Basic Environmental Engineering and Pollution Abatement

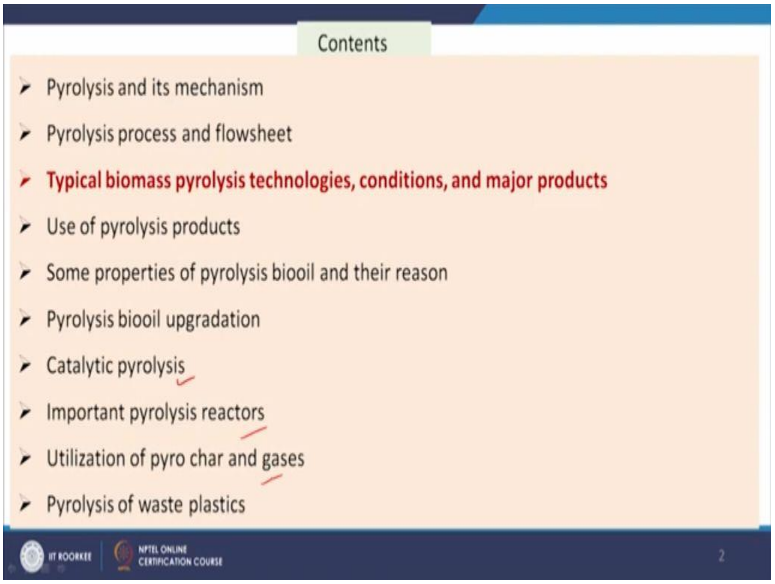
Professor Prasenjit Mondal
Department of Chemical Engineering
Indian Institute of Technology, Roorkee

Lecture – 54

Solid Waste and Hazardous Waste Management - 4

Hello everyone. Now we will discuss on the topic, solid waste and hazardous waste management part-4. And in this class, we will focus on the pyrolysis.

(Refer Slide Time: 00:39)

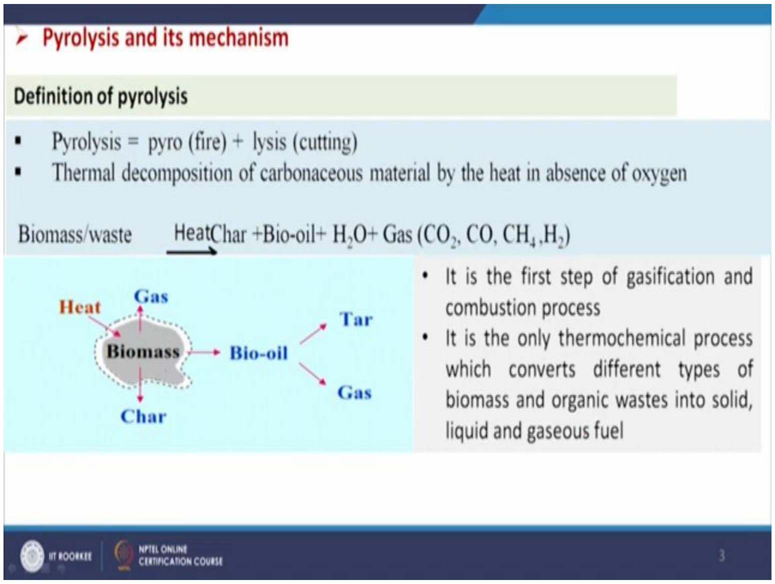


Contents

- Pyrolysis and its mechanism
- Pyrolysis process and flowsheet
- **Typical biomass pyrolysis technologies, conditions, and major products**
- Use of pyrolysis products
- Some properties of pyrolysis biooil and their reason
- Pyrolysis biooil upgradation
- Catalytic pyrolysis
- Important pyrolysis reactors
- Utilization of pyro char and gases
- Pyrolysis of waste plastics

Contents are pyrolysis and its mechanism, pyrolysis process and flowsheet, typical biomass pyrolysis technologies, conditions and major products, use of pyrolysis products, some properties of pyrolysis biooil and their reason, pyrolysis biooil upgradation, catalytic pyrolysis, important pyrolysis reactors, utilization of pyro char and gases, and pyrolysis of waste plastics.

(Refer Slide Time: 01:05)



Pyrolysis and its mechanism

Definition of pyrolysis

- Pyrolysis = pyro (fire) + lysis (cutting)
- Thermal decomposition of carbonaceous material by the heat in absence of oxygen

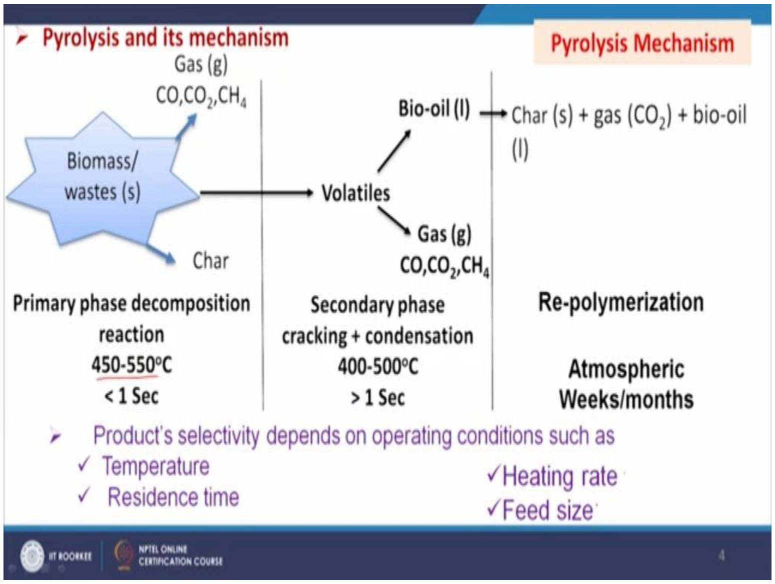
Biomass/waste $\xrightarrow{Heat}$ Char + Bio-oil + H_2O + Gas (CO_2, CO, CH_4, H_2)

- It is the first step of gasification and combustion process
- It is the only thermochemical process which converts different types of biomass and organic wastes into solid, liquid and gaseous fuel

So, if we see the term that is pyrolysis; so Pyro is heat and lysis is the breakdown or the cutting. So, pyrolysis that is the thermal decomposition of carbonaceous materials by the heat in absence of oxygen. And in this method, our feedstock is biomass and waste; and we will apply heat in absence of oxygen or air. Then, we will get char plus bio-oil plus gas, which will containing the water vapour, and other gas components like CO_2, CO, CH_4 and H_2; these are the major component of the gas. So we have biomass, applying heat; we are getting char, we are getting gas. And this gas we can say some vapours phase which is produced after the heat application, some part is liquefied; so, that is bio-oil.

So, that bio-oil contain some liquid molecules and that is also can be converted to tar and gas. So, it is the first step of gasification and combustion process. It is the only thermochemical process, which converts different types of biomass and organic waste into solid, liquid and gaseous fuel. So, that is the unique characteristics of this pyrolysis process; we get liquid, gas as well as the solid material.

(Refer Slide Time: 02:37)



- **Pyrolysis and its mechanism**

Pyrolysis Mechanism

Gas (g)
CO, CO_2, CH_4

Biomass/ wastes (s)

Char

Volatiles

Bio-oil (l) → Char (s) + gas (CO_2) + bio-oil (l)

Gas (g)
CO, CO_2, CH_4

Primary phase decomposition reaction
450-550°C
< 1 Sec

Secondary phase cracking + condensation
400-500°C
> 1 Sec

Re-polymerization

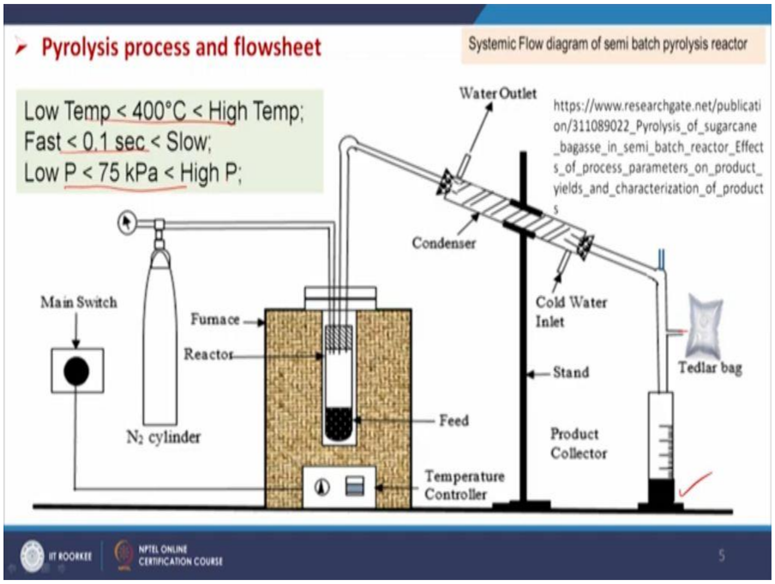
Atmospheric
Weeks/months

- Product's selectivity depends on operating conditions such as
  - ✓ Temperature
  - ✓ Residence time
  - ✓ Heating rate
  - ✓ Feed size

And we see the mechanism in pyrolysis complex reactions takes place, number of reactions can take place simultaneously. So, biomass and waste, we have solid; then it gives us gas and char. This is the primary phase decomposition reactions at 450 to 500 °C less than one second. Then secondary phase these volatiles, so we are getting char, gas and volatile; so that volatiles is further converted to gas, and some part of the gas will be liquefied. So, there is a secondary phase cracking plus condensation at 400 to 500 °C greater than one second. And then re-polymerization also takes place.

So, here the bio-oil, further we convert it to char plus gas plus some bio-oil will also be remaining. So, that way this is called re-polymerization and this reaction is very slow reaction, and takes a long time, like weeks and months for the conversion. So, that is why the quality of bio-oil also gradually degrades if we do not take proper action. Products selectively depend on operating conditions such as temperature, residence time, heating rate and feed size. So, these are the factors which influence the product distribution.

(Refer Slide Time: 04:04)



Pyrolysis process and flowsheet

Systemic Flow diagram of semi batch pyrolysis reactor

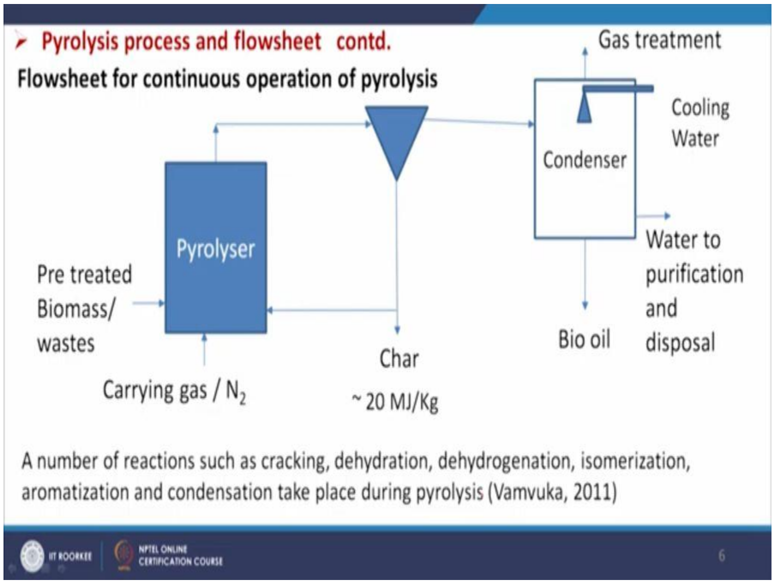
Low Temp < 400°C < High Temp;
Fast < 0.1 sec < Slow;
Low P < 75 kPa < High P;

https://www.researchgate.net/publication/311089022_Pyrolysis_of_sugarcane_bagasse_in_semi_batch_reactor_Effects_of_process_parameters_on_product_yields_and_characterization_of_products

Now, we will see how the pyrolysis gas can be produced with respect to a batch scale set up. Here, we are putting some feed and then it is heated; then high temperature will be there. And we are sending some nitrogen gas, so that inert atmosphere will be there in the absence of oxygen; that condition we are ensuring by that supply of nitrogen. Then, when it will be of high temperature, so then the feed will be pyrolyzed and the vapours will form. So, volatiles will goes off with this nitrogen and it will be cooled down here.

So, this is our cold water in and out; so, in this condenser, so some vapour will be condensed; so, this is our oil part. And some gases will goes up, we can collect it here in the tedlar bag, and get it analyzed; and the bottom part will be remaining some charcoal or char. And depending upon the temperature, we have low temperature and high temperature, this is the normal range; and this means slow or fast pyrolysis. This is the range, fast less than 0.1 second less than slow; and pressure may also be low and high. So, low pressure less than 75 kilo Pascal less than high pressure. So, these are some typical range and this is the batch scale production of pyro oil.

(Refer Slide Time: 05:38)



➢ Pyrolysis process and flowsheet contd.

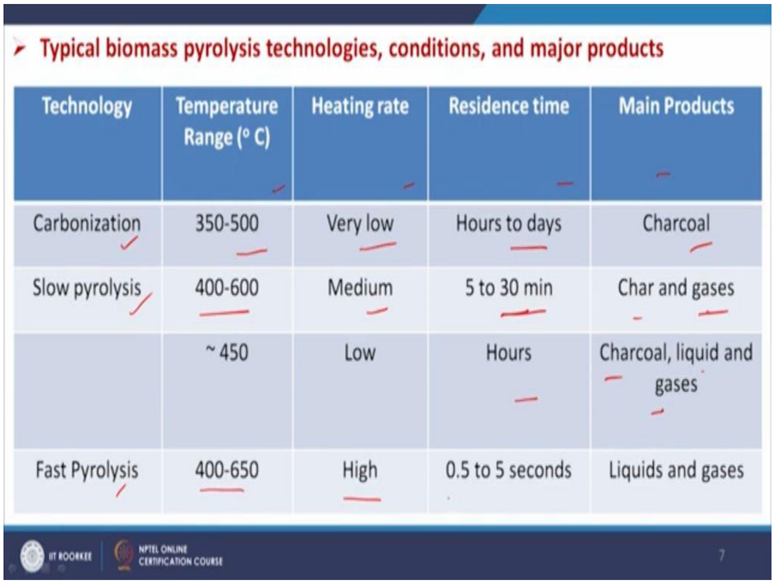
Flowsheet for continuous operation of pyrolysis

A number of reactions such as cracking, dehydration, dehydrogenation, isomerization, aromatization and condensation take place during pyrolysis (Vamvuka, 2011)

And in case of continuous operation, so pretreated biomass and waste; because we know in pyrolyzer, some feedstock properties should be maintained for proper heat transfer and the reactions. So, then here we will be getting some conversions, if we pass the carrying gas nitrogen to provide inert atmosphere. So, then the gas which will be produced here, that is vapours which that will be going into this; and that will also contain some particulates such chars. So, that will be settled here and recycled; so, then getting this one and this is the gas. So, then this further condensed that is vapour basically.

So, it is condensed, some parts will be not condensed, and it will go out as a gas; and it will be treated further and used for the application. And when which part of this vapour is condensed that we are getting as a biooil; and then this cooling arrangement is made, so water to purification and disposal. So, this is the scheme for the pyrolysis of biomass and waste. A number of reactions such as cracking, dehydration, dehydrogenation, isomerization, aromatization and condensation take place during pyrolysis. So, pyrolysis is not a single reactions; in multiple reactions, different types of reactions can take place simultaneously.

(Refer Slide Time: 07:10)



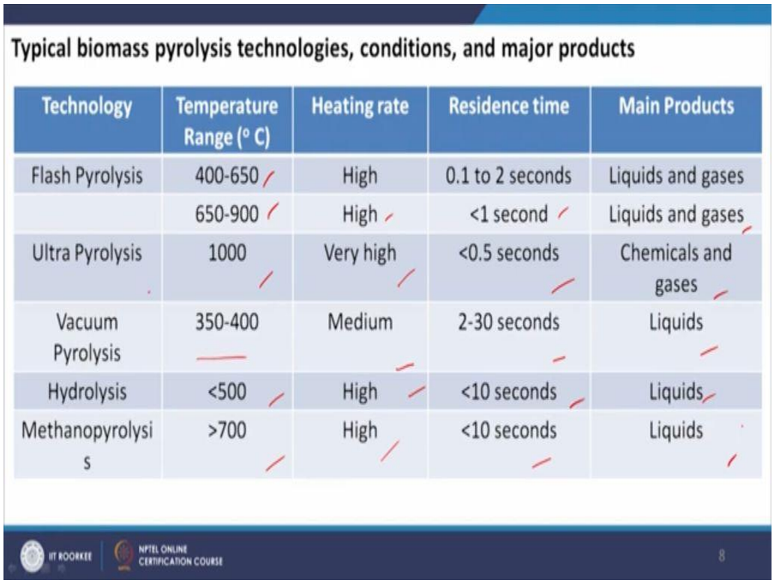
Typical biomass pyrolysis technologies, conditions, and major products

Technology	Temperature Range (° C)	Heating rate	Residence time	Main Products
Carbonization	350-500	Very low	Hours to days	Charcoal
Slow pyrolysis	400-600	Medium	5 to 30 min	Char and gases
	~ 450	Low	Hours	Charcoal, liquid and gases
Fast Pyrolysis	400-650	High	0.5 to 5 seconds	Liquids and gases

Now, we will see the different types of pyrolysis, like say carbonization, slow pyrolysis, fast pyrolysis. Here will see the difference in temperature, heating rate, residence time and product distribution. So, for carbonization you see, suddenly our main objective is to get solid part, or that is the charcoal. So to get the charcoal, we need to apply low heating rate. And our residence time should be more hours to days, and temperature also will be medium; so 350 to 500 ^{o}C. And for slow pyrolysis, this is the temperature range. But, heating rate is more than this medium; and then 5 to 30 minute time and char and gases.

Then, this cracking takes place at this step, then further reaction can take place thereafter. And 450 and low, for hours, and then charcoal, liquid and gases. Here we get char and gas, here you get charcoal, liquid and gases. And in case of the first pyrolysis, this is temperature 400 to 650 ^{o}C, and high heating rate, and residence time 0.5 to 5 seconds, and liquid and gases are produced.

(Refer Slide Time: 08:32)



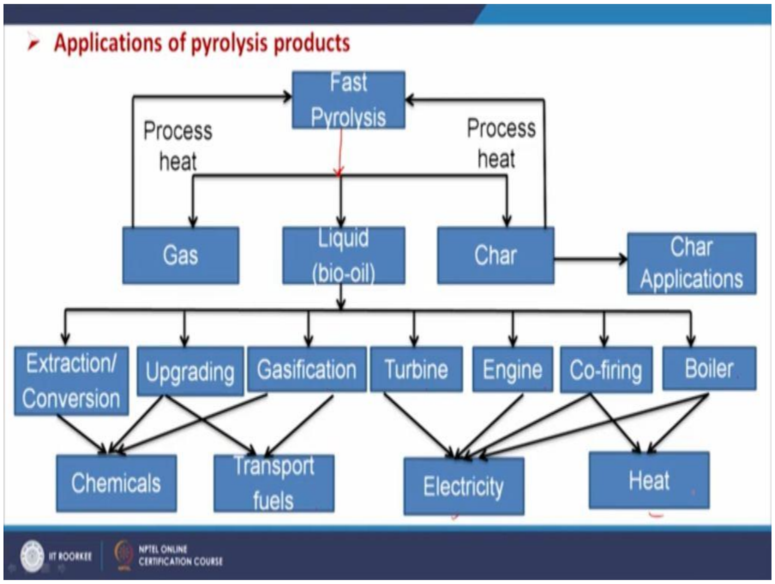
Typical biomass pyrolysis technologies, conditions, and major products

Technology	Temperature Range (° C)	Heating rate	Residence time	Main Products
Flash Pyrolysis	400-650	High	0.1 to 2 seconds	Liquids and gases
	650-900	High	<1 second	Liquids and gases
Ultra Pyrolysis	1000	Very high	<0.5 seconds	Chemicals and gases
Vacuum Pyrolysis	350-400	Medium	2-30 seconds	Liquids
Hydrolysis	<500	High	<10 seconds	Liquids
Methanopyrolysis	>700	High	<10 seconds	Liquids

In flash pyrolysis, this is the temperature range and then this is high heating rate; residence time is less, liquid and gases are produced. And Ultra pyrolysis, 1000 ^{o}C, very high heating rate; and residence time is less, and the chemicals and gases. Vacuum pyrolysis, 350 to 400 ^{o}C temperature is relatively less; and then medium heating rate, low residence time and liquid is basically preferably produced. And hydrolysis is less than 500 ^{o}C, high heating rate, less than 10 seconds; again it gives us liquid. And methanopyrolysis greater than 700 ^{o}C, high heating rate, less than 10 seconds residence time, and gives liquid products.

So, these are the different types of pyrolysis which have been reported in literature, and their product distributions varies, their heating rate varies; and their temperature and residence time also varies.

(Refer Slide Time: 09:27)



Applications of pyrolysis products

Fast Pyrolysis
Process heat
Process heat
Gas
Liquid (bio-oil)
Char
Char Applications
Extraction/ Conversion
Upgrading
Gasification
Turbine
Engine
Co-firing
Boiler
Chemicals
Transport fuels
Electricity
Heat

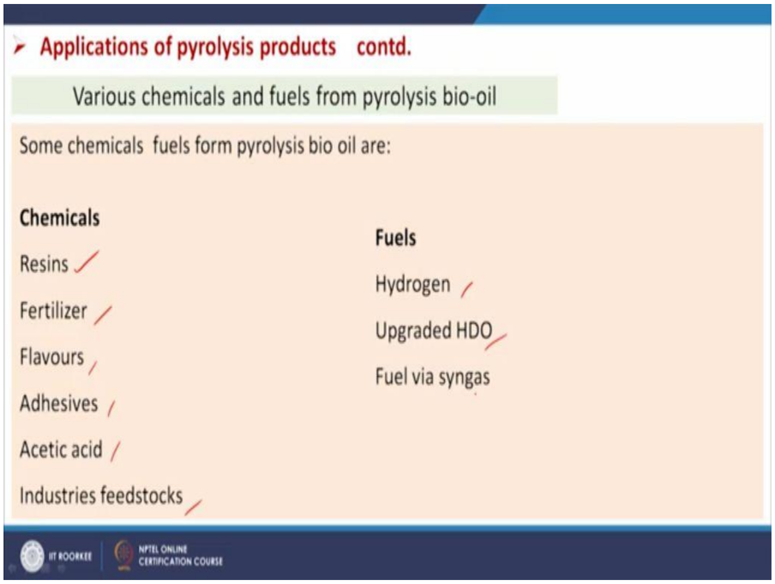
IIT ROORKEE
NPTEL ONLINE CERTIFICATION COURSE

Now, we will see the applications of pyrolysis products. So from the pyrolysis, say fast pyrolysis; we will be getting gas, liquid, and char. So, this gas and char both can be used to provide heat for the fast pyrolysis process, because pyrolysis process is an endothermic reaction; so that can be recovered or the char can be used for other applications also. And then liquid which you are getting that may not be used directly because of its inferior quality. As you mentioned that moisture content is higher, so we have to remove the moisture first.

Then, we have to upgrade it; we will see that its its fuel properties are also not not good and requires upgradation. So, different applications are say extraction or conversion, upgrading; we can use this for gasification purpose. we can use it in turbine, we can use it in engine, we can use it in for co-firing in co-generation plant, or it can be used in boiler. So, these are the different applications which we can have with this pyrolysis bio-oil; and conversion and gasification, upgradation can give us different type of chemicals and transportation fuels, and turbine, boiler, engine, co-firing all these can give us electricity and heat.

So, these are the different applications of liquid fuel which we get through the pyrolysis of biomass and wastes.

(Refer Slide Time: 11:13)



Applications of pyrolysis products contd.

Various chemicals and fuels from pyrolysis bio-oil

Some chemicals fuels form pyrolysis bio oil are:

Chemicals

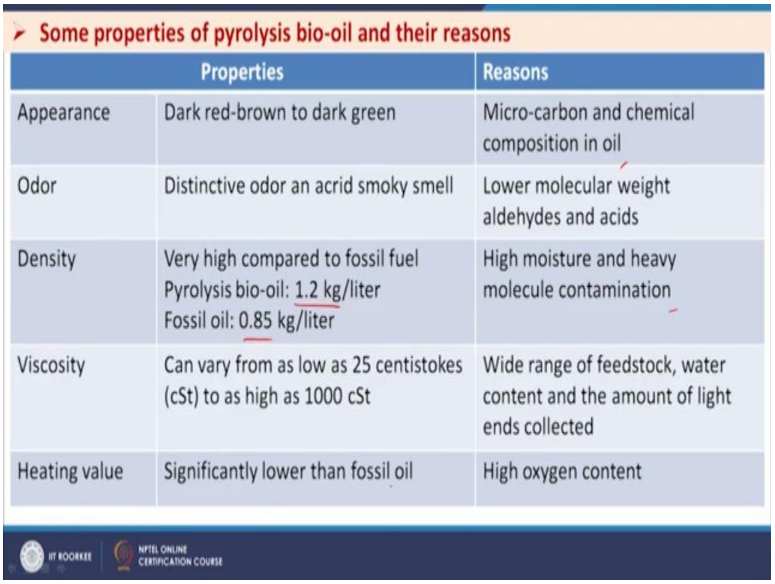
- Resins
- Fertilizer
- Flavours
- Adhesives
- Acetic acid
- Industries feedstocks

Fuels

- Hydrogen
- Upgraded HDO
- Fuel via syngas

Now, various chemicals and fuels from the pyrolysis bio-oil can be produced; some chemicals and fuels from pyrolysis bio-oil are, like resins, fertilizer, flavours, adhesives, acetic acid industrial feedstocks, we can get. And fuels like hydrogen, upgraded HDO, hydro-de-oxygenated oil; and then fuel via syngas, we can use it for the gasification purpose and we can get the syngas; and from syngas to liquid fuel. So, these are the different applications of the bio-oil.

(Refer Slide Time: 11:51)



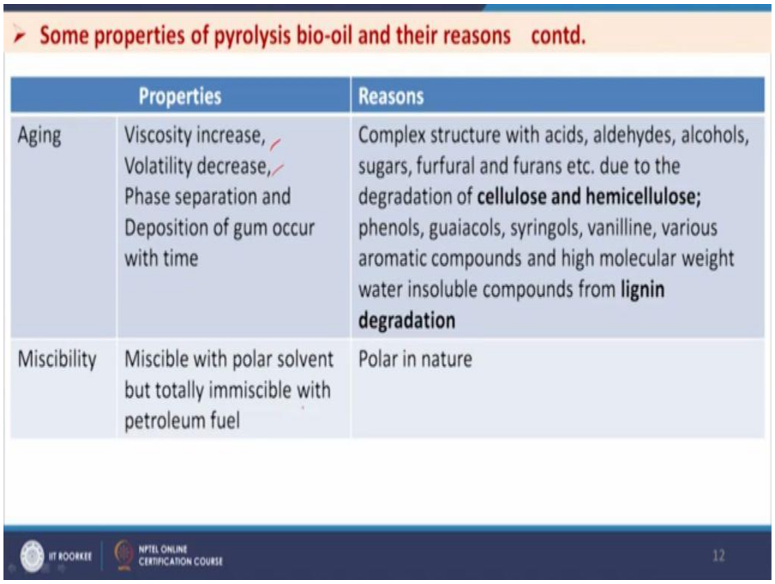
Some properties of pyrolysis bio-oil and their reasons

Properties		Reasons
Appearance	Dark red-brown to dark green	Micro-carbon and chemical composition in oil
Odor	Distinctive odor an acrid smoky smell	Lower molecular weight aldehydes and acids
Density	Very high compared to fossil fuel Pyrolysis bio-oil: 1.2 kg/liter Fossil oil: 0.85 kg/liter	High moisture and heavy molecule contamination
Viscosity	Can vary from as low as 25 centistokes (cSt) to as high as 1000 cSt	Wide range of feedstock, water content and the amount of light ends collected
Heating value	Significantly lower than fossil oil	High oxygen content

And we will see now the properties of bio-oil, some important properties and their reason; like say, appearance it looks like a dark red brown to dark green color. So, because of micro-carbon and chemical composition in the oil, normally it possesses some odour, the distinctive odour and acrid smoky smell. So, that is because of lower molecular weight, aldehydes and acids. Density is very high compared to fossil fuels. Pyrolysis bio-oil is 1.2 kg/L; whereas, fossil fuel is 0.85 kg/L for typical value. So high moisture and heavy molecular contamination; because of that, this density is higher.

And viscosity can vary from as low as 25 centistokes to as high as 1000 centistoke; that is because of wide range of feedstocks, water content and the amount of light ends collected; and heating value significantly lower than fossil fuel because of high oxygen content.

(Refer Slide Time: 12:57)

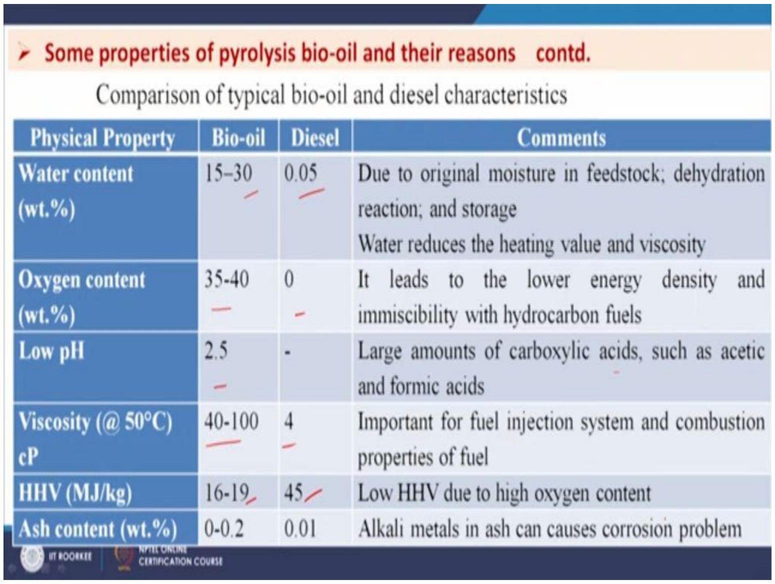


➤ Some properties of pyrolysis bio-oil and their reasons contd.

Properties		Reasons
Aging	Viscosity increase, Volatility decrease, Phase separation and Deposition of gum occur with time	Complex structure with acids, aldehydes, alcohols, sugars, furfural and furans etc. due to the degradation of **cellulose and hemicellulose;** phenols, guaiacols, syringols, vanilline, various aromatic compounds and high molecular weight water insoluble compounds from **lignin degradation**
Miscibility	Miscible with polar solvent but totally immiscible with petroleum fuel	Polar in nature

Now, we will see there is some aging properties of this pyrolysis oil. That is viscosity increase, volatility decrease, phase separations and depositions of gum occurs with time; that means the quality degrades with time. So, because of the complex structure with acids, aldehydes, alcohols, sugars, furfural and furans etc.; due to the degradation of cellulose and hemicellulose; phenols, guaiacols, syringols, vanilline, various aromatic compounds and high molecular weight, water insoluble compounds from lignin degradation. And miscibility, if we see the miscible with bio-oil, is miscible with polar solvent; but totally immiscible with petroleum fuel, because this is polar in nature.

(Refer Slide Time: 13:50)



Some properties of pyrolysis bio-oil and their reasons contd.

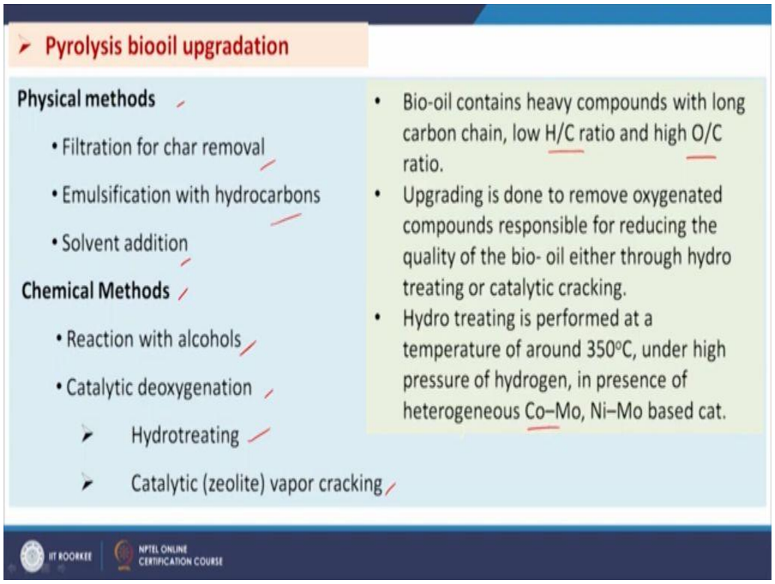
Comparison of typical bio-oil and diesel characteristics

Physical Property	Bio-oil	Diesel	Comments
Water content (wt.%)	15–30	0.05	Due to original moisture in feedstock; dehydration reaction; and storage Water reduces the heating value and viscosity
Oxygen content (wt.%)	35-40	0	It leads to the lower energy density and immiscibility with hydrocarbon fuels
Low pH	2.5	-	Large amounts of carboxylic acids, such as acetic and formic acids
Viscosity (@ 50°C) cP	40-100	4	Important for fuel injection system and combustion properties of fuel
HHV (MJ/kg)	16-19	45	Low HHV due to high oxygen content
Ash content (wt.%)	0-0.2	0.01	Alkali metals in ash can causes corrosion problem

Now, if we compare the properties of this, the pyrolysis bio-oil and petro diesel; then, we see the water content is much more in case of bio-oil 15 to 30 %; whereas, diesel is very very less. So, due to original moisture in feedstock, dehydration reactions and storage, water reduces the heating value and viscosity. So, these are the negative impact of this water. And oxygen content is very high in case of bio-oil 35 to 40 %, whereas diesel has zero. So, it leads to the lower energy density and immiscibility with hydrocarbon fuels; so this is the reason why it is not miscible with the hydrocarbon fuel. And low pH it has 2.5 pH. So, large amounts of carboxylic acids such as acetic and Formic acids are available in it.

Viscosity is also that is 40 to 100 unit; where it is in case of diesel, it is 4. So, this is important for fuel injection system, viscosity is very very important; so low viscosity is desirable. And so this directly bio-oil cannot be used in engine. HHV here is 16 to 19, less HHV with respect to diesel that is 45 MJ/kg. So, low HHV due to high oxygen content as we have discussed; and ash content is 0 to 0.2; whereas, in desert 0.01. So, alkali metals in ash can causes corrosion problem. So, these are the negative aspects of the bio-oil, which is produced to the pyrolysis of biomass and waste. So, it requires upgradation.

(Refer Slide Time: 15:29)



Pyrolysis biooil upgradation

Physical methods

- Filtration for char removal
- Emulsification with hydrocarbons
- Solvent addition

Chemical Methods

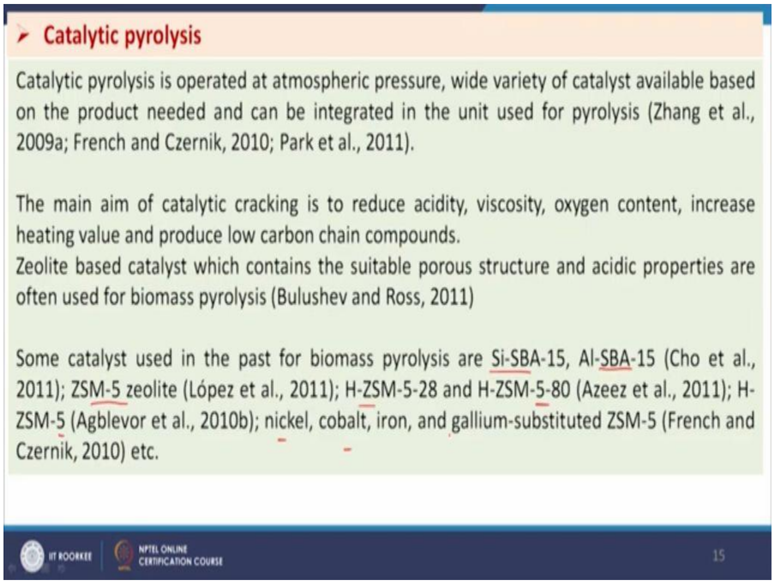
- Reaction with alcohols
- Catalytic deoxygenation
  - Hydrotreating
  - Catalytic (zeolite) vapor cracking

- Bio-oil contains heavy compounds with long carbon chain, low H/C ratio and high O/C ratio.
- Upgrading is done to remove oxygenated compounds responsible for reducing the quality of the bio- oil either through hydro treating or catalytic cracking.
- Hydro treating is performed at a temperature of around 350°C, under high pressure of hydrogen, in presence of heterogeneous Co–Mo, Ni–Mo based cat.

Now, the upgradation can be done through physical route or through chemical route. Like say, physically the filtration for char removal, emulsification with hydrocarbons and solvent addition. So, these are some example through which the quality can be improved. Chemically reaction with alcohols, catalytic deoxygenation; so, by the help of hydrotreating and catalytic vapor cracking. So, these are some routes through which the bio-oil can be upgraded. And bio-oil contains heavy compounds with long carbon chain, low hydrogen by carbon ratio, and high oxygen by carbon ratio. Upgrading is done to remove oxygenated compounds responsible for reducing the quality of the bio-oil, either through hydrotreating or catalytic cracking.

Hydro treating is performed at a temperature of around 350 ^{o}C, under high pressure of hydrogen, in presence of heterogeneous cobalt-molybdenum, nickel-molybdenum based catalyst.

(Refer Slide Time: 16:29)



Catalytic pyrolysis

Catalytic pyrolysis is operated at atmospheric pressure, wide variety of catalyst available based on the product needed and can be integrated in the unit used for pyrolysis (Zhang et al., 2009a; French and Czernik, 2010; Park et al., 2011).

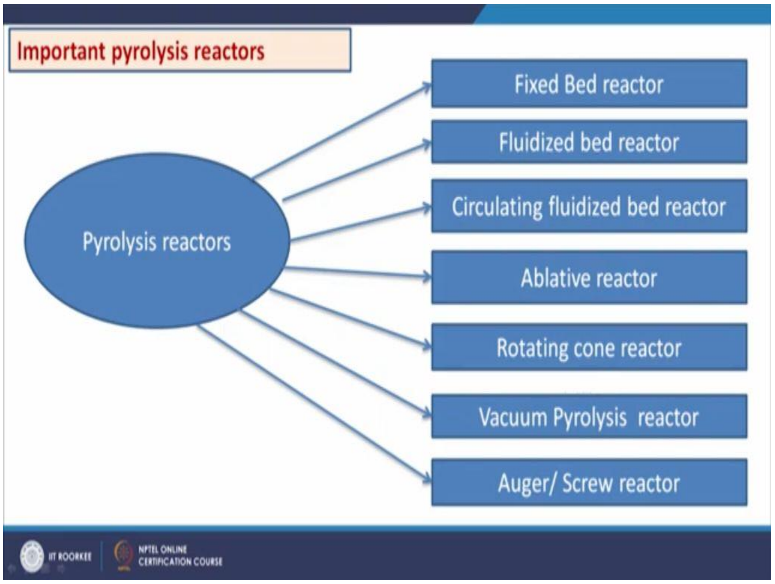
The main aim of catalytic cracking is to reduce acidity, viscosity, oxygen content, increase heating value and produce low carbon chain compounds.
Zeolite based catalyst which contains the suitable porous structure and acidic properties are often used for biomass pyrolysis (Bulushev and Ross, 2011)

Some catalyst used in the past for biomass pyrolysis are Si-SBA-15, Al-SBA-15 (Cho et al., 2011); ZSM-5 zeolite (López et al., 2011); H-ZSM-5-28 and H-ZSM-5-80 (Azeez et al., 2011); H-ZSM-5 (Agblevor et al., 2010b); nickel, cobalt, iron, and gallium-substituted ZSM-5 (French and Czernik, 2010) etc.

Now, we will see the catalytic pyrolysis. So, pyrolysis is a thermal process, no catalyst is used. But, if we use the catalyst, then the temperature requirement may be reduced; and the quality of the pyro-oil or bio-oil produced to the pyrolysis can be improved. So, the catalytic pyrolysis is operated at a atmospheric pressure, wide variety of catalyst available based on the product needed, and can be integrated in the unit used for pyrolysis. The main aim of catalytic cracking is to reduce acidity, viscosity, oxygen content, increase heating value and produce low carbon chain compounds.

Zeolite based catalyst which contains the suitable porous structure and acidic properties are often used for biomass pyrolysis. But, you know, we are using the waste and we are trying to produce bio-oil from it; and that is why the catalyst cost should not be very high. So, low cost catalyst is very very important and many research is also going on to develop low cost catalyst for the upgradation of bio-oil. Some catalyst used in the past for biomass pyrolysis are SI-SBA-15, Al-SBA-15, ZSM-5 zeolite, H-ZSM-5-28, H-ZSM-5-80, H-ZSM-5; a nickel, cobalt, iron and gallium-substituted ZSM-5 catalyst. So, here mostly ZSM based catalyst have been reported, but after that some other type of catalysts are also being investigated in recent years.

(Refer Slide Time: 18:13)



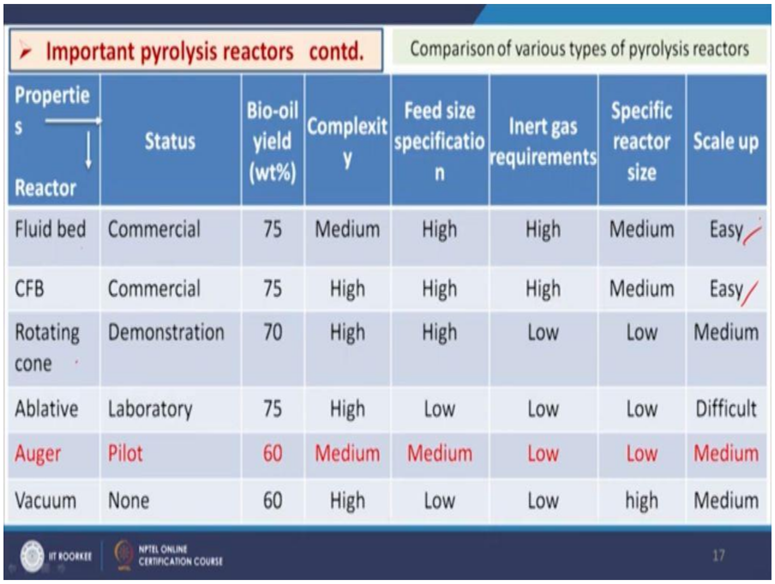
Important pyrolysis reactors

Pyrolysis reactors

- Fixed Bed reactor
- Fluidized bed reactor
- Circulating fluidized bed reactor
- Ablative reactor
- Rotating cone reactor
- Vacuum Pyrolysis reactor
- Auger/ Screw reactor

Now, we will be talking about the pyrolysis reactors. So, there are different types of reactors which have been used for the pyrolysis purpose, like fixed bed reactor, fluidized bed reactor, circulating fluidized bed reactor, ablative reactor, rotating cone reactor, vacuum pyrolysis reactor, auger or screw type reactor.

(Refer Slide Time: 00:32)



Important pyrolysis reactors contd.

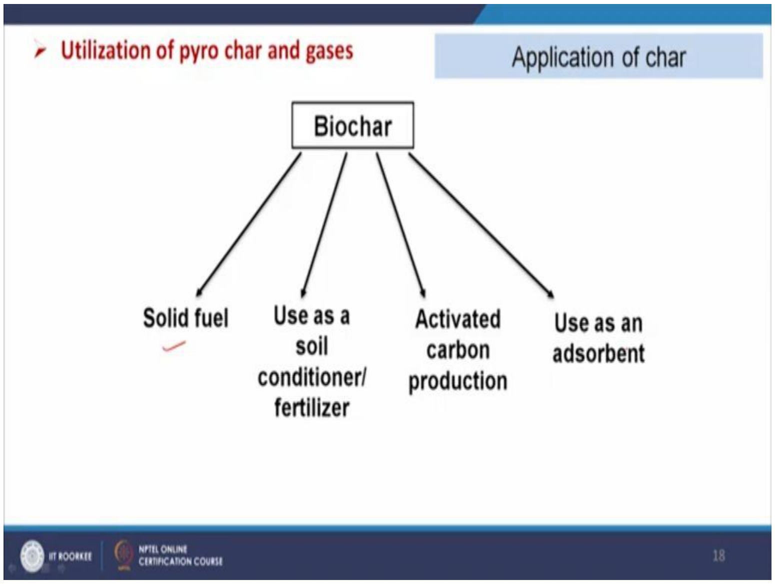
Comparison of various types of pyrolysis reactors

Properties → Reactor ↓	Status	Bio-oil yield (wt%)	Complexity	Feed size specification	Inert gas requirements	Specific reactor size	Scale up
Fluid bed	Commercial	75	Medium	High	High	Medium	Easy
CFB	Commercial	75	High	High	High	Medium	Easy
Rotating cone	Demonstration	70	High	High	Low	Low	Medium
Ablative	Laboratory	75	High	Low	Low	Low	Difficult
Auger	Pilot	60	Medium	Medium	Low	Low	Medium
Vacuum	None	60	High	Low	Low	high	Medium

So, if we compare the different types of reactors with respect to their status, whether it is commercial, demonstrated, or it in laboratory scale. Or, what is the bio-oil yield? What is the complexity and what is the feed size requirement? And inert gas requirements, specific reactor size and scale up possibility. Then, we can see the data in this table, so fluid bed, then circulatory fluidized bed, then rotating cone, ablative, auger and vacuum these different types of reactors are mentioned there.

And status we see the commercial is fluidized bed and CFB circulatory fluidized bed; these 2 are commercially reactor. Others are rotating on demonstration level, ablative laboratory; and these are not that matured one. So, here we see the bio-oil yield are around 60 to 70 %, and complexity level is also different for different types of reactors. And feed size is also different, inert requirement is also different, specific reactor size are also different. But, these are already commercialized; so scale up is very easy for these type of reactors.

(Refer Slide Time: 19:50)



➢ Utilization of pyro char and gases

Application of char

Biochar

Solid fuel

Use as a soil conditioner/ fertilizer

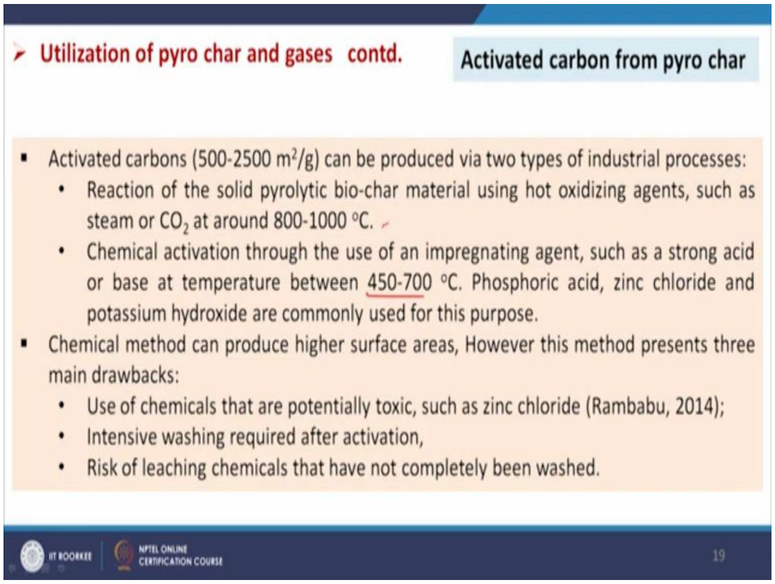
Activated carbon production

Use as an adsorbent

Now, we will see the application of char. So, biochar which is produced through the pyrolysis that can be used for multiple applications; like say solid fuel that can be used as a solid fuel, and that can be used as a soil conditioner and fertilizer. So, char which is produced that will be having surface area and its porous structure. So, when it will be added with the soil, so, it will help the diffusion of oxygen in the soil; and it will help to make the environment more healthy for the growth of the plants.

And activated carbon produced that can be used for adsorption or any other application; and it can be used as an adsorbent also. So, these are different applications of this char.

(Refer Slide Time: 20:38)



- Utilization of pyro char and gases contd.

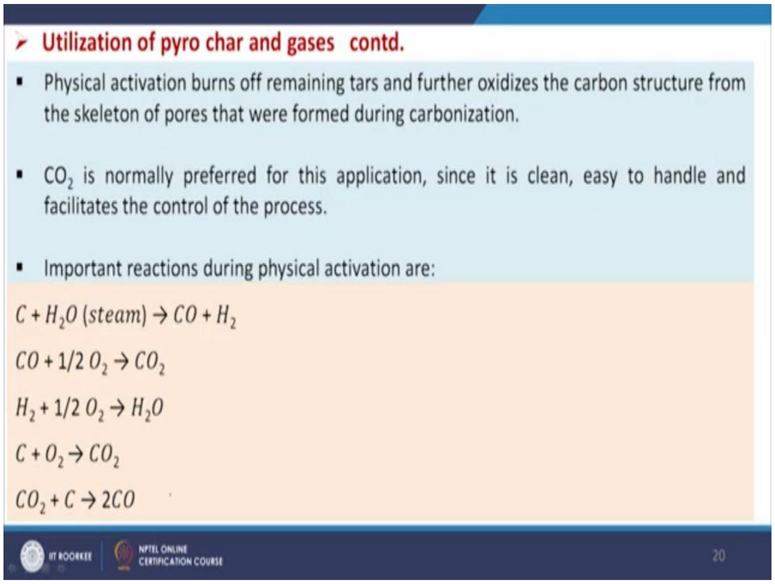
Activated carbon from pyro char

- Activated carbons (500-2500 m^2/g) can be produced via two types of industrial processes:
  - Reaction of the solid pyrolytic bio-char material using hot oxidizing agents, such as steam or CO_2 at around 800-1000 °C.
  - Chemical activation through the use of an impregnating agent, such as a strong acid or base at temperature between 450-700 °C. Phosphoric acid, zinc chloride and potassium hydroxide are commonly used for this purpose.
- Chemical method can produce higher surface areas, However this method presents three main drawbacks:
  - Use of chemicals that are potentially toxic, such as zinc chloride (Rambabu, 2014);
  - Intensive washing required after activation,
  - Risk of leaching chemicals that have not completely been washed.

And activated carbon from pyro char for the production of activated carbon from Pyro char; there are basically 2 types of methods have been used. One is physical activation another is your chemical activation. So, activated carbons 500 to 2500 m^2/g can be produced via 2 types of industrial processes. Reaction of the solid paralytic bio-char material using hot oxidizing agents, such as steam or CO_2 at around 800 to 1000 °C; that is your physical activation. And chemical activation through the use of an impregnating agent, such as strong acid or base at temperature between 450 to 700 °C; phosphoric acid, zinc chloride and potassium hydroxide are commonly used for this purpose.

The chemical methods can produce higher surface areas. However, this method presents 3 main drawbacks. Like say, use of chemicals that are potentially toxic, such as zinc chloride; and intensive washing required after activation, risk of leaching chemicals that have not completely been washed. So, these are some aspects of the activation of the char produced to the pyrolysis of biomass waste.

(Refer Slide Time: 21:53)



Utilization of pyro char and gases contd.

- Physical activation burns off remaining tars and further oxidizes the carbon structure from the skeleton of pores that were formed during carbonization.
- CO_2 is normally preferred for this application, since it is clean, easy to handle and facilitates the control of the process.
- Important reactions during physical activation are:

$C + H_2O\ (steam) \rightarrow CO + H_2$

$CO + 1/2\ O_2 \rightarrow CO_2$

$H_2 + 1/2\ O_2 \rightarrow H_2O$

$C + O_2 \rightarrow CO_2$

$CO_2 + C \rightarrow 2CO$

The physical activation burns off remaining tars and further oxidizes the carbon structure from the skeleton of pores that were formed during carbonization. CO_2 is normally preferred for this application, since it is clean, easy to handle and facilitates the control of the process. Important reactions during physical activations are

$C + H_2O \rightarrow CO + H_2$

$CO + ½\ O_2 \rightarrow CO_2$

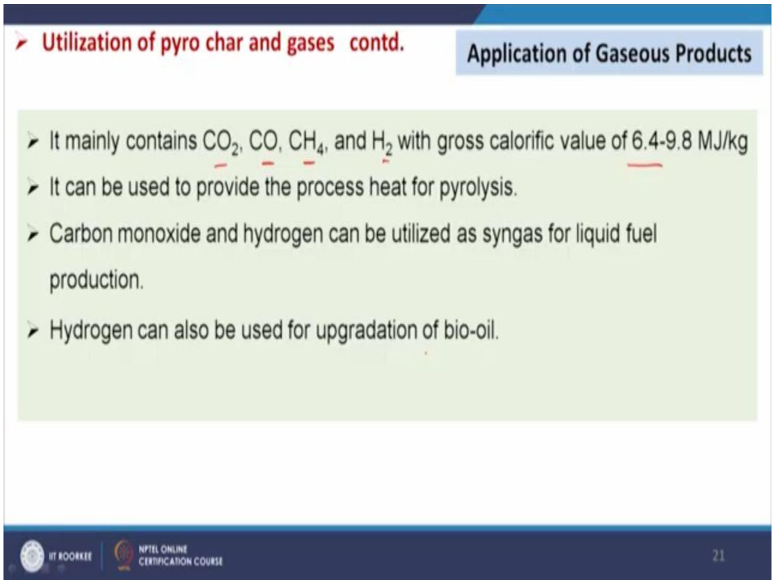
$H_2 + ½\ O_2 \rightarrow H_2O$

$C + O_2 \rightarrow CO_2$

$CO_2 + C \rightarrow 2CO$

So, these are the different reactions takes place during the activation of the char through the physical activation route.

(Refer Slide Time: 26:31)



Utilization of pyro char and gases contd.

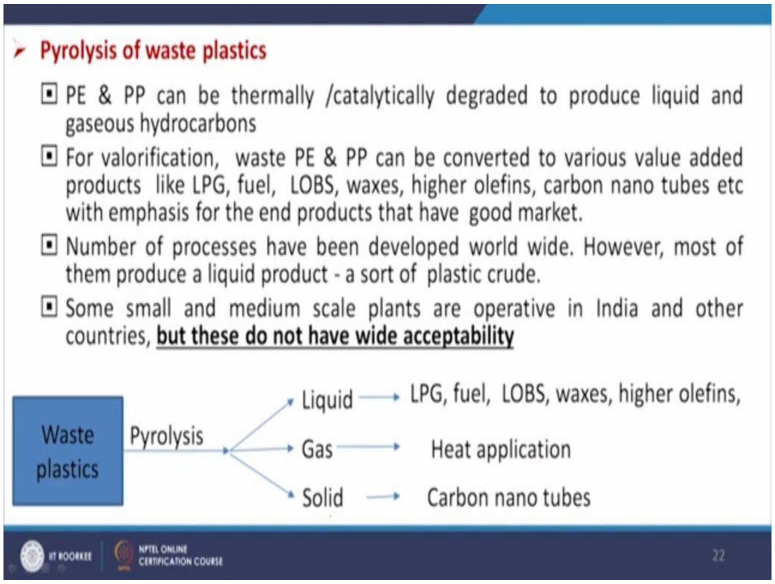
Application of Gaseous Products

- It mainly contains CO_2, CO, CH_4, and H_2 with gross calorific value of 6.4-9.8 MJ/kg
- It can be used to provide the process heat for pyrolysis.
- Carbon monoxide and hydrogen can be utilized as syngas for liquid fuel production.
- Hydrogen can also be used for upgradation of bio-oil.

Now application of gaseous products. So, it mainly contains CO_2, CO, CH_4 and H_2; so and it is containing CH_4 and H_2 certainly it will be having some heating value. The calorific value ranges from 6.4 to 9.8 MJ/kg; and it can be used to provide the process heat for pyrolysis. Carbon monoxide and hydrogen can be utilized as syngas for liquid fuel production. Hydrogen can also be used for upgradation of bio-oil; so, these are the different applications, which can be possible. Now, we will discuss the pyrolysis of waste plastics; so waste plastic also contributes a significant part of MSW.

So, this can also be processed through the pyrolysis for pyrolysis oil production. So, mostly polyethylene and polypropylene are more easier and Polystyrene is also easier for the production of pyrolysis oil through this route.

(Refer Slide Time: 23:38)



➤ **Pyrolysis of waste plastics**

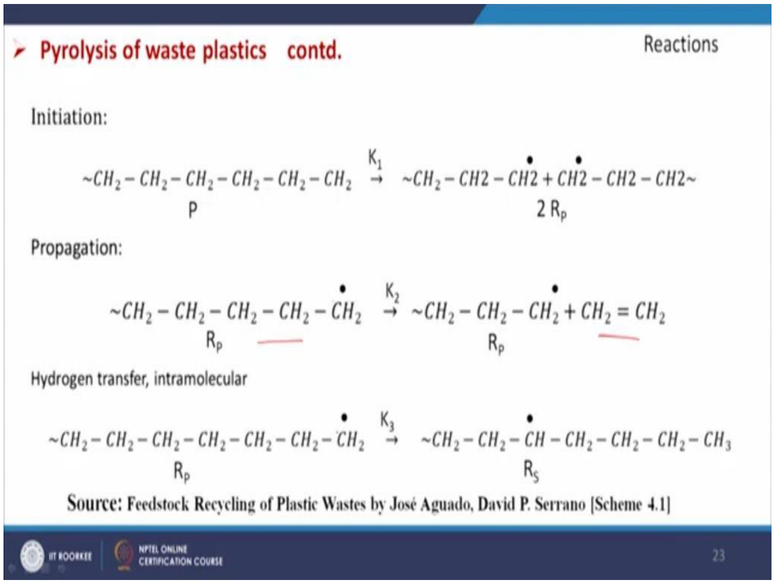
- ▣ PE & PP can be thermally /catalytically degraded to produce liquid and gaseous hydrocarbons
- ▣ For valorification, waste PE & PP can be converted to various value added products like LPG, fuel, LOBS, waxes, higher olefins, carbon nano tubes etc with emphasis for the end products that have good market.
- ▣ Number of processes have been developed world wide. However, most of them produce a liquid product - a sort of plastic crude.
- ▣ Some small and medium scale plants are operative in India and other countries, **but these do not have wide acceptability**

Waste plastics → Pyrolysis
Liquid → LPG, fuel, LOBS, waxes, higher olefins,
Gas → Heat application
Solid → Carbon nano tubes

And that can be produced thermally or catalytically; and these are degraded to produce liquid and gaseous hydrocarbons. So for valorification, waste PE and PP can be converted to various value added products like LPG, fuel, LOBS, waxes. LOBS means Lube Oil Base Stocks, waxes, higher olefins, carbon nano tubes, etc. with emphasis for the end products that have good market. Number of processes have been developed worldwide; however, most of them produce a liquid product a sort of plastic crude. Some small and medium scale plants are operative in India and other countries; but these do not have wide acceptability.

So, waste plastics, if you go for pyrolysis look at liquid LPG, fuel, LOBS, waxes, higher olefins, gas heat applications and solid carbon nanotubes. These are the major root for the application.

(Refer Slide Time: 24:34)



Pyrolysis of waste plastics contd.

Reactions

Initiation:

$$\underset{P}{\sim CH_2-CH_2-CH_2-CH_2-CH_2-CH_2} \overset{K_1}{\rightarrow} \underset{2\,R_p}{\sim CH_2-CH2-\overset{\bullet}{CH2}+\overset{\bullet}{CH2}-CH2-CH2\sim}$$

Propagation:

$$\underset{R_p}{\sim CH_2-CH_2-CH_2-CH_2-\overset{\bullet}{CH_2}} \overset{K_2}{\rightarrow} \underset{R_p}{\sim CH_2-CH_2-\overset{\bullet}{CH_2}}+CH_2=CH_2$$

Hydrogen transfer, intramolecular

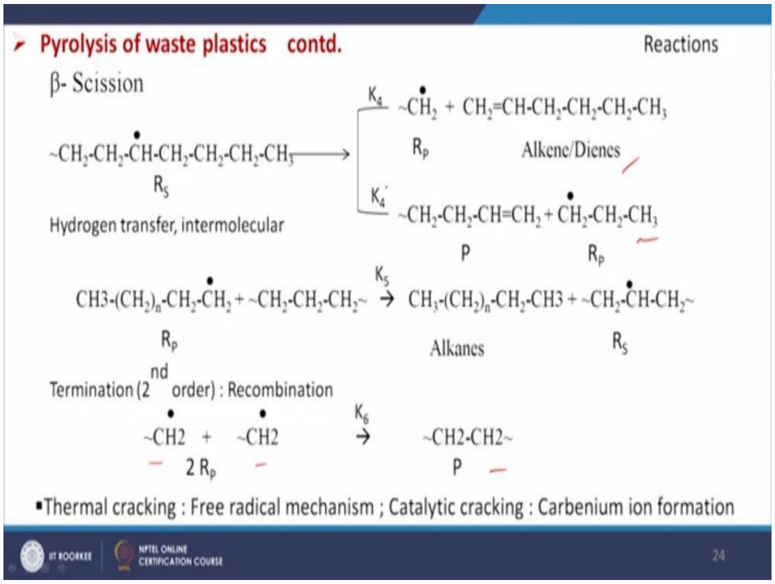
$$\underset{R_p}{\sim CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-\overset{\bullet}{CH_2}} \overset{K_3}{\rightarrow} \underset{R_S}{\sim CH_2-CH_2-\overset{\bullet}{CH}-CH_2-CH_2-CH_2-CH_3}$$

Source: Feedstock Recycling of Plastic Wastes by José Aguado, David P. Serrano [Scheme 4.1]

And we see the reaction part mechanism. So, in case of thermal pyrolysis, so this is a polymeric chain; and then it is broken down and we get free radicals. So, free radical mechanism for thermal pyrolysis initiation, then propagation; so, then say another radical we are getting, so that will be converted to this one. So, this will be $CH_2=CH_2$; and this radical again we will get another radical. So, this is called propagation. And hydrogen transfer intermolecular, so this is one radical.

So, this hydrogen transfer is taking place, the free radical position here; now it is converted to somewhere else, so that way hydrogen transfer intermolecular is possible.

(Refer Slide Time: 25:24)



Pyrolysis of waste plastics contd.

Reactions

β- Scission

$$\underset{R_S}{\sim CH_2\text{-}CH_2\text{-}\overset{\bullet}{C}H\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3} \xrightarrow{K_4} \underset{R_p}{\sim \overset{\bullet}{C}H_2} + \underset{\text{Alkene/Dienes}}{CH_2\text{=}CH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3}$$

$$\xrightarrow{K_4'} \underset{P}{\sim CH_2\text{-}CH_2\text{-}CH\text{=}CH_2} + \underset{R_p}{\overset{\bullet}{C}H_2\text{-}CH_2\text{-}CH_3}$$

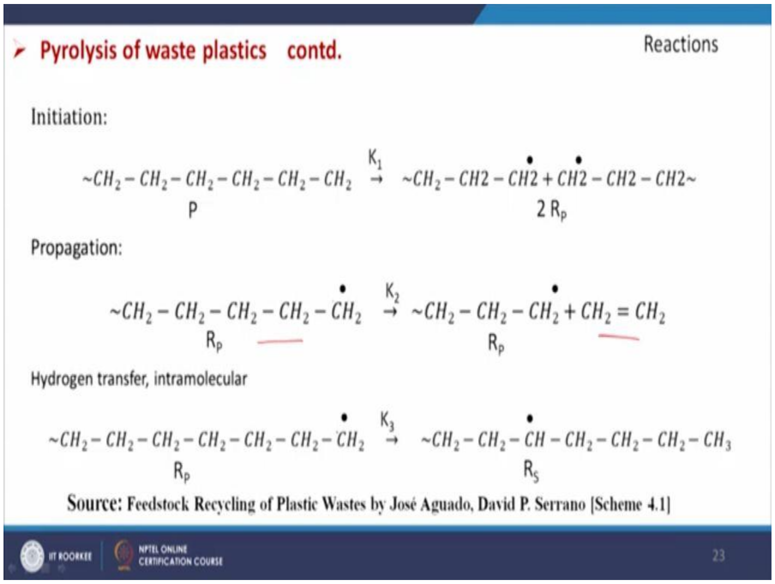
Hydrogen transfer, intermolecular

$$\underset{R_p}{CH3\text{-}(CH_2)_n\text{-}CH_2\text{-}\overset{\bullet}{C}H_2} + \sim CH_2\text{-}CH_2\text{-}CH_2\sim \xrightarrow{K_5} \underset{\text{Alkanes}}{CH_3\text{-}(CH_2)_n\text{-}CH_2\text{-}CH3} + \underset{R_S}{\sim CH_2\text{-}\overset{\bullet}{C}H\text{-}CH_2\sim}$$

Termination (2^{nd} order) : Recombination

$$\underset{2\,R_p}{\sim \overset{\bullet}{C}H2 + \sim \overset{\bullet}{C}H2} \xrightarrow{K_6} \underset{P}{\sim CH2\text{-}CH2\sim}$$

- Thermal cracking : Free radical mechanism ; Catalytic cracking : Carbenium ion formation



Pyrolysis of waste plastics contd.

Reactions

Initiation:

$$\underset{P}{\sim CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2} \xrightarrow{K_1} \underset{2\,R_p}{\sim CH_2 - CH2 - \overset{\bullet}{C}H2 + \overset{\bullet}{C}H2 - CH2 - CH2\sim}$$

Propagation:

$$\underset{R_p}{\sim CH_2 - CH_2 - CH_2 - CH_2 - \overset{\bullet}{C}H_2} \xrightarrow{K_2} \underset{R_p}{\sim CH_2 - CH_2 - \overset{\bullet}{C}H_2} + CH_2 = CH_2$$

Hydrogen transfer, intramolecular

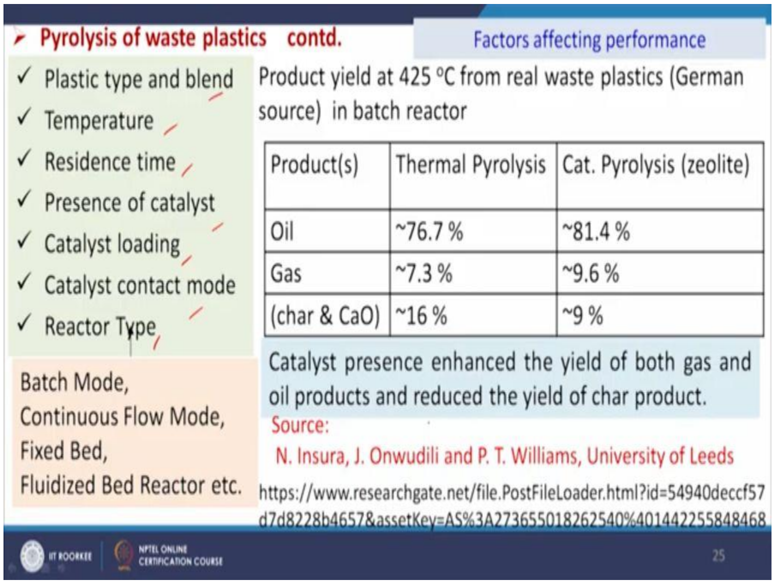
$$\underset{R_p}{\sim CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - \overset{\bullet}{C}H_2} \xrightarrow{K_3} \underset{R_S}{\sim CH_2 - CH_2 - \overset{\bullet}{C}H - CH_2 - CH_2 - CH_2 - CH_3}$$

Source: Feedstock Recycling of Plastic Wastes by José Aguado, David P. Serrano [Scheme 4.1]

And then β-scission, so here we have some radical point, this is the central point; and now α and β, so this position will be cracked. So, this can be give us one CH_2 radical and this is the double bond here, so that is alkene and dienes; or this can break here also, this one can also break. So, then will get this is double one and this $\cdot CH_2\text{-}CH_2\text{-}CH_3$ we can get. So, this is called β -scission and hydrogen transfer intermolecular. So, intermolecular hydrogen, so this is one molecular. So, here we have intermolecular same molecule hydrogen transfer is taking; here we are shifting intermolecular, so one molecule to other molecules. So, this was that initially we had, now the radical is shifted to this one.

So, that way hydrogen transfer is taking place. So, then termination second order recombination, so, different free radicals are combined and giving us another polymer. So, this type of reaction mechanism is responsible for the pyrolysis of waste plastics, and thermal cracking that is free radical mechanism. But, in case of catalytic cracking, this is carbenium ion formation.

(Refer Slide Time: 26:39)



Pyrolysis of waste plastics contd.

Factors affecting performance

- ✓ Plastic type and blend
- ✓ Temperature
- ✓ Residence time
- ✓ Presence of catalyst
- ✓ Catalyst loading
- ✓ Catalyst contact mode
- ✓ Reactor Type

Batch Mode,
Continuous Flow Mode,
Fixed Bed,
Fluidized Bed Reactor etc.

Product yield at 425 °C from real waste plastics (German source) in batch reactor

Product(s)	Thermal Pyrolysis	Cat. Pyrolysis (zeolite)
Oil	~76.7 %	~81.4 %
Gas	~7.3 %	~9.6 %
(char & CaO)	~16 %	~9 %

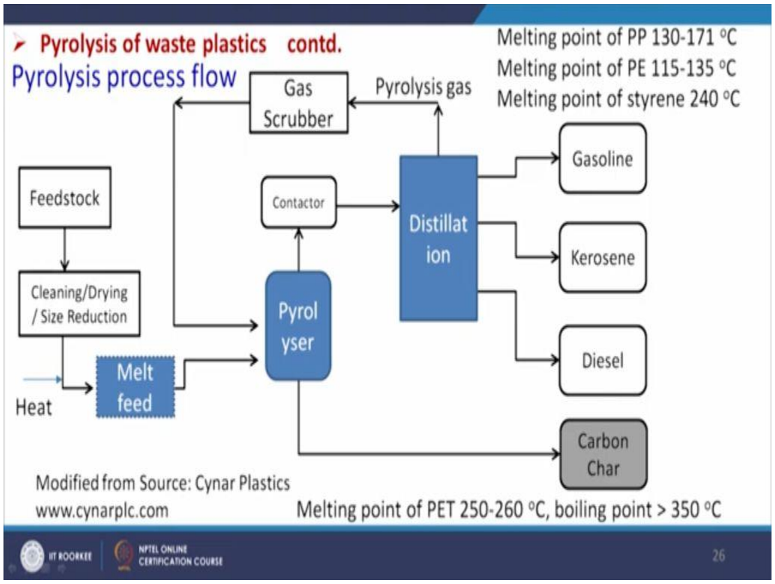
Catalyst presence enhanced the yield of both gas and oil products and reduced the yield of char product.

Source:
N. Insura, J. Onwudili and P. T. Williams, University of Leeds
https://www.researchgate.net/file.PostFileLoader.html?id=54940deccf57d7d8228b4657&assetKey=AS%3A273655018262540%401442255848468

Now, we will see different factors which affect the performance of the pyrolysis process. So, plastic type and blend, temperature, residence time, presence of catalyst, catalyst loading, catalyst contact mode, reactor type, and batch mode, continuous mode and fixed bed, fluidized bed reactor. Reactor may be applied in batch mode or in continuous mode; in continuous mode say fixed bed, fluidized bed reactor mostly used. And product yield at 425 °C from real waste plastics; that is from German source in batch reactor.

We get oil, gas and char CaO, then we are getting thermal pyrolysis 76.7 %; whereas, for catalytic pyrolysis 81.4 %; and gas 7.3 %, it is 9.6 %. Char 16 %, here it is 9 %. So, char percentage is reduced, gas percentage is increasing; oil percentage is also increasing. So, this is one typical trend for the use of catalyst in the pyrolysis that product pattern this changes. Catalyst presence enhanced the yield of both gas and oil products, and reduced the yield of char product. This is the pyrolysis process flow.

(Refer Slide Time: 27:52)



Pyrolysis of waste plastics contd.

Pyrolysis process flow

Melting point of PP 130-171 °C
Melting point of PE 115-135 °C
Melting point of styrene 240 °C

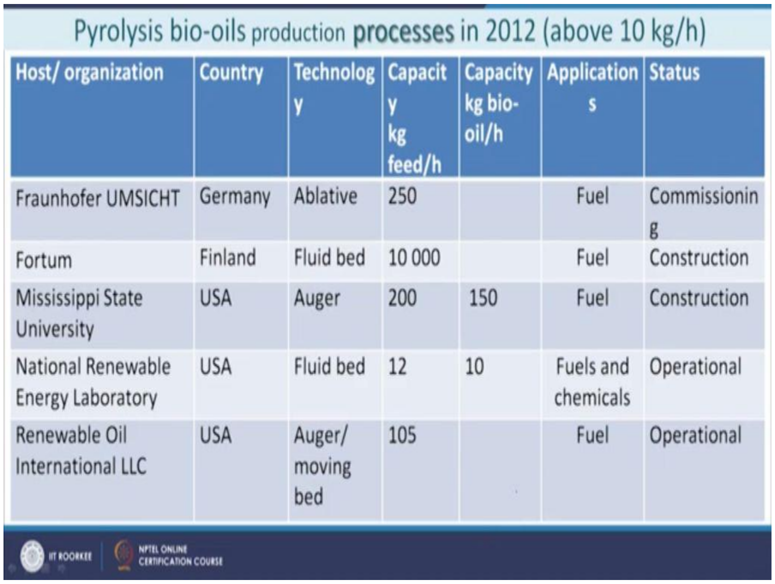
Modified from Source: Cynar Plastics
www.cynarplc.com

Melting point of PET 250-260 °C, boiling point > 350 °C

So, we can take the feedstock, then cleaning, drying, size reduction, then plastics is coming where heating. So, first we can melt it and then melt is, sent to the pyrolyzer reactor; and then after pyrolysis, we get the vapours; then it is condensation basically distillation so, gasoline kerosene, diesel, different fractions we will get. And here we will get the char, so carbon char. So, unlike biomass and wastes, the plastics contains less char content; particularly, for PE and PP. And here the pyrolysis gas which is not condensable; it is coming through the gas scrubber and return to the pyrolysis for supplying the heat.

And what will be the temperature requirement that can be decided by the melting point of the type of the plastics.

(Refer Slide Time: 28:45)

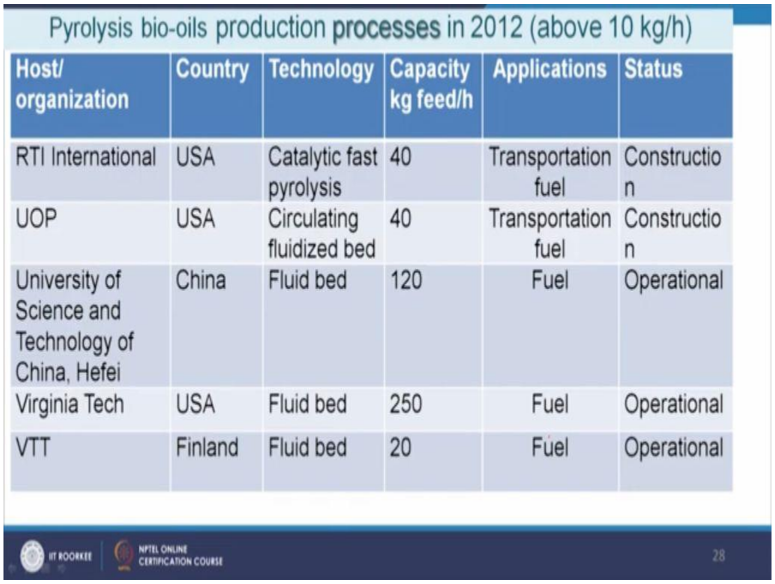


Pyrolysis bio-oils production processes in 2012 (above 10 kg/h)

Host/ organization	Country	Technology	Capacity kg feed/h	Capacity kg bio-oil/h	Applications	Status
Fraunhofer UMSICHT	Germany	Ablative	250		Fuel	Commissioning
Fortum	Finland	Fluid bed	10 000		Fuel	Construction
Mississippi State University	USA	Auger	200	150	Fuel	Construction
National Renewable Energy Laboratory	USA	Fluid bed	12	10	Fuels and chemicals	Operational
Renewable Oil International LLC	USA	Auger/ moving bed	105		Fuel	Operational

Now, some pyrolysis bio-oil production processes in 2012, above 10 kg/h. So, these are the different organization, different country, and different technology, different type of reactors used and capacity, and capacity bio-oil, and different applications. And these are the status.

(Refer Slide Time: 29:11)



Pyrolysis bio-oils production processes in 2012 (above 10 kg/h)

Host/ organization	Country	Technology	Capacity kg feed/h	Applications	Status
RTI International	USA	Catalytic fast pyrolysis	40	Transportation fuel	Construction
UOP	USA	Circulating fluidized bed	40	Transportation fuel	Construction
University of Science and Technology of China, Hefei	China	Fluid bed	120	Fuel	Operational
Virginia Tech	USA	Fluid bed	250	Fuel	Operational
VTT	Finland	Fluid bed	20	Fuel	Operational

These are some other example. In US, China, Finland is provided; here the somewhere catalytic fast pyrolysis. So, different technologies are provided, capacities are provided, and applications and status are also provided. So, we have made sufficient discussion on the on the pyrolysis of biomass and waste and waste plastics. And along with, we have made sufficient discussion on the management of solid and hazardous waste as well. So, up to this in this class, thank you very much for your patience.