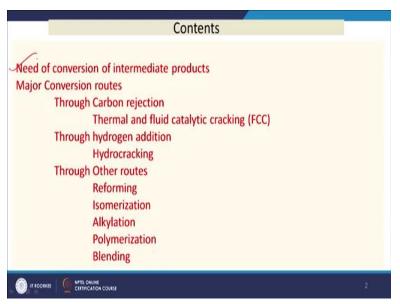
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Lecture-14 Conversion of Intermediate Products

Hi friends now we will discuss on the topic conversion of intermediate products. So, in the previous class we have discussed on the petroleum crude its properties and characteristics then how we can produce different liquid products from the petroleum crude in a refinery and we have seen that different liquid products like naphtha, gasoline, kerosene, ATF and diesel or vacuum residue or atmospheric residue we get.

So, these products have different applications and requirement of these products may change from time to time. So, to meet the requirement in the market the refinery needs to convert these products from one form to other form as per the requirement of the market as well as to maintain the quality of the product and environmental requirement also.

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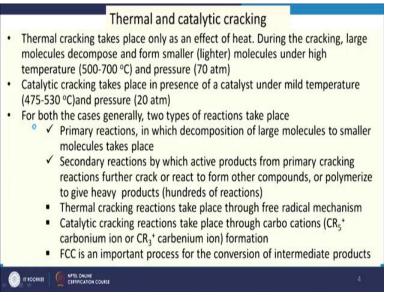
So, this conversion processes we will discuss in this class and the contents are need of conversion of intermediate products then major conversion routes there are basically two major routes one is carbon rejection and another hydrogen addition. And other routes are also we will

discuss that is reforming, isomerisation, alkylation, polymerization and blending. (**Refer Slide Time: 01:53**)



The need of the conversion already we have discussed that we need to meet the market requirement so one product to other product conversion is necessary. And also to improve the product quality I will give some examples that how the some specific property of that particular fuel oil or that particular liquid oil can be improved by these conversion methods. And already have discussed meet the market requirement of different products and then achieve environmental standards.

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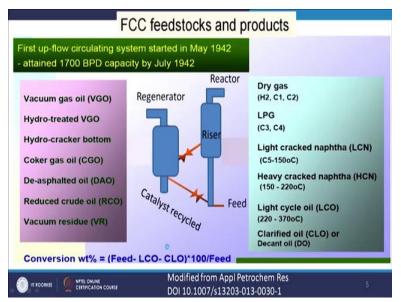


Now we will discuss the carbon rejection routes that is basically cracking it takes place in

presence of catalyst or in absence of catalyst. So, the cracking means the application of heat to crack the bigger molecules of hydrocarbons into the smaller part smaller ones. So, the liquid fractions or we can get more amounts of liquid lighter liquids and that is the main objective of the cracking. And if we apply catalyst then the requirement, the process requirements the high temperature is reduced to some extent.

So, we have two types of cracking one is thermal cracking another is catalytic cracking and the thermal cracking temperature is around say 500 to 700 degree centigrade and pressure is around 70 atmosphere. However if we use catalyst then the temperature may be 475 to 530 degree centigrade and pressure requirement is also less that is 20 atmosphere. If we apply this cracking process may be in thermal or may be in catalytic path.

So, the higher hydrocarbons will be converted to lower one. And the two processes having different mechanism of this conversion so one the thermal route that follows the free radical mechanism where as the catalytic route follows the carbo-cation, productions are carbonium and and carbonium ion productions so there are two CR_{5+} or CR_{3+} that is carbonium and carbonium ion respectively. So, the mechanism is different and requirement of energy is also less for the catalytic route that is why it can take place at lower temperature.



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Now we will see the catalytic route that is fluidized fluid catalytic cracking. So, when catalyst is

used in a fluidised bed and then feed is fed through this reactor. So, this is the riser part of the reactor and this reactor here the catalyst is coming as a recycle. So, this catalyst and the feed is reacting here and then we are getting the product there that side. And this catalyst after use in the reactor is coming to the regeneration part.

And then after regeneration it is again recycle so this is a closed circuit and where the catalyst and fuel is coming in contact and giving us the required product. So, this is our one fuel say which is having less requirement in market. So, you want to convert into other fuel where will be having more requirements. So, this is the concept of the process or this is the descriptions of the FCC process and now what can be the feedstock we can use.

In this process different types of feedstocks have been used like say a vacuum gas oil, hydro treated VGO or vacuum gas oil, hydro cracker bottom then coker gas oil De-asphalted oil, reduced crude oil and vacuum residue so any one of these feedstocks can be processed through this so that we can achieve more valuable products from this. So, what are some examples of these products are say dry gas, we can have LPG, we can have light cracked naphtha.

We can have heavy cracked naphtha we can have light cycle oil and clarified oil. So, this naphtha when the naphtha requirement and LPG requirement is high in that case we can explain the conversion in terms of this that feed how much feed you have taken minus this part. Then remaining part is here so divided into 100 divided by feed. So, this is the conversion of this process. Now we will see the typical conditions under which this FCC reaction takes place.

So, here if we consider here, so obviously catalyst and feed is coming in contact with it so what is the ratio of catalyst and feed I am giving that is important. What is the temperature we are maintaining here so here again riser is there so at what temperature the regeneration of the catalyst is taking place that will also influence the degree of regeneration of the catalyst as a whole the performance of the process, what type of feed we are using that will also influence this one.

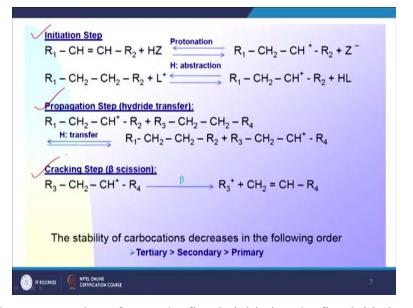
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	FCC Unit	
	Foreign	Indian
Catalyst / Oil Wt. Ratio	7 -9	5-9
Reactor / Riser O/L Temp. ^o C	540	490 - 510
Reactor Contact Time, Sec.	1-8	1.5 - 3
Feed End Pt. ^o c	600-621	540- 560
Regeneration Temp.	700-750	640-660 /730
Carbon On Regenerated Catalyst	0.05-0.10	0.3-0.6 / 0.01-0.02
Regenerator Pressure, Kg/Cm ²	1.75	3.0

So, we will see catalyst to oil ratio there are Indian and foreign units FCC units are there typical properties are shown here that is catalyst to oil ratio 7 to 9 for foreign unit and 5 to 9 Indian unit say reactor riser temperature that is 540 and is a 490 to 510 reactor contact time there is also very important there is 1 to 8 second here 1.5 to 3 second. Feed-end point then that means what type of heat we are using it is 600 to 621 here 540 to 560.

Regeneration temperature that is related with the catalyst here it is 700 to 750 here 640 to 730 and then carbon on regenerated catalyst. So, what is the extent of the regeneration of the catalyst that is the indicator of the carbon deposited on it and then this is for foreign units this 0.05 to 0.1 and this is .3 to .6 or .01 to .02 regeneration regenerated pressure that is 1.75 kg per centimetre square here it is 3 kg per centimetre square.

So, these are the comparison of two FCC units which is in India and in foreign. Now we will see the reaction mechanism and how the cracking takes place when we choose the FCC process. (**Refer Slide Time: 09:11**)



So, in this case there are number of steps the first is initiation the first initiation takes place then is propagation then it is cracking and then we go for isomerisation and cyclization. So, we will see how the cracking reaction initiates. So, we have one hydrocarbon say and then we have catalyst so protonation can take place with this hydrocarbon so 1 H^+ from this is coming here and being added to this CH so this CH⁺.

So then another process may be possible this may be catalyst so that will take 1 hydrogen from this so $R_1CH_2CH^+$ and then we are getting here R_2 , so this way hydrogen that is protonation or hydrogen abstraction takes place that is the initiation. So, we are getting now the carbocation so that carbocation will react with another hydrocarbon and then there will be some hydride transfer. So, this is called propagation step.

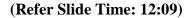
So here we had plus charge and another hydrocarbon so this charge has shifted here and now we are getting this one $n-R_2$ another hydrocarbon and this charge is shifted to this one so that is why this is called hydride transfer. So, 1 hydrocarbon to other hydrocarbon it is transferred. And then cracking step so we are getting this one, this carbocation there will be some cracking in this chain so beta scission it is called.

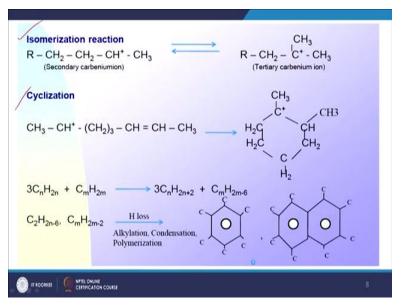
So, beta position see if we have a positive charge here so these positions will be cracked so we are getting R_3^+ and then CH₂CH and R₄ so this will be there some double bond and then R₃ will

be separated as R_3^+ and then we are getting this other product. So, this is called a cracking step so we are getting a smaller hydrocarbon now from a bigger one. So, that is desirable to improve the quality. And now the carbocations which is produced here what type of carbocation so we are discussing here that this hydrogen transfer takes place from one to other hydrocarbon.

So if it is more stable the carbocation is more stable, so this one and this one out of these two which one is more stable? this one or this one this one we have to decide and if you can decide then we can we can predict that this conversion will take place or may not take place. So, it has been seen that if this carbocation is tertiary in nature it may be in secondary or maybe in primary in nature.

So, it is shown that the tertiary has more stability than secondary and then primary. So, that way product nature will also change.

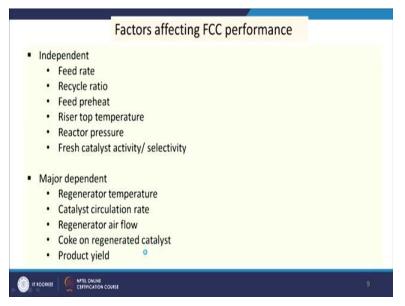




Then isomerisation may also take place so we have on secondary carbenium ion in this case. So, there may be some isomerisation so this H^+ some you see so RCH₂ and C⁺CH₃CH₃ so this can also take place that is called tertiary carbonium ion, so secondary to tertiary formation can also take place and then cyclisation, some cyclization reactions can also take place in this process so as shown here this is our hydrocarbon so this is converted to cyclic form.

This is also 2 hydrocarbons they can make this one okay so that way the cyclization reaction can takes place and alkylation, condensation, polymerization can also take place alkylation may take place condensation may take place and polymerization may take place. So, these are the different type of reactions which can take place during FCC process.

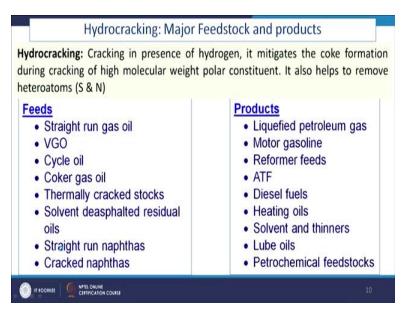
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Now what are the factors that influence the FCC performance? Already we have mentioned some of those that is a feed rate, those are the independent parameters on which it depends the feed rate then recycle ratio, feed preheat, riser top temperature, reactor pressure and press catalyst activity that what is the extent of regeneration of the catalyst and then fresh catalyst selectivity also the how selectivity so that we can get a particular product in higher extent.

And some dependent variables are also there that is regenerated temperature then catalyst circulation rate then regenerator airflow, coke on regenerated catalyst and product yield.

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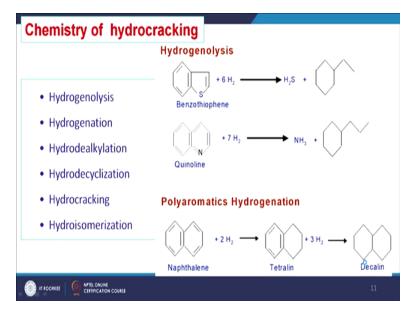


Now we will see other type of cracking in which hydrogen is added so if we add hydrogen then we will be getting more liquid and at the same time we will be able to remove some sulphur nitrogen etcetera. So, that is the advantage of this hydro cracking reactions and we see different types of feeds are also used for this process and different products can also be achieved. So, some examples are straight run gas oil.

So, gas oil which is produced directly through the fractionation in atmospheric distillation so that is that can be used vacuum gas oil which is obtained from the vacuum distillation column that can also be used cycle oil, coker gas oil, thermally cracked stocks and solvent deasphalted residual oils. So, after solvent is deasphalted then what liquid we get that can also be used for hydro cracking and then straight run naphthas and cracked naphthas.

So those are the feedstocks for this hydrocracking process and some products are liquefied petroleum gas LPG, motor gasoline, reformer feeds, ATF, diesel fuels, heating oil solvent and thinners, lube oils and petrochemical feedstocks. So, once we are getting naphtha will be the naphtha is converted to petrochemical feedstocks so that is the use of this.

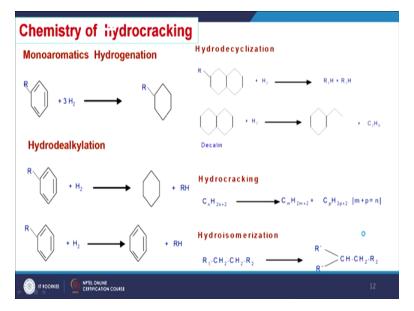
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And we will see the chemistry of this hydrocracking process so like FCC process here also different types of reactions can take place. And obviously hydrogen addition is taking place here so we will get we will get some hydrogen analysis. So, we will be adding hydrogen that hydrogen will break the structure here say benzothiophene so due to the addition of hydrogen this structure will be converted this is broken here so lyses is taking place.

So that is hydrogenolysis due to the addition of hydrogen we are getting some lyses is in the structure the organic compound and then similarly quinoline and this one then hydrogenation say poly aromatics hydrogenation so we have one naphthalene. So, if we add hydrogen so this unsaturation will be removed so in one ring it is shown and in this second step again the both the rings unsaturation is removed.

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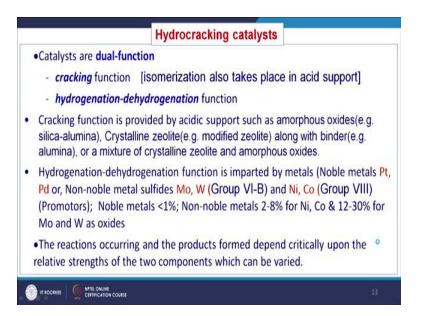


So that way hydrogenation can takes place or hydro dealkylation can take place hydro dealkylation can take place here say this is your one aromatic hydrocarbon we are adding hydrogen so then we are getting hydrogen addition here plus dealkylation. Alkylation dealkylation also taking place alkyl group is removed from this ring so that type of reaction can also place. Another example is here only dealkylation has take place.

And then hydro decyclisation see if we have this type of compound if we add hydrogen then de cyclization this is a cyclic compound due to this there will be some cracking and then hydrogen addition. So, these two different compounds we are getting here which is not having cyclic structure so here decalin, hydrogen it gives this type. So, these are some typical examples and numbers of reactions are may be possible during the reaction conditions.

And then hydro cracking can take place so this is a cracking bigger molecule so it is converted to smaller one. Hydro isomerisation some isomerisation can also take place so this is one hydrocarbon this can be converted to this one so isomeric form of it.

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So different types of reactions can take place during the hydrocracking process or in the hydro crackers. So, if we think about the catalyst and their properties then the catalysts will be having some dual functions one is cracking we have to crack it and another is hydrogenation and dehydrogenation. So, one is cracking another is hydrogenation and dehydrogenation these are the basic process which is available during the whole process that is why the catalyst should have two sides.

One will favour the cracking another will favour the hydrogenation dehydrogenation reactions. So, for the cracking reactions the active sites is acidic in nature and say some examples is silica alumina or say crystalline zeolite modified zeolite along with binder so these are the some examples of acidic sites in a catalyst. And there will be some other sites for hydrogenation and dehydrogenation and these sites are basically containing a metal that is noble metals maybe platinum, palladium or non noble metals like molybdenum and tungsten or nickel cobalt has also been used to increase this hydrogenation and dehydrogenation capacity of the catalyst.

And noble metals less than 1% non noble metals 2 to 8% see if we use noble metal the catalyst will be costly but obviously noble metal in noble metal using catalyst the requirement of noble metals is less but non noble metal requirement is higher than this for example 2 to 8% for nickel cobalt and 12 to 30% for molybdenum tungsten dioxide. So, to reduce the cost of the catalyst the non noble metals have been introduced and the noble metals have been replaced by this although

there are some comparison between the performance obviously the noble metals catalysts are more then the non noble metal catalysts.

Now what type of reactions will take place? What will be the product distribution? that will depend upon the extent of this acidic site and these your basic sites of these two catalysts. So, accordingly the product pattern will change and depending upon the feedstocks also this can be monitored the active sites number of active sites can be monitored. And since and the catalysts can be designed.

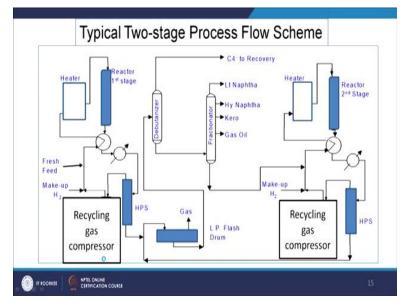
	Catalyst Characteristics			
Desired Reaction	Acidity	Hydrogenation Activity	Surface Area	Porosity
Hydrocracking of Naphtha to LPG Gas oil to gasoline	Strong	Moderate	High	Low to Moderat
Hydrocracking of Gas oil to jet fuel and middle distillate Gas oil to high VI lube oils Solvent deasphalted oils and residues to lighter products	Moderate	Strong	High	Moderate to High
 Hydroconversion of non-hydrocarbon S and N in gas oils Sulfur and metals removal in residues 	Weak	Strong	Moderate	High

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Some example we will show here so this is our desire reactions we want to hydro crack naphtha or LPG, naphtha to LPG or gas oil to gasoline so this is our to say desired reactions we need to do it so our catalyst should have strong acidic site. And then hydrogenation activity is moderate and then surface area high, porosity low to moderate. But when we go for gas oil to jet fuel and middle distillate conversion as gas oil to high viscosity lube oil conversions then we need moderate acidity.

Moderate acidity and hydrogenation activity is very strong so we need to add more hydrogen in this case. So, surface area is high. Similarly when we go for hydro conversion of non hydrocarbon sulphur and nitrogen then obviously we do not need that acidic behaviour because our objective is to remove the sulphur and nitrogen so not to crack the molecules may not be the cracking of the molecules may not be that important. So, in that case we are using weak acidity and then hydrogenation has to be strong because S and N has to react with the hydrogen to give H2S NH3 so that way depending upon the nature of conversions which we are interested to achieve in this process we can design the catalyst as per our requirement.





Now we will see the process how the hydrocracking can take place. So, here we need hydrogen and we need feedstock we have to provide temperature and pressure. So, here we are makeup hydrogen we are providing some pressure and fresh speed so it is coming here so that way it is going and heated preheat it and it again some heating arrangements and it is coming to reactor stage 1 so this is one first reactor for hydrocracking.

So, after reactions the product is again here cooled down and then it is coming for pressure release to high-pressure separator. So, high-pressure separator we are getting some gas so it will be coming and again it will be recycled with hydrogen. So, it is going to this loop and then the liquid part which we are having here that is going for lower pressure plus again we are doing reducing the pressure here.

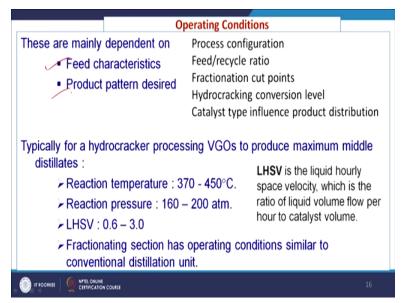
So, low pressure flash drum it is coming so again we are getting some gas molecules gas and the remaining part is going there for debutanizer. So, some again some pressure reduction so debutaniser, butane is recovered here then it is going for different fractionation. So, for

fractionation and in the fractionators we get different products light naphtha, heavy naphtha, kerosene, gas oil etc. So, the residual part again it is going and added with makeup hydrogen and it is entering into the after preheating it is entering into the reactor 2.

So, second stage conversion we are taking the objective is to get more liquid conversions more conversions. So, then it is coming and from second reactor again it is cooled out and then high-pressure separation. So, then high pressure separations we are making a flash so we are getting flash after flashing temperature pressure reduces. So, then the vapours goes there and it is added with the hydrogen for this recycling of this and helps for the hydrocracking.

And in the bottom part of this it is coming and send to the low pressure flash drum so again for the recovery of the gases from it so this is a overall flow sheet which is followed to perform the hydrocracking of different products intermediate products.

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Now we will see the operating conditions these are mainly dependent on feed characteristics and product pattern which we desired that we have already discussed. And some typical example are given here for a hydrocracker processing VGO's to produce maximum middle distillates the reaction temperature is around 370 to 450 degree centigrade and reaction pressure is 160 to 200 atmospheric pressure.

And LHSV that is 0.6 to 3.0 and what is LHSV? that is the liquid hourly space velocity which is the ratio of liquid volume flow per hour to catalyst volume. So, fractionating section has operating conditions similar to conventional distillation unit.

Comparison of Hydrocracking and FCC				
Parameter	FCC	Hydrocracking		
Operating pressure	Low	High 1500-2800 psi		
Operating temperature	High, 900-100 °F	Moderate, 600-780 °F		
Construction costs	Moderate	High		
Product olefins	High	Nil		
Light naphtha octane (RONC)	>100	78-81		
Heavy naphtha octane (RONC)	95-100	40-64		
Distillate cetane index	Low	56-60		
Distillate sulfur content	Moderate to high	Very Low		
Bottoms sulfur content	Moderate to high	Very low		
		17		

So these are some operating conditions now we will see the comparison of FCC and hydrocracking so obviously when we are using hydrogen we need to provide sufficient pressure for the reaction of hydrogen with the liquid part. So, gas phase and liquid phase reaction so we need to increase the high pressure so pressure is high here for FCC we do not need that high pressure. Operating temperature here it is high but in this case temperature is relatively less because hydrogen is present there.

So, construction cost is moderate for FCC, hydrocracker is high because it requires high pressures so cost is also higher, products olefins is high here, here it is nil. So, olefin will not be available because we are providing hydrogen so olefin unsaturations will be removed. And then light naphtha octane number it is greater than 100 but here we get 78 to 81, so unsaturation is not there so octane number is not much with respect 100 where we get in FCC.

But heavy naphtha octane we get in 95 to 100 where 40 to 64 and then they distillate cetane index so cetane index here it is low and we have 56 to 60 and distillate sulphur content obviously in this case will be having moderate to high because sulphur removal does not take place in this

case but here hydrocracking sulphur removal takes place. So, will be very low sulphur will be bottom sulphur content is also very low in this case of hydrocracking. So, that way we can compare the FCC and hydrocracking process.

Now we will see the reforming and isomerisation process so reforming means reforming will reform some products to other one.

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Reforming a	nd Isomerization			
It helps to produce high octane number reformate, main component of motor fuel, aviation gasoline blending or aromatic rich feedstock as well as hydrogen rich gas Feed stocks: either low quality straight run naphtha or cracked naphtha generally mixed with straight run naphtha Reactions (desired) : Naphthene dehydrogenation				
Parffin's dehydrocyclization Linear paraffin's isomerization Naphthene's isomerization	 Isomerization To produce branched C₅-C₆ hydrocarbor (Premium gasoline production) 			
Reactions (Adverse) Hydrocracking	 Reduction of Benzene, aromatics and olefins LPG production 			
Hydrodealkylation Alkylation, Transalkylation and coking	Need for high octane components in gasoline			
	18			

So, basically in this case it helps to produce high octane number reforming so it helps to produce high octane number reformate octane number reformate and different type of reactions which we get here that is naphthene dehydrogen and then paraffin's dehydrocyclisation and the linear paraffin's isomerization and Nephthene's isomerisation. So, dehydrogenation and isomerization are desired product desired reactions.

Whereas adverse reactions which can take place here that is hydrocracking, hydrogenolysis hydrodealkylation and alkylation, transalkylation and coking. So, these are not desired for the reforming. And isomerisation is required to produce branch say C_5 - C_6 hydrocarbons that is gasoline product. So, when we need more gasoline to improve the quality of gasoline this reactions is preferred.

Here also this is also reforming is also preferred to increase the octane number. Then we can add

some blending so blending is possible so that can help to improve the quality of the product as well as to meet the requirement of a specific fraction. So, some example will show here.

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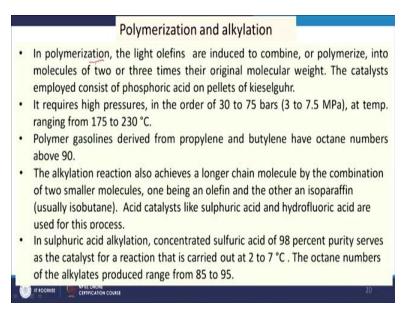
Blending

- Refinery products are blended for the optimal use of all of the intermediate product streams for the most efficient and profitable conversion of petroleum to marketable products with desired specification and environmental standards. Few examples are:
- Typical motor gasolines may consist of straight-run naphtha from distillation, crackate (from FCC), reformate, alkylate, isomerate, and polymerate, in proportions to make the desired grades of gasoline and the specifications.
- Naphthas can be blended into gasoline, or jet fuel streams, depending on the demand.
- In most cases, the components blend nonlinearly for a given property (e.g., vapor pressure, octane number, cetane number, viscosity, pour point), and correlations and programming are required for reliable predictions of the specified properties in the blend.

So, typical motor gasolines that may consist of straight run naphtha from distillation atmospheric distillation so a straight run naphtha which we are getting, that plus crackate from FCC crackers which gasoline we are getting. We can make some proper blend we may get reformate, reforming is also giving us gasoline that part can be blend. Alkylate, isomerate and polymerate so different reactions can give us some gasoline type product so if we can mix it then ultimately gasoline blend will get.

And that may have higher octane number than the straight run gasoline. So, in most cases the components blend non linearly for a given property that means if we mix these different gasoline from different sources. So, after the mixing what will be the property normally it is not that linear it is non linear and some correlations are developed to predict what will with the properties of this.

Then polymerization and alkylation another type of reactions which are also used for the conversion of one intermediate product to other form that is polymerization and alkylation. (**Refer Slide Time: 29:37**)



The in polymerization the light olefins are introduced to combine or polymerize into molecules of 2 to 3 times their original molecular weight so, smaller molecules are converted to higher one. So, the catalysts employed are acidic that is phosphoric acids on pellets of Kieselguhr. So, that is used and we see here it requires high pressure in the order of 30 to 75 bars and temperature is 175 to 230 degree centigrade.

And this polymerization derived gasoline may have higher quality some example is shown here polymer gasoline derived from propylene and butylenes have octane numbers above 90. This alkylation reactions also achieves long-chain molecules by combination of two smaller molecules so one being an olefin and the other as Isoparaffin. So, sulphuric acid can also be used or hydrofluoric acid can also be used for this reactions.

This alkylation when sulphuric acid is used that is 98% concentration and say and the temperature is 2 to 7 degree centigrade. The octane number of these alkaloids may be 85 to 95 so this so polymerizations alkylation's all these processes helps to increase the octane number and to give better quality gasoline.

So, we have discussed different type of reactions which can take place or which you can use to convert one form of liquid to other one to meet the market requirement as well as to improve the quality of that particular liquid fraction, thank you very much for your patience.