may also contain oxygen, nitrogen, and/or sulphur, etc. The main combustible elements are carbon and hydrogen; another combustible element often present in fuels, although rather undesirable, is sulphur. The oxygen necessary for combustion is obtained from air, which is oxygen diluted chiefly by nitrogen.

COMPOSITION OF AIR:

Table gives proportion of oxygen and nitrogen by volume as well as by mass of dry air. In combustion, oxygen is the reactive component of air. The properties of air vary geographically, with altitude and with time. It is usually sufficiently accurate to regard air as 21% oxygen and 79% inert gases taken as nitrogen

Gas	Volume %	Mass %	Molar Mass	Molar Fraction	Molar Ratio
O_2	20.95	23.16	32.00	0.21	1
N_2	78.09	75.55	28.01	0.79	3.76
A	0.93	1.25	38.95		
CO_2	0.03	0.04	44.01		
Air	100.00	100.00	28.95	1.00	4.76

(often called atmospheric nitrogen) by volume.

For each mole of oxygen in air there are $\dfrac{1-0.21}{0.21} = 3.76$ moles of atmospheric nitrogen The molar mass of air is obtained as 28.95 (usually approximated by 29) from the equation $M = \dfrac{1}{n}\sum_i n_i M_i = \sum_i \widetilde{x}_i M_i$ where $\widetilde{x}_i$ is the mole fraction defied as the number of moles of each component n_i, divided by the total number of moles of mixture n. Because atmospheric nitrogen contains traces of other species, its molar mass is slightly different from that of pure molecular nitrogen, i.e., $M_{aN_2} = \dfrac{28.95 - .21 \times 32}{1 - 0.21} = 28.14$. The density of dry air can be obtained from equation of state with universal gas constant, R_o = 8314.3 J/kmol K and M = 28.95: $\rho(kg/m^3) = \dfrac{3.482 \times 10^{-3}\, p\,(Pa)}{T(K)}$.

Thus the value for the density of dry air at 1 atmosphere (1.0133×10^5 Pa) and 25°C is 1.184 kg/m^3. Actual air normally contains water vapor, the amount depending on temperature and degree of saturation. Typically the proportion by mass is about 1 percent, though it can rise to about 4 percent under extreme conditions. The relative humidity compares the water vapor content of air with that required to saturate. It is defined as the ratio of the partial pressure of water vapor actually present to the saturation pressure at the same temperature.

STOICHIOMETRY

Most IC engines obtain their energy from the combustion of a hydrocarbon fuel with air, which converts chemical energy of the fuel to internal energy in the gases within the engine. The maximum amount of chemical energy that can be released (heat) from the fuel is when it reacts (combust) with a stoichiometric amount of oxygen. Stoichiometric oxygen (sometimes also called theoretical oxygen) is just enough to convert all carbon in the fuel to CO_2 and all hydrogen to H_2O, with no oxygen left over.

Stoichiometric Reaction: A stoichiometric reaction is defined such that the only products are carbon dioxide and water. The components on the left side of a chemical reaction equation which are present before the reaction are called reactants, while the components on the right side of the equation which are present after the reaction are called products or exhaust.

Chemical equations are balanced on a basis of the conservation of mass principle (or the mass balance), which can be stated as follows: The total mass of each element is conserved during a chemical reaction. That is, the total mass of each element in the products must be equal to the total mass of that element in the reactants even though the elements exist in different chemical compounds in the reactants and products. Also, the total number of atoms of each element is conserved during a chemical reaction since the total number of atoms of an element is equal to the total mass of the element divided by its atomic mass. The total number of moles is not conserved during a chemical reaction.

In chemical reactions molecules react with molecules, so in balancing a chemical equation, molar quantities (fixed number of molecules) are used and not mass quantities. It is convenient to balance combustion reaction equations for one kmole of fuel. The energy released by the reaction will thus have units of energy per kmole of fuel, which is easily transformed to total energy when the flow rate of fuel is known.

One kmole of a substance has a mass in kilograms equal in number to the molecular mass (molar mass) of that substance. Mathematically, $m = NM$ [kmole] [kg/kmole], where: m = mass[kg], N = number of moles[kmole], M = molecular mass[kg/kmole], 1 kmole = 6.02×10^{26} molecules.

For example, the stoichiometric reaction of propane would be $C_3H_8 + a\,O_2 = b\,CO_2 + d\,H_2O$

Carbon balance gives: $b = 3$; Hydrogen balance gives: $2d = 8 \Rightarrow d = 4$; Oxygen balance gives: $2a = 2b + d \Rightarrow a = 5$. Then, reaction equation becomes $C_3H_8 + 5\,O_2 = 3\,CO_2 + 4\,H_2O$

Very small powerful engines could be built if fuel were burned with pure oxygen. However, the cost of using pure oxygen would be prohibitive, and thus is not done. Air is used as the source of oxygen to react with fuel. Nitrogen and argon are essentially chemically neutral and do not react in the combustion process. Their presence, however, does affect the temperature and pressure in the combustion chamber. Nitrogen usually enters a combustion chamber in large quantities at low temperatures and exists at considerably higher temperatures, absorbing a large proportion of the chemical energy released during combustion. When the products are at low temperature the nitrogen is not significantly affected by the reaction. At very high temperatures a small fraction of nitrogen react with oxygen, forming hazardous gases called NO_x.

Stoichiometric Air/Fuel Ratio: Stoichiometric (or chemically correct or theoretical) proportions of fuel and air are calculated from the stoichiometric reaction on molar basis. The stoichiometric Air to fuel ratio on molar basis is $4.76\,\varepsilon = 4.76\,(\alpha + 0.5\beta)$.

The stoichiometric air/fuel $(A/F)_s$ or fuel/air $(F/A)_s$ ratios depend on fuel composition. Stoichiometric air/fuel $(A/F)_s$ on mass basis can also be calculated.

Figure shows the variation in $(A/F)_s$ as the ratio of hydrogen to carbon ($y = H/C$) varies from 1 (e.g. benzene) to 4 (methane). The complete combustion of a general hydrocarbon fuel of average molecular composition $C_\alpha H_\beta$ with air would be
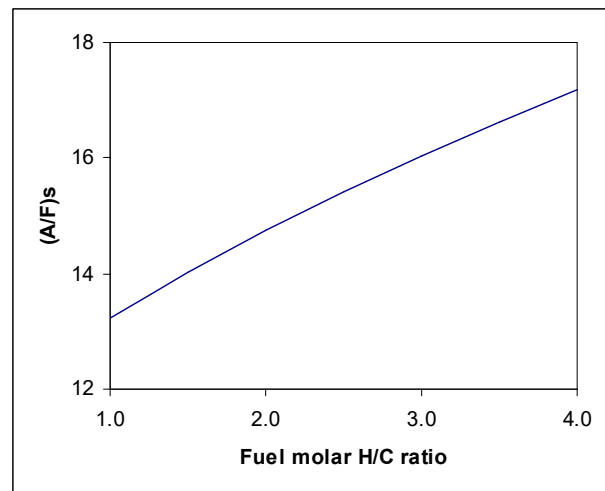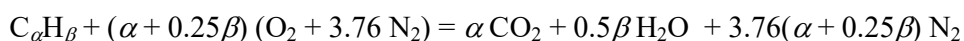

$C_\alpha H_\beta + \varepsilon\,(O_2 + 3.76\,N_2) = v_1\,CO_2 + v_2\,H_2O + v_3\,N_2$
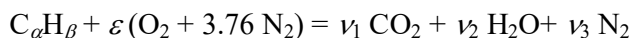
Carbon balance gives: $v_1 = \alpha$; Hydrogen balance gives: $2v_2 = \beta \Rightarrow v_2 = 0.5\beta$;

Oxygen balance gives: $2\varepsilon = 2v_1 + v_2 \Rightarrow \varepsilon = \alpha + 0.25\beta$;

Nitrogen balance gives: $2(3.76)\varepsilon = 2v_3 \Rightarrow v_3 = 3.76(\alpha + 0.25\beta)$.

Then, reaction equation becomes

$C_\alpha H_\beta + (\alpha + 0.25\beta)\,(O_2 + 3.76\,N_2) = \alpha\,CO_2 + 0.5\beta\,H_2O + 3.76(\alpha + 0.25\beta)\,N_2$

This equation can also be written in the following form:

$$CH_{\beta/\alpha} + (1 + 0.25\beta/\alpha)(O_2 + 3.76\ N_2) = CO_2 + (0.5\beta/\alpha)\ H_2O + 3.76(1 + 0.25\beta/\alpha)\ N_2$$

It can be noted that only the ratios i.e., only the relative proportions on a molar basis are used. Thus the fuel composition could have been written CH_y where $y = \beta/\alpha$.

The ratio β/α for the hydrocarbon $C_\alpha H_\beta$ used by the engine may not be known, but the ultimate analysis of the fuel gives the percentage by mass of Carbon, C, and hydrogen, H, and it is easy to see that $\dfrac{H}{C} = \dfrac{1.008\beta}{12.01\alpha}$

$$\left(\frac{A}{F}\right)_s = \left(\frac{F}{A}\right)_s^{-1} = 4.76\varepsilon\,\frac{M_a}{M_F} = 4.76(1 + 0.25y)\left(\frac{28.95}{12.01 + 1.008y}\right).$$

The molar masses of oxygen, atmospheric nitrogen, atomic carbon, and atomic hydrogen are respectively, 32, 28.16, 12.01, and 1.008. It can be noted that $(A/F)_s$ depends only on y, the ratio of hydrogen to carbon moles.

EXAMPLE-1
A hydrocarbon fuel of composition 84.1% by mass carbon, C, and 15.9% by mass hydrogen, H, has a molar mass of 114.15. Determine (a)the number of moles of (i) air required for stoichiometric combustion and (ii) products produced per mole of fuel; (b)$(A/F)_s$ and $(F/A)_s$' (c)the molar masses of the reactants and the products; (d)mole fractions of the product species.
Ans. (a) (i) 59.5 (ii) 64 (b) 15.09; 0.066 (c) 30.36; 28.7 (d) 0.1250 CO_2, 0.1406 H_2O, 0.7344 N_2

The complete combustion of a general fuel of molecular composition $C_\alpha H_\beta O_\gamma N_\delta$ with air would be

$$C_\alpha H_\beta O_\gamma N_\delta + \varepsilon(O_2 + 3.76\ N_2) = \nu_1\ CO_2 + \nu_2\ H_2O + \nu_3\ N_2$$
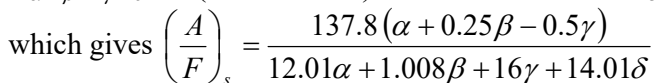
which gives $\left(\dfrac{A}{F}\right)_s = \dfrac{137.8\,(\alpha + 0.25\beta - 0.5\gamma)}{12.01\alpha + 1.008\beta + 16\gamma + 14.01\delta}$

LEAN OR RICH MIXTURE REACTIONS
Fuel-air mixtures with more than or less than the stoichiometric air requirement can be burned. Combustion can occur, within limits, i.e., the proportions of the fuel and air must be in the proper range for combustion to begin. For example, natural gas will not burn in air in concentrations less than 5 percent or greater than about 15 percent. With excess air or fuel-lean combustion, the extra air appears in the products in unchanged form. With less than stoichiometric air requirement, i.e., with fuel-rich combustion, there is insufficient oxygen to oxidize fully the fuel C and H to CO_2 and H_2O. The products are a mixture of CO_2 and H_2O with carbon monoxide CO and hydrogen H_2 (as well as N_2). Carbon monoxide is a colourless, odourless, poisonous gas which can be further burned to form CO_2. It is produced in any combustion process when there is a deficiency of oxygen. It is very likely that some of the fuel will not get burned when there is a deficiency of oxygen. This unburned fuel ends up as pollution in the exhaust of the engine. Because the composition of the combustion products is significantly different for fuel-lean and fuel-rich mixtures, and because the stoichiometric fuel/air ratio depends on fuel composition, the ratio of the actual fuel/air ratio to the stoichiometric ratio (or its inverse) is a more informative parameter for defining mixture composition. Various terminology is used for the amount of air or oxygen used in combustion. 80% stoichiometric air = 80% theoretical air = 80% air = 20% deficiency of air; 120% stoichiometric air = 120% theoretical air = 120% air = 20% excess air

Fuel/Air Equivalence Ratio: For actual combustion in an engine, the fuel/air equivalence ratio is a measure of the fuel-air mixture relative to stoichiometric conditions. It is defined as:

$$\phi = \frac{(F/A)_{act}}{(F/A)_{stoich}} = \frac{(A/F)_{stoich}}{(A/F)_{act}}$$

where: $F/A = m_f/m_a$ = fuel-air ratio; $A/F = m_a/m_f$ = air-fuel ratio; m_a = mass of air; m_f = mass of fuel
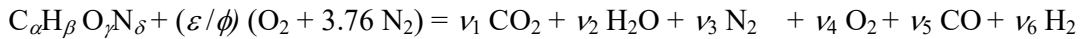
Relative Air/Fuel Ratio: The inverse of ϕ, the relative air/fuel ratio λ, is also sometimes used.

$\lambda = \phi^{-1} = \dfrac{(F/A)_{stoich}}{(F/A)_{act}} = \dfrac{(A/F)_{act}}{(A/F)_{stoich}}$ For fuel-lean mixtures: $\phi < 1, \lambda > 1$, oxygen in exhaust

For stoichiometric mixtures: $\phi = \lambda = 1$, maximum energy released from fuel

For fuel-rich mixtures: $\phi > 1, \lambda < 1$, CO and fuel in exhaust

Lean or Rich Mixture Reactions: At low temperatures and reactant carbon to oxygen ratios less than one, the overall combustion reaction can be written as

$C_\alpha H_\beta O_\gamma N_\delta + (\varepsilon/\phi) (O_2 + 3.76\, N_2) = \nu_1\, CO_2 + \nu_2\, H_2O + \nu_3\, N_2 + \nu_4\, O_2 + \nu_5\, CO + \nu_6\, H_2$

For reactant carbon to oxygen ratios greater than one, we would have to add solid carbon C(s) and several other species.

Convenient approximations for lean and rich combustion are $\phi > 1, \nu_4 = 0; \phi < 1\ \nu_5 = \nu_6 = 0$

Lean Mixture Reactions: For the lean or stoichiometric cases, atom-balance equations are sufficient to determine the product composition (four equations and four unknowns)

For general fuel, fuel-lean combustion reaction can be written as:

$C_\alpha H_\beta O_\gamma N_\delta + (\varepsilon/\phi) (O_2 + 3.76\, N_2) = \nu_1\, CO_2 + \nu_2\, H_2O + \nu_3\, N_2 + \nu_4\, O_2$
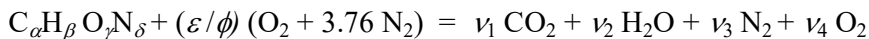
EXAMPLE-2: Combustion of isooctane with 25% excess air or 1.25 times the stoichiometric air requirement ($\phi = 0.8$),

$C_8H_{18} + (12.5/0.8) (O_2 + 3.76\, N_2) = 8\, CO_2 + 9\, H_2O + 58.75\, N_2 + 3.125\, O_2$
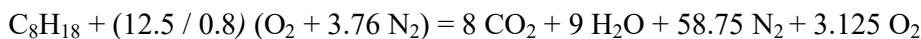
giving mole fractions of product species as $0.1014\, CO_2$, $0.1141\, H_2O$, $0.7448\, N_2$, $0.0396\, O_2$

Rich Mixture Reactions: With fuel-rich combustion the product composition cannot be determined from an element balance alone and an additional assumption about the chemical composition of the product species must be made. If we assume that H_2 is not present in the exhaust, as the reaction rate of hydrogen is faster than that of carbon, then atom balance equations would be sufficient to determine the product composition.

EXAMPLE-3: Combustion of isooctane with 80% stoichiometric air ($\phi = 1.25$)

$C_8H_{18} + (12.5/1.25) (O_2 + 3.76\, N_2) = 3\, CO_2 + 9\, H_2O + 37.6\, N_2 + 5\, CO$
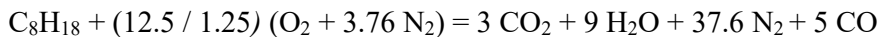
giving mole fractions of product species as $0.0549\, CO_2$, $0.1648\, H_2O$, $0.6886\, N_2$, $0.0916\, CO$.

For the fuel-rich case, assuming equilibrium between the species CO_2, H_2O, CO and H_2. The reaction relating these species (often called water gas reaction) would be $CO_2 + H_2 \rightleftharpoons CO + H_2O$

We introduce an equilibrium constant K for the reaction which is a function of temperature.

$K(T) = \dfrac{\nu_2 \nu_5}{\nu_1 \nu_6}$ K can be determined from a curve fit to JANAF table data:

EXAMPLE-4

In fuel-rich combustion product mixtures, equilibrium between species CO_2, H_2O, CO and H_2 is assumed. For $\phi = 1.25$, for C_8H_{18}—air combustion products, determine the (a) mole fractions and (b) the mass fractions of the product species. (Assume equilibrium constant, $K = 3.5$)

Ans. (a) $0.0839\, CO_2$, $0.1359\, H_2O$, $0.6886\, N_2$, $0.0626\, CO$, $0.0289\, H_2$

(b) $0.1356\, CO_2$, $0.0898\, H_2O$, $0.7081\, N_2$, $0.0644\, CO$, $0.0021\, H_2$

EXAMPLE-5

(a) For stoichiometric combustion of nitromethane, CH_3NO_2, find air/fuel ratio and mole fractions of the product species (b) If nitromethane burns without air compare its exhaust composition with that obtained from stoichiometric combustion. (Assume equilibrium constant, $K = 3.5$)

Ans. (a) $(A/F)s = 1.693$; $0.1718\, CO_2$, $0.2577\, H_2O$, $0.5705\, N_2$

(b) $0.0833\, CO_2$, $0.2500\, H_2O$, $0.1667\, N_2$, $0.2500\, CO$, $0.2500\, H_2$

EQUIVALENCE RATIO DETERMINATION FROM EXHAUST GAS CONSTITUENTS

Exhaust gas composition depends on the relative proportions of fuel and air fed to the engine, fuel composition, and completeness of combustion. These relationships can be used to determine the operating fuel/air equivalence ratio of an engine from knowledge of its exhaust composition. It is common practice to analyze the exhaust of an IC engine. Chemical composition of the hot exhaust is determined by various chemical, electronic, and thermal methods. This may be done by taking a sample of the exhaust gases and running it through an external analyzer. When this is done, there is a high probability that the exhaust gas will cool below its dew-point temperature before it is fully analyzed, and the condensing water will change the composition of the exhaust. To compensate for this, a dry analysis can be performed by first removing all water vapour from the exhaust, usually by some thermo-chemical means.

Exhaust Dew-Point Temperature: When exhaust gases of an IC engine are cooled below the dew-point temperature of the water vapor, moisture starts to condense to liquid. It is important to be able to predict the dew-point temperature since the water droplets often combine with the sulfur dioxide that may be present in the combustion gases, forming sulfuric acid, which is highly corrosive.

It is common to see water droplets come out of an automobile exhaust pipe when the engine is first started and the pipe is cold. Very quickly the pipe is heated above the dew point temperature, and condensing water is then seen only as vapor when the hot exhaust is cooled by the surrounding air, much more noticeable in the cold wintertime.

EXAMPLE-6

The four-cylinder engine of a light truck has been converted to run on propane oil. A dry analysis of the engine exhaust gives the following volumetric percentages:$CO_2$4.90%, CO 9.79%, O_2 2.45%. Calculate the equivalence ratio at which the engine is operating. (Ans. 1.11)

COMBUSTION EFFICIENCY:

Even when the flow of air and fuel into an engine is controlled exactly at stoichiometric conditions, combustion will not be "perfect," and components other than CO_2, H_2O, and N_2 are found in the exhaust products. One major reason for this is the extremely short time available for each engine cycle, which often means that less than complete mixing of the air and fuel is obtained. Some fuel molecules do not find an oxygen molecule to react with, and small quantities of both fuel and oxygen end up in the exhaust. In practice, the exhaust gas of an internal combustion engine contains incomplete combustion products (e.g., CO, H_2, unburned hydrocarbons, soot) as well as complete combustion products (CO_2 and H_2O).

Under lean operating conditions the amounts of incomplete combustion products are small. Under fuel-rich operating conditions these amounts become more substantial since there is insufficient oxygen to complete combustion.

Because a fraction of the fuel's chemical energy is not fully released inside the engine during the combustion process, hence combustion efficiency is defied as the fraction of the fuel energy supplied which is released in the combustion process. Figure shows how combustion efficiency varies with the fuel/air equivalence ratio for internal combustion engines.

SI engines have combustion efficiency in the range of 95% to 98% for lean mixtures. For rich mixtures, where there is not enough air to react all the fuel, the combustion efficiency steadily decreases as the mixture becomes richer. Combustion efficiency is little affected

Combustion efficiency as a function of fuel equivalnec ratio

by other engine operating and design variables, provided the engine combustion process remains stable.

CI engines always operate lean overall and typically have combustion efficiencies of about 98%.
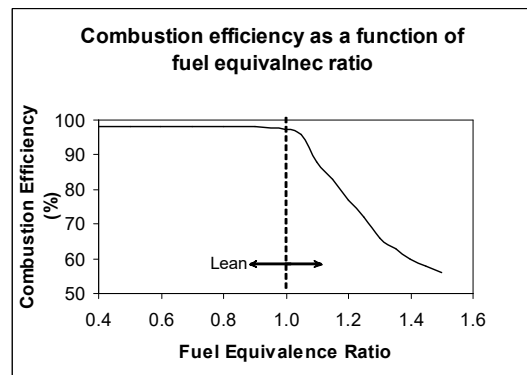
DISSOCIATION

In actual engine performance the combustion usually is not complete even in the presence of excess air, because of dissociation at high temperature and also unsatisfactory mixing of the air and the fuel. When hydrocarbon fuels react with oxygen (air) at high engine temperatures (greater than about 2200 K), dissociation of normally stable components can occur. CO_2, dissociates to CO and O, O_2 dissociates to monatomic O, N_2 dissociates to N, etc. This not only affect chemical combustion, but is a cause of one of the major emission problems of IC engines. Nitrogen as diatomic N_2 does not react with other substances, but when it dissociates to monatomic nitrogen at high temperature it readily reacts with oxygen to form Nitrogen dioxide (NO_x), a major pollutant from automobiles e.g., NO (Nitric oxide) and NO_2 (Nitrogen dioxide). (Note: *N_2O is Nitrous oxide*). In such cases the exhaust gases may contain certain percentages of CO, H_2, NO, OH, H, O, and CH_4. To avoid generating large amounts of nitrogen oxides, combustion temperatures in automobile engines are lowered, which reduces the dissociation of N_2. Unfortunately, this also lowers the thermal efficiency of the engine.
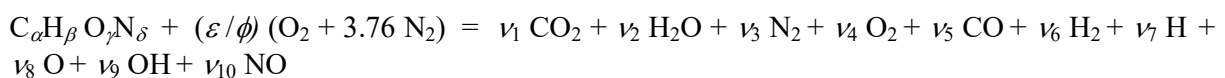
CHEMICALLY REACTING GAS MIXTURES

The working fluids in engines are mixtures of gases. Depending on the problem under consideration and the portion of the engine cycle in which it occurs chemical reactions may:
(1) be so slow that they have a negligible effect on mixture composition (the mixture composition is essentially "frozen");
(2) be so rapid that the mixture state changes and the composition remains in chemical equilibrium;
(3) be one of the rate-controlling processes that determine how the composition of the mixture changes with time.

Chemical Equilibrium: It is a good approximation for performance estimates in engines to regard the burned gases produced by the combustion of fuel and air as in chemical equilibrium. It means that the chemical reactions, by which individual species in the burned gases react together, produce and remove each species at equal rates. No net change in species composition results. For example, if the temperature of a mass of CO_2 gas in a vessel is increased sufficiently, some of the CO_2 molecules dissociates into CO and O_2 molecules. If the mixture of CO_2, CO, and O_2 is in equilibrium, then CO_2 molecules are dissociating into CO and O_2 at the same rate as CO and O_2 molecules are recombining in the proportions required to satisfy the equation $CO + \frac{1}{2}O_2 \rightleftharpoons CO_2$
Owing to the dissociation when carbon and hydrogen react with oxygen of air, the reaction does not proceed to the point where all carbon and hydrogen are consumed, forming CO_2 and H_2O. Instead, the reactions proceed only until an equilibrium condition is reached in which not only the final products of reaction, CO_2 and H_2O, are present, but also certain amounts of the original reaction substances and some intermediate compounds. The second law of thermodynamics defines the criterion for chemical equilibrium, in which minimization of Gibbs free energy is considered.

Practical Chemical Equilibrium: The proportions, at equilibrium, of the different constituents of the products of combustion depend on the original proportions and on the temperature and pressure reached at the end of the reaction. The higher the final temperature, the less complete the combustion reaction. On the other hand, the higher the pressure, the more complete the reaction. In fuel-air mixtures at equilibrium after combustion, the following substances usually are present: CO_2, H_2O, N_2, O_2, CO, H_2, H, O, OH, NO, C, and CH_4. However, free carbon, C, and methane, CH_4, are present in such small portions that they can be disregarded. If we consider, H, O, OH and NO the only species of importance because of dissociation then the reaction equation be written as:

$$C_\alpha H_\beta O_\gamma N_\delta + (\varepsilon / \phi)(O_2 + 3.76\,N_2) = \nu_1\,CO_2 + \nu_2\,H_2O + \nu_3\,N_2 + \nu_4\,O_2 + \nu_5\,CO + \nu_6\,H_2 + \nu_7\,H + \nu_8\,O + \nu_9\,OH + \nu_{10}\,NO$$

Atom balancing yields the four equations. Introduction of six equilibrium constants will yield ten equations for the ten unknowns. A solution can be obtained by solving these equations for the given fuel composition, fuel/air equivalence ratio, and product pressure and temperature.

Chemical Reaction Rates: Whether a system is in chemical equilibrium depends on whether the time constants of the controlling chemical reactions are short compared with time scales over which the system conditions (temperature and pressure) change. Chemical processes in engines are often not in equilibrium. Important examples on non-equilibrium phenomena are the flame reaction zone where the fuel is oxidized, and the air-pollutant formation mechanism. Such non-equilibrium processes are controlled by the rate at which actual chemical reactions which convert reactants to products occur. The rates at which chemical reactions proceed depend on the concentration of the reactants, temperature, and whether any catalyst is present. This field is called chemical kinetics.

Unburned Mixture Composition: During the exhaust stroke of an engine, not all of the exhaust gases pushed out of the cylinder by the piston, a small residual being trapped in the clearance volume. The amount of this residual depends on the compression ratio, and somewhat on the location of the valves and valve overlap. The unburned mixture for a spark ignition engine during intake and compression consists of air, fuel, and previously burned gases. It is therefore, a mixture of CO_2, H_2O, N_2, O_2, CO, and H_2 for fuel-rich mixtures, and fuel (usually vapor). The composition of the unburned mixture does not change significantly during intake and compression. It is sufficiently accurate to assume the composition is frozen. For the compression ignition engine, the unburned mixture prior to injection contains no fuel; it consists of air and previously burned gas. The combustion products or burned mixture gases, during the combustion process and much of the expansion process, are close to thermodynamic equilibrium. As these combustion products cool, recombination occurs. Towards the end of the expansion process, the gas composition departs from the equilibrium composition; recombination no longer occur fast enough to maintain the reacting mixture in equilibrium. During the exhaust process, reactions are sufficiently slow so that for calculating thermodynamic properties the composition can be regarded as frozen. The mass of charge trapped in the cylinder (m_c) is the inducted mass per cycle (m_i), plus the residual mass (m_r), left over from the previous cycle. The residual fraction (x_r) is $x_r = m_r / m_c$. Typical residual fractions in SI engines range from 20% at light load to 7% at full load. In CI engines the residual fraction is smaller (a few percent) due to the higher compression ratio, and in naturally aspirated engines is approximately constant since the intake is unthrottled. If the inducted mixture is fuel and air (or air only), then the burned gas fraction (x_b) in the unburned mixture during compression equals the residual fraction.

Exhaust Gas Recirculation: In some engines, a fraction of the engine exhaust gases is recycled to the intake to dilute the fresh mixture for control of NO_x emissions. If the percent of exhaust gas recycled (%EGR) is defined as the percent of the total intake mixture which is recycled exhaust, EGR (%) = m_{EGR} / m_i, where m_{EGR} is the mass of exhaust gas recycled, then the burned gas fraction in the fresh mixture is $x_b = \dfrac{m_{EGR} + m_r}{m_c} = \left(\dfrac{EGR}{100} \right)(1 - x_r) + x_r$. Up to about 30% of the exhaust can be recycled; the burned gas fraction during compression can, therefore, approach 30 to 40%.

Heat Of Combustion: From steady-flow energy balance equation with no work interaction heat liberated by the combustion reaction of a hydrocarbon fuel with air is the difference between the total enthalpy of the products and the total enthalpy of the reactants. This is called heat of reaction, enthalpy of reaction, heat of combustion, or enthalpy of combustion and is given by:

$$Q = \sum_{PROD} N_i h_i - \sum_{REACT} N_i h_i ,$$

where: N_i = number of moles of component i, $h_i = \left(h_f^0 \right) + \Delta h_i$, h_f^0 = enthalpy of formation, the enthalpy needed to form one mole of that component at standard conditions of 25°C and 1 atm, Δh_i = change of enthalpy from standard temperature for component i.
Q will be negative, meaning that heat is given up by the reacting gases.
Values of h_f^0 and Δh are molar-specific quantities and can be found in tables. The enthalpy of combustion of a particular fuel will be different at different temperatures and pressures.

Heating Value: Heating value (also called calorific value) is defined as the amount of heat released when a fuel is burned completely in a steady-flow process and the products are returned to the state of the reactants. In other word, the heating value of fuel is equal to the negative of the heat of reaction for one unit of fuel, and thus is a positive number. It is calculated at constant pressure or at constant volume assuming both the reactants and the products are at a standard temperature (usually 25°C) for the complete combustion of unit mass of fuel. Complete combustion means that all carbon is converted to CO_2, all hydrogen is converted to H_2O, and any sulfur present is converted to SO_2. Care must be used when using heating values, which almost always are given in mass units (kJ/kg), whereas heats of reaction are obtained using molar quantities. For fuels containing hydrogen, whether the H_2O in the products is in the liquid or gaseous phase affects the value of the heat of reaction. The term higher heating value (or gross heating value) is used when the water formed is all condensed to the liquid phase; the term lower heating value (or net heating value) is used when water formed is all in the vapor phase. The two heating values at constant pressure are related by $Q_{HHV\,p} = Q_{LHV\,p} + \Delta h_{vap}$. The difference Δh_{vap} is the heat of vaporization of the water which is equal to $(m_w/m_f)(h_{fg})_w$, where (m_w/m_f) is the ratio of mass of water produced to mass of fuel burned.

A similar expression for the two heating values at constant volume are related by $Q_{HHV\,v} = Q_{LHV\,v} + \Delta u_{vap}$, where $\Delta u_{vap} = (m_w/m_f)(u_{fg})_w$. The heating value at constant pressure is the more commonly used. The difference between the heating values at constant pressure and constant volume is small. Heating values of fuels are measured in calorimeters. The heating values of common fuels are given in the tables. Higher heating value is usually listed on fuel containers, the higher number making that fuel seem more attractive. For engine analysis, lower heating value is the logical value to use. All energy exchange in the combustion chamber occurs at high temperature, and only somewhere down the exhaust process, where it can no longer affect engine operation, does the product gas get cooled to the dew point temperature. Heat into the engine that gets converted to output work can be given as: $Q_{in} = \eta_c\, m_f\, CV_f$, where: η_c = combustion efficiency, m_f = mass of fuel, CV_f = lower heating value per unit mass of fuel. Usually the heating value is determined in MJ/kg. For gaseous fuels it is more convenient to have the heating value determined in MJ/m^3 at standard pressure and temperature. The heating value per m^3 may be found by multiplying the heating value expressed in MJ/kg by density of the gaseous fuel. Or, if heating value per kmole is known, the heating value per m^3 may be found by dividing the MJ/kmole by the volume of the gaseous fuel per kmole for standard conditions.

Mixture Heating Value: For the reciprocating IC engine, representing an approximately constant admission value machine because of the fixed displacement, the heat energy input per working cycle is much more determined by the mixture heating value, in which also the composition of the mixture given by the air fuel equivalence ratio has to be taken into consideration. Mixture heating value per unit mass of mixture is given by $CV_m = \dfrac{CV_f}{1 + \dfrac{(A/F)_s}{\phi}}$. Mixture heating value per unit

volume of mixture is given by $CV_v = CV_m = \rho_m$, where ρ_m is the density of mixture

EXAMPLE-7
Evaluate the lower heating value per unit mass of stoichiometric mixture and per unit volume of stoichiometric mixture (at standard atmospheric conditions) for isooctane. Assume the fuel is fully vaporised. Lower heating value of isooctane (C_8H_{18}) is 44.3 MJ/kg.
(Ans. 2.75 MJ/kg; 3.41 MJ/m^3)

COMBUSTION TEMPERATURE

One of the most important criteria in an engine is the combustion temperature (and hence pressure). Figure shows the temperatures reached on the combustion of mixtures of fuel and air of different strengths between 50% weak and 50% rich, for a compression ratio of 5/1 of an SI engine. The maximum temperature should theoretically be produced by a stoichiometric mixture strength, but in fact it occurs at about 20% rich. The shape of the temperature curve is due to the dissociation of CO_2 and H_2O into CO, H_2, and O_2 which is slight at a temperature of 2000°C, but increases rapidly above that. In engine combustion the dissociation of CO_2 affects engine behaviour more than that of H_2O which is relatively slight.

Combustion theory allows the dissociation proportions of CO, H_2, and O_2 to be calculated and represented in the combustion equations. Hence the energy released on combustion can be calculated. If the formation of nitric oxide which occurs at the higher temperatures is taken into account the temperatures attained are even lower, due to the absorption of energy to form NO as shown in Figure. At the higher compression ratios of modern engines higher temperatures and pressures are attained and dissociation occurs, not only to a greater extent for NO, but also to some common radicals mainly OH, H, and O, e.g. at 3000°C a stoichiometric mixture of octane and air at equilibrium will contain OH (1.4%), H (0.3%), O (0.3%), and NO (0.3%). Mixture strength, particularly for a spark-ignited engine, can vary considerably due to the way in which the mixture is created and distributed. It is not a controlled process as it is in the diesel engine. One of the results of this is a considerable variation in the cycle to cycle and cylinder to cylinder performance of petrol engines. Figure shows pressure variation for 10 consecutive cycles in a single cylinder SI engine due to inconsistency of combustion. An important parameter is the spark timing. Figure shows the form of the variation of the maximum pressure reached in the cylinder with the advance of the ignition before the TDC position. An estimation of the maximum temperature reached in an IC engine can be obtained by calculating the adiabatic flame temperature (also called adiabatic combustion temperature) of the input air-fuel mixture. This is done by setting $Q = 0$ in heat of reaction equation, yielding $\sum_{PROD} N_i h_i = \sum_{REACT} N_i h_i$. Assuming that inlet conditions of the reactants are known, it is necessary to find the temperature of the products such that this equation will be
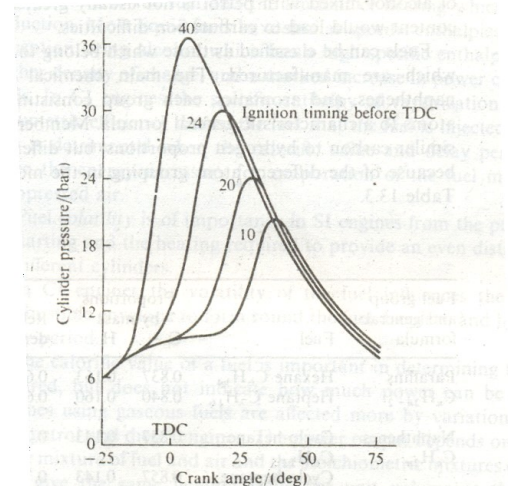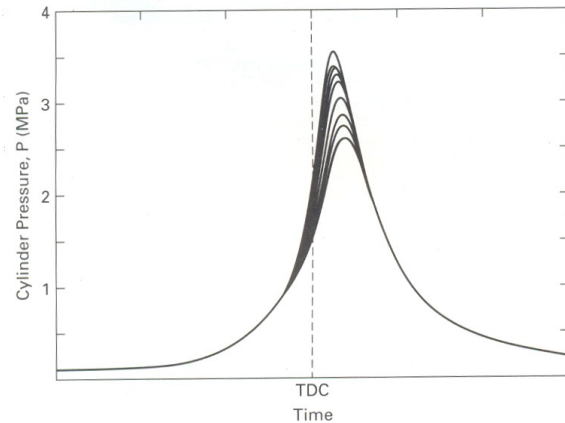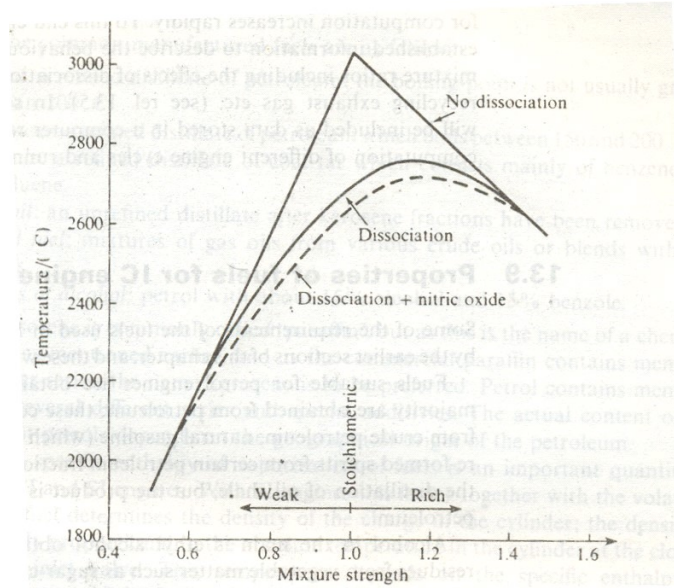
satisfied. This is the adiabatic flame temperature. Because the temperature of the product is not known prior to the calculations, the determination of the adiabatic flame temperature requires the use of an iteration technique. A temperature is assumed for the product gases, and the enthalpy of product is determined for this temperature. If it is not equal to the enthalpy of reactants calculations are repeated with another temperature. When the oxidant is air, the product gases mostly consists of N_2, and a good first guess for the adiabatic flame temperature is obtained by treating the entire product gases as N_2. Adiabatic flame temperature is the ideal theoretical maximum temperature that can be obtained for a given fuel and air mixture. In combustion chambers, the highest temperature to which a material can be exposed is limited by metallurgical considerations. Therefore, adiabatic flame temperature is an important consideration in the design of combustion chambers, gas turbines, and nozzles. The actual peak temperature in an engine cycle will be several hundred degrees less than this since the combustion is usually incomplete, some heat loss takes place, and some combustion gases dissociate at high temperatures. There is some heat loss even in the very short time of one cycle, and combustion efficiency is less than 100% so a small amount of fuel does not get burned. All these factors contribute to making the actual peak engine temperature somewhat less than adiabatic flame temperature. The maximum temperature in a combustion chamber can be controlled by adjusting the amount of excess air, which serves as a coolant.

SELF-IGNITION TEMPERATURE

Bringing a fuel into intimate contact with oxygen is not sufficient to start a combustion process. The fuel must be brought above its ignition temperature (also called self-ignition temperature) to start the combustion. If the temperature of an air-fuel mixture is raised high enough, the mixture will self-ignite without the need of a spark plug or other external igniter. This is the basic principle of ignition in a compression ignition engine. The compression ratio is high enough so that the temperature rises above self-ignition temperature (SIT) during the compression stroke. Self-ignition then occurs when fuel is injected into the combustion chamber. On the other hand, self-ignition (pre-ignition, or auto-ignition) is not desirable in an SI engine, where a spark plug is used to ignite the air-fuel at the proper time in the cycle. The compression ratios of gasoline-fueled SI engines are limited to about 11:1 to avoid self-ignition. Table gives minimum ignition temperatures of various substances in atmospheric air.

Fuel	SIT (°C)
Hydrogen	580
Methane	630
Ethane	515
CO	610
Propane	480
Gasoline	260
Kerosine	210
Diesel	210
Ethanol	365
Methanol	385

When self ignition does occur in an SI engine higher than desirable, pressure pulses are generated. These high pressure pulses can cause damage to the engine and quite often are in the audible frequency range. This phenomenon is often called knock or ping. Figure shows the basic process of what happens when self-ignition occurs. If a combustible air-fuel mixture is heated to a temperature less than SIT, no ignition will occur and the mixture will cool off. If the mixture is heated to a temperature above SIT, self-ignition will occur after a short time delay called ignition delay (ID). The higher the initial temperature rise above SIT, the shorter will be ID. Ignition delay is generally on the order of thousandths of a second. The values for SIT and ID for a given air-fuel mixture are ambiguous, depending on many variables which include temperature, pressure, density, turbulence, swirl, fuel-air ratio, presence of inert gases, etc. Ignition delay is generally a very small fraction of second. During this time, preignition reactions occur, including oxidation of some fuel components and even cracking of some large hydrocarbon components into smaller HC molecules. These preignition reactions raise the temperature at local spots, which then promotes additional reactions until, finally, the actual combustion reaction occurs.
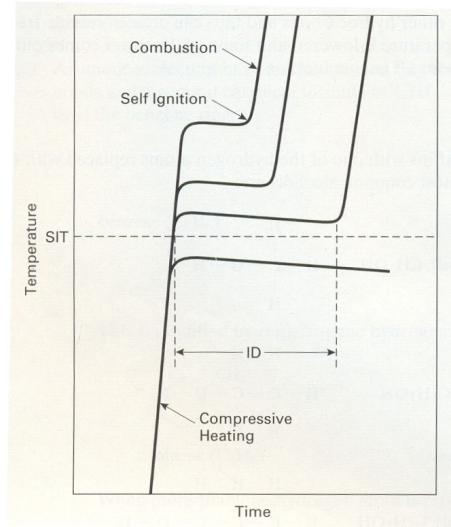
SELF-IGNITION

Figures a, b, c show the pressure-time history within a cylinder of a typical SI engine.

(a) Normal Combustion with No Knock   (b) Combustion with Light Knock   (c) Combustion with Heavy Knock
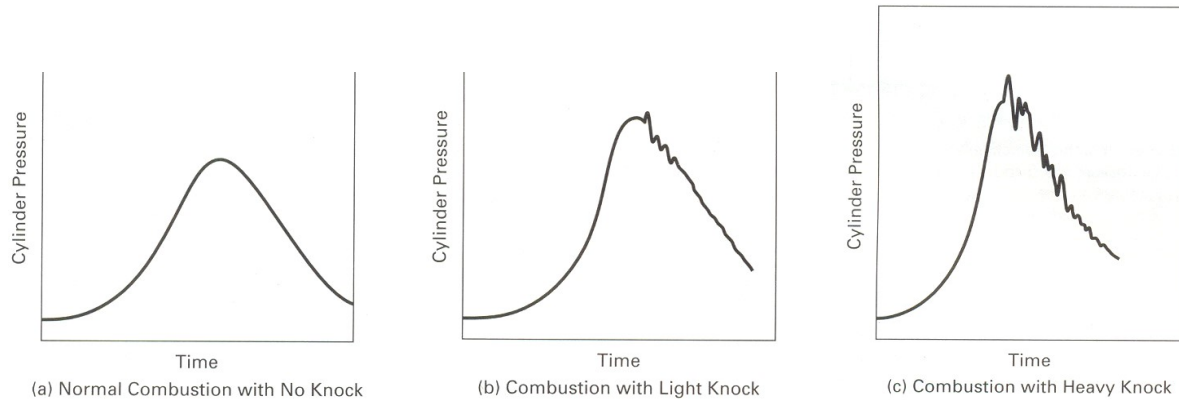
With no self-ignition the pressure force on the piston follows a smooth curve, resulting in smooth engine operation (Fig. a). When self-ignition does occur, pressure forces on the piston are not smooth and engine knock occurs (Fig. b & c). The combustion process is a fast exothermic gas-phase reaction (where oxygen is usually one of the reactants). A flame is a combustion reaction which can propagate subsonically through space; motion of the flame relative to the unburned gas is the important feature. The existence of flame motion implies that the reaction is confined to the zone which is small in thickness compared to the dimensions of the apparatus—in our case the engine combustion chamber. The reaction zone is usually called the flame front.

MECHANICAL ENGINEERING DEPARTMENT
Advanced Internal Combustion Engines (MSc Thermal)
Problem Sheet No. 1

1. A CI engine running at 2400 rpm has an ignition delay of 15° of crankshaft rotation. What is the ignition delay in seconds?   {Ans: 1.04 ms}

2. Draw the chemical structure formula of
   (a) 3,4-dimethylhexane,   (b) 2,4-diethylpenatne,   (c) 3-methyl-3-ethylpentane. These are isomers of what other molecules?
   {Ans: Isomers of (a) & (c) Octane (b) Nonane}

3. Hydrogen is used as a fuel in an experimental engine and is burned with stoichiometric oxygen. Write the balanced chemical reaction equation. Calculate fuel-oxygen ratio and equivalence ratio.   {Ans: 0.126; 1}

4. Draw the chemical structural formula of 2-methyl-2,3-ethylbutane. This is an isomer of what chemical family? Write the balanced chemical reaction equation for one mole of this fuel burning with an equivalence ratio of 0.7. Calculate the stoichiometric air/fuel ratio for this fuel.   {Ans: Isomer of Paraffin family; 15.043}

5. Methanol is burned in an engine with air at an equivalence ratio of 0.75. Write the balanced chemical equation for this reaction. Calculate air-fuel ratio.   {Ans: 8.6}

6. Ethanol is burned in an engine with air at an equivalence ratio of 1.1. Write the balanced chemical equation for this reaction assuming no hydrogen is present in the exhaust. Calculate air-fuel ratio.   {Ans: 8.16}

7. Find the amount of air necessary for combustion with 25% excess air of 100 m^3 of natural gas which has an analysis of 2.5% H_2, 0.5% CO, 92.0% CH_4, 1.0% O_2, 0.2% CO_2, and 3.8% N_2.   {Ans: 1097.8 m^3}

8. A six-cylinder, four-stroke cycle SI engine with multipoint port fuel injectors operating on an Otto cycle at wide open throttle (WOT). The fuel injectors are set to deliver an air-fuel ratio such that gasoline (C_8H_{15}) would burn at stoichiometric conditions. Calculate:
   (a) equivalence ratio if gasoline is replaced with ethanol without readjusting the air-fuel delivered by the fuel injectors
   (b) increase or decrease in brake power using alcohol instead of gasoline under these conditions, with the same air flow rate and same thermal efficiency. Assume ethanol would burn under these conditions with the same combustion efficiency.
   {Ans: (a) 0.616 (b) 37.3% decrease}

9. What would be the percentage increase in engine power if stoichiometric gasoline is replaced with stoichiometric (i) methanol, (ii) ethanol, (iii) nitromethane? Assume the same combustion efficiency, thermal efficiency, and air flow rate for all fuels.
   {Ans: (i) 5.24% (ii) 1.69% (iii) 118.4%}

10. Isooctane is supplied to a four-cylinder spark-ignition engine at 2g/s. Calculate the air flow rate for stoichiometric combustion. If the engine is operating at 1500 rev/min, estimate the mass of fuel and air entering each cylinder per cycle. The engine displaced volume is 2.4 liters. What is the volumetric efficiency?
   {Ans: 30.22 g/s; 0.04 g, 0.6 g; 85.1%}

11. Calculate the exhaust gas composition (molar) of a butane-fuelled spark-ignition engine operating with equivalence ratio of 0.9. Assume the butane (C_4H_{10}) is fully burned within the cylinder.

{Ans: CO_2 = 10.847%, H_2O = 13.558%, N_2 = 73.637%, O_2 = 1.958%}

12. A six-liter, eight cylinder, four stroke cycle SI race car engine operates at 6000 rpm using stoichiometric nitromethane as fuel. Combustion efficiency is 99%, and the fuel input rate is 0.198 kg/s. Calculate:
    (a) flow rate of air into the engine
    (b) volumetric efficiency of the engine
    (c) heat generated in each cylinder per cycle and
    (d) chemical energy in unburned fuel in the exhaust.

{Ans: (a) 0.335 kg/s (b) 94.6% (c) 5.33 kJ (d) 21.6 kW}

13. A 50% coal-water slurry (50% coal and 50% water by mass) is burned in stoichiometric air. Calculate
    (a) air-fuel ratio
    (b) lower heating value per kg of fuel
    (c) heating value per kg of mixture, and
    (d) heating value per m^3 of mixture.

{Ans: (a) 5.75 (b) 16.9 MJ/kg (c) 2.51 MJ/kg (d) 2.584 MJ/m^3}

14. Liquid petroleum gas (LPG) is used to fuel SI engines. A typical sample of the fuel consists of 70% by volume propane (C_3H_8), 5% by volume butane (C_4H_{10}), and 25% by volume propene (C_3H_6). The higher heating values of the fuels are: propane, 50.38 MJ/kg; butane, 49.56 MJ/kg; propene (propylene), 48.95 MJ/kg. Work out the overall combustion reaction for stoichiometric combustion of one kmole of LPG with air, and the stoichiometric F/A and A/F ratios. What are the higher and lower heating values for combustion of this fuel with excess air, per unit mass of LPG?

{Ans: 0.0648, 15.43; 50 MJ, 46.2 MJ}

15. A flexible-fuel vehicle operates with a stoichiometric fuel mixture of one-third isooctane, one-third ethanol, and one-third methanol, by mass. Calculate air-fuel ratio.

{Ans: 10.17}

16. A fuel mixture consists of 20% isooctane, 20% triptane, 20% isodecane, 40% toluene by moles. Write the chemical reaction formula for the stoichiometric combustion of one mole of this fuel. Calculate air-fuel ratio and lower heating value of fuel mixture.

{Ans: 14.52; 43 MJ/kg}

17. The fuel which a coal-burning carbon monoxide generator supplies to an automobile engine consists of CO + ½(3.76) N_2. Calculate stoichiometric air-fuel ratio and higher and lower heating values of the fuel. Estimate the loss of power when this fuel is used for the carburetted engine originally designed to operate on stoichiometric gasoline.

{Ans: 0.854; 3.507 MJ/kg, 3.507 MJ/kg; 37%}

18. A taxicab is equipped with a flexible-fuel four-cylinder SI engine running on a mixture of methanol and gasoline. Calculate the actual equivalence ratio the carburettor is supplying to the engine when it is adjusted to supply stoichiometric air at normal operating conditions using gasoline fuel but is actually operating with 10% (by mass) methanol (M10) fuel. How must the air-fuel ratio change as the fuel flow to the engine shifts from 10% methanol (M10) to 85% methanol (M85) at an equivalence ratio of 0.95?

{Ans: 0.944; From 14.53 to 8.09}

19. Evaluate and compare the lower heating values per unit mass of stoichiometric mixture and per unit volume of stoichiometric mixture (at standard atmospheric conditions) for methane, isooctane, methyl alcohol, and hydrogen. Assume the fuel is fully vaporised. {Ans: 2.75 MJ/kg, 2.75 MJ/kg, 2.69 MJ/kg, 3.40 MJ/kg; 3.11 MJ/m^3, 3.41 MJ/m^3, 3.23 MJ/m^3, 2.92 MJ/m^3}

20. Calculate the low-temperature burned gas composition resulting from the combustion of 7 g/s air with 0.48 g/s of fuel, when fuel is (i) Ethane (C_2H_6) (ii) Ethanol (C_2H_6O). (Assume equilibrium constant, K = 3.5)
    {Ans: (i) CO_2 = 0.093, H_2O = 0.1641, N_2 = 0.7054, CO = 0.025, H_2 = 0.0125;
    (ii) CO_2 = 0.0794, H_2O = 0.119, N_2 = 0.7272, O_2 = 0.0744}

21. An SI engine is operated on isooctane fuel. The exhaust gases are cooled, dried to remove water, and then analyzed for CO_2, CO, H_2, O_2. Using the overall combustion reaction for a range of equivalence ratios from 0.5 to 1.5, calculate the mole fractions of CO_2, CO, H_2, and O_2 in the dry exhaust gas, and plot the results as a function of equivalence ratio. Assume:
    (a) that all the fuel is burnt inside the engine and that the ratio of moles CO to moles H_2 in the exhaust is 3:1, and
    (b) that there is no hydrogen in the exhaust for lean mixtures. For high-power engine operation the air/fuel ratio is 14:1. What is the exhaust gas composition, in mole fractions, before the water is removed?
    {Ans: CO_2 = 0.1096, H_2O = 0.1411, N_2 = 0.7195, CO = 0.0224, H_2 = 0.0074}

22. The exhaust gases of a hydrogen-fuelled engine contain 22.3% H_2O, 7.44% O_2, and 70.2% N_2. At what equivalence ratio is it operating? {Ans: 0.6}

23. The measured dry exhaust gas composition of a propane-fuelled spark-ignition engine is CO_2 = 10.8%, O_2 = 4.5%, CO = 0%, H_2 = 0% (water was removed before the measurement). Calculate the equivalence ratio. {Ans: 0.8 }

24. Gas is sampled from the exhaust manifold of an IC engine and analysed. The mole fractions of species in the exhaust are: CO_2, 0.0585; H_2O, 0.0468; N_2, 0.772; O_2, 0.123. Other species such as CO and unburned hydrocarbons can be neglected. The fuel is a synthetic fuel derived from coal containing only carbon and hydrogen. What is the ratio of hydrogen atoms to carbon atoms in the fuel? Calculate the equivalence ratio at which the engine is operating. Is the IC engine a conventional SI or a CI engine? Explain. {Ans: 1.6, 0.4, CI}

25. The measured engine fuel flow rate is 0.4 g/s, air flow rate is 5.6 g/s, and exhaust gas composition (measured dry) is CO_2 = 13.0%, CO = 2.8%, with O_2 essentially zero. Unburned hydrocarbon emissions can be neglected. Compare the equivalence ratio calculated from the fuel and air flow with the equivalence ratio calculated from exhaust gas composition. The fuel is gasoline with a H/C ratio of 1.87. Assume a H_2 concentration equal to one-third the CO concentration. {Ans: 1.04, 1.046}

26. Butane, C_4H_8 is burned in an engine with a fuel-rich air-fuel ratio. Dry analysis of the exhaust gives the following volume percents:
    CO_2 = 14.95%, O_2 = 0%, CO = 0%, H_2 = 0%, C_4H_8 = 0.75%, with the rest being N_2. Higher heating value of this fuel is 46.9 MJ/kg. Write the balanced chemical equation for one mole of this fuel at these conditions. Calculate the air-fuel ratio, equivalence ratio, lower heating value of the fuel, and energy released when one kg of this fuel is burned in the engine with a combustion efficiency of 98%.
    {Ans: 12.28; 1.2; 43.76 MJ/kg; 42.89 MJ}

27. The exhaust from an SI engine has the following composition (in mole fractions):
$CO_2 = 0.12$; $H_2O = 0.14$; $N_2 = 0.7247$; $CO = 0.01$; $H_2 = 0.005$; $C_8H_{18} = 0.0003$
The fuel is isooctane, C_8H_{18}; as shown above, a small fraction of the fuel escapes from the cylinder unburned. Calculate the combustion *inefficiency* in the engine; i.e., the percentage of the entering fuel energy which is not fully released in the combustion process and leaves the engine in the exhaust gases. What fraction of this inefficiency is due to the unburned fuel emissions?   {Ans: 6.6%, 27%}

28. A gasoline engine operates steadily on a mixture of isooctane and air. An analysis of the combustion products yields the following values (on a dry volumetric basis):
$CO_2 = 11.4\%$, $N_2 = 84.1\%$, $O_2 = 1.6\%$, $CO = 2.9\%$
Find the composition in moles (number of moles per mole of isooctane) of the reactants and the reaction products.   {Ans: Reactants: $O_2 = 12.5$, $N_2 = 47$; Products: $CO_2 = 6.38$, $H_2O = 9$, $N_2 = 47$, $O_2 = 0.895$, $CO = 1.62$}

29. A 2-liter displacement four-cylinder engine, operating at 2000 rev/min and 30% of its maximum power at that speed, has the following exhaust composition (in percent by volume or mole percent):
$CO_2 = 11\%$; $H_2O = 11.5\%$; $N_2 = 74.5\%$; $O_2 = 2\%$; $CO = 0.5\%$; $H_2 = 0\%$; unburned hydrocarbons (expressed as CH_2) = 0.5%.
The fuel is $(CH_2)_n$ with a heating value of 44 MJ/kg. The heating value of unburned hydrocarbons is 44 MJ/kg.
(a) Is the engine a CI or SI engine?
(b) Is there enough oxygen in the exhaust to burn the fuel completely? Briefly explain.
(c) Calculate the fraction of the input fuel energy which exits the engine unburned as (i) CO and (ii) unburned HC.
(d) An inventor claims a combustion efficiency of 100% can be achieved. What percentage improvement in engine specific fuel consumption would result?
{Ans: (a) SI engine; (b) Yes; (c) (i) 0.019, (ii) 0.0417; (d) 6.46%}

30 The following exhaust data were obtained from a four-stroke cycle SI engine. CO_2, O_2, CO, and NO_x molar concentrations are all measured fully dry; HC is measured fully wet as ppm C_1. Determine the fuel/air equivalence ratio for the following three sets of data. Make the following assumptions:
(a) the equilibrium constant $K = 3.5$
(b) the fuel composition is $C_8H_{15.12}$
(c) the unburned hydrocarbon H/C ratio is the same as that of the fuel; and
(d) NO_x is entirely NO.
(i) $CO_2 = 14.0\%$, $O_2 = 0.7\%$, $CO = 0.64\%$, $NO_x = 3600$ ppm, $HC = 3200$ ppm.
(ii) $CO_2 = 13.8\%$, $O_2 = 0.0\%$, $CO = 3.05\%$, $NO_x = 1600$ ppm, $HC = 3450$ ppm.
(iii) $CO_2 = 12.5\%$, $O_2 = 4.0\%$, $CO = 0.16\%$, $NO_x = 4600$ ppm, $HC = 2100$ ppm.
{Ans: (i) 1.0034 (ii) 1.11 (iii) 0.8339}
****

Assignment

1. An engine is operated on an **assigned** fuel. The exhaust gases are cooled, dried to remove water, and then analyzed for CO_2, CO, H_2, and O_2. Assume:
   - (a) that all the fuel is burnt inside the engine
   - (b) that there is no hydrogen and CO in the exhaust for lean mixtures and
   - (c) equilibrium constant $K = 3.5$.

   Using the overall combustion reaction for a range of equivalence ratios from 0.5 to 1.5, calculate
   - (i) the mole fractions and mass fractions of the exhaust gas species in the dry exhaust gas, and plot the results as a function of equivalence ratio.
   - (ii) mole fractions and mass fractions of the exhaust gas species before the water is removed and plot the results as a function of equivalence ratio.

2. Solve problem 30 assuming **assigned** fuel in (b) for the **assigned** data set.

3. Evaluate for **assigned** fuel
   - (i) higher heating value per unit mass of fuel
   - (ii) lower heating value per unit mass of mixture for **assigned** equivalence ratio
   - (iii) lower heating value per unit volume of mixture (at standard atmospheric conditions) for **assigned** equivalence ratio.

   Assume the fuel is fully vaporised.

4. Solve problem 17.

5. Solve problem 29.

****

LIST OF FUELS

  (i) Natural gas (Volume composition: 2.5% H_2, 0.5% CO, 92.0% CH_4, 1.0% O_2, 0.2% CO_2, and 3.8% N_2)

 (ii) LPG (Volume composition: 70% C_3H_8, 5% C_4H_{10}, and 25% C_3H_6)

(iii) Producer gas (Volume composition: 15% H_2, 24% CO, 2% CH_4, 1% O_2, 5% CO_2, and 53% N_2)

(iv) Nitromethane

 (v) Methanol

(vi) Ethanol

(vii) Methylated Spirit (Volume composition: 90% C_2H_6O, 10% CH_4O)

(viii) Gasoline

(ix) Kerosene ($C_{10}H_{22}$)

 (x) Light Diesel

(xi) Heavy Diesel

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Appendix

Element	Molar Mass
C	12.010
H	1.008
O	16.00
N	14.01

Fuel Name	Fuel Formula	Lower Heating Value (MJ/kg)
Coal (Carbon)	C	33.80
Hydrogen	H_2	120.00
Carbon monoxide	CO	10.10
Methane	CH_4	50.00
Nitromethane	CH_3NO_2	10.92
Methanol	CH_4O	20.05
Ethanol	C_2H_6O	26.95
Propene	C_3H_6	48.95
Propane	C_3H_8	46.19
Butane	C_4H_{10}	49.56
Toluene	C_7H_8	40.60
Triptane	C_7H_{16}	44.44
Heptane	C_7H_{16}	44.56
Gasoline	C_8H_{15}	43.00
Isooctane	C_8H_{18}	44.30
Isodecane	$C_{10}H_{22}$	44.22
Light Diesel	$C_{12.3}H_{22.2}$	42.50
Heavy Diesel	$C_{14.6}H_{24.8}$	41.40
Cetane	$C_{16}H_{34}$	43.98