

**Chemical Technology**  
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**Module - 2**  
**Coal Chemical**  
**Lecture - 3**  
**Gasification of Coal, Petrocoke and Biomass**

We are discussing the module 2 of the organic chemical technology course and the lecture 3. Now, we will be discussing about the gasification part because the coal gasification that is very important in the utilization of the coal.

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### **Coverage of Lecture**

- Introduction: Gasification of Coal, Petrocoke and Biomass
- History of Gasification
- Gasification – Indian Context
- Gasification: underground and surface
- Process steps in gasification
- Various Type of Gasifier
- Gasification in Fertiliser industry
- Biomass Gasification and Co-gasification of Coal and biomass for methanol synthesis

So, gasification of the coal and the petro coke and biomass gasification will be discussing in detail. So, these are the coverage of the lecture. First the introduction gasification of the coal, petro coke and biomass, why we are going for the petro coke and the biomass gasification? What are these importance of the gasification of the and the history of the gasification? Gasification in the Indian context gasification, because we are having surface gasification and the underground gasification also.

We are doing process steps in the gasification various type of the gasifier that is being used because we started with the fixed bed. Now, the fixed bed to fluidized bed moving

bed and all other type of the gasifier that we are using. Then gasification in the fertilizer industry because that was the 1 of the major source of the fertilizer also before the availability of the naphtha or the natural gas for the fertilize industry. Because we started 2 fertilizer plant based on the coal that was through the gasification route or you can say the partial oxidation and that was at the Ramakundam in Andhra Pradesh in the Talcher.

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### **Gasification of Coal, Petrocoke and Biomass**

- Gasification of coal, petrocoke, biomass and other carbonaceous materials to produce synthesis gas has gained significant economic and environmental importance in the recent years.
- Petrocoke is by product from refineries
- Biomass is carbon neutral renewable resource

But these two units were closed and so, will be discussing about the gasification what are the constraints if you are going for the gasification route for making of the fertilize. Then the biomass gasification and coke gasification of the bio coal and biomass for methanol synthesis these are the thing also will be discussing about the petro coke gasification. Because, the petro coke that we are getting from the refinery that is being used presently for the as a fuel in the cement plant and other plants. But there is lot of scope for gasification of the petro coke for making the hydrogen or the synthesis gas and now the reliance Jamnagar refinery they are going for the petro coke gasification.

So, we will be also discussing about the petro coke gasification gasification of the coal petro coke biomass and other carbonaceous materials to produce synthesis gas has gained significant economic and environmental importance in the recent years. Apart from the coal gasification, which is being used from beginning of the 19th century now, we are also having the petro coke gasification, which is the byproduct from the refinery. Biomass is a carbon neutral renewable resource, which is available in the abundance and

the nature and so, that biomass that can be utilized for the gasification or for the fermentation for production of the alcohol. That will be discussing while discussing sugar and alcohol how the alcohol you can get from the biomass.

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### **Gasification of Coal, Petrocoke and Biomass**

- Technology of gasification or partial oxidation of heavy feed stock is quite established for over half century,
- The technology of gasification has undergone continuous developments over years to tackle higher ends of refinery bottoms, petcoke, coal and biomass [Sukumar ran nair, 2010]

The technology of the gasification or the partial oxidation of the heavy feed stock is quite established for over half century and so, the only thing development that has taken place because always there is a scope of the development in the any process. The technology the gasification has under gone continuous developments over years to tackle the higher ends of the refinery bottoms petro coke coal and the biomass even in case of the coal. Because the ash content that is varying very widely, now the coal which used to get during the 50s or 60s that was much better coal now the coal quality in many area that is having the very ash content.

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## **Gasification of Coal, Petrocoke and Biomass**

- Gasification of coal to produce coal gas goes to the end of 18<sup>th</sup> century when coal gas was used for heating and lighting.
- However with the availability of natural gas and petroleum products at cheaper rate the interest in coal gasification dwindled.

Gasification of the coal to produce coal gas goes to the end of the 18th century when the coal gas was used for heating and lighting purposes even in that continuation that was the production of the producer gas water gas. Even I remember when I was working Orion, we are having the producer gas plant in the lime for making of the lime from the lime stone. So, that was the actually importance in case of the gasification that water gas producer gas blue gas town gas all those things. So, however with the availability of the natural gas and petroleum product at the cheaper rate the interest in the coal gasification dwindled.

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## **Gasification of Coal, Petrocoke and Biomass**

- Due to increasing cost of oil and gas and the availability of petrocoke and look for alternative feed stock for gasoline and petrochemical, interest was renewed in coal gasification.

During the early stage, because the more the petroleum products that was available at the much cheaper rate due to the increasing cost of the oil and gas again there is been continued interest. In case of the coal or the biomass or the petro coke, so due to the increasing cost of the oil and gas and the availability of the petro coke and look for the alternative feed stock for gasoline and petrochemical. Interest was renewed in the coal gasification, as well as in the gasification of the petro coke and the biomass.

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### **Gasification of Coal, Petrocoke and Biomass**

- India has estimated coal reserves of 253 billion tons and lignite around 28 billion tons and lignite around 28 billion tons.
- Indian coal is mainly non-coking anthracite and bituminous in nature with ash content of over 35%.

India has estimated coal reserve of 253 billion tons and lignite around 28 billion tons and lignite around Indian coal is mainly non-coking anthracite and bituminous in nature with ash content of over 35 percent. Many of the cases coal gasification is now done by the surface and the underground gasification with the increasing heavier crude petro coke production has increased in the petroleum refinery.

So, the all the refinery they are looking for the utilization of the petro coke because then you see that there has been continuous up gradation of the refinery technology and the capacity. Now, the all the refinery they have increased here capacity and so the with the utilization of more and more heavier crude definitely the production of the petro coke that will increase; and so the petro gasification, petro coke gasification instead of the reforming of the naphtha, which is now commonly being used in most of the refinery for production of the hydrogen because hydrogen.

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## **Gasification of Coal, Petrocoke and Biomass**

- Coal gasification is now done by surface and underground gasification.
- With increasing heavier crude, Petrocoke production has increased in Petroleum refinery
- Gasification of biomass is also getting interest during recent years because of availability of biomass in abundance.

That is one of the major actually the raw material, in case of the refinery or the petrochemical in the various pretreatment processes. As well in the process so, just to meet requirement of the hydrogen we are producing. But in the future and some of the refinery they may have the petro coke gasification for production of the hydrogen.

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## **Gasification of Coal, Petrocoke and Biomass**

- Gasification Technology offers the cleanest and most efficient way to convert low and/or negative value carbon based feed stock to syngas.
- The gasification of coal involves the conversion of coal to high content gas (CO and H<sub>2</sub>)
- Syngas can ultimately replace natural gas for Industrial uses, electrical power generation and basic raw material to produce chemical and fuel oil.

Gasification of the biomass is also getting interest during recent years because of the availability of biomass in the abundance. Gasification technology offers the cleanest and most efficient way to convert low and or negative value carbon based feed stock to the



syngas. Because synthesis gas that is the again from the synthesis gas we can produce large number of the chemicals. The gasification of the coal involve the conversion of coal to high content gas that is the C O and H 2, where the C O and H 2 that can be separated because C O that is converted to C O 2 during the and that C O 2. We are using for the making of the urea and hydrogen.

We are getting for other purposes so, this that hydrogen that can be used in the refinery if you are having the petro coke gasification or hydrogen for the fuel shale, because that is also one of the emerging area. Syngas can ultimately replace the natural gas for industrial purposes electrical power generation and basic raw material to produce chemical and fuel oil. Why we are not using the coal gasification or the bio gasification the because the naphtha or the natural gas that is available. But, how long that will last and so, in order to have the alternative feed stock, definitely the gasification of the coal petro coke and biomass that is going to play very important role in meeting the raw material for the chemical process industry

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## **Gasification of Coal, Petrocoke and Biomass**

Commercial Success of Gasification

Technology will depend on the advancement of technologies such as:

- Low cost oxygen production
- Syngas cleanup and
- Cost effective separation of Hydrogen from CO<sub>2</sub>

The commercial success of the gasification technology will depend on the advancement of the technology such as the low cost oxygen production because here in case of the partial oxidation and gasification we need the oxygen. So, oxygen that is we are producing by separation liquidation of the air. And so, that is the highly energy is in the process in case of the liquidation of the air and then the separation for the oxygen and

nitrogen. So that oxygen we are using for the partial oxidation syngas cleanup, because syngas it may contain sulphur compound. So, this syngas that has to be, because the otherwise the sulphur compounds are there, then that will result in the catalyst poisoning.

Cost effective separation of the hydrogen from the  $\text{CO}_2$  that is another requirement because the that is not  $\text{C}_2$ , but  $\text{CO}_2$  so the cost effective separation of the hydrogen from  $\text{CO}_2$ . Because  $\text{CO}$  is converted  $\text{C}_2$  and that is  $\text{CO}_2$  and normally absorption process and various absorption and new absorption that has come and the they have replaced conventional absorbing media  $\text{K}_2\text{CO}_3$ , which was earlier used for the absorbing of this  $\text{CO}_2$ . So, the cost effective separation of the hydrogen from the gases that will be very important. As I told you the, we are having the surface and underground now the recent year there has been interest in the underground gasification also.

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## **Gasification of Coal, Petrocoke and Biomass**

Gasification is the process of converting organic part of solid fuel to combustible gases of high heat value by interaction with steam and oxygen.

Gasification converts the low value fuel to high heat value gas.

Gasification of the biomass by now the emphasis that is being given on the gasification. Because of the availability of the biomass with abundance, because now the gasification you will find lot of the literature lot of the development R and D project are going on the gasification of the biomass to produce synthesis gas to produce hydrogen to produce methanol or the fermentation of the biomass for the production of the alcohol. Gasification is the as I told you the gasification because here in case of the carbonization that was the in absence appear in the gasification that we are doing in presence of oxygen.



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## **Gasification of Coal, Petrocoke and Biomass**

The feed for Gasification can be

- Gas (e.g., Natural gas)
- Liquid (e.g., Light or Heavy oils)
- Solid (e.g., Petroleum Coke, Coal, Lignite or Biomass).

So, gasification is the process of converting organic part of the solid fuel to the combustible gases of high heat value by interaction with the steam and the oxygen. So, the high heat value of gas may be important from the fuel point of view, but gasification converts the low value fuel to high heat value and we can have the synthesis gas from the gasification. The feed for the gasification can be the gas and natural gas, but that is actually the term we are not using the gasification there we are using the term steam reforming where, from the steam reforming of the natural gas or the naphtha that we are getting the synthesis gas the solid.

So, we are discussing about the solid part of the petroleum coke coal lignite or the biomass for the gasification. Here, we are not discussing about the gasification of the reforming of the gases or the naphtha. This is about the availability of the coal and lignite and so, why then now that we are having more interest for the gasification of the coal? Indian coal is mainly non-coking anthracite and bituminous in nature with ash content. As, I told earlier also ash content of the coal in our country is very high.

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### **Gasification of Coal**

- India has estimated coal reserves of 253 billion tons and lignite around 28 billion tons and lignite around 28 billion tons.
- Indian coal is mainly non-coking anthracite and bituminous in nature with ash content of over 35%.

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### **Gasification of Coal**

- Gasification of coal offers as promising source of chemicals as well liquid fuel.
- The gasification of coal involves the conversion of coal to high content gas (CO and H<sub>2</sub>)

Gasification of the coal offers as promising source of chemicals as well as liquid fuel because, depending upon the gasification. Because now we are also having the fast pyrolysis process that is the fast pyrolysis of the biomass. So, you can get the liquid fuel the gasification of the coal involves the conversion of coal to high content gas, means that is the C O and H 2 and that C O and H 2 and again that is what we called as the synthesis gas that is a important source of the many chemicals including the methanol and from methanol to other value added products. You can make that the methanol to olefin methanol to dimethyle either or methanol to polymer. So, this is the history of the

gasification because this is the, if you see the literature you will find are the mention of the coke even long back in China.

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<b>History of Gasification</b>	
<b>Period</b>	<b>Technology</b>
Before 1700	Major fuels were Wood and Charcoal
1700-1750	Industrial revolutions – Coal as fuel
1800-1900	Coal Pyrolysis – Town gas supply, Water gas, Producer Gas
1920	Cryogenic air separation – Oxygen replaces air
1926	Winkler Fluidized Bed Gasifier

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<b>History of Gasification</b>	
<b>Period</b>	<b>Technology</b>
1931	Lurgi Moving Bed Gasifier
1940	Koppers-Totzek Entrained Flow Gasifier
1950s	Texaco and Shell develop Oil Gasification
1970s	Oil crisis
1973	Texaco develops Slurry Process for Coal Gasification

They mentioned the coke, but the before 1700 major fuels were wood and the charcoal that was being used and the even the coke. That was the in the form charcoal that was getting from the carbonization of the wood. The 1700 to 1750 industrial revolution coal as a fuel that came in the with the availability of the coal pyrolysis town gas supply water

gas producer gas. Then the cryogenic air separation that was developed in 1920 and so the oxygen that replaces air and so the efficiency of the, that was high.

The Winkler fluidized bed gasifier that was developed in 1926 and the, because the fluidization that came in the big way not only in the gasification. But also in the petroleum refinery with a fluid cat fluidized bed catalytic cracking and the improvement in the production of the various chemicals. In 1931 Lurgi moving bed gasifier that was developed and 1940 the entrained flow gasifier. These were the earlier development that took place, but the again then lot changing in this configuration 1950 Texaco and Shell develop oil gasification and 1970 that was the oil crisis that took place and then the Texaco develops slurry process for coal gasification.

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<b>History of Gasification</b>	
<b>Period</b>	<b>Technology</b>
1974	Shell and Koppers-Totzek Pressure Gasification JV
1981	High Temperature Winkler Gasification
1984	Lurgi Slagging Gasifier (together with British Gas)
1999	Shell/Krupp-Uhde develops Pressurised Entrained; Flow (PRENFLO) Gasifier
Beyond 2000	Shell Gasification, GE Quench/PHR/FHR, Siemens, Chinese, GPE, Plasma, Headwaters

1974 again the shell and the Koppers Totzek pressure gasification high temperature of Winkler that is gasification process. So, these are the some of the beyond 2000 again shell gasification shell and the even the reliance they are working in big way on the gasification, because that is going to have the future source of the synthesis gas when the resources of the crude oil that will be less anyway.

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1940s	Wood Gasification	Wood	FACT - Cochin
1945-1950	Lurgi Fixed Bed	Coal	Sindri
1960s	Winkler Fluidized Bed	Lignite	Neyveli
1960s	Texaco	Naphtha	FACT - Cochin

Wood gasification as I told you that here because it was the wood from where we are getting the charcoal. So, that was the earlier route for making of the naphtha also, naphtha both the process that has been reported either the steam reforming or the partial oxidation of the naphtha. That is the in the Indian context I am discussing earlier what are the development we discussed in the gasification that was the global what are the changes that has taken place.

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1970s	Krupp-Koppers Entrained Bed Atm.	Coal	Ramagundam Talcher
1970s	Shell	Fuel oil	Sindri
1980s	Shell	Fuel oil	NFL - Bhatinda, Panipat, Nangal
1980s	Texaco	Fuel oil	GNFC - Bharuch

This is how we started in case of the Sindhri, because Sindhri that is the place you see the first to manufacture the fertilizer under the banner of fertilizer and chemical corporation. That was started in the Sindhri and that was the and large number of be Sindri just new to Dhanbad.

So, lot of the coal that is available there and the another as I told you the coal gasification of the coal partial oxidation that was the same under the FCIL banner that was started in the Talcher and the Ramagundam unit of the fertilizer. So, winkler fluidized bed for lignite is the Neyveli Texaco naphtha fact, Cochin. That is fertilizer and chemical Travancore. The fact that is the plant which is making the fertilizer urea as well as they are making also the Caprolactam that is 1 of the raw material the poly monomer for the making of the nylon 6.

This is the, I told you earlier about the Ramakundam and Talcher, these were the two process which came into existence based on the coal gasification of the coal partial oxidation. But again the unit has to be closed because lot of the the cost of production of the synthesis gas from the coal is higher than the what we are getting from the natural gas or the naphtha. Because earlier the naphtha gas availability was less, but with the coming of the SBJA pipeline other pipeline for the natural gas and the processing of your crude oil. More and more percent of the your crude oil from the off shore on shore and at the same time with the availability of the natural gas from the your (( )).

So, that affected the operation of the coal base plant, but again there is, a as I told you the interest and the lesser part in some of the fertilizers especially the NFL. They started using the fuel oil because most of the plant of the national fertilizer limited NFL. They are based on the fuel again they have shifted from the fuel oil even the your if company plant at the Phoolpur that was based on the fuel oil. Now again all those plants they are shifting to the, more cheaper raw material means the from the petroleum route that is the naphtha or the natural gas again the n NFL Bathinda Panipat, which I told you they they started using the fuel oil. Because, at that time the huge amount of the fuel oil that we were getting from the refinery and there is no use except the fuel as a fuel we are using so, the some of the fertilizer plant they were based on the fuel oil. So, as I told you the gasification that can be underground gasification or the surface gasification.



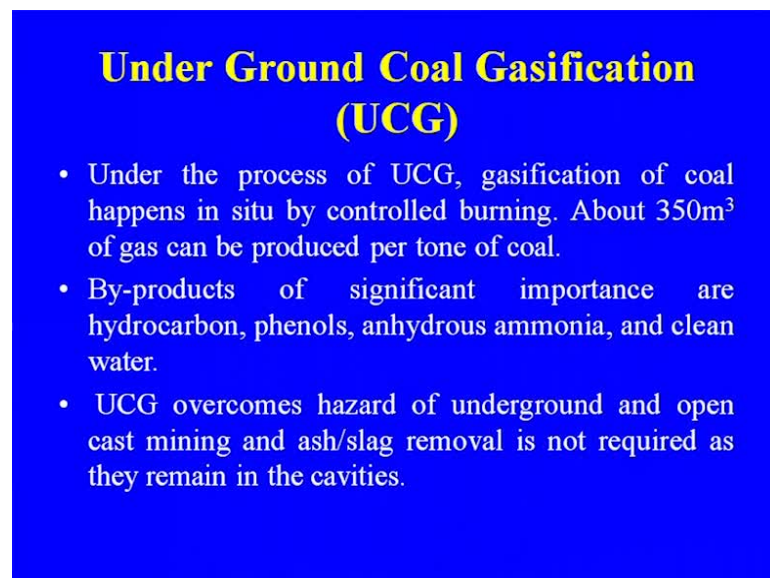
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## Gasification

- Underground Gasification
- Surface Gasification

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## Under Ground Coal Gasification (UCG)

- Under the process of UCG, gasification of coal happens in situ by controlled burning. About 350m<sup>3</sup> of gas can be produced per tone of coal.
- By-products of significant importance are hydrocarbon, phenols, anhydrous ammonia, and clean water.
- UCG overcomes hazard of underground and open cast mining and ash/slag removal is not required as they remain in the cavities.

Underground coal gasification, gasification of the coal happens in in situ<sup>1</sup> by controlled burning about 35 cube meter of gas can be produced per tone of the coal by product of the significant importance are hydrocarbon phenols, anhydrous, ammonia and the clean water. So, this is the some of the by product that we are getting from the not the clean water, but the water we are getting UCG overcome the hazard of the underground and open cast mining and ash slag removal is not required as they remain in the cavities. So, this is the some of the advantage why we are now going for the underground gasification.

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## **Under Ground Coal Gasification (UCG)**

Some of the advantages of UCG are :

- Tapping of energy from vast coal reserves which are not economically viable to mine,
- Increased worker safety,
- Low environmental impact, increased worker safety

Source: Sawhney, P. meeting of Indo-US working group on Coal April, 2008].

Some of the advantages are the tapping of the energy from vast coal reserves which are not economically viable to mine. In that case the underground gasification that is very important increase worker safety, low environmental impact, increased worker safety that as I told you and that is because of the underground gasification.

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## **Surface Gasification**

- Surface gasification involves reaction of coal with hot steam and controlled amount of air or oxygen under high temperature and pressure produces syn gas which can be used as the substitute of Natural gas, for power generation using low Btu gas as fuel, manufacture of chemicals and fertilizer and conversions to liquid fuel by GTL liquid.

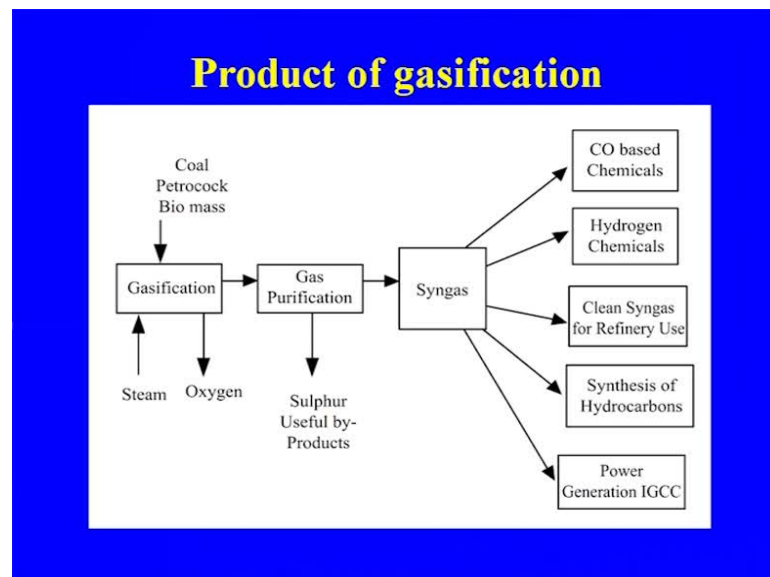
Surface gasification involves reaction of the coal with hot steam and controlled amount of air or oxygen under high temperature and pressure which produces the synthesis gas, which can be used for the substitute of the natural gas for power generation using low

BTU gas as fuel manufacture of chemicals and fertilizer and conversion to liquid fuel by GTL technology, gas To Liquid Technology. Because gas to liquid technology that is coming in a big way to utilize these heavier fraction for producing the gasoline. So, GTI Technology gas to that is based on the fisher top synthesis

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Process steps in the gasification. Some of the process steps involved in case of the gasification first part is the feed preparation. Then the gasification, gasification in the presence of air and the presence of oxygen because many of the plant they are having the

air separation. Because if you are having the oxygen that is always better and so, the syngas cooling because synthesis gas which you are having there that has to be further processed for the separation of hydrogen.

For the conversion of  $\text{CO}_2$ 's  $\text{CO}_2$  or in other process and just like for the methanol synthesis air separation. As I told you that is the one of the very important unit of the any plant, which is based on the partial oxidation or the gasification where oxygen we are using for gasification acid gas removal again acid gas that may be because of the sample compound present in the coal or the even the petroleum coke. Because you see the petroleum coke, how we are getting we are getting more petroleum coke because of the your heavier crude oil. And the heavier crude oil they always contain higher sulphur than the your other crude oil.

So, the acid gas removal even in case of the coal gasification or the petro coke has been very important slag handling system. This is the process of the gasification, whether you are having the coal petro coke or the biomass that will go to the gasification steam oxygen that you have to that will go the gasification section gas purification sulphur useful byproducts. Because always whether it is the refinery or the other plant or even the NFL. Panipat or any fertilizer plant which are using the heavier fraction, they are going for the recovery of the sulphur and by Claus process or the modified Claus process.

Then from the gas purification that will go to synthesis gas with the synthesis gas that will be actually, because you know the synthesis gas means  $\text{CO}$  and  $\text{H}_2$  for the various manufacture of chemicals or it may be hydrogen and nitrogen if hydrogen and nitrogen is there. What we are doing? We are using this nitrogen from the air separation unit in the ammonia plant for making the hydrogen which we are getting from your the syngas and the  $\text{CO}$  if it is remaining after the separation of the hydrogen. That is being used  $\text{CO}$  that is converted to  $\text{CO}_2$ . That  $\text{CO}_2$  along with the ammonia we are making the urea, but if you are having the  $\text{CO}$  because  $\text{CO}$  is also important source of the a large number of the chemicals and already and some of things we discussed in the earlier lecture.

But, again will be discussing in detail by discussing the synthesis gas and the various chemicals which you are getting from synthesis gas in the while discussing the petro chemicals hydrogen chemicals, hydrogen and the chemicals in methanol that may be

important product hydrogen that can be used in the process for making the ammonia or it can be used for the fuel shell or it can be used for other purposes. Various hydrogenation process hydrodesulphurization process clean syngas for refinery use synthesis of the hydrocarbons power generation.

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### **Process Steps in Gasification**

- **Feed Preparation :**

Wet feed system or dry feed system may be used in gasification.

Wet feed system employ grinding and slurring with water and pumping to gasifier while dry system consist of grinding of the feed and employ lock hoppers to pressurize the feed.

Now, let us discuss what are the in detail about the various steps in gasification feed preparation, wet feed system or dry feed system may be used in the gasification. Wet feed system employ grinding and slurring with the water and pumping to the gasifier while dry system consist of grinding of the feed and empty lock hoppers to pressurize the feed and so always the dry actually the a raw material that will be the more economical than the by your the wet feed.

Then, the second part is the gasification that is carried out at the 900 to 1100 centigrade carbon react to the oxygen and steam to form the synthesis gas, synthesis gas that is C O and H 2 and some minor by products which is removed to produce the clean synthesis gas which can be used as a fuel for generation of the steam electricity. Or, it may be used as chemical feed stock like methanol and methanol to again we can go for the manufacture a large number of the chemicals like the formal dehyde or it may be methanol to olefin or methanol to plastic.

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## Process Steps in Gasification

### Gasification:

Gasification is carried out at temperature between 900-1100°C. carbon react with oxygen and steam to raw synthesis gas( CO and H<sub>2</sub>) and some minor by products which is removed to produce clean synthesis gas which can be used as fuel , for generation of steam and electricity or may be used as chemical feed stock.

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## Process Steps in Gasification

### Syn gas cooling

High temperature syn gas produced from gasification is cooled.

### Air Separation

The process produces oxygen for gasification. The process is based on cryogenic separation of air. The process involves liquefaction of air and fractionation to get oxygen, nitrogen and other gases.

Then comes the other steps syngas cooling high temperature syngas produced from the gasification that is cooled because always the wasted boiler that is integral part of the your gasification plant or the steam reforming where we are recovering the heat from the gases. And so, the steam which generated then the air separation this is only normally wherever we are having the steam reforming unit we are using the air directly.

But in case of the partial oxidation process or the gasification we need the pure oxygen for gasification. So, the process based on the cryogenic separation of the air this is



mostly varying using although the pressure swing at the option that has also come for the separation of the oxygen nitrogen. But mostly they all the units they were having and the air separation and that the pressure swing at the option that was developed the process involves liquefaction of air and fractionation to get oxygen nitrogen and other gases because the large number of the other unit gases also we are getting from the air separation acid gas removal.

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## Process Steps in Gasification

### Acid Gas Removal :

This involves removal of impurities like  $H_2S$ ,  $COS$ ,  $NH_3$  and  $HCN$  by absorption using various commercial solvent like monoethanol amine(MEA), methyl diethanol amine(MDEA), methanol (Rectisolvent and Selexol. The solvent is regenerated by stripping the acid gases and recycle.

**Slag Handling System :** The gasifier may be either slagging or non- slagging.

This involves the removal of impurities like  $H_2S$ ,  $COS$ ,  $NH_3$  and the  $HCN$  by absorption using various commercial solvent like mono ethanol amine methyl diethanol. Because as I told you for absorption of the acid gas, these are the some of the development which is that has taken place because with the coming of the petrochemical complex. Now we are we are getting the mono ethanol amine or die ethanol amine so, these are the some of the amine's that can are very commonly the refinery and the fertilizer.

Also methanol that also we are using for the even for the absorption of the  $CO_2$  and in some of the fertilizer plant where they are making methanol just like RCF or the NFL Panipat, they are using methanol and the sodium carbonate. Of course, that was the solvent is regenerated by stripping and the acid gases and the recycle. Slag handling system this gasifier may be either slagging or non slagging type. The reaction it is an exothermic because always you know the whenever the oxidation is there that is

exothermic and produces a gas containing when the C O and H<sub>2</sub> and the because of this exothermic and the endothermic reaction. In case of the steam reforming now there has been development in case of the reforming process also that is the auto thermal refining so, where they are using the both the partial oxidation in the steam reforming the steam.

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## Gasification

- It is an exothermic process and produces a gas containing mainly CO and H<sub>2</sub>.
- The raw synthesis gas contains small quantities of CO<sub>2</sub>, H<sub>2</sub>O and H<sub>2</sub>S and impurities, such as CH<sub>4</sub>, NH<sub>3</sub>, COS,HCN, N<sub>2</sub>, Ar and ash, the quantities being determined by the composition of the feedstock, the oxidant and actual gasification temperature (1300-1400°C).
- A small amount of unconverted carbon is also present and ranges from 0.5 to 1.0 by percent wt in liquid feedstock or 50-200 ppm wt in gaseous feedstock.

The heat generated during the exothermic process that is being used for the in the endo in the endothermic process that is the catalytic reforming the raw synthesis gas is gas contains a small quantity of C O<sub>2</sub> H<sub>2</sub> and H<sub>2</sub> S and impurities. Such as this already I have discussed about the this impurity has to be removed in the air that because the organ that is coming from the and the ash. A small amount of unconverted carbon because during the always whenever carbon rejection is there whenever you are going for the high temperature same thing happen.

In case of the partial oxidation also the carbon is also present as a fine particle and ranges from the 0.5 to 1.0 percent weight in the liquid feedstock or 500 to 50 to 200 percent weight in the gaseous product. These are the reaction that is taking place in case of the gasification combustion Steam reforming reaction and Boudouard reaction these are the some of water gas reaction water shift reaction methanation.

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### Gasification Reactions



For gas as pure methane  $m=4$  and  $n=1$   
hence  $m/n=4$

For oil  $m/n \approx 2$  hence  $m=2, n=1$

For coal  $m/n \approx 1$  hence  $m=1, n=1$

- Source: Chemical Industry Digest. Annual-January 2010, Page- 148]

These are the some of the series of the reaction because you see the partial oxidation or the steam reforming that is a complex initial.

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#### • Combustion



#### Steam Reforming Reaction



#### Boudourard Reaction



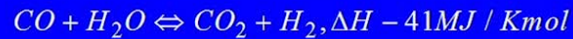
Number of reaction that is taking place simultaneously during the process and this is the reason why we are getting the methane also.

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- **Water Gas Reaction**



- **Water Shift Reaction**



- **Methanation Reactions**



- Source: Chemical Industry Digest. Annual-January 2010, Page- 148

Gasification, now we will discuss about the why we are going for the gasification in the petroleum refinery with increasing use of the heavier crude and processing of the heavy residue has resulted in increased production of the tar petro coke. And asphalt by various residues upgrading technology like visbreaking coking and deasphalting. Because you see the we start with the thermal cracking and then the catalytic cracking and again vis breaking or the delayed coking processes are now extensively used in all the refinery for processing of the heavier residues.

We are getting so, during the process we are getting the petro coke because the during the coking process of vis breaking and that petro coke. Now, the because you see the you take the case of the reliance their capacity plus 60 million tons crude oil processing all the refinery they have been increased their capacity.

So, they are processing and even the crude oil which we are using that is the crude oil which we are using, that is indigenous crude is only 35 to 45 rest it is all imported crude and It is varying in the quality and more and more heavier residue heavier crude oil now it is available in the refinery and so the mixed that is the reason why we are using the mixed crude oil for processing. It is not only the imported or the indigenous crude, but it is the mixed blend of the crude oil that we are processing.

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## Gasification in Petroleum Refinery

- With increasing use of heavier crude and processing of heavy residue has resulted in increased production of tar, petrococoke and asphalt by various residues upgrading technologies processes like visbreaking, coking and deasphalting.
- These residues can be gasified for production of hydrogen, syn. gas, electricity ammonia and chemicals.
- [Handa and Ganesh,2011]

So, the huge amount of your petro coke that is available and that is going to be available in the future. Because of the use of more and more heavier crude so, these residues can be classified for production of the hydrogen syngas electricity ammonia and other chemicals. But production of the hydrogen already some of the units they are going for the production of the hydrogen from the syngas.

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## Various Type of Gassifier

Fixed bed	Fixed bed involve an upward flow of reaction gas through a relatively stationary bed of hot coal. The gas velocity is low.
Moving bed gasifier	Moving bed gasifier operates counter currently where the coal inter the gasifier at the top and moves downward and slowly heated with the product gas. Gasification takes place in the gasification zone.

Source: Vorres, K.S. "Coal gasification" Encyclopedia of Chemical Technology vol 6,p.760

Only problem in case of all the steam reforming as a syngas that is the generation of the C O 2 that C O 2, 1 ton of the hydrogen that produces about 10 tons of the C O 2 when



you are going for the steam reforming. So, that is a big challenge in the refinery, but with the availability of the petro coke we are going for the gasification of the petro coke and for the production of the hydrogen because that is the way. That is petro coke that is being used by the other plants like cement and the paper unit as a fuel so, why not the your refinery itself can use that raw material important raw material, because always the petro coke is better than your coal. Because the carbon contents in much much higher than the coal and so the always the gasification or the partial oxidation that will be very economical.

Now let us discuss because as I told you the the gasification are making of the coke that has been from the ancient time in some or other form. So, we started the gasifier that was the first gasifier that was the fixed bed Lurgi fix fixed bed gasifier. And the fixed bed involves an upward flow of the reaction gases through a relatively stationary bed of hot coal. The gas velocity is low moving bed gasifier operates counter currently where the coal enter the gasifier at the top and moves downwards and slowly heated with the product gas and gasification takes place in the gasification zone.

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<b>Various Type of Gassifier</b>	
Fluidised bed gasifier e.g., <u>Winkler/KBR</u> / <u>U-GAS</u>	Fluidised bed operates at higher gas velocities than fixed bed and uses smaller particle. The gasifier operates at atmospheric pressure and moderate and uniform temperature.
Entrained flow gasifier	Entrained bed operates with parallel flows of reaction gas and pulverised coal which minimize the reaction time and maximize throughput of product.. The residence time is few seconds. Ash is removed as molten slag

Source: Vorres, K.S. “ Coal gasification” Encyclopedia of Chemical Technology vol 6,p.760

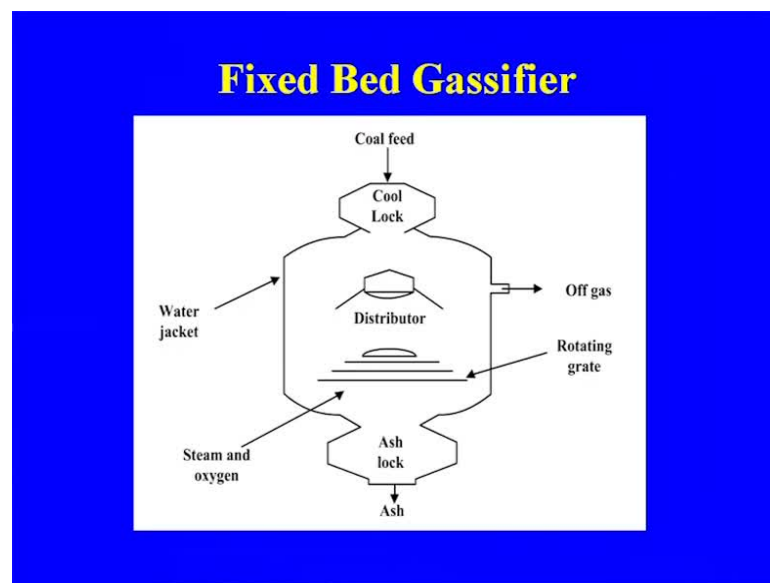
So, this slowly from the mixed to moving bed and moving bed to fluidized bed that is the development in case of the gassifier. Fluidized bed gassifier that operates at higher gas velocity than the fixed bed and uses smaller particle. The gassifier operates at atmospheric pressure and moderate and uniform temperature. So, better actually the



quality of the synthesis gas and it is more energy intensive that is the in case of the fluidized bed. And the better reaction is there now the most of the cases now the new type even in case of the thermal power plant we are using the now the fluidized bed boiler.

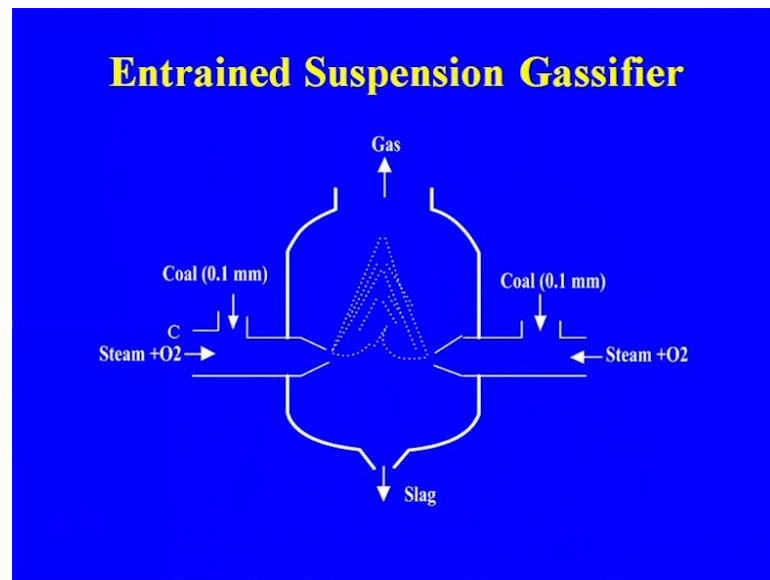
So, in next development in case of the gasifier that was the entrained flow gasifier entrained bed operates with the parallel flows of the reaction gas and pulverised coal. Because in as I told you the in case of the thermal power plant where you are the fluidized bed. So, there we are using the pulverized coal, so pulverized coal which minimize the reaction time and maximize the thorough output of the product. The residence time is few seconds ash is removed as molten slag. This is the in case of the entrained flow gasifier.

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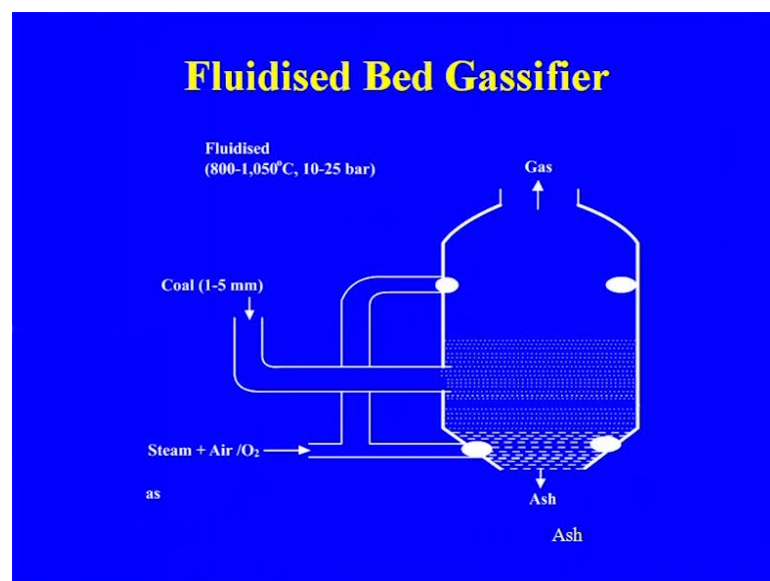
This is the fixed bed gasifier coal feed that is going to the cool lock system and from the cool lock system it is going to the gasifier section rotating grate for removal continuous removal of the ash that has to be there. And depending upon the type of the because if you are having the coal definitely ash going to be more then the petro coke. And this is the water jacket is there here water jacket is there it is not shown, but water jacket is there for cooling steam and oxygen that is going to the gasifier off gases that is there. So, this is the fixed bed that was the older technology that was being used and that was developed by the Lurgi.

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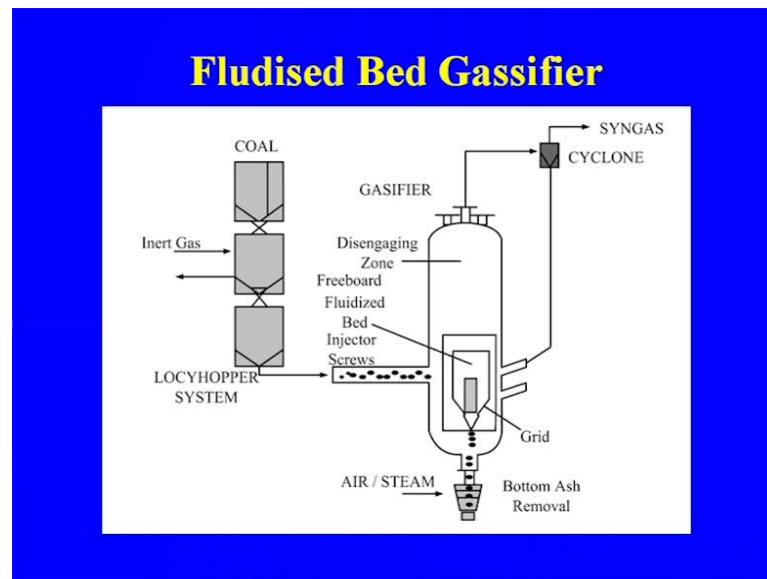
And then, the entrained suspend gasifier that is the again the new development that is taking place that this steam and coal that is going and this is also the type of fluidized system is there. This is the fluidized bed that was the actually the earlier, which I showed that was it is not the fluidized, but it is the moving bed this is the entrained and this is the fluidized bed. Coal and steam that is going from the bottom fluidization that is taking place and the ash that is coming continuously from the bottom of the fluidized bed gasifier.

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This is the again another type of the fluidized bed gasifier where the fluidization is taking place and syngas after going to the cyclone where the particulate matters are separated and then the syngas that will go for further processing.

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New gasifier designs that eliminate the air separation unit, because actually the cost of the air separation is very high. And so, the now the elimination of the air separation unit is there in the new type of the gasifier high temperature syngas cleanup, high efficiency and the lower cost. These are some of the developments that are taking place in the gasifier. New gasifier is the KBR transport gasifier, which is developed by the KBR low rank high ash high moisture coal compatible that is for the KBR. Because always some problem in the when you have the high gas coal for power generation air can be employed as the oxidant. Here actually the you see the oxygen instead of oxygen you can use the air lower cost predicted higher availability predicted.

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### **New Gassifier Designs**

GE Global/ Unmixed Fuel Processor (UOP) :

- Elimination of Air Separation Unit (ASU)
- High Temperature Syn gas Clean up
- Higher efficiency
- Lower cost

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### **New Gassifier Designs**

KBR Transport Gassifier (TRIG™)

- Low rank, high-ash, high-moisture coal compatible
- For power generation, air can be employed as the oxidant
- Lower cost predicted
- Higher availability predicted

Non slagging and refractory issues should therefore be minimal in case of the your coke oven plant this gasifier, higher predicted efficiency lower emissions large scale of the technology. By 2010 that was the actually estimated earlier this technology will be operating at the scale of EGS gas experience already in 2007.

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- Non-slugging, and refractory issues should therefore be minimal
- Higher predicted efficiency
- Lower emissions (due to higher efficiency)
- Large scale up of the technology still required, by a factor of ~30
- By 2010, this technology will be operating at the scale of E-Gas which has >20 years experience already in 2007.

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- Lower temperatures and short gas residence time may lead to some methane formation, which is detrimental in chemical applications.
- Ash disposal problem if carbon conversion predictions are not met in commercial apparatus.

Lower temperature and short gas residence time may lead to the some methane formation, which is detrimental in the chemical application. Because methane that may be non material in case of, but in case of the chemical because whenever you are going for the fertilizer plant the we are removing the C O 2 by nitrogen, but in case of the steam reforming or converting this C O to methane so, but in other application that methane that may be problematic. As, disposal problem carbon conversion prediction are not met in the commercial operation. Again you see the always there has been people

have been looking for the better and better operation. So, instead of the normal gasification now people are also looking for the catalytic coal gasification.

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## Catalytic Coal Gasification- Bluegas™

- Elimination of oxygen plant
  - For SNG objective, little or no catalytic methanation required
  - High thermodynamic efficiency potential
  - Catalyst cost and recoverability
  - Carbon conversion and methane production yields in the gasifier
  - Cost of applying the catalyst effectively to the coal
- Inherently must be done in a fluidized bed which have not been scaled up to larger capacities of entrained gasifiers (yet)

So, elimination of the oxygen for SNG of objective syngas little or no catalytic methanation required high thermodynamic efficiency catalyst cost and recoverability, carbon conversion and methane production yields in the gasifier. So, cost of the applying the catalyst effectively with coal inherently must be done in fluidized bed which have not been scaled up to the larger capacity.

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- Interactions of catalyst with coal ash
- Separation costs of syn gas and methane – cryogenic process
- Excess steam requirements
- Unsuitable for chemical synthesis processes due to CH<sub>4</sub> reforming requirement.



So, some of the advantage are there in case of the, when you are going for the catalytic coal gasification.

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**Coal Gasification in fertilizer Industry**

- Coal gasification for production of synthesis gas and ammonia has been being used many part of the world where large quantity of coal is present.
- Higher energy consumption in coal based ammonia plant has been major constrain
- Relative energy consumption per tonee of ammonia

Gas	Naphtha	Fuel oil	Coal
	1.1	1.15	1.45

[ Murthy and Patnaik, 2001].

Now, we will discuss about the coal gasification in the fertilize industry because as, this is the coal gasification for the production of the synthesis gas and ammonia has been used many part of the world where large quantity of the coal is present. Higher energy consumption in coal based ammonia plant has been major constraint relative energy consumption if you see the gas if you take the gas 1. So, naphtha is one 1.5 time fuel oil 1.15 coal is the maximum energy consumption when you are producing synthesis gas or ammonia this is for the figure is for ammonia.

So, the always the cost of production of the syngas or the ammonia that is higher and that has been the major constrain in utilization of the coal when the, we are having the enough gas of the naphtha. But you will have to always look for the alternative resources because the whatever the resources of the oil are the supply of the oil the volatile market of the crude oil. Definitely, you will have to look after the some of the other raw material also. But again government is thinking to start the coal based fertilizer plant.

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## **Rapid Thermal Processing (RTP™) Process for Conversion of Biomass to Liquid Fuels**

- RTP™ is fully heat integrated technology that yields over 70% liquid products from typical biomass feed stocks.
- It is a fast thermal process where biomass is rapidly heated in the absence of oxygen.
- The biomass is vaporized and the vapour cooled to generate high yields of pyrolysis oil.

These are the this is the another rapid thermal processing for conversion of the biomass to liquid fuels, because I will be discussing about this in detail about the biomass gasification here why the importance of the biomass gasification. So, this is the we are doing the fast pyrolysis also to get the more liquid products so let us know discuss about the biomass gasification. Why we are going for the biomass gasification? Why the, what was the necessity?

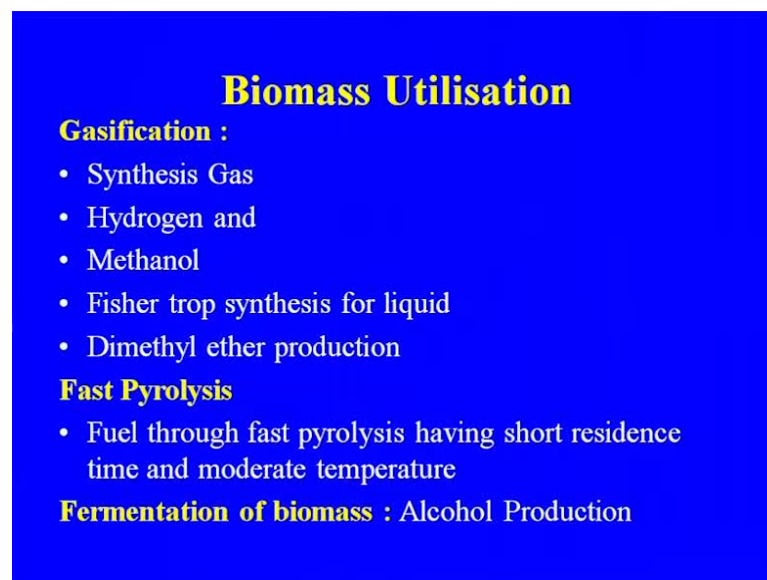
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## **Biomass Gasification**

- Biomass is available in large quantity. Biomass gasification has received considerable interest during recent years as Biomass is carbon neutral renewable resource
- The constantly depleting resources of conventional energy and the steeply escalating price of fossil fuels have led to the need of alternate energy and raw material resources.

Because the biomass is available in large quantity and because of that reason biomass gasification has received considerable interest during the recent years as biomass is the carbon neutral renewable source and always we are taking for either for the renewable energy renewable feedstock, because whatever the resources we are having that is not unlimited, so definitely will have to think of the alternative resources. In case the conventional resources are not available, the constantly depleting resources of the conventional energy and the steeply escalating price of the fossil fuel have led to the need of the alternative energy. And the raw material resources, this is the reason why we are going for the utilization of the biomass.

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**Biomass Utilisation**

**Gasification :**

- Synthesis Gas
- Hydrogen and
- Methanol
- Fisher trop synthesis for liquid
- Dimethyl ether production

**Fast Pyrolysis**

- Fuel through fast pyrolysis having short residence time and moderate temperature

**Fermentation of biomass :** Alcohol Production

So, what are the ways of utilization of the biomass because they are in a various forms of the biomass that can be used. One is the gasification where you can produce the synthesis gas hydrogen and methanol and the fisher trop synthesis for liquid dimethyl dimethyl ether. Production that can be also blended with the gasoline or dimethyl ether to methanol that we can produce. Another, actually the development that has taken place, which I was telling about the fast pyrolysis of the biomass fuel through fast pyrolysis having short residence time and moderate temperature that yield in more liquid products than the gaseous products.

So, that is what we are doing in case of the and again lot of the work that is going on the fast pyrolysis the biomass to get the more economically. Because that is very important,

you see the whenever you are using the fuel or the liquid fuel from the petroleum of that is always cheaper. So, the fast pyrolysis that has to be process has to be optimized then the next major use that is coming in big way that is the fermentation of the biomass for the production of the alcohol. That will be discussing while discussing the sugar and the fermentation industry where the, how the biomass that is being used for the alcohol production syngas and the hydrogen and methanol from biomass?

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## **Synthesis Gas, Hydrogen and Methanol From Biomass**

Methanol and hydrogen produced from biomass are promising carbon neutral fuel

Process steps:

- Pretreatment
- Gasification
- Gas cleaning
- Reforming of higher hydrocarbons
- Gas separation
- Methanol synthesis

Methanol and hydrogen produced from the biomass are promising carbon neutral fuel. And the various process step in case of the biomass that is the pretreatment gasification, gas cleaning, reforming, of the higher hydrocarbons gas separation and the finally, it may be methanol synthesis or you can separate the from the C O to C O and H<sub>2</sub> that H<sub>2</sub>. That can be separated if you are interested for the production of the hydrogen. Then the CO<sub>2</sub> again C O that has to be converted to C O<sub>2</sub> and that CO<sub>2</sub>. If you are not having so, that is a problem as told you the about 10 tons of the C O<sub>2</sub> that may be produced with the 1 ton of the, for producing 1 ton of hydrogen in the steam reforming. So, definitely you will have to look for some alternative thing.

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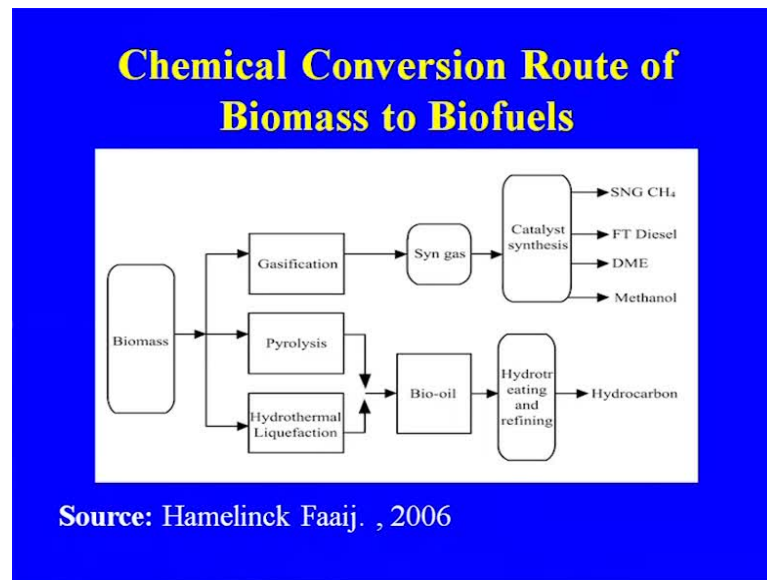
<b>Biomass Feed stock</b>	<b>Typical Pyrolysis oil yield ,wt% of dry feed stock70-75</b>
Hardwood	70-80
Softwood	70-80
Hardwood bark	60-65
Soft wood bark	55-65
Corn fiber	65-75
Bagasse	70-75
Waste Paper	60-80

- **Source** : Reno et al., 2011

So, this is the typical yield of the various biomass if you are having the pyrolysis oil. So, hardwood, softwood, hardwood bark, softwood bark, corn fiber bagasse waste paper. But actually the you see the bagasse or the waste paper or the even hardwood softwood normally, it is being used in large quantity for making of the paper mill. And so, the even the deforestation problem it may not be very economical to have the, but at least the hardwood bark softwood bark that can be used even in case of the bagasse, because you see the bagasse that is being used as the for the only fuel purposes why not to provide the alternative fuel to the sugar mills.

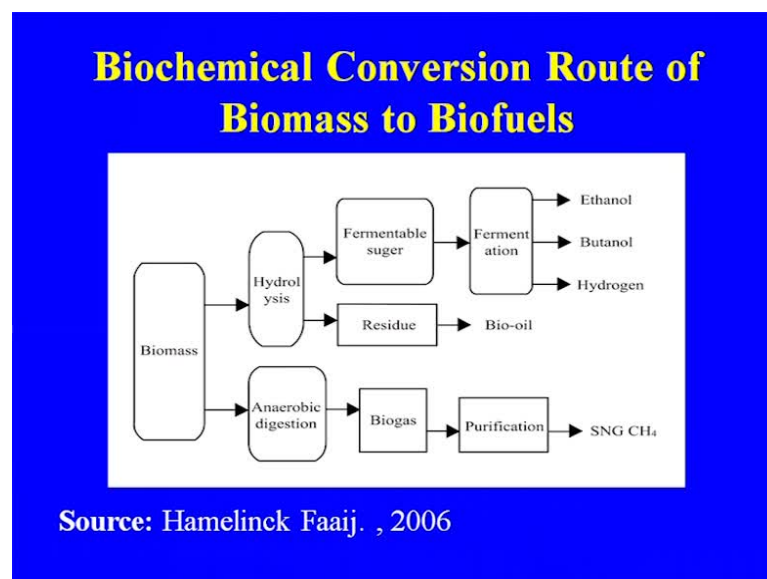
So, that the bagasse that can be used for more value added product through the gasification or for other or alcohol. Waste paper again you cannot afford to go for the fast pyrolysis of the waste paper because this is also being used for the production of the, but this is the how the availability of the pyrolysis oil is there. Waste paper that is being used in huge amount and now the many of the mills in India they are totally based upon the waste paper.

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This is the chemical conversion route for the biomass gasification that is the biomass gasification pyrolysis or hydrothermal liquefaction; that may be there in presence of hydrogen. We may get the synthesis gas that the from the synthesis gas you can go for the FT diesel DME dimethyl ether or the methane and the bio oil hydro treating and refining then the hydrocarbon. So, this is the process that can be used for the gasification of the biomass.

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This is the biomass conversion route for the biomass to biofuel hydrolysis anaerobic digestion this is the for the production of the ethanol again. We will be discussing while discussing the ethanol manufacture from the biomass. Now the recent interest there has been for the coal gasification, coke gasification of the coal and biomass for methyl methanol synthesis because, you see the coal and biomass, if you mix with the coal. So, the coke gasification that can be done and some of the advantage. Because in case of the coke gasification of the coal and biomass combined with the power and methanol production can be of considered as, a potential fuel base for gasification.

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### **Co-gasification of Coal and biomass for methanol synthesis**

- Co-gasification of coal and biomass combined with power and methanol production can be of considered as a potential fuel-base for gasification
- Some of the advantage of integrated biomass-coal cogasification system are possible continuous operation of the coal gasification reactor, lower costs of electric-energy production

Some of the advantage of integrated biomass coal gasification system or possible continuous operation of the coal gasification reactor. Low cost of the electricity, energy production because as such you see the biomass is that is free only the transportation cost would be there. So, definitely if you compare the cost of the coal and the biomass, so definitely the whole process that is going to be the economical. So, this was the actually the about the gasification part the coal gasification petro coke gasification or the biomass gasification. And definitely, in the future because some of the country like China, they are having the huge amount of the coal deposit.

So, they are going for the, already they have started one plant for the coal gasification and from the coal gas to synthesis gas and from synthesis gas to methanol and methanol to plastic. So, that will be the one of the actually the major area, but at the still in India

also we are working for the coal gasification for making of the synthesis gas and from the coal route through, because the in India also the coal deposit is much higher than in comparison to other country. Similarly, the biomass gasification although we are not using the biomass gasification in India, but there is lot of scope for the biomass gasification and this is the reason why the most of the multinationals are there even in Indian industry.

They are getting interest in the utilization of the biomass for the production of the synthesis gas or the production of the alcohol through the fermentation route are as a fuel. Then the same thing if it is the petro coke, petro coke which we are making which we are getting from the refinery. That can be again a source of the good source of the because the petro coke quality is much better than the coal. So, always the cost of the production of the hydrogen as a syngas that will be lower than the coal at the same time we will be utilizing that waste material or the byproduct of the delayed coking or the coking plant.

It may be the waste for the production of the hydrogen that hydrogen that can be used in the refinery for in the various processes just like catalytic reforming, hydro desulpherization. Then hydro desulpherization means removal of the sulphur component of the phase, feed stock for the various process at the same time. Desulpherization of the product, which we are getting after the crude oil distillation or the just like desired desulpherization. So, that hydrogen that can be so as I told you earlier also the reliance they are going to have the petro coke gasification other uses of the petro coke of course.

They are they are instead of the fuel that can be also used the electro for the electrode also, but the gasification part definitely that is going to improve the economy of the any refinery because now the in future we will have the more and more heavier feedstock. So, this is this was, the about the... So, next module that will be the module 3 that will be on the pulp and paper making; so that we will have the 4 lectures lecture 1 about the introduction of the paper industry what are the development has been taken place. Lecture 2 will be it is discussing about the pulping and bleaching and lecture 3 that will be on the your recovery of the chemicals and fourth lecture that will be on the paper making part. So, this is the how we will be proceeding 1 by 1 from the coal to the paper making.