# Energy Conversion Technologies (Biomass and Coal) Prof. Vaibhav V. Goud Department of Chemical Engineering Indian Institute of Technology, Guwahati Lecture 27 Energy from Coal (Carbonization, Gasification and Liquefaction)

Good morning everyone.

Welcome to this first lecture of module 7 on origin and composition of solid fuels. In that we will discuss about the composition and origin of solid fuel that is coal, properties of coal, classification of coal and followed by that we will discuss storage and handling of coal and at the end we will discuss carbonization of coal as well as coal gasification process.

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# Solid Fuels

- Fuels can be defined as substances that liberate heat when reacted chemically with an oxidizer.
- In the current context, the term "solid fuel" refers to various types of combustible solid materials which are used as fuel to produce heat and energy, usually through the combustion.
- The solid fuels are typically derived from organic matter originating from fossil source (e.g. coal, peat) and biomass source (e.g. wood, grass).
- Solid fuels have been used for thousands of years as a source of heat and energy, particularly for cooking food, space heating, and powering industrial processes.
- Solid fuels (wood, coal, biomass)  $-C_aH_bO_c$
- In general, for wood and biomass a b

For coal : a>b

Therefore coal is likely to produce more  $CO_2$  when burned.

3 भारतीय प्रौद्योगिकी संस्थान गुलाहाटी INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI

So, at first what is a solid fuel? So, in that first we will discuss about the fuels and then we will talk about the solid fuels in detail. Fuels can be defined as substances that liberate heat when reacted chemically with an oxidizer. And the oxidizer used during this chemical reaction may be air or pure oxygen or sometimes it may be a steam.

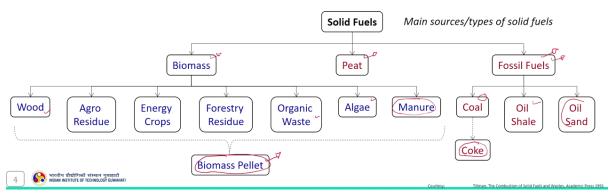
In the current context that is in the context of this module here, the term solid fuel refers to various types of combustible solid materials which are used as fuel to produce heat and energy. And the production of heat is usually carried out through combustion operation. The solid fuels are typically derived from organic matter originating from fossil source that is coal, peat and biomass source that is wood, grass, etc. And these solid fields have been used for thousands of years as a source of heat and energy and primarily for cooking food, space heating application and powering industrial processes.

And these solid fuels are chemically represented in this form that is C, H and O. In general for wood and biomass material this A is less than B that means the carbon contained in the wood and biomass source material is less than that of the hydrogen. However, for the coal this A is greater than B that means coal contains more carbon than hydrogen and therefore when the coal is burnt it produces more carbon dioxide. And if you recollect our discussion in one of the lecture in the module 1, we discussed about the composition of the solid fuels. And there we talked about the biomass composition and composition of coal as well. And there also we discussed that the coal contains more carbon in its composition than that of the biomass.

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#### Origin and Composition of Solid Fuels

- Various solid fuels are derived from organic matters originating from fossil and biomass source. Therefore, based on the origin, the sold fuels are classified as Biomass and Fossil fuels.
- **Biomass** is an organic matter derived from plants, animals, or microorganisms found in nature, which can be used as renewable source of energy.
- · Fossil fuels are formed through accumulation and transformation of organic matter over million of years.



So, now let us discuss about the origin and the composition of the solid fuels. So, the solid fuels are derived from the organic matter originating from fossil source and biomass source and therefore based on the origin the solid fuels are classified as biomass and fossil fuels that means biomass based fuel and fossil based fuels. And here biomass is the organic matter derived from plant, animal or microorganism and which can be used as a renewable source of energy while fossil fuels are formed through accumulation and transformation of the organic material over millions of years. And this chart, it provides the information about the various types of the solid fuels, that is, biomass-based solid fuel, peat, and fossil fuel-based solid fuels.

The biomass-based solid fuels are further subclassified as wood, agro-residue, energy crops, forested residue, organic waste, algae, and manure. And this biomass based organic matter can further be converted into biomass pellets using convenient and suitable pelletization technique. While the fossil fuels are sub classified as oil sand, oil shale and coal. And here the coal is transformed into coke using suitable transformation system or suitable transformation process.

Solid fuels	Origin	Composition
Biomass	Biomass is an organic matter derived from plants, animals, or microorganisms found in nature, which can be used as renewable source of energy.	Biomass mainly consists of cellulose, hemicellulose, lignin, and other organic compounds. However, its composition varies with the source.
Biomass Pellets	Biomass is compressed into pellets/briquettes to increases the energy density. Pellets can be made more effective by torrefaction before pelletization.	It contain cellulose, hemicellulose, lignin, and other organic compounds (varies with the source). Torrefied pellets contain higher content of fixed carbon.

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So, after learning about the various types of solid fuel, let us discuss about the origin and the composition of the solid fuels. Biomass is an organic matter derived from plants, animals or

microorganisms found in nature and which can be used as a renewable source of energy and this biomass mainly consists of cellulose, hemicellulose, lignin and other organic compounds. However, its composition varies with the source. For example, in case of agricultural residue, the composition that is cellulose, hemicellulose, and lignin may be different than that of the forestry residue material. Similarly, the biomass pellets In this case the biomass is compressed into pellets or briquetts to increase its energy density and this pellets can be made more effective by first torrefying the biomass and then converted into pellets. And the biomass pellets also contains cellulose, hemicellulose, lignin and other organic compounds.

However, the torrefied pellets contain higher amount of fixed carbon. Since the biomass material has been torrefied, so ultimately it increases the fixed carbon content of the torrefied material. As a result the torrefied pellets contain more amount of fixed carbon than that of the original biomass sample.

marshes. Peat Over time, the dea partial decomposi oxygen to form pea The peat beds un	ad plants accumulate and undergoes ition/ carbonization due to lack of	It is organic sediment containing cellulose, hemicellulose, and lignin along with minerals and wate content. Its carbon content is less than 60% (daf basis).
Coal the geochemical efforts of the past 300 coalification has coa	ffects of heat and pressure.	It contains organic constituents called macerals as the coalified remnants of the starting biomass. Three groups of macerals are vitrinite liptinite (or

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Another solid fuel is peat and it is formed in waterlogged environment such as bogs and marshes. Over the time the dead plants accumulate and undergoes primary decomposition that is called as a carbonization process and that is mainly due to lack of oxygen and it converts into peat.

And it is also organic sediment containing cellulose, hemicellulose and lignin with minerals and water content and that is the reason the peat has higher moisture content in its composition and its carbon content is less than 60% and that is on dry-ash-free basis. Coal is another solid fuel and the coal it is originated from the peat beds underwent the sedimentation of the minerals and organic matter leading to its coalification. And that is mainly due to the geochemical effect of heat and pressure. And in this case, the peat which is formed in the previous stage, so that peat beds further underwent the sedimentation of minerals and organic matter and that leads to the torrefaction.

And if you recollect our discussion in the one of the lecture in the module 1, we also discussed in detail about the coalfaction process and that mainly due to the geochemical effects of heat and pressure. And this process of peat and the coalfaction has occurred several times to form coal seams under the layers of sedimentary rocks over the past several millions years. And this coal it contains organic constituents called macerals as qualified remnants of starting biomass materials and the three groups of macerals are vitrinite, liptinite and inertinite.

Solid fuels	Origin	Composition
Coke	Coke is derived from carbonization of coal. Coal is heated in the absence of oxygen at high temperatures (~1000 °C) to volatilize the lighter constituents leaving behind a carbon residue containing both ash and sulfur is called <i>coke</i> .	It mainly contains carbon (90-95%), ash, & sulfur. It may contain lower content of moisture and volatile matter.
Oil shale	Oil shale is a fine-grained sedimentary rock containing large amounts of organic matter (called <i>kerogen</i> ), formed from the remains of ancient marine organisms, including plankton and algae, accumulated over millions of years ago.	Kerogen is precursor to petroleum or hydrocarbons. Its composition is highly complex, which include hydrocarbons and $O/N/S$ -containing compounds. It has high carbon content and low H/C ratio.
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Coke is basically derived from the carbonization of coal. So, when the coal is heated in absence of air or we can say the oxygen at high temperature that is close to around 1000 °C to

volatilize the lighter constituents present in the coal sample leaving behind the carbon residue, containing both ash and sulphur and that is termed as coke.

It mainly contains carbon close to around 90 to 95% traces of ash and sulphur. It may contain lower amount of moisture and volatile matter. While this oil shale it is a fine grained sedimentary rock containing large amount of the organic matter that is called as a kerogen and it is formed from the remains of ancient marine organisms including the plankton and algae accumulated over millions of years ago and that gets converted into a organic matter that is called as a kerogen. And, kerogen is a precursor to petroleum or the hydrocarbons. And its composition is highly complex which includes hydrocarbons and oxygen, nitrogen, sulfur containing compounds.

And it has high carbon content and low H by C ratio. And, this is about the origin and the composition of the solid fuels.

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Classification of coal

The **rank of coal** is the basis for the classification of a particular coal relative to other coals, according to the degree of metamorphism, or progressive alteration (American Society for Testing and Materials/ASTM, 2011).

Types of coal, in increasing order of alteration:

Lignite (brown coal);
 Sub-bituminous;
 Bituminous;
 Anthracite

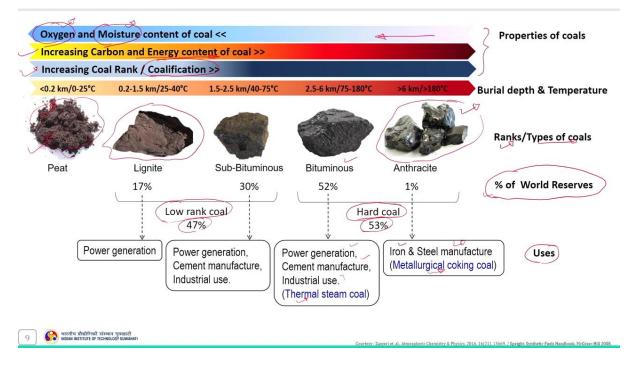
The properties of coal that varies with the rank of coal: (1) HHV, (2) VM, (3) moisture, (4) ash, and (5) FC

8 भारतीय प्रौद्योगिकी संस्थान गुवाहाटी INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI

So, now let us move on to the next topic that is classification of coal. Here the rank of the coal is basis for the classification of a particular coal relative to other coal samples and according to the degree of metamorphism or progressive alteration. And the types of coal in the increasing order of alteration are as follows.

Lignite, that is also termed as brown coal is a low rank coal, followed by the sub bituminous coal, bituminous coal and anthracite. And anthracite is a highest rank coal among these given sample whereas lignite is lowest rank coal. And the properties of the coal that varies with the rank of a coal includes higher heating value, volatile matter content, moisture content, ash content and the fixed carbon content in the coal sample.

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Here it shows the properties of the coal that varies with the rank or we can say type of the coal. Along with that it also shows the percentage of world resource for the specific coal samples as well as its uses. And here it shows the increasing order of oxygen and moisture content of the coal sample. That means the anthracite has lower amount of oxygen and moisture in its composition while the peat has higher oxygen and the moisture content in its composition. However, it shows the increasing carbon and energy content of the coal sample which indicates that peat has lower carbon and energy content than that of the anthracite. And it shows the increasing coal rank and coalification. In that anthracite is considered as the highest rank coal as we just discussed one slide before and peat is considered as low rank coal.

Similarly, even the lignite is also considered as low rank coal. So, according to the ranks and types of the coal the anthracite and the bituminous coal are considered as the hard coal or we can say high rank coal. While sub bituminous lignite are considered as low rank coal. And the percentage of world reserves of bituminous and the anthracite coal is around 53%, while for the lignite and the sub bituminous, it is around 47%. And as far as the use of these types of coal is concerned, the lignite is used for the power generation, while sub bituminous coal is used for power generation as well as for the cement manufacture and industrial use.

And the bituminous coal here it is used for the power generation, cement manufacture, industrial use and thermal steam coal. While the anthracite it is used in iron and the steel manufacturing industries and for metallurgical cooking coal.

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Properties	of coal used for	its evaluation and use
	Density, 🖌 Specific gravity	<ul> <li>It is a measure of how much mass is contained within a space occupied by coal.</li> <li>Useful in evaluation of its quality transportation, storage, and economic value.</li> </ul>
Physical	Pore structure	<ul> <li>It specify the porosity, nature of pores or ultrafine structure of coals.</li> <li>Useful in evaluation of permeability and gas storage capacity of within the coal matrix.</li> </ul>
Properties	Surface area	<ul> <li>It is determined based on the amount of gas adsorbed on coal surface</li> <li>Useful for evaluation of its reactivity and the rate at which it can undergo combustion.</li> </ul>
	Reflectivity	<ul> <li>It is a measure of the percentage of incident light reflected from the surface of coal.</li> <li>Useful in evaluation of the thermal maturity and rank of coal.</li> </ul>

#### 10 🚱 भारतीय प्रौद्योगिकी संस्थान गुवाहाटी INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI

So, after learning about the ranks and the types of the coal, let us discuss about the properties of the coal used for its evaluation and uses which includes the physical properties, mechanical properties, thermal properties and electrical properties. So, let us first discuss about the physical properties which includes density, pore structure, surface area and reflectivity. Density it is the measure of how much mass is contained within a space occupied by a coal and it is useful in evaluation of its quality as well as it is useful in evaluation of its

transport that is related to the transportation cost, storage and economic value, pore structure it specify the porosity and the nature of pores or the ultra fine structure of the coals.

And it is useful in evaluation of permeability and gas storage capacity of within the coal matrix. Surface area also it is determined based on the amount of gas absorbed on the coal surface and it is used for the evaluation of its reactivity and the rate at which it can undergo the combustion. While the reflectivity it is a measure of the percentage of incident light reflected from the surface of the coal and it is used in the evaluation of the thermal maturity and also it is considered as one of the parameter while ranking the coal.

	Strength	<ul> <li>It is a specification of compressibility strength.</li> <li>Useful in underground mining operations, e.g. stronger coal is mined more safely.</li> </ul>
echanical	Hardness / Abrasiveness	<ul> <li>It is a specification of scratch, indentation hardness, and abrasive action of coal.</li> <li>Useful in selecting suitable mills and crushers for coal grinding in power plants.</li> </ul>
operties	Grindability	<ul> <li>It is a measure of relative amount of work needed to pulverize coal.</li> <li>Useful in assessing the ease of pulverizing coal in preparation for combustion.</li> </ul>
	<sup>y</sup> Dustiness index	<ul> <li>It is a measure of amount of dust/produced when coal is handled.</li> <li>Useful in assessing the safety and environmental aspects during its handling.</li> </ul>

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Mechanical properties it includes the strength, hardness, grindability and dustiness index. The strength it is specification of compressibility strength of the material and it is useful in underground mining operation example stronger coal is mined more safely than that of the soft coal, while hardness of the coal is useful in selecting suitable mills and crusher for coal grinding in power plants.

The grindability, it is a measure of relative amount of the work which is needed to pulverize the coal sample and it is useful in assessing the ease of pulverizing coal in preparation for combustion operation. While the dustiness index, it is a measure of amount of the dust which is produced when coal is handled and it is useful in assessing the safety and the environmental aspects during its handling and operation.

	Calorific value	• It is a measure of energy content,
فكما	Heat capacity	<ul> <li>It is a amount of heat required to raise the temperature of a unit quantity of coal by 1 °C</li> <li>Useful in evaluation of its thermal behavior for designing efficient combustion systems.</li> </ul>
Thermal	Thermal conductivity	<ul> <li>It is a rate of heat transfer through unit area, unit thickness, unit temperature difference.</li> <li>Useful in evaluation of how heat is transferred within a fuel bed during combustion.</li> </ul>
Properties	Plastic Property	<ul> <li>During the heating of coal, an unstable intermediate phase, called metaplast.</li> <li>The metaplast is responsible for the plastic behavior of coal.</li> <li>Useful in assessing the coking properties of coal.</li> </ul>
	Free swelling index	<ul> <li>Measure of the increase in volume when a coal is heated without restriction.</li> <li>Useful in assessing the coking properties of coal.</li> </ul>
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Thermal properties include the calorific value and it is measure of the energy content of the given sample. While the heat capacity it is the amount of heat which is required to raise the temperature of a unit quantity of a sample given by 1 °C. Suppose if the sample is coal then the heat which is required to raise the temperature of a unit quantity of coal by 1 °C and that is termed as a heat capacity and it is useful in evaluation of its thermal behavior for designing efficient combustion system. Thermal conductivity it is a measure of heat transfer through unit area, unit thickness and unit temperature difference and it is useful in evaluation of how heat is transferred within the fuel bed during the combustion process. And thermal conductivity of such material it gives this useful information of the rate of heat transfer within the material during thermal processes. Plastic property is also one of the important properties of a coal. Because during the heating of coal an unstable intermediate phase called metaplast is formed and this metaplast is responsible for the plastic behavior of the coal sample and it is useful in assessing the cooking properties of the coal.

While this free swelling index it is the measure of the increase in the volume when coal is heated without restriction and it is also useful in assessing the coking properties of coal.

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Electrical resistivity	<ul> <li>It is a measure of coal's ability to resist the flow of electric current (measured in 'ohm cm').</li> <li>Useful for optimizing the industrial coal processes, such as electric arc furnaces.</li> </ul>
Properties Dielectric constant	<ul> <li>It is a measure of a coal's ability to store electrical energy in an electric field.</li> <li>It decreases with coal rank, may be due to the loss of polar groups (e.g. OH', RCOO').</li> <li>Useful in certain applications where coal-derived materials are used in electrical components or as insulating materials.</li> </ul>

13 🚱 भारतीय प्रौद्योगिको संख्यान गुवाहाटी

An electrical property that is electrical resistivity and the dielectric constant are important in optimizing the industrial coal process such as electric arc furnace. Because this electrical resistivity, it is a measure of the coal's ability to resist the flow of electric current and this information is useful for optimizing the industrial coal processes such as electric arc furnace.

However, this dielectric constant, it measures the coal's ability to store the electrical energy in an electric field, and it decreases with coal rank and this is may be due to loss of polar groups. However, the information about the dielectric constant of the given sample is useful in certain application where coal derived materials are used in electrical components or as a insulating materials.

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#### **Typical Properties of Coal**

• The properties of coal vary considerably with coal type and even from sample to sample within a specific coal types, depending on the source of the coal.

Type of coal	Bulk density	Moisture	Fixed carbon	Ash	с	н	Ο	S	нну
	kg/m <sup>3</sup>	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w	MJ/kg
Lignite	641-865	20-60	28-34	4–5	70	5 (	25	0.4	14.6-19.3
Sub-bituminous	640-900	16-36	42-49	5–9	75	5	20	0.4–0.5	19.3–26.7
Bituminous	673–913	2–16	45–78	3–12	85	5	10	0.4–0.7	26.7–32.5
Anthracite	800–929	1-16	80-86	9–20	94	3	3	0.6-0.8	32.5-36.0

• Typical properties of coal are presented in below table.

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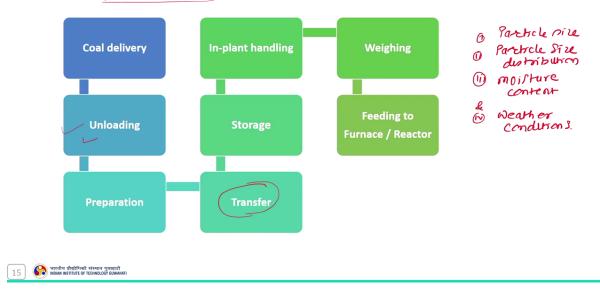
#### artesy: Speight, The chemistry and technology of coal, CRC Press 2013. / Viswanathan, Energy Sources- Fundamentals of Chemical Conversion, Elsevier 2017. / Oakey, Fuel Flexible Energy Generation - Solid, Liquid & Gaseous Fuels, Woodhead Publishing 2015.

Apart from these many properties of the coal there are certain typical properties of the coal that need to be taken into consideration while ranking the coal sample. And these typical properties of the coal these vary considerably with coal type and even from sample to sample within the specific coal types and depending on the source of coal. And these typical properties of the coal are presented in this table here, which shows bulk density, moisture content, fixed carbon content of the sample, ash and the ultimate analysis as well as the higher heating value. And from this table, it appears that the anthracite has the highest fixed carbon content and higher heating value compared to that of the lignite. Because lignite has fixed carbon content in the range of 28 to 34 which is significantly low.

Also the high reading value of the lignite is in the range of 14 to 19 that is substantially lower than that of the anthracite. Even the oxygen content in the anthracite coal sample is significantly lower than that of the lignite coal. While the moisture content, the moisture content in the lignite coal is quite high compared to that of the anthracite. And because of these two properties and high fixed carbon content anthracite has relatively higher heating value compared to that of the lignite and other coal samples.

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#### Coal Handling



Coal handling consists of various steps and systems as shown in the chart:

After learning about the coal types, origin and its composition as well as the different properties of the coal, so the next important topic that needs to be taken into consideration is the handling of a coal. Because this coal handling it consists of various steps and system as shown in this chart here. The coal after washing and upgrading is transported to industrial centers and generally the manner of coal handling is substantially affected by the particle size particle size distribution, moisture content, and weather conditions.

Environmental impact occurs during loading and unloading as well as during the en route affect the natural system. For example, the major adverse environmental impact resulting from the coal dust particle released during the coal loading as well as during the coal unloading and coal dust entrainment during the transport. And this problem can to a certain degree be overcome by storing coal in abandoned pits or silos constructed for this purpose.

#### Storage of Coal

Coal storage is an important part of coal-handling systems at mines and coal processing plants for production and utilization aspects.

- There may be some undesirable events associated with the coal storage -
  - 1) Oxidation and spontaneous combustion,
  - 2) Changes in coal properties which may affect utilization,
  - 3) (Degradation of coal due to multi-handling steps,
  - 4) High cost of the handling steps and the storage facilities (etc.)

16 🚱 भारतीय त्रौद्योगिकी संस्थान गुवाहाटी INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI

And for that reason, the coal storage is an important part of the coal handling system at mines and coal processing plants for production and utilization aspects. There may be some undesirable events which are associated with the coal storage, which may include the oxidation and the spontaneous combustion of the stored sample.

And during prolonged storage, it may undergo certain changes in the coal properties, which may affect its utilization. And it may cause degradation of the coal due to multi handling steps. As well as the high cost which is associated with the handling steps and the storage facility, these are some of the undesirable events which are associated with the coal storage.

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#### Considerations for Safe Coal Storage

- The areas selected for storage should be dry and constructed to permit good drainage.
- The area must be made free of all combustible material (low ignition temperature), such as wood, dry hay, etc.
- The base of storage pile should be a clay or firmly packed earth. The coal should be spread over the entire area in thicknesses of approximately 1–2 ft and compacted.
- · Conical piles should be avoided. The top and sides of pile should be compacted to form a seal and exclude air
- An effective seal can be formed by a continuous layer of fine coal followed by a covering of lump coal to prevent from the action of wind and rain.
- Heating in storage piles should be monitored/detected by driving small diameter pipes at intervals.
- When heating and fires develop in storage piles, smothering by compaction with heavy equipment is generally the best procedure. Water-flooding may allow the fire to spread via spontaneous combustion.

#### 17 🚱 भारतीय त्रौधोगिकी संस्थान गुवाहाटी INDIAN INSTITUTE OF TECHNOLOGY GUWAHAT

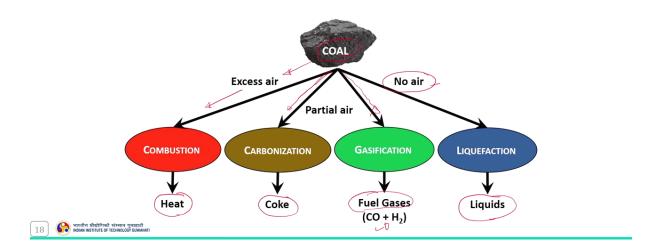
And hence there are certain points which need to be taken into consideration for safe coal storage. That means the area which is selected for the storage, it should be dry and constructed to permit the good drainage and this area must be free of all combustible materials that are low ignition temperature material. Similarly, the area which is used for this storage, the base of this storage field should be clay or firmly packed earth so that the coal should be sprayed over this entire area in the thickness of approximately 1 to 2 feet and then compacted. Somehow this conical pile should be avoided. The top and the sides of the pile should be compacted to form a seal and exclude air.

And to exclude this air an effective seal can be formed by continuous layer of fine coal followed by covering of the lump coal to prevent from the action of wind and rain. And the heating in this storage piles should be monitored and detected by driving small diameter pipes at intervals. And when the heating and the firing develops in the storage piles, then smothering by compaction with heavy equipment is generally the best procedure, as the water flooding may allow the fire to spread via spontaneous combustion. So, these are some of the points which need to be taken into consideration for safe coal storage.

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#### **Coal Conversion Technologies**

- · Coal is a versatile energy resource being used for the production of heat, power, alternative fuels, and chemicals.
- The current coal conversion technologies are summarized as follows:



So, now next move on to the coal conversion technologies. So, coal is a versatile energy resource being used for the production of heat, power, alternative fuels and chemicals. And the current coal conversion technologies which are used to produce heat, power, alternate fuels and chemicals are summarized as follows.

The coal with excess supply of air can be combusted to produce heat as a product, while in limited supply of air can be carbonized to produce coke or in limited supply of air it can be gasified to produce fuel gas that is carbon monoxide plus hydrogen or another alternative technology includes the liquefaction of coal in absence of air to produce liquid product. So, these are different technologies which are available for the conversion of coal to suitable product. So, now let us discuss about these technologies one by one.

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#### 1 Coal Carbonization

- **Carbonization** is the destructive distillation of organic substances in the absence of air accompanied by the production of carbon and liquid and gaseous products.
- Carbonization is essentially used for the production of a carbonaceous residue called *coke* by the thermal decomposition and simultaneous removal of *distillate* and *gaseous products*.
- During this process, small quantities of tar and light oil may be produced.
- The coke is physically dissimilar from charcoal and has the more familiar honeycomb-type structure.
- Initially, the smoke generated from carbonization process was a major problem, which was solved with the new modification of the charring-coking kiln (*the beehive process*, 1759), that laid the foundation for the modern coke blast furnace.

rtesy: Porter, Chemical & Engineering News, 1924, 2(15): 12. / Speight, The chemistry and technology of coal, CRC Press 2013

#### 19 🚱 भारतीय प्रौद्योगिकी संस्थान गुवाहाटी INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI

So, first let us discuss about the coal carbonization process. So, carbonization is the destructive distillation of the organic substances in absence of air accompanied by the production of carbon, liquid and gaseous products. And this carbonization process it is used for the production of the carbonaceous residue called coke by the thermal decomposition and simultaneous removal of distillate and gaseous products. And during this carbonization process, small amount of tar and light oil may be produced.

However, this coke produced during this carbonization process is physically dissimilar from the charcoal and has the more familiar honeycomb type structure. During the early stage of development of this carbonization process, the smoke generation from the carbonization process was a major issue. And it was solved over the period with new and modification of charring coking kiln that laid the foundation for the modern coke blast furnace.

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Products of Carbonization }

• Coke

- → Coke is an essential product of carbonization, used as energy dense solid fuel in various applications.
- → Several types of coke produced through carbonization of coal by varying the process conditions and coal blends.
- → Metallurgical coke (used in blast furnace in iron and steel industry), Low-volatile steam coke, Foundry coke, Blast furnace coke, etc.
- → Coke is used for briquetting such as Phurnacite briquettes, Pitch-bound briquettes, etc.)
- → Gases of high calorific value are obtained by low-temperature or medium-temperature carbonization of coal called coal gas. p
- $\mapsto$  Coal gas is the mixture of CH<sub>4</sub>, H<sub>2</sub>, CO, CO<sub>2</sub>, and HCs.)
- + The gases obtained by the carbonization of any given coal change in a progressive manner with increasing temperature.
- $\mapsto$  It is used for heating, lighting, and power generation.

20 Indian Institute of technology Guwahati

• Coal gas

And the major product of the carbonization process includes coke, coal gas and coal tar. In that this coke is an essential product of the carbonization process and it is used as an energy dense solid fuel in various applications. And accordingly several types of the coke can be produced through the carbonization of the coal by varying the process condition and the coal blends.

And which includes the metallurgical coke mainly used in the blast furnace in iron and the steel industry. It can be also used to produce low volatile steam coke, foundry coke, blast furnace coke etc. Moreover, the coke produced from the carbonization process is also used for the briquetting purpose. Coal gas which is a high calorific value gas can be obtained by low temperature or the medium temperature carbonization of coal. And it is termed as a coal gas and it is a mixture of methane, hydrogen, carbon monoxide, carbon dioxide and other hydrocarbons.

And these gases obtained during the carbonization of the any given coal sample it changes in progressive manner with increasing the temperature. And this gas is used for heating, lighting and the power generation.

- Coal tar
  - → Coal tar is the volatile material that is released during the thermal decomposition of coal and which condenses at room temperature.
  - → The tar may be composed of solid material (pitch) and liquid or semisolid materials (coal tar).

50

- → Coal tar is used as source of precursors for the synthesis of dyes as well as raw materials for the production of solvents, pharmaceuticals, synthetic fibers, and plastics.
- $\mapsto$  Coal tar can also be upgraded to gasoline and other liquid fuels.
- → Benzene, toluene, and xylene (BTX) are extracted from coal tar, which have various industrial applications.
- → Naphthalene is also obtained from coal tar, which is used as precursor for dyes, resins, and surfactants.
- $\mapsto$  (Coal oil, also known as coal distillate, is obtained after further refining of coal tar.

21 🚱 भारतीय प्रौद्योगिकी संस्थान गुवाहाटी INDIAN INSTITUTE OF TECHNOLOGY GUWAHAT

Similarly, this coal tar it is a volatile material that is released during the thermal decomposition of coal and which condenses at room temperature. The tar may be composed of solid material that is called as a pitch and liquid or semi-solid material that is coal tar. And this coal tar it is used as a precursor for the synthesis of dyes as well as raw material for the production of solvents, synthetic fibers and plastics.

Even this coal tar it can be upgraded to produce gasoline and other liquid fuels. For example, the benzene, toluene and xylene can be extracted from coal tar which has very high industrial applications. Even the naphthalene is also obtained from coal tar which is used as a precursor for dyes, resins and surfactants. Even the coal oil which is also known as coal distillate can be obtained after further refining of this coal tar.

# (**Refer slide time:** 32:32)

#### Physicochemical Aspects of Carbonization

• Carbonization can be represented as:

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(C_{\text{organic}} \rightarrow C_{\text{coke/char/carbon}} + Liquids) + Gases
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- The thermal decomposition of coal is a complex sequence of events, which can be described in terms of several important physicochemical changes.
- The carbonization temperature ranges can be different for coal and biomass.
- Biomass, contains less complex organic matter and can be converted into biochar or charcoal at lower temperatures.
- Coal, being a fossil fuel that has undergone millions of years of geological processes, requires higher temperatures to release its carbon content.

Speight, The chemistry and technology of coal, CRC Press 2013.

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So now let us try to understand the physicochemical aspects of the carbonization process in which organic carbon contained in the given sample is carbonized to produce coke, char or carbon along with the liquid and gaseous products. Since this thermal decomposition of the coal is a very complex sequence of the event which can be described in terms of the several important physicochemical changes.

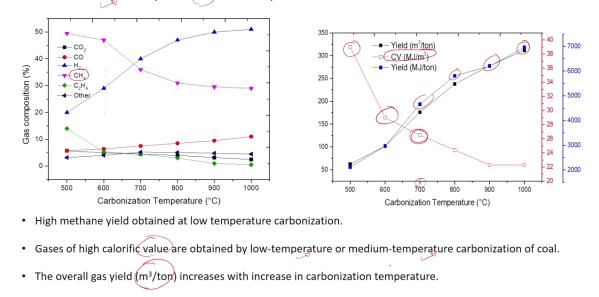
The carbonization temperature it also ranges and can be different for coal sample as well as for the biomass sample. As we know that biomass contains less complex organic matter and hence can be converted into biochar or charcoal at relatively lower temperature. But coal being a fossil fuel has undergone millions of years of geological processes and hence it requires relatively higher temperature to release its carbon content.

# (**Refer slide time:** 33:53)

Process	Temp. range	Processes/changes	Major Products
-	100 – 200 °C	Evolution of residual moisture	H <sub>2</sub> O
-	200 – 500 °C	Evolution of light gases begins (Pyrolysis)	CO, CO <sub>2</sub> , light HC, tar
-	400 – 500 °C	Coal become soft and fluid (coal plasticity). Cross- linking reactions begins (pyrolysis)	High tar yield, Combustible gas, HCs, H <sub>2</sub> S, NH <sub>3</sub>
Low temperature carbonization	500 – 700 °C	Coke produced by Coalite process (650 °C) & Rexco process (700 °C) in vertical tube/retorts.	Reactive coke, Gases, High tar yield, Aqueous liquid
Medium temperature carbonization	₹700 - 900 °C}	Phurnacite briquettes, Pitch-bound briquettes, Low-volatile steam coke processes carried out.	Reactive coke, Domestic briquettes, High tar yield
High temperature Carbonization	900 – 1100 °C	Foundry coke (900 °C), Blast furnace coke (950 – . 1050 °C).	Hard & unreactive coke, Metallurgical coke
Plasma } (	> 1650 °C	- 1	Acetylene, carbon black
23 🛞 भारतीय प्रौद्योगिकी संस्थान गुवाहाटी INDIAN INSTITUTE OF TECHNOLOGY GUWAHA	Π		Courtesy: Speight. The chemistry and technology of coal. CRC Press 2013.

And because of these different carbonization temperature ranges, the carbonization process is classified as low temperature carbonization process, medium temperature carbonization, high temperature carbonization process and plasma carbonization process. In case of low temperature carbonization process, the low temperature carbonization process occurs in the temperature range of 500 to 700 °C. And it produces coke by these two different processes in vertical tube or vertical retorts and it majorly produce reactive coke, gases, tar and aqueous liquid as a product. While the medium temperature carbonization process occur in the temperature range of 700 to 900 °C and mainly carried out using low volatile steam coke process. And the major product of this process includes reactive coke, domestic briquettes and also it gives high tar yield. High temperature carbonization process, it occurs in the temperature range of 900 to 1100 °C.

And in this process the coke is produced by different processes like foundry coke or blast furnace coke operation. And the major product obtained from this process includes hard and unreactive coke and the metallurgical coke. However in case of plasma carbonization process it carries out in the temperature more than 1600 °C and the major product obtained from plasma carbonization process includes acetylene and carbon black. And this table provides the detailed information about the different carbonization process which can be carried out in different temperature ranges along with its major products.



Effect of Carbonization Temperature on Gas Composition & Yields

And these two graph here provides the information about the effect of carbonization temperature on gas composition and the yield.

So, in this case the high methane yield is obtained at low temperature carbonization while the gases of high caloric value are obtained at low temperature or medium temperature carbonization of coal. And the overall gas yield in meter cube per ton is increases with increase in the carbonization temperature. And therefore, the suitable temperature range needs to be selected during the carbonization process to obtain the sufficient product yield.

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#### 2 Coal Gasification

- The coal gasification is thermochemical conversion of coal to produce combustible gases.
- Coal gasification process involve several chemical reactions carried out under high temperature (400–1500 °C) and pressure (0-40 bar), which break and oxidize hydrocarbons into a gaseous product, called *synthesis gas* (syngas).
- Gasification agents: air, oxygen-enriched air, or oxygen. Sometimes steam is added as source of external heat, called *allothermal gasification*.
- Gasification products: Syngas, hydrogen sulfide, various compounds of sulfur and carbon, ammonia, light hydrocarbons, heavy hydrocarbons (tars), and ash/slag.
- Gasification has been used for many years as an alternative to combustion of solid or liquid fuels.
- Gaseous fuel is convenient as it is easier to clean gaseous mixtures than the solid or high-viscosity liquid fuels, as well as the solid and liquid fuels cause severe fouling or corrosion in fuel system.

istry and technology of coal, CRC Press 2013

25 🚯 भारतीय त्रौद्योगिकी संस्थान गुवाहाटी INDIAN INSTITUTE OF TECHNOLOGY GUWAHAT

So, another important process in the solid fuel is coal gasification. Coal gasification is a thermo chemical conversion of coal to produce combustible gases and this is one of the most widely used process which involves the chemical reaction which are carried out under high temperature that is in the range of 400-1500°C and pressure between 0-40 bar.

And during this condition it breaks down and oxidize the hydrocarbon into gaseous product called synthesis gas and commonly referred as syngas. The gasification agent also termed as oxidizing agent used during the gasification process are air, oxygen rich air or oxygen and sometimes the steam is added as a source of external heat called allothermal gasification. And the product of this gasification process includes syngas, hydrogen sulphide, various compounds of sulphur and carbon, ammonia, light hydrocarbon and heavy hydrocarbon along with that it also produces ash that is also called as slag. And this process of gasification it has been used for many years as an alternative to combustion of solid and the liquid fuels. And this gaseous fuel is more convenient to handle as it is easier to clean gaseous mixture than the solid and the highly viscous liquid fuels as well as the solid and the liquid fuels cause severe fouling or corrosion in the fuel system.

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#### Gasification Products

#### Synthesis gas (Syngas)

- The syngas produced by coal gasification contains carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), hydrogen (H<sub>2</sub>), methane (CH<sub>4</sub>), water, and some pollutants such as particulate matter and sulfur compounds.
- Therefore the syngas must be first cleaned from these pollutants before further use.
- In coal gasification process, the oxygen is not separated from the air, and as a result a gas product containing high amount of N<sub>2</sub> gas is formed, called as a *"low-heat-content gas*".
- In coal gasification process) a  $N_2$  barrier (such as the use of pure  $O_2$ ) is applied to keep diluent  $N_2$  out of the system, as a result a product is formed containing mainly CO and  $H_2$  called as a "medium-heat-content gas".

26 INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI

And the product of this gasification process is mainly a synthesis gas; it is commonly referred as syngas. The syngas which is produced by coal gasification it contains carbon monoxide, carbon dioxide, hydrogen and methane. Along with that it also contains water and some pollutants such as particulate matter and sulphur compounds. And for that reason the syngas it must be clean from these pollutants before further use. And in case during the coal gasification process, if the oxygen is not separated from the air, then the gases product contain high amount of nitrogen in its composition and the gas produced during such operation called as low heat content gas.

And for that reason in coal gasification process, a nitrogen barrier is applied to keep this diluent nitrogen out of the product mix. As a result, a product is formed containing mainly carbon monoxide and hydrogen and called as a medium heat content gas. And because of that a suitable oxidizer need to be selected during the coal gasification process to obtain a medium heat contained gas which mainly consists of carbon monoxide and hydrogen.

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- *High-heat-content gas* is essentially pure methane (with traces of H<sub>2</sub>) and often referred to as *synthetic ngtural gas* or *substitute natural gas (SNG)*. To qualify as SNG, it must contain at least 95% methane.
- (High-heat content gas is produced through methanation reaction :  $(CO + 3 H_2) \rightarrow CH_4 + (H_2O)$
- The H<sub>2</sub> is used in excess to ensure complete conversion of toxic CO to CH<sub>4</sub>. This excess quantity of H<sub>2</sub> lowers the heat content to a small degree.

	Syngas type	LHV (MJ/m <sup>3</sup> )	Characteristics	Use
J	Low-heat-content gas	5.6-11.2	High N <sub>2</sub> (~50%), Small qty. of H <sub>2</sub> , CO, CO <sub>2</sub> and trace gases, like CH <sub>4</sub> .	Fuel gas; Raw material for ammonia, methanol, and other chemical synthesis.
Ч	Medium-heat-content gas	11.2-20.5	Predominantly CO and $(H_2)$ small amount of $CH_4$ and other incombustible gases.	Fuel for boiler; Fuel in CHP cycle; Raw material for methane (by methanation), higher hydrocarbons (by FT synthesis), methanol, and a variety of synthetic chemicals.
L	High-heat-content gas	36.5-40.2	Almost pure methane (CH <sub>4</sub> )	Synthetic or substitute natural gas (SNG)
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However, a high heat contained gas is essentially a pure methane with traces of hydrogen and it is often referred to as synthetic natural gas or substitute natural gas. And this type of high heat content gas is produced through methanation reaction in which carbon monoxide reacts with the hydrogen to form methane and water as a product.

And this table here, it provides the information about these different types of syngas that is low heat content gas, medium heat content gas and high heat content gas. In case of low heat content gas, its caloric value ranges from 5 to 11, and is majorly consist of high amount of nitrogen that is close to 50% and small quantity of hydrogen, carbon monoxide,  $CO_2$  and traces of gases like methane. However, this low heat content gas can be used as a fuel gas as well as raw material for the ammonia, methanol and synthesis of the other chemicals. In case of medium heat content gas, its lower heating value ranges from 11 to 20 mega joule per meter cube and it predominantly consists of carbon monoxide and hydrogen.

Along with that it also contains small amount of methane and other incombustible gases. And this medium heat content gas can be used as a fuel for boiler. Also, it can be used as a raw material for methane by methanation reaction, higher hydrocarbon synthesis by FT synthesis process. It can be also used for the synthesis of methanol and variety of other synthetic chemicals. However, this high heat content gas has a low heating value in the range of 36 to 40 and it is almost a pure methane and it can be used as a substitute natural gas and commonly referred as SNG.

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The syngas from coal gasification:

Gas name	Syngas type	Composition (v/v)
Producer gas	Low-heat-content gas. Produced by coal gasification with air.	28% CO, 55% N <sub>2</sub> , 12% H <sub>2</sub> ) 5% CH <sub>4</sub> , and CO <sub>2</sub>
Water gas	Medium-heat-content gas. Produced by passing steam over hot coal bed.	$\left\{ 50\% \text{ H}_2, 40\% \text{ CO}, \text{ small amount of } N_2 \text{ and } \text{CO}_2 \right\}$
Town gas	Medium-heat-content gas. Produced in the coke ovens	55% H <sub>2</sub> , 27% CH <sub>4</sub> , 6% CO, 10% N <sub>2</sub> 2% CO <sub>2</sub>
Synthetic natural ga	s High-heat-content gas Methane. Produced by reacting CO or C with $H_2$ .	Almost pure methane (CH <sub>4</sub> )
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And this table here it depicts the information about the different syngas type produced during the coal gasification process. So, producer gas also termed as a low heat content gas is produced by coal gasification with air and its composition mainly consists of 28% carbon monoxide, 55% nitrogen, 12% hydrogen, 5% methane and CO<sub>2</sub>. While water gas which is a medium heat content gas produced by passing steam over hot coal bed. And its composition mainly consists of 50 percent hydrogen, 40 percent carbon monoxide and small amount of nitrogen and carbon dioxide.

While town gas which is also a medium heat content gas produced by cocoons. And mainly consists of 55 percent hydrogen, 27 percent methane, 6 percent carbon monoxide, 10 percent nitrogen and 2 percent of carbon dioxide. While this synthetic natural gas also referred as high heat content gas. That is methane produced by reacting carbon monoxide or carbon with hydrogen and it mostly consists of pure methane. And this gives detailed information about the different types of the syngas and their gas name. So, as we discussed before the syngas that is the synthetic gas produced during this coal gasification process consists of traces of other gases.

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**Coal Gasification By-Products and Separation Methods** 

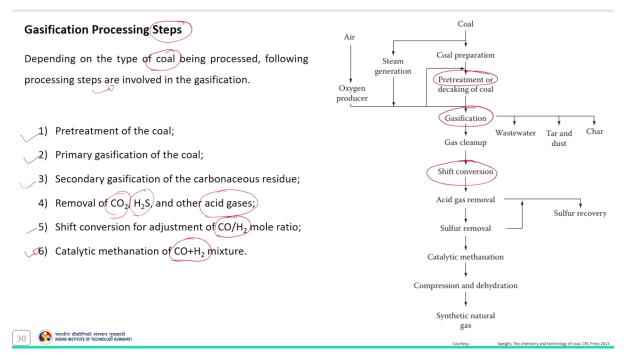
By-Product	Cleaning / Separation Method
CO <sub>2</sub>	Acid gas scrubbing
H <sub>2</sub> S	Acid gas scrubbing, Stretford process, Amine treatment, Rectisol process
COS, CS <sub>2</sub>	Removed with H <sub>2</sub> S
NH <sub>3</sub>	Scrubbing, Ammonia stripping
HF, HCI, HCN	Scrubbing
Suspended particles	Cyclone separators, Electrostatic precipitators, Scrubbing
Ash	Gravity settling
Tar, Coal oils	Scrubbing

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Apart from that it also contains certain other impurities which need to be removed before further use. And for that a different cleaning and separation method need to be used to separate out these pollutant and traces of other gases from these different gases. For example, the byproducts  $CO_2$  can be cleaned using acid gas scrubbing method while the H<sub>2</sub>S can be separated using acid gas scrubbing or amine treatment method. This  $CS_2$ , it can be removed along with the H<sub>2</sub>S.

NH<sub>3</sub>, it can be removed or separated by scrubbing or ammonia stripping method. These gases, it can be removed by scrubbing operation. Suspended particles, it can be separated or removed using cyclone separators, electrostatic or scrubbing method. And the ash produced during this process can be cleaned or separated by gravity settling method, while the tar and coal oils can be cleaned or separated by the scrubbing method. So, likewise this different cleaning or the separation method needs to be used to remove these byproduct gases from the product mix.

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So, after learning about the gasification process as well as the coal gasification byproducts and separation method, let us move on to the next topic that is gasification processing steps. So, depending on the type of the coal being processed, following processing steps are involved in the gasification process.

That is pretreatment of coal, primary gasification of the coal, secondary gasification of the carbonaceous residue, removal of carbon dioxide, hydrogen sulphide and other acid gases and then the shift conversion for the adjustment of carbon monoxide to hydrogen molar ratio followed by the catalytic methanation of carbon monoxide and hydrogen mixture. Alongside this chart here, it provides the information about the different processing steps which are involved in the gasification process.

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1. Pre-treatment
• Gasification technologies require some pre-treatment of the coal feedstock for its suitability for the process.
e.g. The Lurgi process can accept "lump" coal, but not a caking coal. Otherwise, the caking coal form agglomerate plastic mass in the bottom of a gasifier and results in plug up the system thereby reducing process efficiency. Therefore, a pre-treatment is necessary to reduce caking properties of coal.
2. Primary gasification of the coal
<ul> <li>Primary gasification involves thermal decomposition of the raw coal via various chemical processes and many of these reactions involve pressures ranging from atmospheric to 1000 psi.</li> <li>A low-heat-content gas is formed along with solid char product.</li> </ul>
3. Secondary gasification
• Secondary gasification involves the gasification of char (or carbonaceous residue) from the primary gasifier.
• This is done by reacting hot char with water vapors: $C_{char} + H_2O \rightarrow CO + H_2$
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Pretreatment of the feed sample: So, the gasification technology it requires certain pretreatment of the coal feedstock for its suitability for the process. For example, here the Lurgi process can accept lump coal but not a caking coal. Because in case if the caking coal is used during the gasification process then it form agglomerate and plastic mass in the bottom of a gasifier and it results in plug up the system thereby reducing the process efficiency.

And therefore, a predetermined step is essential to reduce the caking properties of coal during the operation. Primary gasification of a coal, it involves the thermal decomposition of raw coal via various chemical processes and many of these reactions involve pressures ranging from atmospheric to even 1000 psi. And in this process a low heat contained gas is formed along with the solid char as a product. And the solid char which is formed during this primary gasification step is used as a raw material for the secondary gasification. Because the secondary gasification step it involves the gasification of char that is a carbonaceous residue from the primary gasifier.

That means the solid char which is formed during this primary gasification step, it can act as a raw material for the secondary gasification step where it involves the gasification of char or we can say a carbonaceous residue. And this is done by reacting this hot char which is formed during this primary gasification step with water vapors. So, likewise this reaction if you can see here this char it undergoes the secondary gasification with water vapor produces carbon monoxide and hydrogen as a product.

### (Refer slide time: 51:26)

- 4. Removal of  $CO_2$ ,  $H_2S_2$  and other acid gases
- CO<sub>2</sub>, H<sub>2</sub>S and acid gases can be removed by using several methods including absorption, adsorption and chemical reactions.

e.g. Benfield process of solvent absorption involve the reaction of 20%–30% potassium carbonate in hot water solution + catalyst with  $H_2S$  and  $CO_2$  to clean the syngas.

- 5. Shift conversion for adjustment of CO/H<sub>2</sub> mole ratio
- Gaseous product from a gasifier generally contains large amounts of CO and H<sub>2</sub>, and traces of other gases.
- If CO and H<sub>2</sub> present in 1:3 mole ratio, it can undergo catalytic methanation: CO +  $3H_2 \neq CH_4$  +  $H_2O$
- Therefore, adjustment of CO/H<sub>2</sub> mole ratio is required to bring it to the ideal ratio of 1:3.)
- This can be accomplished by the waste gas shift (shift conversion) reaction  $(CO + H_2) \neq CO_2 + H_2$

#### 32 🚱 भारतीय प्रौद्योगिकी संस्थान गुवाहाटी

So, another important step in the gasification process is the removal of carbon dioxide, hydrogen sulphide and other acid gases. And this can be removed by using several methods as just discussed few slides back including the absorption, adsorption and chemical reaction method. For example, a solvent absorption involves the reaction of 20 to 30% of the potassium carbonate in hot water solution plus catalyst and it reacts with the  $H_2S$  and  $CO_2$  to clean the syngas. So, this is one of the methods. However, several different separation methods and cleaning process are available to clean the syngas. Followed by that is the shift conversion for the adjustment of carbon to hydrogen molar ratio. Since we know the gaseous product from the gasifier it mainly contains large amount of the carbon monoxide and the hydrogen along with the traces of other gases.

And if this carbon monoxide and hydrogen it is present in 1:3 molar ratios it can undergo catalytic methanation process to form methane. And in case if the CO and hydrogen is not present in the proper molar ratio, then the adjustment of carbon to hydrogen molar ratio is required to bring it to the ideal ratio of 1:3 because this is the ideal ratio for the catalytic

methanation reaction. And this can be accomplished by the water gas shift conversion reaction where the carbon monoxide reacts with the water vapor to form carbon dioxide and hydrogen.

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6. Catalytic methanation of CO+H<sub>2</sub> mixture / Hydrogasification of C+H<sub>2</sub>

 $C + H_2O \rightleftharpoons CO + H_2 - 131 \text{ kJ/mol}$ 

• Catalytic metanation can be used to produce  $CH_4$ , whereas a number of processes use hydrogasification.  $CO + 3H_2 \rightleftharpoons CH_4 + H_2O + 206 \text{ kJ/mol}$  ... Methanation  $UC + 2H_2 \rightleftharpoons CH_4 + (74.8 \text{ kJ/mol})$  ... Hydrogasification

•  $(H_2$ -rich gas for hydrogasification can be manufactured by reacting the char) from hydrogasifier with steam.

• The heat released by methane formation in the primary gasifier is at a sufficiently high temperature, which can be used in the water-gas reaction to produce  $H_2$ , so that less  $O_2$  is used to produce heat.

... Water-gas or steam

• Hence, less heat is lost in the low-temperature methanation step, thereby leading to a higher overall process efficiency.

#### 33 भारतीय प्रौद्योगिकी संस्थान गुवाहाटी INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI

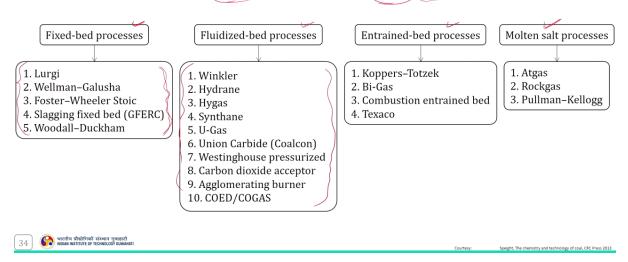
And the next is the catalytic methanation of carbon monoxide and hydrogen mixture or we can say the hydro gasification of carbon and hydrogen. This catalytic methanation step it can be used to produce methane whereas in number of processes a hydro gasification step is used. Now if you look at this particular reaction here it indicates the methanation reaction where the carbon monoxide reacts with the hydrogen to form methane and during this process it releases significant amount of the heat. The hydro gasification reaction in which the carbon reacts with the hydrogen to form methane and it also releases good amount of the heat during the hydro gasification step.

And this hydrogen rich gas for the hydro gasification step it can be manufactured by reacting the char from the hydro gasifier with steam in which the char reacts with the steam to form carbon monoxide and hydrogen. However, this step absorb significant amount of the heat. And as we commonly know this is a water gas or steam reaction and during this step good amount of heat need to be added to convert this char and steam into carbon monoxide and hydrogen and this is termed as water gas or steam reaction. And the heat released by methane formation in the primary gasifier is at sufficiently high temperature which can be used in the water-gas reaction that is in this particular step here to produce hydrogen so that less oxygen is used to produce the heat. Because if the heat is not transferred from this primary gasifier to water gas reaction then in that case excess oxygen need to be used to produce the required heat for the water gas reaction. And hence less heat is lost in low temperature methanation step that is in this step thereby leading to higher overall process efficiency. And this provides the details about the gasification processing steps.

# (Refer slide time: 56:12)

#### **Types of Gasification Processes and Reactors**

- Several processes have been developed for gasification of coal, since the use of coal gas for lighting purpose.
- These gasification processes are classified according to the type of reactor vessel used.



So, likewise several processes have been developed for the gasification of coal since the use of coal gas for the lighting purpose is one of the prime motives of this particular process. So, this gasification process are classified according to the type of reactor or the vessel used during the gasification operation which includes the fixed bed process, fluidized bed process, entrained bed process and molten salt process. And according to these processes the subclassification of these different processes is also given here. Although we will not be discussing in detail about these types of reactor, but it is just provided here for the information purpose. And this is all about the coal carbonization and the coal gasification process. So, in the next lecture, we will discuss about the coal liquefaction, combustion process, combustion stoichiometry and the combustion chemistry.

Thank you.