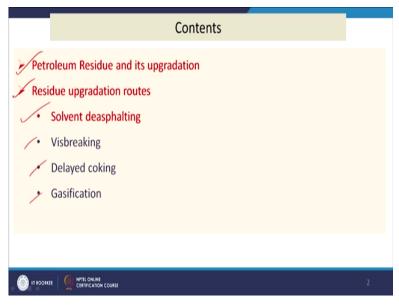
# Technologies for Clean and Renewable Energy Production Prof. Prasenjit Mondal Department of Chemical Engineering Indian Institute of Technology-Roorkee

# Lecture-17 Residue Upgradation 1

Hi friends, now we will discuss on the residue upgradation part. In the previous lecture, we have discussed on the removal of sulphur, nitrogen and metals from the liquid fuels. Now we will concentrate how the vacuum residue or the residual part can be upgraded to liquid fuels through different upgradation routes to make the product and the process more cleaner.

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So, the content of this topic, Petroleum residue and its upgradation then residue Upgradation routes, the solvent deasphalting. Visbreaking, delayed coking and gasification. So, these are different routes which are normally used. In this class we will cover up to solvent deasphalting and the rest will be covered in the next part. So, now, we know that when we process petroleum crude in the atmospheric distillation, it lefts some residue.

And then that atmospheric distillation column residue is processed in vacuum distillation column and again vacuum residue is formed. And so what we are getting crude oil then atmospheric residue and then we are getting vacuum residue.

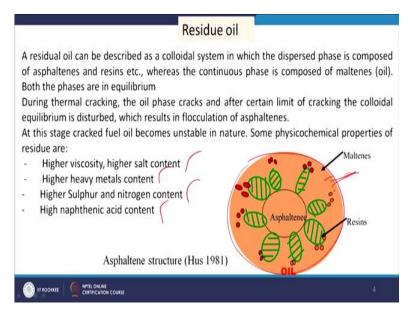
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| Properties | Viscosity, cSt    | S, % | N, % | Asphaltenes % | H/C ratio , (a/a) | CCR, % | °API |
|------------|-------------------|------|------|---------------|-------------------|--------|------|
| Crude oil  | <u>3.5@55</u> °C  | 1-3  | 0.1  | 2.8           | 2                 | 2.8    | 33   |
| AR         | 480 @ 50 °C       | 2.5  | 0.16 | 4.4           | 1.8               | 6.4    | 12.3 |
| VR         | 1030 @ 100 °C     | 3.8  | 0.2  | 10-30 🚽       | 1.3 ,             | 20.5   | 5.8  |
| н          | igher viscosity 🗹 |      |      |               |                   |        |      |

So, if we go from crude oil to different ratio, then we see the quality is degraded. So viscosity increases, sulphur increases, nitrogen increases, asphaltenes increases, H/C ratio decreases and API decreases, CCR increases. So, this clearly indicates that the quality of VR is much poor than the crude oil and refinery is not that much interested with this VR to properly manage it, because this of low value or negative value product for them.

So, we need to convert these VR, so that the; it will be managed properly, and environmental pollution will be reduced. On the other way, the refinery can also add some value addition to the whole process. So, from this table, it is clear to us that residue is having higher viscosity, high sulphur, high average boiling point and, H/C ratio is low and CCR is high. So if we want to upgrade it, obviously, the scope is there, we have to improve the hydrogen H/C ratio. So H/C ratio we need to improve.

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So for doing this, there are number attempts, people tried to do it, and like say solvent, deasphalting, and then thermal processes, hydro treatment etc. So now we will see, what, how the solvent the deasphalting and other process will help to improve it. And to understand that, we have to understand the residue, what the residual oil is? So, Residual oil is a high viscuous oil, in which we have asphaltenes and resins as well as some oil part.

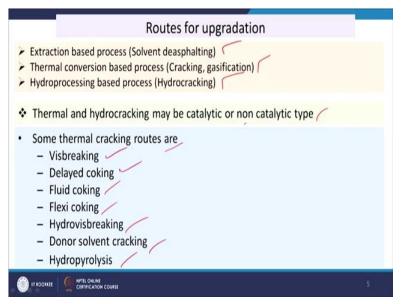
So oil part is called say Maltenes says one here. So, this is a maltene part, this is the emulsion. In this emulsion, we are getting asphaltene and resins in the disperse state and in the continuous phase we are getting the Maltenes. Now, if we can remove asphaltenes and resins from this whole system, then we can get the maltenes which is desirable and we can recover that oil for our applications.

So, how we can do it? Obviously, because the presence of these asphaltenes and resins and other presence of metals are also there. So, it gives here higher viscosity and higher salt content, higher heavy metal content, higher sulphur and nitrogen content and higher naphthenic acid content. So, this content, this is the properties of this now, we need to remove these things, the asphaltenes from this.

So, how it can be done? We can use some solvent. So, that solvent will take these maltenes from this whole emulsion and it will be broken and some maltenes can come to the solvent. So that is one way of solvent deasphalting. Otherwise you can apply thermal heat here. So, heat will break or crack the molten molecules and after a certain extent of cracking this emulsion may break and then that broken emulsion under the conditions the asphaltenes can be separated from the oil.

And hydro processing can also take place to hydrogen addition. So, this maltenes will be converted and then this will be separated.

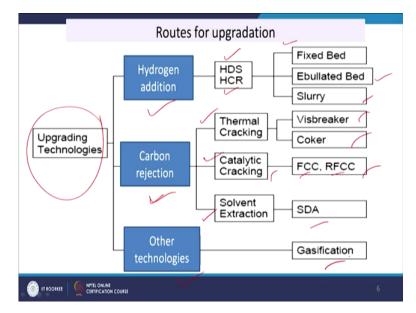
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So, these three major routes which can be applied for the removal of this asphaltenes from the maltenes and to get pure quality oil from the residual part. So, on the basis of this, the methods which are developed one is solvent deasphalting and there is thermal conversion based process that is cracking and gasification and hydro processing based process, hydro cracking.

Now, thermal and hydrocracking maybe catalytic or non catalytic type and some thermal cracking routes are visbreaking, delayed coking, fluid cooking Flexi coking, hydro visbreaking donor solvent cracking and hydropyrolysis. So, these are the different routes people have applied for the upgradations of the residue.

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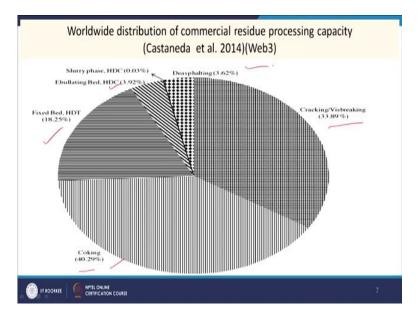


So, the total upgradation technologies we can classify into three major category. One is hydrogen addition method, another is carbon rejection method and another is the other method. So, in hydrogen addition method, we add hydrogen. So, hydro desulfurization and hydro cracking these are two and different types of reactors have been used that is fixed bed, ebullated bed and slurry bed reactor.

Now the carbon rejection method, one is thermal cracking, catalytic cracking and solvent extractions we can apply. So, these thermal cracking visbreaking and delayed coking and coker, it is mentioned here and catalytic cracking FCC, RFCC. Residual Fill Catalytic cracking, FCC is fluid catalytic cracking RFCC, residual fill catalytic cracking and solvent extraction also that will reject carbon.

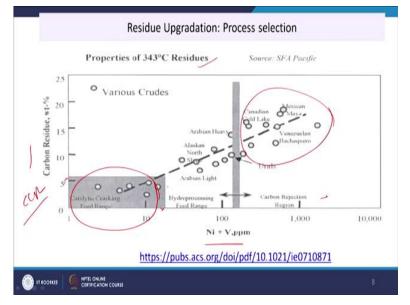
So, carbon rich molecules are settled in the extractor. So, when get separated later on, so, then other techniques are the gasification. So, these are different techniques. Now first we will discuss this one solvent deasphalting process. Before that, we see around the world what type of techniques are used?

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And if you see this figure, coking is mostly use that is 40.29% then, visbreaking or cracking that is 33.89%, the you see here hydrotreating and then hydro cracking and then the deasphalting is 3.62%. So, these are different technologies which have been applied around the world to upgrade the residual part. So, now, we will be conducting this one.

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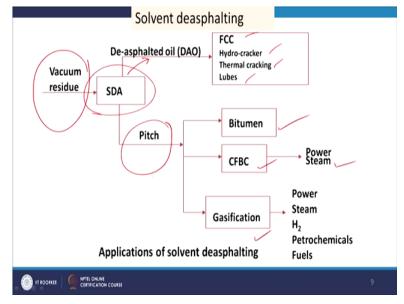


Before that we will see how we can select this technology which is always selected for what type of feedstocks. This slide shows with reference to some properties of 343 degrees centigrade residues. So, various crudes if we take and then we can measure the nickel and vanadium and we can measure the CCR. So, carbon residue, CCR carbon residue Condensed Carbon Residue and nickel and vanadium concentration.

Both amounts can guide us what process will be more suitable. So if more metal is there then more carbon is also there, we can go for carbon rejection. So these are carbon rejection zone metal is also more and carbon is also more. But if we have carbon is less, metal is also less, we can go for fluid catalytic cracking and hydro processing range are the, in between one or more preferable.

So this way we can select a particular route which will be more suitable for a particular feedstock. Now we are coming to solvent deasphalting. So, the term itself says the solvent de asphalting. So, we will be adding some solvent so maltenes will come into the solvent and asphalt will be separated from the feedstock. So, that is the main objective.

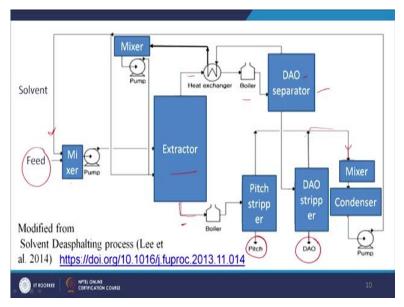
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So, vacuum residue we are using in the SDA process. So, so, asphaltene will be separated at the bottom. So, we are getting asphaltene so pitch we are getting and then solvent plus oil. So that is called deasphalted oil. So, after the deasphating the oil which are getting that is deasphalted oil plus solvent is coming here. So that can be used for different FCC for further purification or improvement of quality.

FCC, Hydro crackers, Thermal cracking, as a Lubes, we can use it as a lube base stock. And pitch or asphaltene spot which you are getting that can be used for Bitumen or road making that can be used in circulatory fluidized based combustor for power production or steam generation. And that can also be gasified, and that steam gas can be used for power applications for Steam, or production hydrogen production petrochemicals or as the fuel itself. So, these are the overall concept of solvent deasphalting process.

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Now we will see this flowsheet which explains this SDA process. So here we are getting feed then feed has to be mixed with some solvent. So solvent we are getting initially we add then we get the recovered solvent. So, solvent plus feed we are mixing here. So it is going to extractor. Extractor has certain conditions: temperature pressure is maintained and RPM etc proper mixing is provided.

Then we get to phase. It is allowed to settle we get two phases. One phase we are getting asphalting phase as it is going there and then heat recovery takes place and then it is coming to pitch stripper. So we get pitch here so again some flashing tap arrangement so it is coming here and then flashing we are getting some liquid part, if solvent comes here, so that can also goes off and it is coming here and then it is going to mixer and condenser.

After condenser this solvent is recycled. And here we are getting the pitch which we are having. And from the extractor, the upward deasphalted oil along with the solvent it is going and in it heat exchange is taking place here then it is going to boiler and then DAO separator, so DAO and deasphalted oil and solvent. We have to separate it now solvent has boiling point and deasphalted oil components also have boiling point.

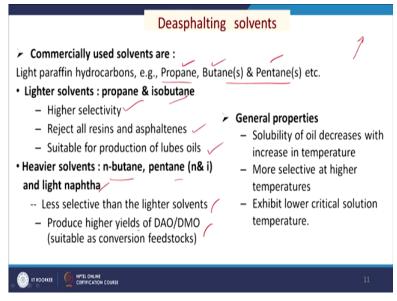
So those are not similar so if we apply heat and then the solvent will be in vapor phase that we can go there and it can mix here and can be added here extractor. And then deasphalted oil along with some solvent it comes then it will be coming to here. So deasphalted oil will be

separated in the stripper section and then solvent will also be come through these routes and then it will be recycled.

So solvent is this it can from the bottom is also recycled, recovered and recycled and from the DAO separator also solvent is recycled and is recovered and recycled. So that way a solvent is recovered and recycled. That recovery of solvent is very, very important. Now people have used two routes for its recovery, what is use of evaporators, sequential and then another is the operation separation of solvents at supercritical conditions of the solvent.

So DAO plus solvent this mixture is it is heated to supercritical conditions of the solvent and then solvent is recovered from it and in that process the efficiency is more. So, now, we will be making some discussion on that line. Before that, we will see the properties of the solvent and the deasphalting solvents. So, what can be the good solvent obviously, the liquid hydrocarbons, low molecular weight hydrocarbons.

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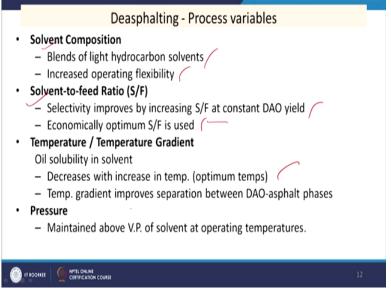
Like say propane, it may butane, it may be pentane. So, normally it may be hexane also, but normally, these propane, butane and pentane have been reported in literature and have been used for the separation. So, once we use low molecular weight hydrocarbon, then the maltene part which will come to this because the density is less here, all the asphaltenes will be removed.

And lighter solvent propane and isobutane that are the higher selectivity that they are having and reject all resins and asphaltenes suitable for production of lube oils. And heavier solvents we use pentane and n-butane, then light naphtha can also be used in that case less selective than lighter solvents and then produce higher yields of DAO and DMO.

So, Deasphalted oil production is higher. So produce higher yields of DAO, so if we use more butane and pentane, it will be able to take more maltenes because its condition changes, it takes it operates at higher temperature. So high temperature means more maltenes can come here. So now we will see the general properties of the solvents. So, solubility of oil decreases with the increase in temperature, then more selective at higher temperatures exhibit lower critical solution temperature.

So, lower the critical temperature that recovery part will be easy. Now, process variables for this process so what is the, we are interested to get the oil part from the residue? So, solvent, how much solvent we are using that will play a role, solvent to feedstock ratio and the solvent composition, solvent to feedstock ratio.

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So selectivity improves by increasing solvent to feedstock ratio at constant DAO yield. And economically, we have to optimise it. Obviously if we say more solvent, more purity of the product will get and but we have to optimise about with the economy and the solvent composition blends of light hydrocarbon solvent can be used and then its increased operating flexibility.

If we use the blends, then flexibility will increase and temperature also important because this temperature gradient will help the transfer of the oil phase from the residue to our solvent while

solubility in solvent decreases with increase in temperature and temperature gradient improved separation between DAO asphalt phases. And pressure also maintained above the vapour pressure of the solvent.

|  | Comparis     | on of solve               | $nt (c_3 - c_5)$                                      |                          |                           |
|--|--------------|---------------------------|---|--------------------------|---------------------------|
| Solvent  | Feed<br>(SR) | Propane (C <sub>3</sub> ) | Propane – butane<br>(C <sub>3</sub> /C <sub>4</sub> ) | Butane (C <sub>4</sub> ) | Pentane (C <sub>s</sub> ) |
|  |              | DAO                       |   |                          |                           |
| Yield, wt% 🧹   | 100          | 29 🛩                      | 46.8 🗸  | 67.3                     | 82.8                      |
| API gravity 🧹  | 6.6          | 21 🛩                      | 16 🗸  | 12.1 🗸                   | 10.3                      |
| Viscosity, cSt @ 100°C   | 1900         | 35                        | 110   | 340                      | 800                       |
| CCR, wt%   | 22.1         | 1.5                       | 5.0   | 10.6                     | 14.0                      |
| Sulphur, wt%   | 4.29         | 2.60                      | 3.0   | 3.6                      | 3.9                       |
| Asphaltenes, wt%   |              |                           |   |                          |                           |
| "V" ppm  | 70           | 1.1                       | 2.5   | 7                        | 23                        |
| "Ni", ppm  | 21           | 0.3                       | 0.7   | 2.1                      | 7                         |
|  |              |                           | ASPHAL  | r                        |                           |
| Sp. Gravity  |              | 1.047                     | 1.089   | 1.116                    | 1.175                     |
| Sof. Pt. (R&B), "C   |              | 160                       | 225   | 270                      | 390                       |
| PEN. (25°C, 100g, 5 sec.) 1/10 mm  |              | 5                         | 0   | 0                        | 0                         |
| (Feed : Arabian medium V.R)  | tocillumente | idocomo con               | n/odan knight/m                                       | oban kondo               |                           |
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Now, we will see the comparison of some solvent and that DAO and deasphalting process. So, so, if we have some SR that we have, we have feed then we have propane, we have propane, butane or we have butane we have pentane. So different solvents we are using in the deasphalting process, then will be getting DAO as well as you will be getting asphaltenes. Then we will see how the properties of DAO asphaltenes are changing with the variation of this solvents.

So, here yield, DAO yield let us say 29% and then we are fine it is propane is used, if we use propane butane 46.8, if we use butane against 67.3 if it is pentane then 82.8. So, with the increase in carbon number, we are getting more DAO. We are getting more DAO but the same time we will be getting lower quality. So, higher solvent recovery is possible here higher oil recovery is possible by this way.

And then but the quality you see the API gravity is decreased here 21, here 16, here 12.1, here 10.3. So, we are getting more oil, but we are compensating we are compromising with the quality, we are using higher carbon number in the solvent. So, viscosity is also similar way increases. That means more oil is coming to the solvent. And then CCR, it also increased and the oil part which is coming to the solvent are having higher carbon than its so that is why CCR has also increased in this case.

And sulphur content also increased because the bottom which is going to the VR that is coming to the DAO part that is why sulphur is also increasing. The metal content is also increased with the increase of the carbon number in the solvent. Then we see this asphaltene then also softening point, if we see softening point increases and then penetration point decreases. It is not that soft. So penetration is not possible in this case.

And specific gravity also increases. Why it is? Because more denser particles or molecules are coming to the DAO part with their use of heavier hydrocarbon or hydrocarbon with more carbon number. So, this is the comparison of different types of solvents when it is used for deasphalting purpose.

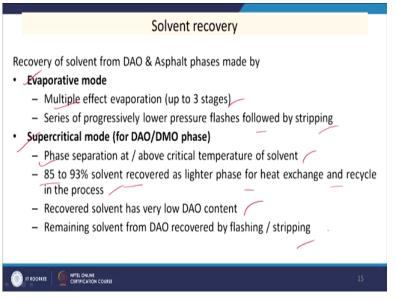
| Ger                      |           | g conditions of<br>pe of solvent | fsda         |
|--------------------------|-----------|----------------------------------|--------------|
| Operating conditions     | Propane   | Butane                           | Pentane      |
| Extraction range<br>(°c) | 50 - 80   | 100 – 130                        | 170 – 210    |
| Pressure range<br>(MPa)  | 3.5 – 4.0 | <u>~</u> 4.0                     | <u>~ 4.0</u> |
| Solvent ratio<br>(vol.)  | 6-9       | 4-7                              | 3 - 5        |

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And now we will compare the about the operating conditions if we use propane, butane and pentane. Then extraction temperature is different for propane it is 50 to 80, butane it is 100 to 130 and pentane is 170 to 210. So that is one reason why we are getting more heavier part in the in the solvent, in the DAO part and then pressure range we are getting 3.5 to 4 mega Pascal, in case of propane, Butane is 4 and pentane is 4. And solvent ratio is higher. So butane solvent ratio is lesser, Pentane is further lesser.

So higher the solvent than the feedstock higher solvent to feedstock ratio will be getting more pure quality product or better quality product so that propane when we use, then, we can use the feedstock for lube oil based off production. Then we are coming to solvent recovery.

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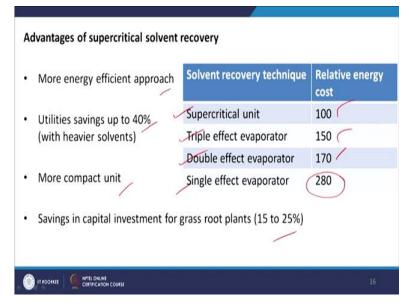


So evaporative mode and supercritical mode already we have discussed. So, in case of you have evaporative mode we can use multiple effect evaporation up to three stages and series of progressively lower pressure flashes followed by stripping. Just in the flow sheet also we have seen some stripping is there, flashing was there and then stripping was there.

So, supercritical mode if it is used then it becomes more energy efficient say phase separation at above critical temperature of solvent above critical temperature up or at the critical temperature solvent can is possible and 85 to 90% solvent recovered as lighter phase for heat exchange and recycle in the process and recovered solvent has very low DAO content, that the purity of the recovered solvent is higher if we use the supercritical mode of operation.

And then, remaining solvent from DAO is recovered by flashing and stripping. So, solvent recovery is higher quality is higher, but we have to optimise with the cost also economic factor also. Now, we see the comparison of different process.

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If Supercritical unit Triple effect evaporator, double effect evaporator and single effect evaporator, if we use single effect that 280 unit say energy cost and it is double it is 170 triple effect 150 and for supercritical 100. So, if we use supercritical unit, the relative energy cost is less and it also more energy efficient approach and utilities saving up to 40% with heavier solvents, more compact unit, this one and savings in capital investment for grass root plants is 15 to 25%.

So, this is the advantage of applying super critical condition. Now, we will discuss on deasphalting tower for the extractor which we had in this case extractor.

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| DEASP   | HALTING TOWER / EXTRACTOR   |
|---|---|
| Column internals<br>Baffle trays / Louvre trays<br>Rotating disc contractor<br>(RDC)<br>Packing (random /<br>structured)<br>Parallel interceptor plate<br>(PIP) assemblies<br>Baffles<br>Being used in all PDA plants in<br>the country<br>UOP/ FW offers choice of PIP<br>or RDC | <ul> <li>Structured packing<br/>Currently used in all ROSE units<br/>Advantages claimed         <ul> <li>Better quality of DAO</li> <li>Higher circulating solvent purity</li> <li>Higher capacity for existing SDA units</li> <li>Lower operating cost</li> </ul> </li> <li>PIP assemblies<br/>Used in UOP/FW SDA pilot units<br/>Advantages claimed         <ul> <li>Increased separation efficiency (lower S/F ratio)</li> <li>Reduced size of extractor vessel</li> <li>Reduction in capital and operating costs</li> </ul> </li> </ul> |

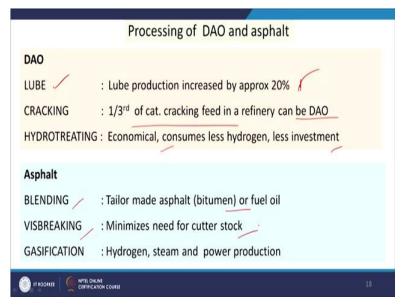
So, here we can get some internals. So, column internal internals may be Baffle trays, it may contain rotating disc contractor. It may have packing or it may have parallel interceptor plate.

So, these different types of options are available. So, baffle plates baffles are, mostly used in PDA plants in India and that RDC and PIP that UOP and foster wheeler, they offer the choice for the PIP or RDC.

And structure packing used for rose units that is called residual oil supercritical extraction unit ROSE unit. So, currently used in all ROSE units are packing. And the advantage of this is that better quality of DAO and higher circulating solvent purity, higher capacity for existing solvent deasphalting units and the lower operating cost. And PIP assemblies if it is used that I have mentioned that UOP and foster wheeler has given their options which are PIP or rotating disc contractor.

But it has some advantage that PIP has some advantage that increased separation efficiency and reduce size of extraction vessel and reductions in the capital and operating costs. So, these are the comparison of different deasphalting design column design. Now we will see the processing of DAO and asphaltene. So, what we can do with the DAO and asphaltene.

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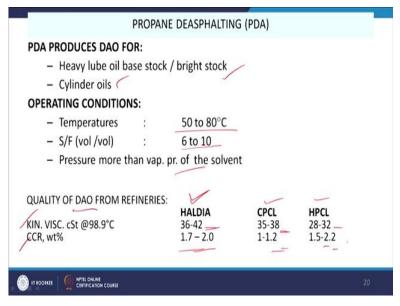


So, once we can get DAO we can get lube oil and lube production increased by approximately 20% and that due to the use of this deasphalted oil and cracking one third of catalytic cracking feed in a refinery can be of DAO and hydro cracking economical consumes less hydrogen less investment. So, we see that that if we can produce DAO so that can improve the economics of the plant also because it will give more products which are available in market.

Then asphalts can be used as a blending, it can be used as a bitumen or fuel oil or road making and it can be going to visbreaking so that many ways minimise the need of cutter stock and then it can be gasified also. Here, we will see some technology licences. So, if we Kellogg brown and root, they are giving the technology rose, residuum oil supercritical extraction. And more than 33 supercritical units are used in commercial scale with this capacity.

And UOP, Foster wheeler solvent deasphalting process, they are also 50 units and IFP France there are 7 unit and then IIP Dehradun and EIL in India they have 2 conventional plants and RIPP China they have 5. So, these are some basis of 2002 data also it is a very old data, but Exxon Mobil offers PDA technology. So, in India we are having the conventional PDA technology.

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And we will see the what that PDA is Propane deasphalting. Propane Deasphalting use propane as a solvent for the removal of asphalting from the vacuum residue or any heavy lube oil base stock can be produced from this process. And cylinder oil can also be produced and the operating condition is 50 to 80 degrees centigrade and 6 to 10 solvent to feed ratio and pressure more than the vapour pressure of the propane. So, these are the conditions.

And we see the IOC Haldia, CPCL and HPCL. They are producing DAO with this quality the kinetic viscosity and CCR. So, these values are provided here. So, obviously, you see the viscosity is reduced and the CCR is also reduced. So, by this process and good amount of DAO is recovered from the vacuum residues which are cleaner in nature.

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| PROPANE DEASPHALTING - STATUS |                        |                                      |  |
|-------------------------------|------------------------|--------------------------------------|--|
| Plant                         | Capacity, MMT/A        | Technology                           |  |
| HPCL, Mumbai                  | 548,000 /              | IIP / EIL                            |  |
| CPCL, Chennai                 | 574,000                | IIP / EIL 🧹                          |  |
| IOC Haldia                    | 650,000                | Romanian/ expansion by EIL<br>/ ROSE |  |
| - All plants produce          | e LOBS(BS)             |                                      |  |
| - Solvent recovery            | : evaporation mode / s | supercritical mode                   |  |
| - Development of<br>&HPCL     | now-how for supercrit  | ical mode is done by IIP,EIL         |  |
|                               |                        | 21                                   |  |

Now, we see the propane deasphalting status. So we shall see HPCL, Mumbai, CPCL, Chennai, IOC Haldia. So, their capacity is this 5,48,000 MMT per annum and for this CPCL it is 5,74,000 MMT per annum and this is for 6,50,000 MMT per annum. And these are the technology licenser IIP/EIL and this is in case Romanian, expansion by EIL, ROSE. So, these are the some deasphalting technology which is implemented in the country.

So all plants produce Lube oil based stock and solvent recovery, evaporation mode or supercritical a supercritical mode, IIP and EIL have developed a knowhow on this process. So, so far we have discussed on the Solvent deasphalting part and next class we will discuss the other part of the vacuum residual Upgradation. So thank you very much for your patience.