

SCHOOL OF MECHANICAL ENGINEERING

DEPARTMENT OF AUTOMOBILE ENGINEERING

Unit - 1 - COMBUSTION OF FUELS – SME1606

UNIT -1

COMBUSTION OF FUELS

Stoichiometry - calculation of theoretically correct air required for combustion of liquid and gaseous fuels, volumetric and gravimetric analysis of the dry products of combustion, mass of dry gas per kg of fuel burnt, mass of carbon in the exhaust gas, mass of carbon burnt to carbon-monoxide per kg of fuel, heat loss due to incomplete combustion, exhaust gas analysis by Orsat apparatus.

STOICHIOMETRY

This section develops relations between the composition of the reactants (fuel and air) of a combustible mixture and the composition of the products. Since these relations depend only on the conservation of mass of each chemical element in the reactants, only the relative elemental composition of the fuel and the relative proportions of fuel and air are needed.

Complete oxidation of simple hydrocarbon fuels forms carbon dioxide (C02) from all of the carbon and water (H₂0) from the hydrogen, that is, for a hydrocarbon fuel with the general composition CnHm,

$$C_n H_m + \left(n + \frac{m}{4}\right)O_2 \longrightarrow nCO_2 + \frac{m}{2}H_2O$$

Even in the idealized case of complete combustion, the accounting of all species present in combustion exhaust involves more than simply measuring the CO2 and H20. Since fuels are burned in air rather than in pure oxygen, the nitrogen in the air may participate in the combustion process to produce nitrogen oxides. Also, many fuels contain elements other than carbon, and these elements may be transformed during combustion. Finally, combustion is not always complete, and the effluent gases contain unburned and partially burned products in addition to CO2 and H20. Air is composed of oxygen, nitrogen, and small amounts of carbon dioxide, argon, and other trace species. Since the vast majority of the diluent in air is nitrogen, for our purposes it is perfectly reasonable to consider air as a mixture of 20.9% (mole basis) O2 and 79.1 % (mole basis) N2 • Thus for every mole of oxygen required for combustion, 3.78 mol of nitrogen must be introduced as well. Although nitrogen may not significantly alter the oxygen balance, it does have a major impact on the thermodynamics, chemical kinetics, and formation of pollutants in combustion systems. For this reason it is useful to carry the "inert" species along in the combustion calculations. The stoichiometric relation for complete oxidation of a hydrocarbon fuel, CnHm, becomes

$$C_n H_m + \left(n + \frac{m}{4}\right) (O_2 + 3.78N_2) \longrightarrow nCO_2 + \frac{m}{2} H_2O + 3.78\left(n + \frac{m}{4}\right)N_2$$

Thus for every mole of fuel burned, 4.78(n + m14) mol of air are required and 4. 78(n + m14) + m14 mol of combustion products are generated. The molar *fuel/air* ratio for stoichiometric combustion is 11 [4. 78(n + m14)].

Gas compositions are generally reported in terms of mole fractions since the mole fraction does not vary with temperature or pressure as does the concentration (moles/ unit volume). The product mole fractions for complete combustion of this hydrocarbon fuel are

$$y_{CO_2} = \frac{n}{4.78(n + m/4) + m/4}$$
$$y_{H_2O} = \frac{m/2}{4.78(n + m/4) + m/4}$$
$$y_{N_2} = \frac{3.78(n + m/4)}{4.78(n + m/4) + m/4}$$

Calculation of theoretically correct air required for combustion of liquid Fuels

Air is a mixture of about 21% oxygen, 78% nitrogen, and 1% other constituents by volume. For combustion calculations it is usually satisfactory to represent air as a 21% oxygen, 79% nitrogen mixture, by volume. Thus for every 21 moles of oxygen that react when air oxidizes a fuel, there are also 79 moles of nitrogen involved. Therefore, 79/21 = 3.76 moles of nitrogen are present for every mole of oxygen in the air. At room temperature both oxygen and nitrogen exist as diatomic molecules, O2 and N2, respectively. It is usually assumed that the nitrogen in the air is non reacting at combustion temperatures; that is, there are as many moles of pure nitrogen in the products as there were in the reactants. At very high temperatures small amounts of nitrogen react with oxygen to form oxides of nitrogen, usually termed NOx. These small quantities are important in pollution analysis because of the major role of even small traces of NOx in the formation of smog. However, since these NOx levels are insignificant in energy analysis applications, nitrogen is treated as inert here. The molecular weight of a compound or mixture is the mass of 1 mole of the substance. The average molecular weight, M, of a mixture, as seen earlier, is the linear combination of the products of the mole fractions of the components and their respective molecular weights. Thus the molecular weight for air, Mair, is given by the sum of the products of the molecular weights of oxygen and nitrogen and their respective mole fractions in air. Expressed in words:

 M_{air} = Mass of air/Mole of air = (Moles of N₂ /Mole of air)(Mass of N₂ /Mole of N₂) + (Moles of O₂/Mole of air) (Mass of O₂ /Mole of O₂)

Or $M_{air} = 0.79 M_{nitrogen} + 0.21 M_{oxygen} = 0.79(28) + 0.21(32) = 28.84$

The mass fractions of oxygen and nitrogen in air are then $mf_{oxygen} = (0.21)(32)/28.84 = 0.233$, or 23.3%

and $mf_{nitrogen} = (0.79)(28)/28.84 = 0.767$, or 76.7%

Theoretical Air and Air-Fuel Ratio -The minimum amount of air which will allow the complete combustion of the fuel is called the Theoretical Air (also referred to as Stoichiometric Air). In this case the products do not contain any oxygen. If we supply less than theoretical air then the products could include carbon monoxide (CO), thus it is normal practice to supply more than theoretical air to prevent this occurrence. This **Excess Air** will result in oxygen appearing in the products.

The standard measure of the amount of air used in a combustion process is the Air-Fuel Ratio (AF), defined as follows:

$$AF = \frac{m_{air}}{m_{fuel}}$$

Thus considering only the reactants of the methane combustion with theoretical air presented above, we obtain:

CH₄ +2(O₂ +3.76N₂) ↔ Reactants
fuel 2 kmol air

$$AF = \frac{m_{air}}{m_{fuel}} = \frac{2(4.76) [kmol] 29 [kg/kmol]}{1 [kmol] (12 + 4) [kg/kmol]}$$

$$AF = 17.3 \frac{kg - air}{kg - fuel}$$

Analysis of the Products of Combustion - Combustion always occurs at elevated temperatures and we assume that all the products of combustion (including the water vapor) behave as ideal gases. Since they have different gas constants, it is convenient to use the ideal gas equation of state in terms of the universal gas constant as follows:

 $\mathsf{P},\mathsf{V}=m.\mathsf{R},\mathsf{T}=\frac{m}{M}\,\mathsf{R},\mathsf{M},\mathsf{T}$

where: m is mass [kg], V is volume [m^3], P is pressure [kPa] and T is temperature [K]

 $R\left[\frac{kJ}{kg.K}\right] \text{ is the gas constant}$ $M\left[\frac{kg}{kmol}\right] \text{ is the molar mass of the substance}$ thus: P. V = N.R_u.T where: R_u = R.M = 8.314 $\left[\frac{kJ}{kmol.K}\right]$ is the Universal Gas Constant N = $\frac{m}{M}$ is the number of kmols

Volumetric and gravimetric analysis

Fuels are generally comprised of a number of different elements in a vast array of molecular forms. The main elements in flammable materials are Carbon C, Hydrogen, H, Oxygen, O, Nitrogen, N, and Sulphur with other trace elements to boot.

The components of a mixture (whether liquid, solid or gas) can take be expressed in many ways: volumetric, gravimetric, dry, wet, ash free, as supplied etc. etc. It is important right from the start to know exactly what these mean so that, when combustion calculations are carried out, we have the right numbers.

Gravimetric and Volumetric Ratios

The two fundamental methods of defining the quantities of mixture are by weight (gravimetric) or by volume (molar). For clarity, the following symbols are often (but not exclusively) used.

c i = the gravimetric fraction (mass fraction) of element / molecule i

y i =the volumetric fraction (molar fraction) of element / molecule i

Of course, the sum of mass or mole fractions for all species in a mixture will be unity:

$$\sum_{N} \mathscr{W}_{i} = \sum_{N} \mathscr{X}_{i} = 1$$

To convert from mole fraction to mass fraction we must know the molecular weight, M (kg/kmol), of the individual chemical species. We then calculate the mass of all species by multiplying the volume fraction by the molecular weight. Then we divide the mass of the individual element/molecule by the total mass.

$$\chi_i = \frac{\psi_i M_i}{\sum_{N} \psi_i M_i}$$
- Molar to mass

$$\psi_{i} = \frac{\chi_{i} / M_{i}}{\sum_{N} \chi_{i} / M_{i}}$$
- Mass to molar

So, if we are given a coal of composition C 95%, H 4%, Cl 0.5%, S 0.5% by weight. Then the molar composition is calculated thus:

Element	🗆 i (mass)	🗆 i / Mi	□ i (volumetric)
С	95	7.917	66.25
Н	4	4.0	33.47
Cl	0.5	0.014286	0.195
S	0.5	0.015625	0.131
Total	100	11.95	100.046

Mass of dry gas per kg of fuel

Mass of carbon in the exhaust gas

The mass emission of pollutants are calculated by means of the following equation :

$$M_{i} = \frac{V_{mix} * Q_{i} * k_{H} * C_{i} * 10^{-6}}{d}$$

Mi = Mass emission of the pollutant i in g/km

Vmix = Volume of the diluted exhaust gas expressed in m3/test and corrected to standard conditions 293 K and 101.33 kPa

Qi = Density of the pollutant i in kg/m3 at normal temperature and pressure (293 K and 101.33 kPa)

kH = Humidity correction factor used for the calculation of the mass emissions of oxides of nitrogen. There is no humidity correction for HC and CO.

Ci = Concentration of the pollutant i in the diluted exhaust gas expressed in ppm and corrected by

the amount of the pollutant i contained in the dilution air.

d = distance covered in km

Mass of carbon burnt to carbon-monoxide

Carbon monoxide (CO) is a byproduct of incomplete combustion and is essentially partially burned fuel. If the air/fuel mixture does not have enough oxygen present during combustion,

it will not bum completely. When combustion takes place in an oxygen starved environment, there is insufficient oxygen present to fully oxidize the carbon atoms into carbon dioxide (CO2). When carbon atoms bond with only one oxygen atom carbon monoxide (CO) forms.

An oxygen starved combustion environment occurs as a result of air/fuel ratios which are richer than stoichiometry (14.7 to 1). There are several engine operating conditions when this occurs normally. For example, during cold operation, warm-up, and power enrichment. It is, therefore, normal for higher concentrations of carbon monoxide to be produced under these operating conditions. Causes of excessive carbon monoxide includes leaky injectors, high fuel pressure, improper closed loop control, etc



Fig. 1.1 Effect of A/F Ratio on Exhaust CO

Heat loss due to incomplete combustion

The gasoline-powered internal combustion engine takes air from the atmosphere and gasoline, a hydrocarbon fuel, and through the process of combustion releases the chemical energy stored in the fuel. Of the total energy released by the combustion process, about 20% is used to propel the vehicle, the remaining 80% is lost to friction, aerodynamic drag, accessory operation, or simply wasted as heat transferred to the cooling system.

The heat transfer from cycle to cycle varies for different points in an engine. Below figure shows the heat transfer at three different locations in the combustion chamber for a single cylinder during one cycle. There is significant variation in the heat transfer for these points.







* Areas where heat transfer is important

- Intake system: manifold, port, valves
- > In-cylinder: cylinder head, piston, valves, liner

- > Exhaust system: valves, port, manifold, exhaust pipe
- Coolant system: head, block, radiator
- Oil system: head, piston, crank, oil cooler, sump

✤ Information of interest

- Heat transfer per unit time (rate)
- > Heat transfer per cycle (often normalized by fuel heating value)
- > Variation with time and location of heat flux (heat transfer rate per unit area)
- ✤ Heat transfer mostly from hot burned gas
- > That from unburned gas is relatively small
- > Flame geometry and charge motion/turbulence level affects heat transfer rate
- Order of Magnitude
- ➢ SI engine peak heat flux ∼ 1-3 MW/m2
- Diesel engine peak heat flux ~ 10 MW/m2

For SI engine at part load, a reduction in heat losses by 10% results in an improvement in fuel consumption by 3%

- Effect substantially less at high load

ORSAT APPARATUS.

An Orsat gas analyser is a piece of laboratory equipment used to analyse a gas sample (typically fossil fuel flue gas) for its oxygen, carbon monoxide and carbon dioxide content. Although largely replaced by instrumental techniques, the Orsat remains a reliable method of measurement and is relatively simple to use.

The apparatus consists essentially of a calibrated water-jacketed gas burette connected by glass capillary tubing to two or three absorption pipettes containing chemical solutions that absorb the gasses it is required to measure. For safety and portability, the apparatus is usually encased in a wooden box.

The absorbents are:

Potassium Hydroxide (Caustic Potash)

Alkaline pyrogallol

Ammoniacal Cuprous chloride

The base of the gas burette is connected to a levelling bottle to enable readings to be taken at constant pressure and to transfer the gas to and from the absorption media. The burette contains slightly acidulated water with a trace of chemical indicator (typically methyl orange) for coloration.

By means of a rubber tubing arrangement, the gas to be analyzed is drawn into the burette and flushed through several times. Typically, 100ml is withdrawn for ease of calculation. Using the stopcocks that isolate the absorption burettes, the level.

The gas is then passed into the caustic potash burette, left to stand for about two minutes and then withdrawn, isolating the remaining gas via the stopcock arrangements. The process is repeated to ensure full absorption. After leveling the liquid in the bottle and burette, the remaining volume of gas in the burette indicates the percentage of carbon dioxide absorbed.

The same technique is repeated for oxygen, using the pyrogallol, and carbon monoxide using the ammoniacal cuprous chloride.



Fig 1.3 ORSAT APPARATUS

TEXT / REFERENCE BOOKS

- 1. Mishra D P., "Fundamentals of Combustion", PHI Pvt Ltd, 1st Edition, 2008.
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Unit - 2 – THERMODYNAMICS OF COMBUSTION – SME1606

UNIT -2

THERMODYNAMICS OF COMBUSTION

EQUATION OF STATE

An equation of state provides a relationship among \mathbf{P} , \mathbf{T} and \mathbf{V} (or \mathbf{r}) of a substance. Ideal gas behavior (neglect intermolecular forces and volume of molecules themselves):

- P=rRT
- Pv=RT
- PV=mRT
- R=R_{universal}/MW, R_{universal}=8314 J/kmol K

Assumption is appropriate for nearly all systems. since high temperatures associated with combustion generally result in sufficiently low densities for ideal gas behavior to be a reasonable approximation. Real gas laws try to predict true behavior of a gas better than ideal gas law by putting in terms to describe attractions and repulsions between molecules. These laws have been determined empirically or based on a conceptual model of molecular interactions or from statistical mechanics. Examples: **van der Waals** and **Redlich-Kwong** equations.

FIRST LAW OF THERMODYNAMICS

In Words: Heat added to system in going from state 1 to state 2 (Q) minus work done by system in going from state 1 to state 2 (W) equals change in total system energy (E) in going from state 1 to state 2.

$$Q_{12} - W_{12} = \Delta E_{12}$$

$$E = m \left(u + \frac{1}{2} V^2 + gz \right)$$

$$q_{12} - w_{12} = \Delta e_{12} = e_2 - e_1$$

$$\dot{Q}_{12} - \dot{W}_{12} = \frac{dE}{dt}$$

$$\dot{q} - \dot{w} = \frac{de}{dt}$$

CONTROL VOLUME

In Words: Rate of heat transferred across control surface from the surroundings to control volume minus rate of all work done by control volume (including shaft work, but excluding flow work) equals rate of energy flowing out of control volume minus rate of energy flowing into control volume plus net rate of work associated with pressure forces where fluid crosses the control surface, called flow work

Assumptions:

- CV is fixed relative to coordinate system
- Properties of fluid at each point within CV, or on the CS, do not vary with time
- Fluid properties are uniform over inlet and outlet flow areas
- Only one inlet and outlet stream keep this form simple, but can be easily relaxed to allow for multiple inlet/outlet streams.



Fig. 2.1 Variation of specific heat vs. temperature

Example:

- Enthalpy often approximated as $h(T)=C_pT$
- In combustion chemistry, enthalpy must take into account variable specific heats, h(T)=C_p(T)T
- If $C_p(T)$ can be fit with quadratic, solution for flame temperature for certain classes of problems f < 1 and T < 1,250 K leads to closed form solutions
- For higher order fits or f > 1 and/or T > 1,250 K, iterative closure schemes are required for solution of flame temperature

IDEAL-GAS MIXTURES: SOME USEFUL FORMULAS

- Mole fraction of species i, c_i
- Sum of all constituent mole fraction is unity
- Mass fraction of species i, Y_i
- Sum of all constituent mass fractions is unity
- Converting mole fraction to mass fraction
 - MW = molecular weight
- Converting mass fraction to mole fraction

$$\chi_i \equiv \frac{N_i}{N_1 + N_2 + \dots + N_i + \dots} = \frac{N_i}{N_{total}}$$
$$\sum_i \chi_i = 1$$

$$Y_i \equiv \frac{m_i}{m_1 + m_2 + \dots + m_i} = \frac{m_i}{m_{total}}$$
$$\sum_i Y_i = 1$$

$$Y_{i} = \frac{\chi_{i} M W_{i}}{M W_{mixture}}$$
$$\chi_{i} = \frac{Y_{i} M W_{mixture}}{M W_{i}}$$

ABSOLUTE (STANDARD) ENTHALPY, hi, AND ENTHALPY OF FORMATION, h[°]_{f,i}

- For chemically reacting systems concept of absolute enthalpy is very valuable
- Define:

- Absolute enthalpy = enthalpy that takes into account energy associated with chemical bonds (or lack of bonds) + enthalpy associated only with T
- Absolute enthalpy, h = enthalpy of formation, h_f + sensible enthalpy change, Dh_s
- In symbolic form:

 $h_i(T) = h_{f,i}^{\circ}(T_{ref}) + \Delta h_{s,i}(T_{ref})$

- In words first equation says:
 - Absolute enthalpy at T is equal to sum of enthalpy of formation at standard reference state and sensible enthalpy change in going from T_{ref} to T
- To define enthalpy, you need a reference state at which enthalpy is zero (this state is arbitrary as long as it is same for all species).
 - Most common is to take standard state as T_{ref}=298.15 K and P°=1 atm (Appendix A)
 - Convention is that enthalpies of formation for elements in their naturally occurring state at reference T and P are zero.
 - Example, at T_{ref}=25 °C and P°=1 atm, oxygen exists as a diatomic molecule, so:

$$h_{f,O_2}^{\circ}(T_{ref}, P^{\circ}) = h_{f,O_2}^{\circ} = 0$$

Note: Some text books use H for enthalpy per mol (Glassman), some books use h for enthalpy per mol, some use for enthalpy per mol. Use any symbol you like, just know what equations require.

GRAPHICAL INTERPRETATION OF ABSOLUTELY ENTHALPY, HEAT OF FORMATION AND SENSIBLE ENTHALPY

Physical interpretation of enthalpy of formation: net change in enthalpy associated with breaking the chemical bonds of the standard state elements and forming news bonds to create the compound of interest



Fig. 2.2 Variation of enthalpy with temperature

ENTHALPY OF COMBUSTION AND HEATING VALUES

The **heat of combustion**, also known as **heating value** or **heat of reaction**, is numerically equal to **enthalpy of reaction**, but with opposite sign

- Heat of combustion (or heat of reaction) = enthalpy of combustion (or) = enthalpy of reaction)
 - If heat of combustion (or heat of reaction) is positive \rightarrow Exothermic
 - If heat of combustion (or heat of reaction) is negative \rightarrow Endothermic
 - If enthalpy of combustion (or enthalpy of reaction) is positive →
 Endothermic
 - If enthalpy of combustion (or enthalpy of reaction) is negative →
 Exothermic

The upper or higher heating value, **HHV**, is the heat of combustion calculated assuming that all of water in products has condensed to liquid. This scenario liberates most amount of energy, hence called 'upper'. The lower heat value, **LHV**, corresponds to case where none of water is assumed to condense

LATENT HEAT OF VAPORIZATION

In many combustion systems a liquid \leftrightarrow vapor phase change may occur

- **Example 1**: A liquid fuel droplet must first vaporize before it can burn
- Example 2: If cooled sufficiently, water vapor can condense from combustion products

Latent Heat of Vaporization (also called enthalpy of valorization), h_{fg}: Heat required in a constant P process to completely vaporize a unit mass of liquid at a given T

- $h_{fg}(T,P) \equiv h_{vapor}(T,P) - h_{liquid}(T,P)$

- T and P correspond to saturation conditions

Latent heat of vaporization is frequently used with **Clausius-Clapeyron** equation to estimate P_{sat} variation with T

$$\frac{dP_{sat}}{P_{sat}} = \frac{h_{fg}}{R} \frac{dT_{sat}}{T_{sat}^2}$$

- Assumptions:
 - Specific volume of liquid phase is negligible compared to vapor
 - Vapor behaves as an ideal gas
- If h_{fg} is constant integrate to find $P_{sat,2}$ if $T_{sat,1}$ $T_{sat,2}$, and $P_{sat,1}$ are known
- We will do this for droplet evaporation and combustion, e.x. D^2 law.

ADIABATIC FLAME TEMPERATURE

For an adiabatic combustion process, with no change in KE or PE, temperature of products is called **Adiabatic Flame Temperature**

- Maximum temperature that can be achieved for given concentrations of reactants
- Incomplete combustion or heat transfer from reactants act to lower temperature

$$H_{reac}(T_i, P) = H_{prod}(T_{ad}, P)$$
$$h_{reac}(T_i, P) = h_{prod}(T_{ad}, P)$$

Adiabatic flame temperature is generally a good estimate of actual temperature achieved in a flame, since chemical time scales are often shorter than those associated with transfer of heat and work. Most common is constant-pressure **adiabatic** flame temperature. Conceptually simple, but in practice difficult to evaluate because requires detailed knowledge of product composition, which is function of temperature.

CHEMICAL EQUILIBRIUM

Adiabatic flame temperature is calculated assuming complete combustion. All fuel is completely oxidized to form CO₂, H₂O and excess O₂ and N₂ are carried through unaffected. Assumption reasonable for T < 1250 K, but most combustion systems operate at higher T. Species that are normally stable at ambient conditions dissociate. Concentration is determined by a balance between oxidation and formation. Balance is a function of T, P and concentration.

Note: The chemical equilibrium relations we will use still only approximate the species concentrations in a combustion process. That is, they rest on the assumption that the conditions are constant for a sufficiently long time for all the reactions to reach equilibrium.

CHEMICAL EQUILIBRIUM FOR A FIXED-MASS SYSTEM

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$

$$CO + \frac{1}{2}O_2 \rightarrow (1 - \alpha)CO_2 + \alpha CO + \frac{\alpha}{2}O_2$$

If final temperature of combustion reaction is high enough, CO_2 will dissociate. Can calculate adiabatic flame temperature as function of a (a = fraction of CO_2 dissociated). Must consider second law: $dS \ge 0$.

$$S_{mix}(T_f, P) = \sum n_i \overline{s}_i(T_f, P_i)$$

Composition of system will shift toward point of maximum entropy when approaching from either side, since dS is positive. Once maximum entropy is reached no further changes since would violate second law $(dS)_{U,V,m} = 0$.



Fig. 2.3 Variation of Temperature and Specific heat

SECOND LAW OF THERMODYNAMICS: GIBBS FREE ENERGY

To arrive at equilibrium relations, employ 2^{nd} Law of Thermodynamics. State 2^{nd} Law in terms of Gibbs free energy, **G=H-TS**. For a closed system at constant T and P, the Gibbs free energy is minimum at thermodynamic equilibrium.

$$dS = \frac{\delta Q}{T} + dS_{irrev}$$

$$\delta Q = dH - VdP$$

$$TdS = dH - VdP + TdS_{irrev}$$

$$dG = -SdT + VdP - TdS_{irrev}$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,n_i}$$
$$V = \left(\frac{\partial G}{\partial P}\right)_{T,n_i}$$
$$-TdS_{irrev} = \sum_i \frac{\partial G}{\partial n_i}\Big|_{T,P} dn_i$$

$$\sum_{i} \frac{\partial G}{\partial n_i} \bigg|_{T,P} dn_i = 0$$

ADIABATIC COMBUSTION EQUILIBRIUM

Previously we have considered:

Known Stoichiometry + 1st Law (Energy Balance) \rightarrow Adiabatic Flame Temperature Known P and T + 2nd Law (Equilibrium Relations) \rightarrow Stoichiometry

Now we can combine these:

1st Law (Energy Balance) + 2nd Law (Equilibrium Relations) → Adiabatic
 Flame Temperature + Stoichiometry

Guess a T=T_{guess}

Do equilibrium calculation to solve for species concentrations at T_{guess} Plug into 1st Law

- We want $F(T_{guess})=0$
- If $F(T_{guess}) > 0$, then initial guess was too high
- If $F(T_{guess}) < 0$, then initial guess was too low

Increment T_{guess}

TEXT / REFERENCE BOOKS

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Unit – 3- COMBUSTION KINETICS – SME1606

UNIT -3

COMBUSTION KINETICS

COMBUSTION KINETICS

Thermodynamic laws, establishh limits to natural and artificial processes, i.e. bounds to the possible paths, but the path actually followed, and the pace (the process rate), depends on other circumstances. For instance, Thermodynamics does not say that a piece of paper will burn in air, not even after being ignited, and does not deal with the burning rate; it just says that the system paper/air might reach a more stable equilibrium state (more entropy) by burning, and determines that end state (which might be reached also by secularly-slow oxidation). It is Kinetics science which deals with how fast things happen: instantly (i.e. more quickly than monitored, as in explosions), evolving at a sizeable pace (i.e. in the monitoring time-span, as in combustion), or at a negligible rate (i.e. more slowly than monitored, as in slow oxidation). For instance, a piece of paper enclosed in a transparent container with more air than the theoretical one, may not burn completely if ignited (e.g. by a concentrated light), because, as oxygen concentration gets reduced, convection and diffusion might not supply enough oxygen to maintain the minimum heat release needed for propagation. Hydrocarbon fuels cannot burn in N2/O2 mixtures if xO2<12% (<5% for H2 fuel), and hydrocarbon fuels cannot burn in CO2/air mixtures if xO2<15% (<6% for H2 fuel). At room temperature, without ignition, the piece of paper in air will oxidize very slowly (unnoticeable to the eye). Topics covered below are: rate of physical mixing and its effects on ignition, propagation and extinction, and rate of chemical reaction once mixed (including a review of reaction mechanisms). Some basic models of global combustors and of flame structure are dealt with apart.

PHYSICAL MIXING AND ITS EFFECTS ON IGNITION, PROPAGATION AND EXTINCTION

It cannot be stressed enough that kinetics is what finally controls combustion (or any other reaction); Thermodynamics indicates if the reaction is natural (i.e. may proceed in an isolated system) or artificial (i.e. requires some exergy input from outside). Thermodynamics says that a fuel and air may naturally react, but if the kinetics is too slow, an observer concludes that there is no reaction. Some illustrative examples are: the burning of a piece of paper or a candle inside a closed container; the fuel will not burn completely if there is not enough room inside for a good air-convection to the flame, even if with more than stoichiometric air is enclosed. A vivid example of the controlling effect of mixing is presented in Fig. 3.1, showing two similar candle flames, one on the ground. The other on a space platform (no buoyancy effects); candle flames on earth are long, slender and yellow, whereas under weightlessness they are nearly spherical, blue, and burn much slower (sometimes get extinguished), due to the lack of air draught by buoyant convection.



Fig.3 1. Candle flames on earth (left) and on a space station under weightlessness (right).

One of the basic features of combustion is its self-spreading power: under usual conditions, a fuel/air mixture, once ignited, generates a flame-front that sustains itself, i.e. that transmits the activation to the fresh mixture through heat and mass transfer. Two limit cases can be considered for this propagation according to the state of the mixture: combustion propagation when fuel and air are at each other side of the flame (i.e. for a non-premixed mixture), and combustion propagation when both fuel and air are at the same side of the flame (i.e. for a premixed flame).Mass transfer is essential to combustion, which is a special case of combined heat and mass transfer reacting system; and not only inside the combustor itself, but for other combustion-related reactors as in the after-burning catalysts, fuel reformers, etc.

MIXING

Mixing is a pre-requisite for combustion. Mixing (i.e. decreasing bulk differences), is a natural process (i.e. it does not require an energy expenditure), so that, if fuel and oxidizer gases are brought to contact and enough time allowed, a perfect mixing would take place in their energy level (temperature), relative speeds and chemical composition (with the natural stratification in the presence of gravity or another force field). But mixing is a slow physical process if not forced by convection (large-scale transport) and turbulence (large-scale to small-scale transport). Turbulent mixing is the rule in all practical fluid flows at scales larger than the millimeter, from the piping of water, fuels, gases..., to the wakes behind vehicles of any sort, to all atmosphere, ocean and stellar motions (there are some exceptions, as the laminar diffusing contrails left by jet aircraft).

Two extreme cases of mixing are considered in combustion: combustion in a premixed system (prepared well-before-hand, or well-stirred), and combustion in the common-interface layer where non-premixed fuel and air come into contact. For premixed combustion, the mixture ratio specification is established before-hand, whereas for non-premixed combustion, the mixture ratio specification depends on the actual feeding flow-rates of fuel and air.

Mixture ratio specification

Mixture ratio specification may use different units: molar fraction of fuel in the mixture *x*F, mass fraction *y*F, fuel-to-air ratio *f* (molar or mass), air-to-fuel ratio *A* (molar or mass), equivalence ratio φ (the actual fuel/air ratio relative to the stoichiometric one, with the same value in molar and mass basis), air relative ratio λ (the air/fuel ratio relative to stoichiometry, with the same value in molar and mass flow rate of products), etc.

Diffusion

Actual mixing of chemical species is governed by mass transfer laws, very similar to heat transfer laws for conduction (diffusion) and convection. In a homogeneous media, without phase changes or chemical reactions, the basic kinetic law for mass diffusion is Fick's law. There are also secondary fluxes associated to other possible gradients (e.g. mass-diffusion due to a temperature gradient, known as Soret effect, and mass-diffusion due to a pressure gradient; alternatively, there may be heat-diffusion due to a pressure gradient, known as Dufour effect, and heat-diffusion due to a pressure gradient, known as Dufour effect, and heat-diffusion due to a pressure gradient), but most of the times those cross-coupling fluxes are negligible. Besides, selective force fields may yield diffusion (e.g. ions in an electric field). Notice that only molecular diffusion is considered here, i.e. for particle sizes $<10^{-8}$ m; particles in the range 10^{-8} .. 10^{-6} m (soot, mist, smoke), are studied with Brownian-motion mechanics, and particles $>10^{-6}$ m with Newton mechanics. To better grasp the similarity between species diffusion and heat diffusion, the balance equations for mass-transfer and heat-transfer, applied to a unit-volume system, are here presented jointly:

with *wi* being the mass-production rate by chemical reaction, and $a=k/(\rho cp)$ the thermal diffusivity. Notice that there is only one driving heat-transfer-function, *T*, but many mass-transfer functions, *yi* (one for each species), although most problems are modelled as a binary system of one species of interest, *i*, diffusing within a background mixture of averaged properties.

Typical values for Di and a are given in Mass diffusivity data. Because of the nearlyequal values of Di and a for gases ($Di \approx a \approx 10^{-5} \text{ m}^2/\text{s}$), the thermal and solutal relaxation times in absence of convection, are nearly equal ($trel \approx L^2/Di \approx L^2/a$), in spite of the fact that the coefficients in (1) are widely different ($Di \approx 10^{-5} \text{ m}^2/\text{s}$ and $k \approx 10^{-2} \text{ W/(m} \cdot \text{K})$), T is not bound, and ρi is bound to $\rho i \ll 1 \text{ kg/m}^3$ for diffusion in air under normal conditions. In liquids and solids, mass diffusion relaxation times are much smaller than their thermal counterparts.

Convection

A quicker mixing process than diffusion is convection, where bulk fluid-flow transports species as if encapsulated, instead of having to migrate by its own random fluctuations. As in the study of convective heat transfer, the fluid flow should be solved in conjunction to diffusion, but, as in heat transfer, one usually resorts to empirical correlations to compute mass-transfer non-dimensional parameters (Sherwood Sh, or mass-Nusselt number) in terms of non-dimensional stimuli (e.g. Reynolds number of the imposed flow Re, Rayleigh number of the imposed thermal gradient Ra, etc.). Thus, instead of solving the whole fluid-dynamic problem with (2-3) and momentum equation, empirical correlations applicable just to the boundary values are often used as:where both, the solutal and thermal convection correlations are sketched ($Sc \equiv v/Di$, $Pr \equiv v/a$). Notice, however, that the boundary conditions in practical solutal-convection problems can be very different to the classical heat-convection problems where a single fluid sweeps a hot or cold rigid boundary. The case of a submerged jet is a good case of similarity between solutal convection (e.g. a jet of fuel gas emerging to ambient air) and thermal convection (e.g. a jet of hot air emerging to ambient air). Phase changing systems are more conspicuous, although most of the times the process of phase change (e.g. the evaporation of liquid fuels studied below) can be separated from the more complex gas-phase combustion. But, in the burning of solid fuels the process are entangled because there may be decomposition reactions within the solid (as in wood burning), or heterogeneous combustion at the interface (as in coal burning and metal burning). For instance, when aluminium particles burn in a carbon-dioxide atmosphere $(2Al+3CO2 \rightarrow Al2O3+3CO)$, the initial and final phases take place with a detached vapour flame (at some 2600 K), consuming two thirds of the mass, whereas an intermediate stage takes place at the surface, controlled by a carbon layer (perhaps Al4C3) formed by heterogeneous reaction of carbon monoxide there (and not by an alumina layer as thought; *Tm*(Al2O3)=2320 K).

EVAPORATION

Evaporation (sometimes called vaporisation) is the net flux of some species, at the interface between a condensed phase and a gas mixture, due to a normal concentration-gradient of that species in the gas close to the interface. Examples: the evaporation of water from a glass of water in air (the level decreases some 1 mm/day); the evaporation of ethanol from a glass of wine in air (water evaporates too); the evaporation of ammonia from an open bottle of water ammonia solution in air (water evaporates too); the evaporation of naphthalene in air (sometimes called sublimation). Volatiles liquids and volatiles solids are smelly. It is often simpler and more efficient to transport fuels in condensed form, and safer to burn them with non-premixed flames, in which case, fuel droplet evaporation from the injector spray constitutes a first stage to the combustion of the generated vapors within the oxidizer stream (droplet burning is dealt with below; we follow on here just with the evaporation process). Evaporation should not be confused with boiling (which may also be properly called vaporization), which is the change of phase within the liquid phase due to an increase in temperature or a decrease in pressure. Perhaps the most clarifying difference is that boiling is a bulk process (bubbles form at hot points, usually the walls of a heated container), and may take place in pure substances, whereas evaporation is a free- surface process (no bubbles form, and the interface region cools) that only happens in mixtures. Evaporation is a basic topic in combustion of condensed fuels, as well as a more general mass-transfer topic in mechanical engineering (humidification, drying, cooling towers) and chemical engineering (reactors, materials processing, oxidation, electrochemistry, scrubbing, desalination by reverse osmosis and other membrane processes, etc.). Evaporation and condensation in a mixture are always combined mass-and-heat transfer problems (boiling and condensation in a pure substance and the Stefan problem of melting or solidification, are just heat transfer problems). We only consider here evaporation of a pure liquid, typically water, in air (a mixture), controlled by diffusion of both, species and heat. When considering the vaporization of practical fuel droplets (like diesel oil), the variation with time of the composition and vaporization temperature may be very important due to multi-component equilibrium; however, it is common practice in theoretical analysis to assimilate commercial fuels to pure-component reference-fuels, usually n-octane for gasoline's, and n- dodecane or n-tetradecane for diesel oils.

Evaporation from a planar surface

Let us start by the simplest one-dimensional planar diffusion-controlled evaporation problem. Consider a test-tube with water in open air. Assuming that the air in the tube is quiescent, but the air outside is stirred enough as to maintain constant conditions at the mouth (T0, p0, $\phi0$), and assuming a steady state (the water level is thought to be kept steady by some slow liquid supply from the bottom; in the real test-tube case, the liquid level would slowly decrease), Eq. (2) with its initial and boundary conditions would solve the problem, although the first integration can be skipped directly establishing the series of mass conservation.

where ρ is the density of the mixture (assumed constant in a first approximation), $\rho i=yi\rho$, and *v*liq the speed of liquid injection (really, the liquid-level descent with time). Notice that, with the constant-density approximation in the gas phase, the global velocity is also constant along the tube. Dividing by ρ and integrating, the value of the global velocity is obtained:yi1 being the mass-fraction of species *i* at the mouth (assumed to be that of the ambient), yi0 the mass-fraction at the bottom of the gas column (i.e. close to the liquid surface), assumed to be that of two-phase equilibrium, i.e. Raoult's law (see Mixtures), and z1-z0 being the depth (the diffusion length). This result might have been anticipated by a simple dimensional analysis of the function $v=v(Di,\Delta yi,\Delta z)$.

For water evaporation in ambient air, the mass-fraction of water-vapour, yi, at the ambient and at liquid-level equilibrium are related to the pure vapour pressure at that temperature by Raoults' law: where *M*i and *M*m are the molar mass of species *i* (the volatile liquid, e.g. water) and the mixture (practically that of ambient air, for small x's), respectively, and φ is the relative humidity of the ambient. The evaporation speed, (6), with the relation $\rho v = \rho liq v liq$ from (5), and the linearization in (6) yields. e.g. the evaporation rate for water at 20 °C in ambient air at 20 °C, 100 kPa and 60% humidity ratio, for a 1 cm diffusion layer, is: where Di was found from Mass diffusivity data, and the vapour-pressure value obtained from steam tables (or from Clapeyron equation, or Antoine fitting). Notice that the evaporation rate increases with vapour pressure (e.g. ethanol evaporates some 10 times faster than water at 20 °C vliq=12 mm/day), whereas for a less volatile fuel like n-decane it is <0.1 mm/day), and it falls with deepness (e.g. 0.13 mm/day for water down 10 cm in a test-tube). It was J. Dalton in 1801, just after he introduced the partial-pressure concept, who first said that the evaporation rate is proportional to the difference in partial pressure of water vapour from the saturated boundary layer, to that of the air far aside, and that it increases with free air velocity. The first analytical model of evaporation is due to J. Stefan in 1872.

The effect of wind speed is to decrease the boundary layer thickness, directly related to the diffusion depth, Δz , we have assumed known, consequently increasing the evaporation rate. Evaporation not only implies a mass transfer but also a heat transfer, since the vaporization enthalpy at the liquid surface must come from either the liquid side or the air side, at the steady state. This heat- transfer implication was not apparent in the numerical application of (8) just done, because the two temperatures were assumed known, but in reality, the temperature at the liquid interface will depend on the heat transfer and energy balance (the effect of a possible radiation trapping there, e.g. from sun rays, will enter here also); for a small amount of liquid the liquid quasi-steady temperature would be the wet-bulb temperature (see <u>Humid air</u>), a little below ambient temperature, making the approximation above acceptable.

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SCHOOL OF MECHANICAL ENGINEERING

DEPARTMENT OF AUTOMOBILE ENGINEERING

Unit – 4 - FLAMES – SME1606

UNIT -4

FLAMES

Flame length

Flame length is the most characteristic parameter of a non-premixed flame established at the mouth of an injector; the most common example may be the flame of a cigarette lighter. Flame length depends on the measuring principle: visible light, other radiations, temperature field, concentration fields, and the averaging principle for fluctuating flames. It also depends on buoyancy; e.g. propane/air jet flames issuing from a 0.8 mm tube, linearly increase their height with exit velocity up to 12 m/s ($Re\approx1000$), with heights of 0.25 m for buoyant flames (on the ground) and 0.33 m for non-buoyant flames (under microgravity). Further increasing of exit velocity causes a transition to turbulent flames with heights receding to 0.18 m for buoyant flames, until they blow out at 33 m/s, whereas for non-buoyant flames heights further increase to 0.39 m, until some 35 m/s, when they shorten to some 0.29 m before blow out at 40 m/s. Notice that, at high speeds, buoyancy should not be as relevant as it appears in practice (perhaps the behaviour would tend to match, if blow-out did not prevent it).

A quick guess for the laminar flame length, *L*fl, may be given by the distance travelled by the jet at the exit speed w0 during the period of fuel diffusion *t*dif, from *y*F=1 at the jet centre, to the stoichiometric value *y*F=*y*F,stq at the flame front; i.e. *L*fl=*t*difw0, with tdif= $(1-yF,stq)(D0/2)^2/Di$ and thence:

$$Lfl=(1-yF,stq)w0D0^{2}/(4Di).$$
 (1)

For instance, for the propane/air jet-flame above-mentioned, at w0=12 m/s, with D0=0.8 mm, $Di=10^{-5}$ m²/s and yF,stq=1/(1+16)=0.06, we get Lfl=0.18 m, against the 0.25 m measured.Notice that with this model (only applicable to laminar jet flames, Re<1000) the flame length is proportional to the volumetric flow-rate, and increases with stoichiometric air/fuel ratio (e.g. carbon-monoxide flame are much shorter than hydrocarbon flames, $LCO/LCH4\approx0.2$, $LH2/LCH4\approx0.2$, $LC4H10/LCH4\approx3$). Turbulent non-premixed flames flicker with a wide frequency spectra, but the main first natural

Non-premixed flames may radiate a lot of energy. For gas-jet flames of a few kilowatts issuing from a few-millimetre injector, from 10% (for methane/air) to 50% (for propane/air) of their heat release is lost by radiation, mainly by blackbody emission at some 2500 K. from the in-flame soot (with a smooth maximum at CWien/T=2900/2500=1.2 μ m, but with a more pronounced peak between 4 μ m and 5 μ m due to molecular band emission by H2O and CO2.Similarly to the temperature field, soot production in a gas-fuel jet flame, concentrates in the mixing shell where the flame locates at small heights, and wide-spreads to the centre downstream (e.g. for a steady methane jet of 10 mm diameter issuing in air at 80 mm/s, soot volume fractions profiles have a two-bell shape up to some 50 mm height, and one central bell-shape further along the axis). In most practical non-premixed burners, air is coaxially fed with the fuel, what may increase the flame length and pollutant emissions if the co-flow pattern reduces the mixing. To prevent this, special swirl-inducing nozzles are used to quickly mix fuel and air, greatly reducing flame length. Flame stabilization by porous feeding: oil lamps and the candle flame Condensed fuels can be ignited by a spark if they are above their flash-point temperature (at least locally); if not, they have to be heated before ignition starts, perhaps just holding close a match for a while, providing the heating and the igniter at the same time. Once ignited, the non-premixed flame will travel along the fuel surface, usually becoming unstable, and even extinguishing by poor ventilation (lack of air). All these problems are solved when the flame can get stabilized around the tip of a porous solid that pumps liquidfuel by capillary suction towards a well-ventilated region, what is the foundation of oil lamps and candles; a torch being a hybrid device between a candle and an oil lamp (a torch is a wooden or tow shaft dipped in wax, tallow or pitch, and set alight by an igniter). Some oil lamps developed in the 19th century used gravity-pumping instead of capillary pumping. A detailed description of the historical developments of oil lamps (where the fuel is already in the liquid state), and of candles (where the fuel is in the solid state, but a local molten pool is maintained by heat radiation from the flame), can be found aside, in History of Fuels. Torches, oil lamps and candles).

The length of this type of flames depends to some extent on the length of the wick, what can be controlled in oil lamps (too long wicks will burn themselves if unable to pump enough liquid). The structure of a typical candle flame is depicted in Fig. 4.1. Initially, the wick holds some solid wax in its pores (from previous use or from manufacturing). The wax can be of animal origin (esters of fatty acids. like stearin beeswax) or of mineral origin (long-chain paraffins, beyond and eicosane, C20H42,*T*m=36.4 °C).

When a match is brought nearby, first the wax melts (between 50 °C and 60 °C), then the vapours heat up to the flash point (around 230 °C, i.e. 600 K), ignition starts, and a quasi-steady-state regime is reached; a 20 mm in diameter candle burns some 5..10 g/h of fuel, yielding some 60..120 W (LHVwax=44 MJ/kg), with a flame height of 40..45 mm in still air, and a maximum flame diameter of some 8..10 mm.

These flames radiate a lot of energy, and, although most of this low temperature blackbody-radiation is in the infrared spectrum, the small visible part more than justified their prominent use for artificial lighting since prehistoric times, until the development of electric light at the end of the 19th century. A typical candle flame has a colour temperature of some 1700 K, what is responsible for the typical yellow colour of non-premixed flames. A volume fraction of soot less than 1 ppm already gives luminous blackbody emission. This is similar to the incandescent radiation from a filament electrically heated to near 3000 K as in the traditional incandescent bulb-lamp (white light corresponds to the solar spectrum, nearly a perfect blackbody at 5800 K). Soot formation is a relatively slow chemical process of nucleation and aggregation, and it is enhanced by increasing the residence time within the flame and by the presence of polycyclic aromatic hydrocarbons (PAH), so that, when flickering occurs in turbulent flames, soot production quickly rise.



Fig. 4.1. Mixing processes and structure of a candle flame.

Fuel sprays

Because of the advantage of easy storage and high energy intensity, liquid fuels are used in the majority of vehicle-engines (cars, trucks, trains, ships, and aircraft), and in a sizeable part of stationary engines and power plants. The combustion is performed by injection of the liquid fuel in an oxidiser gas stream(usually air), and it is of utmost importance for a good burning to promote the interface area between liquid and gas, where, in most cases, a nonpremixed flame will be established; the exception is when the injected liquid can be left to fully evaporate and a subsequent premixed flame produced, as in gasoline engines.



Fig. 4.2. Jet break-up, droplet formation and evaporation in a diesel injector.

The scattering of the injected liquid into fine droplets (spray, or atomization; see Fig. 4.2), is usually achieved mechanically by creating a high-speed jet (>100 m/s, what requires very high pressure jumps, currently up to 200 MPa in some diesel injectors), which disintegrate into droplets (much smaller than the jet diameter), by shear forces. Think about how fast the processes follow each other: in few а milliseconds, a thin liquid stream in turbulent motion (which may cavitate and flashboil when approaching the tip of the fuel injector), forms a spray that breaks down to a myriad of droplets, which evaporate, ignite, burn, and generate unwanted emissions. Wall impingement is undesirable in most circumstances, increasing emissions by poor combustion cold walls; in gasoline injection near even at the manifoild, wetted surfaces introduce an undesirable time-lag in the fuel control loop.

The break-up length, i.e. the length where the first droplets appear (at the jet surface), tends to zero in atomized jets. Other methods of spraying, as impinging jets, airentrained or water-entrained jets, are less used in combustion. Steady non-premixed flames occur in liquid-fired gas turbines, boilers and furnaces, whereas unsteady non-premixed flames occur in diesel engines. Typically, a jet of liquid fuel is injected (at some 350 K once warmed by the hot engine), inside hot air (heated to some 950 K by adiabatic compression). Due to the fine atomization achieved by the high pressure injector, a cloud of fuel vapor, well-mixed with air, develops around the liquid jet already after a few millimeters from the injector; at a distance of a few centimeters.

This rich vapor mixture already attains its auto ignition temperature (the minimum for diesel/air is 480 K, but up to 800 K are measured before proper ignition), pyrolyses and burns, attaining more than 2500 K and showing chemi luminescent radiation; beyond that, soot starts to form at the tip of the jet due to thermal pyrolysis of air-depleted vapors, and soot formation continues until there is liquid remaining. In the dual-fuel diesel engine, a lean mixture of air / natural gas is usually formed in the admission manifold, and, once compressed to the normal compression ratio of the diesel engine, is ignited by a injection of a small amount of diesel oil at the usual high pressure near the top dead centre; the temperature increase during compression of the mixture is high enough to auto-ignite the oil (480 K for diesel/air) but not enough to auto-ignite the gaseous mixture (850 K for methane/air), helped also by the larger auto ignition delay of methane than that of diesel oil. Notice that LPG injection, and heated gasoline and diesel injection, can give rise to flash-boiling (i.e. if the injection enthalpy is higher than the saturated-liquid enthalpy at the discharge pressure), with a very effective atomization. Presently, it is only of interest in gasoline injectors in the intake manifold.

Droplet combustion

A single droplet of fuel burning in air, is not of any practical use (except for research), but it is of paramount importance for the understanding of spray combustion, a very practical arrangement used in all. liquid-fuel burners, all diesel engines, and kerosene gas-turbines. The key parameter to be found is the droplet burning time, what governs the path length before burnout (and consequently the minimum size of the combustion chamber required), and the required residence time for unsteady processes (and consequently the minimum period in reciprocating engines).

We here assume that the combustion has already been started, either by a spark in cold air (above the flash-point temperature), or by auto ignition in hot air (above auto ignition temperature). Pressure, assumed constant during droplet combustion, has an influence on several aspects of the droplet-burning process, including flame dynamics, combustion chemistry, evaporation rate, heat-up period, and ignition delay time. For instance, droplet combustion experiments show that, after ignition, the flame increases in size initially by thermal expansion and internal convection, but later decreases in size, following the shrinking of the droplet (but not linearly proportional as deduced below with a simple model). To further simplify the single-droplet problem, we assume it to be spherically-symmetric (a good approximation under microgravity, because, on Earth, a vertical plume develops; by the way, microgravity also allows easy droplet positioning by levitation). Additionally, we focus just on the quasi-steady rate of burning, after the initial processes of ignition (heating, species diffusion, and reaction activation) had been settled. As for droplet evaporation, we can imagine a liquid source at the centre of the drop to keep a strict steady state.

In this steady-rate regime, sketched in Fig. 4.3, the droplet temperature keeps a constant value *T*0 (a heat-and-mass diffusion trade-off value to be found, lower than its boiling point), with heat from the flame diffusing inwards and forcing evaporation, which supplies fuel vapours with a mass fraction *y*F0 close to the liquid, diffusing outwards and feeding a non-premixed flame, located at $r1/r0\approx10$, fed also from the outside by a diffusive flow of oxygen from the air, with both fuel and oxidiser concentrations approaching zero at the flame (with slopes proportional to the stoichiometry). Products being generated at the flame (we assume the single-step reaction model F+vOO→vPP), and part of the heat released, diffuse outwards. A possible inert gas, notably nitrogen foe combustion in air, completes the set of species playing (one must have at every point *y*F+*y*O+*y*P+*y*N=1).



Droplet combustion. a) Temperature and species-concentration profiles (combustion in air).b) Evolution of drop radius, area, and volume, with time.

We start the analysis of droplet combustion by rewriting the equations for droplet evaporation (9-11), i.e., the global mass balance, species mass balance, and energy balance, for a spherical volume of radius r (now it must be r0 < r < r1), with yF+yP+yN=1 and only the fuel flowing (from the source at the origin, to the sink at the flame; there is no sink for yP or yN at r0): i.e. getting the well-known r^2 -law (similar to Langmuir's law (1918) for droplet evaporation), stating that the droplet life-time, tburn, is proportional to the square of the initial radius; often, the diameter, d, is use Spalding and Godsave in 1953. Notice that this constant K for the burning problem will differ in value from that of the simple evaporation problem. If the steady-state temperature of the drop, T0, and its corresponding vaporization enthalpy, *h*LV0, are approximated by the boiling-point values (*T*b and *h*LVb, or any other suitable value, because the influence on (31) is not large), the energy balance gives directly the burning rate; afterwards, the species balances can be used to get the actual droplet temperature and other internal unknowns, as fuel-mass-fraction near the liquid surface, and products-mass-fractions. The simplification introduced along (31), 1/r1 << 1/r0, is justified by practical results $(r1/r0 \ge 10)$. Later, the flame position r1 will be found from (27), but the droplet life-time is directly given by the integrated energy equation (28) because we know the flame temperature T1, which is the adiabatic flame temperature, Tad, (we neglect radiation losses) given by, where LHVmolar stands for the lower heating value of the fuel in molar basis, $T^{\oplus}=298$ K is the standard reference in Thermochemistry, ni are the molar coefficients of the products (including any possible inert species), and *cp*,*i* their molar thermal capacities.

One can make the approximation of considering just one thermal-capacity value for the products mixture, *cp*, usually that of air at some appropriate conditions intermediate between the extreme temperatures; the values $cp=34 \text{ J/(mol}\cdot\text{K})=1200 \text{ J/(kg}\cdot\text{K})$ may be used for combustion in air (care is needed, however, to account for the mol-ratio or the mass-ratio of products, including inerts, relative to the fuel. As a rule of thumb, an order-of-magnitude value for the adiabatic temperature of Tad=2500 K may be used for a first approximation In summary, for a given fuel droplet in a given environment, data are: initial droplet radius (e.g. $r_{0,ini=10^{-5}m}$), ambient air temperature, pressure and oxygen concentration (e.g. T_{∞} =300 K, p=100 kPa, vO ∞ =0.23), thermal properties of ambient air (for the given state, $cp=1000 \text{ J/(kg \cdot K)}, \lambda=0.024 \text{ W/(m \cdot K)}, \text{ and } MO=0.029 \text{ kg/mol}), \text{ properties of fuel (e.g.$ for n-dodecane, a pure-substance model for diesel oil (a commercial distillate), ρ liq=780 kg/m³, *T*b=489 K. *h*LVb=257 kJ/kg, MF=0.170 kg/mol, vO=37/2=18.5, vP=12+13=25, LHVmass=45 MJ/kg, and Tad=2600 K), the latter obtained from the thermochemical analysis:

Stoichiometry: C12H26 + (37/2)O2 = 12CO2 +13H2O + 7575 kJ/mol

the latter obtained from LHVmolar= $-\Sigma vihf$,i=-[-12(-393.52)-13(-241.82)+(-291)]=7575 kJ/mol and thence LHVmass=7.575/0.170=44.6 MJ/kg. The actual mixture used in the case of burning in air is:

Mixture used: C12H26 + 18.5O2 + 69.6N2= 12CO2 + 13H2O + 69.6N2 + 7575 kJ/mol

Particle combustion

We consider here the combustion of solid particles, liquid particles being considered above under Droplet combustion. The main differences to the latter are:

• Particles shape can depart a lot from the spherical shape, because there are no surface tension effects as in droplets. Fine solid particles, however, are usually the result of a milling process that tends to produce not too-elongated particles.

• In the case of metallic particles, the combustion products are usually solid oxides (even at the high-temperatures involved).

• Inert solid material (ash) may be a sizeable part of solid fuel (e.g. in some coals), leaving a poroussolid layer around the burning fuel core, significantly distorting mass and heat transfer.

• Contrary to liquids, the combustion of solids can take place at the interface (heterogeneous combustion). This is because liquids cannot get hot enough to sustain a rapid surface-oxidation process with the adsorbed oxidiser; they vaporise before. But solids can indeed get very hot and yield a sizeable rate of chemical recombination at their surface layer. For a reaction scheme

• Under some circumstances, two combustion fronts may develop: the heterogeneous one at theparticle surface mentioned above, and a homogeneous detached flame as in droplet burning.

• Solid particles are far more difficult to ignite than droplets (they have higher flash points). Ignition and combustion of pulverized coal particles is of major interest to modern coal-fuelled power plants. Combustion of metal powders and polymeric dust in air is a major safety concern in many powder industries (e.g. flour in food processing, saw-dust in wood processing).

The nature of coal combustion depends a lot on composition and temperature. Leaving aside coal composition (see <u>Coal analysis, in Fuel properties</u>), the effect of temperature on pure-carbon combustion is as follows (temperature range is very sensitive to humidity):

• For T0 < 1500 K, i.e. when the surface temperatures (after ignition) does not go over 1500 K, a heterogeneous combustion process is established at the surface according to C+O2 \rightarrow CO2.

• For 1500 K<70<2500 K, a heterogeneous endothermic reaction sets at the surface, according to C+CO2 \rightarrow 2CO, driven by a gas-phase homogeneous combustion with a blue free flame at some distance from the surface, according to CO+(1/2)O2 \rightarrow CO2.

• For 2500 K<70<3500 K, the external free-flame disappears, leaving just the heterogeneous combustion at the surface according to C+(1/2)O2 \rightarrow CO.

• For T0>3500 K, evaporation is so effective (carbon sublimates at 3910 K at 100

kPa) that a detached flame develops as in droplet combustion, according to

C+(1/2)O2 \rightarrow CO, although oxygen dissociation becomes important too.

The surface temperature in carbon combustion depends on how quick heterogeneous reactions proceed relative to the species-diffusion rates, what depends on geometry, trace contaminants, catalysts, etc. In the simplest case of diffusion-limited combustion at low ambient temperatures, once the heterogeneous reaction C+O2 \rightarrow CO2 is established, a surface temperature is in the range 1000 K<T0<1500 K is obtained, with a radial profiles as sketched in Fig. 4.4a, whereas for higher temperatures, 1500 K<T0<2500 K, a detached flame appears, with a radial profiles as sketched in Fig. 4.4c.



Fig. 4.4. Combustion of a carbon particle: *a*) Radial temperature and species concentration profiles when 1000 K<T0<1500 K (the only product, P, is CO); *b*) Correlation of species concentration close to the surface, with surface temperature, for 1000 K<T0<1500 K; *c*) Radial temperature and species concentration profiles when a detached flame appears (1500 K<T0<2500 K).

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SCHOOL OF MECHANICAL ENGINEERING

DEPARTMENT OF AUTOMOBILE ENGINEERING

Unit - 5 - ENGINE COMBUSTION – SME1606

UNIT-V

FUELS FOR I C ENGINES

Types of fuels, liquid and gaseous fuels, heating value of fuels, higher and lower heating values, chemical structure of hydro-carbons SI engine fuels, volatility characteristics, desirable characteristics of SI engine fuels, knock rating and additives, alternate fuels for SI engines, CI engine fuels, desirable characteristics, Cetane rating and additives

Types of Fuels

Since the heat energy is derived from the fuel, a fundamental knowledge of the types of fuels and their characteristics is essential to understand the combustion phenomenon.

The characteristic of fuel has a considerable influence on the design, efficiency, output and particularly the reliability and durability of the engine. Further, the fuel characteristics play an important role in the atmospheric pollution caused by the automobile engines.

Internal combustion engines can be operated on different types of fuels such as

- Solid fuels
- ✤ Liquid fuels
- Gaseous fuels

The design of the engine usually depends upon the type of fuel used.

Solid fuels

This type of fuel was used in early engines. During the initial stages of engine development, solid fuels (such as finely powdered coal) were used. However, due to the problem of handling the fuel as well as in disposing off the solid residue or ash (after combustion), solid fuels find little practical application today.

Further, there are storage and feeding problems associated with solid fuels as compared to gaseous and liquid fuels. However, attempts are being made to produce gaseous or liquid fuels from charcoal for their use in engines.

Liquid fuels

The liquid fuels are mostly used in modern internal combustion engines. Basically, they are the derivatives of liquid petroleum. The commercial types are:

- > Benzyl
- > Alcohol
- Petroleum products

Petroleum (obtained from crude oil) is a mixture of many hydrocarbons with varying molecular structure. It also contains small amounts of

- > Sulphur
- Oxygen
- ➢ Nitrogen
- Impurities (such as water, sand etc.)

Advantages of liquid fuels over solid fuels

- ➢ 1. High calorific value.
- ➢ 2. Low storage capacity required.
- ➤ 3. Cleanliness and free from dust.
- ➢ 4. Practically no ashes.
- ➤ 5. Non-deterioration in storage.
- ➢ 6. Non-corrosion of boiler plates.

Disadvantages

- ▶ 1. Highly expensive.
- ➤ 2. High risk of fire.
- ➢ 3. Expensive containers are required for storage and transport

Gaseous fuels

Gaseous fuels are ideal for internal combustion engines. They mix more homogeneously with air. However, their use is restricted in automobiles due their storage and handling problems. Gaseous fuels are suitable for stationary power plants near the source of availability of the fuel. They can be liquefied under pressure to reduce the storage volume, but this process is very expensive and risky.

Advantages of gaseous fuels

- 1. The supply of fuel gas, and hence the temperature of furnace is easily and accurate Controlled.
- 2. The high temperature is obtained at a moderate cost by pre-heating gas and air with Combustion of waste gases.
- 3. They are directly used in internal combustion engines.
- 4. They are free from solid and liquid impurities.
- 5. They do not produce ash or smoke.
- 6. They undergo complete combustion with minimum air supply.

Disadvantages

- 1. They are readily inflammable.
- 2. Air requires large storage capacity.

Heating value

For fuels where the precise fuel composition is not known, the enthalpy of the reactants cannot be determined from the enthalpies of formation of the reactant species. The *heating value* of the fuel is then measured directly.

The heating value QHv or calorific value of a fuel is the magnitude of the heat of reaction at constant pressure or at constant volume at a standard temperature [usually $25^{\circ}C$ (77''F) for the complete combustion of unit mass of fuel.

Complete combustion means that all carbon is converted to CO, all hydrogen is converted to H and O, and slny sulfur present is converted to SO,. The heating value is usually expressed in joules per kilogram or joules per kilomole of fuel.

The term *higher heating value* QHHv (gross heating value) is used when the H,O formed is all condensed to the liquid phase; the term *lower heating value* QLHv (or net heating value) is used when the H,O formed is all in the vapor Phase.

Heating value of fuels are measured in calorimeters. For gaseous fuels, it is most convenient and accurate to use a continuous-flow atmosphere pressure calorimeter.

CHEMICAL STRUCTURE OF PETROLEUM

Depending upon the number of carbon and hydrogen atoms the petroleum products are classified into different groups. They are

(i) Paraffin series (CnH2n+2)

(ii) Olefin series (CnH2n)(iii) Naphthene series (CnH2n)(iv) Aromatic series (CnH2n-6)

Various aromatic compounds are formed by replacing one or more of the hydrogen atoms of the benzene molecules with an organic radical such as paraffins, naphthenes and olefins. By adding a methyl group (CH3). Benzene is converted to toluene (C6H5CH3) the base for the preparation of Trinitrotoluene (TNT) which is a highly explosive compound.

Family of	Chemical	Molecular	Saturated /	Stability
Hydrocarbons	Formula	Structure	Unsaturated	
Paraffin	C _n H _{2n+2}	Chain	Saturated	Stable
Olefin	C _n H _{2n}	Chain	Unsaturated	Unstable
Naphthene	CnH2n	Ring	Saturated	Stable
Aromatic	C _n H _{2n-6}	Ring	Highly Unsaturated	Most unstable

Table 5.1 Properties of Hydrocarbons

SI engine fuels

Gasoline which is mostly used in the present day SI engines is usually a blend of several low boiling paraffin, naphthenes and aromatics in varying proportions. Some of the important qualities of gasoline are discussed below.

- ✤ Volatility
- ✤ Starting and warm up
- Operating Range Performance
- Crank case dilution
- Vapour lock characteristics
- Antiknock quality
- Gum Deposits
- Sulphur Contents.

Volatility

It is the most important characteristics of a SI engine fuel. Volatility is a physical concept that loosely defined as the tendency to evaporate at a temperature lower than their boiling temperature. It is the most dominant factor that controls the air-fuel ratio inside the combustion chamber.

One of the most important requirements for proper and smooth combustion is the availability of a highly combustible air-fuel mixture at the moment of the start of the ignition inside the combustion chamber.

A highly volatile (of low molecular weight) fuel generates a rich fuel air ratio at low starting temperature, to satisfy the criteria at the starting of the ignition. But, it will create another problem during running operation; it creates vapour bubble which choked the fuel pump delivery system. This phenomenon is known as vapour lock. A vapour lock thus created restricts the fuel supply due to excessive rapid formation of vapour in the fuel supply system of the carburetor. High volatility of fuel can also result in excessive evaporation during storage in a tank which will also pose a fire hazards.Low volatile fuel like kerosene and distillates can be used for SI engines for tractors.

Starting and warm up

A certain part of the gasoline should vapourize at the room temperature for easy starting of the engine. Hence the portion of the distillation curve between 0 and 10% boiled off have relatively low boiling temperature. As the engine warms up, the temperature will gradually increase to the operating temperature.

Operating Range Performance

In order to obtain good vaporization of the gasoline, low distillation temperature are preferable in the engine operating range. Better vaporization tends to produce both more uniform distribution of fuel to the cylinder as well as better acceleration characteristics by reducing the quantity of liquid droplets in the intake manifold.

Crank case dilution

Liquid fuel in the cylinder causes loss of lubricating oil(by washing away oil from the cylinder walls) which deteriorates the quality of lubrication and tends to cause damage to the engine through increased friction. The liquid gasoline may also dilute the lubricating oil and weaken the oil film between rubbing surfaces. To prevent this situation, the upper portion of

the distillation curve should exhibit sufficiently low distillation temperatures to ensure that all gasoline in the cylinder is vapourized by the time the combustion starts.

Vapour lock characteristics

High rate of vapourisation of fuel can upset the carburetor metering or even stop the fuel flow to the engine by setting up a vapour lock in the fuel passages. This characteristic demands the presence of relatively high boiling temperature throughout the distillation range.

Antiknock quality

Abnormal burning or detonation in an SI engine combustion chamber causes a very high rate of energy release, excessive temperature and pressure inside the cylinder adversely effects its thermal efficiency. Therefore, the characteristic of fuel should be such that it reduces the tendency to detonation and this property is called its antiknock property. The antiknock property of a fuel depends on the self-ignition characteristics of its mixture and varies largely with the chemical composition and molecular structure of fuel. In general, the best SI engine fuel will be that having the highest antiknock property, since this permits the use of higher compression ratios and thus the engine thermal efficiency and the power output can be greatly increased.

Gum deposits

Reactive hydrocarbons and the impurities in the fuel have a tendency to oxidize and form liquid and solid gummy substances. Unsaturated hydrocarbons are more prone to form gum deposits. Gum deposits may lead to clogging of carburetor jets and enlarging of the valve stems, cylinders and pistons.

Sulphur content

Hydrocarbon fuels may contain free sulphur, hydrogen sulphide and other sulphur compounds which are objectionable for several reasons. The sulphur is the corrosive element of the fuel that can corrode fuel lines, carburetors and injection pumps and it will unite with oxygen to form sulphur dioxide that, in presence of water at low temperatures, may form sulphurous acid. Since sulphur has a low ignition temperature, the presence of sulphur can reduce the self-ignition temperature, then promoting knock in the SI engine.

Important characteristics of SI engine fuels

Every SI engines are designed for a particular fuel having some desired qualities. For a good performance of a SI engine the fuel used must have the proper characteristics. The followings are requirements of a good SI engine fuels or Gasolines.

- It should readily mix with air to make a uniform mixture at inlet, ie. it must be volatile
- It must be knock resistant
- It should not pre-ignite easily
- It should not tend to decrease the volumetric efficiency of the engine.
- It should not form **gum** and **varnish**
- Its Sulphur content should be low as it is corrosive
- It must have a high calorific value

Rating of SI engine fuels:-

The knock resistance is the most important characteristic of the fuel for SI engine. The fuels differ widely in their ability to resist knock depending on their chemical composition. In addition to the chemical properties of the hydrocarbons in the fuel other operating parameters such as fuel-air ratio, ignition timing, dilution, engine speed, shape of combustion chamber, ambient conditions, compression ratio etc. affect the tendency to knock in the engine cylinder. Therefore, in order to determine the knock resistance characteristic of the fuel, the engine and its operating variables must be fixed at standard values.

Here also there are two reference fuels viz. iso-octane (C8H18) chemically being a very god antiknock fuel, has been assigned an octane number of 100 and normal heptane (C7H16), it has very poor antiknock qualities and is assigned an octane number of 0.

Def. The octane number of a fuel is defined as the percentage, by volume, of iso-octane in a mixture of iso-octane and normal heptanes, which exactly matches the knocking intensity of the fuel in standard engine under a set of standard operating conditions.

The octane number at the higher range of scale will produce greater antiknock effect compared to the same unit at the lower end of the scale e.g. octane number increase from 90 to 91 produces greater antiknock effect than a similar increase from 30 to 31. The addition of some chemicals like tetra ethyl lead(TEL) to iso-octane produces fuels of greater antiknock qualities.

Antiknock Quality

Abnormal burning/detonation in SI engine cause a very high rate of energy release, temperature and pressure. This adversely affects the thermal efficiency. The fuel characteristics should resist this tendency. This property of fuel is called its antiknock quality. With no self-ignition, the pressure force on piston follows a smooth curve, resulting in smooth engine operation. When self-ignition occurs, pressure forces on piston are not smooth and engine knock occurs.

U		
Additives	Туре	Function
Oxidation inhibitors	Aromatic amines and phenols	Inhibit gum formation and oxidation
Corrosion inhibitors	Carboxylic acids and carboxylates	Inhibit corrosion of ferrous metals
Metal deactivators	Chelating agent	Inhibit gum formation Catalyzed by certain metals
Anti-icing additives	Surfactants and glycols	Prevent icing in carburetor and fuel system
Detergents	Amines and amine carboxylates	Prevent deposits in carburetor throttle body
Deposit control additives	Polybutene amines Polyether amines	Remove and prevent deposits throughout carburetor intake ports and valves
Blending agents	Ethanol, methanol, tertiary butyl alcohol, methyl tertiary ether	Extend gasoline supply, increase apparent octane quality with some loss in mileage
Antiknock compounds	Lead alkykl, organo-manganese compounds	Increase octane quality

Table 5.2 Gasoline additives

Gasoline additives

CI Engine Fuels

Knock characteristics

Knock in the CI engine occurs because of an ignition lag in the combustion of the fuel between the time of injection and the time of actual burning. As the ignition lag increases, the amount of fuel accumulated in the combustion chamber increases and when combustion actually takes place, abnormal amount of energy is suddenly released causes an excessive rate of pressure rise which results in an audible knock. Hence, a good CI engine fuel should have a short ignition lag and will ignite more readily. Furthermore, ignition lag affects the starting, warm up, and leads to the production of exhaust smoke in CI engine. The present day measure in the cetane rating, the best fuel in general, will have a Cetane rating sufficiently high to avoid objectionable knock.

Volatility

The fuel should be sufficiently volatile in the operating range of temperature to produce good mixing and combustion.

Starting Characteristics

The fuel should help in starting the engine easily. This requirement demands high enough volatility to form a combustible mixture readily and a high cetane rating in order that the self-ignition temperature is low.

Smoking and odor

The fuel should not promote either smoke or odour in the engine exhaust. Generally, good volatility is the first prerequisite to ensure good mixing and therefore complete combustion.

Viscosity

CI engine fuel should be able to flow through the fuel system and the strainers under the lowest operating temperatures to which the engine is subjected to.

Corrosion and Wear

The fuel should not cause corrosion and wear of the engine components before or after combustion. These requirements are directly related to the presence of sulphur, ash and residue in the fuel.

Handling Ease

The fuel should be a liquid that will readily flow under all conditions that are encountered in actual case. This requirement is measured by the pour point and the viscosity of the fuel. The fuel should also have a high flash point and a high fire point

Rating of fuels:-

Rating of fuels is normally done for their antiknock qualities. The rating of fuels is done by defining two parameters cetane number and octane number for diesel and gasoline respectively. Here the detailed description of the rating is given.

Rating of CI engine fuels:-

The knock resistance depends on chemical properties as well as on the operating and design conditions of the engine. So the knock rating of a diesel fuel is found by comparing the fuel at a specific condition with primary reference fuels. The reference fuels are normal cetane C16H34, which has been assigned a cetane number of 100 and alpha methyl naphthalene, C11H10, with a cetane number of 0.

Def. Cetane number of a fuel is defined as the percentage by volume of normal cetane in a mixture of normal cetane and alpha methyl naphthalene which has the same ignition characteristics (ignition delay) as the test fuel when combustion is carried out in a standard engine under specified operating conditions.

The knock should be directly related to the ignition delay as it is the major factor in controlling of the autoignition in the CI engine. Knock resistance property of a diesel oil can be improved by adding small quantities of compounds like amyl nitrate, ethyl nitrate or ether.

Additives

Some compounds called additives or dopes are used to improve the combustion properties of fuels. The main combustion problems that arise when the operating conditions become severe are knocking and surface ignition. That can be tackled by a lot of ways of which one is using additives.

For an additive to be acceptable, it must satisfy some basic requirements. These are as follows:-

- It must be affective in desired reaction that is knock resistance or surface ignition or both.
- It should be soluble in fuel under all conditions.
- ✤ It should be stable in storage and have no adverse effect on fuel stability.
- It should be in the liquid phase at normal temperature, and volatile to give rapid vaporization in the manifold.
- ✤ It must not produce harmful deposits.
- * Its water solubility must be minimum to minimize handling loses.

Additive	Туре	Function
Detergents	Polyglycols, basic nitrogen-containing surfactants	Prevent injector deposits, increase injector life
Dispersants	Nitrogen-containing surfactants	Peptize soot and products of fuel oxidant; increase filter life
Metal deactivators	Chelating agents	Inhibit gum formation
Rust and corrosion inhibitors	Amines, amine carboxylates, and carboxylic acids	Prevent rust and corrosion in pipelines and fuel systems
Cetane improvers	Nitrate esters	Increase cetane number
Flow improvers	Polymers, wax crystal	Reduce pour point modifiers
Antismoke additions or smoke suppressants	Organic barium compounds	Reduce exhaust smoke
Oxidation inhibitors	Low-molecular weight amines	Minimize deposits in filters and injectors
Biocides	Boron compounds	Inhibit growth of bacteria and microorganisms

Automotive diesel fuel additives

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