Lec 20: Petroleum Refinery Processes.

Welcome to the MOOCs course organic chemical technology. Title of today's lecture is petroleum refinery processes.

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Before going into the details of today's lecture, we will have a recapitulation of what we have discussed in last couple of lecture on petroleum industry. We started discussing on petroleum industry with some introduction importance of petroleum industries in chemical industries and its contribution towards the economics of the nation, etc., those things we have discussed.

Then we have discussed the occurrence of crude petroleum, how it occurs, whatever the organic matter that is present in marine deposits, they will be undergoing anaerobic processing by some kind of specific bacterial attack. So that whatever the carbohydrates and then proteins, etc. that are present in this organic matter, they would be consumed by the bacteria and then fats would be produced. These fats would be accumulated over the years to form crude oil reserves or petroleum reserves, that is what it happens, those things we have discussed.

Then chemical composition of a crude, whatever the crude that you get, what is the chemical composition? So then crude that we have seen, it is having paraffins, naphthene components like cyclic components, etc., aromatics, etc. Then as per this kind of components we have seen that they are present in the crude petroleum. Then we have classified the crude petroleum like paraffin base and then naphthene base and then

intermediate base, crude petroleum like 3 categories we had. So, in the paraffin base primarily majority of the components whatever are there, they would be either normal paraffins or isoparaffins.

If the naphthene base crude is there, so that means majority of the components would be dominated by the cyclics and then aromatic components, etc. If you have intermediate base, then both paraffins and naphthene may be present in the large quantities that is what we have seen. Then production of petroleum, so for that purpose what we have done, what are the methods like exploration methods, production methods, finding out the results by the exploration methods then using certain kind of production methods to get the crude petroleum, those details we have seen. Then petroleum refinery products we have seen, so then when you do the fractionation of crude petroleum, then you get several products like you know gas fraction, like light fractions, intermediate fractions, heavy fractions, residues, etc. we have seen and then under each category what are the major components or major products that are available or you know that you get those things we have seen.

Then characteristics of petroleum refinery, what do you mean by characteristics of petroleum refinery? So, whether it is a primary refinery or intermediate refinery or complex refinery, those kind of details we have seen. Primary usually you have single distillation column, fractionation column, so where you try to separate out the residues as well, etc. and then remaining of the crude whatever is there that you sell to other refineries for their further processing. In the intermediates you have more detailed kind of thing whereas the complex it is suitable for any kind of a crude to handle and then with flowchart also we have seen what are the different types of fractions we get, how each fraction is further processed to get different types of products, etc. those things also we have seen as part of characteristics of petroleum refinery.

Then choice of crude that also we have seen you know let us say you have you know different types of crude like you know as already we have seen paraffin base, naphthene base and then intermediate base. Naphthene base, intermediate base, paraffin base, so that depends on your product. Let us say if you want more like petrol like kind of product then you should go for the paraffin base you know crude. If you want to produce more lubrications, lubricating compounds, waxes, etc. then you should go for the naphthene base crude.

If you want both of them it is better to go for the intermediate base crude, such kind of choice of crude petroleum also we have discussed. Then common processes of petroleum refinery we have listed out that list is provided here again.

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Common refinery conversion processes include pyrolysis and cracking, reforming, polymerization, alkylation, isomerization, hydrodealkylation, hydrogenation, impurities removal or purification of the products, etc. So why are we discussing these processes individually because in subsequent chapters especially another 2 to 3 chapters we are going to discuss about the production of petrochemicals or petrochemicals industry that is production of  $C_1$  to  $C_2$  chemicals,  $C_3$  to  $C_4$  chemicals, aromatics, etc. How to produce or how these are being produced industrially that is what we are going to see with flowchart engineering problems, economics and then other details like reactions, raw materials all those things we are going to see in detail as we have been discussing for any of the product.

In their flowchart primarily, you may be seeing like reforming unit or reformer. There may be isomerization unit, there may be hydrogenation reactor. So, these units are presented just you know a kind of box or you know kind of proper representation if it is a simplified engineering diagram, but we do not discuss much detail of these kind of thing. There may be units like you know cracking, there may be units like pyrolysis and so on so different units may be there. So, there it is not possible to discuss in detail about individual these things because they may be occurring if not all multiple of such processes or units may be in occurring in different types of flowcharts that we are going to discuss in coming 2 weeks or 3 weeks of the course.

So there if we discuss repeatedly it is going to consume lot of time that is the reason we are going to have a minimum possible discussion so that we have minimum knowledge required so that to understand what is a pyrolysis process, what is a reforming process, what happens in alkalization, what happens in isomerization if at all that is occurring in

petrochemicals, industries, etc. You know it will not be difficult for us to understand. So, then what are the minimum things that you are expecting? Why I am saying that minimum things because if you go in details of all these things you know they may consume lot of time and then design and then all those things are you know very complicated. All those things are you know part of a proper petroleum refinery course or petrochemicals courses, but here we are discussing it a part of it as a you know organic chemical technology course. So, under the organic chemical technology a part of it only we are studying, a part of petroleum refinery processes only we are studying.

So, we see some details which are sufficient enough rather saying minimum details, some details you know they would be sufficient enough for us to understand the process. So, for each of these process now we are going to discuss some introduction. What are the reactions or reaction mechanisms available you know for a given process and then what are the reaction conditions or process variables, etc. If at all catalyst are required so what are the catalyst or in general used, how it is being regenerated because most any catalyst you take it may undergo some kind of deactivation or ageing kind of problem. So those details we are going to see.

Then what are the equipment that are being used for such kind of processes, those design of those equipments, etc. We are going to discuss for each of these processes now.

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So, let us start with pyrolysis and catalytic cracking. In petroleum industry what do you mean by pyrolysis, what do you mean by catalytic cracking, etc. This minimum understanding is required.

So, under the head of pyrolysis and catalytic cracking processes of petroleum refineries we will be discussing some introduction concept, some reaction mechanisms, reaction conditions, catalytic cracking process design and operation. So, what are the equipments are available, how they are being designed and operation and then petroleum coking process design and operation. Petroleum coking process we are calling because here also if you whatever the residues, etc. would be there which you may not be able to convert to some kind of products by any of the other processes that will start, then that you can do the pyrolysis so that to get different types of products. These products may be including the gases, light fractions or light end, etc. and so on, gas oils, etc. may be forming little quantities like gas oil, etc. but definitely they will be forming in addition to the coking. Basically, what are we doing this residue whatever is there that you will try to get up to the stage of coking because coking is nothing but whatever the free carbon that is formed. Coking means whatever the free carbon formation is there, which will not undergo any kind of reaction further either in the presence of catalyst or in the absence of the catalyst only that it can undergo combustion to produce CO and CO<sub>2</sub> which is not required from the petroleum industry point of view.

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So, let us start with the introduction concept of pyrolysis and then catalytic cracking. What is pyrolysis? It is nothing but a thermochemical conversion which occurs at high temperatures in the absence of oxygen. So, what it does in general, it is used to crack larger molecules into the smaller ones, because we have seen the crude petroleum compositions paraffin, snapthenes, asphalt, etc. are there. So that is  $C_1$  to  $C_{40}$  different types of organic chemicals are present.

So bigger molecules whatever are there they can be converted into the smaller molecule by the use of pyrolysis processes. So, this pyrolysis can be non-catalytic pyrolysis or simply thermal pyrolysis you can call. The other one is the catalytic cracking or catalytic pyrolysis either way you can call. So, these are 2 types of approaches that are possible in petroleum industries. Remember primarily we are going to discuss or we are discussing those things which have already been implemented in industries.

We are not talking anything about the ongoing research point of view. Ongoing research you know they are keep developing new concepts, new catalyst, new operating conditions, etc. but we can consider them fruitful, economically feasible when they are implemented in the chemical plants or petroleum plants successfully. So those which have been not tested in the refineries those details we are not discussing in this particular course. In non-catalytic pyrolysis higher molecular weight compounds are also produced simultaneously.

What does it mean by we are going to see in the reaction mechanism also. Let us say when you take a larger alkane and then you do the pyrolysis so alkyl groups will be forming. Those alkyl groups are free radicals they will be reacting with you know some other radicals to terminate the reaction but that does not take place easily. So, what happens these free radicals further decomposing to the olefins and then smaller alkyl radicals. So, these olefins whatever are forming they would be undergoing some kind of a polymerization.

So that is possible in non-catalytic pyrolysis through reaction mechanism we are going to discuss. So, because of formation of such kind of olefins by now we already discussed in the previous couple of lecture that olefins are not good from the petroleum industry products point of view. So, you can take them and then separate them and do the polymerization to get the different polymers, etc. that is a different things but from the petroleum or petrol compounds like you know diesel petrol gasoline, gas oil, etc. if you wanted to produce so these olefin should not be there but they are forming in pyrolysis of crude petroleum in general. So those you know obviously the temperature conditions are also large high temperatures in the pyrolysis so they will undergo some kind of a polymerization to form a bigger molecule so that is also possible. Then coming to the catalytic cracking what is the purpose of utilizing a catalyst in pyrolysis? So, the main purpose of the catalyst to use any of the chemical process is to reduce the severity of the temperature and pressure that is required for the process chemical process to occur.

Let us say if chemical process is there if the conditions are not severe enough to undergo then there is no point of using catalyst that is one particular use of catalyst. Other important characteristic of the catalyst or you know purpose of the catalyst is that it should increase the selectivity of a specific product whichever you are targeting it. So, both are either of two conditions you know should be fulfilled by utilizing the catalyst such catalyst only one has to use. So, to lower the temperatures and pressures of the process to obtain higher selectivity of cracking with less side reactions that is the other purpose. Commercial thermal pyrolysis started in 1913 in United States then fixed bed cracking was applied in 1936.

Moving and fluid bed catalytic cracking were introduced in 1945. We are going to discuss more details about these kind of reactors though we have already discussed about them in the first week of the course that is in the first chapter of the course where we were discussing common unit operations and then unit processes of organic chemical technology.

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Coming to the reactions involved in the pyrolysis and cracking of petroleum crude various approaches or reaction mechanisms were proposed for endothermic thermal pyrolysis and catalytic cracking. The pyrolysis that is occurring at high temperature that means the process is endothermic until and unless you provide sufficient energy the reaction is not going to move forward. So, such kind of endothermic thermal pyrolysis and catalytic cracking whatever are there for them various reaction mechanisms were proposed.

However, none of them were found to be you know exactly explaining the experimental results though they provided best overall approach of pyrolysis and cracking. So, we see those details only. We discussed for the first case of thermal pyrolysis reaction mechanism where thermal cracking is taking place, thermal polymerization is taking place and coking is also taking place. In general, what do you mean by whatever the pyrolysis or thermal pyrolysis process is there primarily you know cracking is taking place that is larger molecules are being reduced into the smaller molecules. Then some kind of larger molecules are also taking place or some kind of larger molecules also forming.

These larger molecules may be bigger than what was there in the feed that is also quite possible as I explained. We are going to discuss the same with reaction mechanism anyway and then obviously any of the thermal process you know especially when you take organics or hydrocarbons and do some kind of high temperature thermal process definitely free carbon or carbon deposits would be forming so that we called coking. So, coking also need to be explained. If you start with thermal cracking which is based on the free radical theory. Free radicals are electrically neutral highly reactive particles.

How they form? They form whatever the C-C bonds or C-H bonds that are present in the hydrocarbons you know some kind of rupture of such bonds will take place. So that each particle retaining one of the pair of shared electrons that make up the bond. For example, you have n-butane. So, when you apply the high temperature or when you do the pyrolysis of this molecule then what happen obviously butyl radical will form. So that is counted as cracking or thermal cracking.

This butyl free radical since it is a free radical it is having so much of energy it cannot stay as it is either it will react with some other radicals or some other molecules or it will further decompose into the you know other molecules or other radicals and you know that process continues. So, what happens this butyl radical will form propylene and then methyl radical. See now here propylene has formed which is nothing but olefin or alkenes we call  $C_nH_{2n}$ form they are having. So, these you know what happens they may go under kind of polymerization because for the polymerization also high temperature is required in general. So that you know this whatever propylene is there polypropylene may takes place may form okay so bigger molecule is made form right.

Whereas now again another free radical has formed that is methyl now here it is also free radical so it cannot stay calm right. It will also react with some other you know molecule or radicals and then give some other products but it cannot further undergo decomposition fractionation like you know butyl radical has given propylene and then methyl radical because it is already having only one carbon it cannot further decompose. So this methyl radical will react with the other molecules let us say other hydrocarbon generalized expression RH we are having so then it will give methane and then this alkyl radical. Let us say if it is alkyl then it will be alkyl radical okay. So now here what you understand from the reaction see methane has formed that is  $C_1$  component has formed.  $C_1$ ,  $C_2$  components are what they are in general in gases form. So, what does it mean? Thermal pyrolysis it is possible that you know gases components or gases fraction may be higher compared to the catalytic cracking that is what we are going to understand very soon again when we discuss about catalytic cracking right.

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So now depending on the size of R if R star is a large alkyl group it breaks down into a olefin same thing like you know just now we have seen butyl radical forming propylene and then methyl radical and then form a small free radicals. So, it is forming it is going to form olefin and then small free radical. So that small free radical further reacts as in reaction C to produce a chain reaction right.

So now this CH<sub>3</sub> again going to react with RH to give CH<sub>4</sub> and all like that okay. So, this kind of process chain reaction continues until and unless it is being terminated. How it will be terminated? It will be terminated only when free radical species react with each other or with solids such as coke or surface of the reactor. This free radical has to react with the surface of the reactor or with the coke or two free radicals reacting together to form a molecules under such condition only this chain reactions will be terminated otherwise they will keep on you know progressing. Now again see olefins are forming and then smaller components like methane, etcetera are forming.

Now thermal polymerization in pyrolysis thermal polymerization also occur because just now we have seen olefins are forming. These olefins will easily get polymerized to form larger molecules okay. What kind of olefins let us say propylene just now in the previous slide we have shown the same reaction is shown here. Let us say butyl radical is forming a smaller molecule propylene that is olefin and then methyl radical. So, this propylene will undergo because it is unsaturated one olefinic nature so it can easily undergo polymerization not easily that much easily but compared to the saturated hydrocarbons unsaturated hydrocarbons may undergo you know polymerization easily and they form a bigger molecules. They are so large that they are larger than the molecules that are present in the feedstock okay and then sometimes condensation of aromatics may also take place if the more aromatics are naphthene based crude you have taken. Coke formation free carbon always occurs to a degree when hydrocarbons undergo complete degradation so that is unavoidable at certain stage definitely coke formation would take place. How much coke formation it is taking that is going to be you know one of the important factor to decide. So obviously we understand now in the thermal pyrolysis more gases and more coke formation taking place. Typical reaction representation for the coke formation may be done like this here.

So, whatever this free carbon that is forming that is contributing to the coke formation. It is not good also how why that we are going to discuss in the subsequent slides anyway when we are going to discuss about the catalytic cracking process as well as catalytic reforming processes.

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Now second reaction mechanism is the catalytic cracking mechanism. So here now depending on the catalyst the reaction mechanism varies. So that is the reason catalytic cracking mechanisms are specific to the reactions.

How the you know reactant species are being adsorbed on the catalyst surface, how the reaction is taking place on the catalyst surface and inside the pores of the catalyst, how the products are coming out of the pores to the surface and then from the surface to the bulk. All that depends on the type of the catalyst and then its porosity, its other characteristics all those things. That is the reason reaction mechanisms of catalytic cracking is dependent on the catalyst and the feedstock that you have taken. But however, some of the

observations if you see catalytic cracking produces no  $C_1 C_2$ ,  $C_1 C_2$  fractions that are not present. So, what does it mean by less gas fractions would be there because when you do the pyrolysis of the crude it is going to have some liquid products, some gases products and then some free carbon you know these things should be there.

So in the catalytic cracking it does not produce a  $C_1 C_2$  fractions and isomerizes to secondary and tertiary hydrocarbons. These hydrocarbons are very essential or desirable compounds for the current petrol. So, this fraction whatever is there that depends on its boiling range. If the boiling range of these hydrocarbons whatever forming if they are between having 60 to 200 degree centigrade boiling range then we can consider them as naphtha and then we can use for the reforming process and different processes that we are going to see anyway.

In general, relatively little free carbon coke is formed. These are the observations generalized observation though reaction mechanisms are specific to the catalyst and then feedstock that you have taken. But whenever you do the catalytic cracking of any of the crudes these are you know common observations. Okay. Aromatic rings would also be forming which are stable in general as we already discussed with example previous lecture right. Cyclic compounds are you know very difficult to break them and make linear components out of them whereas the linear components may be easily broken down.

For example, you have this structure benzene with  $CH_2CH_3$  that is ethyl chain is there. So, breaking any of these bonds is very difficult but this bond you can easily break. This bond also you can easily break as per your requirement. So, this fraction is stable but not this fraction.

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Now reaction conditions of pyrolysis and cracking process if you see any of the reaction not only with respect to the pyrolysis and cracking what are the important parameters especially endothermic reactions the kind of reactions like pyrolysis cracking that we are having.

Obviously, the reaction time you have to optimize it and then temperature, pressure are important. But in addition to the optimum time, temperature and pressure in this case catalyst to feed ratio is also important if it is a catalytic process. If you have catalytic cracking process then catalyst to feed ratio is also important. If you have a thermal pyrolysis simply or non-catalytic pyrolysis simply then these things are important. These are obviously again specific to the process or the feed material that you have taken its reactivity what are the products desired and then what is the coking tendency different factors are there.

You cannot generalize you know how much time is the process optimum time. We are going to see a table some of the reactions are taking place in just a fraction of second and then whereas some of the reactions are going for the hours. Some of the reactions are taking over 1000 degree centigrade some of the reactions are taking you know less than 500 degree something like that. So, it depends on the feed, its reactivity, its products required product formation what are the product that you are desiring and then how much coking tendency is there. All these things are important in addition to this if it is a catalytic cracking process then catalyst its activity all those things are also very important.

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Feed	Process	Reactor conditions		
		Time (s)	Temperature (°C)	Pressure (atm. gage)
	The	rmal pyroly	* Ceier	at son E
Methane /	Acetylene production	0.1	1350	()- 11 men (+)
Ethane	Ethylene production	1	800	11
Gas oil,	Thermal cracking	60	600	20 🗸
Residual crude	Coking <sub>7</sub>	O'	500	(1-3)
	Cat	alytic crack	ing	
Gas oil 🛪	High yield of petrol		(480) 4 1	0.7 - 1
	fraction		<u> </u>	1

Some examples are shown in the table here. Let us say we have taken a few examples under the thermal pyrolysis case where methane is undergoing a slim production process where the reaction time optimum time is just 0.1 seconds whereas the reaction temperature is 1350 degrees centigrade pressure atmospheric gauge pressure. So, this is 0 gauge here if you wanted to have just in a normal pressure under the atmosphere conditions you should have add plus. If you wanted to have the pressure in the atmosphere gauge so then whatever the reading is that you have to do minus 1. So that means this process is occurring atmospheric pressures because these pressures whatever are given they are given atmospheric gauge pressure.

If it is 0 that means the conditions within the reactor are atmospheric conditions. So, then atmosphere condition is there. Other process is that ethane is taken and ethylene production process has been done time is increased to 1 second temperature reduced to 800 degrees centigrade pressure increased to 11 atmospheric gauge pressure. You have taken the gas oil and then thermal cracking process if you do then optimum time is 60 seconds temperature decreased to 600 degrees centigrade pressure increased to 20 gauge pressure. Now what you can see from here as you move down you know volatility is decreasing as the volatility is decreasing required temperature for the process is decreasing here.

But whatever the time required for the process that is increasing as well as the pressure is increasing. So, we cannot generalize for all of them but some observations are provided like this. Let us say if you take residual crude and do the coking process then time you cannot optimize it depends on the residual crude fraction. Whereas these things are you know their compositions are more or less same these are individual components and gas

oil compositions are you know more or less you know remains same in general in a product. So residual crude you know very difficult to say its composition it may vary one crude to the other crude.

So, then time optimization is very difficult to say but the coking takes place approximately at 500 degrees centigrade whereas the pressure again decreases to the 1 to 3 atmospheric gauge pressure. This is about thermal pyrolysis examples. If you take a catalytic cracking example let us say if you have the gas oil and then you try to do a process to produce high yield of petrol fraction. Light fractions you wanted to improve with high yield of petrol in that one.

So, space velocity 0.323 hour inverse what do you mean by space velocity? You know what is the mass rate of the feed that has been supplied to the reactor per mass of or per kg of catalyst. So, this is kg per hour and this is kg. So, what is the mass rate? How many kgs per hour of gas oil is supplied to the reactor per kg of the catalyst that you do. So, then whatever the velocity is coming that whatever the parameter coming that is known as the space velocity it is having hour inverse units.

It is very much important from the heterogeneous reactions point of view. We have seen these things WHSV, LHSV, etc. we have seen in the beginning of the course if not in this course in organic chemical technology course these things have been discussed in detail. Catalyst to oil weight ratio is 5 to 20. Now here you see the temperature is only 480 degrees centigrade.

So, since it is a catalytic process the temperature has reduced. If you wanted to do the same thing without catalyst so the temperature requirement would be very high and then you might not be getting the high yield of petrol as well. This is the pressure. So, these are some kind of observations.

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If you see more observations you know from variations in the reaction conditions point of view whenever you do pyrolysis or catalytic cracking of a petroleum crude what you can find you know this kind of observation as listed below. So, some of them are higher molecular weight feeds crack more readily though they produce more coke or their coking tendency is high.

Then high pressure increases rates of polymerization which is not good because you wanted to reduce the size of the molecule larger molecules you are reducing into the smaller ones by pyrolysis or catalytic cracking but larger molecules forming that is forming because of thermal polymerization. So that polymerization rate increases by increasing the pressure or at high pressure. But however, this high pressure whatever is there that also increases the throughput. So, you have to make a balance you cannot avoid it. Advantage of catalytic cracking is that it lowers the pressures and then temperature requirements as just seen in the previous slide.

In the plant where, low contact time high temperature conditions are existing quenching to avoid back or side reactions is required. Let us say in the previous slide where we have seen such kind of example like a acetylene production or ethylene production these reactions are also reversible and then here the time of contact is very low and then temperature is very high. Under such conditions you know if you do not control the temperature what happens reversible reactions or some side reactions may takes place. So that you have to control how you can control you can provide sufficient quenching to the reaction section or the reactor section. (Refer Slide Time: 36:08)



Now catalytic cracking process design and operations we see here following points are very much essential to understand introduction, selection of catalyst, process variables, process characteristics, equipment design.

Since it is a catalytic process so in the introduction what is the catalyst deactivation how regeneration of the catalyst express all those things we are going to discuss. Then selection of catalyst is also very essential what factor should you consider for the selection of a catalyst, what are the process variables, how they are affecting the catalytic cracking of petroleum, crude, etc. those things we are going to discuss. And then process characteristics that means thermal pyrolysis versus catalytic cracking if you are doing which product is having you know better characteristics those things we are going to see fixed bed, fluid bed, moving bed, etc. these kind of reactors are used so those details also we are going to discuss.

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So, under the introduction catalyst deactivation, regeneration type of reactors, etc. would be discussed. What do you mean by catalyst deactivation? As just now explained any hydrocarbon you take and then you do high temperature processing pyrolysis, catalytic pyrolysis whatever. Definitely some amount of free carbon formation would be there that is nothing but the coking or the coke formation would be there. So maybe in catalytic process that coking may be less, less coke may be forming but definitely that would be forming.

These coke particle what they do? They will deposit on the surface of the catalyst and then they reduce the surface area that is available for the reaction to undergo subsequently. So that is known as the catalyst deactivation. So, because of deposition of this free carbon or coke particles onto the catalyst surface you know activity of the catalyst gradually decreases and then at certain times they will completely deactivated. So, some of the catalyst are very expensive that you cannot replace with the new catalyst you have to regenerate. So how you can do? Simply you can burn off or combust the coke particles whatever formed on the catalyst surface.

How you can do? You can do the combustion at high temperature using oxygen or air. So that whatever the C is there or carbon is there that would be forming CO,  $CO_2$ , etc. And then taken out as flue gases and then clear catalyst surface you know would be available for the subsequent reactions. So that is catalyst regeneration. So, cracking on acidic catalyst is endothermic operation in which tarry material coke deposit gradually and deactivate the catalyst. Catalyst regeneration, reactivation is possible by oxidation of coke which is exothermic known as the regeneration process.

So now in the cracking on acidic catalyst is endothermic process. So, then we are going to see in the fluidized bed reactor or the purpose of fluidized bed reactor or moving bed is this is one of the important one that the catalyst regeneration can be done within the process. You do not need to shut down the reaction and then do the regeneration, refill the catalyst that all batch wise not required. Within the process you can do the regeneration. So, when you are doing the regeneration exothermic reaction takes place or whatever the combustion of carbon particle is there giving flue gas like CO, CO<sub>2</sub>, etc.

You know lot of energy being liberated. That energy may be used for the endothermic reactions, cracking reaction which is occurring in the different part of the reactor. So, this energy may be used there itself. Early fixed bed units by Houdry which is in USA went on stream in 1936. These units employed at 10 minutes make clean cycle and using expensive tubular reactors. In general, what happens if you take a packed bed reactor, packed or fixed bed reactors those things we have already discussed in the first week of the course.

Let us say you have a column within this column certain fraction or the entire fraction or the entire reactor tubular section whatever is there that is packed with some kind of material, packing material. Now whatever the reacting medium is there that passes through this bed. This bed is maintained at certain temperature, pressure which are required for the reaction to take place for the so-called heterogeneous reaction. So, whatever the crude is there that would be passed through and then you get the cracked crude products you can get from here. So, in this process obviously what happens this catalyst whatever the catalyst particle are there that would be deactivated because of the carbon deposition.

Now if you want to regenerate this catalyst especially in the petroleum refinery platinum is mostly used and then you know how expensive it is. If you cannot reuse the platinum catalyst again your process is not going to be economically feasible or the product cost is going to be very expensive and then you may not find the market. So, regeneration is important for that purpose you have to stop the process and then you know do the regeneration, refill the bed and all those things is required. So, there are certain designs like you know here if you wanted to do here hours or even days are required this kind of design if you have. But you know other kind of designs are there where you know the column whatever is there that is filled with certain kind of tubes.

Now these tubes are packed with whatever the catalyst particles which are essential for the reaction to undergo. Now you do the reduction kind of reaction by passing the reactants through this you know tubes within the column and then collect the products. After 10 minutes what you do? You stop them and then you separately supply the oxidizing agents like air, etc. So, whatever the coke that has been deposited that would be combusted and then taken out as a flue gas and then after the all combustion is taken place whatever the remaining are there on the catalyst surface they will also be removed and then you can have the regenerated catalyst without disturbing this you know structure of the packing. So, these

kind of designs are also used in general I think we are going to discuss in one of the refinery process.

But however, in this one also there is a cycle for 10 minutes or some process it may be 10 minutes some process it may be 50 minutes or 1 hour also. So, there is a cyclic kind of operation is there such kind of cyclic operation you know they will delay the process especially when you have competitive world market then you cannot afford to have such larger delay in the process. So, in order to overcome them fluid bed and then a moving bed reactors have been developed and then they are developed such a way that within the reactor catalyst regeneration takes place and then recirculated back to the reactor zone. How it is going to happen that we are going to see through flow chart as well or schematically we are going to see them.

In the reactors molten heat transfer salts circulated in the shell side. Reactors were constructed of expensive alloys to withstand alternative reducing and oxidizing conditions crude first you are doing the reducing reactions reduction reaction size reduction reactions and then later on you are doing the oxidation. So different extremes of reactions are there so that is very difficult to handle.



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Because of such reasons fixed bed design was obsolete within 10 years and was replaced by moving with large pellet catalyst and fluid bed reactors with the catalyst. In both of these designs catalyst is moved from cracking to regenerating section within the column within single column you have both sections one is the reaction or the reactor section another one is the regeneration section that we are going to see pictorially anyway in the next slide. Because these designs eliminated the disadvantage of cyclic operation with heat control not only they avoided the cyclic operation but also heat transfer is very better in this kind of reactors compared to the fixed bed reactors.

Next important aspect of catalytic cracking is selection of catalyst when you do the catalyst selection composition is very much essential. If you have a particular group of metals any metals of that particular group if you can take as a catalyst so then composition you have to see form also you have to see whether pellets are suitable or powders or granules are suitable all those things you have to see. And then some catalyst are not easy to regenerate so regenerative properties of the catalyst also important. Poisoning some catalyst if you have sulphur nitrogen kind of components in the feed then those catalyst may be poisoning the catalyst.

If you have lead arsenic kind of metals they may be damaging the platinum catalyst permanently. So, you have to be careful about the presence of such kind of components and metals in the crude feedstock. Ageing is nothing but when you do the continuously regeneration if you are doing then some kind of surface area would be lost and then ageing of the catalyst may be taking place. So, all these factors you have to select before making a selection of catalyst. Now we discuss about the individual aspects of these properties of a catalyst or requirements of a catalyst. Composition acid treated silica, alumina are found to be best one for the catalytic cracking of the crude petroleum.

However, bentonite and kaolin which in general consist of a silica and then alumina at different proportions they are being replaced by high purity synthetic oxides of alumina and silica of varying proportions as shown here. Form, if you have a moving bed reactor then 3 to 4 mm pellets are suitable. If you have a fluidized bed reactor for the catalytic cracking then 20 to 80 mesh micro spherical particles are suitable. So, what is this mesh number, etc. those things we have already discussed several times.

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Regenerative properties, burning rate must be high and CO<sub>2</sub> to CO rates should be low for better heat control in fluidized beds.

Poisoning, sometimes catalyst may be permanently poisoned by metals particularly group 3 and 4 of reducible oxide type such as iron, nickel, vanadium, copper, etc. you know you should be very careful. So, catalyst should have high tolerance to sulphur if steam reactivation is being done. Reactivation or activation of catalyst is done by different processes.

One is the steam process, another one is the high temperature hydrogen treatment, etc. these kind of different processes are there. Steam is the better one from the economics point of view and then safety point of view as well. So, when you do the steam reactivation so you should be careful that the catalyst having high tolerance to the sulphur. Ageing, reduction in surface area from continued steam reactivation causes catalyst reactivity loss.

However, high silica compositions if you are taking they would be more susceptible to ageing.

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Next is the process variables of a catalytic cracking processes. Here what are the points to be considered? Conversion, temperature, pressure, catalyst to oil ratio, catalyst activity, etc. are important.

We see each of them. Conversion it should be flexible and should be dependent on petrol, gas, oil, product rates, etc. as per the product rate, as per the product distribution or spectrum it should be decided, it should be flexible. Once through up to 50% yield is sufficient. If you are doing recycle then above 50% yield of petrol is expected or it is taken as a standard. What do you mean by once through? Whatever the crude is there you pass through a reactor once and then collect the product.

From the product if the petrol yield is up to 50% so then it is sufficiently fine. But if you are sending some of the products back to the reactor as a recycle then you are expected to have more than 50% of petrol yield in the product. That should be taken as a standard. Temperature in the catalytic cracking coking also takes place.

So, you cannot avoid it. So, you have to make sure that as minimum coking as possible takes place not much. So, there should be a balance between cracking and coking rate. So that to decide the appropriate temperature and for the most of the catalytic cracking processes 500 degrees centigrade is found to be the best average value. Increasing pressure reduces unsaturation that is a good one. But it also reduces the octane number which is not good one.

It increases the coke production which is also not good but increases the reactor throughput so which is good. Now see here 2 positives are there and then 2 negatives are there. So, you have to make a balance. You have to make a tradeoff and accordingly you have to select the pressure as per your requirement as per your feed as per your catalyst that you are going to use in the process.

In general, 0.421 atmospheric gauge pressure is found to be the best average or best range.

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Next is the catalyst to oil ratios how it is going to affect the catalytic cracking of petroleum crude that we are going to see. Possible to recycle catalyst faster with less coke deactivation but it increases recirculation cost.

5 to 20 weight ratio used with 0.3 to 0.6 percent coke levels in the reactor. Catalyst activity so it should be balanced at a constant value dependent on mechanical catalyst losses and additions dropping to 10 to 25 percent of initial value. So, the losses should not be there. It should be as much less as possible but less than 10 percent is in general not possible because the process is so complicated.

But you have to make sure that it is not more than that one. But it also depends on the form of the catalyst. If you have a fluidized bed reactors the powdered form of granulated form of catalyst is better one. This granule sizes are very small not very small like you know nanometers or something like that 20 to 80 mesh size in general they are taking. So, there would be a kind of dusting if you have such small particles. If you have pellets of 3 to 4 mm so dusting, etc. may not be there. So, but if you have a powder of 20 to 80 mesh size

and there is a dusting possibility and because of the dusting there may be some amount of catalyst loss so that you have to make sure as minimum as possible.

Sometimes deliberate additional discard is also practiced additionally. Though there is no loss you try to discard some amount of the catalyst especially where cracking capacity is very tight. Because if the more catalyst is present you know what happens you know rather cracking taking place coking may take place. Undesirable reactions may take place under such conditions deliberately some catalyst is discarded.

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Coming to the process characteristics that is thermal pyrolysis process and then catalytic cracking of petroleum crude when you do if you compare the products so then which one is having better advantages that is what we are going to see. Distinctive features of catalytic versus thermal cracking as a conversion operation are catalytic cracking produces high quality petrol having 80 to 90 octane number from any crude that is very much better option and then this may be used as a naphtha for reforming reactions.

In the next topic we are going to discuss this one and then more selective cracking and less light ends are forming. More isomerization taking place so then that may lead to you know increased octane number. Greater portion of aromatics this may also lead to you know increased octane number. Less polymerization so larger molecules formation will not be there or it will be less. Relatively, little coke, coke formation cannot be avoided but in the catalytic cracking the coke formation is almost negligible or very small amount it is present. Greater ability to tolerate high sulfur feedstocks and then uniformity of temperature and pressure control can be obtained by you know catalytic cracking.

So, all these advantages are coming or all these advantages you are having because of a catalytic cracking of a petroleum crude rather pyrolysis of the petroleum crude.

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Equipment design we have a fluid bed and moving bed design. Fluidized bed by using dense phase liquid like fluidization a compact design is possible in which regenerative heat is transferred as sensible heat of clean catalyst to reactor section. What does it mean? Within the reactor we have the regeneration also regeneration of a catalyst also.

So, this regeneration is exothermic so it is releasing the energy. So, this energy may be utilized in the reactor section where the reactions are endothermic that is what it means by. With low rates of dusting and dense phase operation the cyclones are small enough to place inside the shell because the gases streams are forming. Obviously when you do the catalytic cracking not only the desired product some gases, cokes would also be forming.

These gases may be taking away some of the catalyst particle. They should not be lost. So, for the collection of those catalyst particles what you do? You use the cyclone separator. But in this dense phase fluidization process what happen? Low rates of dusting is taking place because of that one you can use the small size cyclones within the shell itself. We are going to see in the next slide pictorially this one. Short lengths of straight stand pipes reduce the erosion. Coming to the moving bed catalyst pellets move at a fixed rate by gravity flow downward through the reactor generator in succession elevated to reactor again by a gas lift.

Pictorially we are going to see it next slide. Uniform liquid and vapor liquid feed distribution necessary. Other design drawbacks compared to the fluidized bed units are excessive steam requirements and then poorer heat economy.



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So pictorially if you see here what you have this is nothing but the fluidized bed. Now here this is the column we are talking about. This column we are having within the column one particular section is the reactor section.

Another particular section or the top section is the regenerator section as mentioned here regenerator and then reactor here. So, reactor section is fed with the catalyst and then this catalyst is maintained at certain pressure as per the reaction requirements. So, to this one feed is supplied from the bottom and then steam is used as a fluidizing medium for the reaction to take place. So, because this is we are talking with respect to catalytic cracking not generalized one. So here steam may be utilized. So, reaction is taking place whatever the cracked products are there they will be taken to the distillation column where fractionation takes place to collect the gas, petrol, gas oil separately whereas the heavy ends, etc.

Residues, etc. are there you know they may be taking to the reactor as a recycle or some fraction of the products may also be taken as a recycle to the process depends on the once through or recycle process. If you are doing the recycle process this is what you can do it. So, after certain reaction time the catalyst deactivation may take place. So, whatever the deactivated catalyst would be taken through this line and then they would be sent to regenerator section using the airlift. So, these catalysts which are deactivated when they

enter the regenerator here also temperature pressure are maintained such a way that you know they should be suitable for the oxidation of a free carbon deposited on the catalyst surface should be taking place easily.

So, when this oxidation of carbon takes place which is this carbon free coke or carbon that is there on the catalyst surface then you know flue gases would be formed those gases would be collected, tested, their composition and then released accordingly if releasable. Otherwise you know proper processing is required. So once the regeneration process is taking place so these gases may also carrying some of the catalyst.

So those catalyst particles are separated by these cyclones. Since the rates are low rates are supplied here so the catalyst particle, etc. carrying are going away with the flue gases would also be low. So then smaller cyclones are sufficient. So, then those smaller cyclones may be installed within the shell in the regenerator top of the regenerator section within the shell we can do this one. So, within the shell we have the regenerator section and then reactor section. Once the catalyst is being reactivated so those catalyst would be taken regenerated catalyst would be taken to the reactor again and then the process continues.

So, you do not need to go for the cyclic operations of catalyst regeneration and all those things that is the advantage of a fluid bed reactor. Next one is the moving bed. Here what we have we do not have the reactor section and regenerator section within one column or within one shell we do not have we have separately here. So here reactor section the temperature pressure are maintained sufficiently as per the catalytic cracking requirements and then steam is supplied to this reactor once the temperature pressure are attained as per the requirement the catalyst are fed. So, at high temperature pressure these catalyst particles interact with the feed which is coming from the top and then products would be forming those products would be collected. So, whatever the spent catalyst whatever are there after certain time obviously catalyst deactivation takes place those spent catalyst or deactivated catalyst would be drawn from the bottom of the reactor and sent to the regenerator.

To, this regenerator air is supplied so that you know combustion of a carbon that is deposited in the catalyst particle can take place and then flue gases would be collected out. So, whatever the regenerated catalyst are there they would be taken to a lift engaging hopper and then using a lift gas or air these catalyst particles are lifted to the top where you know catalyst dispensing hopper is there and then again fed back to the reactor. So, this process continuously goes on without so what is the advantage of these two reactors fluid bed and then moving bed you do not need to stop the process or you do not need to go for the cyclic process for the catalyst regeneration.

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Now petroleum coking process design and operation here we will be discussing about introduction process variables equipment design for coking. Introduction residual petroleum so let us say when you do the fractionation of crude so some residues would be formed or when you do the refining process some heavy end forms which you cannot further process you can only do for the asphalt collections or for the lubrications, etcetera which is not going to be much profitable.

So, the such kind of heavy end fractions as well as the residual petroleum from the refineries whatever are there they can also be pyrolyzed and upgraded to values. What do you mean by upgraded to the values you know different components or the compounds or homologs you can produce by the pyrolysis of residual petroleum or heavy end fractions from the refineries. So typical yields if you do the coking of petroleum refinery residuals or the high heavy end fractions then light ends you can get up to 5 weight percent petrol you can get 20 percent so this may not be pure enough so then this can be used as a naphtha for the naphtha reforming purpose which is our next topic and then you produce aromatics, etcetera. These are feedstocks for the different types of chemicals or it will also increase the octane number. Gas oils you can get 60 to 65 weight percent and then coke is 10 to 15 percent see how much better advantage is there by doing the coking of the residual petroleum.

You are getting light ends you are getting petrol gas oil so much of gas oil you are getting and then coke is very less 10 to 15 percent only. So that means out of the overall heavy end fractions only 10 to 15 percent is only going waste as a coke. In fact, this is also having different advantages but not within the petroleum refinery industries but for some other industries.

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Process variables obviously temperature and pressure are important temperature increasing the temperature results in the higher yields of the gas because it is non-catalytic and then petrol as well as the coke where gases are more olefinic. Olefinic gases are forming like you know ethylene gases these kind of gases are forming. Petrol required hydrogenation for stability what does it mean by whatever the petrol that approximately 15 to 20 percent that we are getting here you know this is not stable so for that purpose you have to do the hydrogenation.

And then best temperature is 500 degrees centigrade pressure higher pressure yields more gas and coke so it is not good. You look for more the liquid products in general best pressure range is 1 to 3.5 atmospheric gauge.

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Coming to the equipment design for coking process 3 types of equipments or units are possible one is the delayed coking unit another one is the fluid bed another one is the moving bed coking unit. We discuss about them now delayed coking rapid heating in pipe stills followed by coke formation and settling in large coke drums is taking place. Units are cleaned by cutting with high speed water jets whatever the coke formation here that is taking place within the pipes that you have to separate out for that you know high speed water jets are used.

Under the fluid bed units it is working principle is similar to fluid bed catalytic cracking unit as we have seen. Product coke is circulated to an air fluidized burner and then to the reactor where steam is fluidizing agent. Coke particles increase in size in the units so a portion is removed ground and return for average particle size control. Coming to the moving bed it is working principle is similar to whatever the catalytic cracking unit we have discussed a few slides before pictorially.

In the next class we will be discussing about other refinery processes.

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The references for the today's lecture are presented here. But however, the entire lecture notes is prepared from this reference book. Thank you.