

## Energy Conversion Technologies (Biomass and Coal)

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### Lecture 28

#### Practice Example (Combustion of Biomass & Coal)

Good morning everyone.

Welcome to the second lecture of module 7. If you recollect our discussion in the previous lecture, we discussed about two different coal conversion processes that is carbonization and gasification. However, in this lecture which is a continuation of same topic that is energy from coal we will discuss other two coal conversion processes that are liquefaction and combustion process. So, let us first begin with the coal liquefaction.

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#### ③ Coal Liquefaction

- *Coal liquefaction is a process used to convert coal, a solid fuel, into a substitute for liquid fuels such as diesel and gasoline. (Speight, 2013)*
- Coal liquefaction process was extensively used in many countries during World War II due to the unsecure supply of petroleum.
- Successful research on coal liquefaction by direct hydrogenation began in the early 20<sup>th</sup> century.
- If the crude oil supplies are completely disrupted, Coal liquefaction may be used in future for the production of oil for transportation and heating.

Coal liquefaction is a process used to convert solid fuel. So, solid fuel here is referred as a coal into substitute for liquid fuel such as diesel and gasoline. And, this coal liquefaction process was extensively used during World War II due to unsecure supply of petroleum and the successful research on coal liquefaction by hydrogenation began in the early 20th century.

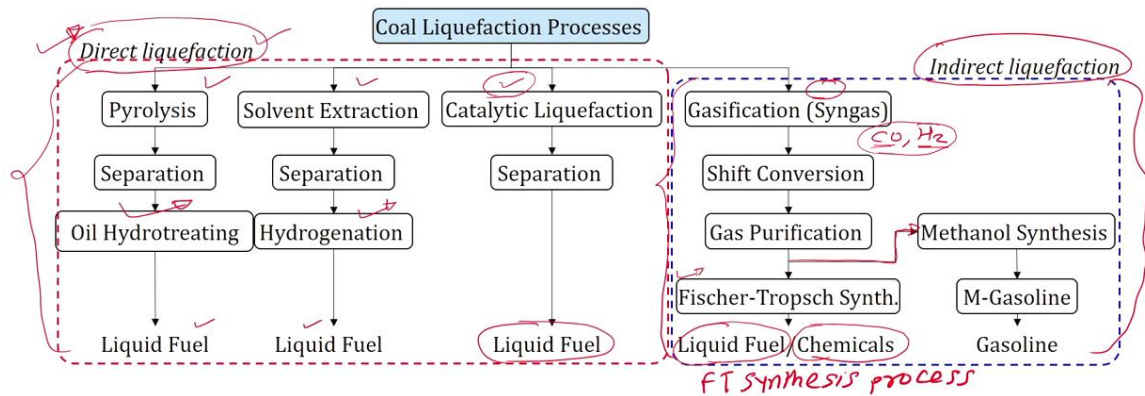
If the crude oil supplies are completely disrupted then the coal liquefaction may be used in future for the production of the oil for transportation and the heating application. And that is the importance of the coal liquefaction process, because in case the supply of the crude oil completely disrupted in future then the coal liquefaction process may be used to produce oil. And produced oil after using certain upgradation technique and refining can be used as a fuel for transportation or can be used as a fuel for the heating purpose.

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### Coal Liquefaction Processes

The coal liquefaction processes can be classified as:

- Direct Coal Liquefaction (DCL): (i) pyrolysis, (ii) solvent extraction, (iii) catalytic liquefaction
- Indirect Coal Liquefaction (ICL): (i) Liquefaction through Gasification



These coal liquefaction processes are classified as direct coal liquefaction and indirect coal liquefaction. This direct coal liquefaction process is further sub classified as pyrolysis, solvent extraction and catalytic liquefaction process. And this direct coal liquefaction refers to the direct thermochemical conversion or you can say the hydrogenation of coal at relatively high temperature and pressure to produce liquid fuel as a product. Similarly, the catalytic liquefaction of coal produces liquid fuel as a product.

So, all these processes are direct liquefaction process here and these processes are carried out at relatively high temperature and pressure. However, this indirect coal liquefaction process, it begins with the gasifying coal. So, in this case the coal first needs to be gasified with oxygen or steam and then converting these produce gases that are carbon monoxide and hydrogen after purification to liquid. So, liquid produce here are liquid fails and the

petrochemical by the Fischer-Tropsch synthesis process. However, the produce gases after purification can directly be converted into a methanol using methanol synthesis process.

And because of that this particular process is termed as indirect coal liquefaction process. Because in this case the coal is first gasified with the oxidizing agent or you can say the oxidizer that is oxygen and steam to produce a gaseous product that is carbon monoxide and hydrogen. And these produced gases after purification converts into a liquid fuel and there It carried out using the Fischer-Tropsch synthesis process. Also it produces the petrochemicals and the process also used is the same that is the Fischer-Tropsch synthesis process. And that is why it is termed as indirect coal liquefaction process.

However in these processes the coal is directly converted into a liquid fuel using a thermochemical conversion. And that is why these processes are termed as direct coal liquefaction process. And if you recollect we discuss in detail about FT synthesis process that is conversion of gases to liquid or petrochemicals in one of the lecture in module 4 as a reason we are not discussing this part again in this module. Rather we will be discussing in detail about the direct co-liquefaction processes. So, let us first begin with the pyrolysis process.

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#### i. Pyrolysis

- Pyrolysis processes involves heating coal to temperatures 300–815 °C and pressure 0–7 MPa, which results in the conversion of the coal to gases, liquids, and char.
- The char is hydrogen deficient, thereby enabling inter- or intramolecular hydrogen transfer processes to be operative, resulting in relatively hydrogen-rich gases and liquids.
- The liquid product (oil) yield is limited in the range 5–35%, as the char produced often amounts to more than 45% of the feed coal.
- Therefore, such processes have often been considered to be uneconomical or inefficient use of the carbon in the coal.

Commercial coal pyrolysis processes: Lurgi–Ruhrgas Process, Char-oil Energy Development Process, Occidental Flash Pyrolysis Process, Toscoal Process, Clean Coke Process, Coalcon Process.

So this pyrolysis process it involves heating coal. So as the solid fuel we are referring here as a coal. So, it involves heating this coal to a temperature around as mentioned here 300 to 800 degree Celsius approximately and the pressure used is around 0 to 7 mega Pascal. Sometime the process is carried out at atmospheric pressure as well as sometime it is carried out at relatively high pressure and it results in the conversion of coal to gas liquid and char as a product. So, during this process the produced char is hydrogen deficient that means the char is mostly consists of the more carbon rather than the hydrogen and that is why it is termed as hydrogen deficient.

However, this process results into a higher hydrogen rich gas and the liquid as a product. And that is mainly because of the enabling of inter or intramolecular transfer of hydrogen during the process. And mainly in this process if you look at this particular numbers here, so the liquid product that is oil yield it is limited here in the range of 5 to 35%, and in terms of char it produce more amount of char that is close to around 45 percent that of the feed coal. And therefore such processes are often considered uneconomical or you can say inefficient use of carbon in the coal during this process. And there are number of commercial coal pyrolysis processes which are available and the list of such processes is shown here. So, now let us move on to the next process that is solvent extraction process.

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#### ii. Solvent extraction process

- Solvent extraction processes are those processes in which coal is mixed with a solvent (H-donor solvent, i.e. tetralin) that is capable of providing atomic or molecular hydrogen to the system at temperatures up to 500 °C and pressures up to 35 MPa.
  - More severe conditions are more effective for sulfur and nitrogen removal, as well as to produce a lower-boiling liquid product that is more suitable to downstream processing.
  - Recently, the tar sand bitumen and/or heavy oil are being used as process solvents in this process.
- Commercial solvent extraction processes: Consol Synthetic Fuel Process, Costeam Process, Extractive Coking Process, Extraction By Supercritical Fluids, Exxon Donor Solvent Process, Pott-broche Process, The Solvent Refined Coal Process, Uop Process.

So, in coal extraction process the coal is mixed with solvent and the solvent used here is hydrogen donor solvent example is tetralin. And as we can see here, this particular solvent which is used in the solvent extraction process is providing the atomic and the molecular hydrogen to the system and roughly at a temperature up to 500 °C and pressure up to 35 mega Pascal. And if more severe condition than mentioned above are used, then it is more effective for the removal of sulfur and nitrogen from the fuel, as well as to produce a low boiling liquid product that is more suitable to the downstream processing. Since the low boiling products are getting produced at severe conditions that is mostly a liquid product.

So, handling or the operations of such low boiling product would be more suitable while carrying out the downstream processing of such intermediate products. And recently the tar sand bitumen or the heavy oils are being used as solvents in this process and also the commercial solvent extraction processes which are available for the extraction of such a liquid product are listed here. So, the next is catalytic liquefaction process.

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### iii. Catalytic liquefaction

- In this process a suitable catalyst is used to add hydrogen to the coal in a liquid medium with the catalyst dispersed throughout or in a fixed-bed reactor at 350 – 550 °C temperature and 5 – 30 MPa pressure.
- Otherwise, the catalyst is mixed with coal and the combined coal-catalyst system is injected into reactor.

Advantage: It eliminates the need for a hydrogen donor solvent, however, there is still the need for an external supply of hydrogen.

#### Limitations:

The catalyst gets deactivated by the mineral matter in the coal as well as by coke lay-down during the process.

Moreover, the process efficiency is limited as the direct hydrogenation of the coal needs intimate contact of the catalyst and the coal, which depends on the coal particle size.

So, in this process a suitable catalyst is used to add hydrogen to the coal in liquid medium with catalyst being dispersed throughout or sometimes in a fixed bed reactor at a temperature range of 350 to 550 °C and pressure around 5 to 30 mega Pascal. Or in some cases the

catalyst is mixed with the coal and this combined coal catalyst mixture is injected into the reactor.

And the advantage associated with this coal liquefaction process is- it eliminates the need of hydrogen donor solvent during this catalytic liquefaction process. However, there is a still need of the hydrogen and that need to be supplied externally during this process. And the limitations which are associated with this process include the catalyst deactivation because of the presence of the mineral matter in the coal as well as formation of the coke during this process. And these two factors may result into the deactivation of the catalyst. And in this case even the process efficiency is limited, as the direct hydrogenation of the coal needs intimate contact of the catalyst and the coal particle and it depends on the coal particle size.

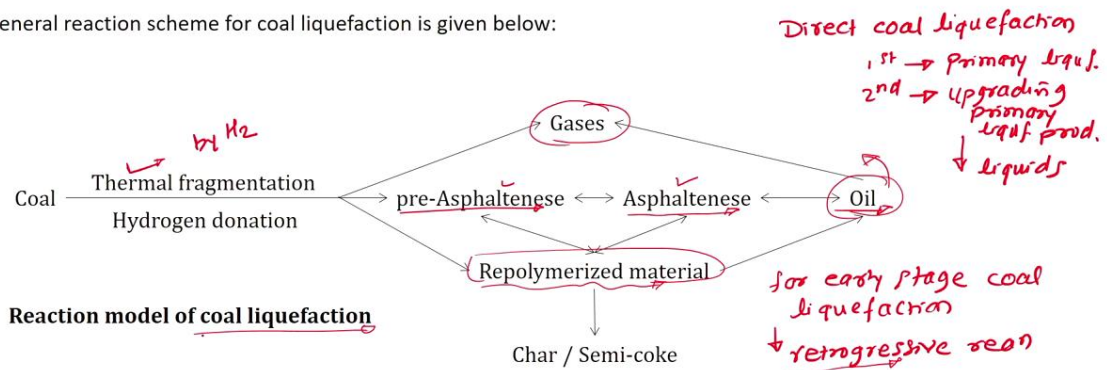
For example, here if the coal particle size is not in the appropriate range, then it may not be able to diffuse into the catalyst pores and as a result it decreases the process efficiency. Therefore, the appropriate coal particle size needs to be used during this catalytic liquefaction process to improve the process efficiency. So, this is all about the direct coal liquefaction process. So, now let us discuss about the physicochemical aspects of the direct coal liquefaction process.

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#### Physicochemical Aspects of Direct Coal Liquefaction

- The reaction mechanism involving conversion of coal to oil is very complex and hypothetical.
- The variable chemical and physical properties of coal make it difficult to understand the true fundamental processes that take place in a DCL process.

A general reaction scheme for coal liquefaction is given below:



The reaction mechanism involved in the direct coal liquefaction process that is the conversion of coal to oil is very complex and hypothetical, and the variable chemical and the physical properties of the coal. So, if you recollect again our discussion in one of the lecture in this module we discuss about the varying properties of the coal between the even types of the coal as well as sometimes between the samples of the same types of the coal also gives varying chemical and the physical properties. And it makes difficult to understand the true fundamental process that takes place during the direct co-liquefaction process. However, a general reaction scheme for the co-liquefaction is given here. And this direct co-liquefaction, it proceeds through two loosely defined stages that is first stage is primary liquefaction and the second stage is upgrading primary liquefied product and that produces liquids like synthetic crude oils.

And this primary liquefaction here it involves the thermal fragmentation of coal macromolecular structure to produce free radicals which are kept by hydrogen. And this hydrogen donation may be by the hydroaromatic solvents or you can say other donating species in the coal or by gas phase hydrogen. And this primary liquefaction steps produces the pre-asphaltenes as well as the asphaltenes and oil along with C1 to C4 hydrocarbon and inorganic gases such as ammonia and the hydrogen sulphide. The pre-asphaltene which is formed here along with the asphaltene is often called as a liquefied product. Because these two products are coal fragments soluble in the certain solvent, but they are in fact solid at the ambient temperatures.

And this incorporation of this re-polymerized insoluble organic material in the reaction scheme is conceptually very important especially for early stage coal liquefaction process. Because, retro aggressive reactions can occur to a significant extent and this occurrence of this retro aggressive reaction have negative impact on the oil yield that is we can term it as a liquid yield here. And that is mainly referred to the reaction in which this liquid fuel molecules break down into the gaseous product.



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- The main desired reactions or steps involved in the production of liquid fuel via coal liquefaction are:

- 1) Coal dissolution (disintegration or dispersion of coal macromolecules),
- 2) Reduction of molecular size to allow access to catalyst pores,
- 3) Removal of hetero-atoms such as N, O and S,
- 4) Hydrogenation of aromatic rings and ring opening of saturated rings,
- 5) Reduction of molecular size to 5–20 carbon atoms and
- 6) Increase in the atomic H/C ratio to about 2 : 1.

- On the other hand, undesired side reactions comprise:

- 1) Retrogressive reactions,
- 2) Condensation of polar materials on catalyst surfaces (deactivation),
- 3) Removal of side chains from aromatic and saturated rings (gas formation), and
- 4) Dehydrogenation of aromatics (decrease of solvent quality and loss of hydrogen).

And in summary, the main fundamental steps that are necessary to transform this coal to gasoline or distillates via direct liquefaction are coal dissolution in which the disintegration or the dispersion of the coal macromolecules will take place, followed by the reduction of this molecular size to allow access to catalyst pores. And if you recollect our discussion just one slide back, there we mentioned that the catalytic liquefaction process is relatively inefficient and that is mainly because of the poor contact of the catalyst pores with the coal particles.

And if this reduction of the molecular size to allow to have access to the catalyst pores then eventually it results into increase in the process efficiency followed by the removal of the hetero atoms such as nitrogen, oxygen and sulphur from the coal, and then the hydrogenation of the aromatic rings and the ring opening of the saturated rings. And next to that is the reduction of the molecular size to 5 to 20 carbon atoms. And then it increases in the atomic H by C ratio to about 2 is to 1. And these are the main desired reaction or we can say the steps which are involved in the production of the liquid fuel via coal liquefaction. However, there are undesired side reactions which comprises of retrogressive reaction as we have mentioned here because it results into decrease in the oil or you can say the liquid yield and the condensation of the polar materials on the catalyst surface and due to deposition of this polar materials on the catalyst surface the catalyst deactivation occurs.

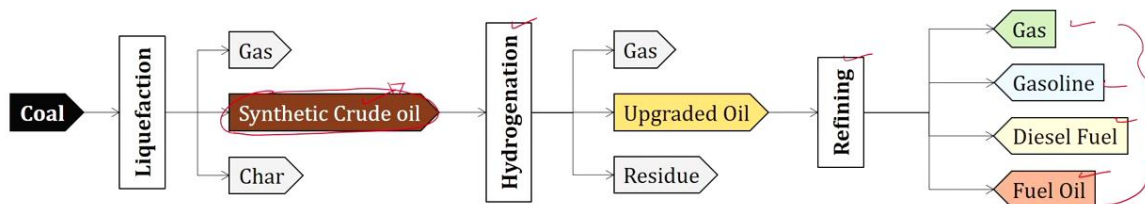


As a result it decreases the process efficiency as well and the removal of the side chain from aromatic and the saturated rings. Because mostly the gas formation and then the dehydrogenation of the aromatics that decrease of solvent quality as well as the loss of hydrogen during this process. And the successful completion of these steps during the coal liquefaction process results into the formation of the liquid product.

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#### Coal Liquefaction Products

- Direct liquefaction produce a synthetic crude oil, known as *syncrude*.
- Syncrudes from coal liquefaction are generally different from those produced by petroleum refining, as they may contain substantial amounts of phenols.
- Therefore, coal liquids need further upgrading and refining to match specification of petroleum fuel products.
- Syncrude can be further upgraded and refined into various petroleum grade products such as: fuel gas, gasoline, diesel fuel, fuel oil, etc.



The direct liquefaction process, it produces a liquid product that is a synthetic crude oil known as syn-crude. So, this is a product which is obtained during the direct liquefaction process. And this syncrude obtained from the coal liquefaction are generally different from those produced by petroleum refinery, as they may contain substantial amount of the phenols in its composition. And therefore, this coal liquid it needs further upgrading and the refining to match specification of petroleum fuel products. This syncrude produced after the coal liquefaction process can be further upgraded and refined into various petroleum grade products such as fuel gas, gasoline, diesel fuel and fuel oil. So, this is all about the coal liquefaction process. So, let us move on to the next topic that is combustion process.

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### Combustion process (biomass/coal)

**Combustion** refers to the rapid oxidation of fuel accompanied by the production of significant amount of heat. Complete combustion of a fuel is possible only in the presence of an adequate supply of oxygen.

e.g. 1 mole of Carbon is oxidized in excess air to produce 1 mole of CO<sub>2</sub> and 393.52 kJ of heat energy.



(coal)

- The principles of combustion chemistry are significantly different when applied to solid fuels, as compared to the liquid and gaseous fuels.
- When a solid fuel particle is exposed to a hot flowing gas stream, it undergoes three stages/zones of mass loss –

✓ → Drying,

✓ → Devolatilization (solid particle pyrolysis), and

✓ → Char oxidation/combustion.

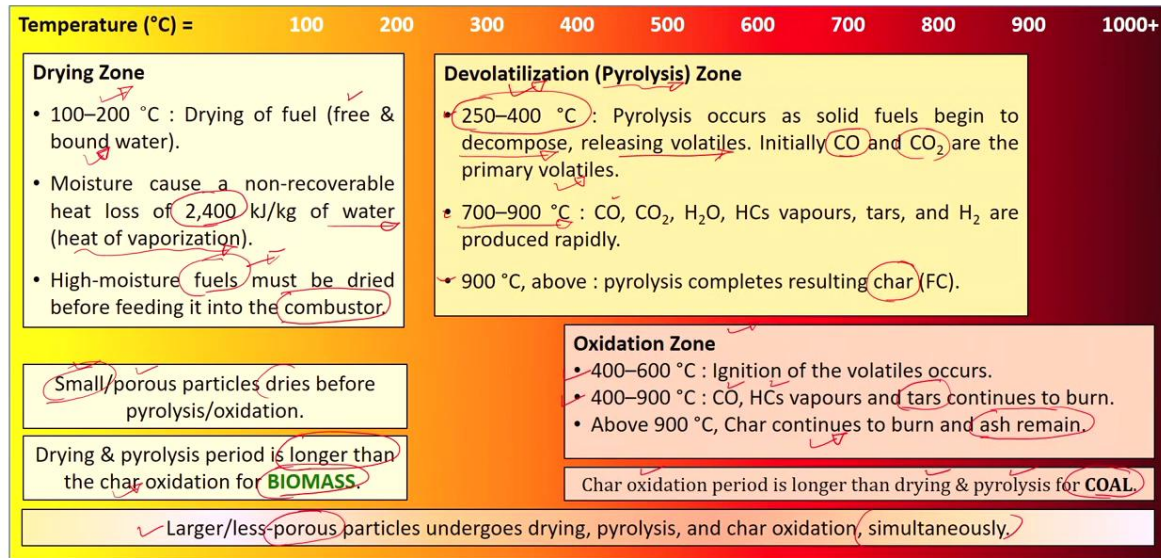
Therefore, the proximate composition of the fuel significantly affect these three steps.

Combustion here it refers to the rapid oxidation of the fuel that is solid fuel accompanied by the production of significant amount of the heat. And this complete combustion of the fuel is possible only in the presence of adequate supply of air or oxygen. For example, here in this case if you take a look at this particular equation here which indicates that this one mole of carbon is oxidized in excess air to produce 1 mole of CO<sub>2</sub> and this much amount of the heat energy and that is per mole of carbon. And these principles of the combustion chemistry are significantly different when applied to fuel that is here we are referring as a coal as compared to the liquid and the gaseous fuels. And when a solid fuel particle is exposed to hot flowing gas streams, it undergoes three different stages or zones of mass loss that is drying that is the first stage followed by the devolatilization.

Normally it is termed as solid particle pyrolysis and the third stage is char oxidation and we refer it as a combustion process. And therefore the proximate composition of the fuel significantly affects these three steps during the combustion process.

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## Zones of combustion



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So, the first is the drying zone or we can say the drying stage in which the drying of fuel takes place in the temperature range of 100-200 °C. And during this stage free and the bound moisture or you can say the water release from the fuel. And this moisture it causes a non-recoverable heat loss of 2400 kJ/kg of water, and that is heat of vaporization of water.

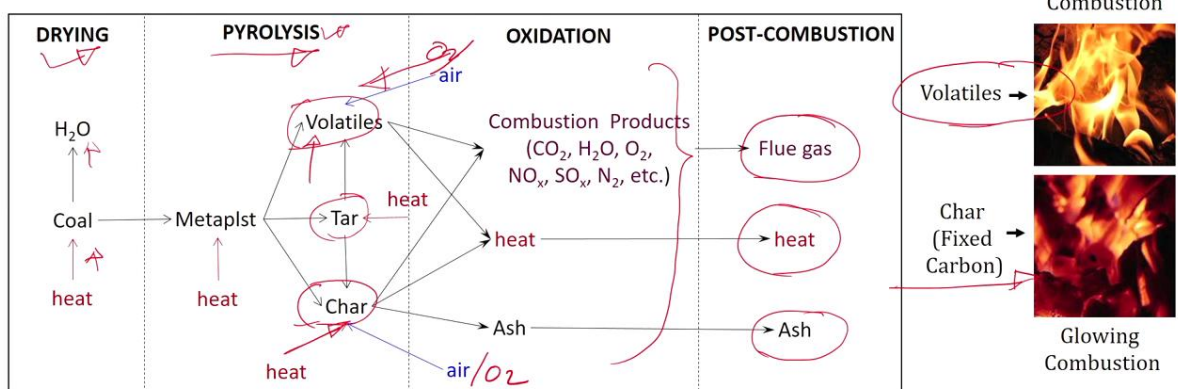
And hence the high moisture fuels must be dried before feeding into the combustor or in the other word I would mention that the high moisture fuels need to be avoided for the combustion process. And the next zone is the devolatilization zone that is also termed as a pyrolysis zone which is represented here according to three different temperature ranges. So, at first the pyrolysis occurs in the temperature range of 250 to 400 °C as the solid fuels begin to decompose releasing the volatiles. And during this initial stage carbon monoxide and carbon dioxide are the primary volatiles released during this early pyrolysis stage followed by rapid production of carbon monoxide, carbon dioxide, hydrocarbon vapors, tar and hydrogen in the temperature range of 700 to 900 degree Celsius. And above 900 °C the pyrolysis completes resulting into a char as a product.

And followed by that is the oxidation zone, in which the ignition of the early volatiles occurs in the temperature range of 400 to 600 °C, followed by the burning of carbon monoxide, hydrocarbons and tar in the temperature range of 400 to 900 °C. And above this 900 degree

Celsius the char continues to burn and only ash remains at the end of the oxidation zone. So, in this case the small and the porous particles these dries before pyrolysis and the oxidation and this drying and the pyrolysis period is longer than the char oxidation for biomass as a solid fuel. However, in case of coal the char oxidation period is longer than the drying and the pyrolysis of the coal sample. And if the larger and the less porous particles undergoes drying, pyrolysis, and the char oxidation simultaneously and for that reason small and the porous particles are used during this process.

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#### Combustion models (Reaction Pathways)



- The volatiles produced by solid fuel particle pyrolysis include both noncondensable gases and condensables.
- Condensables includes both lighter and heavy molecules such as naphthalene, anthracene, fluorine, and other PAHs.
- Tars produced by pyrolysis are very large molecules. Secondary reactions of tar increase the volatile & char yields.
- Volatiles undergoes flaming combustion, whereas char (containing fixed carbon) shows glowing combustion.

So, now let us try to understand this combustion model and its reaction pathways. So, this schematic here it represents the overall schematic of solid fuel combustion. Here the first stage is drying stage. During this drying process moisture in the feed that is free or the bound moisture released by the application of heat to the sample. And the next stage is a pyrolysis stage in which the pyrolysis of the solid fuel particle produces the volatiles including both non-condensable and the condensable gases.

The condensable includes both lighter and the heavy molecules such as naphthalene, anthracene, fluorine and other gases. And the tar produced by pyrolysis are very large molecules and thus the secondary reaction of tar, it increases the volatiles as well as the char yield during the secondary cracking reaction. And these produced volatiles undergo flame

combustion as shown here in the schematic with adequate supply of oxygen or air. While this char containing a fixed carbon shows glowing combustion as shown here in the schematic with application of heat and adequate supply of air or oxygen. And this post oxidation or we can say the combustion process it releases flue gas along with significant amount of the heat as a product and the solid remains as ash.

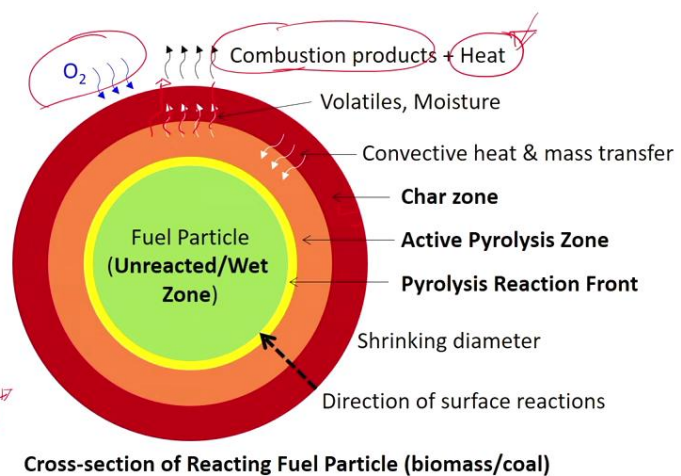
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Pyrolysis involves both chemical and physical changes. The physical changes include the particle shrinkage. In coal and biomass, pyrolysis becomes heat transfer limited at  $\sim 500^\circ\text{C}$ .

The volatiles are combustible and they consume any oxygen being transported toward the surface of the fuel particle.

The char oxidation does not proceed until volatile evolution is essentially complete.

Char oxidation process is influenced by the fuel particle diameter; temperature; and oxygen availability.



So, now after understanding about these reaction pathways, let us try to understand this combustion model taking a single fuel particle into consideration. So, once this portion of the solid fuel particle reaches the reaction temperature then the fuel undergoes pyrolysis to form volatiles and char as a product. So, it forms these volatiles which are shown here and the char as a product and the specific location where the thermal degradation reaction occurs is called as an active pyrolysis zone here. And a very sharp and distinct interface between this unreacted zone and the pyrolysis zone, it moves as a function of the temperature gradient and is termed as pyrolysis reaction front. So, this particular portion in the schematic represent as pyrolysis reaction front.

The initial reaction of the coal to metaplast can be considered as pyrolysis initiation if you look at this particular slide here. So, this initial reaction of coal to metaplast it can be considered as a pyrolysis initiation. And the degradation of the metaplast can be considered



as a subsequent pyrolysis reaction. That is this metaplast it degrades to form volatile tar and the char as a product and this can be considered as a subsequent pyrolysis reaction. And the pyrolysis it involves both chemical and the physical changes and the physical change includes the particle shrinkage.

In coal and biomass the pyrolysis becomes heat transfer limited at around 500 °C. And the volatiles released during this process they consume oxygen being transported towards the surface of the particle and form the combustion product along with the heat. And this char oxidation it does not proceed until the volatiles evaporation completes. And the char oxidation process is influenced by the fuel particle diameter, temperature and the oxygen availability. And in this case the availability of the oxygen is important step here because of insufficient supply of the oxygen it may results into the incomplete combustion and will release only carbon monoxide as a product along with the relatively less amount of the heat than that of the completely combusted product and that is termed as a combustion chemistry. So, let us discuss about this combustion chemistry in more detail.

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#### Combustion Stoichiometry

- Oxygen of air reacts with the combustible substances (fuel) resulting in the formation of combustion gases (e.g.  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{O}$ , etc) along with release of heat.
- Pure oxygen gas or air can be used as oxidizers for fuel combustion. Air is assumed to contain 21% Oxygen ( $\text{O}_2$ ) and 79% Nitrogen ( $\text{N}_2$ ), with traces of other gases.
- $\text{N}_2$  reduces combustion efficiency by absorbing heat from the combustion of fuels and diluting the flue gases.
- $\text{N}_2$  increases the volume of combustion by-products which then have to travel through the heat exchanger and up the stack faster to allow the introduction of additional fuel air mixture.
- $\text{N}_2$  also can combine with  $\text{O}_2$  (at high flame temperatures) to produce the toxic pollutants-  $\text{NO}_x$  consisting nitric oxide (NO) and nitrogen dioxide ( $\text{NO}_2$ ) via various mechanisms (endothermic reactions).

During this combustion process the oxygen of the air it reacts with the combustible substances that is fuel. So, here we are referring it as a coal and results into the formation of combustion gases that is  $\text{CO}_2$ , carbon monoxide, sulphur dioxide and  $\text{H}_2\text{O}$ . And here we are

referring to sulphur dioxide because as we know the coal sample contains certain amount of the sulphur in its composition. So, as a result the sulphur dioxide will be present in the combustion product gaseous stream. And along with that it releases significant amount of the heat.

However, in some cases the pure oxygen gas is also used as an oxidizer for the combustion of a fuel or normally the air being used as an oxidizer for the fuel combustion. Air is assumed to contain 21 percent of the oxygen and 79 percent of nitrogen with traces of the other gases. And the presence of this nitrogen in the oxidizer, it reduces the combustion efficiency by absorbing the heat produced during the combustion of a fuel and also results in diluting the flue gases. Since this nitrogen does not take part into the combustion process. So, it leaves as it is along with the product gases that are flue gases without getting reacted and hence it increases the volume of combustion byproducts.

Moreover, this nitrogen also can combine with the oxygen that is at relatively higher temperature that is a flame temperature to produce a toxic pollutant in the form of  $\text{NO}_x$  which is consisting of nitric oxide and nitrogen dioxide via various mechanisms that is endothermic reactions.

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- C,  $\text{H}_2$  and S in the fuel combine with oxygen in the air to form  $\text{CO}_2$ , water vapour and  $\text{SO}_2$ .
  - $\text{C} + \text{O}_2 \rightarrow \text{CO}_2 + 393.5 \text{ kJ/mol of product}$  (1)
  - $\text{C} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO} + 110.5 \text{ kJ/mol}$  (2)
  - $\text{S} + \text{O}_2 \rightarrow \text{SO}_2 + 296.1 \text{ kJ/mol}$  (3)
  - $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} + 285.8 \text{ kJ/mol}$  (4)
- Each mole of CO formed means a loss of 283 kJ of heat. This heat can be recovered if CO is completely combusted further.
  - $\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 + 283 \text{ kJ/mol}$  (5)

$$\begin{array}{r}
 283 \\
 + 110.5 \\
 \hline
 393.5 \text{ kJ/mol}
 \end{array}$$
- The combustion of solid fuels (coal and biomass) is more complex than the combustion of liquids and gases due to the complex chemical composition of solids.
  - $\text{C}_a\text{H}_b\text{O}_c + \text{O}_2$



And if you recollect our discussion in one of the module, we discussed about the combustion of the solid fuels. And there we learnt that the elements such as carbon, hydrogen and sulphur in solid fuel only take part into the combustion or you can say the oxidation reaction. And the other element does not take part into the combustion and the oxidation reaction. And when the solid fuel is used for the combustion process, so the carbon, hydrogen and sulfur get oxidized to produce carbon monoxide.

If it is partially oxidized, then it produces the carbon monoxide as a product. Or it will form  $\text{CO}_2$ , water vapor and sulfur dioxide as a product. So, for example, here if the carbon present in the solid fuel is completely oxidized or combusted in presence of adequate supply of oxygen or the air. Then it produces  $\text{CO}_2$  as a product along with that it releases this much amount of the energy. And in case if the carbon in the fuel is partially oxidized and that is mainly due to inadequate supply of oxygen or air during the combustion process then it may results into the formation of carbon monoxide and in this process this much amount of energy gets released.

However, in case of sulfur, the sulfur is oxidized completely to produce sulfur dioxide and this much amount of the energy. Similarly, the hydrogen in the solid fuel get oxidized to produce water vapor and this much heat energy. So, here if you look at this reaction number 2. So, for this each mole of CO form means a loss of around 283 kJ of heat. And this heat can be recovered if CO is completely oxidized further in the combustion process to produce  $\text{CO}_2$  as a product and during this process it release out 283 kilo joule per mole of heat.

So, once we combine these two heat values that are 283 plus 110.5 it comes out to be 393.5 kilojoules per mole. And that is the amount of energy which gets released if the carbon in the fuel is completely oxidized in presence of adequate supply of oxygen and air to produce  $\text{CO}_2$  as a product. And during this reaction it releases this much amount of the energy.

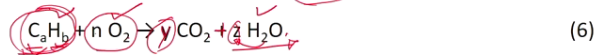
However, in case if the partial combustion of the carbon occurs during the combustion process then it releases only 110.5 kJ/mole of heat energy. And that is why it is termed as loss of around 283 kJ/mole of energy due to this partial oxidation or the partial combustion of carbon during the combustion process. And this can be recovered by completely oxidizing the carbon monoxide further in the combustion process by this reaction as it is represented here.

And this combustion of the solid fuels is more complex than that of the liquid and the gaseous fuel.

And that is mainly due to the complex chemical composition of the solid fuels. And normally the coal and the biomass sample is represented as per the following chemical formula that is  $C_aH_bO_c$ . And the stoichiometry of combustion of this hydrocarbon fuel with adequate supply of oxygen can be described as follows.

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- Stoichiometrically, the combustion of a hydrocarbon presented by  $C_xH_y$  can be described as follows:

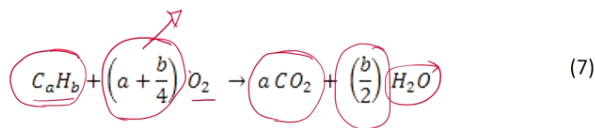


By mass balance in Eq (6): C balance:  $a = y$

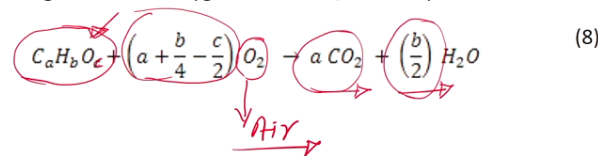
$$H \text{ balance: } b = 2z, \Rightarrow z = b/2$$

$$O \text{ balance: } 2n = 2y + z, \Rightarrow 2n = 2a + b/2 \Rightarrow n = a + b/4$$

Therefore, Eq. (6) becomes:



- The biomass and coal also contains large amount of oxygen. Therefore, above equation can be modified as:



So, normally the combustion of hydrocarbon fuel it represented as C suffix X and H suffix Y and it can be described as follows that is  $C_aH_b$ . And if this hydrocarbon fuel is oxidized with adequate supply of oxygen then it produces y moles of  $CO_2$  plus z mole of water vapor.

Now, by mass balance in equation 6, the carbon balance for example, here, so a is equal to y in terms of the H balance. So, b equal to 2 into z and you can also rearrange this term here that is z equal to b by 2 and the oxygen balance that is 2 into n, 2 into y and z equal to we can just rearrange this term and it comes out to be n equal to a plus b by 4. And once you substitute this term in equation number 6, so the modified form of the equation 6 is represented in this way  $C_aH_b$  plus this is a value of n. That means these many moles of oxygen required to completely oxidize this hydrocarbon fuel to form a moles of  $CO_2$  and b/2

moles of  $\text{H}_2\text{O}$  and along with that it releases significant amount of the heat energy. So, here we just try to bring this entire equation in the form of a and b.

And as we know the biomass and the coal contains large amount of the oxygen and that is what I mentioned in the previous slide. Normally the biomass and the coal is represented as per the following chemical formula that is  $\text{CH}$  and  $\text{O}$ . And if instead of the hydrocarbon we consider the biomass or coal as a fuel for the combustion operation, then it is represented as  $\text{C}_a\text{H}_b\text{O}_c$ . So, there is large amount of the oxygen is present in the feed sample itself.

And therefore, this above equation, this can be modified in this form. The value of n also will get modified it will be a plus b by 4 minus c by 2. That is because of the presence of oxygen in the feed sample and it will give a moles of  $\text{CO}_2$  and b by 2 moles of  $\text{H}_2\text{O}$ . And in this case we have to make one more assumption here that all the fuel and the oxidizers are completely combusted or oxidized to form the product as a result the oxygen is not seen in the product stream. That means the entire oxidizer or you can say the oxidant is completely utilized during this combustion process along with the fuel to produce product.

And hence the oxygen cannot be seen in the product stream. So, now suppose instead of oxygen if air is used as an oxidizer or oxidizing agent during the combustion process. So, there will be a change in this equation number 7 and 8.

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- In real combustion process, air is used as oxidizer instead of pure oxygen.

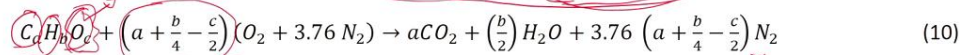
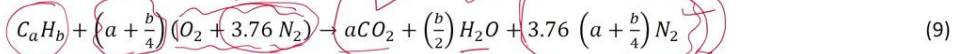
- The composition of air (at molar or volume basis):

⇒ 20.9% (oxygen  $O_2$ ) + 78.1% (nitrogen  $N_2$ ) + 0.9% ( $CO_2$ , He,  $H_2$ , and others) = 100 % v/v

⇒ A good approximation of this by molar or volume is: 21% oxygen, 79% nitrogen

- Thus, each mole of  $O_2$  is accompanied by  $0.79/0.21 = 3.76$  moles of  $N_2$ .

- For air as an oxidant, the Eq (7) can be written as:



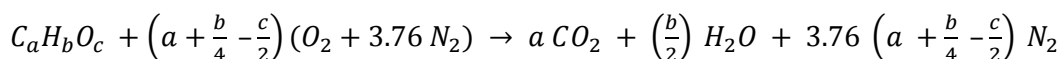
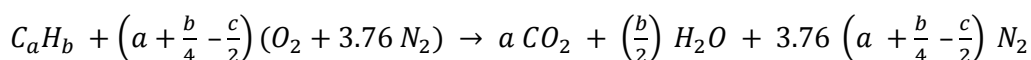
- The amount of air required for combusting a stoichiometric amount of mixture is called **stoichiometric** or **theoretical air**.

- In Eq(9),  $(a + b/4)$  moles of stoichiometric air required for complete oxidation of 1 mole of fuel ( $C_a H_b$ ).

- Moisture or humidity also can be added to the oxidant as some fraction of n moles of  $O_2$ .

Because as we know the composition of the air on molar or volume basis, it contains 20.9 percent oxygen and 78.1 percent nitrogen and remaining 0.9 percent is other gases. However, when we consider air as an oxidizer or oxidant for the combustion process, so normally we neglect the composition of other gases while doing the calculation of stoichiometric amount of the air which is required for the combustion process. And the summation of these three comes out to be around 100% that is on the volume basis.

And hence this oxygen and the nitrogen are approximated to 21 percent oxygen and 79 percent nitrogen. And normally during the combustion process while calculating the statuette amount of the air which is required for the combustion process, so these other gases are neglected during the calculation process. And hence this percentage oxygen and percentage nitrogen can be approximated to 21% oxygen and 79% nitrogen and that is by molar or volume basis. And thus 1 mole of oxygen here it is accompanied by 3.76 moles of nitrogen that is 0.79 divided by 0.21 which comes out to be around 3.76 moles of nitrogen. So, with help of this given information now the equation 7 can be rewritten as.



So, this is a fuel which is oxidized using air as an oxidant. So, now here this component represents air however in the equation 7 if you remember it was just the pure oxygen. But since now the oxygen is replaced with air as an oxidant so this term here it represent the air and it forms  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and along with that now the additional term coming in this equation 9 is nitrogen. However, it was absent when pure oxygen is used as an oxidizing medium during the combustion process. But due to use of air as an oxidant since as I mentioned earlier the one mole of oxygen it is accompanied by 3.76 moles of nitrogen. And this nitrogen does not take part during the combustion process and it remains unaffected during the combustion process.

As a result we can see here these many moles of nitrogen are coming out as it is along with the other combustible product that is  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . And hence it dilutes the product gases as well as it increases the volume of product gas. And similarly the equation 8 can be rewritten in the following way. Here the only difference is the oxygen is present in the feedstock and thus the amount of air which is required for combusting a stoichiometric amount of mixture is called as a stoichiometric or the theoretical air.

And in the equation 9 the term  $a + b/4$  indicates the moles of stoichiometric amount of the air which is required for the complete oxidation of 1 mole of fuel that is hydrocarbon fuel. And similarly in equation 10 if you see here,  $a + b/4 - c/2$  moles of stoichiometric amount of air which is required for the complete oxidation of 1 mole of fuel that is  $\text{CaHbOc}$  because here the oxygen is already present in the feed material. And even the moisture and the humidity can also be added to oxidant as some fraction of moles of oxygen, but normally these terms are neglected during the calculation of the stoichiometric amount of the air which is required for the combustion of a specific fuel.

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- The relative masses of the molecules are obtained by multiplying the number of moles of each species in the molecule by their respective molecular weights (g/mole).
- The stoichiometric amount of air (mass) can be calculated as :

$$(m_{\text{air}})_{\text{sto}} = (n_{\text{air}} \times M_{\text{air}})_{\text{sto}} \quad (11)$$

- Molecular weight of air:

$$M_{\text{air}} = \sum x_i M_i = x_{\text{O}_2} M_{\text{O}_2} + x_{\text{N}_2} M_{\text{N}_2}$$

Air contain approximately 21% Oxygen ( $\text{O}_2$ ) and 79% Nitrogen ( $\text{N}_2$ ) by volume.

Using  $M_{\text{O}_2} = 32.00$  g/mole and  $M_{\text{N}_2} = 28.01$  g/mole, yields

$$M_{\text{air}} = 0.21 \times 32.00 + 0.79 \times 28.01 = 28.85 \text{ g/mole} \approx 29 \text{ g/mole}$$

Composition of air by mass:

$$\text{Oxygen} = (0.21 \times 32.00) / 28.85 = 23\% \text{ approx}$$

$$\text{Nitrogen} = (0.79 \times 28.01) / 28.85 = 77\% \text{ approx}$$

20

Now, similarly these relative mass of molecules can be obtained by simply multiplying the moles of each species in the molecule by their molecular weights. Say for example, here as the stoichiometric amount of the air need to be calculated that is on the mass basis, so it can be calculated like this.

So, it can be calculated as mass of air that is a stoichiometric quantity equal to number of moles of air into its molecular weight that is a stoichiometric quantity and the molecular weight of the air as we know it is a mixture of nitrogen and the oxygen. So, it can be calculated using this equation. That is summation of fraction of specific species multiplied by its relative molecular weight. So, this indicates the fraction of oxygen into its molecular weight plus fraction of nitrogen into its molecular weight.

And as we discussed earlier, air contain approximately 21% oxygen and 79% nitrogen. So, with help of this given information and the molecular weight of oxygen is 32 g/mol and the nitrogen is 28.01 gram per mole, so once we substitute this value in the above equation that is equation of molecular weight of air, it comes out to be around 28.85 gram per mole and it can be approximated to 29 gram per mole. And now we can calculate the composition of air by mass that is oxygen is 0.21 into its molecular weight divided by the molecular weight of air.

And it comes out to be around 23 percent approximately and similarly the nitrogen it comes out to be around 77 percent approximately. But remember that this is by mass and this is by mole or volume.

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- % Excess Air (%EA)
- ✓ if actual air used is less than the stoichiometric amount, the mixture is described as fuel rich mixture
  - ✓ if actual air used is in excess, the mixture is described as fuel lean mixture
- ∴ To ensure complete combustion, the actual air is supplied is in excess of stoichiometric air.
- The amount of air in excess of the stoichiometric amount is called "excess air"

So, there is another important concept in the combustion stoichiometry that is termed as percentage excess air. Practically, fuels are often combusted in amount of air different than that of the stoichiometric ratio. And in case if actual air used is less than the stoichiometric amount of air then the mixture is described as fuel rich mixture.

Which indicates that the amount of air which is used during this combustion operation is less than the stoichiometric amount of air required for the combustion as a result the mixture is fuel rich mixture. So, mixture here in the sense is the combustible mixture. So, in that combustible mixture it is a fuel rich mixture that means the percentage of fuel is more than that of the amount of air which is required for the combustion. And this fuel rich mixtures are less efficient but may produce more power and burn cooler or in case if actual air if actual air used is in excess then the mixture is described as fuel lean mixture. So, which indicates that the air which is used during this combustion it is in excess of that of the fuel.



And as a result the combustible mixture is fuel lean mixture that means the amount of fuel is less than that of the amount of air which is being used during this combustion operation. And this fuel lean mixture these are more efficient but may cause higher temperatures which can lead to the formation of nitrogen oxides. And therefore, to ensure complete combustion the actual air is supplied is in excess of stoichiometric air. And this amount of air in excess in excess of the stoichiometric amount is called excess air. So, basically the amount of air which is used in excess of the stoichiometric amount of the air which is required for the combustion operation and that is why it is termed as excess air.

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$$\begin{aligned} \% EA &= \frac{m_{air,act} - m_{air,stio}}{m_{air,stio}} \times 100 \\ &= \left( \frac{m_{air,act}}{m_{air,stio}} - \frac{m_{air,stio}}{m_{air,stio}} \right) \times 100 \\ \% EA &= \left( \frac{m_{air,act}}{m_{air,stio}} - 1 \right) \times 100 \end{aligned}$$

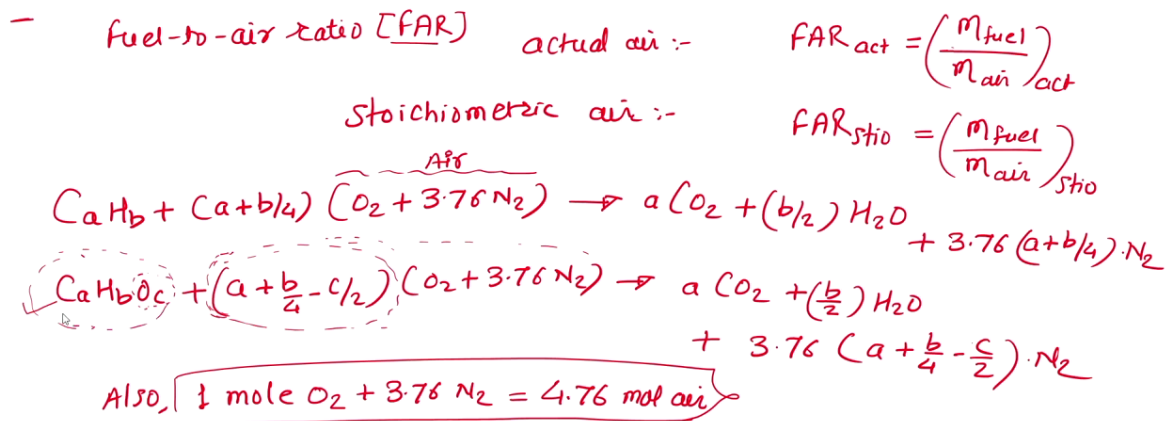
Subscript :- act = actual  
stio = stoichiometric amount.

And this percentage excess air can be calculated using this equation that is mass of air actually which is required for the combustion minus mass of air stoichiometric amount divided by mass of air stoichiometric amount into 100. So, if you just simply rearrange this equation, so it will be mass of air actual by mass of air stoichiometric amount minus mass of air stoichiometric amount divided by mass of air stoichiometric we have just separated this term here. So, this will cancel out and we will get the equation in the form of mass of air that is actual amount mass of air stoichiometric amount minus 1 into 100. This gives percentage excess air which is required during the combustion operation. And here the subscript indicates actual and indicates stoichiometric amount.

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FUEL-TO-AIR RATIO &  
Equivalence ratio

FUEL-AIR RATIO



And thus to quantify this combustible mixture the fuel to air ratio and equivalence ratio are introduced and these are important aspect of the combustion operation that ensures efficient and safe combustion. So, let us first discuss about this fuel to air ratio. So, let us first discuss about fuel to air ratio and this particular ratio that is fuel to air ratio and equivalence ratio are introduced to quantify the combustible mixtures. For example, fuel to air ratio that is also abbreviated as FAR for actual amount of air. It is represented as F that is fuel to air ratio actual equal to mass of fuel by mass of air and this is on actual basis.

Similarly, stoichiometric air can be represented in the form of fuel to air ratio stoichiometric amount the ratio of is a ratio of mass of fuel by mass of air and this is stoichiometric amount. And if you recollect our discussion just few slides back we described the combustion of hydrocarbon for air as an oxidant and the equation is represented in the form that is plus into 3.76 and this term here it represent air as oxidant.

It gives an amount of  $CO_2$  plus  $b$  by 2  $H_2O$  plus 3.76. Similarly, for biomass and coal as a solid fuel the equation can be represented in the form there we need to consider the percentage of oxygen which is present in the specific given solid sample either it is biomass or coal. And it gives plus water plus  $a$  plus  $b$  by 4 minus  $c/2$  nitrogen. Also here if you see

this 1 mole of oxygen is accompanied by 3.76 moles of nitrogen and it comes out to be 4.76 moles of air.

So, for example, here if the solid fuel used is biomass or coal, then the moles of air required for the combustion of the given solid fuel is this much into 4.76 because as I mentioned 1 mole of oxygen accompanied by 3.76 moles of nitrogen that means 4.76 into these many moles of air is required to carry out the combustion of the given solid fuel.

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$$FAR_{sto} = \left( \frac{\bar{m}_{fuel}}{((a + b/4 - c/2) \cdot 4.76 \cdot M_{air})} \right)_{sto} \quad \text{--- (15)}$$

The range of  $FAR_{sto}$  is from zero to infinity

- The air-fuel-ratio (AFR) is also used to describe combustible mixture which is simply the reciprocal of FAR [FUEL-AIR ratio]

$$AFR = \frac{1}{(FAR)_{sto}}$$

Note:- AFR & FAR are the mass ratios.

And this fuel to air ratio based on the stoichiometric amount of air is represented in the following way  $a + b/4 - c/2$  into 4.76 and this is molecular weight of air. And this total it is based on the stoichiometric amount of air which is required for combusting this much mass of fuel. And this equation we can number it as 15. And the range of this fuel to air ratio is from 0 to infinity and in the similar line the air to fuel ratio that is represented as AFR. So, this is fuel to air ratio.

Similarly, the air to fuel ratio is also used to describe combustible mixture, and which is simply the reciprocal of fuel to air ratio. So, for example, once we know fuel to air ratio, then air to fuel ratio is simply the reciprocal of and that is the stoichiometric fuel to air ratio. So,

please make a note of one thing here that is this air to fuel ratio and fuel to air ratio are in the terms of mass ratios. So, this is all about the fuel to air ratio.

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Equivalence ratio ( $\phi$  and  $\lambda$ )

- Normalizing the actual FAR by the stoichiometric FAR gives the equivalence ratio ( $\phi$ )

$$\text{Equivalence ratio :- } \phi = \frac{(FAR)_{act}}{(FAR)_{sto}} = \left( \frac{m_{air,sto}}{m_{air,act}} \right) = \left( \frac{n_{air,sto}}{n_{air,act}} \right) = \left( \frac{n_{O_2,sto}}{n_{O_2,act}} \right)$$

$$(FAR)_{act} = \left( \frac{m_{fuel}}{m_{air}} \right)_{act}$$

$$(FAR)_{sto} = \left( \frac{m_{fuel}}{m_{air}} \right)_{sto}$$

$$\phi = \frac{\left( \frac{m_{fuel}}{m_{air}} \right)_{act}}{\left( \frac{m_{fuel}}{m_{air}} \right)_{sto}} = \left( \frac{m_{air,sto}}{m_{air,act}} \right)$$

Similarly, the equivalence ratio is another one important concept in the combustion stoichiometry. So, this equivalence ratio also denoted as phi and lambda. The equivalence ratio it can be calculated by normalizing the actual fuel to air ratio by the stoichiometric fuel to air ratio. So, if you just divide the actual fuel to air ratio by the stoichiometric fuel to air ratio, it gives the equivalence ratio. And this equivalence ratio is represented using this equation that is fuel to air ratio actual by fuel to air ratio stoichiometric amount. So, this equivalence ratio phi can be represented by using this equation that is fuel to air ratio actual by fuel to air ratio stoichiometric quantity.

That is equal to mass of air stoichiometric quantity divided by mass of air that is actual. And so, just to know how we have reached to this particular term here, we can simply solve this equation that is fuel to air actual is equal to mass of fuel by mass of air actual. And fuel to air ratio stoichiometric equal to mass of fuel by mass of air stoichiometric quantity. And if you replace these two equations in the above equation that is phi equal to mass of fuel by mass of air actual by mass of fuel mass of air stoichiometric quantity. And just rearranging this

equation this mass of fuel this will get cancel out here. It will get mass you will get the equation in the form of this mass of fuel will cancel out and we will get the equation in the form of mass of air stoichiometry by mass of air actual.

So, this is the term as we have mentioned in the previous equation. And similarly, this can be represented in the form of moles of air by actual. And in case if the oxygen is used as an oxidant then so this is the actual and this is stoichiometric quantity.

(Refer slide time: 1:10:15)

$\phi < 1$  : fuel lean mixture  
 $\phi = 1$  :- stoichiometric mixture  
 $\phi > 1$  : fuel rich mixture

Similar to fuel-to-Air ratio,  $\phi$  ranges from zero to infinity corresponding to the limits of pure air and fuel, respectively.

- Alternatively, an equivalence ratio based AFR is frequently used by combustion and is denoted by lambda ( $\lambda$ )

Lambda is defined as the ratio of the actual AFR to the stoichiometric AFR

$$\text{Equivalence ratio : } \lambda = \frac{(AFR)_{act}}{(AFR)_{sto}} = \frac{(m_{air,act})}{(m_{air,sto})} = \frac{1}{\phi}$$

Now in this case if this phi is less than 1 and it is termed as fuel lean mixture or if phi is equal to 1 then it is or stoichiometric mixture and in case if the phi is greater than 1 then it is fuel rich mixture. So, similar to this fuel to oil ratio is equivalence ratio that is phi also ranges from 0 to infinity and that is corresponding to the limits of and that is corresponding to the limits of pure air and fuel, respectively. And alternatively an equivalence ratio based on air to fuel ratio is frequently used by combustion scientist and is denoted by lambda.

And this lambda here is defined as the ratio of the actual air to fuel ratio to the stoichiometric air to fuel ratio. So, the equivalence ratio that is in the form of lambda it can be represented in the form of air to fuel ratio. This is actual by air to fuel ratio stoichiometric quantity. That is equal to mass of air divided by mass of air stoichiometric quantity. And if you remember the

previous equation that is phi it is the ratio of mass of air that is stoichiometric to the mass of air actual. And here it is just reverse of that and that is the reason the lambda is inverse of phi.

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$\lambda < 1$  : fuel rich mixture  
 $\lambda = 1$  : stoichiometric mixture  
 $\lambda > 1$  : fuel lean mixture

And if this lambda is less than then it is a fuel rich mixture and if it is equal to 1, it is a stoichiometric mixture and if it is greater than 1, then it is fuel lean mixture. So, this is all about the combustion stoichiometry and I hope it is clear now how to calculate the fuel to air ratio as well as air to fuel ratio equivalence ratio and the percentage excess air for the given fuel; and how to represent the combustion stoichiometry for the given fuel if it is a biomass or if it is just a hydrocarbon fuel. Since we know the biomass and coal contains oxygen in its composition. Therefore, the combustion equation for the biomass as well as the coal is different than that of the pure hydrocarbon fuels.

This is all about the combustion stoichiometry. So, in the next lecture, we will practice few example on the concept covered in this module.

Thank you.