Waste to energy conversion

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Lecture – 22
Energy Production from Waste Plastics – 1

Good morning. Now we will start discussion on a new module Energy Production from Waste Plastics. Waste plastics are the part of municipal solid waste and these are of basically two types: thermo setting and thermo plastic. Municipal solid waste contains more amounts of thermo plastics which are recyclable in natures. So, these can be recycled, but these recyclable plastics are of different types and different routes are available for its recycling. Out of these routes liquid fuel production is important one and recommended by CPCB.

But if we think about different options for liquid fuel production from plastics then we will see chemical biological routes are not suitable, because these are not biologically degradable and only thermal route is suitable. And out of three thermal routes that is incineration, gasification, and pyrolysis; pyrolysis gives liquid product in higher amount directly.

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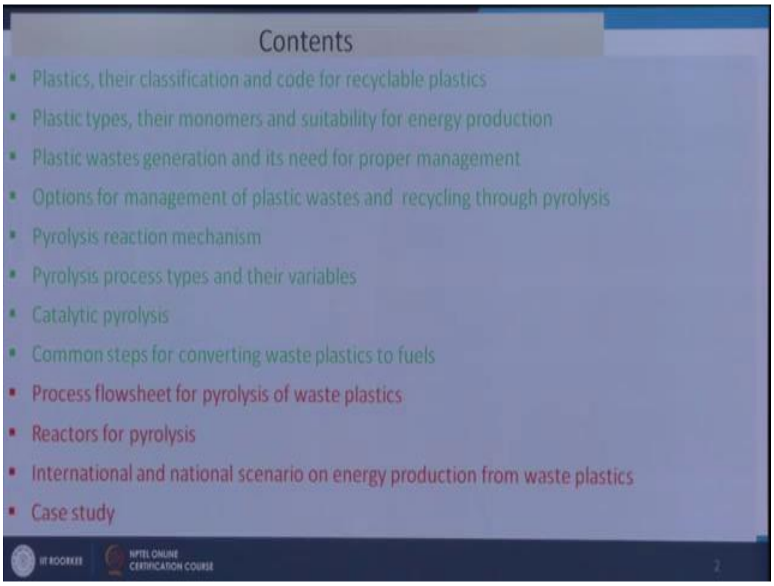

So, in this module we will discuss on plastics, their classification and code for recyclable plastics. Plastic types: they are monomers and suitability for energy production, plastic waste generation and its need for proper management, options for management of plastic waste, and recycling through pyrolysis; pyrolysis reaction mechanism, pyrolysis process types and their variables. Catalytic pyrolysis, common steps for converting waste plastic to fuels, process flow sheets for pyrolysis of waste plastics, reactors for pyrolysis, international and national scenario on energy production from waste plastics and also will provide some case study.

Now let us see what the plastics are and what is their classification? So, it is clear that plastics is a material consisting of any of wide range of synthetic or semi synthetic organic compounds that are malleable and can be molded into solid objects; that plastics are basically organic compounds or polymeric compounds and these contain some other molecules also like additives, so fillers plasticizers and colorants. So, these additives impart some toxicity to the plastics.

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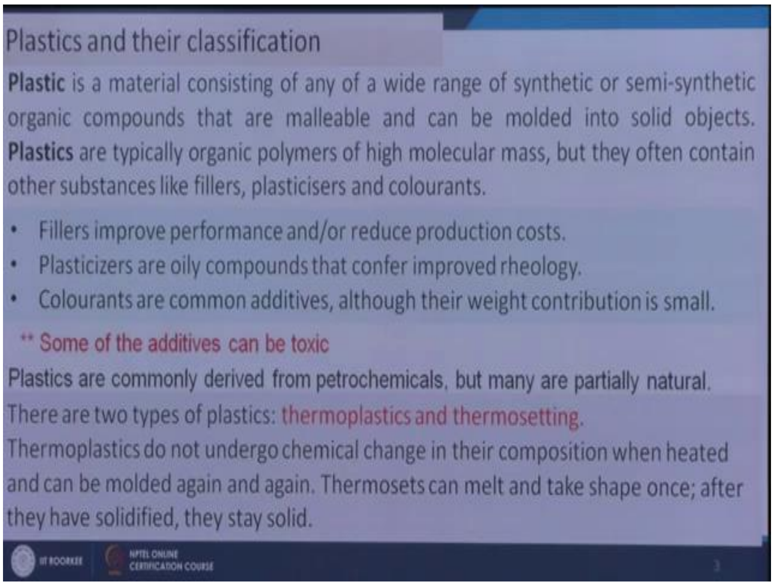

As we have discussed the thermo plastics and thermo setting two types of plastics are there: this thermo plastics are more important for the oil production.

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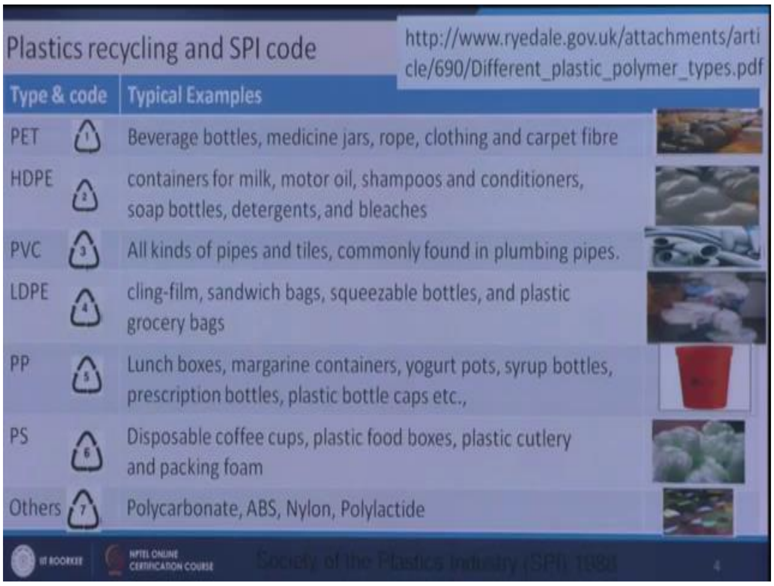

And we will see the variation of thermo plastics available in the municipal solid waste. So, PET, HDPL, d p polypropylene, polystyrene and others PVC, so these seven category or seven numbers have been given by society of the plastic industry in 1988 and some examples of this different types of plastics are shown here with photographs.

So, why this classification if we see the molecular structure of these different types of polymers then it is very clear that the polystyrene, polypropylene, polyethylene, and PET these are having and PVC also these are having similar type of monomers in their molecules. So, in the polymers the monomer is similar that is C 2 H 2 these bond.

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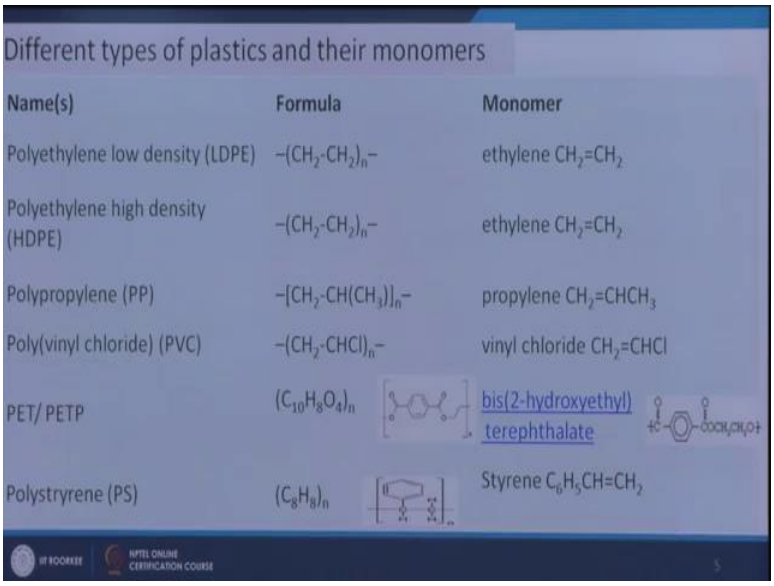

So, monomer is ethylene. So, this double bond is opened and single bond is coming and n number of this monomer is attached to give the polymer. Similarly this is for polyethylene where the monomer is, this is ethylene and this is for polypropylene monomer is propylene. For polyvinyl chloride- vinyl chloride is the monomer and this is the polymer. PET is also having this bis 2-hydroxyethyl terephthalates, so this and this is the polymer. Polystyrene is also styrene monomer and it is giving n number of styrene it is giving us polystyrene.

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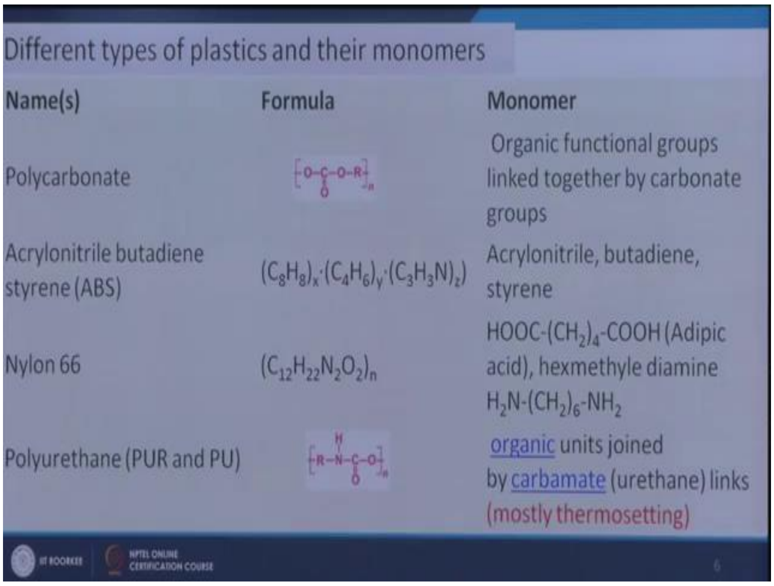

But now if we see the others that is polycarbonate, so polycarbonate carbonate is attached with the r or the organic functional groups. So, this r may change and so the monomers will also change acrylonitrile butadiene styrene ABS polymer we are having three molecules in the monomer: that is acrylonitrile, butadiene, and styrene. Nylon 66: here also the monomer is composed of adipic acid and hexamethyle diamine. And polyurethane is also r can change in this monomer and in the polymer will be having different types of monomer molecules.

But this polyurethane most of the polyurethane are thermo setting in nature, but few are thermo plastics. So, what information we are getting from the molecular structure that if we want to produce energy from this or the liquid fuel from this. So, all will not be equally a suitable. Obviously, these molecules the HDPL, DP, PP and polystyrene only hydrogen and carbon containing molecules will be more suitable for the oil production. But PET is having terephthalate acid, terephthalate so that will not be suitable for energy productions or liquid fuel production. The others these will also not be suitable for this productions, because some were getting nitrogen (Refer Time: 06:23) more oxygen. So, those will be creating more pollutants.

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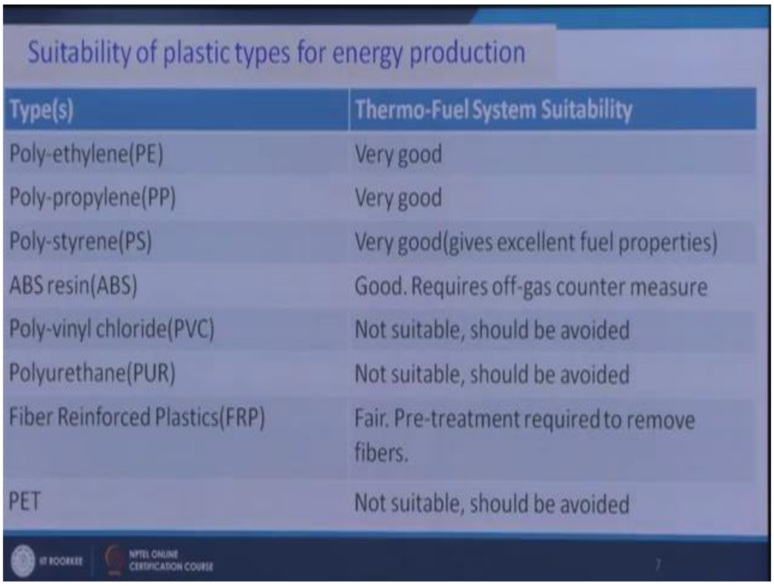

Suitability of plastic types for energy production

Type(s)	Thermo-Fuel System Suitability
Poly-ethylene(PE)	Very good
Poly-propylene(PP)	Very good
Poly-styrene(PS)	Very good(gives excellent fuel properties)
ABS resin(ABS)	Good. Requires off-gas counter measure
Poly-vinyl chloride(PVC)	Not suitable, should be avoided
Polyurethane(PUR)	Not suitable, should be avoided
Fiber Reinforced Plastics(FRP)	Fair. Pre-treatment required to remove fibers.
PET	Not suitable, should be avoided

Here this table gives us the suitability of different types of plastics for oil production. So, polyethylene very good, polypropylene very good, and then polystyrene it is also good and gives excellent fuel properties. And PVC and PET are not suitable. PVC gives HCL and PET also give some other toxic during the presence of terephthalate acids and terephthalates. Now we will see the plastic waste generation and its need for the proper management.

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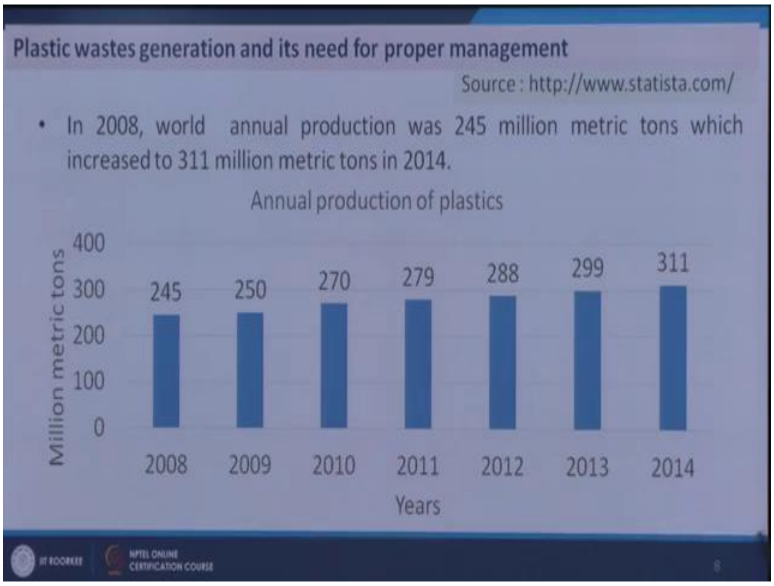

Around the world in 2014 that was 311 million metric tons of plastic waste generation, whereas in 2008 it was 245; that means, the generation is increasing around the world.

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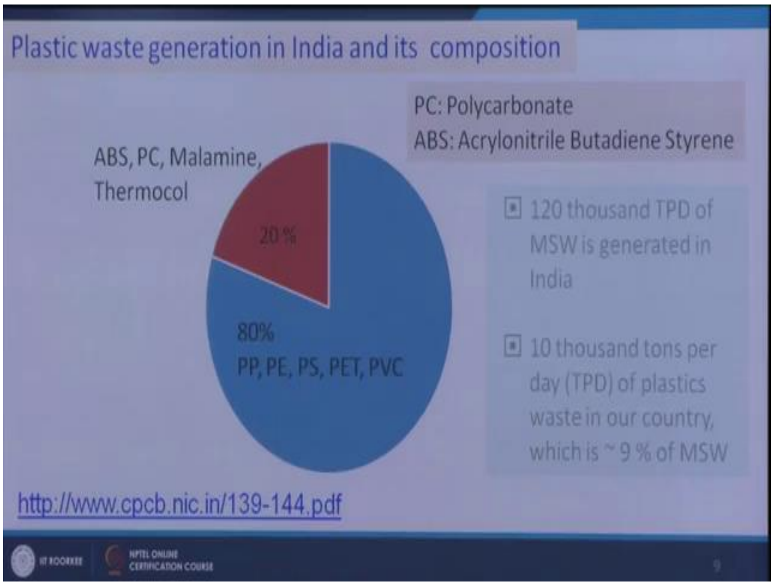

And in India you will see 12 thousands ton per day MSW municipal solid waste is generated out of which around 10 thousand tons is waste plastics that is around 9 percent of the MSW. And this 9 percent of MSW is composed of different types of plastics mostly 80 percent is of thermo plastics that is polypropylene, polyethylene, polystyrene, PET and PVC. So, this can be recycled all this PET and PVC are not so suitable for this oil production, but efforts are on to make new technology taking more care for the removal of toxic pollutants which is coming out during the process. And in future we may get process for the processing of these two feed stocks also.

In India the waste plastics is wide spread littering and on the landscape due to the lack of proper management techniques; still then government is trying to ban plastic but it is not being working. So, it is difficult to ban the plastic. So, options have to be identified for its proper management. Amongst interesting information is here that around 8 million tons of plastic waste are drowned in the ocean each year. So, huge amount of plastic waste is going to oceans and creating pollution.

So, we have to develop some proper management. And these are the options for management of plastic waste. The recycling: the recycling are basically of four types: the primary recycling, secondary recycling, tertiary recycling, and quaternary recycling. So, primary recycling means plastics will be use to produce similar type of product. Secondary product characteristics will differ from those of the original plastics products. Third category will produce the products which will be having characteristics of basic chemicals and fuels. From the waste (Refer Time: 09:32) as part of the municipal waste stream or as aggregative waste.

So, this is our concern we are concerning with the third part and that is quaternary recycling process in this process the insulation and burning of the waste plastics are done, but this practice is not used in India.

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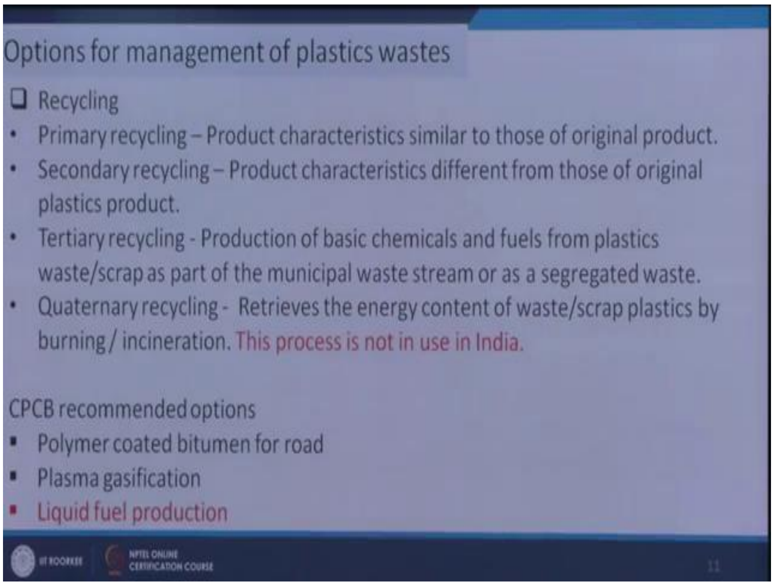

So, we are here for tertiary recycling. So, tertiary recycling can be done as for the CPCB guidelines recommendations that are polymer coated bitumen for road preparation or plasma gasifications or through liquid fuel production. So, liquid fuel productions we are going to discuss on this part.

As we have discussed that the pyrolysis gives both liquid gas and solid. So, three types of products are obtained to the pyrolysis of feed stocks. And the liquid fuel which we get through the pyrolysis of waste plastics is superior in quality with respect to other biomass and wastes. So, here we can get LPG from the liquid; we can get LPG we can get fuel, we can get LBOS, we can get waxes or higher olefins. And the solid which is generated through the waste plastic through the pyrolysis this solid it also in superior quality and that can be used for carbo nano tubes production.

But there are good number of work and reported in literature on the production of liquid fuel from this and some commercials operations are also available around the world. But in India also some operations are going on, but this do not have wide acceptability. There is this is there is some debate also whether we should go for this or not and development is going on.

Now, we will see one estimation; how to find out the yield. So, the statement is in a laboratory a 50 gram waste plastic sample is pyrolized in a batch reactor, weight is 750 gram. The weight of collected value is 37 gram and final weight of the reactor is 755 gram. So, calculate the yield of gas liquid and solid fractions.

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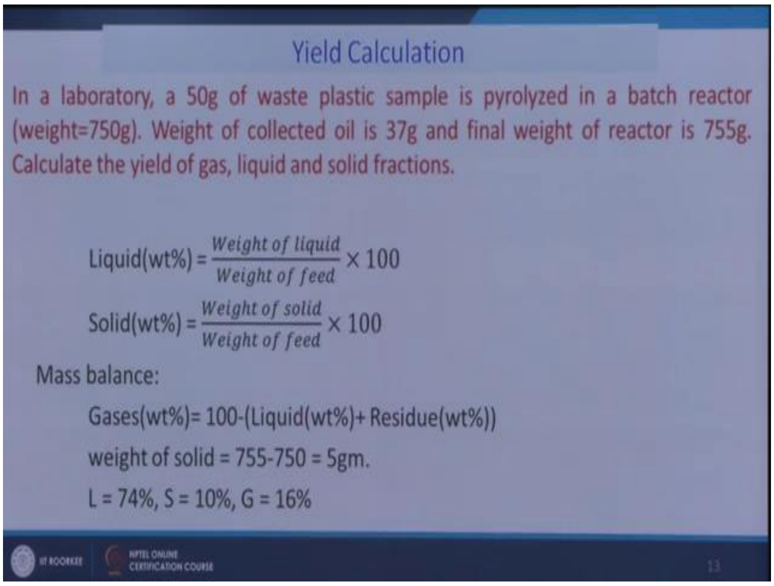

So, percentage of liquid will be weight of the liquid divided by weight of the feed into 100. And percentage of solid weight of the solid divided by weight of the feed into 100. And the rest will be the gas percentage that is 100 minus liquid percentage minus solid percentage.

Now, liquid percentage weight of liquid and weight of feed, so out of 50 gram we are getting 37 gram of oil. So, there is liquid, so the percentage for liquid is 37 divided by 15 to 100 that is coming 74 percent. Similarly, if we see the weight of the batch reactor at initially it is 750 gram after the pyrolysis reactions it is 755 gram; that means some carbon or some char is deposited in a reactor. So, 755 minus 750 that is 5 gram is the weight of the char produced during the process. So, percentage of solid will be weight of solid that is 5 gram divided by weight of feed that is equal to 50 gram so that is into 100 so that is coming is equal to 10 percent. So, what will be the gas? The 100 minus 74 minus 10 that is equal to 16 percent. So, that way the yield estimation can be done.

Now, we will go to discuss on the reaction mechanism. So, we have taken one example with reference to polyethylene. So, polyethylene molecules monomer is ethylene. So, numbers of ethylenes monomers are attached to give bigger molecules a polymer. So, when we apply heat, so then free radicals are formed. So, here some free radical formations as for example is given here. So, we have here 7 carbon; 1- 6 carbon 1, 2, 3, 4, 5, 6.

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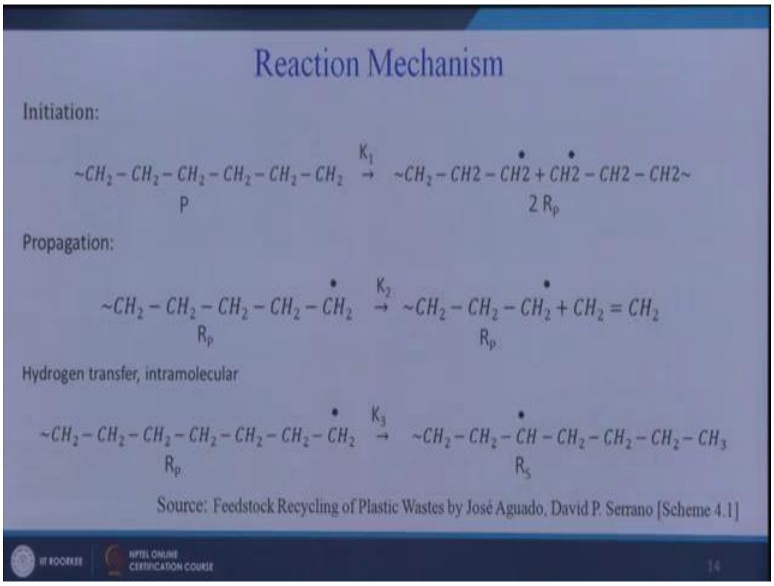

So, after heating we are assuming that two equals in having free radical heat generated this and this one then. Once the free radical are generation generated, so the propagation will take place.

So, first initiation step second step is propagation. So, these in this propagation step what happens you see this is our free radical and then free radical will generate some lower molecule and will give another free radical. So, this is the propagation step. It is giving us a lower molecular weight molecule and compound and then it is also giving one periodical. So, this is our propagation step.

Another step which is responsible for the reactions of pyrolysis is hydrogen transfer intra molecular. The same molecular or same free radicals we are having in this same free radical the hydrogen will transfer from one position to other position. So, here the free radical CH 2 we are having. So, one hydrogen from any of this position of carbon may shift to here. So, it will give us CH 3 and that positions will be having one hydrogen less. So, in this case we have shown here. So, this is the position when the free radical has been generated at carbon. And this CH 2 now is getting another hydrogen and getting CH 3.

So, this is hydrogen transfer intra molecular. Next, if which will have that is beta scission; beta scission means there will be some breaking in this free radicals and some smaller molecule will be formed.

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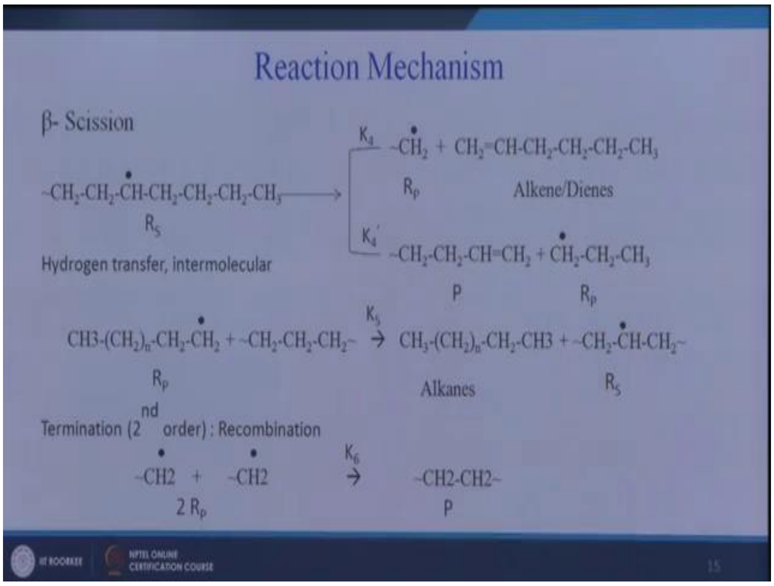

But if we have one free radical here in this C position dot. So, the beta scission means the breakdown of the chain will take place in beta carbon. So, this is alpha carbon, this is beta carbon, so here also alpha carbon, so here also beta carbon. So, by this scission we will be getting two routes: one is this route K four and K four dash that is equal to say we are assuming this is shifting to this. So, we are getting this free radical CH 2 dot.

And then the rest here some double bond will form. So, we will be getting CH 2-CH-CH 2-CH 2-CH 2-CH 3. So, this is one way of formation of lower molecule by beta scission. Another, this can shift to the rightward directions. So, then it will be shifting here. So, this is our CH 3-CH 2-CH 2 dot CH 3-CH 2-CH 2 dot will be our free radical. And this there will be some double bonding, so CH 2-CH 2-CH-CH 2. So, another molecule we are getting with having the lower molecular weight than the original one.

Another type of reactions which takes place during pyrolysis there is hydrogen transfer inter molecular. So, two different molecules in between two different molecules there may be some hydrogen transfer say- one free radical here another polymer is here. So, hydrogen is being transferred from this. So, it will be creating one periodical here. So, we are assuming hydrogen transfer from this position. So, CH 2-CH dot-CH 2 we are getting 1 free radical. And this free radical is now converted to 1 molecule compound. And this is your intermolecular hydrogen transfer.

Another type of reaction that is the end of this pyrolysis reaction that is termination in second order, this is recombination of the free radical which are formed, so these are the free radicals. So, any of these free radical can combine and make a molecule. So, here we example to 2 CH 2 we are getting CH 2-CH 2 with this.

Now from this mechanism some important things are very clear to us. The one is that the different molecules with different molecular weight are generated during the pyrolysis process. Another important is that we are getting alkene, we are getting alkanes. So, alkenes and alkanes both type of molecules we are getting from the pyrolysis of polyethylene. So, the alkenes high molecular rate alkanes will gives us parapines or wax. So, wax can be generated through this pyrolysis or these will be the part of diesel and petrol etcetera. So, diesel, petrol, wax etcetera will be generated from this pyrolysis reaction.

But these reactions are shown with reference to polyethylene, but if the polypropylene polystyrene or any other polymers are used, so reaction mechanism will be same, but the products will be different. Now we will see how pyrolysis process can be carried out. So, pyrolysis process basically is of two types: one is thermal pyrolysis another is catalytic pyrolysis. So, thermal pyrolysis means: heat will be used for the initiation and then propagations and other reactions, only heat. The process involves operation at high temperature, and formations of liquid products have wide distribution of carbon number. Just we have discussed in the mechanistic part there are different number of molecules with different molecular weight can be generated.

But now if we use the catalyst that reduces the temperature requirement for the process as well as the narrow down the carbon number in the molecules in the product. So, the quality of the liquid product obtund is better and it helps to narrow down the product distributions of the carbon number to gasoline and diesel range. So, that is why the catalytic pyrolysis in case of plastics are more attractive than the thermal one.

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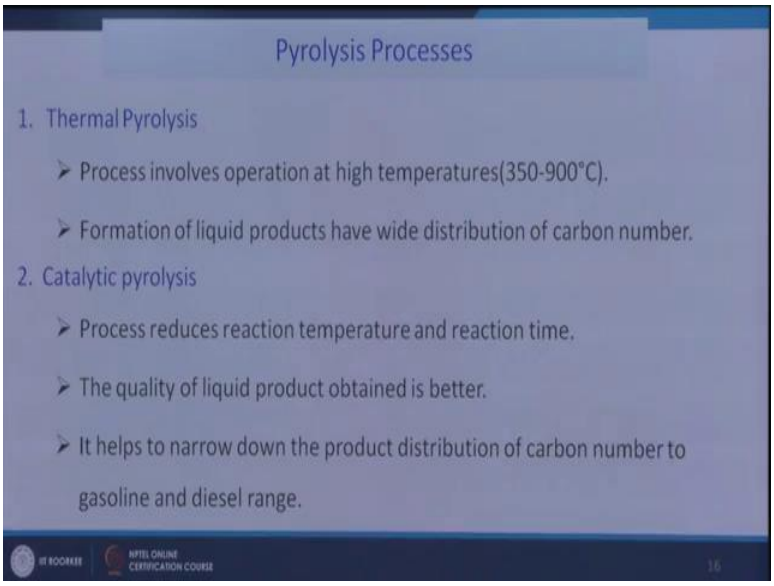

Now, we will see what are the factors on which the performance of pyrolysis is process will depend. So, plastic type and blend as we have seen the different types of plastics are there, so they are different monomers they are having. So, what types of plastics are used, what are the ratios of those plastics that will influence the performance of the pyrolysis process?

Then temperature just we have discussed three 50 to 800 or 900 centigrade joules if catalysts is used what temperature will be used. And temperature will influence the distribution of the product. Residence time will also influence the distribution of the product and preferences of catalyst; different catalysts are having different active sites.

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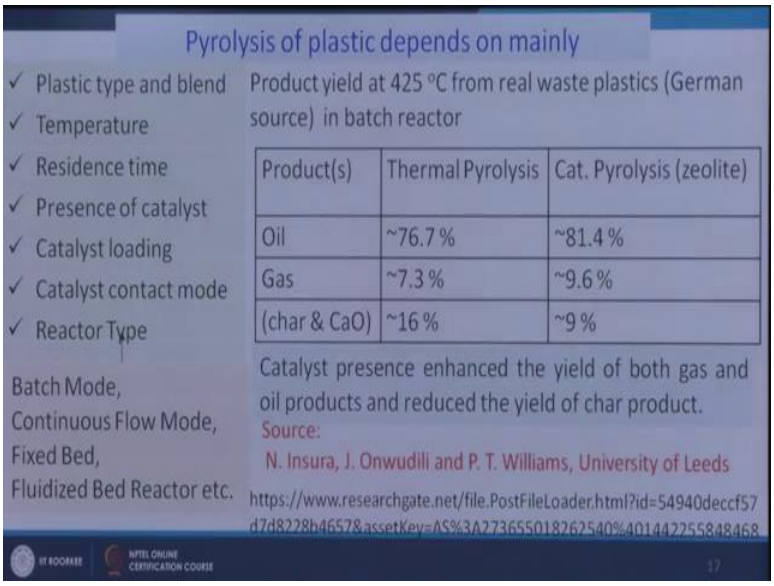

So, nature of active sites will influence the product and the selectivity of the product and the performance of the catalyst will be influencing the product distribution as well as the performance of the process. And catalyst loading: so what is the amount of catalyst we are loading in the reactor that also influence the performance of the catalytic process and catalyst contact mode, how it is contacting it means we are using a fix wave reactor or fluidized reactor what is the resistance time and how the mixing is taking place all those things will influence the performance of the pyrolysis process.

And different types of reactors can be used batch mode, continuous mode, fluidized mode, moving mode. So, different types of can be used. Now one data is given here that gives us some example how the use of catalyst improves the performance of the process. So, this is at 425 degree centigrade from real waste plastics in German based waste plastics were used in batch reactor and this was reported by this source. So, here we see that use of catalyst is increasing oil yield, increasing gas yield, but decrease in char and CO yield.

So, CO actually used in this study to capture the CO 2 produced during the process. So, it is very clear to us that use of catalyst is give some more oil and more gases which are desirable.

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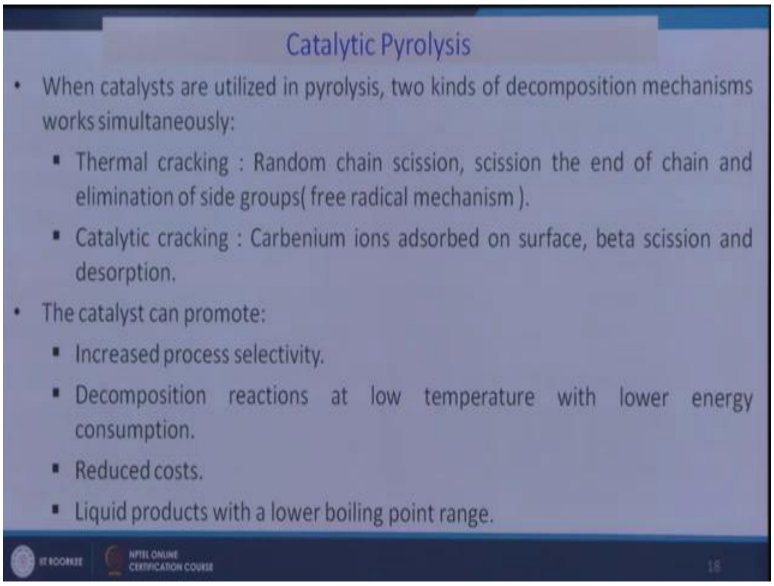

Now, catalytic pyrolysis how differs from the thermal one. Now when the catalysts are used there are two mechanisms: one is thermal cracking and another is catalytic cracking. Thermal cracking we have already explained the mechanism through the beta scission and we have seen that free radical mechanism is responsible for that.

But if we use hydrogenous catalyst, that case carbonium irons are form which are absorbed on the surface of the catalyst and beta scission and disruption takes place. So, the mechanism changes slightly when we use the catalytic cracking. Due to that reason we get more selectivity, more product and more desired product. And the catalyst can promote increased process selectivity, decomposition reactions and low temperature with lower energy consumptions and reduces cost. And liquid products with a lower boiling point range are available if we use the catalyst.

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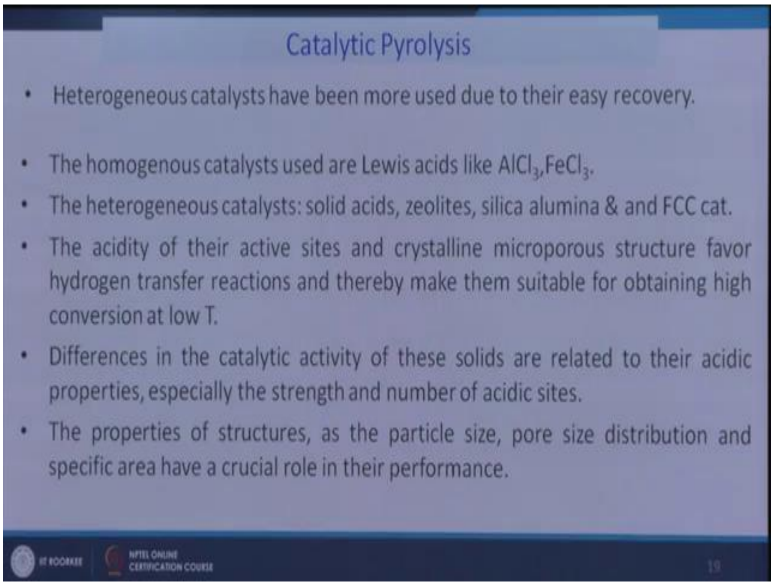

Now catalytic paralysis if we use heterogeneous or we may use homogeneous type of catalyst, but heterogeneous catalysts are preferable because the catalyst can be easily separated after use. And then a homogeneous catalyst which has been used in literature are basically like say ALCl 3, APCL 3, etcetera. So, how the catalyst helps in the reaction the active sides? The active sides which are available and acidity of these active sides as well as the microporous structure. So, these two things are very very important with acidity of their active sites and crystalline microporous structure, these two favors the hydrogen transfer reactions.

There is intra molecular and intermolecular hydrogen transfer a reaction which is the part of the pyrolysis process is favored by these properties the acidity of the active sites as well as the crystalline microporous structure. That is why we get more product and at lower temperature. So, differences in the catalytic activity of these solids are related to their acidic properties, especially the strength and number of acidic sites. The properties of structure as well as the particle size pore size distribution and specific area have a crucial role in the performance of the catalyst basically the heterogeneous catalyst.

Now we will see; what are the different steps which can be used for the conversion of waste plastic to fuels.

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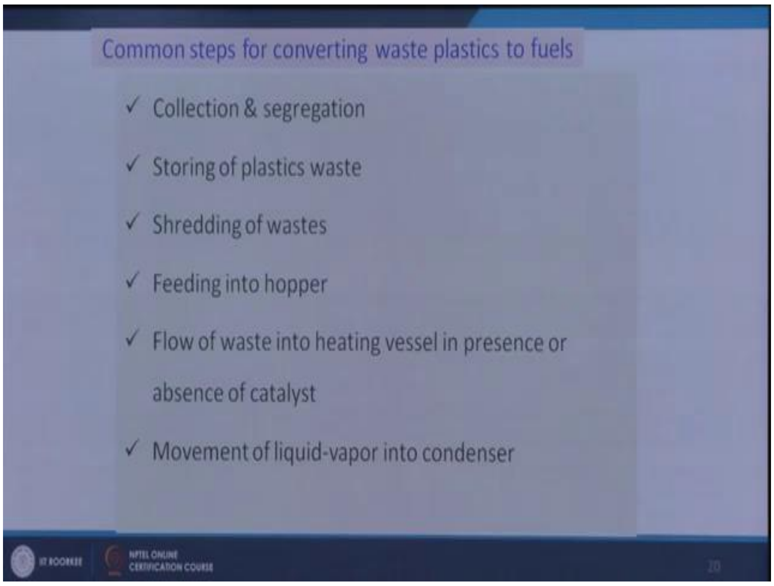

So, as this is the part of municipal solid waste obviously we have to collect it then we have to segregate it, then storing of plastic waste we have to store for a longer time so that we can use it and shredding of wastes we have to cutting and shredding then feeding into hopper. Then you go for flow of waste into heating vessel in presence or absence of catalyst.

So, once the all those things are up to this feeding to hopper these are the pre treatment steps; these are the pre treatment steps, after pre treatments we are going to flow of waste into heating vessel in presence or absence of catalyst. So, we may use the catalytic pyrolysis or only thermal pyrolysis depending upon the process; and then movement of liquid vapor into condenser.

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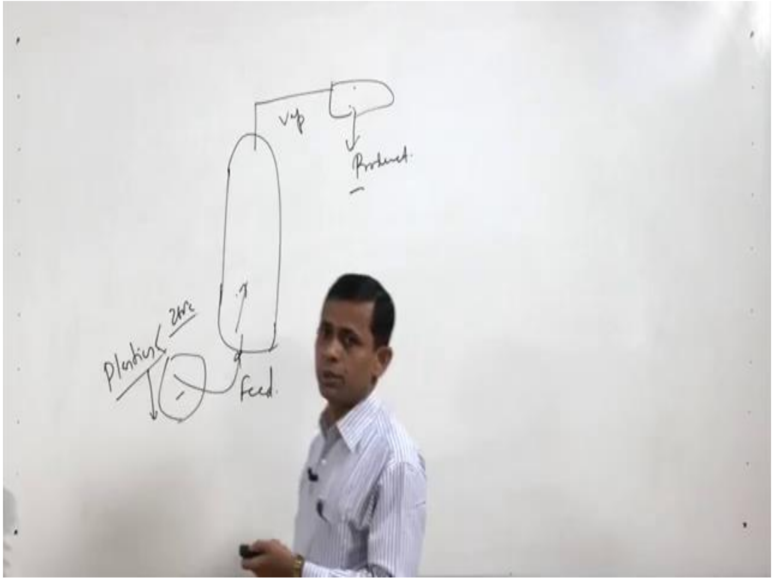

So, if we use one reactor here, so we will be putting some feed. So, what will be the feed in this case? The flow of waste into heating vessel in presence or absence of catalyst; in presence and absence of catalyst whatever may be the test, but this is our feed stocks. This is our plastics our feed, the boiling range of this PP- polypropylene polyethylene PET etcetera is within 260 degree centigrade. So, after that it will be liquefied. So, efforts are there that this has been liquefied fast and pumped or in some cases the solids have also been used.

So, flow of waste into heating vessels in presence or absence of catalyst. So, there may be some another heating vessels and here are the liquid is sent or directly the feed is sent into the reactor. And then from this we will get the vapor that will be cooled and we will get the product. So, this is the steps and then we will get movement of liquid vapor into condenser. So, this liquid vapor is going we are using condenser it is producing the product.

So, these are the common steps for converting this and collection of liquid fuels; here we will be collecting the liquid fuel collection. So, up to this in this part of this module; so we will discuss in the next part.

Thank you very much for your patience.