Waste to energy conversion
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Lecture – 12
Syngas Utilization-1

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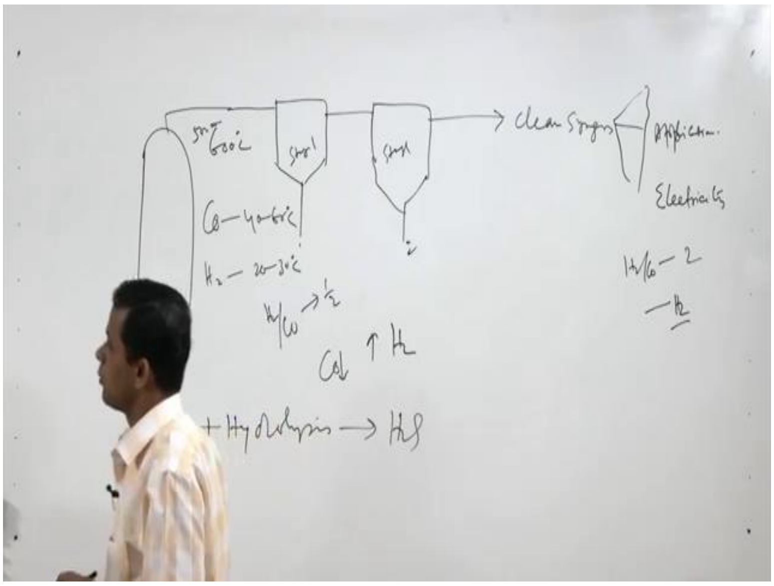

Good morning everyone. In the last module, we have discussed on the gasification and we have come to know that in a gasifier the syngas is produced and it exits from the gasifier at high temperature, so 600 to 500 to 600 centigrade temperature, so that hot syngas it is cleaned. So, particulate the stage one, then for other stage two, or acid gas then clean syngas for different applications. So, for different downstream applications, we need to achieve certain quality of the syngas, it must be free from the all sort of impurities like acid gases etcetera, and it will be having certain H 2 CO ratio as per the requirement except the electricity production. Electricity production does not need any requirement.

So, once we will discuss on this utilization part or sections of this, we should concentrate first on the cooling and clean up option. And another important point is that syngas here the typical composition CO is 40 to 60 percent say; and H 2, it is a 20 to 30 percent, but here we need, so H 2 by C this ratio is almost half. But we need somewhere H 2 by CO ratio 2 or in somewhere all hydrogen complete hydrogen. Therefore, we need to cool the syngas, we need to remove the impurities from it as well as we need to control the H 2 y C ratio. So, all those things we have to do first then we will go for different applications.

So, in this module, we will discuss on syngas utilization options, syngas cooling and conditioning that includes acid gas removal and shift reactions. Shift reaction will increase the hydrogen concentration in the syngas, and reduce CO concentration in the syngas. And then we will discuss on the processes for the production of some chemicals or some other utilities like say production of electricity etcetera.

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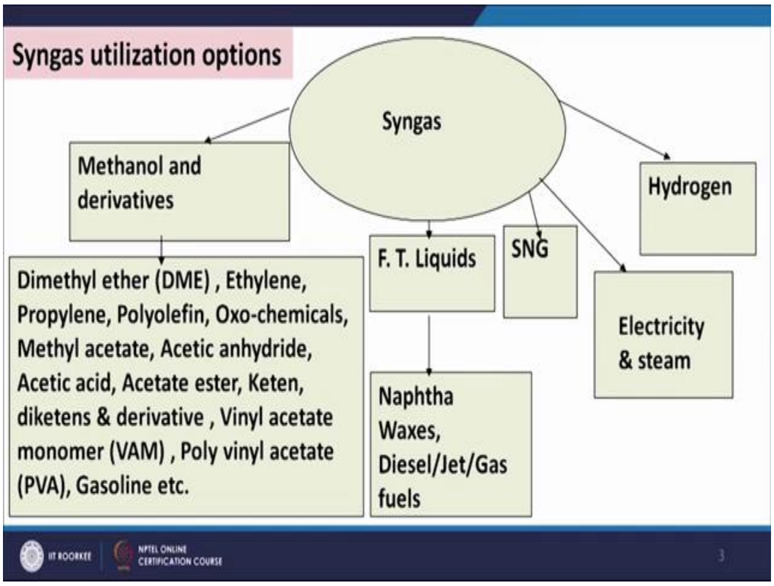

Syngas utilization options

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

Hydrogen

Electricity & steam

Here you can see that from syngas we can get hydrogen, we can get electricity, we can get SNG, we can get F.T fuels that is diesel petrol and other F.T fuels, and we can get methanol, and many chemicals. Once we can get methanol that can be converted to DME that can be converted into many other chemical such some of the chemicals are mentioned here like ethylene, propylene, polyolefin, oxo chemicals, methyl acetate acetic anhydride etcetera, etcetera all some list are given here. So, we can utilize syngas in different routes. We will be discussing some important routes here like say electricity SNG, hydrogen, F.T and methanol synthesis and DME synthesis.

So, we have to come to know that we need to clean the syngas and cool the syngas. So, cooling can be done by direct quenching it or by indirect cooling, any methods can be used direct quench helps to remove the particulates also. The once the syngas is cooled then the part comes for clean off, so that for the clean off means the removal of undesirable impurities. Obviously, the acid gases COS, H 2 S etcetera there is no knocks in this case, it will be nitrogen because we have supplied control amount of oxygen. There will be no shocks also because you have supplied control amount of oxygen. So, if sulphur present in the fixed stocks, it will be available in H 2 S. So, our major concern H 2 S, COS and CO 2. So, these three are major concern we have to remove it, but if chlorine is present in case of your feedstocks then that is another addition will be assail or chloride.

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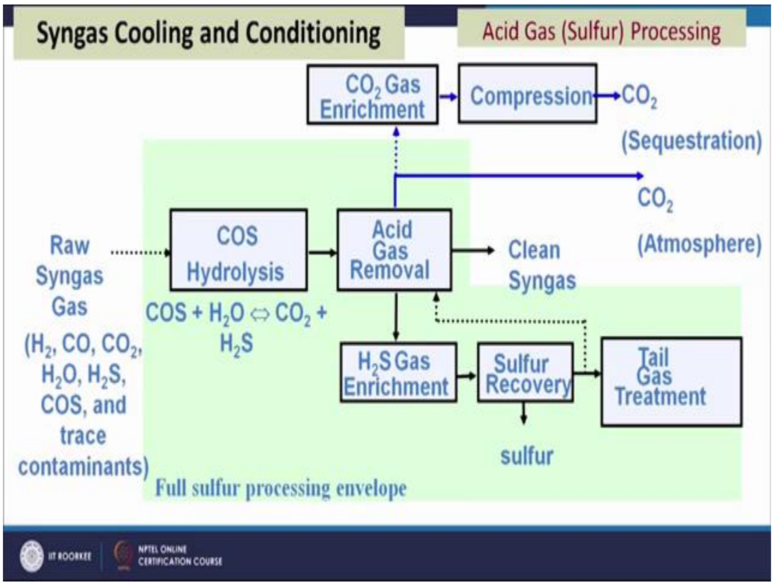

Syngas Cooling and Conditioning

Acid Gas (Sulfur) Processing

Now, this flow sheet say that at first the syngas raw syngas continuing different compositions and some other trace contaminants are mentioned here. The first step is hydrolysis of COS. So, COS will be converted to H 2 S by hydrolyses, it will give us H 2 S so plus CO 2 H 2 S plus CO 2. Then second step is to remove H 2 S and CO 2 from the syngas and that is acid gas removal unit, this acid gas removal unit gives us clean syngas gas as well as it H 2 S rich gas and CO 2 to rich gas. So, CO 2 rich gas, we can pressurize it, and we can use as a source of carbon oxide, or we can see study it. There are number of methods for carbon dioxide sequent station.

And for H 2 S gas which is (Refer Time: 06:33) to it H 2 S that is used for sulfur recovery there are number of methods for sulfur recovery we will discuss now. And after recovering the sulfur from the H 2 S rich syngas the tail gas is go is going for treatment. So, this is the acid gas treatment process. And for the removal of H 2 S and CO 2, there are number of technologies available; and most of the commercial technologies are based on the absorption process and the recent trend is to developed adsorption process or warm gasification.

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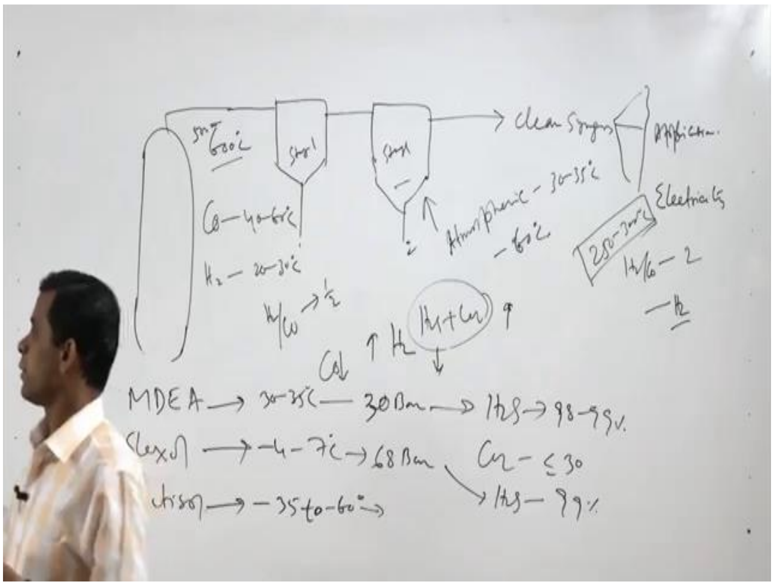

Now, if you see on the flow sheet, then it is clear to us this is 500 to 600 degree centigrade. Now, it is again say most of the cases say 250 to 300 centigrade is required. So, cooling if we can treat this hot gas at warm condition, then it will be more economically feasible. But in conventional cleaning stages for H 2 S and CO 2 suppuration for H 2 S and CO 2 separation, the conventional cleaning processes uses absorption base technology absorption base technology which are both chemical and physical absorption in nature. So, the temperature of the gas used in the systems either atmosphere atmospheric temperature around 30 to 35 degree centigrade or it may be below 0 degree centigrade up to minus 70 minus 60 degree centigrade is used.

So, if we use conventional absorption process, so obviously we have to reduce the temperature here below it must be temperature, again we have to increase the temperature here to 250 to 300 degree centigrade say for particular application. So, once temperature down again it is increasing, so this thermal processes will reduce the overall efficiency of the process. But in place of this, if one process is available or can be developed which can separate H 2 S and CO 2 at warm condition that is one clean process based on absorption that can be more economically feasible and attractive. But this is latest development and very few commercial plants are available on this technology. The most of the old commercial plants are base on the absorption technology.

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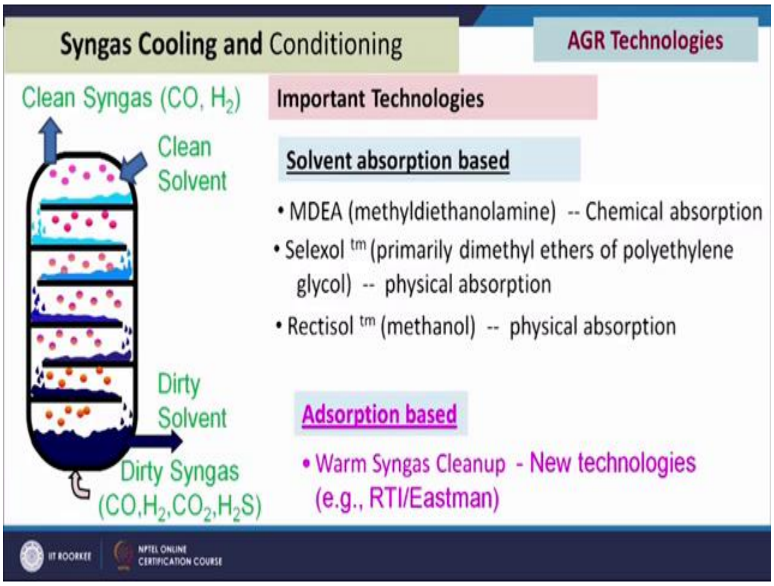

Syngas Cooling and Conditioning

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)

And there are basically three major absorbance has been reported, and used commercially those are MDEA that is methyldiethanolamine, selexol that is primarily dimethyl ethers of polyethylene glycol, and rectisol that is refrigerated methanol. So, this refrigerated methanol rectisol and selexol these two absorbance captures this H 2 S and CO 2 by physical absorption. Whereas, MDEA captures this impurities from the syngas through chemical absorption, due to this reason the temperature for this MDEA process is around atmospheric temperature whereas, for these two selexol and rectisol the temperature is below 0 degree centigrade.

So; obviously, the cost is higher in case of rectisol and selexol process, but obviously, there will be some advantage of this rectisol process also it will be giving more selectivity and more efficiency for separation. Now, we will compare this three syngas or acid gas methods that is MDEA, selexol and rectisol. So, MDEA that is 30 to 30 five degree centigrade and temperature is same 30 to 35. And pressure is 2.94, it is around 30 bar around 30 bar and it gives 98.99 percentage of 98 to 99 percent of H 2 S selectivity and removals. So, H 2 S removal, H 2 S removal is around 98 to 99 percent and CO 2 removal is around less than equal to 30 percent. So, up to 30 percent CO 2 removal, it is possible using this chemical absorption method.

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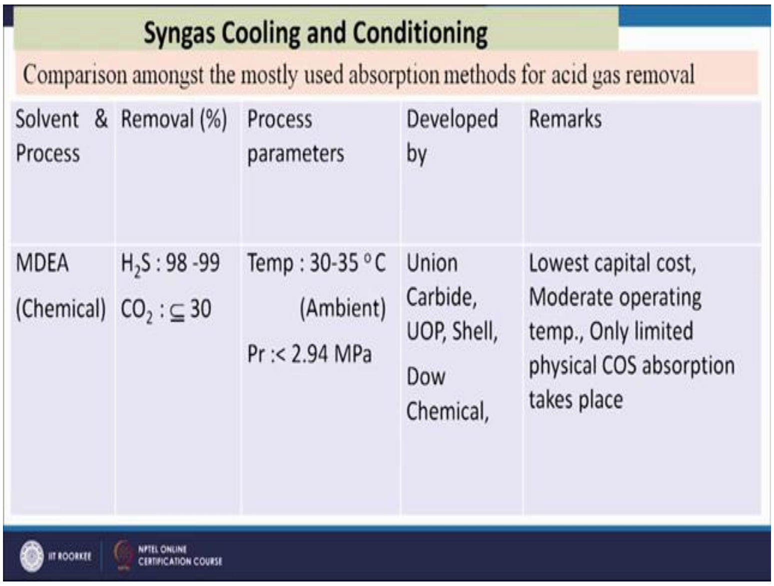

Syngas Cooling and Conditioning

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

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And this is developed by Union Carbide UOP, Shell, Dow Chemical; all those licensors are using these in their plant. And this is low capital cost. And selexol process, this is also having temperature is less than 0 minus 4 to minus 7 degree centigrade and pressure is also similar say this is the around the 68 or around 68 bar. And then here H 2 S removal is again 99 percent. And carbon dioxide removal can vary, so 99 percent H 2 S removal carbon dioxide can vary.

For rectisol methods this temperature is up to minus 60 degree minus 35 to minus 60 degree centigrade. So, very low temperature at this temperature the H 2 S capture capacity is very high for this absorbent and CO 2 is also captured almost completely. So, 99.5 this is having 99.5 to 99.9 percent H 2 S removal and CO 2 removal is also around 98.5 percent, so 98.5 percent. So, on efficiency wise, the rectisol is the superior one that is why in spite of higher cost the rectisol has been used in commercial plant. MDEA has also been used in commercial plant because of its low cost, but selexol is less used with comparison to these two.

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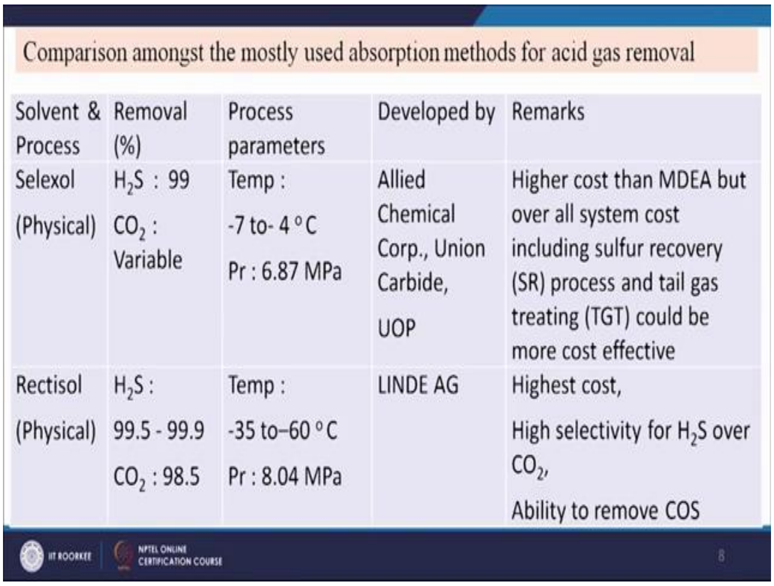

Comparison amongst the mostly used absorption methods for acid gas removal

Solvent & Process	Removal (%)	Process parameters	Developed by	Remarks
Selexol (Physical)	H_2S : 99 CO_2 : Variable	Temp : -7 to- 4 °C Pr : 6.87 MPa	Allied Chemical Corp., Union Carbide, UOP	Higher cost than MDEA but over all system cost including sulfur recovery (SR) process and tail gas treating (TGT) could be more cost effective
Rectisol (Physical)	H_2S : 99.5 - 99.9 CO_2 : 98.5	Temp : -35 to–60 °C Pr : 8.04 MPa	LINDE AG	Highest cost, High selectivity for H_2S over CO_2, Ability to remove COS

Here the technology licensors are given the rectisol is developed by LINDE AG, and the important features we have discussed. Now, we will see the mechanism of syngas clean off at hot conditions or warm clean off of the syngas at high temperature if we use some methyl oxides then H 2 S is converted to the metal oxide metal sulfide and steam. If we further increase the temperature, then the regionalization occurs, so sulfide is converted to metal oxide again.

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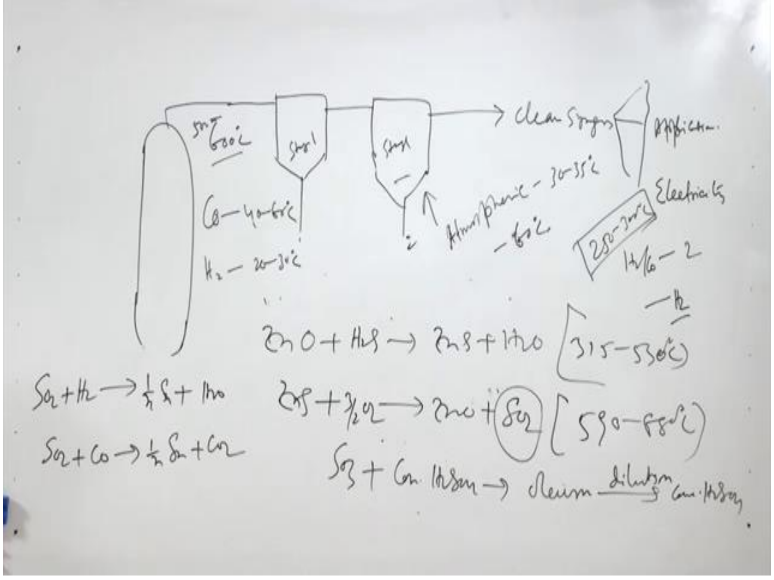

So, for example, if we use Zn O plus H 2 S then it will give us Zn S plus H 2 O at high temperature that is around say 315 into 530. So, 315 to 530 degree centigrade, so this reaction takes place. Further Zn is heated and then it gives us this is heat it gives us in presence of oxygen Zn O plus is SO 2 Zn O plus SO 2. These, temperature is 590 to 680 degree centigrade. Now, once SO 2 is produced, which is coming out from the adsorbed materials, so that will be having high concentration of SO 2, so that SO 2 can be used for further applications. Like say SO 2 can be used directly for the production of sulfuric acid because SO 2 will be converted to SO 3 by vanadium pentoxide V 2 O 5 then it will give SO 3. SO 3 to concentrated H 2 SO 4, it will give olium 3 dilution it will give concentrated H 2 SO 4, so that way we can get sulfuric acid from this.

Or we can we can recover sulfur directly that is the reaction is like this SO 2, SO 2 we have that will be reacting with hydrogen and it will give us 1 by n S n that is elemental sulfur and H 2 O. Or this SO 2 can react with CO SO 2 can react with CO and it can gives us 1 by n S n plus CO 2, so that way directly we can recover the sulfur or Claus process is also there for the sulfur recovery. For absorption method also using like rectisol, selexol or MDEA, when it is regenerated or desorption proceeds then the H 2 S comes out. So, that H 2 S can further be used for sulfur recovery through Claus process.

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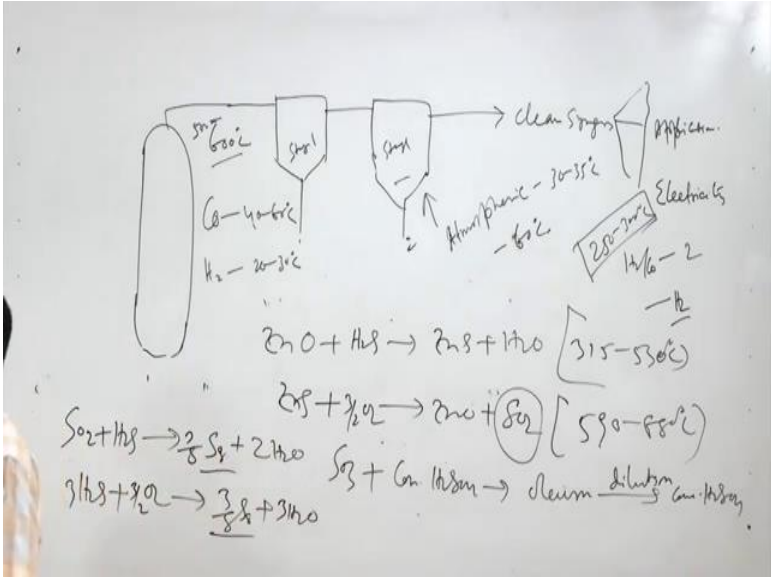

Now, we will see the reactions involved in Claus process. In this Claus process H 2 S partially reacts with oxygen and forms SO 2 and H 2 O. Then SO 2 and H 2 S, SO 2 and

H 2 S this reacts in presence of some catalyst AP O 3 or Al 2 O 3, and it gives us 3 by 8 S 8 plus H 2 O. This is or H 2 S can also reacts with oxygen and directly it can gives 3 by 8 S 8 plus 3 H 2 O, 2 O 2. So, this elemental sulfur is generated and that can be produced can be processed for different production.

Now, we will concentrate on the conditioning part that means how to increase the hydrogen concentrations in the syngas and it is CO conditioning in the syngas. For this shift reaction is carried into the shift reactor. So, shift reactor we see it can be placed here before acid gas removal or it can be place after acid gas removal. So, this syngas conditioning or shift gas reactors can be shift reactors can be replaced before or after the acid gas removable. If we place in different positions, then we will be having different phenomena.

Particularly here, the temperature is higher, temperature is lower, because the syngas after cleaning the temperature will be lower, but this shift reactors will be having or requiring certain temperature this shift reactor will also be requiring certain temperature. So, when we will be using after switch shift reactor and source shift reactor before this acid gas removal this will be having different efficiency. And as here the syngas is containing more impurities the catalyst will also be different. So, now, we have got two types of shift reactions or reactors. So, one is your high temperature shift reaction another is low temperature shift reaction. So, shift reaction temperature may be of high temperature and low temperature.

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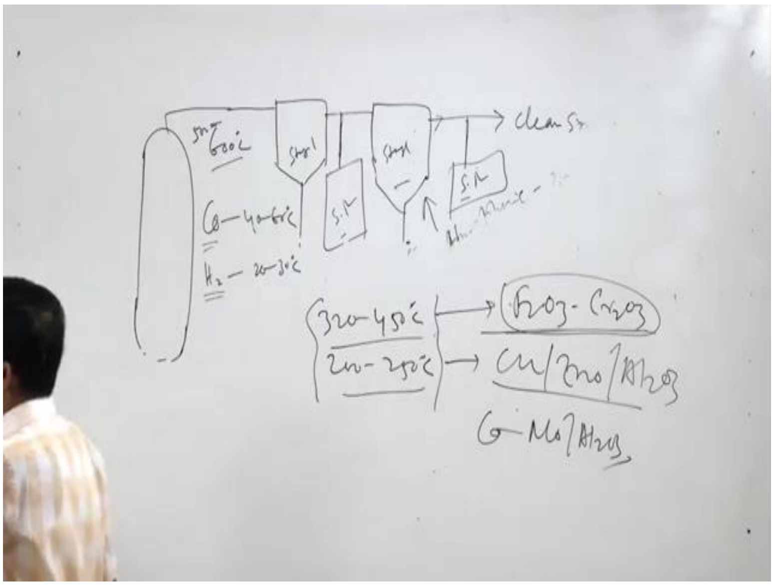

So, high temperature means say 320 to 450 degree centigrade; and low temperature means say 200 to 250 degree centigrade. So, these two reactors under these two conditions two different catalysts have been used. So, high temperature catalyst is basically Fe 2 O 3 Cr 2 O 3; and in this case low temperature that is your Cu Zn O Al 2 O 3. So, these are two catalyst has been used. Now, development in the catalyst section catalyst side has given another catalyst which can be used for a wider range that is cobalt, molybdenum, Al 2 O 3 catalyst.

Now, if we think about these two catalyst there are some differences this F e 2 O 3, Cr 2 O 3, this catalyst typically has a relatively less selectivity that Cu Zn O Al 2 O 3 has higher selectivity for hydrogen productions; however, these as lower resistance to sulfur chloride impurities. Now to achieve the conditioning of the syngas, we may use the switch shift reactions or we may use source shift reactions. But whatever reactions we use we need to follow both high temperature and low temperature shift reactions. In case of switch shift reaction, typical two high temperature shift reactors and one low temperature shift reactors are used.

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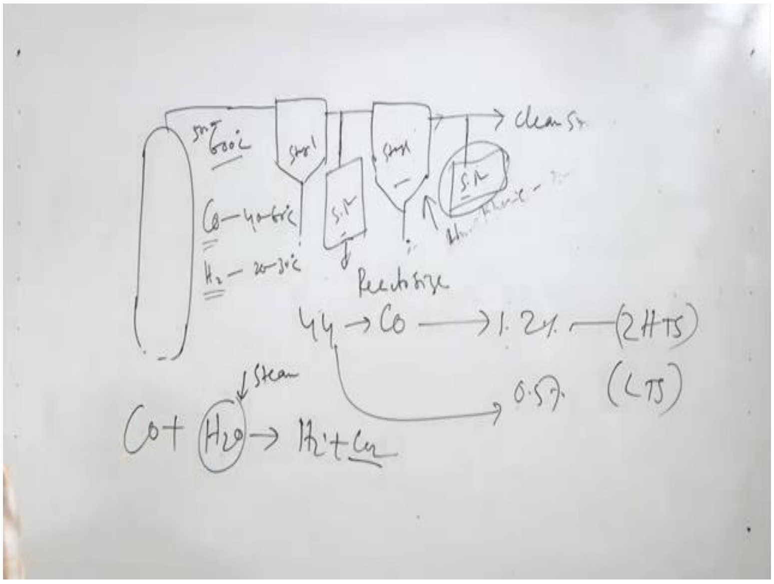

And this say 44 percent of CO can be reduced to around 2 percent or 1 percent around say 2 percent or 1 to 2 percent by two high temperature shift reaction. And when we want to get less than 1 percent of CO, then another LTS is required, so we can get after around 44 percent to 0.5 percent. The similar thing we can get here using source shift reaction also, but in this case more steam is required, so the catalyst which is used in case swift shift reactor that are more costly, but high efficiency. So, reactor volume is less in this case, but for source shift reaction the catalyst are less cheaper relatively, but the reactors size is bigger, so bigger reactor size. So, this is the different between the switch shift and source shift reactor.

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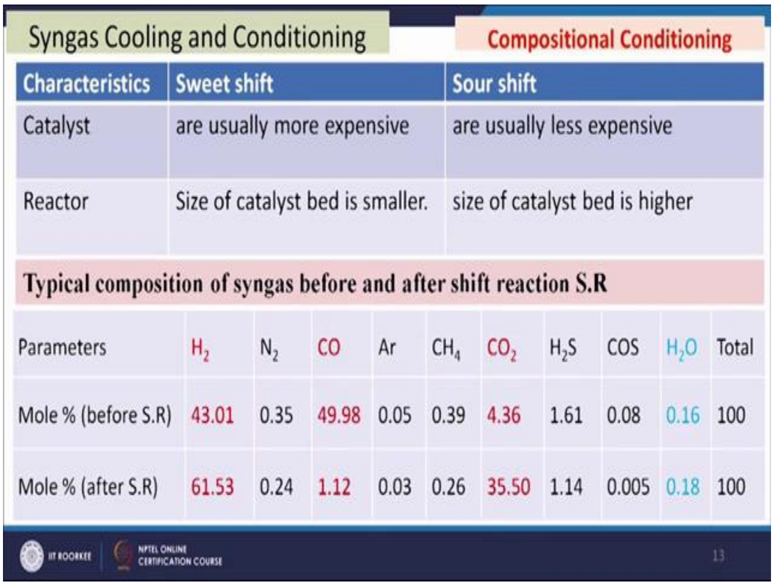

Syngas Cooling and Conditioning

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

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Here some typical example is given how the quality of the syngas changes after shift gas reactions. So, the basic reactions is CO plus H 2 O, it will give your H 2 plus CO 2. So, this is the basic reaction. Now, in this reaction, hydrogen is increasing. So, here hydrogen you see hydrogen is increasing from 43.01 to 61.53, and CO is reducing 49.98 to 1.18, CO 2 is also increasing because CO 2 is increasing. But H 2 O we are not getting much change, because we also need some additional steam, but here it is not changing because when the syngas is taken for the analysis then that during analysis temperature reduced and S 2 is condensed that is why this value is not changing much.

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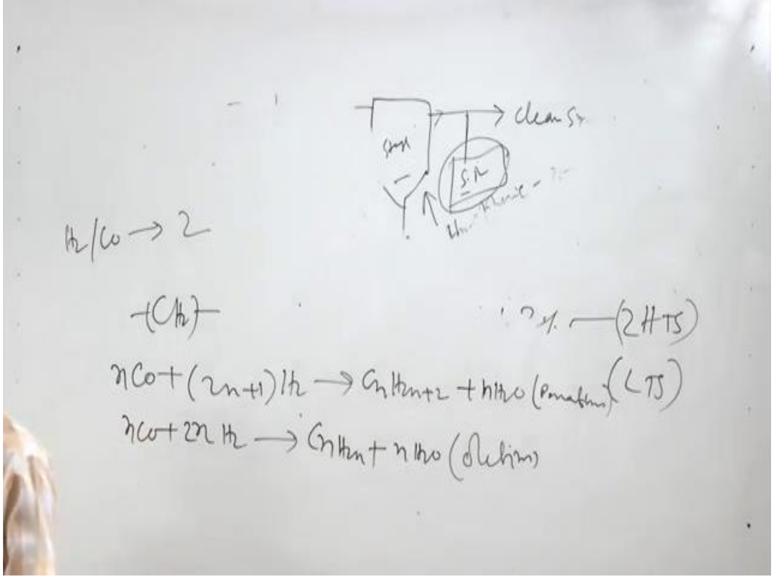

$H_2/CO \rightarrow 2$

$-(CH_2)-$

% — (2 HTS)

$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$ (Paraffins) (LTS)

$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$ (Olefins)

Now, will discuss on Fischer-Tropsch synthesis. So, in case of Fischer-Tropsch synthesis CO and H 2 containing syngas, the ratio having H 2 by CO is equal to 2. So, this syngas is reacted in a FT reactor, where syngas is converted to wax and that wax, and that wax is further process through hydrocracker and then it is after distillation we get different fractions naphtha, kerosene, distillates; and the lower part of it the wax is definite it is recycle for hydrocracker.

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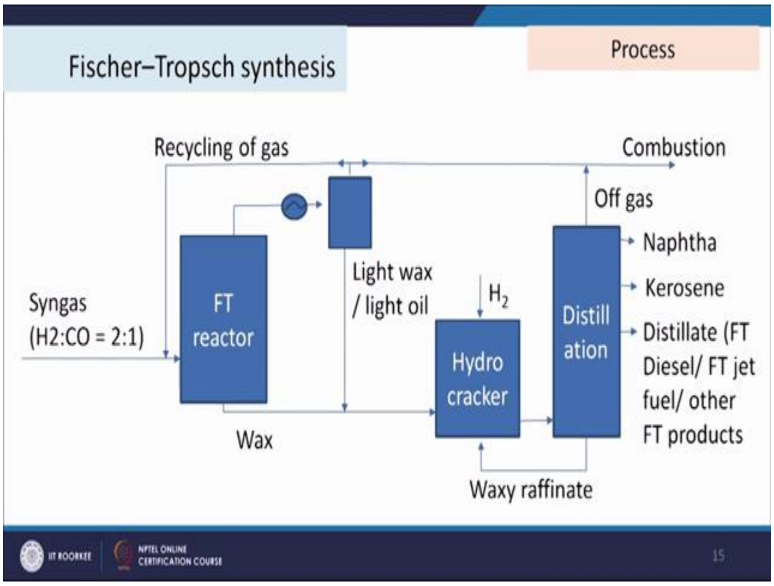

Fischer–Tropsch synthesis

Process

Recycling of gas

Combustion

Off gas

Syngas (H2:CO = 2:1)

FT reactor

Light wax / light oil

H_2

Hydro cracker

Distill ation

Naphtha

Kerosene

Distillate (FT Diesel/ FT jet fuel/ other FT products

Wax

Waxy raffinate

And the light fractions which is generated in f t reactors that goes and after condensation it gives light wax and light oil which is processed with this wax part through the hydrocracker to produce the lighter fractions which is fractionated in distillation column. So, this is the flow sheet of the Fischer-Tropsch synthesis and this reactor part play a significant roll the basic reactions which take place in these are CO plus 2 H 2 that keeps us CH 2 CH 2 N. So, we get paraffin and we get olefins basically the paraffin are wax. So, n CO plus 2 n plus 1 H 2 will give us C n H 2 n plus 2 plus n H 2 O, this is for paraffin. And n CO will react with 2 n H 2, and it will give us n C n H 2 n plus n H 2 O, so this is your olefin and this is your paraffin and shift reactions also takes place in this reactor.

So, the Fischer-Tropsch synthesis the reactor temperature may be high and low. So, high temperature means 325 to 370 degree centigrade; low temperature mean 220 to 270 degree centigrade. And the catalyst either may be FT based iron based or cobalt based.

So, iron based catalyst is fuel flexibilities is there and cobalt based catalyst is not so flexible with fuel, but it is better to use syngas with high S 2 CO ratio. And it is basically used for the syngas produce from natural gas and Z Sm 5 supported bimetallic elliptic catalyst has also been developed in later stage.

In this case, the gas oil is phase velocity is maintained around 700 per hour and pressure is 15 to 30 bar. Under this conditions only the variations of the high temperature and low temperature the product distribution will change. So, you see here the C plus for high temperature the C plus fractions is 5 to 8 percent whether the wax fraction is less only 4 percent. But it is low temperature, FT synthesis we will get higher wax that is equal to 50 percent around and we will get C plus fractions less 20 to 30 percent. And the gasoline will be more in case of high temperature FT synthesis reactors that is 2 is to 1 gas gasoline is to diesel ratio and when the low temperature reduced to gasoline is to diesel ratio 1 is to 2; and scythian number also were is in this two cases.

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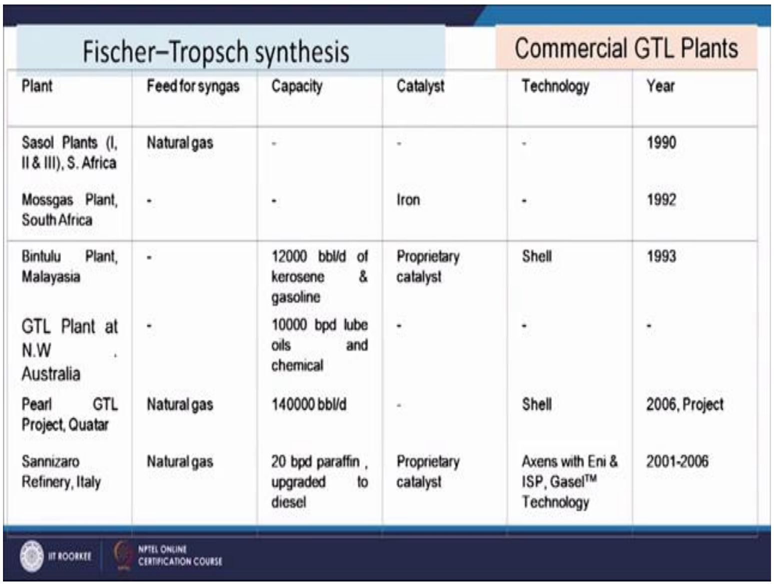

Fischer–Tropsch synthesis

Commercial GTL Plants

Plant	Feed for syngas	Capacity	Catalyst	Technology	Year
Sasol Plants (I, II & III), S. Africa	Natural gas	-	-	-	1990
Mossgas Plant, South Africa	-	-	Iron	-	1992
Bintulu Plant, Malayasia	-	12000 bbl/d of kerosene & gasoline	Proprietary catalyst	Shell	1993
GTL Plant at N.W . Australia	-	10000 bpd lube oils and chemical	-	-	-
Pearl GTL Project, Quatar	Natural gas	140000 bbl/d	-	Shell	2006, Project
Sannizaro Refinery, Italy	Natural gas	20 bpd paraffin , upgraded to diesel	Proprietary catalyst	Axens with Eni & ISP, Gasel™ Technology	2001-2006

Next we will see some applications of this gas syngas into different purposes. So, Sasol plants at South Africa, Sasol gas based plant it is in 1990 it is established and for all these are for FT synthesis. So, another is Mossgas plants - South Africa, Bintulu plant - Malaysia, GTL plant at Australia, Pearl GTL project – Qatar, and Sannizaro refinery – Italy.

So, here one is very interesting information we get that all the plants are having very large capacity. So, 12,000 bp barrel per day, 10,000 barrel per day, 1,40,000 barrel per day, but these technology will not be suitable for the case of biomass and waste gasification. The syngas which is produced from the biomass and waste the capacities is not much the plant capacity is less, but here the plant capacity is very bigger. So, biomass and waste gasification and corresponding utilization of in syngas to FT synthesis will be feasible only when we will be getting more in compact reactors with higher efficiency and heat transfer. And efforts are going on and in near feature, we will get more compact reactors and the scenario will be change and biomass the syngas from biomass and waste will also be suitable for FT synthesis. So, up to this in this module.

Thank you very much for your patience.