

**Technologies for Clean and Renewable
Energy Production
Prof. Prasenjit Mondal
Department of Chemical Engineering
Indian Institute of Technology-Roorkee**

**Lecture-13
Refining of Crude Oil for Fuels Production**

Hi friends, now I will discuss on the topic refining of crude oil for liquid fuels production. So, in the last two three classes we have discussed on the petroleum and then how it is produced its properties and characteristics and different products which you can get through the refining also. Now we will be discussing more about the refining part that how the crude oil is refined to get different products what are the process steps and what are the reactors which are involved or the reaction steps which are involved for the production of the different liquid products.

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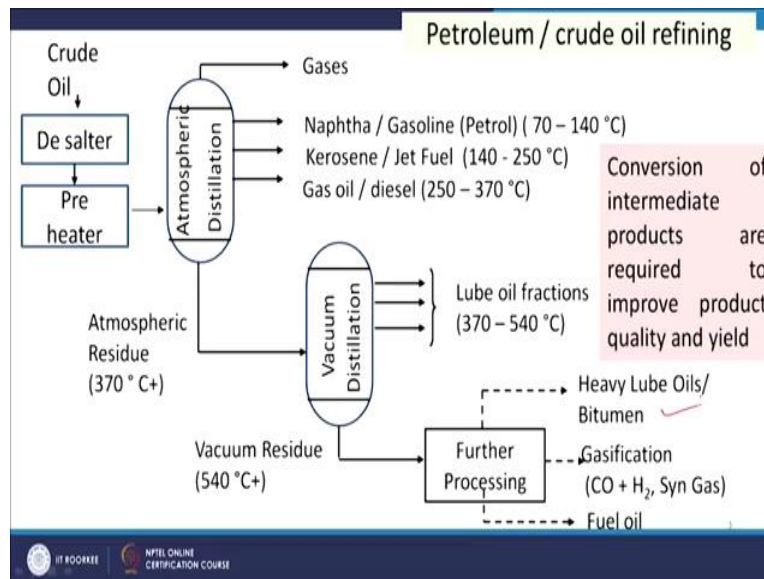


So, the contents of these refinery flowsheet, desalting, atmospheric distillation, vacuum distillation and conversion processes, so if we see the conventional flowsheet of petroleum crude refining then it we see that after taking the crude it is to some extent processed at production site and then it is transported to refinery. And then refinery perform some preliminary operation or pre-treatment step then it is sent to the atmospheric distillation column.

And then residue of the residual part of the atmospheric distillation column it goes to vacuum distillation column for further recovery of liquids from it and then the residual part of the

vacuum distillation column is further processed in the as downstream up-gradation or downstream processing.

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And then different heavy lube oil, bitumen, syngas or fuel oil etcetera, are produced. Now we will start from here the desalter the first step at the refinery. So, the main objective of the desalter is to remove the salt sediments and water present in crude. Because we know this crude oil when it is getting into, entry into the atmospheric distillation and fractionated into different fractions into products that is naphtha, gasoline, kerosene, gas oil etcetera.

Here the salt concentration should be less than certain value that is 2.9 ppm but here the crude which is produced in some cases has very high concentration of salt so that has to be removed. Now we will see, prior starting the discussion we will see the quality of some Indian crude that means what are the different fractions we can get from Indian crude.

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Composition of typical Indian crude oil				
Composition (% mass/mass)	Bombay High ✓	North Gujrat Mix ✓	Assam Mix ✓	Middle East Crude
Gases	1.9	0.4	2.4	2.1
Naphtha (IBP-140)	18.6	4.4	12.5	10.7
Kerosene (140-250)	20.9	10.1	16.6	16.1
Diesel (250-370)	24	19.2	26.6	18.1
VGO (370-530)	28.4	31.2	30	22.5
SR (530 +)	6.2	34.7	11.9	30.5

So, that is Bombay High, North Gujarat mix, Assam mix, we get gaseous 1.9% 0.4 for north Gujarat mix and 2.4 for Assam mix. So, in general this is which is for LPG content is very high in Indian crude not less. And SR that is vacuum residue part is also less in this case Bombay high and Assam mix although it is higher for north Gujarat mix and it is comparable to middle-east crude that is 30.5 this gives us some idea that we can get different amount of product different products in different amount.

But then if our requirement is specific say we need more diesel but these crude are having certain capacity if we turn 100 ton then it will give us 24 it is in 19.2 it is 26.6 say but I need 50 ton so I have to convert other product into this specific one. So, that a conversion of this process of the products into the required part is also very important that we will discuss later. Now we are coming to desalting part.

Desalting as you know the purpose of this process is to remove the undesirable impurities specifically the salts and water and some sediments also if it is available. And one or two step process is used for this purpose.

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Desalting

- The **purpose of desalting** is the removal of undesirable impurities, especially salts and water, from the crude oil prior to distillation. Initially it is carried out at the production field and finally at refinery.
- One or two-step process is used depending upon the desired salt content in the desalted crude oil.
- For refining purposes, a salt concentration of maximum 1.5 PTB (pound of salt as NaCl per thousand barrels i.e., 2.9 ppm) is desired.
- Appreciable amount of suspended solids (sand, clay, or soil particles, or even particles product from corrosion of pipelines and other upstream equipment) can be removed by desalting.
- The total solid concentrations in formation waters range from as little as 200 PPM to saturation i.e. approximately 250,000 PPM. Most sea waters contain approximately 35,000 PPM total solids

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And as I have mentioned that 2.9 ppm salt is allowable in refinery in the distillation column but in some cases it is having very high say 250,000 ppm and normal it is 200 ppm. So, it is very high quantity of salt. So, if we see the salt content in sea water it is 35,000 ppm whereas in some crude it is having more than much more than this. So, the removal of salt is very essential for its further processing in the refinery and that is done in desalting step.

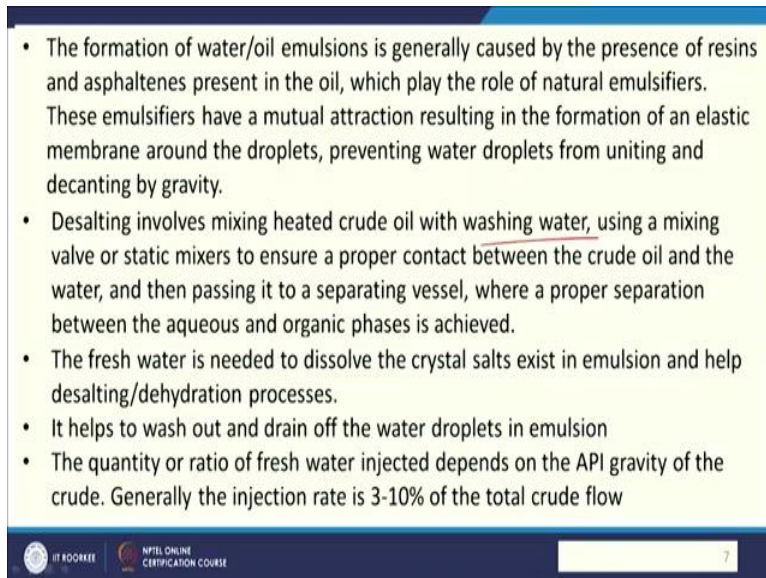
And what is the mechanism? How it works? So if we see the water is present in the crude either as a separate phase or it makes a water in oil emulsion. So, when it is available in separate phase it is easy to separate, it can be simple gravity can also separate it. So, gravity oil-water separator, surge tanks or desalting vessels all those will easily separate this water but water which is in emulsified form that is not very easy to separate.

And that emulsified water also contains the salt of the crude oil so our objective to remove that emulsified water along with the salt from the crude oil that is the desalting step. And as we have discussed that salt is present in the form of crystalline solids or soluble in the emulsified water. So, if we want to remove this salt so one way we can if we are able to remove the emulsified water then salt will come.

But that salt which is in crystallized and as a solid form that cannot be removed for that we have to add some more water. So, water is added, heat is applied so that the external or the solid salts can be dissolved in it. And heat will also help to break the emulsion and emulsified water along with the brine will also with the salt so the brine solution will come out from the crude so this is the principle of this.

The desalting step so how it is done the initially salt separation takes place at the production side as I have mentioned that is the separate phase of the water can be separated easily then it is transported to the refinery side.

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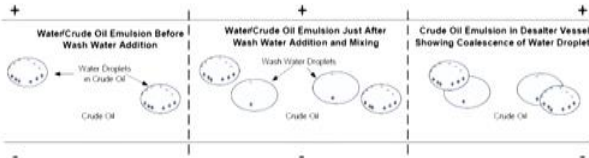
- The formation of water/oil emulsions is generally caused by the presence of resins and asphaltenes present in the oil, which play the role of natural emulsifiers. These emulsifiers have a mutual attraction resulting in the formation of an elastic membrane around the droplets, preventing water droplets from uniting and decanting by gravity.
- Desalting involves mixing heated crude oil with washing water, using a mixing valve or static mixers to ensure a proper contact between the crude oil and the water, and then passing it to a separating vessel, where a proper separation between the aqueous and organic phases is achieved.
- The fresh water is needed to dissolve the crystal salts exist in emulsion and help desalting/dehydration processes.
- It helps to wash out and drain off the water droplets in emulsion
- The quantity or ratio of fresh water injected depends on the API gravity of the crude. Generally the injection rate is 3-10% of the total crude flow

And then desalting takes place and water is added and then mixed and it is using mixing valve for static mixers to ensure a proper contact between the crude oil and the water and then passing it to a separating vessel where the separation of phases takes place water and oil phase. Then how much fresh water will need that will obviously depend upon the salt content normally 3 to 10% is used and this salt content is also indirectly assumed by its degree API or specific gravity.

So, specific gravity also helps to decide how much salt how much water fresh water needs to be added. So, once we are giving the place water then it will dissolve the solid salts and we need to break the emulsified droplets also. So, how we will do it some emulsifiers are also added some chemicals can be added or heating can also work on it or some electricity can be applied.

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- Mixing aids i.e., demulsifying agents are added, which mix with the emulsion and help smaller drops to join together more easily.
- Free injected volume of wash water is broken into emulsion sized drops for even distribution.



- The electrical grid due to electrical voltage gradient distorts the originally spherical water droplets with positive and negatively charged ends to more elliptical shapes; based on their internal charges and their position in the desalter the droplets are attracted by positive and negative electrodes

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So, if we apply electric field then the circular layer which we showed saw that brine droplets this brine droplets has one here say water droplets in circle in the crude oil this is containing different types of molecules which is which is at the surface of it and it is giving a stability to this. So, we have to break this so now this positive and negative if charges which are available at the surface. Now if we apply a positive and negative field electric field by apply by using a positive and negative electrode then these will be oriented.

The positive and negative ions will be oriented and it will be the deformed it will be deformed and rupture can also take place. If we apply very high voltage then this will rupture and small particles will form. So, that may be more stable so this is the phenomenon, which can take place in the crude related to emulsified water droplets. So, we are adding fresh water here and this fresh water when we are adding this is not having that much of plus minus ions on it.

But when it will be getting some time to be in contact and proper mixing will be there and then we can see there will be some coalescence. The droplets which we are adding the fresh water droplets and emulsified water droplets can coalesce and it will settle, this is a mechanism for the renewal of this. And the mixing of this that will depend upon easy mixing of this will depend upon the rupturing of this emulsified layer.

So, that emulsion the breaking of the emulsifying droplets of the water in it and this application of electric field is used in the resulting devices in the refinery.

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• Important variables affecting desalting performance are:

- (1) settling time, (2) demulsifier injection,
- (3) heat, (4) addition of fresh water,
- (5) effective mixing of oil and water as well as chemicals for breaking the emulsion
- (6) electricity

Gravitational residence time is based on Stokes' equation as follows:

$$v = \frac{2r^2 (\Delta\rho)g}{9\eta}$$

Where v is the downward velocity of the water droplet of radius r , $\Delta\rho$ is the difference in density between the two phases, and η is the viscosity of the oil phase.

Maximizing the size of the coalesced water drops (electric field)

Maximizing the density difference between water drops and the oil phase (heating, freshwater addition)

Minimizing the viscosity of the oil phase (heating and fresh water addition)



And the factors which affect the performance of the desalting process are settling time see if we have one desalter, desalter is a horizontal vessels so the crude oil along with water flows horizontally and then applied then voltage is applied electric field is generated. So, in this case the settling times of the crude in this the oil particles in this desalter. Then demands demulsifying injections how much demulsifies we are adding how much heat we are adding.

Then addition of fresh water how fresh water we are adding and effective mixing of oil and water so that two different phase the other we transfer up salts from the organic to aqueous phase and how many chemicals for breaking the emulsion we are using as well as electricity the electricity will also help to break the emulsion. So, now if we see the settling time so if we consider a Stokes law region the settling time or settling velocity will be this one.

So, now R is the radius of the droplets and $\Delta\rho$ is a variation in a difference in the density of the liquid and water and your and the oil phase and then this η is the viscosity of the oil phase. So, now if we want to get less residence time we have to get more v , more v we can get by increasing r the diameter of the droplets which is done by application of heat or by application of electric field.

We can get the more $\Delta\rho$ value so that more $\Delta\rho$ value means $\rho_1 - \rho_2$ that has to be increased. ρ is the oil phase and this is water phase so if we use more water so that the variation this difference will change. If we increase the temperature then also density of water will change and oil will change so that $\Delta\rho$ will also change and viscosity will also change with the temperature.

So, when maximizing the size of the coalesced water drops we can get electric field. So, electric field we are applying the particles are will come together the water droplets will come together it will be bigger one so it will settle quickly and maximizing the density difference between water droplets and oil phase by heating and fresh water addition just we have discussed.

And minimizing the viscosity of the oil phase less of this more the ν so we will be getting less distance time and more efficiency or more performance of the desalting process.

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The electrostatic attraction between droplets can be represented as $F = \frac{KE^2d^6}{S^4}$

F = Electrostatic force between two adjacent droplets (N)
 E = Voltage gradient (V/m)
 K = Dielectric constant for crude oil-water system
 D = Diameter of water droplets
 S = Centre to centre distance between two adjacent droplets

At a certain voltage, water droplets begin to rupture, forming smaller water droplets with higher interfacial tension and produces more stable emulsion. This occurs at the critical voltage gradient defined as

$$E_c = k\sqrt{\frac{T}{d}}$$

E_c = Critical voltage gradient (V/m); K = Dielectric constant for crude oil-water system; T = Surface tension; d = Diameter of droplet



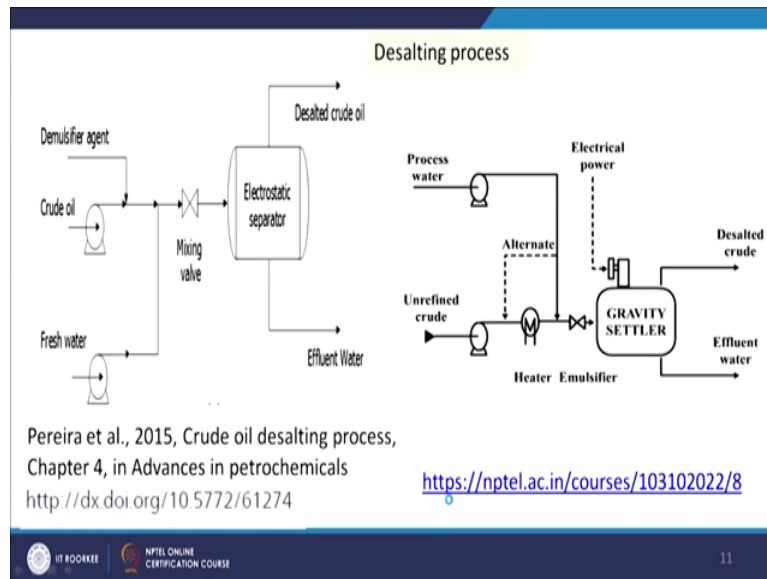

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But how much electricity will apply that will also guided by this formula $F = KE^2d^6/S^4$. So, here F is equal to electrostatic force between two adjacent droplets and the E is a voltage gradient. So, how much gradient we are applying and K is the dielectric constant and d is the diameter of water droplets and S is center to center distance between two adjacent droplets.

So, these are the factors which decide what will be the electrostatic force to adjacent droplets. Now there is some critical voltage if we apply more voltage then the particles can be emulsified and water droplets can be broken into smaller one and can be more stable one. So, this critical voltage is given as this formula is $E_c = k(T/d)^{1/2}$ when T is the surface tension d is the diameter of droplet.

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Now we will see the desalting process, desalting as you know that this is a horizontal vessel separation takes place. So, here we will be adding water fresh water and our crude oil. So, fresh water is added here this is going to this place and crude oil is coming here and demulsifying agent is also added. And we are giving proper mixing and then through valve and then it is separated. So, oil phase will go up low density and water phase will come from the bottom as a density is higher.

So, this is the process for the desalting now mixing valve we have used we have added here demulsifier agent but some configuration is also there without the demulsifying agent the heat can also be working it can also work as heater emulsifier. So, look in this case unrefined crude and process water enters into this gravity settler and it where electric field is applied where electric field is applied.

So, we are in some case we are using the demulsifier agent in some case electric field is applied and in reality electric field is applied and it has more efficiency for the separation of the salts from the crude oil. So, we will get desalted crude and we will get effluent water.

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Typical operating conditions for desalting

- Typical 120°C to 130°C - can vary with crude API

Temperature, °C	crude specific gravity
100	0.825
125	0.875
135	0.910
145	0.965

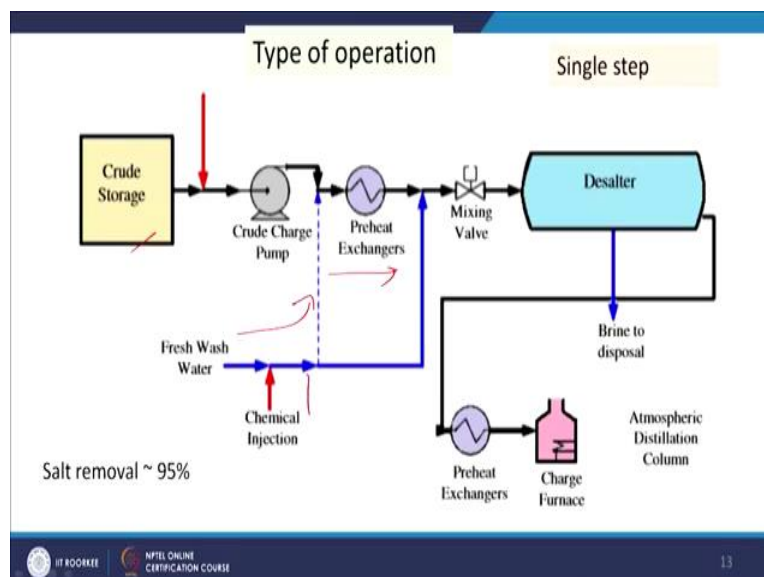
Pressure

- About 2 to 3 kg/cm² above bubble pressure to prevent vaporisation
- Typical residence time : 20 to 30 minutes (Dictated by electrode area)
- Mixing valve : Typical pressure drop 1.07/0.5 kg/cm²
- Wash water : 4 to 6% volume on crude

The typical operating conditions of desalting units is temperature around 120 degree centigrade to 130 degree centigrade and it will depend upon as I have mentioned that depend upon the API gravity of the crude. So, here it is shown crude API gravity increasing so we are having higher temperature. And pressure is around 2 to 3 kg per centimetre square above bubble pressure to prevent vaporization.

Typical residence time is 20 to 30 minutes that is dictated by electrode area and mixing valve typical pressure drop is 1.07 to 0.5 kg per centimetre square and wash water addition is around 4 to 6% somewhere it is 10 to 7% also mentioned. And there may be single step or two-step process so if the salt content is less, we can go for single step if it is more then we can go for double step. If we want to get more purity we can go for double step.

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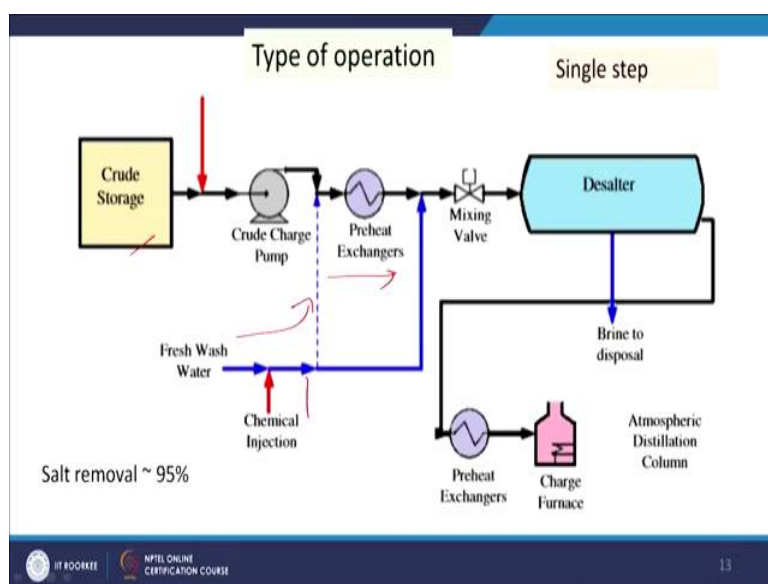


For a single step you see crude storage then it is we are taking it to pre heat exchanger and we are adding fresh water along with chemical injection. So, chemical injection fresh water and crude it is coming and heated and it is mixed then desalting. So desalting oil phase and water phase so brine to dispose and this water we are using and then we are using for fractionation in atmospheric distillation column.

The single step desalting process here we can get around 95% of solid removal and well concentration is also less we can go for it and high concentration we can go for 2 step to get more cleaning of the salt for removal of the salt from it and in this case the water which is added in the first step is coming out from the water generated in the second step. So, that is used here and then in the first step we are getting water.

So, this water we are taking some at the disposal and some part we are using here also and then the second part it is coming the oil part from the first desalter it is going to second desalter for further removal of the salts from it and we also add fresh water. So, this water is again going there and some part is going to this part. So, that way we are getting the removal of the salts from the crude oil with the water.

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And after heating it comes here to atmospheric distillation so this is two-step process for desalting. Next we are coming to atmospheric distillation unit. So, atmospheric distillation unit this here the fractionation takes place. So, vapours are formed at higher temperature then it goes up and then condensation takes place then the vapour condensed and it is it comes here so we will get liquid product and here also in between we can also get different other products.

And then pump around is used to get the more purity of this product different fractions and this is after desalting crude is coming here and normally atmospheric distillation is a very large vertical steel cylindrical column with diameter of around say 65 centimetre to 11 meter and height up to 60 meter and here normally we are having say 40 to 50 actual trays in it. And we have 2 to 3 trays there is some pump around and temperature here 8 to 10 degree above water dew point that is 120 to 130 degree centigrade typical and flash zone below cracking temperature that is 350 to 385 degrees centigrade and here it is 120 130 degree centigrade and pressure drop we get here pressure drop in condenser 0.3 to 0.5 kg per centimetre square and for tray there is some pressure drop that is equal to 0.08 to 0.1 kg per centimetre square.

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Atmospheric distillation		
Major products • LPG • Light naphtha • Heavy naphtha • Aviation turbine fuel (ATF) • Kerosene • Light gas oil [high speed diesel • Heavy gas oil components] • Atmospheric residue	LPG	Vapour Pressure 16.87 Kg/Cm ² Max
		Volatility (Evap. Temp. 2°C For 95% Vol. At 760 mmHg)
	Gasoline	Distillation
		Rec. Upto 70°C 10-40%
		Rec. Upto 100°C 30-65%
		Rec. Upto 180°C 80% (Min.)
		FBP 215°C
		RVP At 38°C 35-70 kPa/cm ²
		(Sulphur And Benzene Spec. Being Revised)

And in this process we get different products and those products are LPG, light naphtha, heavy naphtha, aviation turbine fuel, kerosene, light gas oil and heavy gas oil that is your high speed diesel and then atmospheric residue. We will see now some properties of these different fractions so LPG obviously most important is your vapour pressure that is 16.87 kg per centimetre square and volatility evaporation temperature for 95% volume at 760 millimetre mercury level.

So this is the pressure and this will be having 95% of the LPG vapour from at 2 degree centigrade and gasoline we get recovered up to 70 degrees 10 to 40% that we discussed that this is not a single compound it is a mixture of compounds. So, if we heat and the vapour which is formed if we cool it down then up to 70 degree we will be getting 10 to 40% in liquid and then

up to a 100 degree we will getting 30 to 65% and after 180 degree will be getting 80% minimum.

So, this is a gasoline property and final boiling point is to 215 degree centigrade and red vapour pressure at 30 degrees 35 to 70 kilo Pascal per centimetre square.

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Atmospheric distillation			
ATF		Kerosene	
Aromatics max	22.0	Vol. % Below 200°C	20
Distillation		FBP	300°C max.
10% vol.	205 max.	Flash point (Abel)	35°C min.
FBP	300 max.	Smoke point	18 mm min.
		Sulphur	0.25 wt. % Max.
Smoke point	26 mm min.		
Freezing point	-47°C max.		
Flash point (Abel)	38°C min.		
RVP at 38°C	35-70 kPa/cm ²		

Similarly the ATF has its own characteristics aromatics how much it is present then distillation again say 10% 205 degree centigrade and the final volume point is 300 degree centigrade it has some smoke point that is 26 millimetre that is minimum. Smokes point means when it is burned if we sorry if we apply heat then the fuel will produce smokes and what is the length of this height smoke height that is called at the smoke point.

So, freezing point is -47 degree centigrade maximum, flash point 38 degree centigrade that is minimum and then RVP is 35 to 70 kg kilopascal per centimetre square. So, for similarly for kerosene we are having volume percentage below 200 degree centigrade is 20 final boiling points 300 degree centigrade and flash point 35 degree centigrade minimum and smoke point 18 millimetre minimum sulphur is 0.25 weight percent.

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Atmospheric distillation		
High speed diesel		
Distillation		(revised)
90% vol.	366°C	(85% < 350°C) (95% < 370°C)
Flash point (Abel)	32°C	(35°C)
Sulphur	0.25 wt. %	(0.05 wt. % Being revised further down)
Cetane no.	45	(48, 51 later)
Fuel oil		
Sulphur	3.5 to 4.5 wt. %	
Viscosity @ 50°C, cst	80, 125, 180, 370	
Flash point	66°C min.	

High speed diesel it also has some this 90% volume should come at 366 degree centigrade and flashpoint is 32 degree sulphur is 0.25% and cetane number is 45 and these are the revised data. And fuel oil we have some sulphur content high sulphur viscosity is also higher in this case than flashpoint is also higher in this case.

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Major design variables	
• Desalter temperature • Pre-flash • Heater outlet temperature • Flash zone temperature • Over flash • Column / flash zone pressure • Type of condenser (partial / total) • Location and number of pump arounds • Stripping steam • No. of trays	

Now if we think about the design variables for the atmospheric distillation column. Atmospheric distillation column and desalter both are considered simultaneously. So, desalter temperature and pre flash then heater outlet temperature and flash zone temperature, over flash and then column and flash zone pressure and type of condenser whatever condenser we are using for cooling the vapour and to get in, get it into condensed form.

They also influence the performance and it is also design parameter and location and number of pump around and stripping of stream and number of trays how many trays we use that is also important design consideration. Next we are coming to vacuum distillation so after atmospheric distillation after 370 degree centigrade the residual part we need to process in a vacuum distillation.

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- The vacuum distillation column normally has 10 to 40 mmHg absolute pressure (most often achieved by using multiple stages of steam jet ejectors), which increases the volume of vapor formed per volume of liquid distilled. Thus, such columns have very large diameters, 15 meters or more. Heights ranging up to about 50 meters.
- Most of the column uses packing material for the vapor-liquid contacting because such packing has a lower pressure drop than distillation trays.
- A very low-pressure increase from the top of the column top to the bottom is maintained

Modified from
http://en.citizendium.org/wiki/Vacuum_distillation

So, in this case we create some vacuum that is say 10 to 40 millimetre mercury absolute pressure is maintained in this case. So, once the vacuum is created so at lower temperature also more than 370 degree centigrade the some compounds from the residue atmosphere residue will be vaporized. As the pressure is less or vacuum is created so more volume will be available so the size of this type of column is generally bigger and diameter is more that is say 15 meters or more and height is also say around 50 meter.

And in this case we see we need to maintain a pressure gradient from the top to the bottom so they are less pressure and they are higher pressure the gradient is also maintained. And here also the packed bed is preferably used in this case because most of the column uses packing material for the vapour liquid contacting because such packing has a lower pressure drop than distillation trays. So, here it is coming here so we are getting some time and then different products we are getting LVGO.

And HVGO with you heavy gas oil and light gas oil vacuum obtained from the vacuum distillation column. So, you have gas oil now we have HVGO and we are having LVGO and then residual part we will get from the vacuum distillation unit that can be further upgraded.

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VDU Design issues		
• Preheat train • Heater outlet temperature • Flash zone temperature • Type of vacuum / pressure • Steam rates (ejector / stripping / velocity) • Type of internals • Top temperature • Number location of pump arounds • Ejector vs vacuum pumps or combination	• Fuel based	• Lube based
	Prepare feedstock for FCC, hydrocracker	Prepare feedstock for lube plant
	Products	Products
	Diesel	Spindle oil
	Light vacuum gas oil (LVGO)	Light neutral
	Heavy vacuum gas oil (HVGO)	Intermediate neutral
	Slop distillate	Heavy neutral
	Vacuum residue	Vacuum residue

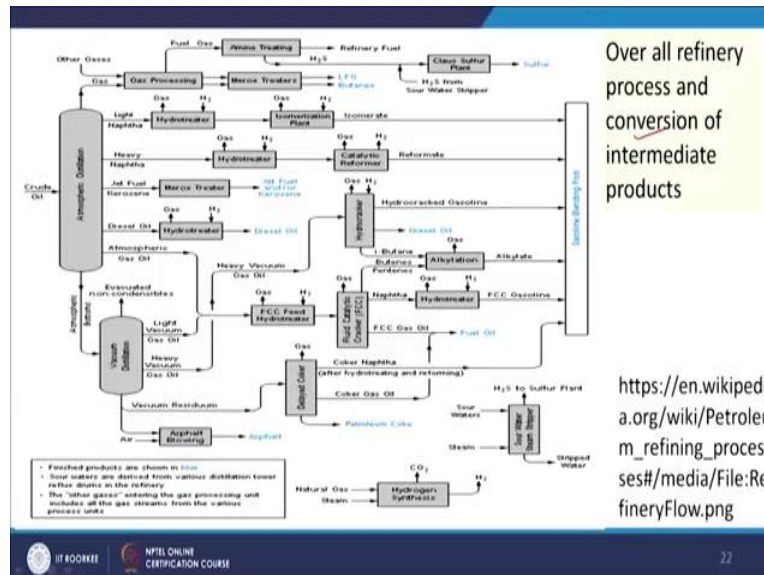
And video design issues are like say preheat train say heater outlet temperature then flash zone temperature, type of column or pressure, type of vacuum and then steam rates and then type of internals, top temperature, number of location of pump around here also just like this just like atmospheric distillation we can use some pump around and ejector versus vacuum pumps or combination. So, how the vacuum has been created at the steam ejector or vacuum pump so that also a matter of consideration for its design.

And this VDU vacuum distillation unit can produce feedstock for FCC or can produce feedstock for lube plant so that way it can be fuel ways and lube based process. So, for fuel base the products are diesel light vacuum gas oil heavy vacuum gas oil, slope distillates and vacuum residue. Whereas for lube based the products are spindle oil, light neutral, intermediate neutral, heavy neutral and vacuum residue.

Now we have discussed how the crude oil is pretreated or desalted and then it is passed through the atmospheric distillation and get different liquid products from it and the residue from the atmospheric distillation is further distilled in the vacuum distillation column and we get different products LVGO, HVGO and the residue. Now we have also mentioned that the specific need may be different at different country of a particular product and accordingly the refinery may not give us the liquid product in the same ratio.

So, we need to convert the one type of product to other one to meet the requirement as well as to meet the quality of the product. So, to improve the quality of the product as well as to meet the specific requirement of a certain product we need to convert one product to other.

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So, here different operations are used those are called conversion processes in the refinery and those conversion processes are some examples are catalytic, FCC process, hydrotreating process etcetera and apart from these alkylation reforming process or a polymerization process are also used in some cases to achieve the target to fulfil the requirement as well as the quality of different products. So, this way the crude oil is converted to different usable forms and upto this in this class thank you very much for your patience.