Technologies for Clean and Renewable Energy Production

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Lecture-08
Gasification of Coal- 2

Hi friends now we will discuss on the topic gasification of coal. This is a second part of this topic in the first part we have discussed about the gasification process, its mechanism, then different types of reactors applicable for coal gasification and their comparison. Now we will see how the syngas produced after gasification can be made suitable for different types of downstream application.

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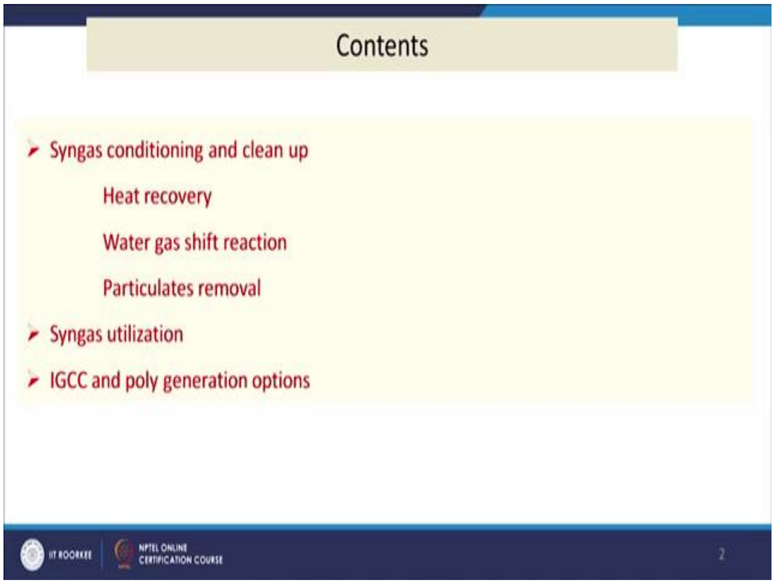

Contents

- Syngas conditioning and clean up
  - Heat recovery
  - Water gas shift reaction
  - Particulates removal
- Syngas utilization
- IGCC and poly generation options

And the content of this class is syngas conditioning and cleanup and then syngas utilization and IGCC and poly generation options. As we have seen in the previous class that when syngas is produced in the gasifier its temperature is very high and it contains number of impurities like say particulates, acid gases like SOx, carbon dioxide, H_2S etc. So, these need to be removed and another fact is that for different type of downstream applications we need different type of syngas quality.

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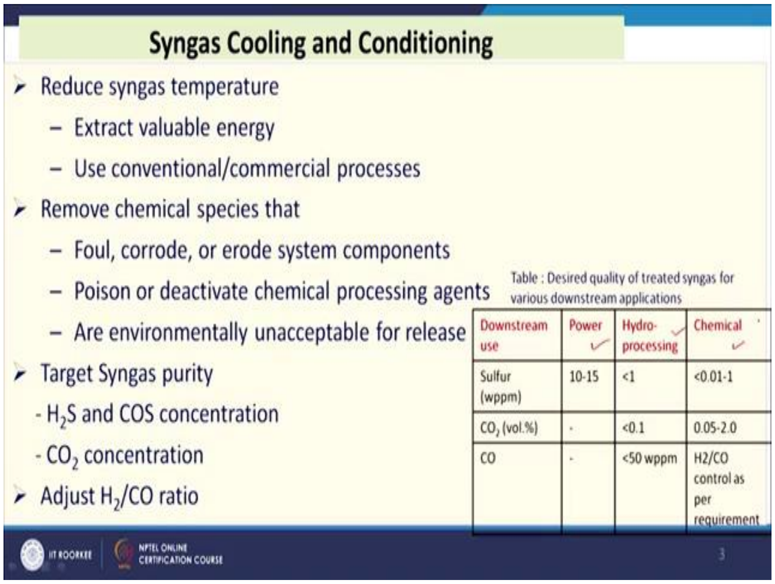

Syngas Cooling and Conditioning

- Reduce syngas temperature
  - Extract valuable energy
  - Use conventional/commercial processes
- Remove chemical species that
  - Foul, corrode, or erode system components
  - Poison or deactivate chemical processing agents
  - Are environmentally unacceptable for release
- Target Syngas purity
  - H_2S and COS concentration
  - CO_2 concentration
- Adjust H_2/CO ratio

Table : Desired quality of treated syngas for various downstream applications

Downstream use	Power ✓	Hydro-processing ✓	Chemical ✓
Sulfur (wppm)	10-15	<1	<0.01-1
CO_2 (vol.%)	-	<0.1	0.05-2.0
CO	-	<50 wppm	H2/CO control as per requirement

So, as shown here in this table if we see for power application for hydro processing and for chemical applications of the syngas we need different types of quality here sulphur, CO_2 and CO concentration is provided for 3 different applications so you see here sulphur for power application requirement is 10 to 15 ppm weight basis whereas for hydro processing it should be less than 1 ppm and for chemical less than 0.01 to 1 ppm.

So, the degree of removal of sulphur compounds from the syngas is required in different extent for carbon monoxide carbon monoxide we see for power application there is no such requirement where for hydro processing it is, it should be less than 50 ppm on weight basis. And for chemical applications the carbon monoxide and hydrogen ratio should be maintained as per requirement. Different applications have different requirement of hydrogen is to CO ratio.

But if we see the CO and H_2 composition in the raw syngas then CO is almost 2 times more than that of hydrogen but in downstream applications in some cases even we need the reverse ratio that is H_2 is to CO as 2, so some conditioning or conversion of CO to H_2 is required and that is why now in this class we will discuss how we can achieve this target. How the high temperatures syngas can be used and cooled to lower temperature heat recovery can be done.

And then the acid gases can be removed to make it suitable for different downstream applications to remove the pollutants which create problems during the processing and to maintain the H_2 CO ratio. So, we should we here reduce syngas temperature during cooling we need to reduce the syngas temperature and we need to extract the valuable energy from it. And chemicals are removed which can foul, corrode or erode system components or which can poison or deactivate chemical processing agents or are environmentally unacceptable.

Now we will see how the syngas can be cooled there are basically two mode of operation one is quench mode operation and another is boiler mode.

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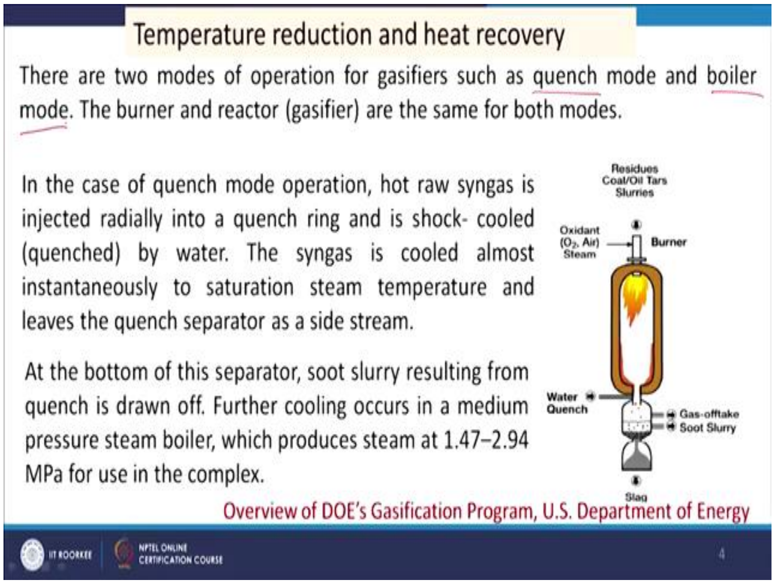

Temperature reduction and heat recovery

There are two modes of operation for gasifiers such as quench mode and boiler mode. The burner and reactor (gasifier) are the same for both modes.

In the case of quench mode operation, hot raw syngas is injected radially into a quench ring and is shock- cooled (quenched) by water. The syngas is cooled almost instantaneously to saturation steam temperature and leaves the quench separator as a side stream.

At the bottom of this separator, soot slurry resulting from quench is drawn off. Further cooling occurs in a medium pressure steam boiler, which produces steam at 1.47–2.94 MPa for use in the complex.

Overview of DOE's Gasification Program, U.S. Department of Energy

So, on is quench mode and another is boiler mode, in both the mode the reactor part is similar but the difference is the cooling process. So, in the quench mode the syngas which is produced here is first pass through the quench ring and it is cooled by shock. The temperature of the syngas is reduced to the temperature of saturated steam then it goes from the side stream. And the slag or ash materials comes down.

This way we can reduce the high temperatures syngas to a lower value. And in this case we see 1.47 to 2.94 mega Pascal steam can be produced.

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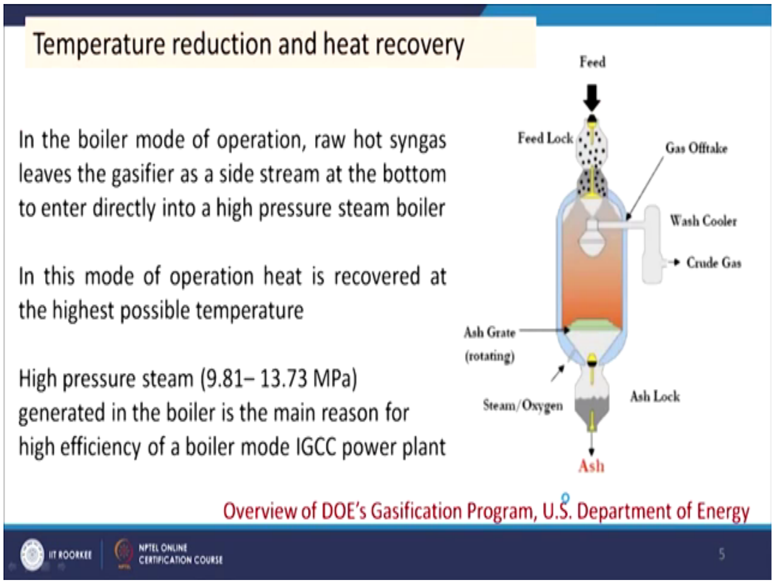

Temperature reduction and heat recovery

In the boiler mode of operation, raw hot syngas leaves the gasifier as a side stream at the bottom to enter directly into a high pressure steam boiler

In this mode of operation heat is recovered at the highest possible temperature

High pressure steam (9.81– 13.73 MPa) generated in the boiler is the main reason for high efficiency of a boiler mode IGCC power plant

Overview of DOE's Gasification Program, U.S. Department of Energy

Now in case of boiler mode the syngas is produced here it is going from the side and ash is coming bottom at the bottom. So, there is no direct quenching but it is sent to a boiler for heat recovery and exchange of heat as a result the syngas temperature reduces. So, this process gives us some advantage we can get high temperature steam here with respect to the quench mode and high pressure steam here with respect to the quench mode.

We see there are 9.81 to 13.73 mega Pascal steam can be generated and as you know higher the pressure in the steam and higher the temperature there is a possibility to have more efficiency in the turbine. So, that is why this mode of operation that is boiler mode of operation is preferred in IGCC application. Now we will see the how the particulates can be removed from the syngas.

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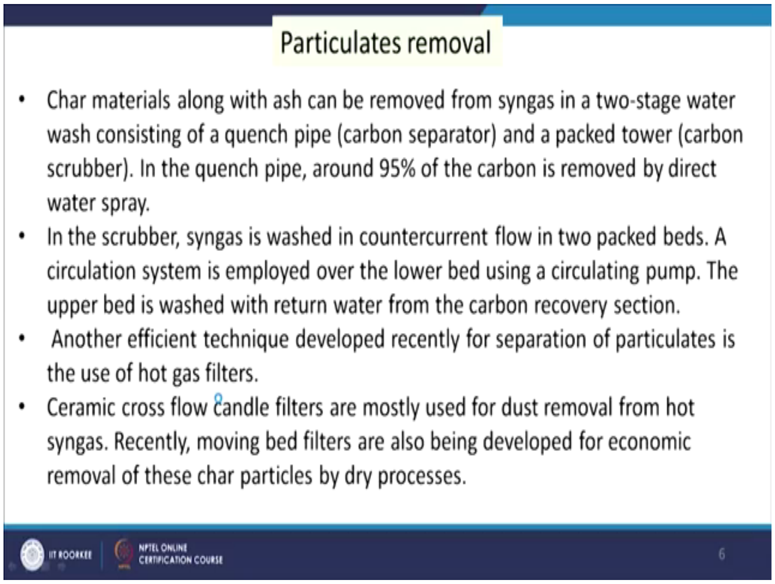

Particulates removal

- Char materials along with ash can be removed from syngas in a two-stage water wash consisting of a quench pipe (carbon separator) and a packed tower (carbon scrubber). In the quench pipe, around 95% of the carbon is removed by direct water spray.
- In the scrubber, syngas is washed in countercurrent flow in two packed beds. A circulation system is employed over the lower bed using a circulating pump. The upper bed is washed with return water from the carbon recovery section.
- Another efficient technique developed recently for separation of particulates is the use of hot gas filters.
- Ceramic cross flow candle filters are mostly used for dust removal from hot syngas. Recently, moving bed filters are also being developed for economic removal of these char particles by dry processes.

As you know the some of the reactor configurations uses very fine particles of coal and those fine particles can be carried over if it is not completely burned or in some applications also tar particles comes. So, those particles we need to remove, so for the removal of those particles there are some configuration that is here char materials along with ash can be removed from syngas in two-stage water wash consisting of a quench pipe carbon separator and a packed tower.

Just we are spraying water and removing the particulates in a packed tower. In quench pipe around 95% of the carbon is removed by direct water spray. So, these are two basic operations through which the particulates are removed. So, you see in this case the temperature of the syngas should be down made down prior to its application. Another way of efforts are also there to use different types of oxides at high temperature to remove the gases or we can use ceramic cross-flow candle filters to remove the particulates at higher temperature.

So, high temperature particulate separation this technology is being developed and extensive research is also going on around the globe for this application. Now by spraying water we can remove the particulates but there are a number of types of spray systems.

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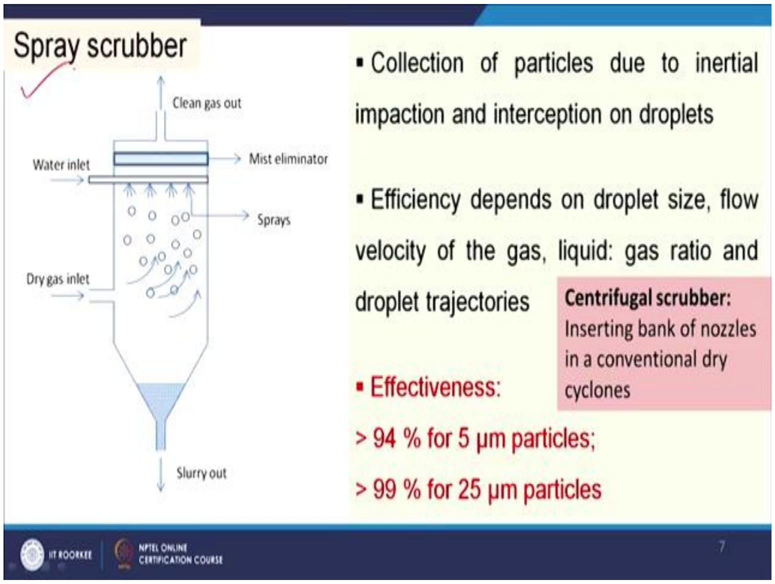

Spray scrubber

- Collection of particles due to inertial impaction and interception on droplets
- Efficiency depends on droplet size, flow velocity of the gas, liquid: gas ratio and droplet trajectories
- Effectiveness:

> 94 % for 5 µm particles;

> 99 % for 25 µm particles

Centrifugal scrubber: Inserting bank of nozzles in a conventional dry cyclones

So, this is here spray scrubber so in this very scrubber so dry gas inlet at the bottom and water injection at the top and then there will be interaction between the droplets as well as the particulates. So, the mechanism is the inertial impaction and interception on the droplets this is the mechanism of the separations of the particulates from the syngas in presence of droplets of the water. So, it will settle and in this case no packed bed is used only spray scrubber and its efficiency say 94% for 5 micrometer particles.

And greater than 99% for 25 micrometer particles and the efficiency of this system will depend on droplet size and flow velocity of the gas and liquid is to gas ratio. These are the factors which influence the efficiency of the system.

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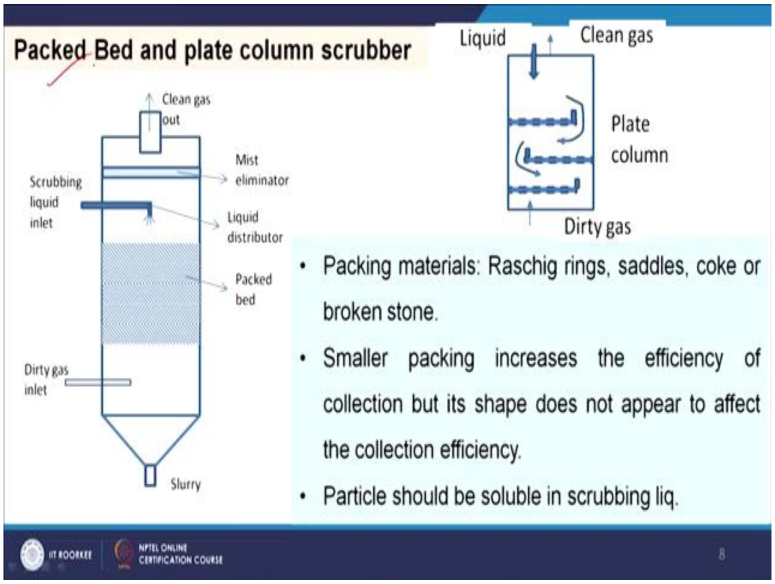

Packed Bed and plate column scrubber

- Packing materials: Raschig rings, saddles, coke or broken stone.
- Smaller packing increases the efficiency of collection but its shape does not appear to affect the collection efficiency.
- Particle should be soluble in scrubbing liq.

Then packed bed and plate column another type of spray system also used in this packed bed one packing material is used like say raschig rings, saddles, coke or broken stone, so these are normally used for the capturing of the particulates in this. It is a dry gas will come here and again from the clean gas will goes up and spray system will be there but we have one packed bed. So, this is one type of design.

Another type of design dry gas or dirty gas from the bottom from the top clean gas and liquid from the top and there are a number of plates. So, plates overflow liquid will come here again plate overflow liquid will come here plate overflow liquid will come so that way the interactions of gas and liquid takes place liquid droplets and particulates separates. So, this system also help to remove some gas molecules from the syngas.

Now we will see how the acid gas components can be removed acid gas components like say SOx, carbon dioxide, H_2S etc present in the syngas that can be removed through specific treatment steps.

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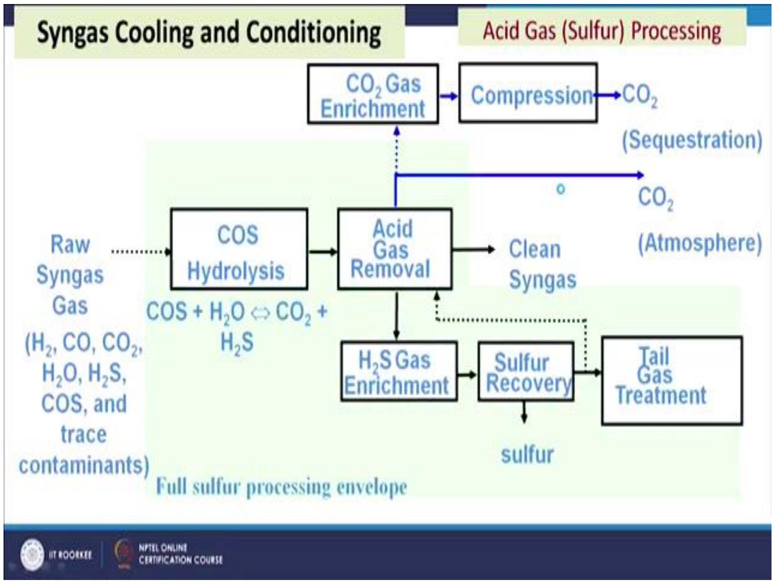

Syngas Cooling and Conditioning

Acid Gas (Sulfur) Processing

Raw Syngas Gas (H_2, CO, CO_2, H_2O, H_2S, COS, and trace contaminants)

COS Hydrolysis

$COS + H_2O \Leftrightarrow CO_2 + H_2S$

Acid Gas Removal

Clean Syngas

CO_2 Gas Enrichment

Compression

CO_2 (Sequestration)

CO_2 (Atmosphere)

H_2S Gas Enrichment

Sulfur Recovery

sulfur

Tail Gas Treatment

Full sulfur processing envelope

So, this flow sheet shows us the raw syngas which is having hydrogen, carbon monoxide, carbon dioxide, H_2O, H_2S, COS and trace contaminants so the first the COS reacts with H_2O to form H_2S and CO_2 so that is hydrolysis of COS then H_2S and CO_2 acid gas components we need to remove. So, how we can remove it, carbon dioxide removal if you can selectively separate the carbon dioxide then that can be enriched and it can be sequestered.

So, carbon dioxide enrichment and then compression and carbon dioxide sequestration so one way we can get. On the other way we have H_2S so we can remove the H_2S enrichment specifically then we use them selectively and then after selective separation of H_2S we can use this gas for sulphur recovery and we can get sulphur and once we can get sulphur we can produce sulphuric acid. So, after removal of sulphur or H_2S, now we can go for further treatment of the tail gas.

So, this is the flow sheet for acid gas removal but now we will see how this can be done. So, the H_2S and CO_2 removal has been made by absorption and adsorption based technology.

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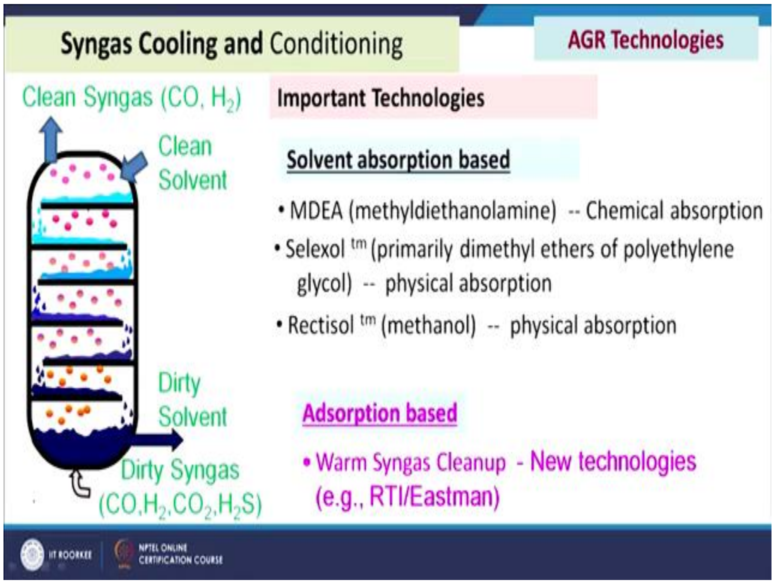

Syngas Cooling and Conditioning

AGR Technologies

Important Technologies

Solvent absorption based

- MDEA (methyldiethanolamine) -- Chemical absorption
- Selexol ^{tm} (primarily dimethyl ethers of polyethylene glycol) -- physical absorption
- Rectisol ^{tm} (methanol) -- physical absorption

Adsorption based

- Warm Syngas Cleanup - New technologies (e.g., RTI/Eastman)

So, here this figure shows absorption based technology from the bottom we are sending dirty syngas and from the top we are using clean solvent. Solvent will be selective to capture say carbon dioxide or H_2S or may be able to capture both. So, then the clean syngas will go up with CO and H_2 there will be no H_2S there will be no CO_2 or very less amount of CO_2 and H_2S. So, different types of solvent has been used this solvent which capture the acid gases either by physical or chemical absorption.

So MDEA we are having a chemical absorption what is MDEA one solvent that is methyldiethanolamine, Selexol another solvent that is primarily dimethyl ethers of polyethylene glycol there is also physical absorption and Rectisol that is nothing but the refrigerated methanol so that is also physical absorption. Now in the recent years some adsorption based technologies are also developed that is warm syngas clean up, that RTI and Eastman Company they have developed this technology. They use some metal oxides so which captures H_2S.

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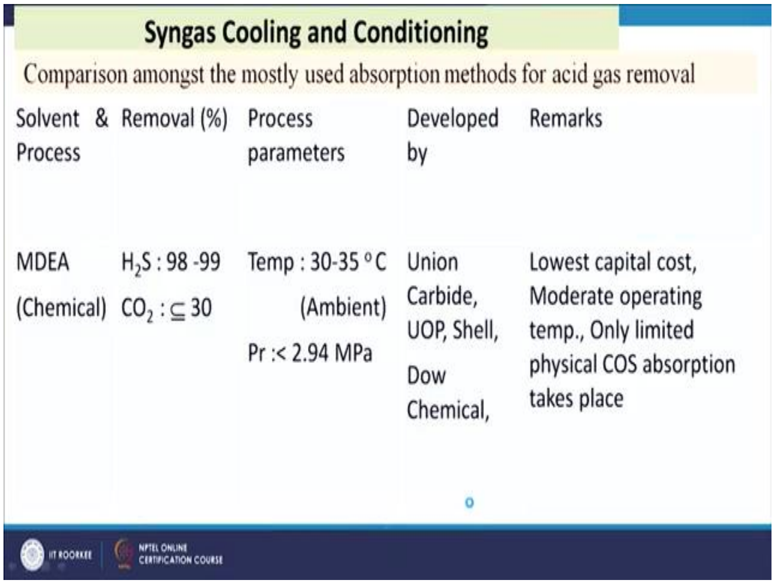

Syngas Cooling and Conditioning

Comparison amongst the mostly used absorption methods for acid gas removal

Solvent & Process	Removal (%)	Process parameters	Developed by	Remarks
MDEA (Chemical)	H_2S : 98 -99 $CO_2 : \subseteq 30$	Temp : 30-35 °C (Ambient) Pr :< 2.94 MPa	Union Carbide, UOP, Shell, Dow Chemical,	Lowest capital cost, Moderate operating temp., Only limited physical COS absorption takes place

Now we will see the comparison among these processes so if we see the MDEA process it is a chemical absorption methods so it removes H_2S 98 to 99% whereas CO_2 is 30% so more selective towards H_2S removal and process parameters 30 to 35 degree centigrade and pressure is 2.94 mega Pascal or less. These are the technology suppliers who have developed the technologies and here we see the cost is low it is not high this is not costly method.

Then Selexol another method H_2S 99% and CO_2 can be variable and temperature is -7 to -4 degree centigrade whereas pressure is 6.87 mega Pascal. These are technology licensers and here higher costs than MDEA but overall system cost including sulphur recovery process and tail gas treating could be more cost-effective. Another is your Rectisol process H_2S is 99.5 to 99.9% and CO_2 is 98.5% so temperature - 35 to -60 degree centigrade and pressure 8.04 mega Pascal.

But this is developed by Linde AG and it is the most costly method but high selectivity to H_2S over CO_2 and ability to remove COS. So, these are the characteristics of these different methods and out of these methods Rectisol has been used widely.

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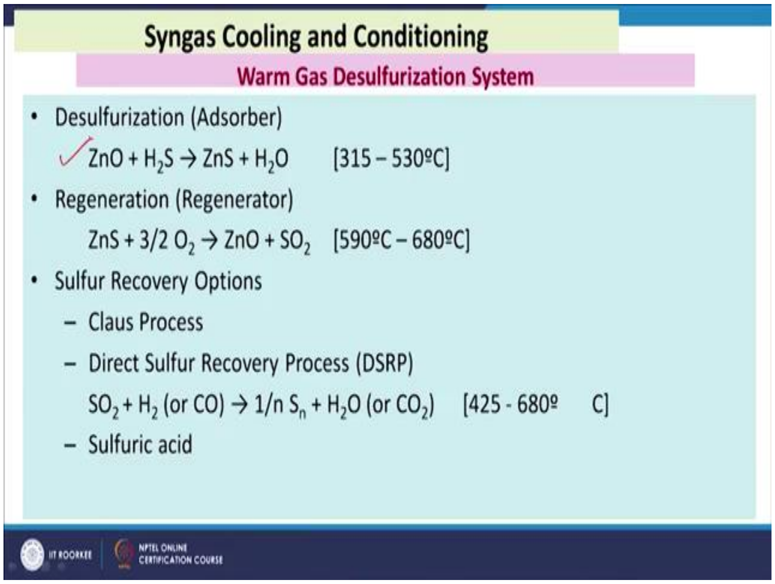

Syngas Cooling and Conditioning

Warm Gas Desulfurization System

- Desulfurization (Adsorber)
  ✓ $ZnO + H_2S \rightarrow ZnS + H_2O$ [315 – 530ºC]
- Regeneration (Regenerator)
  $ZnS + 3/2\ O_2 \rightarrow ZnO + SO_2$ [590ºC – 680ºC]
- Sulfur Recovery Options
  - Claus Process
  - Direct Sulfur Recovery Process (DSRP)
    $SO_2 + H_2$ (or CO) $\rightarrow 1/n\ S_n + H_2O$ (or CO_2) [425 - 680º C]
  - Sulfuric acid

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Now we are coming to warm gas desulphurization as you discussed that some metal oxides are used. So, say ZnO and H_2S reacts and ZnS formed at 315 to 530 degree centigrade and this is your adsorber and then the adsorbent has to be regenerated so regenerator is also there when ZnS reacts with oxygen and again form ZnO at higher temperature 590 to 680 degree centigrade. So, that way it can remove the H_2S from the syngas and sulphur recovery options is also there.

Sulphur can be recovered from the syngas through closed process or direct sulphur recovery process, there are two processes and then direct sulphur recovery process SO_2 + H_2 or CO that reacts 1 by n Sn + H_2O or CO_2 at 425 to 680 degree centigrade temperature. And sulphuric acid can also be produced from the sulphur.

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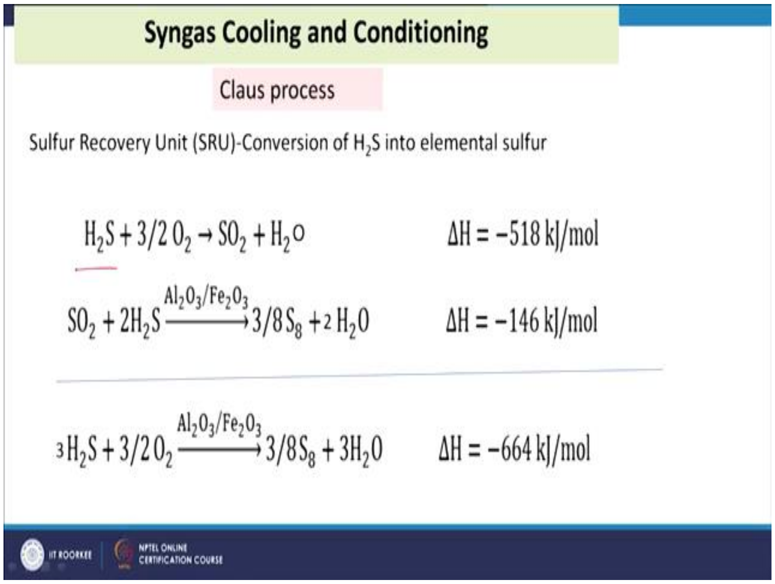

Syngas Cooling and Conditioning

Claus process

Sulfur Recovery Unit (SRU)-Conversion of H_2S into elemental sulfur

$$H_2S + 3/2\,O_2 \rightarrow SO_2 + H_2O \qquad \Delta H = -518\ kJ/mol$$

$$SO_2 + 2H_2S \xrightarrow{Al_2O_3/Fe_2O_3} 3/8\,S_8 + 2\,H_2O \qquad \Delta H = -146\ kJ/mol$$

$$3H_2S + 3/2\,O_2 \xrightarrow{Al_2O_3/Fe_2O_3} 3/8\,S_8 + 3H_2O \qquad \Delta H = -664\ kJ/mol$$

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So, this is the claus process so if we have H_2S + 3 by 2 O_2 then it is giving us $SO_2 + H_2O$ this is the del H value of this reaction then SO_2 reacts with H_2S again and then gives 3 by 8 S8 + $2H_2O$ and this reactions is also possible. So, these are the reactions of the claus process through which we can get elemental sulphur.

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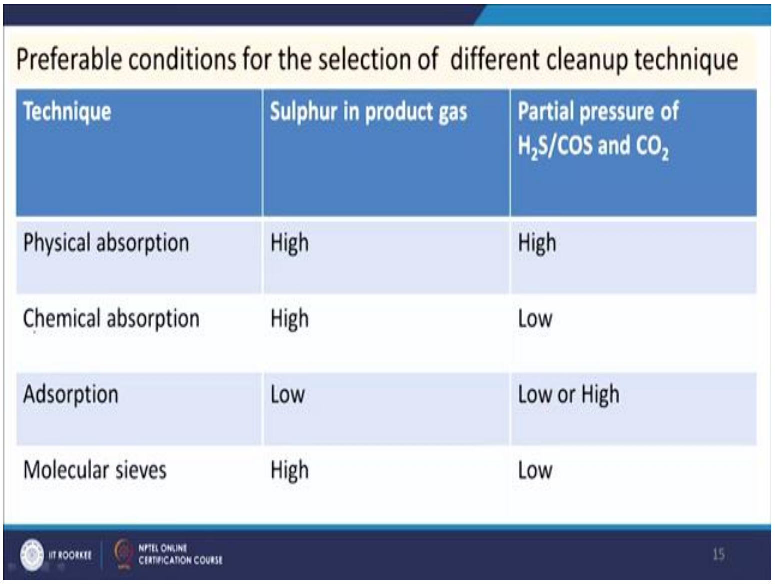

Preferable conditions for the selection of different cleanup technique

Technique	Sulphur in product gas	Partial pressure of H_2S/COS and CO_2
Physical absorption	High	High
Chemical absorption	High	Low
Adsorption	Low	Low or High
Molecular sieves	High	Low

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Now we will see the different methods for the removal of acid gas components from the syngas so physical absorption, chemical absorption, adsorption and molecular sieves. Molecular sieves are also used for the shape selective or size selective separations of the other molecules from the syngas. So, if sulphur in product gas is high and partial pressure of H_2S or COS and CO_2 is also high then we should go for physical absorption.

But if sulphur concentration is high but this pressure is low then you can go for chemical absorption. But for adsorption process certainly the sulphur compound concentration must be less, so low sulphur and then low or high-pressure we can go for adsorption. And for molecular sieves high sulphur and low partial pressure of CO_2, COS and H_2S. Now after the removal of the acid gas now we will see how the CO is to H_2 ratio is maintained or how the H_2 concentration in syngas can be increased.

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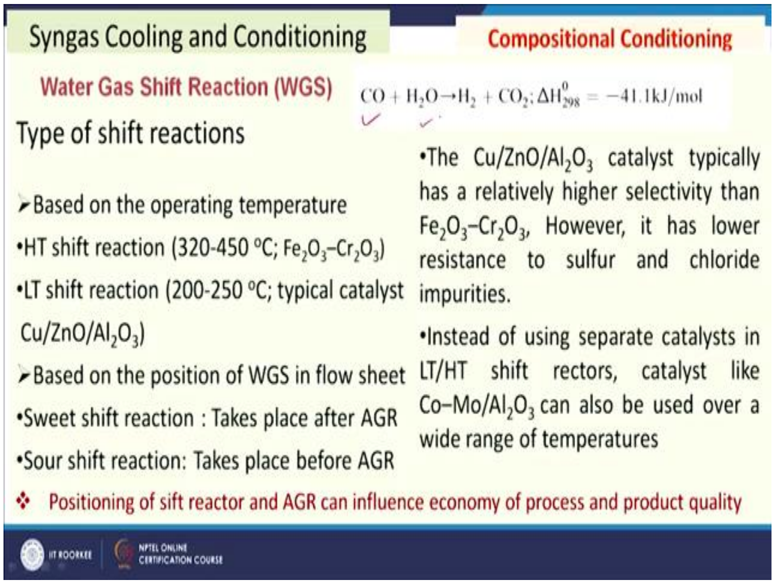

Syngas Cooling and Conditioning

Compositional Conditioning

Water Gas Shift Reaction (WGS)

$CO + H_2O \rightarrow H_2 + CO_2; \Delta H^0_{298} = -41.1 kJ/mol$

Type of shift reactions

➢Based on the operating temperature

- HT shift reaction (320-450 °C; Fe_2O_3–Cr_2O_3)
- LT shift reaction (200-250 °C; typical catalyst $Cu/ZnO/Al_2O_3$)

➢Based on the position of WGS in flow sheet

- Sweet shift reaction : Takes place after AGR
- Sour shift reaction: Takes place before AGR

- The $Cu/ZnO/Al_2O_3$ catalyst typically has a relatively higher selectivity than Fe_2O_3–Cr_2O_3, However, it has lower resistance to sulfur and chloride impurities.
- Instead of using separate catalysts in LT/HT shift rectors, catalyst like Co–Mo/Al_2O_3 can also be used over a wide range of temperatures

❖ Positioning of sift reactor and AGR can influence economy of process and product quality

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So, that is done by shift reaction water gas shift reaction the reaction is CO + H_2O it gives H_2 + CO_2 and this is the exothermic reaction. So, this reaction is performed in presence of catalyst. And this shift reaction can take place before the removal of acid gas from the syngas or after the removal of acid gas from the syngas. So, if this water gas shift reaction takes place before the removal of acid gas removal then it is called sour shift water shift reactions.

And if it is placed after the acid gas removal then it is called sweet water gas shift reaction. So, we have two types of reactions sweet shift reactions and sour shift reactions. These two reactions uses different catalyst, uses different temperature range. So, we can have two types of shift reaction also on the basis of temperature one is high temperature shift reactions another is low temperature shift reactions.

So high temperature means it is 320 to 450 °Clow means 200 to 250 °C. And you see the catalysts are different Fe_2O_3 Cr_2O_3 is used for high temperature shift reactions whereas copper zinc oxide alumina oxide is used for low shift reaction. Now instead of using separate catalyst in low temperature and high temperature shift reactions catalysts like cobalt molybdenum alumina oxide can also be used over a wide range of temperatures. So these are the development of the catalyst sites for shift reaction.

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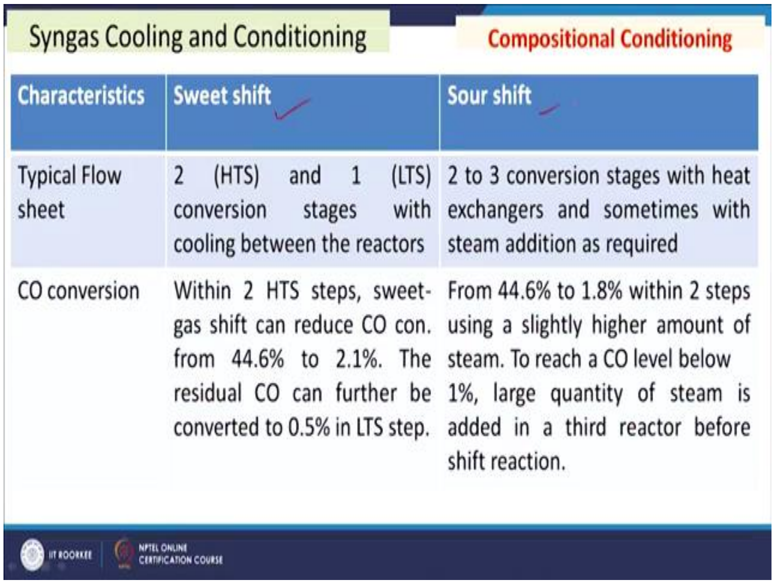

Syngas Cooling and Conditioning

Compositional Conditioning

Characteristics	Sweet shift	Sour shift
Typical Flow sheet	2 (HTS) and 1 (LTS) conversion stages with cooling between the reactors	2 to 3 conversion stages with heat exchangers and sometimes with steam addition as required
CO conversion	Within 2 HTS steps, sweet-gas shift can reduce CO con. from 44.6% to 2.1%. The residual CO can further be converted to 0.5% in LTS step.	From 44.6% to 1.8% within 2 steps using a slightly higher amount of steam. To reach a CO level below 1%, large quantity of steam is added in a third reactor before shift reaction.

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And these are the comparison of sweet shift and sour shift if we see the typical flow sheet then it contains sweet shift 2 HTS and one LTS and sour shift reaction contains 2 to 3 conversion stages which heat exchangers and sometimes with steam addition as required. And conversion if we use CO conversion how the H_2 can be; how much H_2 can be produced? Within two HTS steps the sweet gas shift can reduce CO concentration from 44.6% to 2.1%.

Whereas sour shift can produce 44.6 to 1.8% within two steps. Same both the process we can reduce the concentration of CO below 1% and hydrogen concentration can be increased.

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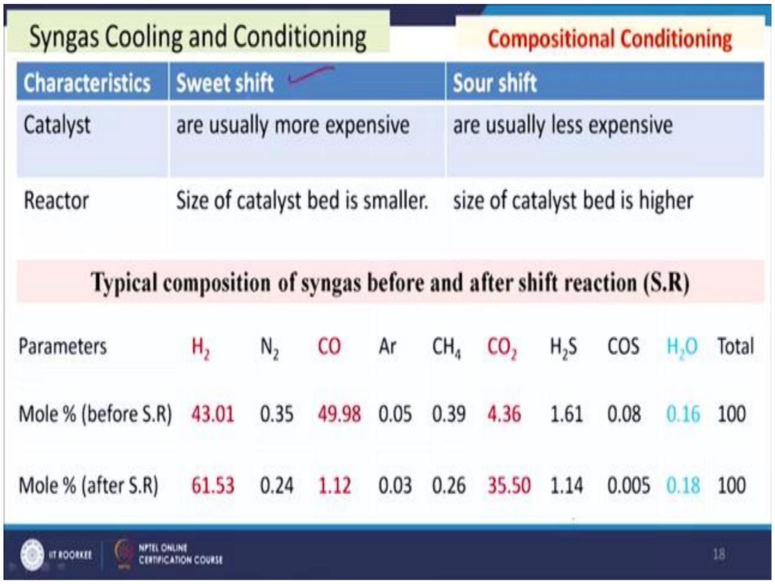

Syngas Cooling and Conditioning

Compositional Conditioning

Characteristics	Sweet shift	Sour shift
Catalyst	are usually more expensive	are usually less expensive
Reactor	Size of catalyst bed is smaller.	size of catalyst bed is higher

Typical composition of syngas before and after shift reaction (S.R)

Parameters	H_2	N_2	CO	Ar	CH_4	CO_2	H_2S	COS	H_2O	Total
Mole % (before S.R)	43.01	0.35	49.98	0.05	0.39	4.36	1.61	0.08	0.16	100
Mole % (after S.R)	61.53	0.24	1.12	0.03	0.26	35.50	1.14	0.005	0.18	100

Now you see the catalyst of sweet shift reactions are more expensive than the sour shift reactions and reactor size is also smaller in case of sweet shift reactions then sour shift reaction. And this table shows the typical composition of syngas before and after shift gas reactions. If we see hydrogen, carbon monoxide and CO_2 this concentration changes significantly CO_2 4.36 to 35.50% then CO 49.98 to 1.12% and here hydrogen 43.01 to 61. 53%.

Now how we will use the syngas once the syngas is cooled then its acid gas are removed then conditioning is done then we can use it the syngas can be used in different applications.

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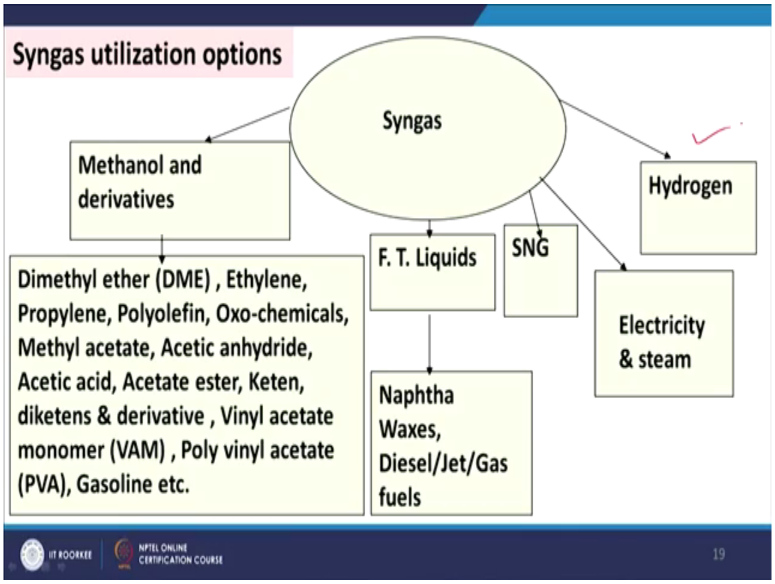

Syngas utilization options

Syngas

Methanol and derivatives

Dimethyl ether (DME) , Ethylene, Propylene, Polyolefin, Oxo-chemicals, Methyl acetate, Acetic anhydride, Acetic acid, Acetate ester, Keten, diketens & derivative , Vinyl acetate monomer (VAM) , Poly vinyl acetate (PVA), Gasoline etc.

F. T. Liquids

Naphtha Waxes, Diesel/Jet/Gas fuels

SNG

Electricity & steam

Hydrogen

Like it can be used for hydrogen production that we have seen if we use rigorous shift water shift reactors then obviously we will get more hydrogen and all carbon monoxide can be converted to hydrogen through these reactions. Or we can use it for electricity or steam productions. The syngas can further be combusted and heat can be generated and can be used in electricity generation. It can be converted to SNG, it can be converted to FT fuels that is naphtha, waxes, diesel, gas fuels etc.

Or it can be converted to methanol, so once methanol is derived as a chemical basic chemicals then from methanol we can get a number of chemicals. So, as shown here so number of chemicals we can get from the methanol or this syngas can be utilized in different way. Now IGCC and poly generation options, this option is becoming very relevant and applicable in recent years. As you see the gasification process is costlier than the conventional combustion based process.

So, we have to utilize the syngas in such a way that the economy is improved. So, the high cost of the process can be compensated by the high value of the products, in products which is produced from the syngas that is why poly generation electricity, chemicals, hydrogen etcetera all productions are considered and integrated and that is called poly generation options. So you see here we use coal or any carbonaceous material then the syngas is produced then particulate removal gas clean up then shift reaction conditioning.

Then we are getting desired concentration of H_2 and CO in the syngas then we can use it for synthesis gas conversion, we can use it for FT synthesis etcetera and then carbon dioxide sequestration's we will also get and will be able to produce the electricity in the gas turbine and again in the steam turbine so electricity we can get. So, that way we can be able to improve the economy of the process.

Now we will see how different parts of the gasification system or gasification process contributes on the overall economy.

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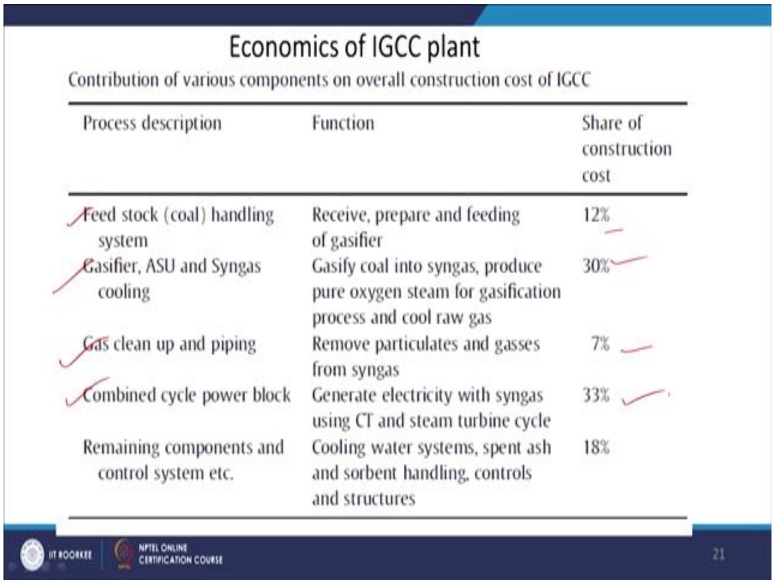

Economics of IGCC plant

Contribution of various components on overall construction cost of IGCC

Process description	Function	Share of construction cost
Feed stock (coal) handling system	Receive, prepare and feeding of gasifier	12%
Gasifier, ASU and Syngas cooling	Gasify coal into syngas, produce pure oxygen steam for gasification process and cool raw gas	30%
Gas clean up and piping	Remove particulates and gasses from syngas	7%
Combined cycle power block	Generate electricity with syngas using CT and steam turbine cycle	33%
Remaining components and control system etc.	Cooling water systems, spent ash and sorbent handling, controls and structures	18%

So, feedstock is around 12% feedstock handling system around 12% share of the construction cost and gasifier air separation unit and syngas cooling around 30% and then gas cleanup and piping it is around 7% and combined cycle power block that is turbines etc so it will be giving 33% and then remaining components and control systems it is around 18%. So, these are the contribution of different parts of the gasification units on the overall construction cost. So, thank you very much for your patience.