Green and Sustainable Technologies
Combustion, Pyrolysis, and Gasification

Dr. Renuka Ariyawansha

Department of Environmental Technology, Faculty of Technology

renukaa@sltc.ac.lk

Outline

Combustion definition

Combustion Equations - Heat of Combustion & Formation

Conditions necessary for combustion to take place

Industrial combustibles

Pyrolysis

Gasification

1.0 Definition - Combustion

▪The combustion is a product of several chemical reactions.

▪Produced during the course of complete or partial oxidation of carbon and hydrogen of usual combustibles.

▪They are exothermic reactions of oxydo-reduction (*also called redox reaction, any chemical reaction in which the oxidation number of a participating chemical species changes*).

*An exothermic reaction is **a reaction in which energy is released in the form of light or heat**. Thus in an exothermic reaction, energy is transferred into the surroundings rather than taking energy from the surroundings as in an endothermic reaction.*

▪The oxidized matter, which losses an electron is **combustible (able to catch fire and burn easily/a combustible substance),** and the reduced matter, which gains an electron, is the **comburant**.

Cont. Definition

- In practice, it is termed the combustible of the original product.

- One or more elements are found to be oxidized during the course of the reaction and other elements do not directly participate in the reaction.

- These elements are found in the fumes and ash,

- which contain gaseous and solid products respectively of the combustion.

Cont. Definition

- The combustibles usually are composed of hydrocarbons (the combustion of hydrogen has a higher energy value than carbon).

- The more commonly employed comburant is pure oxygen or mixed in air of nitrogen.

- However, halogens such as fluorine, chlorine, iodine, or ozone can also be used or being employed as comburant.

- The industrial interest of combustion is in the form of heat.

Cont. Definition

- Since combustion is accompanied by radiation of light, which is found in the flame within the limited space of combustion: it is live combustion.

- On the contrary, it is termed slow combustion, for example, when it is produced during the course of storage of humid products.

- **Heat of combustion :**

  The calorific value is the total energy released as heat when a substance undergoes complete combustion with oxygen under standard conditions
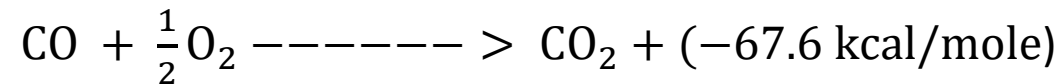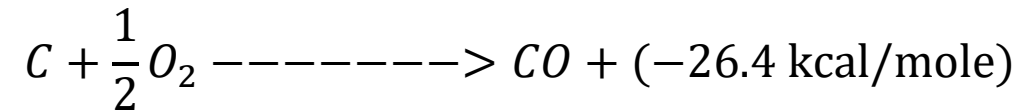
  It may be expressed with the quantities:
  - energy/mole of fuel
  - energy/mass of fuel
  - energy/volume of the fuel

2.0. Combustion Equations - Heat of Combustion & Formation

At atmospheric pressure and 298 K (25 °C) .

$$C + O_2 \; ------------ > \; CO_2 + (-94.05 \text{ kcal/mole})$$

This reaction could be written in two steps.

$$C + \frac{1}{2}O_2 \; --------> \; CO + (-26.4 \text{ kcal/mole})$$

$$CO + \frac{1}{2}O_2 \; ------ > \; CO_2 + (-67.6 \text{ kcal/mole})$$

Chemical Composition	State	$(Hc)_{298}$ kcal/mole
Carbon C	Solid	- 94.052
Hydrogen H_2 (H_2O gas)	gas	- 57.598
Hydrogen H_2 (H_2O liquid)	gas	- 68.317
Carbon monoxide CO	gas	- 67.636
Methane CH_4	gas	-212.79
Acetylene C_2H_2	gas	-310.6
Ethylene C_2H_4	gas	-320.0
Ethane C_2H_6	gas	-372.8
Propane C_3H_8	gas	-530.8
n-Butane C_4H_{10}	gas	-687.9
n-Pentane C_5H_{12}	gas	-845.3
Benzene C_6H_6	liquid	-781.0
Methanol CH_3OH	liquid	-173.6
Ethanol C_2H_5OH	liquid	-326.66

for a simple hydro-carbon of formulae $C_x H_y$

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \; \text{-------} > x\,CO_2 + \frac{y}{2}H_2O$$
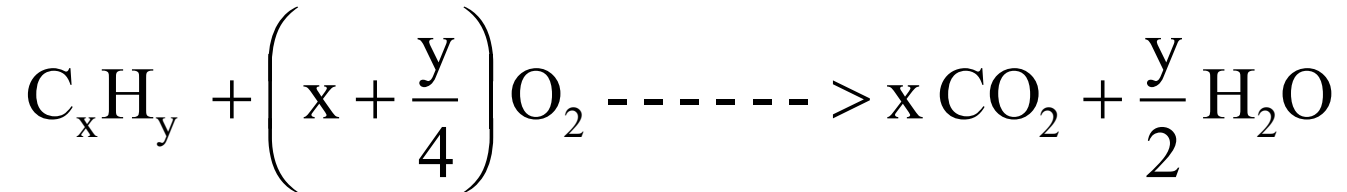
For a complex hydrocarbon of the form $C_x\,H_y\,O_z\,N_u\,S_v$,

$$C_x\,H_y\,O_z\,N_u\,S_v + \left(x + v + \frac{y}{4} - \frac{z}{2}\right)(O_2 + 3.77\,N_2) \; \text{-------} >$$

$$xCO_2 + v\,SO_2 + \frac{y}{2}H_2O + \left[3.77\left(x + v + \frac{y}{4} - \frac{z}{2}\right) + \frac{u}{2}\right]N_2$$
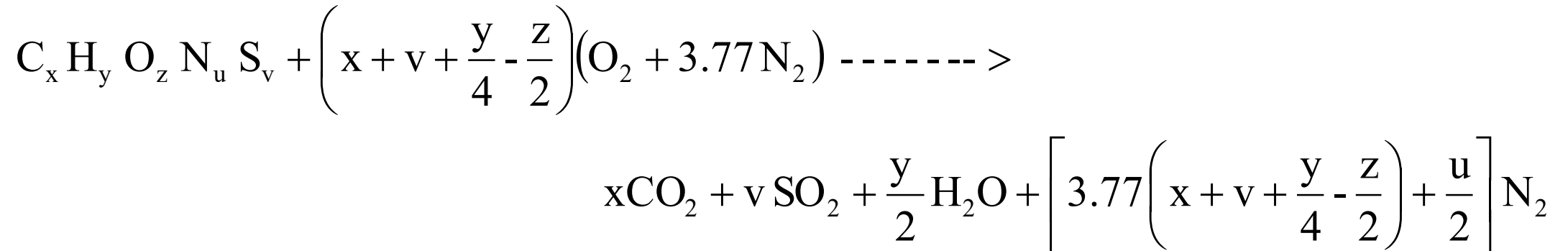
Chemical Composition	State	$(H_f)_{298}$ kcal/mole
H_2O	gas	- 57.6
H_2O	liquid	- 68.32
H_2O_2	gas	- 31.83
HF	gas	- 64.2
HCl	gas	- 22.06
H_2S	gas	- 4.81
SO_2	gas	- 70.96
SO_3	gas	- 94.45
CO	gas	- 26.42
CO_2	gas	- 94.05
CH_4 methane	gas	- 17.86
C_2H_6 ethane	gas	- 20.19
C_3H_8 propane	gas	- 24.75
n-butane	gas	- 29.71
C_4H_{10} iso-butane	gas	- 31.35
C_2H_4 ethylene	gas	- 12.55
C_2H_2 acetylene	gas	- 54.23

$$C_2H_6 + \frac{7}{2}O_2 \text{ -------> } 2\,CO_2 + 3\,H_2O \text{ --------- } (1) \text{ with } H_c(1) = -372.8$$

$$C_{(graphite)} + O_2 \longrightarrow CO_2 \text{ ----------}(2) \text{ with } H_c(2) = -94.05$$

$$H_2 + \frac{1}{2}O_2 \text{ -------> } H_2O \text{ -------------- } (3) \text{ } H_c(3) = -68.32$$

$$2\,C + 3\,H_2 + \frac{7}{2}O_2 \text{ ------- > } 2\,CO_2 + 3\,H_2O \text{ ----------}(4)$$
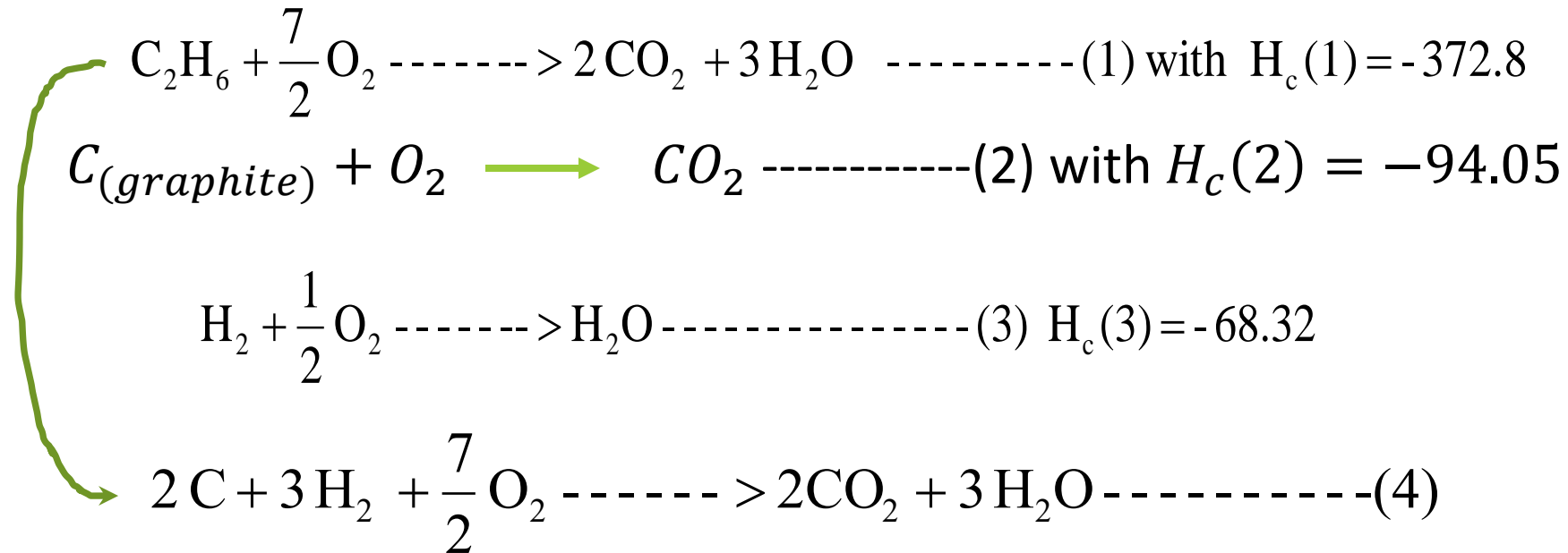
A much better approach is to consider 'Hess Law' where the energy change in the overall chemical reaction is equal to the sum of the energy changes in the individual reactions comprising it.

In other words;

$$\Delta H_{(reaction)} = \sum \Delta H^o_{f\ (product)} - \sum \Delta H^o_{f\ (reactant)}$$

3. Conditions necessary for combustion

Principal conditions necessary for combustion

a) Presence of a combustible and a comburant

b) Temperature at a point of the system which is greater than or equal to the temperature of inflammation.

c) Concentration of chemical elements comprised within Ignitable Limits (Limits of Inflame ability).

These different conditions are;

◦ Inflammation temperature

◦ Auto-inflammation (Flash Point)

◦ Source of Ignition

◦ Point of spark

◦ Spontaneous temperature of inflammation

Ignitable   Limits

Definition

A gaseous mixture cannot ignite, if the proportions of the combustible gas in the combustible - comburant mixture are comprised between the ignitable limits.

 The limit inferior Li correspond a poor mixture and the limit superior Ls is a rich mixture.

Air

Fuel

Ls

Li

Stoichiometry
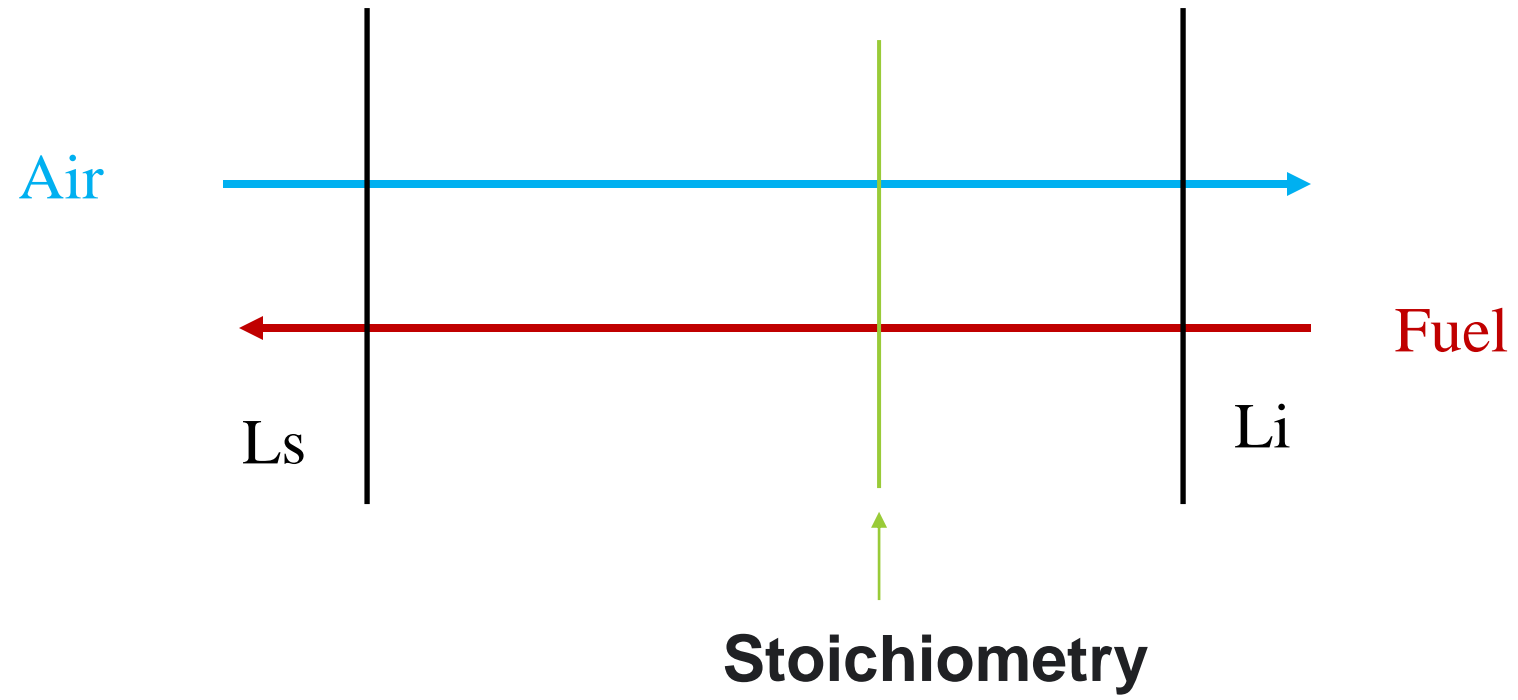
The molecular formula is:

O_2 + 3.77 N_2 = 4.77 moles of air

The notion of ignitable limits is very important for the question of safety

Combustible		Temperature of Auto-Ignition - Flash Point (^{o}C)
Hydrogen	H_2	570
Carbon Monoxide	CO	610
Methane	CH_4	580
Acetylene	C_2H_2	305
Ethylene	C_2H_4	
Ethane	C_2H_6	490
Propane	C_3H_8	480
n-Butane	C_4H_{10}	420
n-Pentane	C_5H_{12}	310
Benzene	C_6H_6	600
Methanol	CH_3OH	
Ethanol	C_2H_5OH	510
Carbon		700
Charcoal		325
Char		360
Coke		700

Factors which influence the ignitable limits:

Energy of inflammation:

Direction and sense of propagation

Dimensions of the container

Initial temperature of the gaseous mixture

Pressure

Inert gas

Humidity

https://youtu.be/fFaOweIbzwc

3.3 Direction and sense of propagation

There are two types of flames
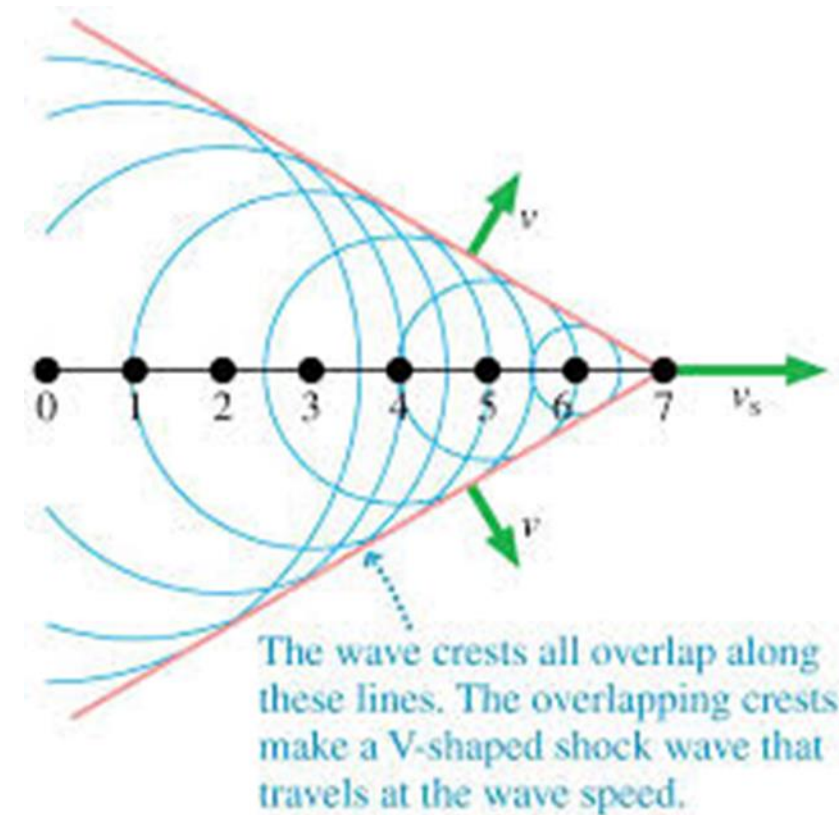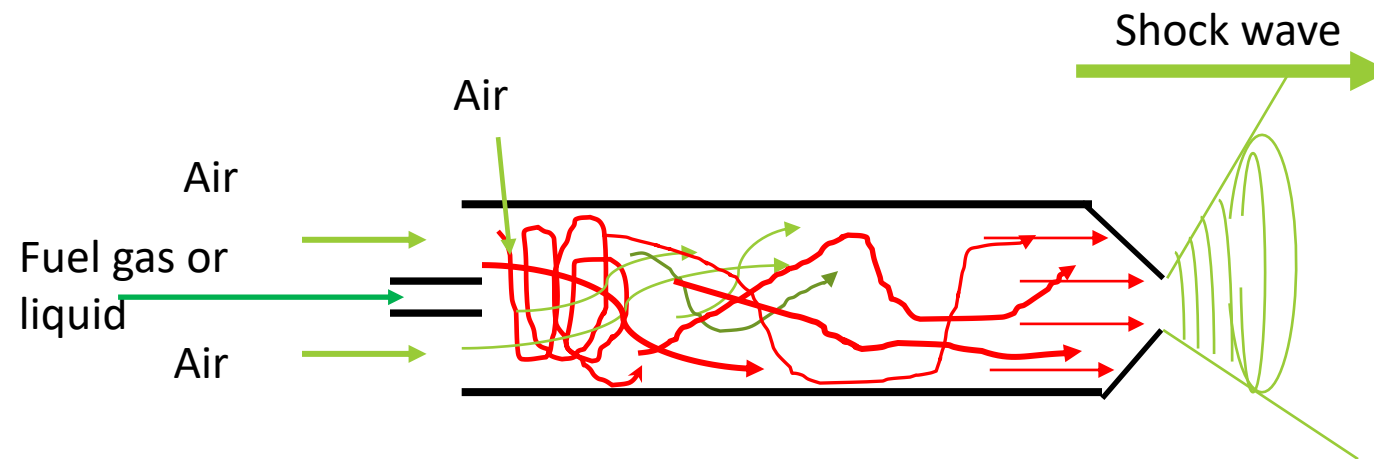
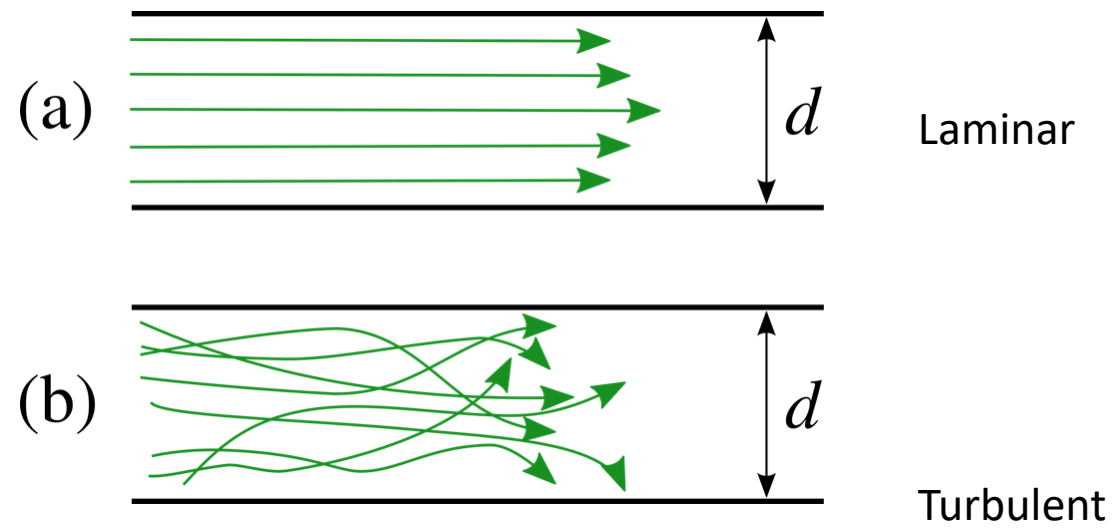A. Premixed or Bunsen type of flame

A. Diffusional flames
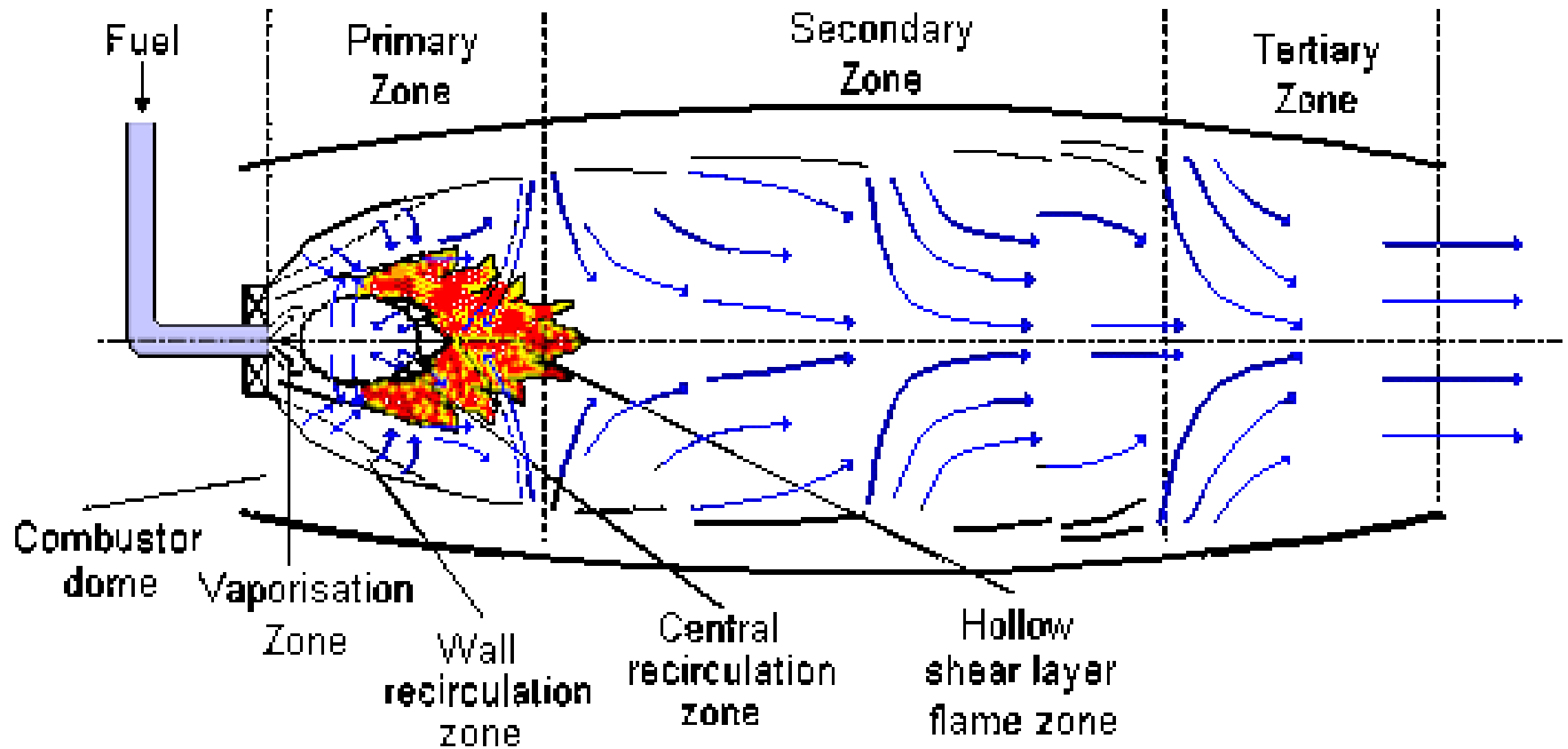
And they can be either;

Laminar or turbulent

flame
nichrome wire
cork

UPPER OXIDIZING ZONE
UPPER REDUCING ZONE
HIGHER-TEMPERATURE ZONE
LOWER OXIDIZING ZONE
LOWER REDUCING ZONE
LOWER-TEMPERATURE ZONE
AIR FLOW
GAS FLOW
gas

air hole open
plenty of air in
gas in from fuel supply

air hole closed
shortage of air in
gas in from fuel supply

This image is not to be copied or re-used.

Flame Temperature Distribution
Bunsen Burner Flame

1540°C
1550°C
1560°C
1540°C
1470°C
1560°C
1520°C
1450°C
350°C
300°C

AXIAL DISTANCE (mm)

RADIAL DISTANCE FROM CENTERLINE (mm)

Level	T(K)
9	2000
8	1800
7	1600
6	1400
5	1200
4	1000
3	800
2	600
1	400

Laminar flame   Turbulent flame

(a) Laminar

(b) d Turbulent

Shock wave

Air

Air

Fuel gas or liquid

Air

The wave crests all overlap along these lines. The overlapping crests make a V-shaped shock wave that travels at the wave speed.

Fuel

Primary Zone

Secondary Zone

Tertiary Zone

Combustor dome

Vaporisation Zone

Wall recirculation zone

Central recirculation zone

Hollow shear layer flame zone

Fuel

Fuel injector

Baffle to shelter & sustain the flame

Dilution air

Air

Flame

Hot gas

Diffuser to slow airflow

Combustion air

Perforated liner

Combustor control volume

4. Industrial combustibles

- Gaseous combustibles burn very easily.

- Liquids should be in the form of fine droplets introduced inside a chamber having a temperature higher than that of ignition so that the contact surface with oxygen will be greater.

- Solid combustion can be considered like liquids where heterogeneous reactions take place and the second phase of oxidation takes place in the gas phase.

- Primary and secondary air are needed for complete combustion
- Secondary combustion is a gas phase reaction

4.1 Composition of industrial combustibles

- Carbon

- Hydrogen

- Sulphur and oxygen

- Inert compounds such as N_2, H_2O and inorganic compounds, oxides as well as pure elements.

4.12 Pure dry combustible

Except water and ash.

4.13 The immediate analysis:

It is the first experimental study, which permits to separate carbon from ash, humidity, and volatile matter.

4.14 The element analysis:

Furnishes the exact composition of the combustible.

It is sometimes a very delicate operation to determine the correct composition.

4.21 Solid Combustibles:

- Anthracite

- Lignite

- Peat

- Wood and other vegetative matter (dry)

Industrial products

Crude oil

Coal

Charcoal

The quantity of ash does not have much influence on efficiency, but it creates problems in combustion chambers, exhaust fans and increases the cost of fly-ash particle separation.

4.22 Combustible liquids

Fuel oil, mazout is derived after producing petrol by distillation of tars of crude oils or bituminous.

4.23 Combustible gases

- Natural hydrocarbons.

- Gases of Gasogens, produced from coke

- Thermal cracking

(decomposition of hydrocarbons having long links chains by heat).

These combustibles are classed according to three categories:

Poor:

The constitute essentially CO, N_2 & CO_2.

They are formed at high temperatures inside furnaces, gas mixed with air, or gas from gasogens.

Rich:

High quantity of CO and H_2, it contains small quantity of hydrocarbons. They are produced by the water shift reaction for example:

Very Rich:

These are essentially formed of hydrocarbons; butane, propane rich etc. and natural gas.

Table 4. Composition of different types of gases by volume.

Combustible Gas	CO	H_2	CO_2	N_2	O_2	CH_4
Gasifiers						
Coal	24	16.5	7.5	50	1	1
Char	27	14	4.5	50.5	1	3
Wood	21	17	12	49	Trac	0.5
High temperature						
Furnace	27.5	3	10	58		0.5
Natural Gas		1		3	1	96

4.3 Solid Combustion Bio-mass (vegetative)

4.31 Different Phases of De-volatilisation

Pyrolysis of wood between 400 °C - 600 °C

Maximum Temperature (T_m)	T_m C <100	T_m C <250	T_m 250>T_m C<600	T_m C>600
Product	Moist	Brown wood	Char, gas, heavy tar, water	Char, gas, light tar, water
Nomenclature	Drying	Torrefaction	Carbonisation	Gasification

4.4 Types of Pyrolysis:

Slow Pyrolysis: At low temperatures (<500 C),

  rate of heating 10 ^{O} C/s.

Flash Pyrolysis: Rate of heating is rapid 10 - 1000 ^{O} C/s Retention times are less than 2s.

Rapid Pyrolysis: The time of retention in the gas phase is less than 0.05s.

  Heating rate is 10^3 to 10^5 ^{O}C/s.

.

4.5 Pyrolysis Products:

- Gases

- Tars

- Chars

- Water

The endothermic reactions of pyrolysis for most wood require 1050 kJ/kg of biomass (without moisture and ash).

Moisture removal from biomass 1100 kcal/kg (4598 kJ/kg) of moisture removed

4.6 Thermo Chemistry of Gasification

4.6 Chemical Reactions

- In a gasifier there are number of chemical reactions to produce CO, H_2 and CO_2.

- The degree of equilibrium of the reactions determines the quality of gas produced.

- Consider that a fixed bed counter-current injection of air and vapour is taking place under the grill of the gasifier.

- After ignition, there will be four distinct zones of reactions in the reactor:

Combustible

Gases

Drying

Pyrolysis

Gasification

Combustion

Throat

Grill

Air
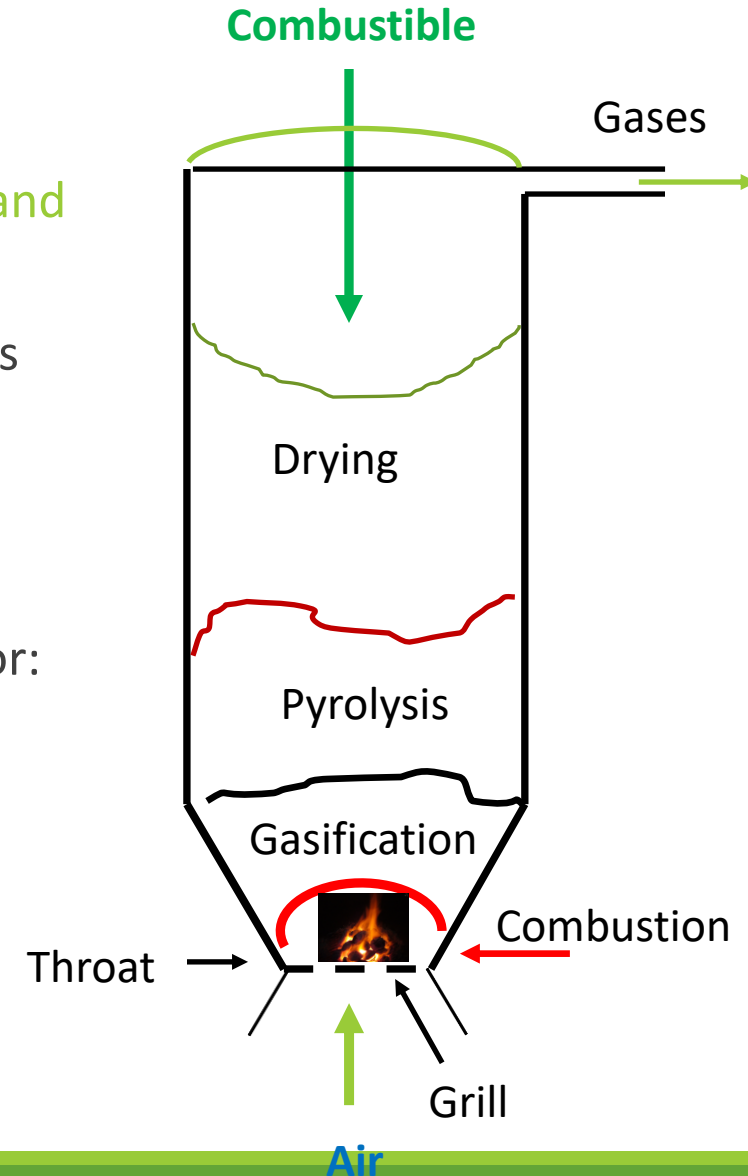
1. just above the grill where the zone of <u>oxidation</u> takes place,

2. and above that <u>gasification</u>,

3. <u>pyrolysis</u> and

4. <u>drying</u>.

Several reactions take place in each of these zones.

They are of two types:

i. Endothermic and

ii. Exothermic.

The endothermic reactions are:

Devolatilization $C + heat \longrightarrow CH_4 + $ Condensable hydrocarbons + char

Water shift reaction: $C + H_2O + heat \longrightarrow CO + H_2$

Catalytic conversion: $C + 2H_2O + heat \longrightarrow CO_2 + 2H_2$

Reverse Boudourad : $C + CO_2 + heat \rightleftharpoons 2CO$

Exothermic reactions are

Oxidation:

$C + O_2 \longrightarrow CO_2 + heat$

Hydrogasification:

$C + 2H_2 \longrightarrow CH_4 + heat$

Conversion reaction:

$H_2O + CO \longrightarrow CO_2 + H_2 + heat$

Methane formation (Catalytic):

$CO + 3H_2 \longrightarrow CH_4 + H_2O + heat$

Exothermic reactions are

Methane formation (Catalytic):

$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O + heat$

Methane formation (Catalytic):

$2CO + 2H_2 \longrightarrow CH_4 + CO_2 + heat$

Vapour Injection:

$H_2O \longrightarrow \frac{1}{2} O_2 + H_2 + heat$

In the zone of oxidation, the carbon reacts with the oxygen of the air to produce CO_2.

This exothermic reaction is essentially to furnish the required energy for gasification, pyrolysis and dehydration.

Therefore, some of the carbon is always used in the combustion process for gasification reactions.

For this reason, the efficiency of gasification, if the sensible heat of producer gas is not accounted for, reduces to 80% of the initial calorific value of the combustible.

In certain conditions of gasification, when water vapor is injected into the air of combustion,

a) a water shift reaction takes place producing CO and H_2.
b) this reaction is endothermic.
c) it consumes a part of the heat produced by the exothermic oxidation reactions.

In the combustion phase,

◦ only inert gases are generally formed such as CO_2, H_2O and N_2,

whereas in the gasification phase the products are

◦ CO, CO_2, H_2, CH_4, C_2H_4, C_3H_6, NH_3, N_2, H_2O, the vapour of tar and organic liquids of low molecular weight.

The producer gas composition depends on the <u>degree of equilibrium attained</u> of the different reactions mentioned above.

Definition: The combustion is an exothermic chemical reaction. We have defined the heat of combustion for a combustible element and the calorific value is a generalization of this notion of heat of combustion.

•The calorific value can be either determined experimentally or calculated directly by using the equation of reactions and the heat of formation or combustion.

Combustion Temperature

Heat of combustion + Enthalpy of Air = Enthalpy *of products + Heat losses*

ΔHc + Enthalphy of Air (M_{air} C_{pair} ΔT_1) = $\sum E^p$ + Heat losses

ΔHc + M_{air} x C_{pair} x $\Delta T_{1 =}$ M_{CO2} $C_{pCO2}\Delta T_2$ + M_{H20} C_{pH20} ΔT_2 + M_{N2} C_{pN2} ΔT_2 + Heat loses

ΔT_2 = Temperature of combustion

Gasification

Beginnings

- Gasification has grown from a simple conversion process used for making "town gas" for industrial lighting to an advanced, multi-product, carbon-based fuel technology of today and tomorrow.

- Gasification was first used commercially in the 1800s for industrial and residential heating and lighting.

- As the use and distribution infrastructures for electricity and natural gas evolved, town gas use declined and gasification development paused.

- However, history has shown that the technology is revisited when access to natural gas, oil and petroleum products are limited through scarcity or high prices.

- Today, gasification technology development is enjoying a renaissance as a means for producing electrical energy, synthetic natural gas, liquid fuels or chemical products from coal, biomass, or other carbon containing materials under increasingly stringent environmental constraints.

Discovery and Earliest Experimentation

In 1609, Jan Baptista Van Helmont, a Belgian chemist and physician, discovered that gas could be produced from heating wood or coal.[1] Following this discovery, several others aided in developing and refining the gasification process:

1669: Thomas Shirley performs various experiments with carbonated hydrogen.

Late 1600s: John Clayton experiments with capturing gas produced from coal.

1788: Robert Gardner becomes the first to obtain a patent dealing with gasification.

1791: John Barber receives the first patent in which "producer gas" was used to drive an internal combustion engine.

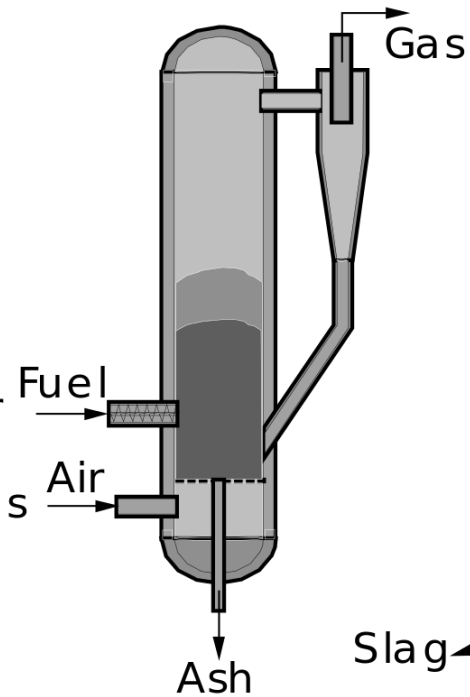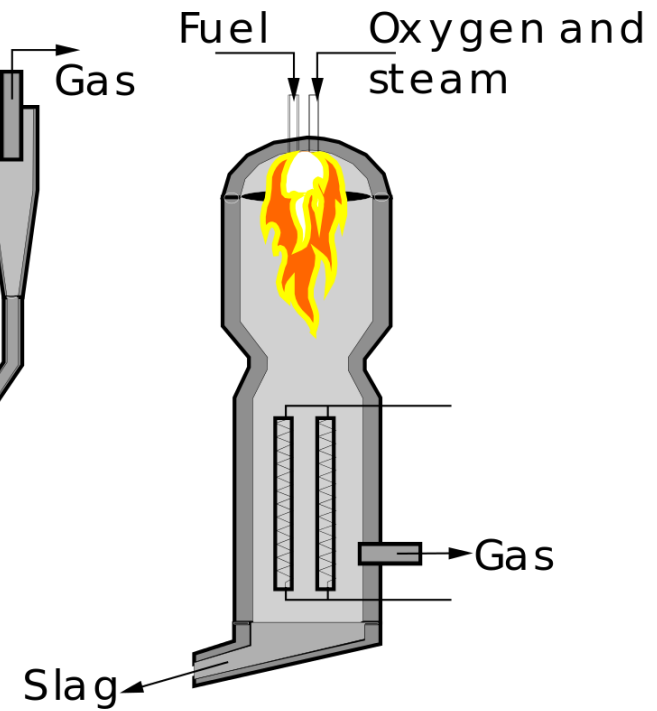1798: Biomass gasification is first conceived when Philippe Lebon led efforts to gasify wood.
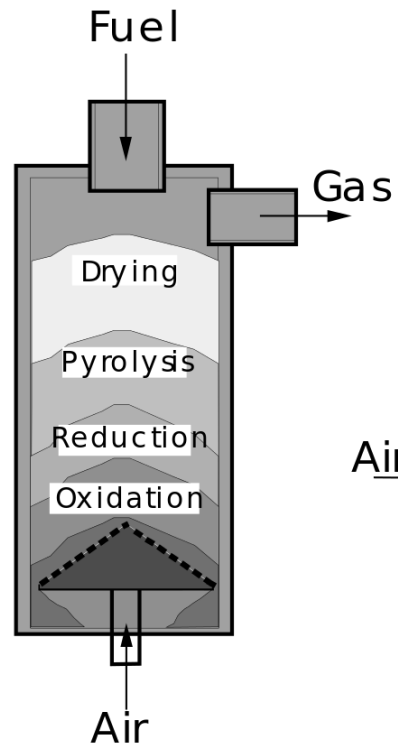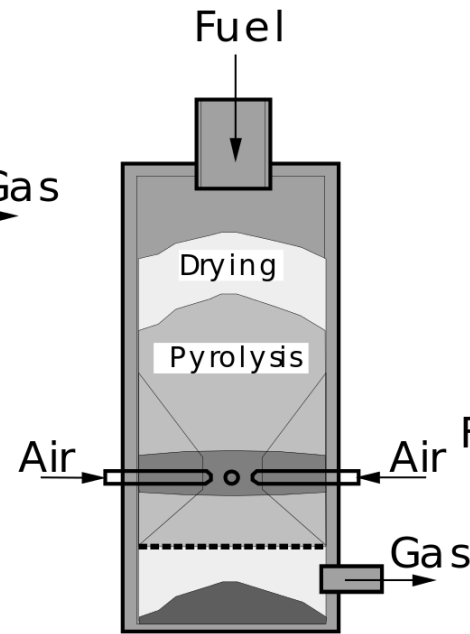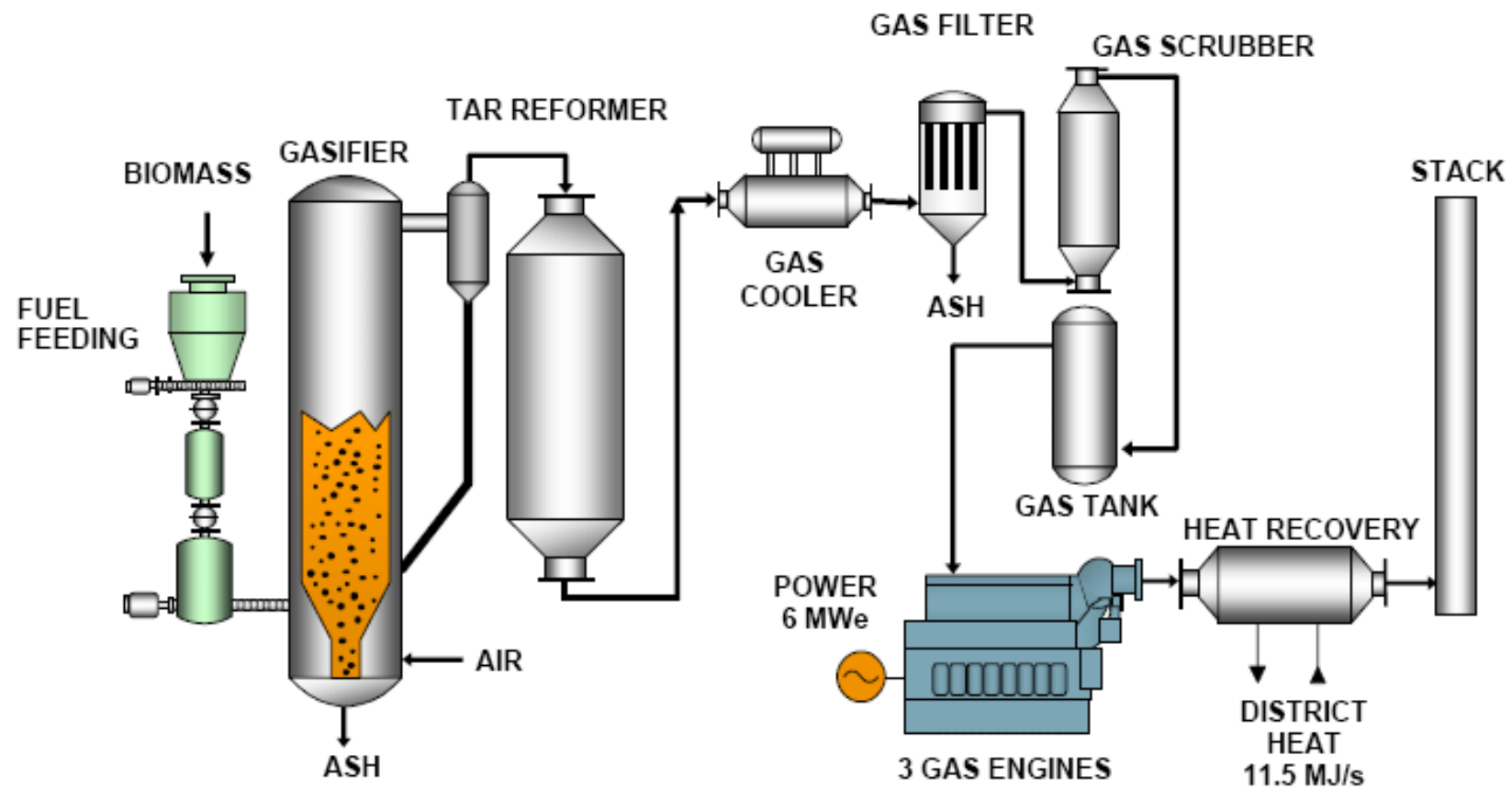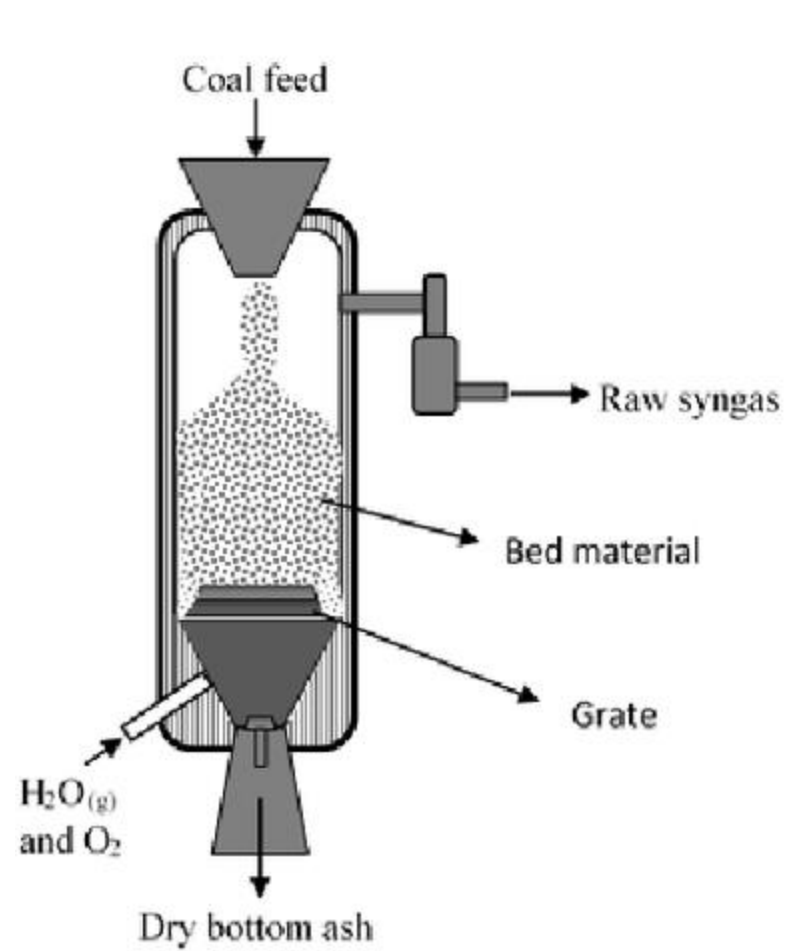
UPDRAFT   DOWNDRAFT   FLUIDIZED BED   ENTRAINED BED

Coal feed

Raw syngas

Bed material

Grate

$H_2O_{(g)}$ and O_2

Dry bottom ash

A. Lurgi Dry Bottom Gasifier

Coal feed

Stirrer

Raw syngas

Gasification zone

Bed material

Tuyere

Combustion zone

Refractory

Slag tap
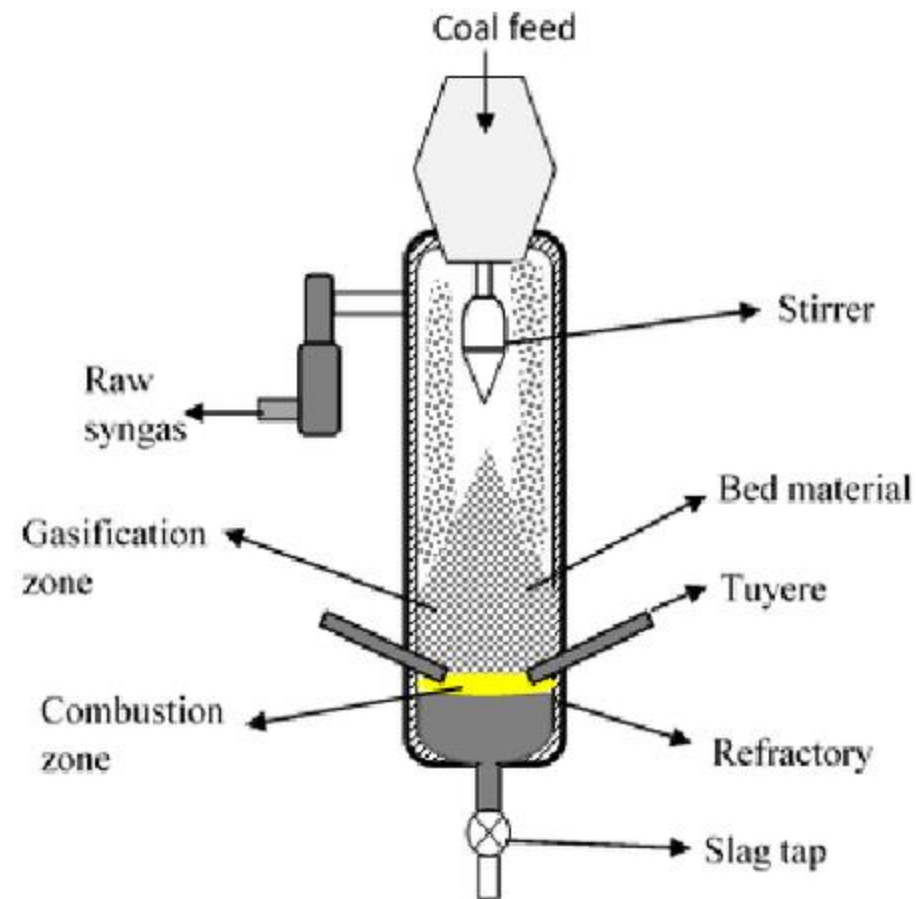
B. British Gas Lurgi Gasifier

Thermo Chemistry of Gasification

Chemical Reactions

In a **gasifier there are number of chemical reactions to produce** CO, H$_2$ and CO$_2$.

The degree of equilibrium of the reactions determines the quality of gas produced.

Consider that a fixed bed counter-current injection of air and vapour is taking place under the grill of the gasifier.

After ignition, there will be four distinct zones of reactions in the reactor:

1. just above the grill where the zone of <u>oxidation</u> takes place,

2. and above that <u>gasification</u>,

3. <u>pyrolysis</u> and

4. <u>drying</u>.

   Several reactions take place in each of these zones.

   They are of two types:
   i. Endothermic and
   ii. Exothermic.

The endothermic reactions are:

Devolatilisation C + heat $\longrightarrow$ CH_4+ Condensable hydrocarbons + char

Water shift reaction: $C + H_2O$ +heat $\longrightarrow$ $CO + H_2$

Catalytic conversion: $C + 2H_2O$ + heat $\longrightarrow$ $CO_2 + 2H_2$

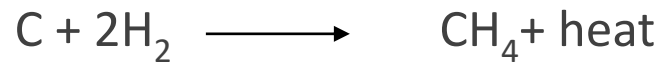Reverse Boudourad : $C + CO_2$ + heat $\rightleftharpoons$ $2CO$

The Boudouard reaction is an important process inside a blast furnace. *The reduction of iron oxides is not achieved by carbon directly, as reactions between solids are typically very slow, but by carbon monoxide. The resulting carbon dioxide undergoes a (reverse) Boudouard reaction upon contact with* coke *(*grey, hard, and porous fuel with a high carbon content and few impurities, made by heating coal or oil in the absence of air—a destructive distillation process) *carbon.*
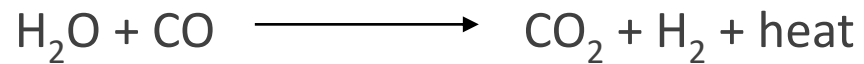
Exothermic reactions are

Oxidation:

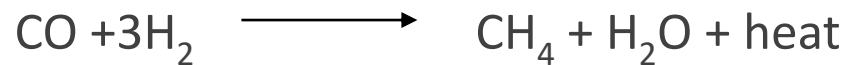$$C + O_2 \longrightarrow CO_2 + heat$$

Hydro-gasification:

$$C + 2H_2 \longrightarrow CH_4 + heat$$

Conversion reaction:

$$H_2O + CO \longrightarrow CO_2 + H_2 + heat$$

Methane formation (Catalytic):

$$CO + 3H_2 \longrightarrow CH_4 + H_2O + heat$$

Exothermic reactions are

Methane formation (Catalytic):

$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O + heat$

Methane formation (Catalytic):

$2CO + 2H_2 \longrightarrow CH_4 + CO_2 + heat$

Vapour Injection:

$H_2O \longrightarrow \frac{1}{2} O_2 + H_2 + heat$

- In the zone of oxidation, the carbon reacts with the oxygen of the air to produce CO_2.

- This exothermic reaction is essentially to furnish the required energy for gasification, pyrolysis and dehydration.

- Therefore, some of the carbon is always used in the combustion process for gasification reactions.

- For this reason, the efficiency of gasification, if the sensible heat of producer gas is not accounted for, reduces to 80% of the initial calorific value of the combustible.

In certain conditions of gasification, when water vapor is injected into the air of combustion,

◦ a water shift reaction takes place producing CO and H_2.

◦ This reaction is endothermic.

◦ It consumes a part of the heat produced by the exothermic oxidation reaction.

In the combustion phase,

◦ only inert gases are generally formed such as

◦ CO_2, H_2O and N_2,

whereas in the gasification phase the products are

◦ CO, CO_2, H_2, CH_4, C_2H_4, C_3H_6, NH_3, N_2, H_2O, the vapour of tar and organic liquids of low molecular weight.

The producer gas composition depends on the <u>degree of equilibrium attained</u> of the different reactions mentioned above.

The Effect of Temperature, Pressure and Retention/Residence Time on Gasification

A. The case of gasification with air

The equilibrium conditions depend on the temperature and pressure.

The temperature of gasification or treatment determines the gas composition at equilibrium.

The pressure influences the manner in which the absolute rates of reactions of mass and heat transfer take place and it modifies the equilibrium conditions in favour of $CH_4 + CO_2$.

- For example, in the equation C + 2H$_2$ $\longrightarrow$ CH$_4$, the quantity of CH$_4$ increases with an increase in pressure (at constant temperature) and reduces with increase in temperature (at constant pressure).

- In other words, at high pressure and low temperatures, formation of CH$_4$ is favored.

- The reciprocal actions on solid/gas and residence time influence the degree of equilibrium.

B. The case of gasification with water vapor

- Most of the studies indicate that higher ratios of air/vapour have very little effect on the end results of gasification.

- Both residence time and temperature have low dependency on formation of CO_2.

- CH_4 increases with an increase in residence time and temperature.

- C_2H_6 is similar to CH_4.

- However, maximum production of C_2H_6 takes place between 650 to 700^OC at a low residence time of 2 s.

- At elevated pressures, the pyrolysis reactions become exothermic and the conversion to char increases by 12% based on weight of cellulose at 1 Bar and 16% at 6 bar pressure.

- When the temperature increases from 800 to $900^O C$, the molecular fraction of CO and H_2 increases, but CO_2 diminishes.

- However, the molecular fraction of CO_2 increases while CO and H_2 diminishes with increase in pressure from 1 bar to 20 bars.

Theoretical Determination of the Optimum Quantity of Air and Water for Gasification

Basic Hypothesis: The principle reactions of gasification are the following:

$C + CO_2 \rightleftharpoons 2CO$ (1)

$C + H_2O \rightleftharpoons CO + H_2$ (2)

$C + 2H_2 \rightleftharpoons CH_4$ (3)

$CO + H_2O \rightleftharpoons CO_2 + H_2$ (4) (Through 1&2)