CHAPTER THREE

FUEL AND COMBUSTION

FUELS AND COMBUSTION

- Any material that can be burned to release thermal energy is called a ***fuel***.
- Most familiar fuels consist primarily of ***Hydrogen*** and ***Carbon***. They are called hydrocarbon fuels(C_nH_m).
- Hydrocarbon fuels exist in all phases
- ***Examples***:-
  - Coal------------------- Solid
  - Gasoline------------- Liquid
  - Natural gas---------- Gas
- The main constituent of coal is ***carbon*** and also contains varying amounts of ***oxygen***, ***hydrogen***, ***nitrogen***, ***sulfur***, ***moisture***, and ***ash***.

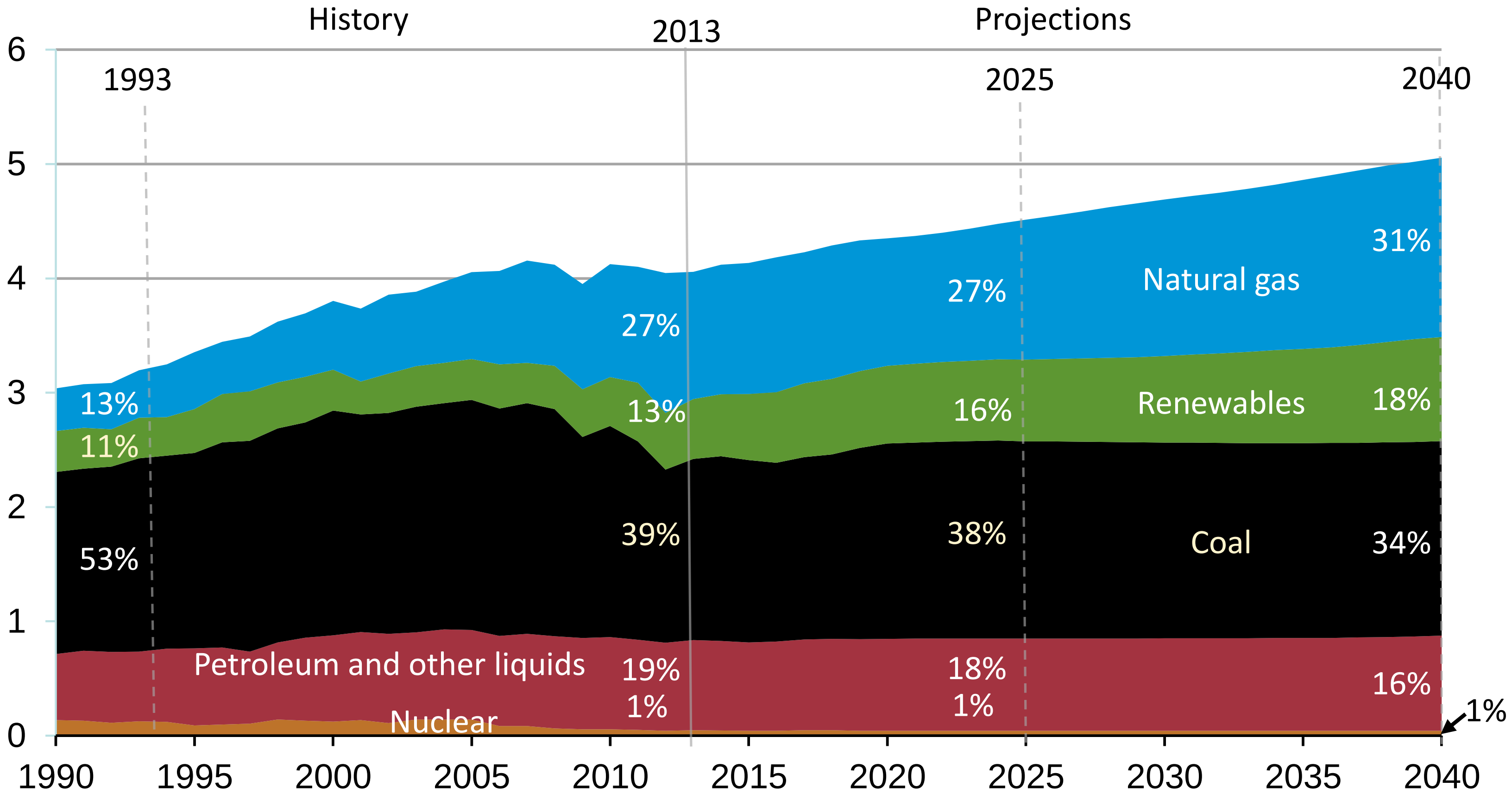
Classification of chemical fuels by phase and availability

Naturally available	*Synthetically produced*
Solid	*Coke*
Coal	*Charcoal*
Wood	*Inorganic Solid Waste*
Vegetation	
Organic Solid Waste	
Liquid	
Crude oil	*Syncrudes*
Biological oils	*Petroleum distillates*
Fuel plants	*Alcohols*
	Colloidal fuels
	Benzene
Gas	
Natural gas	*Natural gas*
Marsh Gas	*Hydrogen*
Biogas	*Methane*
	Propane
	Coal gasification

Energetic study of fuels and their use

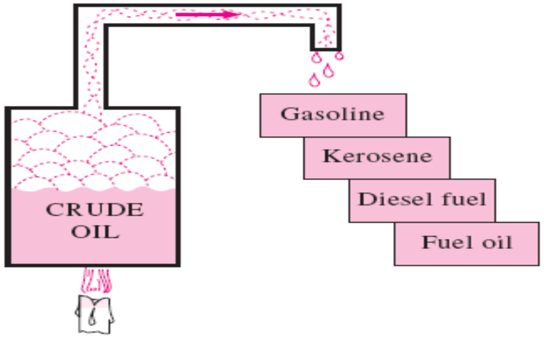
Electricity net generation

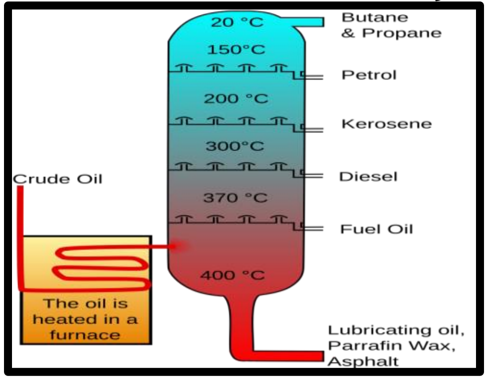
Trillion kilowatthours



Energetic study of fuels and their use

- Most liquid hydrocarbon fuels are a mixture of numerous hydrocarbons and are obtained from ***crude oil by distillation***. The most volatile hydrocarbons vaporize first, forming what we know as gasoline. When more than one type fuel is simultaneously burned to meet the total heating requirement, the boiler is said to have a ***combination firing***.





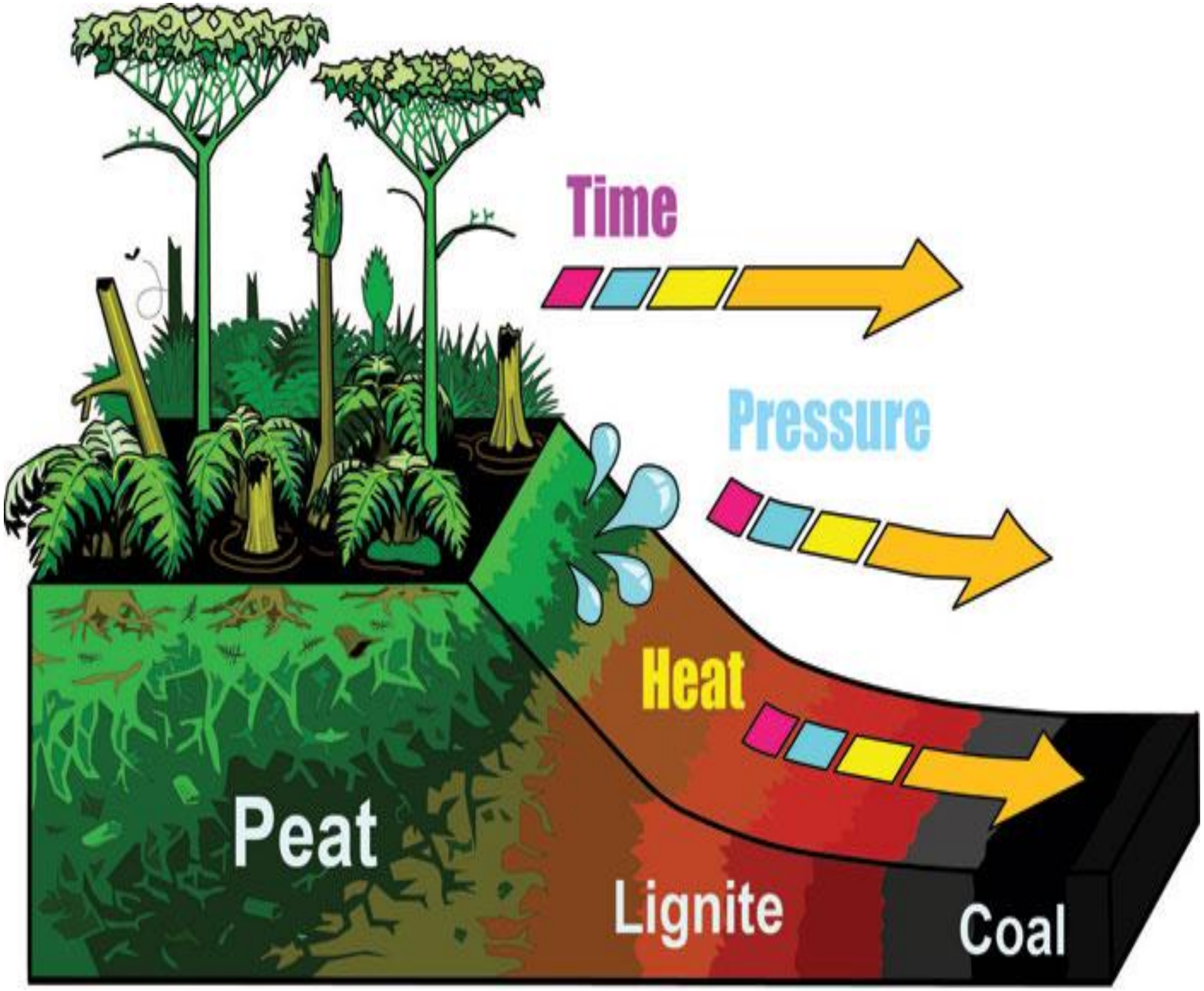
Coal

- An encompassing description of coal has been given by van Krevelen, in which he states: ***"Coal is a rock, a sediment, a conglomerate, a biological fossil, a complex colloidal system, an enigma in solid-state physics and an intriguing object for chemical and physical analyses."***
- In short, **coal** is a chemically and physically heterogeneous, "combustible," sedimentary rock consisting of both organic and inorganic material. **Organically**, coal consists primarily of ***carbon, hydrogen, and oxygen***, with lesser amounts of sulfur and nitrogen.
- ***Inorganically***, coal consists of a diverse range of ash-forming compounds distributed throughout the coal.

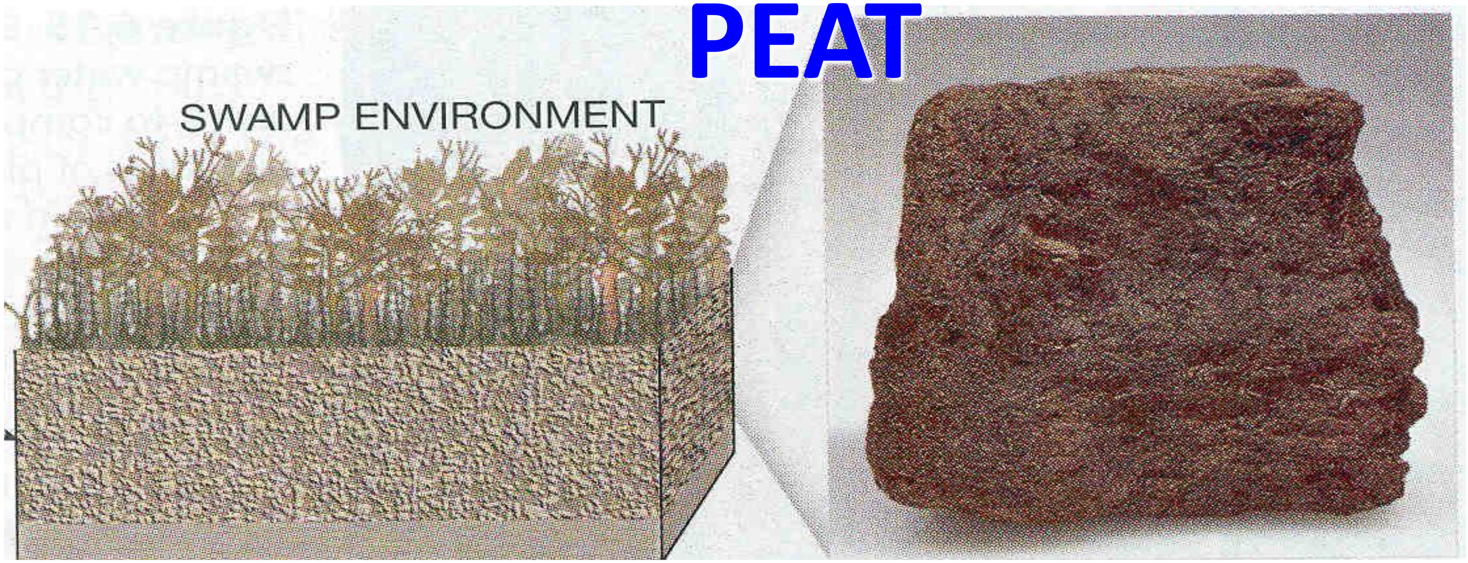
Coal

- The inorganic constituents can vary in concentration from several percentage points down to parts per billion of the coal.
- *Coal is the most abundant fossil fuel in the United States, as well as in the world*.
- At the end of 2000, recoverable coal reserves in the United States, which contains the world's largest coal reserves, totaled 274 billion short tons compared to a total world reserve of 1083 billion short tons .
- On an oil-equivalent basis, there is approximately twice as much recoverable coal in the world as oil and natural gas combined.

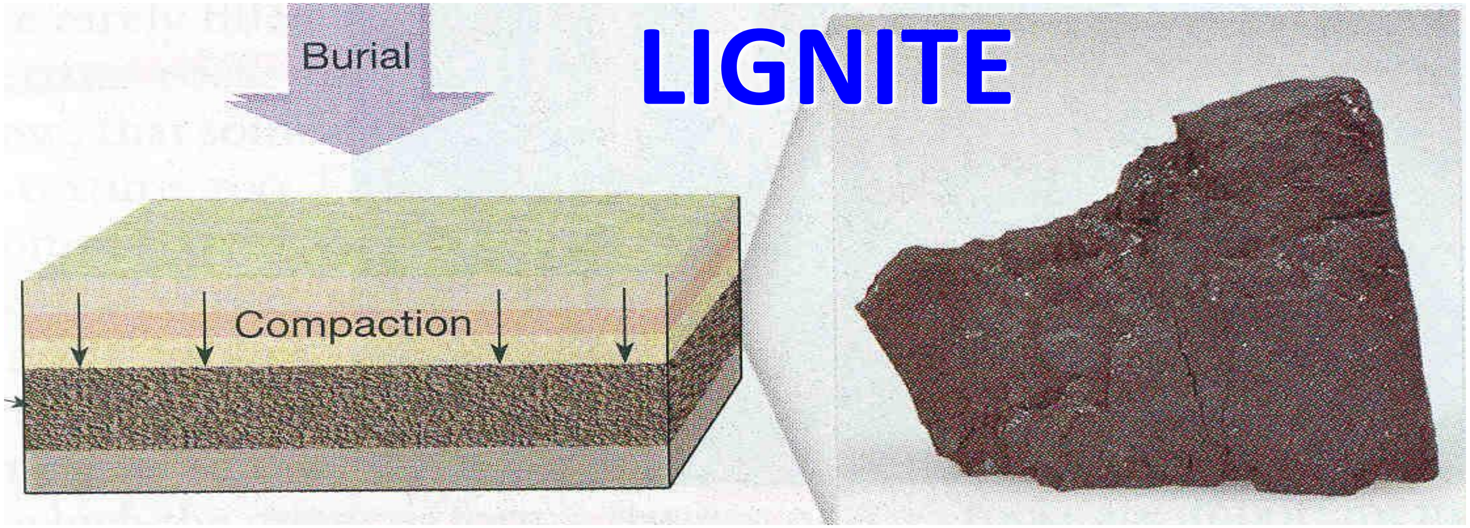
Process of formation of coal



Process of formation of coal



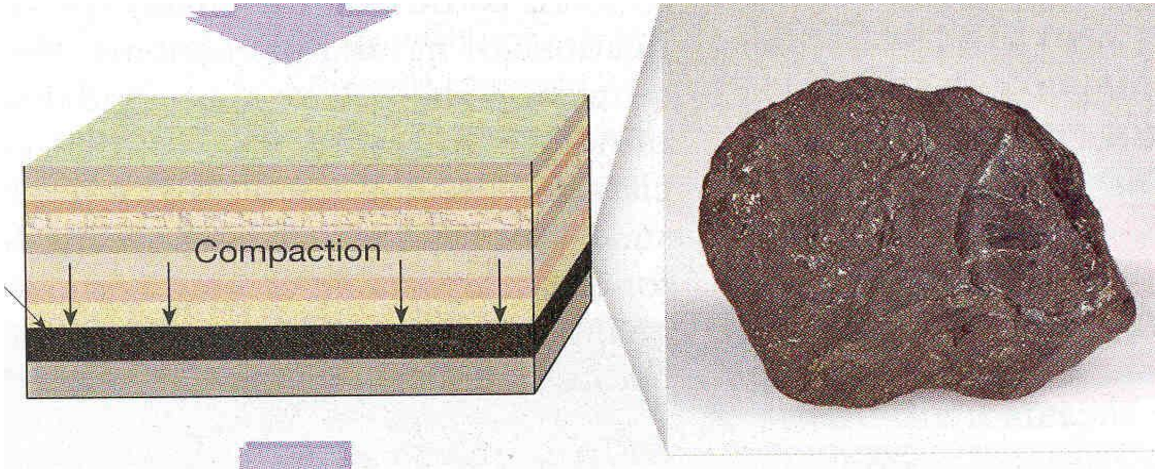
PEAT



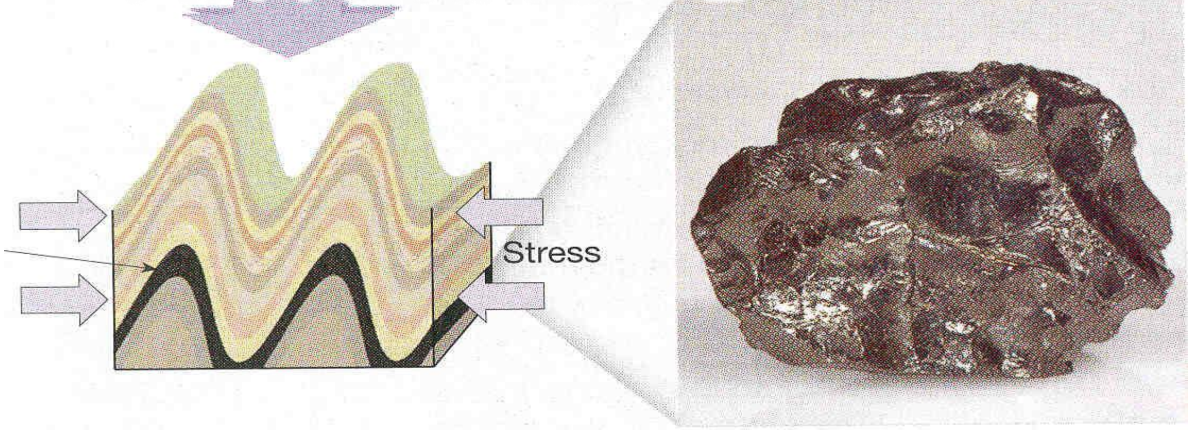
LIGNITE

Process of formation of coal

BITUMINOUS



ANTHRACITE



Process of formation of coal

- With increase percentage of carbon.
- Decrease volatile matter.
- Decrease moisture content.
- Increasing heating value.

Process of formation of coal

- ***Anthracite***:- contains:-
  - more than 86% fixed carbon and
  - less volatile matter.
  - It is difficult to burn anthracite
- ***Bituminous*** :- the largest group. Contains:-
  - 46-86% of fixed carbon and
  - 20-40% of volatile matter.
- The lower volatile, the higher the heating value.
- ***Lignite***:- lowest grade coal. Containing :-
  - moisture as high as 30%
  - high volatile matter.

Process of formation of coal

- According to ASTM (American Society of Testing and Materials).
  - Peat is not regarded as a rank of a coal.
- Peat contains up to 90% moisture and is not attractive as utility fuel.
- Rank carries the meaning of ***degree maturation*** (***carbonization***) and is a measure of carbon content in coal.
- Lignite is considered to be low rank and anthracite to be high rank.

COAL ANALYSIS

- There are two types of coal analysis.
    1. Proximate analysis.
    2. Ultimate analysis.

PROXIMATE ANALYSIS

- Indicates the ***behavior of coal when it is heated***.

1. When 1 gram sample of coal is subjected to a temperature of about 105^0C for a period of 1 hour, the loss in weight of the sample gives the ***moisture*** content of the coal.
2. When 1 gram sample of coal is placed in covered platinum crucible and heated to 950^0C and maintained at that temperature for about 7 minute.

- There is a loss in weight due to the eliminating of ***moisture*** and ***volatile matter***.

COAL ANALYSIS

3. When 1 gram sample of coal is placed in uncovered platinum crucible and heated to 720^0C until the coal is completely burned, a ***constant weight reached***, which indicates that there is only ***ash*** remaining in the crucible.

- Complete combustion of coal is determined by repeated weighing of the sample.
- Percentage by mass

$$\text{Fixed carbon} + \text{volatile matter} + \text{moisture} + \text{ash} = 100$$

$$\mathbf{FC = 100 - (VM + M + A)}$$

COAL ANALYSIS

- This difference does not represent all the carbon that was in the coal.
- Some of the carbon may have been in the form of hydrocarbons which may have been distilled off while determining the volatile matter.
- The amount of volatile matter indicates:-
  - The coal will burn with a short or long flame.
  - It tends to produce smoke.
- The more volatile the coal, the more it will smoke.

ULTIMATE ANALYSIS

- The ultimate analysis gives the chemical elements that comprise the coal substance, together with ash and moisture.
- The coal substance consists of organic compounds of ***carbon***, ***hydrogen*** and ***oxygen*** derived from the original vegetable matter.
- The analysis shows the following components on ***mass basis***:-

$$\mathbf{C + H + O + N + S + M + A = 100\%}$$

COAL PROPERTIES

- There are certain properties of coal which are important in power plant application.

1. ***Sulphur content***:-
   - sulphur content in a coal is combustible and generates some energy by its oxidation to SO_2.
   - SO_2 (sulphurdioxide) is a major source of atmospheric pollution.
   - The operating cost of SO_2 removal equipment need to be considered while selecting a coal with a high sulphur.

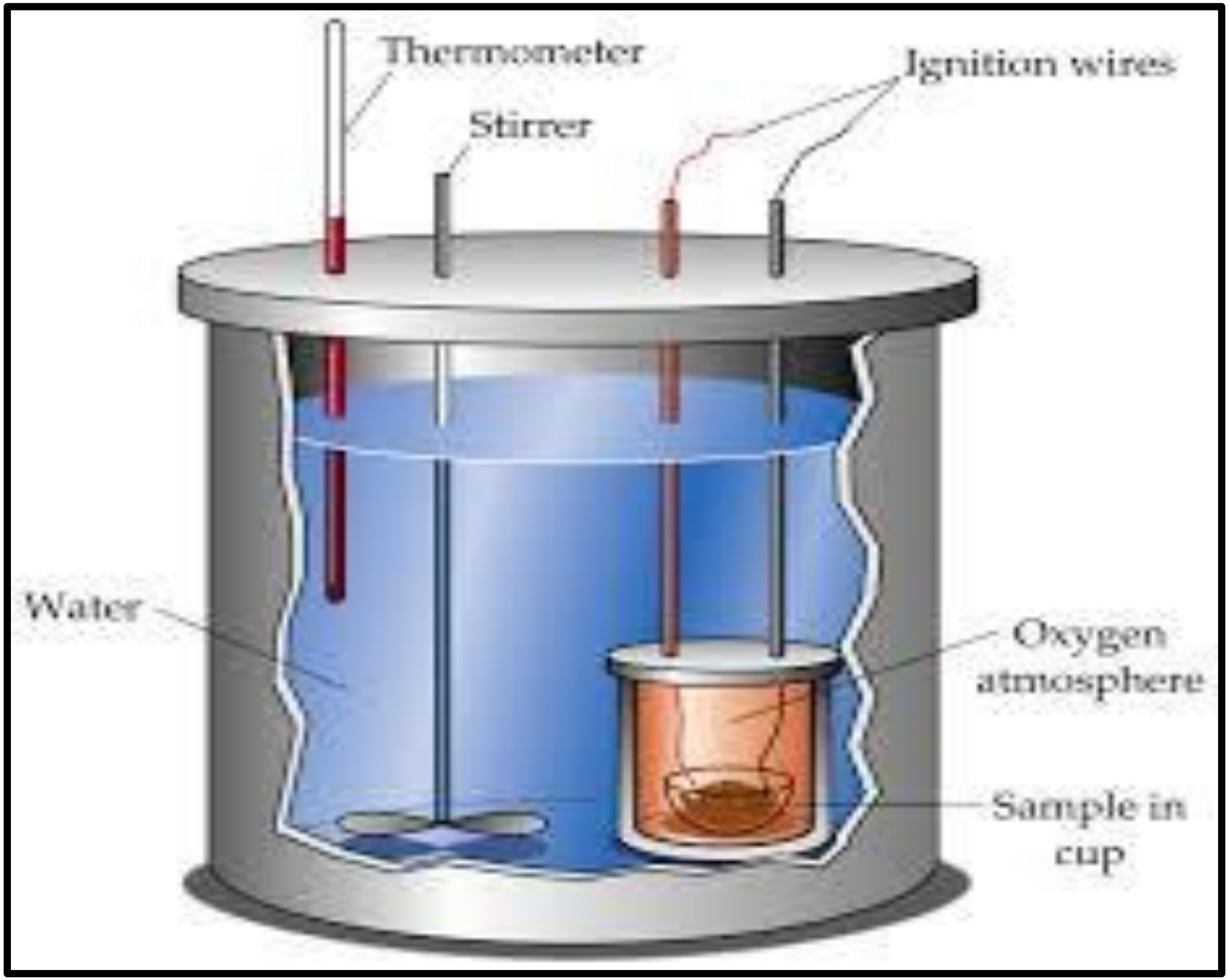
2. Heating value (calorific value)

The heat transferred when the products of complete combustion of a sample of fuel are cooled to the initial temperature of air and fuel.

- It is normally determined in a standard test in a **bomb calorimeter**,
  - ✓ where a coal sample of known mass is burnt with pure oxygen supply completely in a stainless steel bomb or vessel surrounded by a known mass of water and the rise in water temperature is noted.

- Two different heating values are cited for fuel.
  1. Higher heating value (HHV)
  2. Lower heating value (LHV)

Bomb calorimeter



2. Heating value (calorific value)

- ***Higher heating value***:- assumes that the water vapor in the products condenses and thus includes the ***latent heat of vaporization*** of the water vapor formed by combustion.
- ***Lower heating value***:-assumes that the water vapor formed by combustion leaves the vapor it self.

$$LHV= HHV - m_W h_{fg}$$

- If the ultimate analysis is known, the HHV of ***anthracite*** and ***bituminous*** coals can be determined approximately by using ***Dulong*** and ***Petit*** formulas as

$$HHV = 33.83C + 114.45(H\text{-}O/8) + 9.38S \text{ in MJ/Kg}$$

- The latent heat of vaporization h_{fg} at the ***partial pressure of water vapor*** in the combustion products as 2.395MJ/Kg.
- The lower heating value of coal is given by

$$LHV = HHV- 2.395\ m_w$$

ASH SOFTENING TEMPERATURE

- The ash softening temperature is *the temperature at which the ash softens and becomes plastic*.
- This is some times below the melting point of the ash.
- The design of the steam generator greatly depends on *the ash softening temperature of the coal*.
- If the furnace temperature is higher than the ash softening temperature all the ash will melt and would come out of the furnace bottom continuously as molten slag.
- For a furnace that would discharge ash in the form of solid, a high ash softening temperature would be required.

Combustion

Definition

- A chemical reaction during which a fuel is oxidized and a large quantity of energy is released is called ***combustion*.**
- The oxidizer most often used in combustion processes is *air*, for obvious reasons—it is
  - ✓ *Free*
  - ✓ *Readily available.*
- Pure oxygen O_2 is used as an oxidizer only in some specialized applications, such as *cutting* and *welding*, where air cannot be used.

Combustion

- On a **mole** (**volume**) basis **dry air** is composed of:-
    - 20.9 percent oxygen,
    - 78.1 percent nitrogen,
    - 1 percent argon, and small amounts of carbon dioxide, helium, neon, and hydrogen.
- dry air can be approximated as 21 percent oxygen and 79 percent nitrogen by mole numbers.

$$1 \text{ kmol } O_2 + 3.76 \text{ kmol } N_2 = 4.76 \text{ kmol air}$$

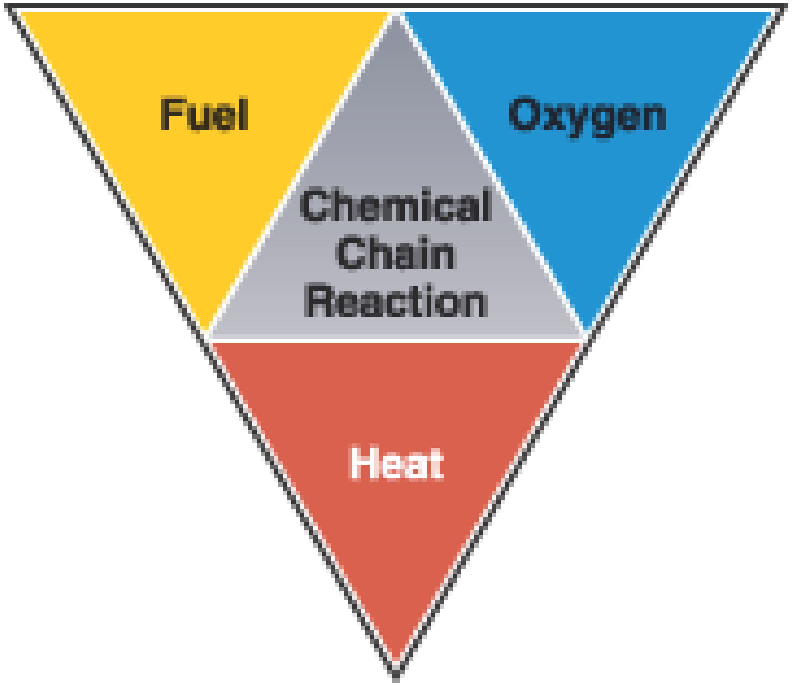
- During combustion, ***nitrogen*** behaves as an ***inert gas*** and does not react with other elements.
- The presence of nitrogen greatly affects the outcome of a combustion process.
- Nitrogen usually enters a combustion chamber in large quantities at low temperatures and exits at considerably higher temperatures. Absorbing a large proportion of the chemical energy released during combustion.

Combustion

- Nitrogen is assumed to remain perfectly inert.
- At ***very high temperatures***, such as those encountered in ***internal combustion engines***, a small fraction of nitrogen reacts with oxygen, forming hazardous gases such as ***nitric oxide***.
- Air that enters a combustion chamber normally contains some ***water vapor*** (or moisture), which also deserves consideration.
- For most combustion processes, the moisture in the air and the H_2O that forms during combustion can also be treated as an ***inert gas***, like nitrogen.

Fire Triangle and Tetrahedron

- Three basic factors required for combustion:
  - Fuel
  - Oxygen
  - Heat
- Chemical chain reactions keep the fire burning.

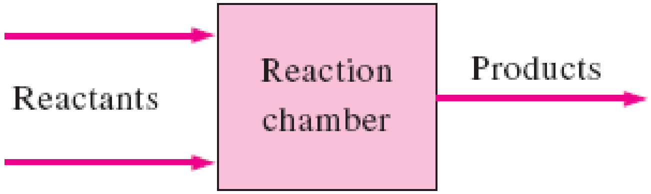


Combustion Fundamentals

- At ***very high temperatures***, however, some water vapor dissociates into H_2 and O_2 as well as into H, O, and OH.
- When the combustion gases are cooled below the ***dew-point temperature*** of the water vapor, some moisture condenses.
- ***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.***

Combustion Fundamentals

- During a combustion process, the components that exist before the reaction are called ***reactants*** and the components that exist after the reaction are called ***products***.



- Consider, for example, the combustion of 1 kmol of carbon with 1 kmol of pure oxygen, forming carbon dioxide,

$$C + O_2 \rightarrow CO_2$$

- If carbon is burned with air instead of pure oxygen, both sides of the combustion equation will include N_2.
- The N_2 will appear both as a reactant and as a product.

Combustion Fundamentals

- ***We should also mention that bringing a fuel into intimate contact with oxygen is not sufficient to start a combustion process. (Thank goodness it is not. Otherwise, the whole world would be on fire now.)***

1. The fuel must be brought above its ignition temperature to start the combustion.

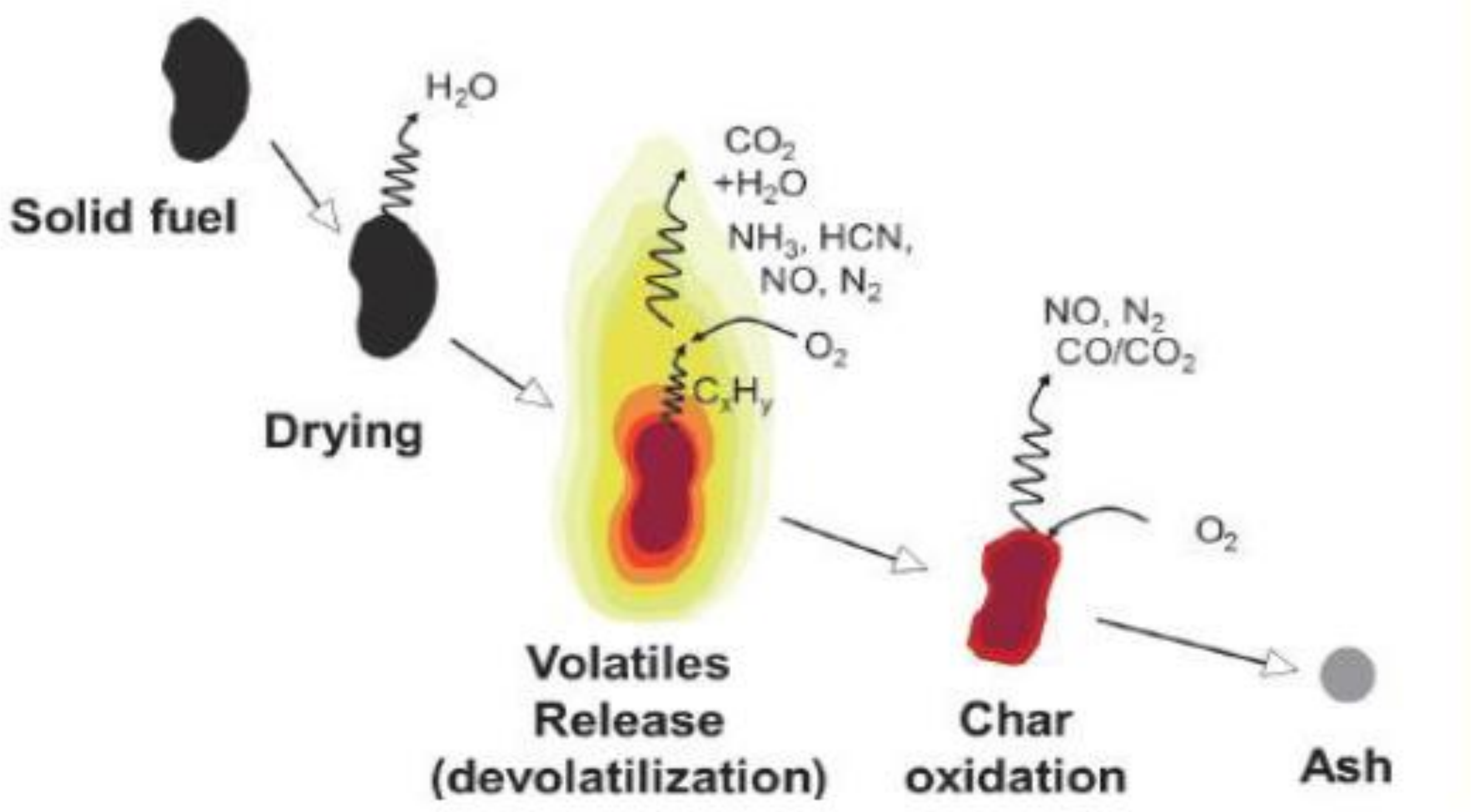
- The minimum ignition temperatures of various substances in atmospheric air are :-
  - 260°C for gasoline.
  - 400°C for carbon.
  - 580°C for hydrogen.
  - 610°C for carbon monoxide.
  - 630°C for methane.

Combustion Fundamentals

2. The proportions of the fuel and air must be in the proper range for combustion to begin.

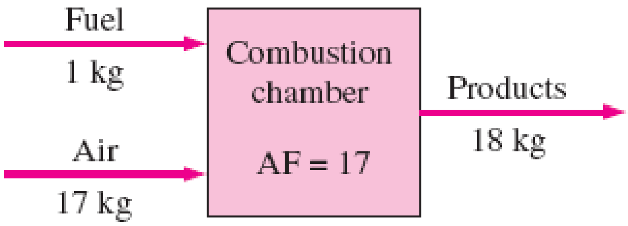
Example, natural gas does not burn in air in concentrations less than 5 percent or greater than about 15 percent.

Combustion Fundamentals



Combustion Fundamentals

- Chemical equations are balanced on the basis of the conservation of mass principle (or the mass balance).
- The total mass of each element is conserved during a chemical reaction.



- ***The total number of atoms of each element is conserved during a chemical reaction .***
- ***The total number of atoms 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.***

$$C + O_2 \rightarrow CO_2$$

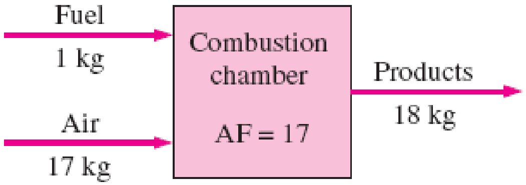
Combustion Fundamentals

- A frequently used quantity in the analysis of combustion processes to quantify the amounts of fuel and air is the ***air–fuel ratio***.
- It is usually expressed on a mass basis and is defined as the ratio of the mass of air to the mass of fuel for a combustion process.

$$\underset{\text{fuel}}{CH_4} + \underset{\text{2 kmol air}}{2(O_2 + 3.76N_2)} \leftrightarrow \text{Reactants}$$

$$AF = \frac{m_{air}}{m_{fuel}} = \frac{2(4.76)\,[\text{kmol}]\;\;29\left[{}^{\text{kg}}\!/_{\text{kmol}}\right]}{1\,[\text{kmol}]\;\;(12+4)\left[{}^{\text{kg}}\!/_{\text{kmol}}\right]}$$

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



16 kg oxygen

2kg hydrogen
16kg oxygen

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

$$AF = \frac{\text{mass}_{\text{air}}}{\text{mass}_{\text{fuel}}} = \frac{\text{mole}_{\text{air}}}{\text{mole}_{\text{fuel}}}$$

$$\text{mass} = \text{mole}(n) \times \text{molecular mass}(M)$$

$$FA = \frac{\text{mass}_{\text{fuel}}}{\text{mass}_{\text{air}}}$$

2kg hydrogen

THEORETICAL AND ACTUAL COMBUSTION PROCESSES

- A combustion process is complete if all the carbon in the fuel burns to CO_2, all the hydrogen burns to H_2O, and all the sulfur (if any) burns to SO_2.

$$C + O_2 \rightarrow CO_2$$

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$$

- All the combustible components of a fuel are burned to completion during a complete combustion process.
- The combustion process is incomplete if the combustion products contain any unburned fuel or components such as C, H_2, CO, or OH.
- Insufficient oxygen is an obvious reason for incomplete combustion, but it is not the only one.

THEORETICAL AND ACTUAL COMBUSTION PROCESSES

- Incomplete combustion occurs even when more oxygen is present in the combustion chamber than is needed for complete combustion.
- This may be attributed to ***insufficient mixing*** in the combustion chamber during the limited time that the fuel and oxygen are in contact.
- Oxygen has a much greater tendency to combine with hydrogen than it does with carbon.
- The hydrogen in the fuel normally burns to completion, forming H_2O, even when there is less oxygen than needed for complete combustion.
- Some of the carbon, however, ends up as CO or just as plain C particles (soot) in the products.
- **The minimum amount of air needed for the complete combustion of a fuel is called the *stoichiometric* or *theoretical air*.**

THEORETICAL AND ACTUAL COMBUSTION PROCESSES

- When a fuel is completely burned with theoretical air, no uncombined oxygen is present in the product gases.
- The theoretical air is also referred to as the chemically correct amount of air, or 100 percent theoretical air.
- A combustion process with less than the theoretical air is bound to be incomplete.
- The ideal combustion process during which a fuel is burned completely with theoretical air is called the ***stoichiometric*** or ***theoretical combustion*** of that fuel

THEORETICAL AND ACTUAL COMBUSTION PROCESSES

- For **example**, the theoretical combustion of methane is

$$CH_4 + 2(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2O + 7.52N_2$$

- Notice that the products of the theoretical combustion contain no unburned methane and no C, H_2, CO, OH, or free O_2.
- In actual combustion processes, it is common practice to use more air than the Stoichiometric amount to :-
  - ✓ Increase the chances of complete combustion
  - ✓ Control the temperature of the combustion chamber.

THEORETICAL AND ACTUAL COMBUSTION PROCESSES

- The amount of air in excess of the stoichiometric amount is called ***excess air***.
- The amount of excess air is usually expressed in terms of the stoichiometric air as ***percent excess air*** or ***percent theoretical air***.

For example, 50 percent excess air is equivalent to 150 percent theoretical air, and 200 percent excess air is equivalent to 300 percent theoretical air.

- The stoichiometric air can be expressed as 0 percent excess air or 100 percent theoretical air.

THEORETICAL AND ACTUAL COMBUSTION PROCESSES

- Amounts of air less than the stoichiometric amount are called deficiency of air and are often expressed as percent ***deficiency of air***.

For example, 90 percent theoretical air is equivalent to 10 percent deficiency of air.

- The amount of air used in combustion processes is also expressed in terms of the ***equivalence ratio***.
- which is the ratio of the actual fuel–air ratio to the stoichiometric fuel–air ratio.

$$\text{equivalence Ratio} = \frac{\text{Actual fuel} - \text{air ratio}}{\text{theoretical fuel} - \text{air ratio}}$$

Combustion Stoichiometry

$$C_nH_m + (n+\frac{m}{4})(O_2 + 3.76N_2) \rightarrow nCO_2 + \frac{m}{2}H_2O + 3.76(n+\frac{m}{4})N_2$$

- Thus for every mole of fuel burned, 4.76(n + m/4) mol of air are required and 4. 76(n + m/4) + m/4 mol of combustion products are generated.
- The molar fuel/air ratio for stoichiometric combustion is 1/[4. 76(n + m/4)].
- 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

Combustion Stoichiometry

$$y_{CO_2} = \frac{n}{4.78(n + \frac{m}{4}) + \frac{m}{4}}$$

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

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

- The large quantity of nitrogen diluent substantially reduces the mole fractions of the combustion products from the values they would have in its absence.

Exercises

The balanced chemical equation for the complete combustion of a general hydrocarbon fuel C_xH_y is given by

$$C_xH_y + \left(x+\frac{y}{4}\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$

$$C_8H_{18} + 12.5\,(O_2 + 3.76\,N_2) \rightarrow 8\,CO_2 + 9\,H_2O + 47\,N_2$$

$$CH_4 + 2(O_2 + 3.76N_2) \leftrightarrow \text{Reactants}$$

fuel 2 kmol air

$$AF = \frac{m_{air}}{m_{fuel}} = \frac{2(4.76)\,[\text{kmol}]\;\;29\left[{}^{kg}/_{kmol}\right]}{1\,[\text{kmol}]\;\;(12+4)\left[{}^{kg}/_{kmol}\right]}$$

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

Example

Elemental analysis of food waste

FW Elemental Composition	%
C	45.405
H	7.655
O	42.915
N	3.945
S	0.4

The biochemical reaction equation used for this analysis is taken from Wu et al [15], and is reproduced in equation below

$C_nH_aO_bN_cS_d + c_1H_2O = c_2CO_2 + c_3CH_4 + c_4NH_3 + c_5H_2S$

C: $n = c_2 + c_3$
H: $a + 2c_1 = 4c_3 + 3c_4 + 2c_5$
O: $b + c_1 = 2c_2$
N: $c = c_4$
S: $d = c_5$
Where,
$c_1 = n - a/4 - b/2 + (3/4)*c + d/2$
$c_2 = n/2 - a/8 + b/4 + (3/8)*c + d/4$

Example

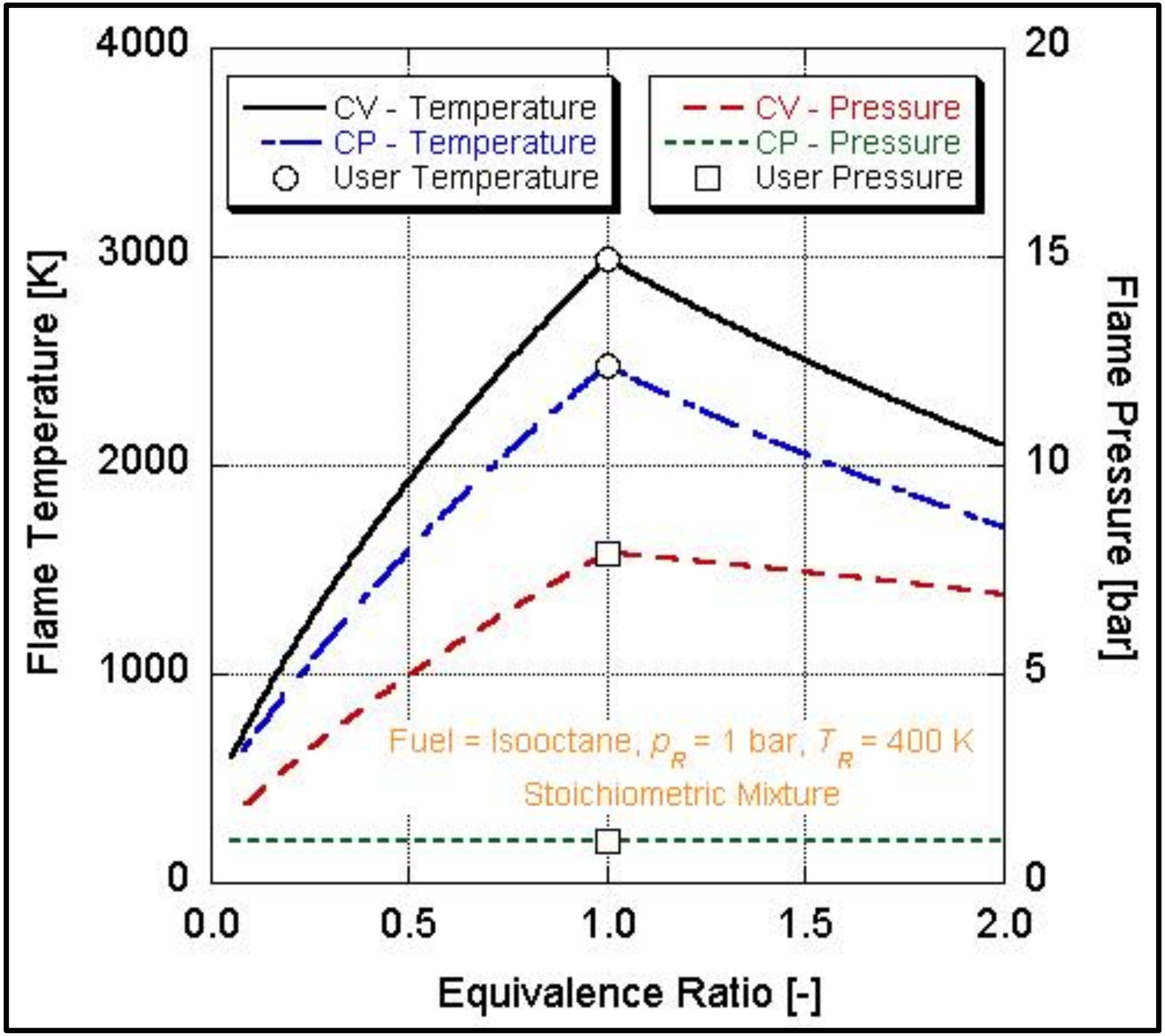
$c_3 = n/2 + a/8 - b/4 - (3/8)*c - d/4$
$c_4 = c$
$c_5 = d$

Balance of biochemical reaction

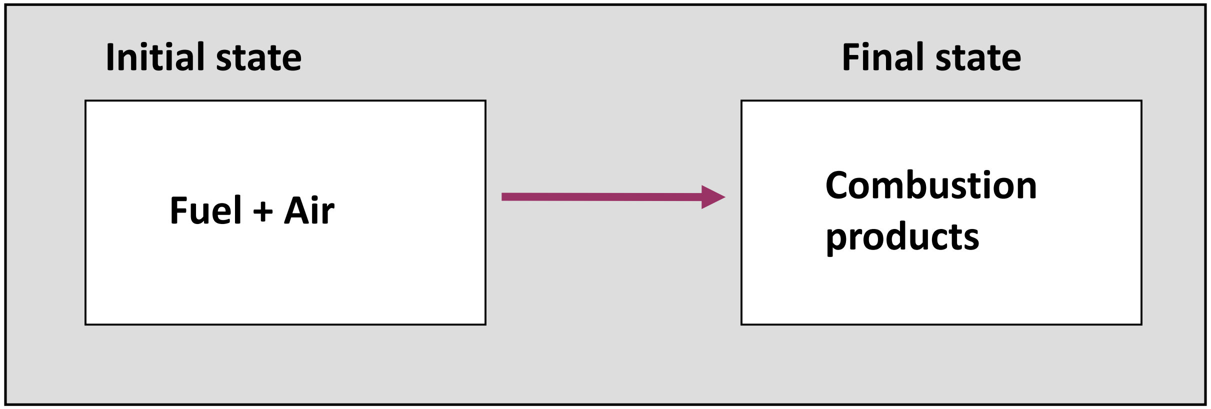
MOLAR RATIOS AND COEFFICIENT CALCULATIONS

	Left	Right
C	N	n/2 + n/2 = n
H	a + 2*[n – a/4 – b/2 + (3/4)*c + d/2] = 2n + a/2 - b + (3/2)*c + d	4[n/2 + a/8 - b/4 - (3/8)*c - d/4] + 3c + 2d = 2n + a/2 -b + (3/2)*c + d
O	b + [n – a/4 – b/2 + (3/4)*c + d/2] = n –a/4 + b/2 + (3/4)*c + d/2	2*[n/2 – a/8 + b/4 + (3/8)*c + d/4] = n –a/4 + b/2 + (3/4)*c + d/2
N	C	C
S	D	D

Combustion Stoichiometry



Complete combustion ...



Initial state

Fuel + Air

Final state

Combustion products

Complete combustion ...
(total reactions)

$C + O_2 \rightarrow CO_2$ + energy

$H_2 + 1/2\ O_2 \rightarrow H_2O$ + energy

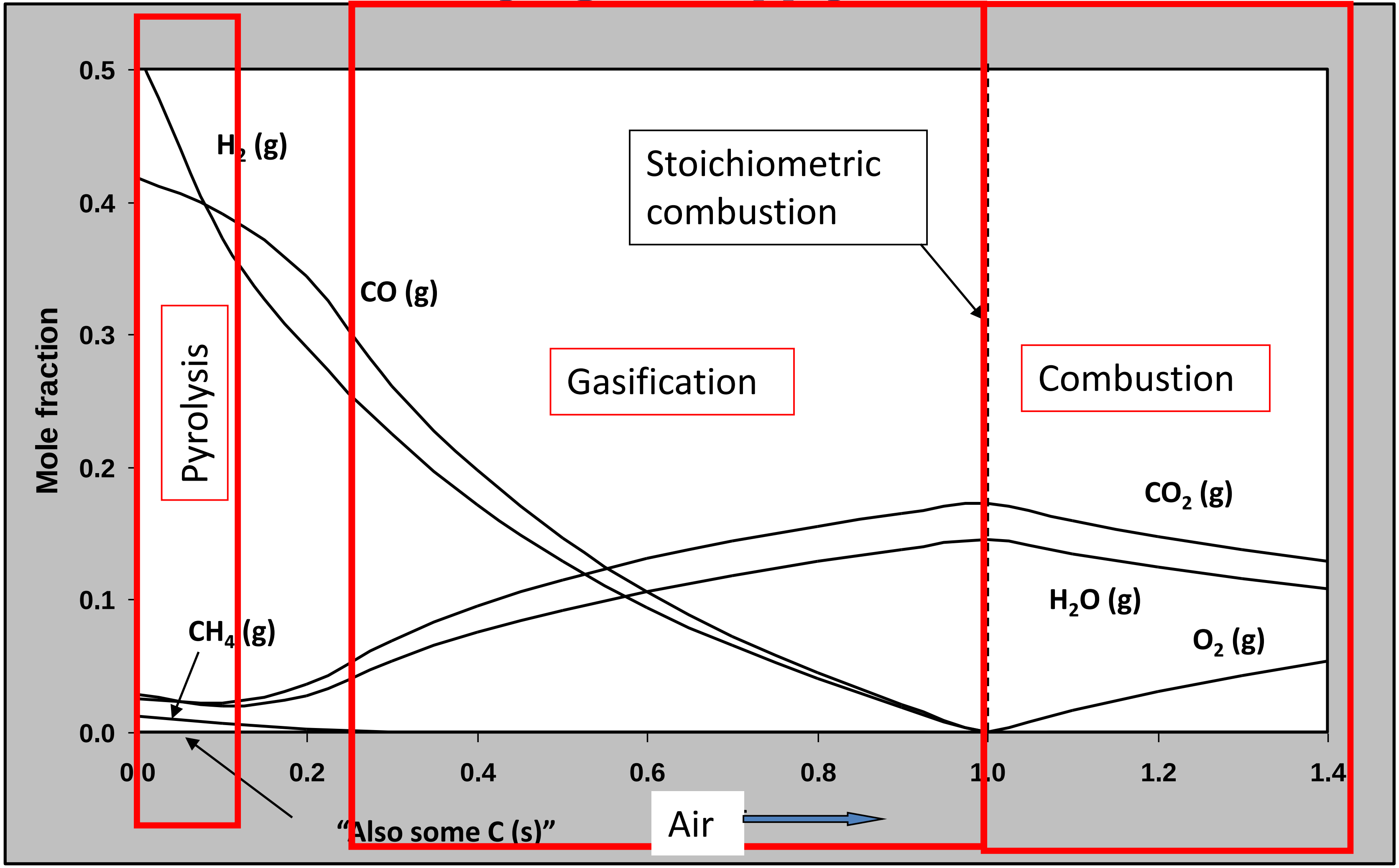
$S + O_2 \rightarrow SO_2$ + energy

Total completion of the combustion process requires ...

1. sufficiently of oxygen (>stoichiometric)
2. high temperature (> 850 °C)
3. long residence time (some sec.)
4. good turbulence (mixing fuel-air)

COMBUSTION

Dominating gases for thermal processing of wood with varying air supply at 800 °C



COMBUSTION

- Almost 90 % of primary energy generated in the world is obtained through combustion processes.
- Oxidation reactions involving fuels are usually strongly exothermic.
- In industrial processes the most common oxidizer is ambient being free and easy to get. Ambient air composition (By Volume) :
- 78 % N2
- 21 % O2
- 1 % Ar
- X_{N2} = Moles of N_2/Moles of Air =78/100= 0.78
- X_{O2} = Moles of O_2/Moles of Air = 21/100= 0.21
- X_{Ar} = Moles of Ar/Moles of Air = 1/100= 0.01
- This is what is defined as dry air and is almost constant everywhere in the world. However, in general, actual air condition is :
- Actual Air = Dry Air + Humidity (Moisture)
- Air = O_2 + 3.76 N_2

COMBUSTION

- So if we need precisely evaluate performances of a plant we need to know humidity composition.
- In general, in chemical reaction, mass is conserved but not molecules.
- However, in general, we even not interested in what happens to molecules unless we don’t need every detail descriptions of the combustion chemical reaction.
- Fuel Mixture : Biomass is basically made up of C,H,O,N,S
- At high temperature these 5 atoms forms gaseous compounds (Volatile reaction)
- But fuel is more complicated that this.

COMBUSTION

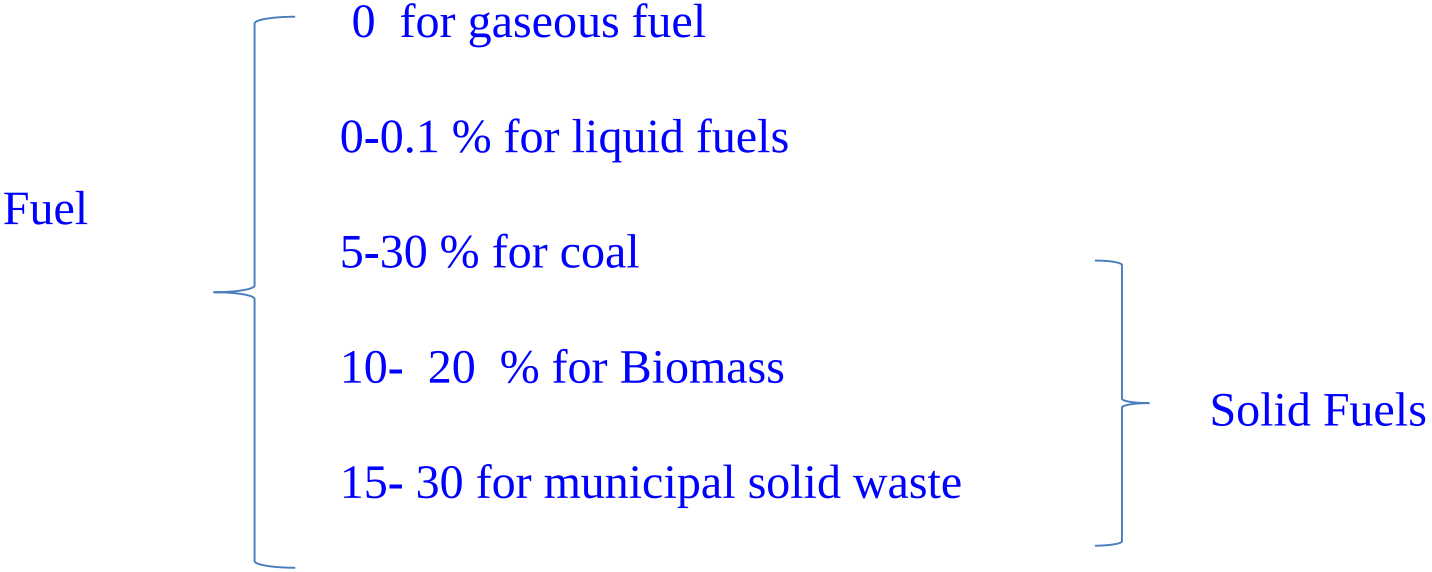
Fuel

- Mixture of C,H,O,N,S : Volatile Fraction
- Moisture (H_2O) liquid phase
- Ashes : Very complex mixture of compounds , they are almost chemically inert and so they don’t Participate in the processes.

COMBUSTION

- Note : Even if they don't participate in the combustion process , but we need to consider them in writing mass and energy balance.
- Almost the same holds for water vapor.
- Ash contents usually one of the indicators of the quality of the fuel.
- If the fuel contains large amount of ash, the design of the combustor will be complicated and the cost of combustor increases.
- In general ashes:
-

y_{ash} = kg of ash/kg of fuel;



Fuel

0 for gaseous fuel

0-0.1 % for liquid fuels

5-30 % for coal

10- 20 % for Biomass

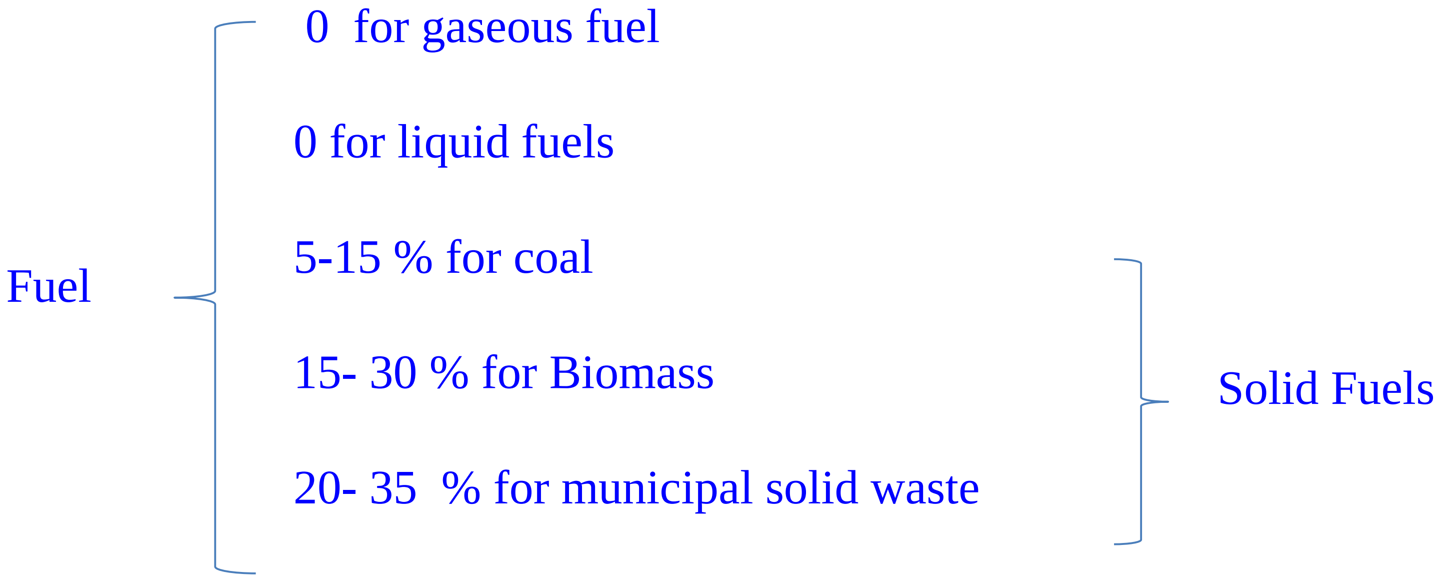
15- 30 for municipal solid waste

Solid Fuels

COMBUSTION

Moisture content

y_{water} = kg of water/kg of fuel;



Fuel

- 0 for gaseous fuel
- 0 for liquid fuels
- 5-15 % for coal
- 15- 30 % for Biomass
- 20- 35 % for municipal solid waste

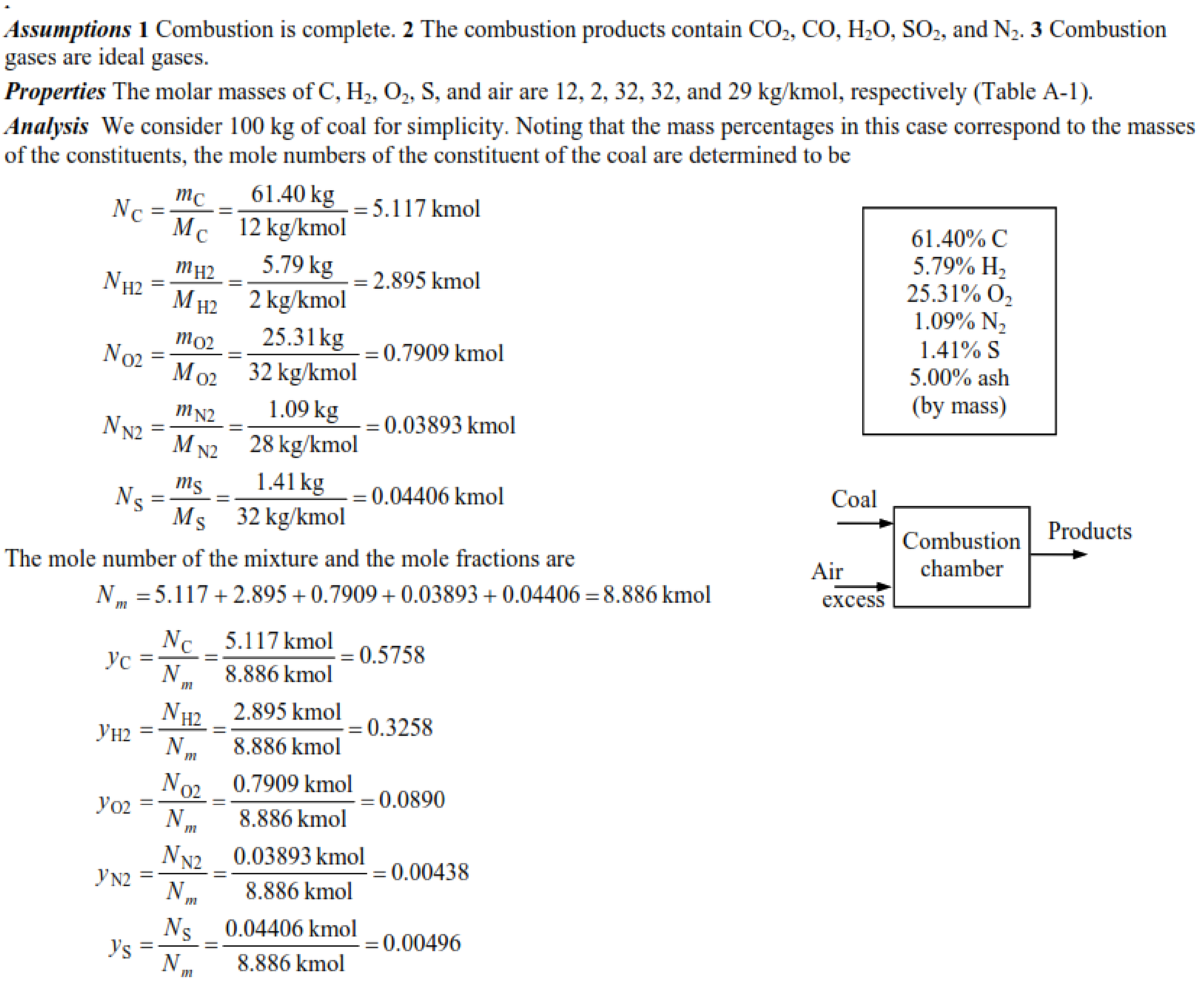
Solid Fuels

Exercise and Solution

- A coal from Utah which has an ultimate analysis (by mass) as 61.40 % C, 5.79 % H2, 25.31 % O2, 1.09 % N2 ,1.41 % S and 5 % ash (non combustibles) is burned with 25 % excess air in an industrial boiler. Assuming complete combustion and the pressure in the boiler smokestack is 1 atm. Calculate the minimum temperature of the combustion products before liquid water begins to form in the smokestack.

Exercise and Solution

- Coal whose mass percentages are specified is burned with 25 % excess air. The dew-point temperature of the products is to be determined.



Assumptions **1** Combustion is complete. **2** The combustion products contain CO_2, CO, H_2O, SO_2, and N_2. **3** Combustion gases are ideal gases.

Properties The molar masses of C, H_2, O_2, S, and air are 12, 2, 32, 32, and 29 kg/kmol, respectively (Table A-1).

Analysis We consider 100 kg of coal for simplicity. Noting that the mass percentages in this case correspond to the masses of the constituents, the mole numbers of the constituent of the coal are determined to be

$$N_C = \frac{m_C}{M_C} = \frac{61.40\text{ kg}}{12\text{ kg/kmol}} = 5.117\text{ kmol}$$

$$N_{H2} = \frac{m_{H2}}{M_{H2}} = \frac{5.79\text{ kg}}{2\text{ kg/kmol}} = 2.895\text{ kmol}$$

$$N_{O2} = \frac{m_{O2}}{M_{O2}} = \frac{25.31\text{ kg}}{32\text{ kg/kmol}} = 0.7909\text{ kmol}$$

$$N_{N2} = \frac{m_{N2}}{M_{N2}} = \frac{1.09\text{ kg}}{28\text{ kg/kmol}} = 0.03893\text{ kmol}$$

$$N_S = \frac{m_S}{M_S} = \frac{1.41\text{ kg}}{32\text{ kg/kmol}} = 0.04406\text{ kmol}$$

61.40% C
5.79% H_2
25.31% O_2
1.09% N_2
1.41% S
5.00% ash
(by mass)

The mole number of the mixture and the mole fractions are

$$N_m = 5.117 + 2.895 + 0.7909 + 0.03893 + 0.04406 = 8.886\text{ kmol}$$

$$y_C = \frac{N_C}{N_m} = \frac{5.117\text{ kmol}}{8.886\text{ kmol}} = 0.5758$$

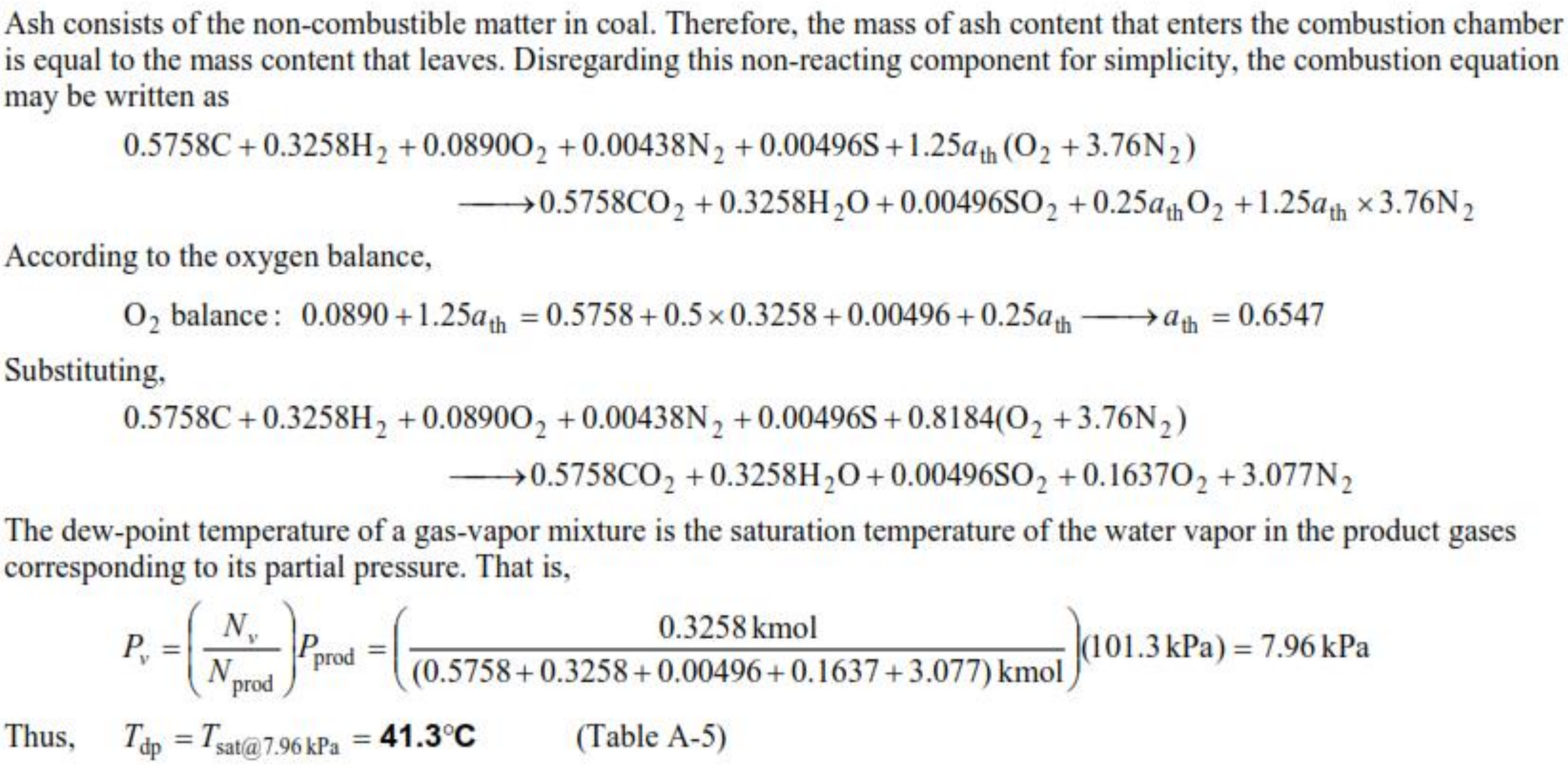
$$y_{H2} = \frac{N_{H2}}{N_m} = \frac{2.895\text{ kmol}}{8.886\text{ kmol}} = 0.3258$$

$$y_{O2} = \frac{N_{O2}}{N_m} = \frac{0.7909\text{ kmol}}{8.886\text{ kmol}} = 0.0890$$

$$y_{N2} = \frac{N_{N2}}{N_m} = \frac{0.03893\text{ kmol}}{8.886\text{ kmol}} = 0.00438$$

$$y_S = \frac{N_S}{N_m} = \frac{0.04406\text{ kmol}}{8.886\text{ kmol}} = 0.00496$$

Exercise and Solution



Ash consists of the non-combustible matter in coal. Therefore, the mass of ash content that enters the combustion chamber is equal to the mass content that leaves. Disregarding this non-reacting component for simplicity, the combustion equation may be written as

$$0.5758\text{C} + 0.3258\text{H}_2 + 0.0890\text{O}_2 + 0.00438\text{N}_2 + 0.00496\text{S} + 1.25a_{\text{th}}(\text{O}_2 + 3.76\text{N}_2)$$
$$\longrightarrow 0.5758\text{CO}_2 + 0.3258\text{H}_2\text{O} + 0.00496\text{SO}_2 + 0.25a_{\text{th}}\text{O}_2 + 1.25a_{\text{th}} \times 3.76\text{N}_2$$

According to the oxygen balance,

$$\text{O}_2 \text{ balance: } \; 0.0890 + 1.25a_{\text{th}} = 0.5758 + 0.5 \times 0.3258 + 0.00496 + 0.25a_{\text{th}} \longrightarrow a_{\text{th}} = 0.6547$$

Substituting,

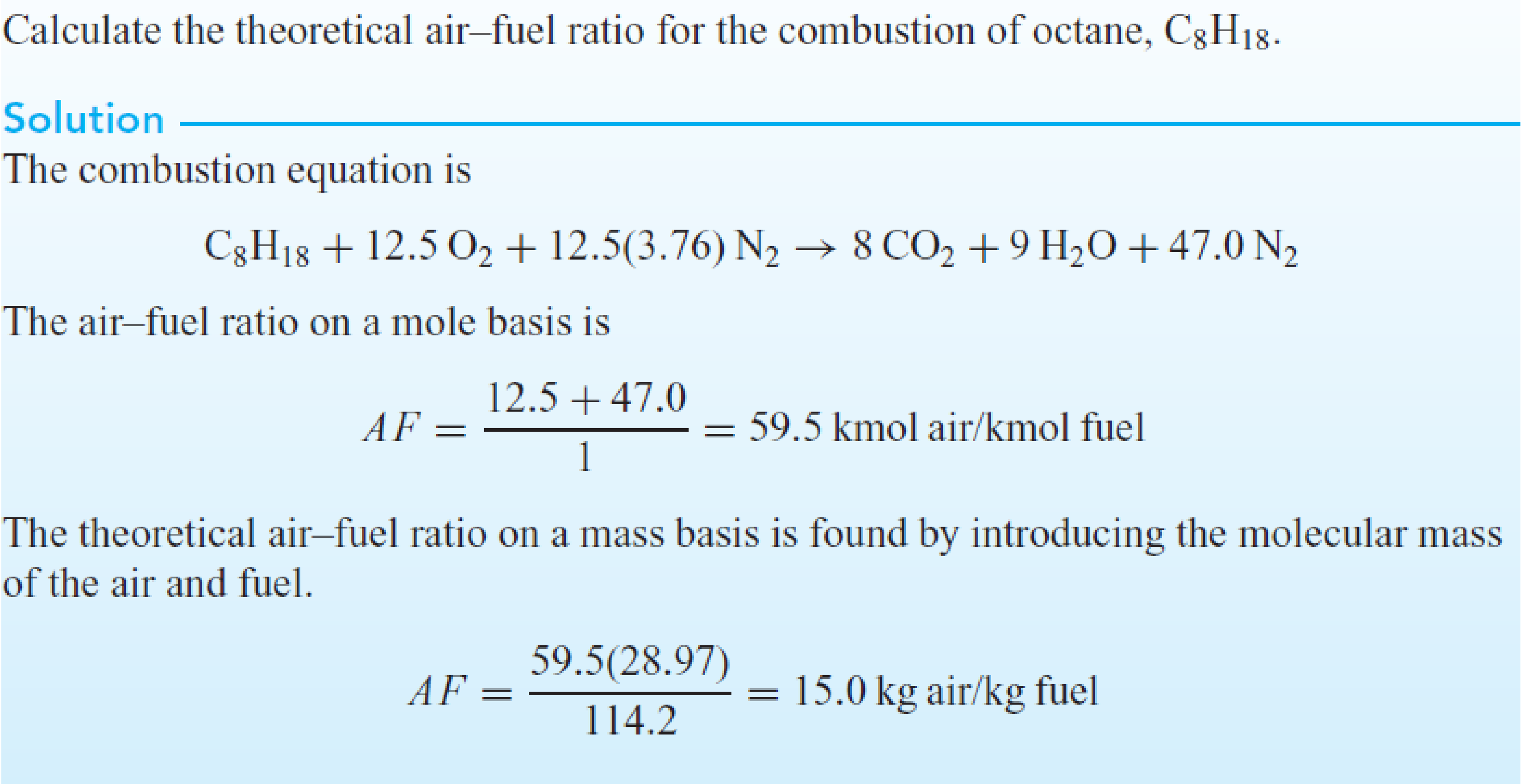
$$0.5758\text{C} + 0.3258\text{H}_2 + 0.0890\text{O}_2 + 0.00438\text{N}_2 + 0.00496\text{S} + 0.8184(\text{O}_2 + 3.76\text{N}_2)$$
$$\longrightarrow 0.5758\text{CO}_2 + 0.3258\text{H}_2\text{O} + 0.00496\text{SO}_2 + 0.1637\text{O}_2 + 3.077\text{N}_2$$

The dew-point temperature of a gas-vapor mixture is the saturation temperature of the water vapor in the product gases corresponding to its partial pressure. That is,

$$P_v = \left(\frac{N_v}{N_{\text{prod}}}\right)P_{\text{prod}} = \left(\frac{0.3258\text{ kmol}}{(0.5758 + 0.3258 + 0.00496 + 0.1637 + 3.077)\text{ kmol}}\right)(101.3\text{ kPa}) = 7.96\text{ kPa}$$

Thus, $T_{\text{dp}} = T_{\text{sat@7.96 kPa}} = \mathbf{41.3^\circ C}$ (Table A-5)

Exercise



Calculate the theoretical air–fuel ratio for the combustion of octane, C_8H_{18}.

Solution

The combustion equation is

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

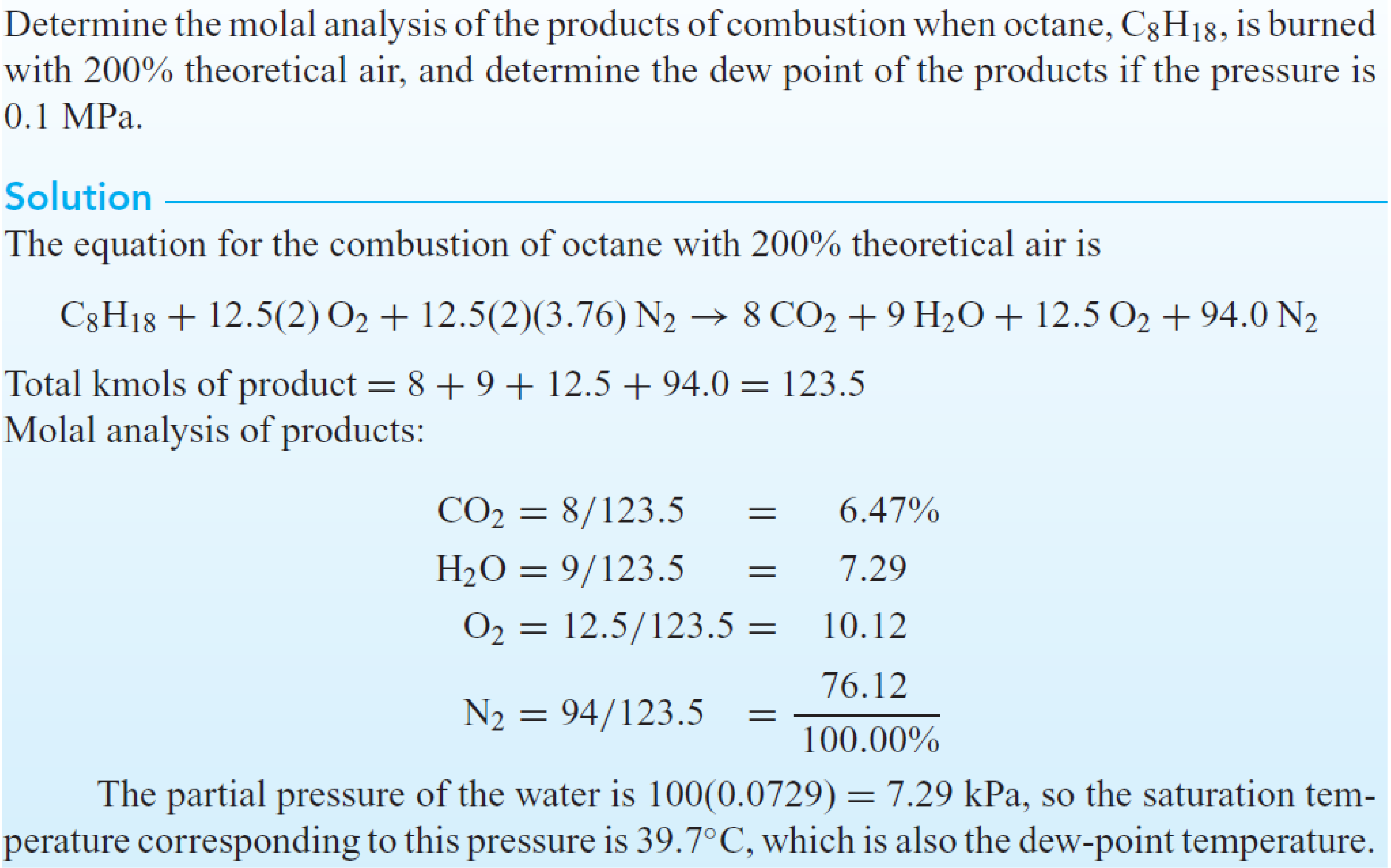
The air–fuel ratio on a mole basis is

$$AF = \frac{12.5 + 47.0}{1} = 59.5 \text{ kmol air/kmol fuel}$$

The theoretical air–fuel ratio on a mass basis is found by introducing the molecular mass of the air and fuel.

$$AF = \frac{59.5(28.97)}{114.2} = 15.0 \text{ kg air/kg fuel}$$

Exercise



Determine the molal analysis of the products of combustion when octane, C_8H_{18}, is burned with 200% theoretical air, and determine the dew point of the products if the pressure is 0.1 MPa.

Solution

The equation for the combustion of octane with 200% theoretical air is

$$C_8H_{18} + 12.5(2)\,O_2 + 12.5(2)(3.76)\,N_2 \rightarrow 8\,CO_2 + 9\,H_2O + 12.5\,O_2 + 94.0\,N_2$$

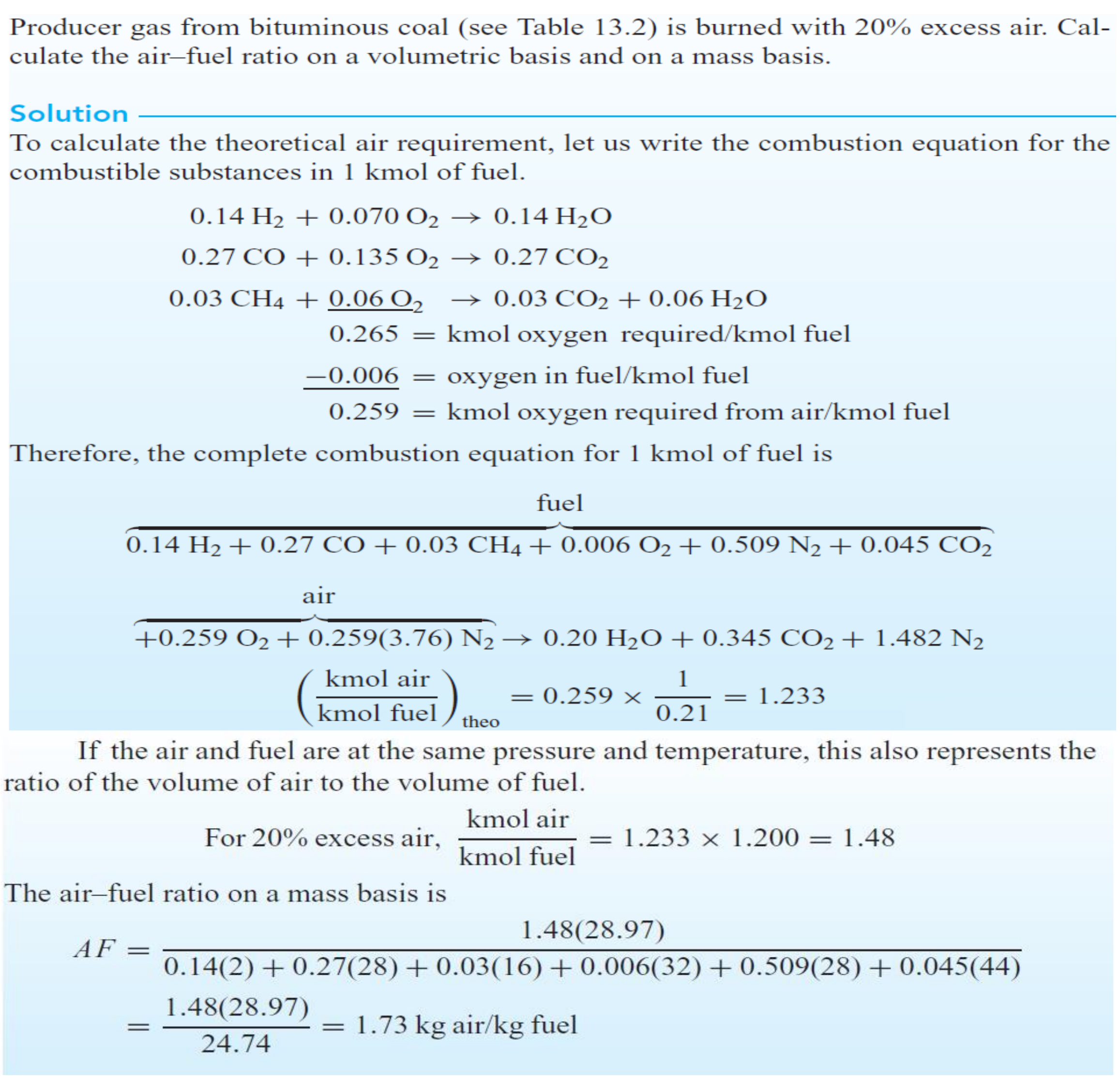
Total kmols of product $= 8 + 9 + 12.5 + 94.0 = 123.5$

Molal analysis of products:

$$\begin{aligned} CO_2 &= 8/123.5 &&= 6.47\% \\ H_2O &= 9/123.5 &&= 7.29 \\ O_2 &= 12.5/123.5 &&= 10.12 \\ N_2 &= 94/123.5 &&= \underline{76.12} \\ & && \ 100.00\% \end{aligned}$$

The partial pressure of the water is $100(0.0729) = 7.29$ kPa, so the saturation temperature corresponding to this pressure is 39.7°C, which is also the dew-point temperature.

Exercise



Producer gas from bituminous coal (see Table 13.2) is burned with 20% excess air. Calculate the air–fuel ratio on a volumetric basis and on a mass basis.

Solution

To calculate the theoretical air requirement, let us write the combustion equation for the combustible substances in 1 kmol of fuel.

$$
\begin{aligned}
0.14\,H_2 + 0.070\,O_2 &\rightarrow 0.14\,H_2O\\
0.27\,CO + 0.135\,O_2 &\rightarrow 0.27\,CO_2\\
0.03\,CH_4 + \underline{0.06\,O_2} &\rightarrow 0.03\,CO_2 + 0.06\,H_2O\\
0.265 &= \text{kmol oxygen required/kmol fuel}\\
\underline{-0.006} &= \text{oxygen in fuel/kmol fuel}\\
0.259 &= \text{kmol oxygen required from air/kmol fuel}
\end{aligned}
$$

Therefore, the complete combustion equation for 1 kmol of fuel is

$$\overbrace{0.14\,H_2 + 0.27\,CO + 0.03\,CH_4 + 0.006\,O_2 + 0.509\,N_2 + 0.045\,CO_2}^{\text{fuel}}$$

$$\overbrace{+0.259\,O_2 + 0.259(3.76)\,N_2}^{\text{air}} \rightarrow 0.20\,H_2O + 0.345\,CO_2 + 1.482\,N_2$$

$$\left(\frac{\text{kmol air}}{\text{kmol fuel}}\right)_{\text{theo}} = 0.259 \times \frac{1}{0.21} = 1.233$$

If the air and fuel are at the same pressure and temperature, this also represents the ratio of the volume of air to the volume of fuel.

$$\text{For 20\% excess air,}\quad \frac{\text{kmol air}}{\text{kmol fuel}} = 1.233 \times 1.200 = 1.48$$

The air–fuel ratio on a mass basis is

$$
\begin{aligned}
AF &= \frac{1.48(28.97)}{0.14(2) + 0.27(28) + 0.03(16) + 0.006(32) + 0.509(28) + 0.045(44)}\\
&= \frac{1.48(28.97)}{24.74} = 1.73\ \text{kg air/kg fuel}
\end{aligned}
$$

Note

- Predicting the composition of the products is relatively easy when the combustion process is assumed to be complete and the exact amounts of the fuel and air used are known.
- All one needs to do in this case is simply apply the ***mass balance*** without needing to take any measurements.
- Things are not so simple, however, when one is dealing with ***actual combustion processes***.
- Actual combustion processes are hardly ever complete, even in the presence of excess air.
- It is impossible to predict the composition of the products on the basis of the mass balance alone.

Note

- To measure the amount of each component in the products directly.
- A commonly used device to analyze the composition of combustion gases is the ***Orsat gas analyzer***.
- Sample of the combustion gases is collected and cooled to ***room temperature*** and ***pressure***, at which point its volume is measured.
- The sample is then brought into contact with a chemical that absorbs the CO_2.
- The remaining gases are returned to the room temperature and pressure, and the new volume they occupy is measured.
- The ratio of the reduction in volume to the original volume is the volume fraction of the CO_2, which is equivalent to the mole fraction if ideal-gas behavior is assumed.
- The volume fractions of the other gases are determined by repeating this procedure.
- In Orsat analysis the gas sample is collected over water and is maintained saturated at all times.
- The vapor pressure of water remains constant during the entire test.

60

Note

- For this reason the presence of water vapor in the test chamber is ignored and data are reported on a ***Dry Basis***.
- The amount of H_2O formed during combustion is easily determined by balancing the combustion equation.

COMBUSTION

- The balanced combustion equation is obtained by making sure we have the same number of atoms of each element on both sides of the equation.
- That is we make sure the mass is conserved.

$$C_8H_{18} + A\,O_2 \rightarrow B\,CO_2 + D\,H_2O$$

$$\boxed{C_8H_{18} + 12.5\,O_2 \rightarrow 8\,CO_2 + 9\,H_2O}$$

$$C_8H_{18} + 12.5\,(O_2 + 3.76\,N_2) \rightarrow 8\,CO_2 + 9\,H_2O + 47\,N_2$$

COMBUSTION

- Mole numbers are not conserved but we have conserved the mass on a total basis as well as a specie basis.
- The complete combustion process is also called the **Stoichiometric combustion**, and all coefficients are called the **Stoichiometric coefficients**.
- In most combustion processes oxygen is supplied in the form of air rather than pure oxygen.
- Air is assumed to be 21% oxygen and 79% nitrogen on a **volume basis**.
- **For ideal gas mixtures, percent by volume is equal to percent by moles.**

COMBUSTION

- Complete combustion of the fuel will not occur unless there is an **excess of air** present greater than just the theoretical air required for complete combustion.
- To determine the amount of excess air supplied for a combustion process, let us define the air-fuel ratio, AF as

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

- the theoretical air fuel ratio
  - ✓ Mole basis $AF_{th} = \frac{12.5(1+3.76)}{1} = 59.5\frac{kmol\ air}{kmol\ \ fuel}$
  - ✓ Mass Basis

$$AF_{th} = 59.5\frac{kmol\ air}{kmol\ \ fuel}\ \frac{28.97\ \frac{kg\ air}{kmol\ air}}{[8(12)+18(1)]\frac{kg\ \ fuel}{kmol\ \ fuel}}$$

$$= 15.12\frac{kg\ air}{kg\ \ fuel}$$

COMBUSTION

Percent Theoretical and Percent Excess Air

- In most cases more than theoretical air is supplied to insure complete combustion and to reduce or eliminate carbon monoxide (CO) from the products of combustion.
- The amount of excess air is usually expressed as percent theoretical air and percent excess air.

$$\text{Percent theoretical air} = \frac{AF_{actual}}{AF_{th}} 100\%$$

$$\text{Percent theoretical air} = \frac{N_{O_2\ actual}}{N_{O_2\ th}} 100\%$$

$$\text{Percentexcessair} = \frac{AF_{actual} - AF_{th}}{AF_{th}} 100\%$$

$$\text{Percent excess air} = \frac{N_{O_2\ actual} - N_{O_2\ th}}{N_{O_2\ th}} 100\%$$

COMBUSTION

- Write the combustion equation of octane with 120% theoretical air (20% excess air).

$$C_8H_{18} + 1.2(12.5)\,(O_2 + 3.76\,N_2) \rightarrow$$
$$8\,CO_2 + 9\,H_2O + (0.2)(12.5)\,O_2 + 1.2(47)\,N_2$$

- Note that (1)(12.5)O_2 is required for complete combustion to produce 8 kmol of carbon dioxide and 9 kmol of water.
- therefore, (0.2)(12.5)O_2 is found as excess oxygen in the products.
- Second method to balance the equation for excess air:-

$$C_8H_{18} + 1.2\,A_{th}\,(O_2 + 3.76\,N_2) \rightarrow$$
$$8\,CO_2 + 9\,H_2O + 0.2\,A_{th}\,O_2 + 1.2(47)\,N_2$$

$$O: \quad 1.2\,A_{th}(2) = 8(2) + 9(1) + 0.2\,A_{th}(2)$$
$$A_{th} = 12.5$$

COMBUSTION

Incomplete Combustion With Known % Theoretical Air

- Consider combustion of C_8H_{18} with 120 % Theoretical air where 80 % C in the fuel goes into CO_2 :-

$$C_8H_{18} + 1.2(12.5)\,(O_2 + 3.76\,N_2) \rightarrow$$
$$0.8(8)\,CO_2 + 0.2(8)\,CO + 9\,H_2O + X\,O_2 + 1.2(47)\,N_2$$

- **Why is X>2.5?**
- Then the balanced equation is

$$O: \quad 1.2(12.5)(2) = 0.8(8)(2) + 0.2(8)(1) + 9(1) + X(2)$$
$$X = 3.3$$

$$C_8H_{18} + 1.2(12.5)\,(O_2 + 3.76\,N_2) \rightarrow$$
$$6.4\,CO_2 + 1.6\,CO + 9\,H_2O + 3.3\,O_2 + 1.2(47)\,N_2$$

COMBUSTION

Combustion Equation When Product Gas Analysis Is Known

Example

- Propane gas C_3H_8 is reacted with air such that the dry product gases are 11.5% CO_2, 2.7% O_2, and 0.7% CO by volume.
  - ✓ What percent theoretical air was supplied?
  - ✓ What is the dew point temperature of the products if the product pressure is 100 kPa?

$$X\, C_3H_8 + A\,(O_2 + 3.76\, N_2) \rightarrow$$

$$11.5\, CO_2 + 0.7\, CO + 2.7\, O_2 + B\, H_2O + A(3.76)\, N_2$$

COMBUSTION

- The unknown coefficients A, B, and X are found by conservation of mass for each species.

$$\begin{array}{ll}
C:\ X(3) = 11.5(1) + 0.7(1) & X = 4.07 \\
H:\ X(8) = B(2) & B = 16.28 \\
O:\ A(2) = 11.5(2) + 0.7(1) & \\
\qquad\qquad + 2.7(2) + B(1) & \boxed{A = 22.69} \\
N_2 : A(3.76) = 85.31 &
\end{array}$$

- The balanced equation is

$$\begin{aligned}
&4.07\, C_3H_8 + 22.69\,(O_2 + 3.76\ N_2) \to \\
&\quad 11.5\, CO_2 + 0.7\ CO + 2.7\ O_2 + 16.28\ H_2O + 85.31\ N_2
\end{aligned}$$

Second method to find A:

- Assume the remainder of the 100 kmol of dry product gases is N_2.

$$kmol\ \ N_2 = 100 - (11.5 + 0.7 + 2.7) = 85.1$$

$$A = \frac{85.1}{3.76} = 22.65 \quad (\,fairly\ \ good\ \ check\,)$$

COMBUSTION

- **Generally we should write the combustion equation per kmol of fuel.**
- To write the combustion equation per unit kmol of fuel divide by 4.07:

$$C_3H_8 + 5.57\,(O_2 + 3.76\,N_2) \rightarrow$$

$$2.83\,CO_2 + 0.17\,CO + 0.66\,O_2 + 4.0\,H_2O + 20.96\,N_2$$

COMBUSTION

- The actual air-fuel ratio is

$$AF_{th} = \frac{5.57(1+3.76)kmol\ air\ \ 28.97\ \dfrac{kg\ air}{kmol\ air}}{1kmol\ \ fuel[3(12)+8(1)]\dfrac{kg\ \ fuel}{kmol\ \ fuel}}$$

$$= 17.45\frac{kg\ air}{kg\ \ fuel}$$

- The theoretical combustion equation is

$$C_3H_8 + 5\,(O_2 + 3.76\ N_2) \rightarrow$$

$$3\,CO_2 + 4.0\ H_2O + 18.80\ N_2$$

- The theoretical air-fuel ratio is

$$AF_{th} = \frac{(5)(1+3.76)kmol\ air\ \ 28.97\ \dfrac{kg\ air}{kmol\ air}}{1kmol\ \ fuel[3(12)+8(1)]\dfrac{kg\ \ fuel}{kmol\ \ fuel}}$$

$$= 15.66\frac{kg\ air}{kg\ \ fuel}$$

COMBUSTION

- The percent theoretical air is

$$\text{Percent theoretical air} = \frac{AF_{actual}}{AF_{th}}100\%$$
$$= \frac{17.45}{15.66}100 = 111\%$$

$$\text{Percent theoretical air} = \frac{N_{O_2\,actual}}{N_{O_2\,th}}100\%$$
$$= \frac{5.57}{5}100 = 111\%$$

- The percent excess air is

$$\text{Percent excess air} = \frac{AF_{actual} - AF_{th}}{AF_{th}}100\%$$
$$= \frac{17.45 - 15.66}{15.66}100 = 11\%$$

COMBUSTION

DEW POINT TEMPERATURE:

- The dew point temperature for the product gases is the temperature at which the water in the product gases would begin to condense when the products are cooled at constant pressure.
- The dew point temperature is equal to the saturation temperature of the water at its partial pressure in the products.

$$T_{\mathrm{DP}} = T_{\mathrm{sat}} \text{ at } P_{\mathrm{v}} = y_{\mathrm{v}} P_{\mathrm{products}}$$

$$y_{\mathrm{v}} = \frac{N_{\mathrm{water}}}{\sum_{\mathrm{products}} N_e}$$

COMBUSTION

Dew Point Temperature:

$$y_v = \frac{4}{2.83 + 0.17 + 0.66 + 4 + 20.96} = 0.1398$$

$$P_v = y_v P_{products} = 0.1398(100\,kPa)$$

$$= 13.98\,kPa$$

$$T_{DP} = T_{sat} \text{ at } 13.98\,\text{kPa}$$

$$= 52.44^o C$$

- **What would happen if the product gases are cooled to 100^0C or to 30^0C?**

COMBUSTION

Dew Point Temperature:

Example

- An unknown hydrocarbon fuel, C_XH_Y is reacted with air such that the dry product gases are 12.1% CO_2, 3.8% O_2, and 0.9% CO by volume.
  - ✓What is the average make-up of the fuel?

- We assume 100 kmol (Do you have to always assume 100 kmol?) of dry product gases; then the percent by volume can interpreted to be mole numbers.

COMBUSTION

- We do not know how much air was supplied or water formed to get the 100 kmol of dry product gases. But, we assume 1 kmol of unknown fuel.

$$C_X H_Y + A\,(O_2 + 3.76\,N_2) \rightarrow$$
$$12.1\,CO_2 + 0.9\,CO + 3.8\,O_2 + B\,H_2O + D\,N_2$$

- The 5 unknown coefficients A, B, D, X, and Y are found by conservation of mass for each species, C, H, O, and N plus one other equation.
- Here we use the subtraction method for the nitrogen to generate the fifth independent equation for the unknowns.

COMBUSTION

- The unknown coefficients A, B, and X are found by conservation of mass for each species.

$$N_2: D = 100 - (12.1 + 0.9 + 3.8) = 83.2$$

$$O_2: \quad A = \frac{D}{3.76} = \frac{83.2}{3.76} = 22.13$$

$$O: \quad A(2) = (12.1)(2) + (0.9)(1) + (3.8)(2) + B(1)$$

$$B = 11.54$$

$$C: 1(X) = 12.1(1) + (0.9)(1)$$

$$X = 13.0$$

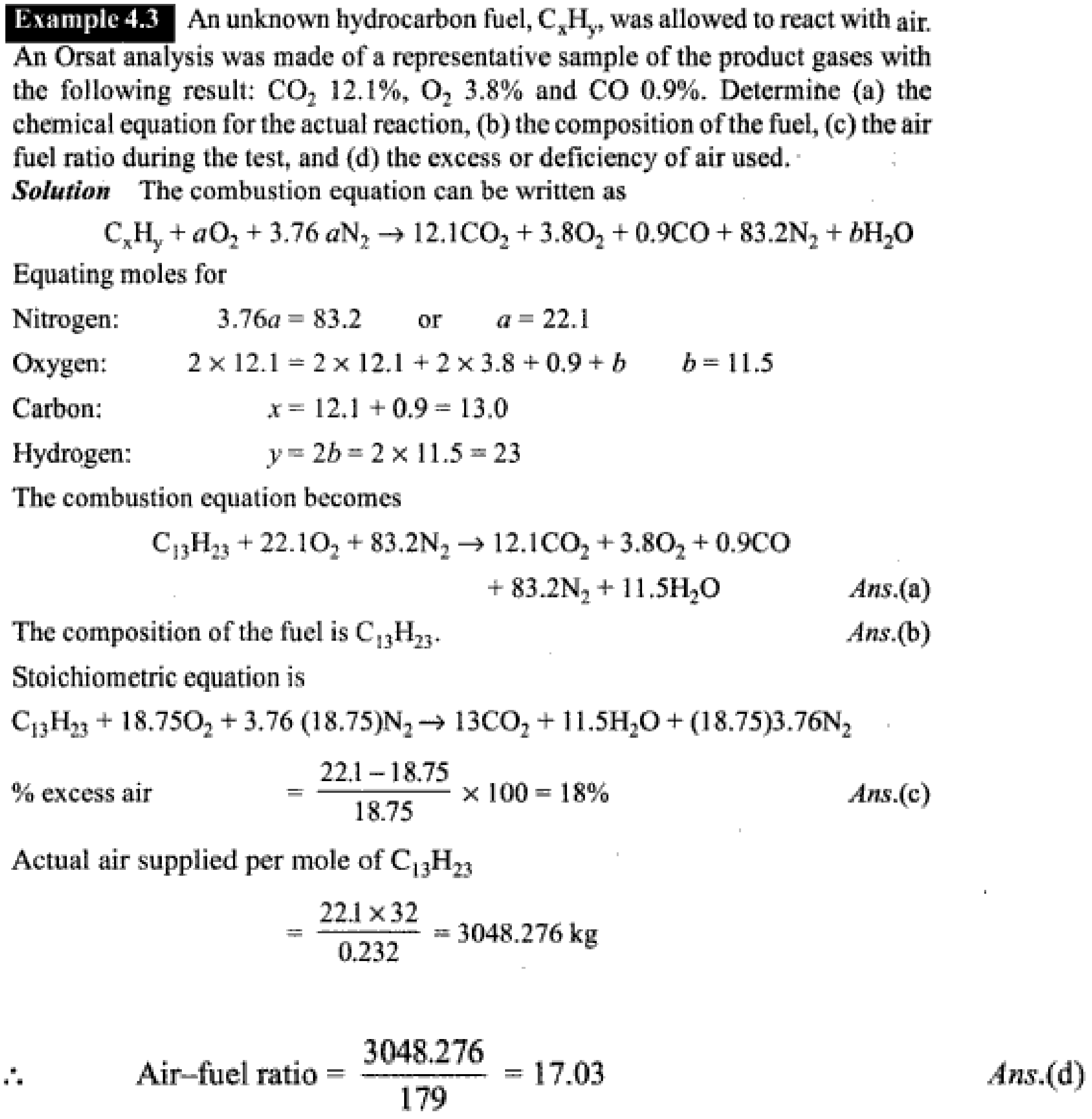
$$H: \; 1(Y) = B(2)$$

$$Y = 23.08$$

- The balanced equation is

$$C_{13}H_{23.08} + 22.13\,(O_2 + 3.76\,N_2) \rightarrow$$

$$12.1\,CO_2 + 0.9\,CO + 3.8\,O_2 + 11.54\,H_2O + 83.2\,N_2$$



Example 4.3 An unknown hydrocarbon fuel, C_xH_y, was allowed to react with air. An Orsat analysis was made of a representative sample of the product gases with the following result: CO_2 12.1%, O_2 3.8% and CO 0.9%. Determine (a) the chemical equation for the actual reaction, (b) the composition of the fuel, (c) the air fuel ratio during the test, and (d) the excess or deficiency of air used.

Solution The combustion equation can be written as

$$C_xH_y + aO_2 + 3.76\,aN_2 \rightarrow 12.1CO_2 + 3.8O_2 + 0.9CO + 83.2N_2 + bH_2O$$

Equating moles for

Nitrogen: $3.76a = 83.2$ or $a = 22.1$

Oxygen: $2 \times 12.1 = 2 \times 12.1 + 2 \times 3.8 + 0.9 + b$ $b = 11.5$

Carbon: $x = 12.1 + 0.9 = 13.0$

Hydrogen: $y = 2b = 2 \times 11.5 = 23$

The combustion equation becomes

$$C_{13}H_{23} + 22.1O_2 + 83.2N_2 \rightarrow 12.1CO_2 + 3.8O_2 + 0.9CO + 83.2N_2 + 11.5H_2O \qquad \textit{Ans.}(a)$$

The composition of the fuel is $C_{13}H_{23}$. *Ans.*(b)

Stoichiometric equation is

$$C_{13}H_{23} + 18.75O_2 + 3.76\,(18.75)N_2 \rightarrow 13CO_2 + 11.5H_2O + (18.75)3.76N_2$$

$$\text{\% excess air} = \frac{22.1 - 18.75}{18.75} \times 100 = 18\% \qquad \textit{Ans.}(c)$$

Actual air supplied per mole of $C_{13}H_{23}$

$$= \frac{22.1 \times 32}{0.232} = 3048.276 \text{ kg}$$

$$\therefore \qquad \text{Air–fuel ratio} = \frac{3048.276}{179} = 17.03 \qquad \textit{Ans.}(d)$$

Exercises

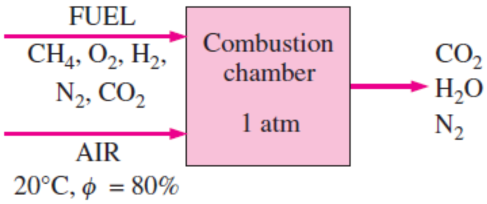


FIGURE 15–12

Schematic for Example 15–3.

EXAMPLE 15–3 Combustion of a Gaseous Fuel with Moist Air

A certain natural gas has the following volumetric analysis: 72 percent CH_4, 9 percent H_2, 14 percent N_2, 2 percent O_2, and 3 percent CO_2. This gas is now burned with the stoichiometric amount of air that enters the combustion chamber at 20°C, 1 atm, and 80 percent relative humidity, as shown in Fig. 15–12. Assuming complete combustion and a total pressure of 1 atm, determine the dew-point temperature of the products.

Solution A gaseous fuel is burned with the stoichiometric amount of moist air. The dew point temperature of the products is to be determined.

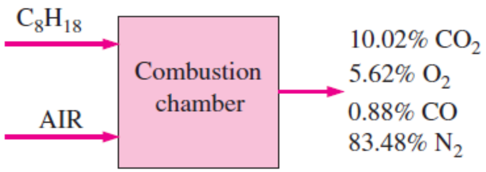


FIGURE 15–13

Schematic for Example 15–4.

EXAMPLE 15–4 Reverse Combustion Analysis

Octane (C_8H_{18}) is burned with dry air. The volumetric analysis of the products on a dry basis is (Fig. 15–13)

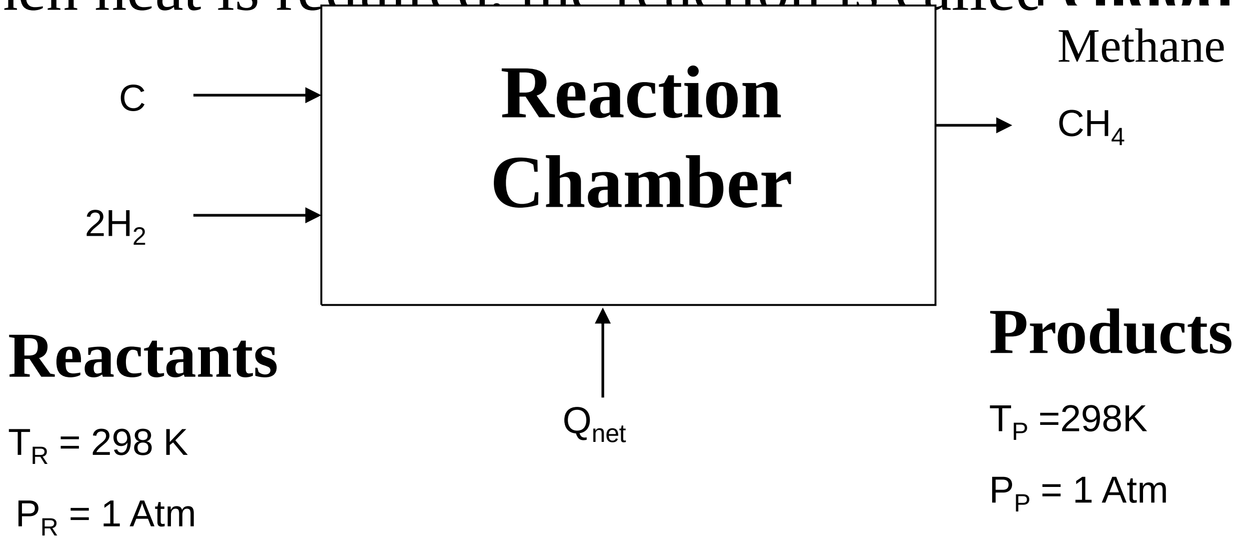
CO_2: 10.02 percent
O_2: 5.62 percent
CO: 0.88 percent
N_2: 83.48 percent

Determine (*a*) the air–fuel ratio, (*b*) the percentage of theoretical air used, and (*c*) the amount of H_2O that condenses as the products are cooled to 25°C at 100 kPa.

COMBUSTION

Enthalpy of Formation

- When a compound is formed from its elements (e.g. Methane, CH_4, from C and H_2), heat transfer occurs.
  - ✓When heat is given off, the reaction is called **exothermic**.
  - ✓When heat is required, the reaction is called **endothermic**.



C

$2H_2$

Reaction Chamber

Methane

CH_4

Reactants

T_R = 298 K

P_R = 1 Atm

Q_{net}

Products

T_P =298K

P_P = 1 Atm

Enthalpies of Reactions

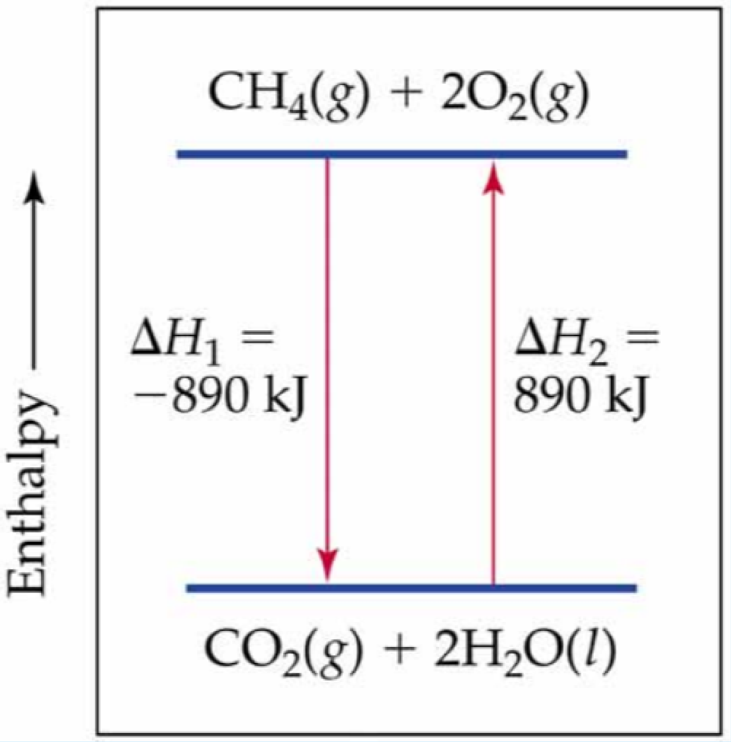
The enthalpy change for a reaction is equal in magnitude, but opposite in sign, to ΔH for the reverse reaction.

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

$\Delta H = -890$ kJ

$CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g)$

$\Delta H = 890$ kJ



Enthalpies of Reaction

- The enthalpy of reaction is dependant on the states of the reactants and products.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \quad \Delta H = -890 \text{ kJ}$$

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \quad \Delta H = -802 \text{ kJ}$$

$$2H_2O(l) \rightarrow 2H_2O(g) \; \Delta H = +88 \text{ kJ}$$

Hess's Law

Result of enthalpy being a state function

Hess's law: if a reaction is carried out in a number of steps, ΔH for the overall reaction is the sum of ΔH for each individual step.

$$
\begin{array}{ll}
CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + \cancel{2H_2O(g)} & \Delta H = -802\text{ kJ} \\
\cancel{2H_2O(g)} \rightarrow 2H_2O(l) & \Delta H = -88\text{ kJ} \\
\hline
CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) & \Delta H = -890\text{ kJ}
\end{array}
$$

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COMBUSTION

Enthalpy of Formation

$$C + 2H_2 \rightarrow CH_4$$

- The conservation of energy for a steady-flow combustion process is

$$E_{in} = E_{out}$$

$$Q_{net} + H_{\text{Reactants}} = H_{\text{Products}}$$

$$Q_{net} = H_{\text{Products}} - H_{\text{Reactants}}$$

$$Q_{net} = \sum_{\text{Products}} N_e \overline{h}_e - \sum_{\text{Reactants}} N_i \overline{h}_i$$

$$Q_{net} = 1\overline{h}_{CH_4} - (1\overline{h}_C - 1\overline{h}_{H_2})$$

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Enthalpy of Formation

- The enthalpy of formation (or heat of formation) ΔH_f is the enthalpy change associated with forming 1 mole of a compound from its constituent elements.

$$2C(graphite) + 3H_2(g) + 1/2O_2(g) \rightarrow C_2H_5OH(l)$$

$$\Delta H_{rxn} = \Delta H_f = -277.7 \text{ kJ}$$

Note: only one mole of product formed!

  - If there is more than one state for a substance, the more stable one is used.
    - C(graphite) is more stable than C(diamond).

Standard Enthalpies

- Standard enthalpy, ΔH^{o}, is the enthalpy measured when everything is in its standard state.
  - ΔH_f^{o} - standard enthalpy of formation: ΔH for forming one mole of product directly from its reactants with products and reactants in standard states.
    - The standard enthalpy of formation of the most stable form of any element is zero.
  - ΔH_{vap}^{o} – standard enthalpy of vaporization: ΔH for converting liquids to gases with products and reactants in standard states.
  - ΔH_{fus}^{o} – standard enthalpy of fusion: ΔH for melting solids.
  - ΔH_{sub}^{o} – standard enthalpy of sublimation: ΔH for converting solids to gases
  - ΔH_{comb}^{o} – enthalpy of combustion: ΔH for combusting a substance with oxygen)

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Enthalpies of Reaction

from enthalpies of formation

- We can use Hess' Law to calculate enthalpies of a reaction from enthalpies of formation.

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$$

$$\Delta H^\circ_{\text{rxn}} = \sum n\Delta H^\circ_f(\text{products}) - \sum m\Delta H^\circ_f(\text{reactants})$$

Heat Capacity and Specific Heat

- Objects can emit or absorb heat, which causes an object to change temperature.
  - An objects heat capacity is the amount of energy required to raise its temperature by 1 K (or 1^0C).
  - The greater the heat capacity, the greater the heat required to produce a given rise in temperature.

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Enthalpy of chemical change (reaction)

Enthalpy of reaction is the heat released or absorbed as a result of a chemical reaction

$$\Delta H_{rxn} = \Sigma H_{products} - \Sigma H_{reactants}$$

COMBUSTION

Enthalpy of Formation

- We need to establish a common reference state for the enthalpies of reacting components.
- The enthalpy of the elements or their stable compounds is defined to be **zero** at 25^{0}C (298 K) and 1 atm (or 0.1 MPa).

$$Q_{net} = 1\bar{h}_{CH_4} - (1(0) - 1(0))$$

$$= \bar{h}_{CH_4}$$

$$\bar{h}_f^o$$

- This heat transfer is called **the enthalpy of formation** for methane
- The superscript (o) implies the 1 atm pressure value and the subscript (f) implies 25^{o}C data.

COMBUSTION

Enthalpy of Formation

- During the formation of methane from the elements at 298 K, 0.1 MPa, heat is given off (an exothermic reaction) such that

$$Q_{net} = \bar{h}^o_{f\ CH_4} = -74{,}850 \frac{kJ}{kmol_{CH_4}}$$

- The enthalpy of formation, $\bar{h}^o_f$, is tabulated for typical compounds.
- The enthalpy of formation of the elements in their stable form is taken as **zero**.

Enthalpy of Formation

- The enthalpy of formation of the elements found naturally as diatomic elements, such as nitrogen, oxygen, and hydrogen, is defined to be zero.

Substance	Formula	M	$\bar{h}_f^o$ kJ/kmol
Air		29	0
Oxygen	O_2	32	0
Nitrogen	N_2	28	0
Carbon Dioxide	CO_2	44	-393,520
Carbon Monoxide	CO	28	-110,530
Water (vapor)	H_2Ovap	18	-241,820
Water (liquid)	H_2Oliq	18	-285,830
Methane	CH_4	16	-74,850
Acetylene	C_2H_2	26	+226,730
Ethane	C_2H_6	30	-84,680
Propane	C_3H_8	44	-103,850
Butane	C_4H_{10}	58	-126,150
Octane (vapor)	C_8H_{18}	114	-208,450
Dodecane	$C_{12}H_{26}$	170	-291,010

COMBUSTION

ENTHALPY OF FORMATION

- The enthalpies are calculated relative to a common base or reference called **the enthalpy of formation**.
- The enthalpy of formation is the heat transfer required to form the compound from its elements at 25^{0}C (77 F) or 298 K (537 R), 1 atm.
- The enthalpy at any other temperature is given as

$\bar{h}^o$

$$\bar{h} = \bar{h}_f^o + (\bar{h}_T - \bar{h}^o)$$

- Here the term is the enthalpy of any component at 298 K.

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COMBUSTION

Enthalpy of Formation

- **If tables are not available**, the enthalpy difference due to the temperature difference can be calculated from:

$$(\bar{h}_T - \bar{h}^o) = \bar{C}_P (T - 298)$$

- When the reactants and products are at temperatures other than 298 K, the enthalpy is given by
- The heat transfer is

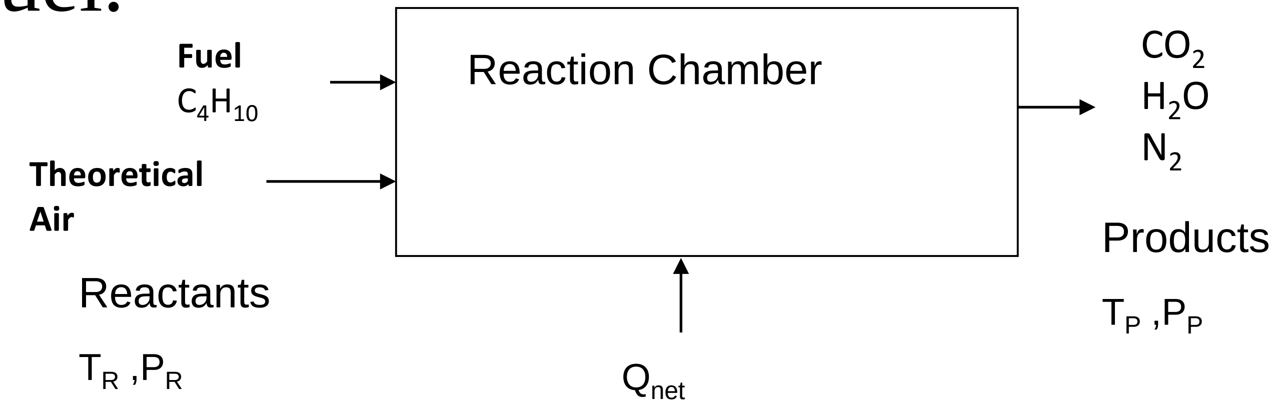
$$\begin{aligned} Q_{net} &= H_P - H_R \\ &= \sum_{\text{Products}} N_e[\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_e - \sum_{\text{Reactants}} N_i[\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_i \end{aligned}$$

COMBUSTION

Enthalpy of Formation

Example:

- Butane gas C_4H_{10} is burned in theoretical air as shown below. Find the net heat transfer per kmol of fuel.



Fuel
C_4H_{10}

Theoretical Air

Reactants

T_R ,P_R

Reaction Chamber

Q_{net}

CO_2
H_2O
N_2

Products

T_P ,P_P

- Balanced combustion equation:

$$C_4H_{10} + 6.5(O_2 + 3.76 N_2) \rightarrow 4CO_2 + 5H_2O + 24.44 N_2$$

COMBUSTION

Enthalpy of Formation

- The steady-flow heat transfer is

$$Q_{net} = H_P - H_R$$

$$= \sum_{\text{Products}} N_e[\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_e - \sum_{\text{Reactants}} N_i[\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_i$$

- Reactants: $T_R = 298$ K

Comp	N_i kmol/kmol fuel	$\bar{h}_f^o$ kJ/kmol	$\bar{h}_T$ kJ/kmol	$\bar{h}^o$ kJ/kmol	$N_i[\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]$ kJ/kmol fuel
C_4H_{10}	1	-126,150	-	-	-126,150
O_2	6.5	0	8,682	8,682	0
N_2	24.44	0	8,669	8,669	0

$$H_R = \sum_{\text{Reactants}} N_i[\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_i$$

$$= -126{,}150 \frac{kJ}{kmol\, C_4H_{10}}$$

COMBUSTION

Enthalpy of Formation

- Assume products: $T_P = 1000$ K

Comp	N_e kmol/kmol fuel	$\bar{h}_f^o$ kJ/kmol	$\bar{h}_T$ kJ/kmol	$\bar{h}^o$ kJ/kmol	$N_e[\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]$ kJ/kmol fuel
CO_2	4	-393,520	42,769	9,364	-1,440,460
H_2O	5	-241,820	35,882	9,904	-1,079,210
N_2	24.44	0	30,129	8,669	+524,482

$$H_P = \sum_{\text{Products}} N_e[\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_e$$

$$= -1{,}995{,}188 \frac{kJ}{kmol\, C_4H_{10}}$$

$$\boxed{\begin{aligned} Q_{net} &= H_P - H_R \\ &= -1{,}869{,}038 \frac{kJ}{kmol\, C_4H_{10}} \end{aligned}}$$

COMBUSTION

Adiabatic Flame Temperature

- The temperature the products have when a combustion process takes place adiabatically is called the adiabatic flame temperature.

Example:

- Liquid octane, C_8H_{18}(liq) is burned with 400% theoretical air. Find the adiabatic flame temperature when the reactants enter at 298 K, 0.1 MPa and the products leave at 0.1MPa.

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Adiabatic Flame temperature

Adiabatic flame temperature (constant pressure) of common fuels

Fuel	Oxidizer	T_{ad} (°C)	T_{ad} (°F)
Acetylene (C_2H_2)	Air	2500	4532
Acetylene (C_2H_2)	Oxygen	3480	6296
Butane (C_4H_{10})	Air	1970	3578
Cyanogen (C_2N_2)	Oxygen	4525	8177
Dicyanoacetylene (C_4N_2)	Oxygen	4990	9010
Ethane (C_2H_6)	Air	1955	3551
Ethanol (C_2H_5OH)	Air	2082	3779[1]
Gasoline	Air	2138	3880[1]
Hydrogen (H_2)	Air	2254	4089[1]
Hydrogen (H_2)	Oxygen	3200	5792[2]
Magnesium (Mg)	Air	1982	3600[3]
Methane (CH_4)	Air	1963	3565[4]
Methanol (CH_4O)	Air	1949	3540[4]
Natural gas	Air	1960	3562[5]
Pentane (C_5H_{12})	Air	1977	3591[4]
Propane (C_3H_8)	Air	1980	3596[6]
Propane (C_3H_8)	Oxygen	2526	4579
MAPP gas Methylacetylene (C_3H_4)	Air	2010	3650
MAPP gas Methylacetylene (C_3H_4)	Oxygen	2927	5301
Toluene (C_7H_8)	Air	2071	3760[4]
Wood	Air	1980	3596
Kerosene	Air	2093[7]	3801
Light fuel oil	Air	2104[7]	3820
Medium fuel oil	Air	2101[7]	3815
Heavy fuel oil	Air	2102[7]	3817
Bituminous Coal	Air	2172[7]	3943
Anthracite	Air	2180[7]	3957
Anthracite	Oxygen	≈2900[see 1]	≈5255
Aluminum	Oxygen	3732	6750[4]
Lithium	Oxygen	2438	4420[4]
Phosphorus (white)	Oxygen	2969	5376[4]
Zirconium	Oxygen	4005	7241[4]

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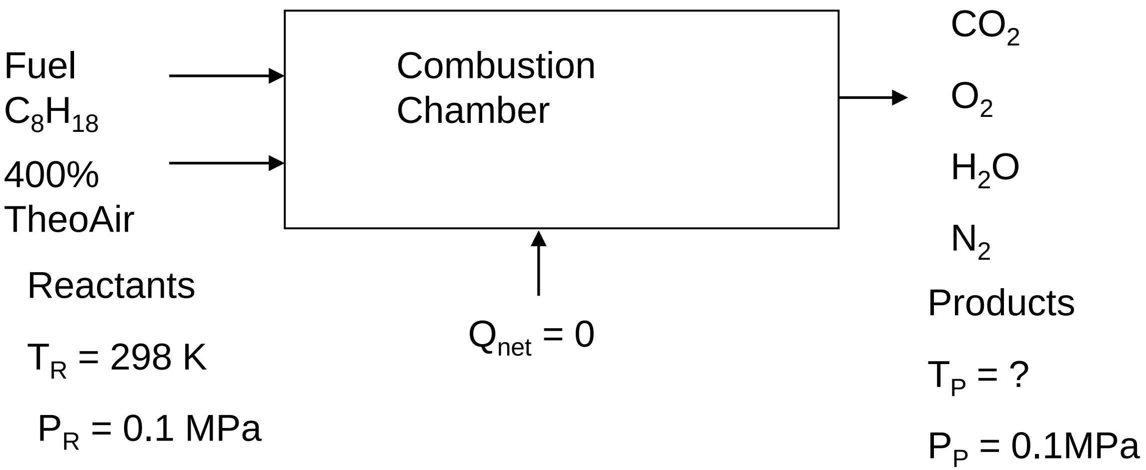
COMBUSTION

Adiabatic Flame Temperature

- The combustion equation is



$$C_8H_{18} + 4(12.5)\,(O_2 + 3.76\,N_2) \rightarrow$$
$$8\,CO_2 + 37.5\,O_2 + 9\,H_2O + 188\;N_2$$

- The steady-flow heat transfer is

$$Q_{net} = H_P - H_R$$
$$= \sum_{\text{Products}} N_e[\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_e - \sum_{\text{Reactants}} N_i[\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_i$$
$$= 0 \;(Adiabatic\ Combustion)$$

COMBUSTION

Adiabatic Flame Temperature

- Thus, $H_P = H_R$ for adiabatic combustion. We need to solve this equation for T_P.
- Since the reactants are at 298 K, $(\bar{h}_T - \bar{h}^o)_i = 0$,

$$H_R = \sum_{\text{Reactants}} N_i \bar{h}^o_{f\,i}$$

$$= 1(-249{,}950) + 4(12.5)(0) + 4(12.5)(3.76)(0)$$

$$= -249{,}950 \frac{kJ}{kmol\, C_4H_{10}}$$

COMBUSTION

Adiabatic Flame Temperature

$$H_P = \sum_{\text{Products}} N_e[\bar{h}_f^o - (\bar{h}_{T_P} - \bar{h}^o)]_e$$

$$= 8(-393{,}520 + \bar{h}_{T_P} - 9364)_{CO_2}$$

$$+ 9(-241{,}820 + \bar{h}_{T_P} - 9904)_{H_2O}$$

$$+ 37.5(0 + \bar{h}_{T_P} - 8682)_{O_2}$$

$$+ 188(0 + \bar{h}_{T_P} - 8669)_{N_2}$$

$$H_P = (-7{,}443{,}845 + 8\bar{h}_{T_P,CO_2} + 9\bar{h}_{T_P,H_2O}$$

$$+ 37.5\bar{h}_{T_P,O_2} + 188\bar{h}_{T_P,N_2})\frac{kJ}{kmol\, C_4H_{10}}$$

COMBUSTION

Adiabatic Flame Temperature

- Thus, setting $H_P = H_R$ yields

$$8\bar{h}_{T_P,CO_2} + 9\bar{h}_{T_P,H_2O} + 37.5\bar{h}_{T_P,O_2} + 188\bar{h}_{T_P,N_2} = 7{,}193{,}895$$

- To estimate T_P, assume all products behave like N_2 and estimate the adiabatic flame temperature from the nitrogen data.

$$242.5\bar{h}_{T_P,N_2} = 7{,}193{,}895$$

$$\bar{h}_{T_P,N_2} = 29{,}665.5\frac{kJ}{kmol\ \ N_2}$$

$$T_p \cong 985\,K$$

COMBUSTION

Adiabatic Flame Temperature

- Because of the tri-atomic CO_2 and H_2O, the actual temperature will be somewhat less than 985 K. Try 960 K and 970K.

	N_e	$\bar{h}_{960\,K}$	$\bar{h}_{970\,K}$
CO_2	8	40,607	41,145
H_2O	9	34,274	34,653
O_2	37.5 $\sum_{\text{Produts}} N_e \bar{h}_{T_P,e}$	29,991	30,345
N_2	188	28,826	29,151
		7,177,572	7,259,362

- Interpolation gives: T_P = 962 K

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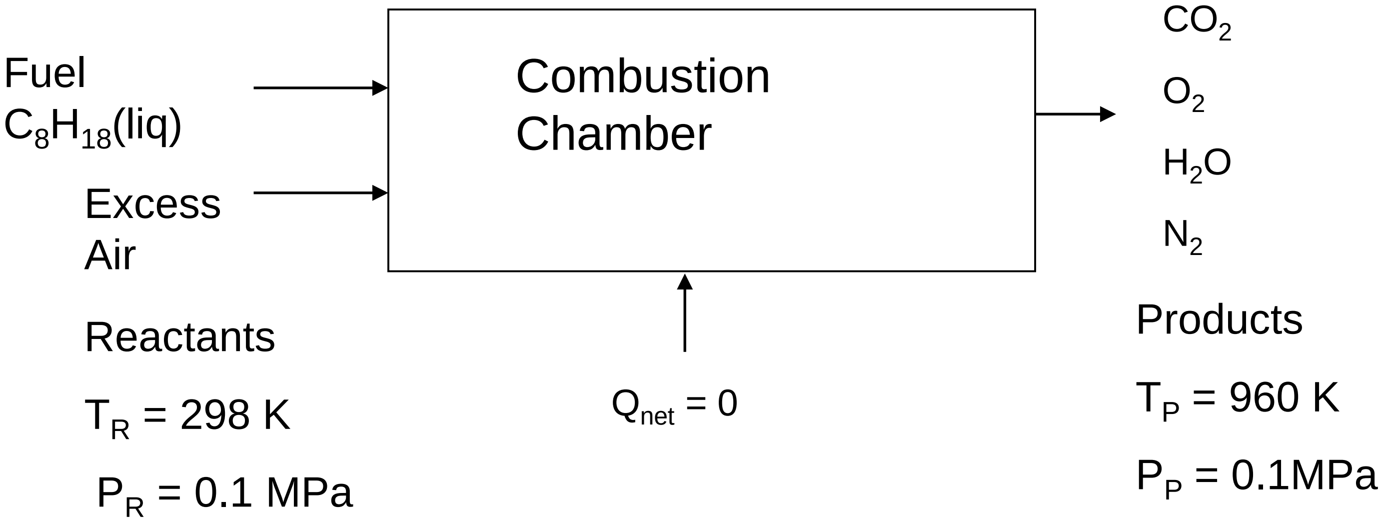
COMBUSTION

Adiabatic Flame Temperature

Example

- Liquid octane, C_8H_{18}(liq) is burned with excess air. The adiabatic flame temperature is 960 K when the reactants enter at 298 K, 0.1 MPa and the products leave at 0.1MPa. What percent excess air is supplied?



Fuel

C_8H_{18}(liq)

Excess Air

Combustion Chamber

CO_2

O_2

H_2O

N_2

Reactants

$T_R = 298$ K

$P_R = 0.1$ MPa

$Q_{net} = 0$

Products

$T_P = 960$ K

$P_P = 0.1$MPa

COMBUSTION

Adiabatic Flame Temperature

- Let A be the excess air; then combustion equation is:-

$$C_8H_{18} + (1 + A)(12.5)\,(O_2 + 3.76\,N_2) \rightarrow$$

$$8\,CO_2 + 12.5A\;O_2 + 9\;H_2O + (1 + A)(12.5)(3.76)\;N_2$$

- The steady-flow heat transfer is

$$Q_{net} = H_P - H_R$$

$$= \sum_{\text{Products}} N_e[\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_e - \sum_{\text{Reactants}} N_i[\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_i$$

$$= 0 \quad (\mathit{Adiabatic\ Combustion})$$

- Here, since the temperatures are known, the $\bar{h}_{T_P}$ are known.

COMBUSTION

Adiabatic Flame Temperature

- The product gas mole numbers are unknown but are functions of the amount of excess air, A. The energy balance can be solved for A.

$$A = 3$$

- Thus 300% excess, or 400% theoretical, air is supplied.

Example

- Tabulate the adiabatic flame temperature as a function of excess air for the complete combustion of C_3H_8 when the fuel enters the reaction chamber at 298 K and the air enters at 400 K.

COMBUSTION

- The combustion equation is:

$$C_3H_8 + (1+A)(5)\,(O_2 + 3.76\,N_2) \rightarrow$$
$$3\,CO_2 + 5A\;O_2 + 4\;H_2O + (1+A)(5)(3.76)\;\;N_2$$

- Where A is the value of excess air in decimal form.
- The steady-flow heat transfer is

$$Q_{net} = H_P - H_R$$
$$= \underset{\text{Products}}{\sum} N_e[\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_e - \underset{\text{Reactants}}{\sum} N_i[\bar{h}_f^o + (\bar{h}_T - \bar{h}^o)]_i$$
$$= 0 \quad (\mathit{Adiabatic\ Combustion})$$

% Excess Air	Adiabatic Flame Temp. K
0	2459.3
20	2191.9
50	1902.5
100	1587.1
217	1200

COMBUSTION

The Enthalpy of Reaction and Enthalpy of Combustion

- When the products and reactants are at **the same temperature**, the enthalpy of reaction h_R, is the difference in their enthalpies.
- When the combustion is assumed to be complete with theoretical air supplied the enthalpy of reaction is called the **enthalpy of combustion**, Δh_C.
- The enthalpy of combustion can be calculated any value of the temperature but it is usually determined at 25^0C or 298 K.

$$\Delta\bar{h}_C = H_P - H_R \quad when\ T_P = T_R = 25^o C = 298\,K$$

$$= \sum_{\text{Products}} N_e \bar{h}^o_{f\;e} - \sum_{\text{Reactants}} N_i \bar{h}^o_{f\;i}$$

COMBUSTION

The Enthalpy of Reaction and Enthalpy of Combustion

Heating Value

- The heating value, HV, of a fuel is the absolute value of the enthalpy of combustion or just the negative of the enthalpy of combustion.
- The lower heating value, LHV, is the heating value when water appears as a gas in the products.

$$LHV = \left|\Delta \bar{h}_C\right| = -\Delta \bar{h}_C \ \text{with}\ H_2O_{gas}\ \text{in products}$$

COMBUSTION

The Enthalpy of Reaction and Enthalpy of Combustion

Heating Value

- The lower heating value is often used as the amount of energy per kmol of fuel supplied to the gas turbine engine.
- The higher heating value, HHV, is the heating value when water appears as a liquid in the products.

$$HHV = \left|\Delta \bar{h}_C\right| = -\Delta \bar{h}_C \ \text{with}\ H_2O_{liquid}\ \text{in products}$$

- The higher heating value is often used as the amount of energy per kmol of fuel supplied to the steam power cycle.

COMBUSTION

The Enthalpy of Reaction and Enthalpy of Combustion

Heating Value

- The higher and lower heat values are related by the amount of water formed during the combustion process and the enthalpy of vaporization of water at the temperature.

$$HHV = LHV + N_{H_2O}\bar{h}_{fg\,H_2O}$$

COMBUSTION

The Enthalpy of Reaction and Enthalpy of Combustion

Heating Value

Example

- The enthalpy of combustion of gaseous C_8H_{18} at 25^0C with liquid water in the products is -5,512,200 kJ/kmol.
  - ✓Find the lower heating value of liquid octane.

$$LHV_{C_8H_{18}\ gas} = HHV_{C_8H_{18}\ gas} - N_{H_2O}\bar{h}_{fg\,H_2O}$$

$$= 5{,}512{,}200\frac{kJ}{kmol\ \ C_8H_{18}} - 9\frac{kmol\ \ H_2O}{kmol\ \ C_8H_{18}}(44{,}010)\frac{kJ}{kmol\ \ H_2O}$$

$$= 5{,}116{,}110\frac{kJ}{kmol\ \ C_8H_{18}}$$

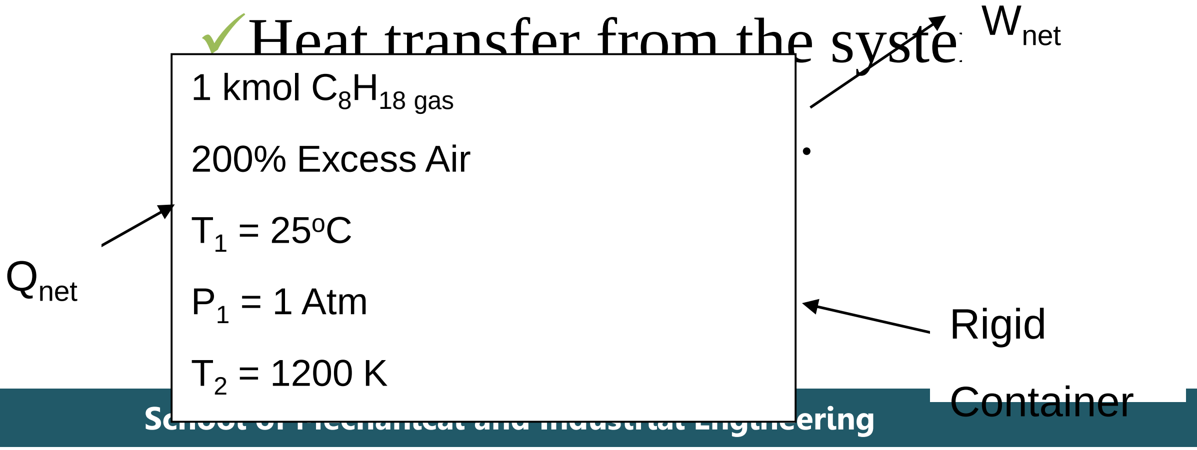
COMBUSTION

The Enthalpy of Reaction and Enthalpy of Combustion

Closed System Analysis:

Example:

- A mixture of 1 kmol C_8H_{18} gas and 200% excess air at 25^0C, 1 atm is burned completely in a closed system (a bomb) and is cooled to 1200 K. Find the
  - ✓ Heat transfer from the syste



COMBUSTION

The Enthalpy of Reaction and Enthalpy of Combustion

Closed System Analysis:

$$E_{in} - E_{out} = \Delta E$$

$$Q_{net} - W_{met} = U_p - U_R$$

$$W_{net} = 0(Rigid\ container)$$

$$Q_{Net} = U_P - U_R = H_P - (PV)_P - H_R - (PV)_R$$

$$Q_{Net} = U_P - U_R = H_P - H_R - (PV)_P - (PV)_R$$

- Assume that the reactants and products are ideal gases, then

$$PV = NR_U T$$

$$Q_{net} = H_P - H_R - \sum_{product} N_e R_u T_e - \sum_{Reactants} N_i R_u T_i$$

$$= \sum_{products} N_e \left[\bar{h}_f^0 + \left(\bar{h}_T - \bar{h}^0\right) - R_u T\right]_e$$

$$- \sum_{Reactants} N_i \left[\bar{h}_f^0 + \left(\bar{h}_T - \bar{h}^0\right)\right]_i$$

COMBUSTION

The Enthalpy of Reaction and Enthalpy of Combustion

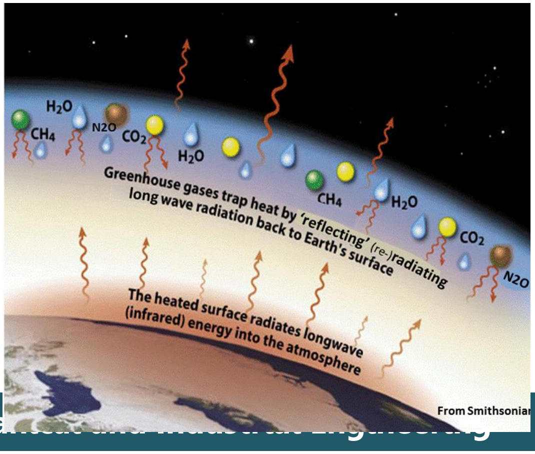
- The balanced combustion equation for 200% excess (300% theoretical) air

$$C_8H_{18} + (3)(12.5)(O_2 + 3.76N_2) \rightarrow 8CO_2 + 25O_2 + 9H_2O + 141N_2$$

$$\begin{aligned}
Q_{net} &= 8(-393{,}520 + 53{,}848 - 9{,}364 - 8.314(1200))_{CO_2} \\
&\quad + 9(-241{,}820 + 44{,}380 - 9{,}904 - 8.314(1200))_{H_2O} \\
&\quad + 25(0 + 38{,}447 - 8{,}682 - 8.314(1200))_{O_2} \\
&\quad + 141(0 + 36{,}777 - 8{,}669 - 8.314(1200))_{N_2} \\
&\quad - 1(-208{,}450 + \bar{h}_{298K} - \bar{h}^{o} - 8.314(1200))_{C_8H_{18}} \\
&\quad - 25(0 + 8{,}682 - 8{,}682 - 8.314(1200))_{O_2} \\
&\quad - 141(0 + 8{,}669 - 8{,}669 - 8.314(1200))_{N_2} \\
&= 1.12 \cdot 10^{6} \frac{kJ}{kmol\ C_8H_{18}}
\end{aligned}$$

Pollutant formation - Greenhouse gas emission

- **Fossil fuels** are mainly **carbon based**.
- The combustion of fossil fuel results in formation of **Carbon Dioxide (CO_2)**
- **After combustion** of the fuels, the **CO_2 is usually released into the atmosphere**
- This **gas absorbs the infrared part of radiation from the earth** and reradiates it back to the earth, **creating the effect of a greenhouse.**
- Due to green house effect of carbon dioxide, the average global temperature of earth is **increasing**.
- The **increased temperature** of the earth due to greenhouse gas effect will results in erratic weather pattern, floods, droughts, submerging of low-lying areas due to melting of ice at poles,etc.



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