Technologies for Clean and Renewable Energy Production
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Lecture-09
Direct Liquefaction of Coal

Hi friends, now we will discuss on the topic direct liquefaction of coal. In the previous class, we have discussed on gasification of coal and we have seen that coal is gasified to produce syngas and that syngas can be used for different downstream application. One application was FT synthesis that is the Fisher-Tropsch synthesis through which we can get different types of liquid fuels.

So, that liquid film production from the coal was an indirect route and this is important, the production of liquid from the coal because, we can use liquid fuel more easily in different engines. And if we want to produce it through this indirect route, then obviously, it is involving number of steps, conversion steps. So more the steps, lesser the efficiency, overall efficiency of the process.

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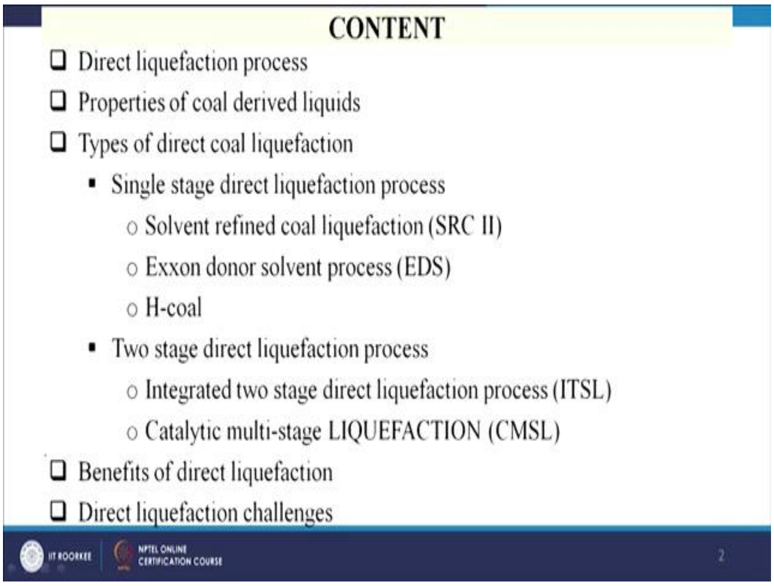

CONTENT

- ☐ Direct liquefaction process
- ☐ Properties of coal derived liquids
- ☐ Types of direct coal liquefaction
  - ▪ Single stage direct liquefaction process
    - ○ Solvent refined coal liquefaction (SRC II)
    - ○ Exxon donor solvent process (EDS)
    - ○ H-coal
  - ▪ Two stage direct liquefaction process
    - ○ Integrated two stage direct liquefaction process (ITSL)
    - ○ Catalytic multi-stage LIQUEFACTION (CMSL)
- ☐ Benefits of direct liquefaction
- ☐ Direct liquefaction challenges

So, people thought if the coal can be converted directly to liquid and in the introductory class, we have seen that coal contains different aromatic rings a chain of aromatic rings we have seen like this very bigger, it is very complex structure that is why it is solid and less reactive. It is not that high reactive, we have to heat it at higher temperature then only there will be some combustion at lower temperatures there will be no combustion unlike say plant materials.

So, that is why it is solid now, and here also we know that carbon concentration is also very high with respect to hydrogen. Now, if we can break this some of the rings here and say some double rings are there see, if we can break some double ring and we can add some hydrogen here this thing's then it will be converted to some organic compound having lower molecular weight and that will be liquid form that can be liquid form.

So, we will be able to get liquid fuel from coal by this process, but what is the; what is needed here for this conversion one is hydrogen we have to provide sufficient amount of hydrogen and as you know coal is not that reactive. So, hydrogen has to be provided at higher pressure. So, high pressure hydrogen is required and coal particles has to be very particle size will be very, very small, the very small particles will be made slurry in some solvent and then solvent coal slurry.

Obviously, more solvent is acquired and then hydrogen at high pressure that will be giving us this conversion, that may give us this conversion and we can use some catalyst the rate of the reaction can also be improved. So that way, directly coal can be converted to liquid. And as you have discussed that this technology was developed many years ago in Germany in lab scale or small scale production, but for commercial scale production very recently the plant has come in China.

So, we will discuss here and our content is direct liquefaction process. And then properties of coal derived liquids, the types of direct coal liquefaction, that a single stage direct liquefaction process or two stage direct liquefaction process and then we will see the benefits of direct liquefaction process and direct liquefaction challenges. Now, we see in direct liquefaction process different coals are converted to coal liquid.

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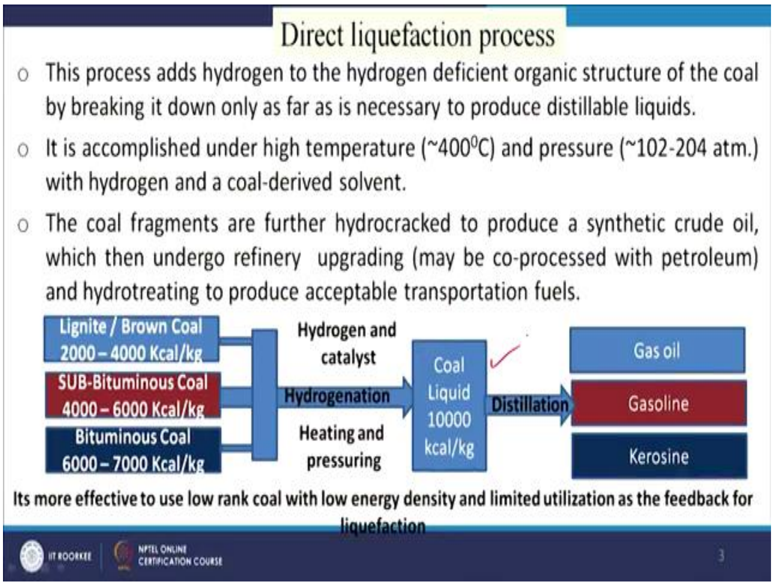

Direct liquefaction process

- This process adds hydrogen to the hydrogen deficient organic structure of the coal by breaking it down only as far as is necessary to produce distillable liquids.
- It is accomplished under high temperature (~400^{0}C) and pressure (~102-204 atm.) with hydrogen and a coal-derived solvent.
- The coal fragments are further hydrocracked to produce a synthetic crude oil, which then undergo refinery upgrading (may be co-processed with petroleum) and hydrotreating to produce acceptable transportation fuels.

Its more effective to use low rank coal with low energy density and limited utilization as the feedback for liquefaction

It can be lignite or brown coal, it may be sub bituminous, it may be bituminous coal. Very interesting here, lower the quality of coal more easy to convert it into liquid fuel and you see here anthracite is not shown. So, when we are getting the coal liquid, we compare the heating value with respect to these different types of coals, this is much higher than this. So, energy intensity is increased in the liquid fuel that is one advantage.

And you see here we need hydrogenation step, we need hydrogen and catalyst, we need high temperature and pressure. So, these are the requirement for the direct liquefaction of coal, here any type of coal can be used, there is no limitation of its quality, but preferably lower quality coals can be used. And then we will get gas oil, gasoline and kerosene. So, this is the overall process for direct liquefaction of coal.

So, it is accomplished under high temperature that is around 400 or more than 400 °C and 102 to 204, atmospheric pressure, very high pressure it takes. So, what will be happening just we have discussed, the coal is fragmented, the complex structure is broken down and it is fragmented and then hydrogenation takes place. So, we will be getting some coal liquid that coal liquid may be requiring for further upgradation that is obviously for hydrogenation that we are going to discuss.

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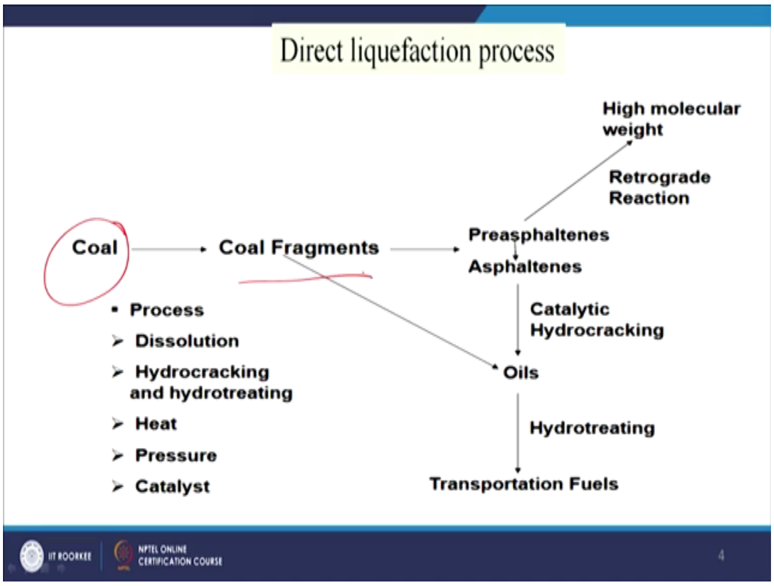

Direct liquefaction process

Coal → Coal Fragments → Preasphaltenes → Asphaltenes

- Process
  - Dissolution
  - Hydrocracking and hydrotreating
  - Heat
  - Pressure
  - Catalyst

So, now, we are having coal this coal we are getting coal fragments and this is what is the process the dissolution, hydrocracking and hydrotreating heat pressure and catalyst. So, coal slurry formation then application of heat and pressure maybe catalyst or may not be catalyst. So, that will be getting coal fragments, then coal fragments will be having some oil part and some also solid part it will be having.

So, that solid part it is called preasphaltenes or asphaltenes that is having high molecular weight then what we will do with this another step we can go for hydrocracking, catalytic hydrocracking. So, we can get more oils from this asphaltenes also and then further hydrotreating will give us transportation fuel. So, hydrogen addition may not be in a single step it may be step wise. So, we can increase the hydrogen concentration in the liquid and it will be more usable form in transportation fuels.

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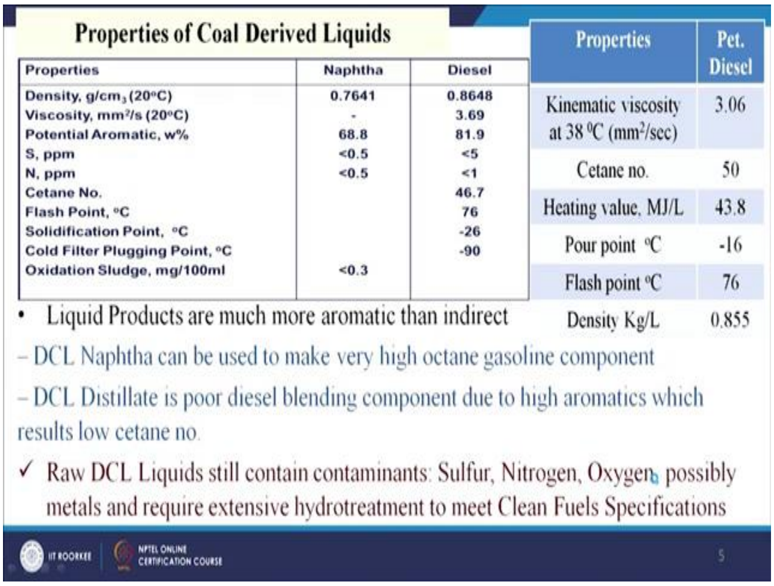

Properties of Coal Derived Liquids

Properties	Naphtha	Diesel
Density, g/cm$_3$ (20°C)	0.7641	0.8648
Viscosity, mm^2/s (20°C)	-	3.69
Potential Aromatic, w%	68.8	81.9
S, ppm	<0.5	<5
N, ppm	<0.5	<1
Cetane No.		46.7
Flash Point, °C		76
Solidification Point, °C		-26
Cold Filter Plugging Point, °C		-90
Oxidation Sludge, mg/100ml	<0.3	

Properties	Pet. Diesel
Kinematic viscosity at 38 °C (mm^2/sec)	3.06
Cetane no.	50
Heating value, MJ/L	43.8
Pour point °C	-16
Flash point °C	76
Density Kg/L	0.855

- Liquid Products are much more aromatic than indirect

– DCL Naphtha can be used to make very high octane gasoline component

– DCL Distillate is poor diesel blending component due to high aromatics which results low cetane no.

✓ Raw DCL Liquids still contain contaminants: Sulfur, Nitrogen, Oxygen, possibly metals and require extensive hydrotreatment to meet Clean Fuels Specifications

Now properties of coal derived liquids we see this table shows the properties that is density, viscosity, potential aromatic percentage, sulphur, nitrogen, cetane number, Flashpoint, solidification point, cold filter plugging point and oxidation sludge, it is also given. So, naphtha which is generated from the coal liquid and diesel these two properties are shown here and this table we can see that the comparison of some properties would say and we can get the cetane number here.

So, cetane number we can have diesel around 50 here we are getting say 46.7 so, relatively lower than that, but as the coal liquid is coming from the coal which is having very complex aromatic structure. So, aromatic compounds in coal liquid will be more. So, octane number will be higher in case of that, but cetane number is not that higher with respect to the petrol-diesel? So, direct coal liquid naphtha can be used to make very high octane gasoline component.

So, that is one advantage of this or the positive point of this on terms of the quality of the coal liquid we will derive to gasoline and DCL distillate is a poor diesel because the value that cetane number is lower than that of the petrol diesel and raw DCL liquid still contains sulphur, nitrogen, oxygen possibly metals also. And so, we need to upgrade this for the removal of these components from the coal derived liquid for its effective application.

Now, we will see; what are the different steps through which the liquid fuel can be produced from the coal.

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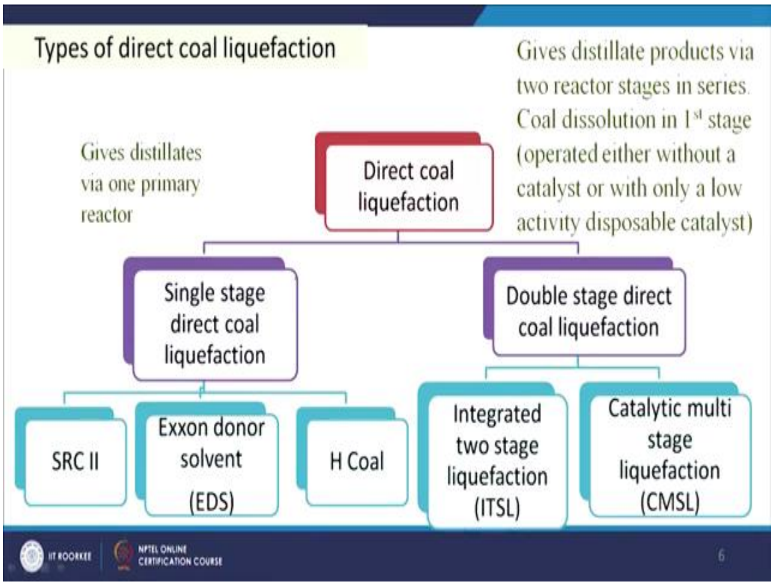

Types of direct coal liquefaction

Gives distillates via one primary reactor

Gives distillate products via two reactor stages in series. Coal dissolution in 1st stage (operated either without a catalyst or with only a low activity disposable catalyst)

Direct coal liquefaction

Single stage direct coal liquefaction

Double stage direct coal liquefaction

SRC II

Exxon donor solvent (EDS)

H Coal

Integrated two stage liquefaction (ITSL)

Catalytic multi stage liquefaction (CMSL)

So, we have one single stage direct coal liquefaction or double stage direct coal liquefaction. So, the single stage that means gives distillates via one primary reactor and double stage gives distillate products via 2 reactor stages in series. So, coal dissolution in first stage operated either without a catalyst or with only a low activity disposable catalyst. So, in case of single stage reactors, there are some technologies like SRC II and then Exxon donor solvent EDS and H coal.

And in double stage we are having integrated 2 stage liquefaction it ITSL and catalytic multistage liquefaction CMSL.

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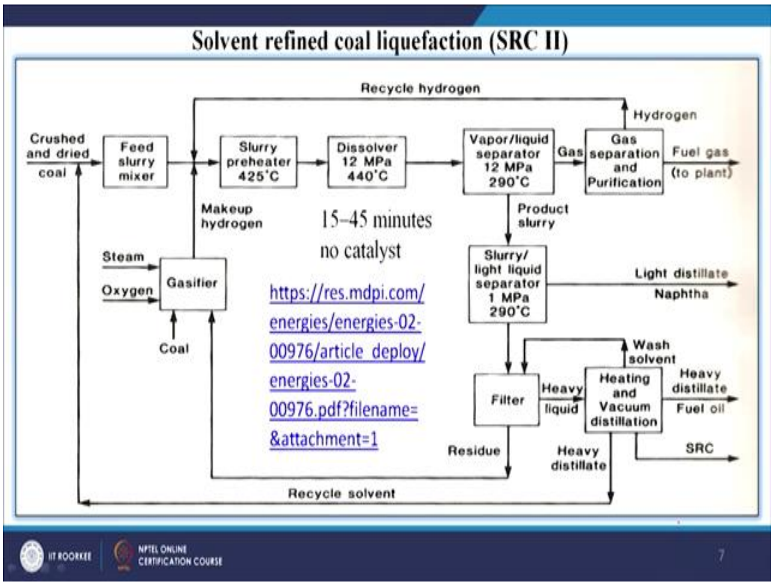

Solvent refined coal liquefaction (SRC II)

15–45 minutes no catalyst

https://res.mdpi.com/energies/energies-02-00976/article_deploy/energies-02-00976.pdf?filename=&attachment=1

Now, we will see SRC II that is solvent refined coal liquefaction. So, we will be using solvent only no catalyst will be used in this case. So, we are using coal here crushed and grinded very small particles then, we have to make slurry. So, I need some solvent, so, how will we get the solvent? It will be coming from the process which is generated in the process, this is heavy distillate it is recycle back and it is creating this slurry.

So, in this slurry is coming, I need hydrogen. So, hydrogen we may get from the gasification process using again some amount of coal here and this hydrogen is coming here or we can get the hydrogen here also which is produced in this process. So, then hydrogen addition is made slurry is formed. So, we have to pressurise it, so after slurry preheater it is coming to dissolver where high pressure of hydrogen is created. So, 12 mega Pascal or 440 degrees centigrade, this 15 to 45 minutes time period is required here without any catalyst.

So, this will give us the conversion. So, what we will get we will be having the mixture now we will be having vapour liquid separation where the vapour the hydrogen which you have added that can be recovered and where also after gas separation, we will get the fuel gas and solid part will come here then it is coming slurry light liquid separation at 1 mega Pascal and 290 degree centigrade. So, we are getting light distillate naphtha and then again filter then residue.

So this residue is your solid part. So, this is again used in the gasifier for the hydrogen production and this liquid part from this filter it will be having the heavy liquid, so, that heavy liquid will be distilled or heating and vacuum distillation then it will give us heavy distillate fuel oil and wash solvent will be coming as a vapour and that can be recycled and this it will give us SRC coal that is solvent refined coal the rest part which is remaining.

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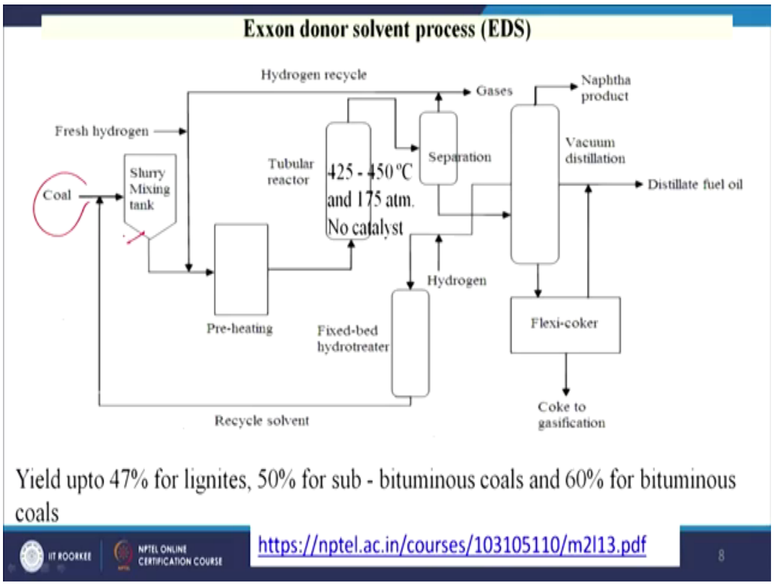

Exxon donor solvent process (EDS)

Yield upto 47% for lignites, 50% for sub - bituminous coals and 60% for bituminous coals

https://nptel.ac.in/courses/103105110/m2l13.pdf

Now, we are coming to Exxon donor solvent process. So, that is also one step process. So, here coal slurry making where the solvent is coming from the process which is generated during this process. And then recycled solvent slurry making hydrogen is coming from this process and it is preheating then it is going to tubular reactor. So, a condition is 425 to 450 °C and 175, atmospheric pressure no catalyst is used,

In this case pressure is higher than the previous one temperature is also slightly higher or in the same range, but the pressure is higher. So, then it is coming for separation so gas separation hydrogen will goes here, we will go here and then we will go for liquid separation so we will get naphtha and we will get distillate fuel then from the solid we can get Flexi Coker and coke formation here and that liquid will also go here.

So, then and from this part we will get some liquid that can be going through hydro-treating, to improve its quality and that can be used as a recycle solvent. So, this is the flow sheet of EDS process that is Exxon donor solvent process. The yield can be up to 47% for lignites, 50% for sub bituminous and 60% for bituminous type of coal.

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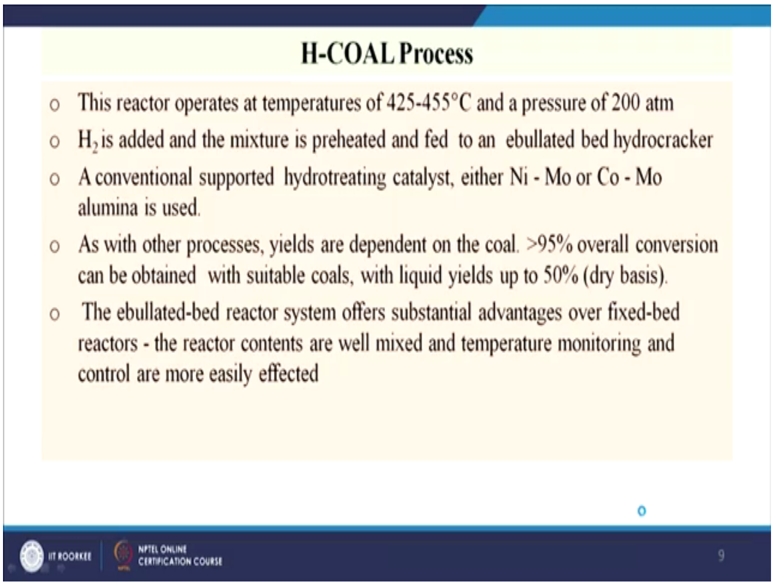

H-COAL Process

- This reactor operates at temperatures of 425-455°C and a pressure of 200 atm
- H_2 is added and the mixture is preheated and fed to an ebullated bed hydrocracker
- A conventional supported hydrotreating catalyst, either Ni - Mo or Co - Mo alumina is used.
- As with other processes, yields are dependent on the coal. >95% overall conversion can be obtained with suitable coals, with liquid yields up to 50% (dry basis).
- The ebullated-bed reactor system offers substantial advantages over fixed-bed reactors - the reactor contents are well mixed and temperature monitoring and control are more easily effected

The H Coal process is another process which is also single step process and this reactor operates at temperature 425 to 455 °C. And here conventional supported hydro-treating catalyst either nickel molybdenum or cobalt molybdenum in alumina is used. So, unlike two other processes in this process, catalyst is used and H2 is added and mixed in a pre heated and fed to an Ebullated bed hydrocracker, the hydro cracker reactor bed is also not fixed unlike the other process.

So, here the yields are dependent on coal and greater than 95% overall conversion, can be obtained because you are using the Ebullated bed reactor and yields liquid yields up to 50% on dry basis. So, as we are using the Ebullated bed reactor, it has some advantage that is well mixed and temperature monitoring. So, that is giving some better efficiency than the previous one.

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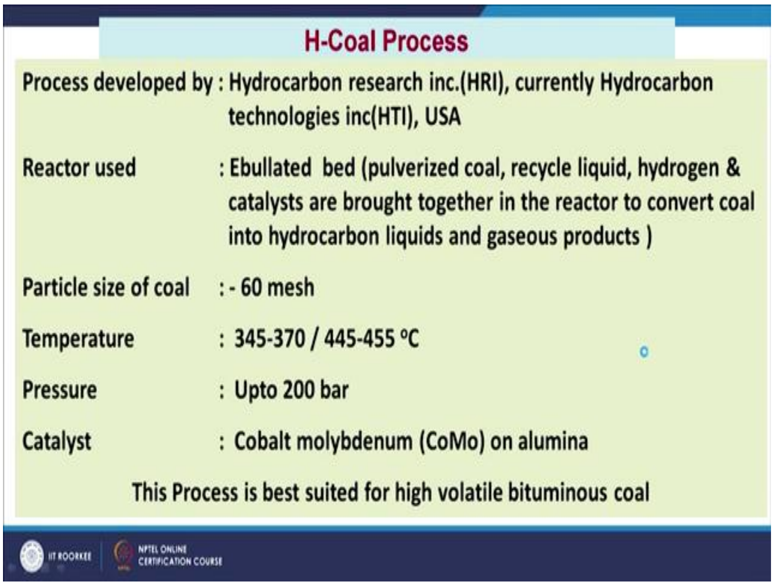

H-Coal Process

Process developed by : Hydrocarbon research inc.(HRI), currently Hydrocarbon technologies inc(HTI), USA

Reactor used : Ebullated bed (pulverized coal, recycle liquid, hydrogen & catalysts are brought together in the reactor to convert coal into hydrocarbon liquids and gaseous products)

Particle size of coal : - 60 mesh

Temperature : 345-370 / 445-455 °C

Pressure : Upto 200 bar

Catalyst : Cobalt molybdenum (CoMo) on alumina

This Process is best suited for high volatile bituminous coal

And then H-Coal process, H-Coal process this is derived; it is developed by HRI Hydrocarbon research incorporation and currently hydrocarbon technologies HTI USA and in this case ebullated bed reactor is used. So, pulverised coal, recycle liquid, hydrogen and catalyst are brought together in the reactor to convert coal into hydrocarbon liquids and gaseous products just we have discuss these things.

And the similar way this also takes place and particle size is minus 60 Mesh and temperature 345 to 370 and this is 445 to 455 °C and up to 200 bar pressure and catalyst is cobalt molybdenum on alumina. So, this is one technology which is used for the direct coal liquefaction.

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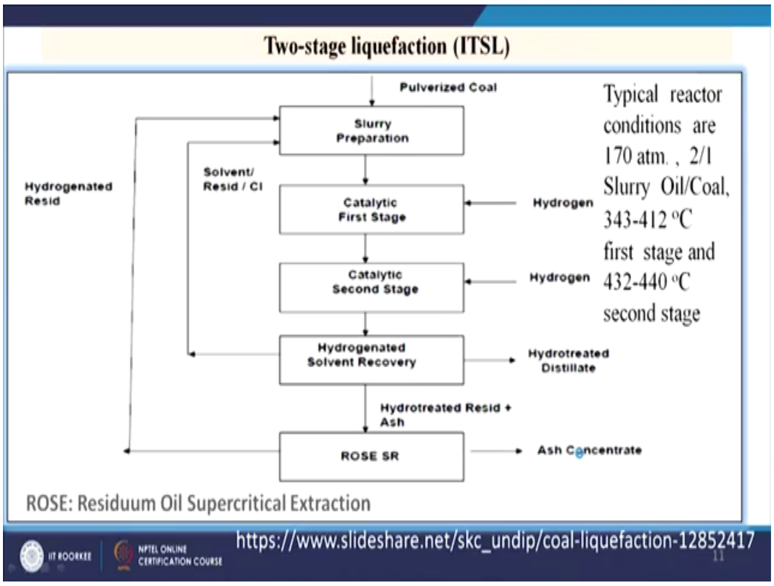

Two-stage liquefaction (ITSL)

Typical reactor conditions are 170 atm. , 2/1 Slurry Oil/Coal, 343-412 °C first stage and 432-440 °C second stage

ROSE: Residuum Oil Supercritical Extraction

https://www.slideshare.net/skc_undip/coal-liquefaction-12852417

So, now 2 stage liquefaction if you see the one is our ITSL two stage liquefaction. So, here we are using coal here. So, that coal we have to make slurry, so some solvent is needed. So, those solvent will also come from the process. So, here is after Rose SR solvent recovery and another is your solvent recovery in this hydro generated solvent recovery. So, these two solvent sources it is coming and making the slurry. Then this slurry the first step will be catalytic first stage.

So, here hydrogen is added then it will go to catalytic second stage again hydrogen will be added then it is going for hydrogenated solvent recovery. So, hydrogenated distillate we are getting and then the solid, the heavier part that is resid plus ash, then we will go for solvent recovery and that is residuum oil supercritical extraction that is ROSE, residuum oil supercritical extraction this method if we use we will get here ash contents and heavier solvent will go to this.

So, this is the flowsheet of these two stage liquefaction process here we can get 170 atmospheric pressure and here 343 to 412 °C for the first stage and the second stage 432 to 440 °C.

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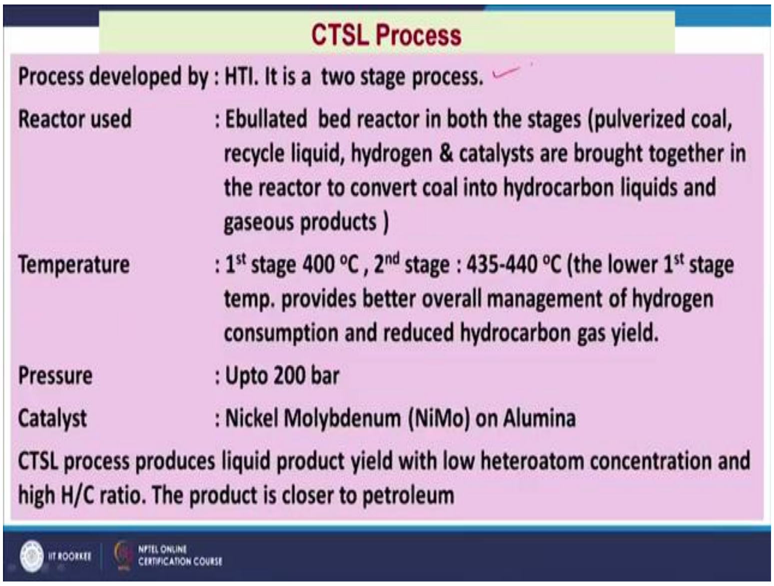

CTSL Process

Process developed by : HTI. It is a two stage process.

Reactor used : Ebullated bed reactor in both the stages (pulverized coal, recycle liquid, hydrogen & catalysts are brought together in the reactor to convert coal into hydrocarbon liquids and gaseous products)

Temperature : 1st stage 400 °C , 2nd stage : 435-440 °C (the lower 1st stage temp. provides better overall management of hydrogen consumption and reduced hydrocarbon gas yield.

Pressure : Upto 200 bar

Catalyst : Nickel Molybdenum (NiMo) on Alumina

CTSL process produces liquid product yield with low heteroatom concentration and high H/C ratio. The product is closer to petroleum

Now, CTSL process that is also a two stage process so, it is ebullated bed reactor in both the stages, in the first stage 400 to 400 °C, second stage 435 to 440 °C, the lower first stage temperature provides better overall management of hydrogen and also it is 200 bar. So, what is the difference between these and previous one? The nickel molybdenum catalyst NiMo on alumina and CTSL process produces liquid product yield with low heteroatom concentration and high H by C ratio, Hydrogen by carbon ratio, the product is closer to petroleum.

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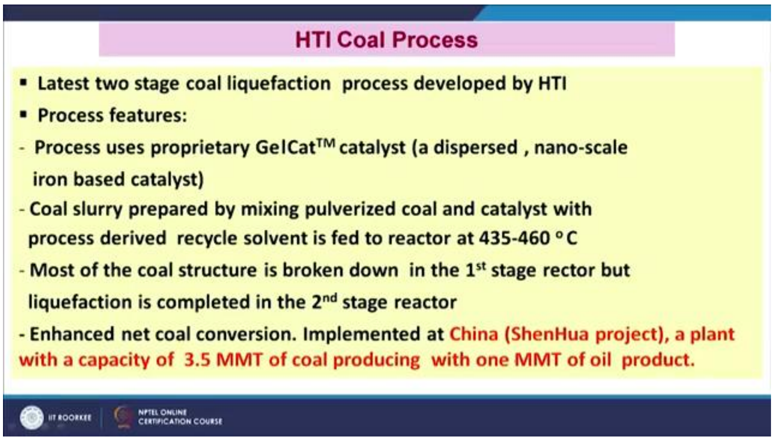

HTI Coal Process

- Latest two stage coal liquefaction process developed by HTI
- Process features:
  - Process uses proprietary GelCat™ catalyst (a dispersed , nano-scale iron based catalyst)
  - Coal slurry prepared by mixing pulverized coal and catalyst with process derived recycle solvent is fed to reactor at 435-460 °C
  - Most of the coal structure is broken down in the 1st stage rector but liquefaction is completed in the 2nd stage reactor
  - Enhanced net coal conversion. Implemented at China (ShenHua project), a plant with a capacity of 3.5 MMT of coal producing with one MMT of oil product.

Another is HTI coal process. So, HTI coal process again two stage process. So, the difference is that this uses the proprietary catalyst a dispersed nano-scale iron based catalyst. So, in the CTSL process we had nickel molybdenum on alumina catalyst. Now, HTI coal process we are having GelCat^{TM} catalyst that is nano-scale iron based catalyst that is the most important difference. And coal slurry prepared by mixing pulverised coal and catalyst with process derived recycle solvent is fed in the reactor 435 to 460 °C.

In the first stage obviously, the breaking of the coal structure, in the second stage is for liquefaction and then this process is used at China ShenHua project in 2008 that is having the capacity of 3.5 million metric tonnes of coal producing with one MMT of oil.

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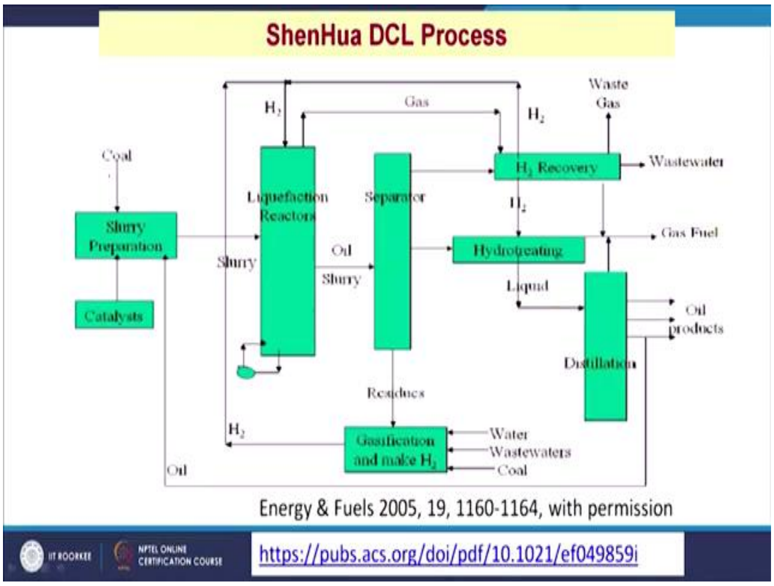

ShenHua DCL Process

Energy & Fuels 2005, 19, 1160-1164, with permission

https://pubs.acs.org/doi/pdf/10.1021/ef049859i

This is the ShenHua DCL project flowsheet, so you see coal is here, slurry preparation takes place, catalyst is added, solvent is coming from the process derived solvent. So, it is coming and then this is going for liquefaction reaction, then separation, then hydrogen recovery hydrogen will come and hydrogen recovery we will get here. So, then the liquid part go for hydro-treating it will give us liquid and then by distillation different fractions of liquid we will get and from this part bottom of this the residual part we can go for gasification and hydrogen we can make. So, that hydrogen can be used here. So, this process is used commercially.

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ShenHua DCL Plant

- World's 1st DCL commercial plant
- Production Capacity: 24,000 BPD (mainly diesel)
- Plant Cost: $1.5 billion USD
- 4 years of construction (2004-2008)

https://www.slideshare.net/tswittrig/shenhua-ccs-program-strategy-and-accomplishments-for-china-ren-xiankun-2009

And this is the first plant in the world on DCL direct coal to liquid that is first DCL commercial plant in China production capacities 24,000 barrel per day and this four year of construction 2004 to 2008.

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Oil Products from SenHua DCL Pilot Plant

https://gcep.stanford.edu/pdfs/wR5MezrJ2SJ6NfFl5sb5Jg/16_china_zhangyuzhou.pdf

These are the some photographs of different fuels derived from the coal directly in this ShenHua DCL plant. Then catalytic multistage liquefaction, so, in this case more than two step is allowable are used.

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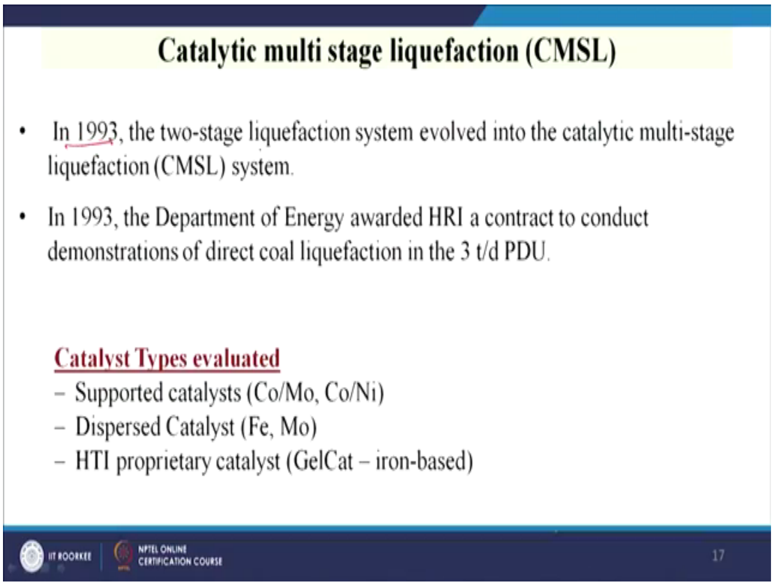

Catalytic multi stage liquefaction (CMSL)

- In 1993, the two-stage liquefaction system evolved into the catalytic multi-stage liquefaction (CMSL) system.
- In 1993, the Department of Energy awarded HRI a contract to conduct demonstrations of direct coal liquefaction in the 3 t/d PDU.

Catalyst Types evaluated

- Supported catalysts (Co/Mo, Co/Ni)
- Dispersed Catalyst (Fe, Mo)
- HTI proprietary catalyst (GelCat – iron-based)

In 1993 the two stage liquefaction system evolved into catalytic multistage liquefaction system. In 1993, Department of Energy awarded HRI a contract to conduct demonstrations of direct coal liquefaction in 3 ton per day capacity, therefore a demonstration plant. So, different types of catalyst has been used, you see the same company HRI they are developing the technology.

So, here supported catalyst, Co-molybdenum, Co-nickel and dispersed catalyst Fe, Mo and HTI proprietary GelCat iron based catalyst.

So, now, we will see the, what is the scope of the DCL process in India? So, we do not have any additional plant in India.

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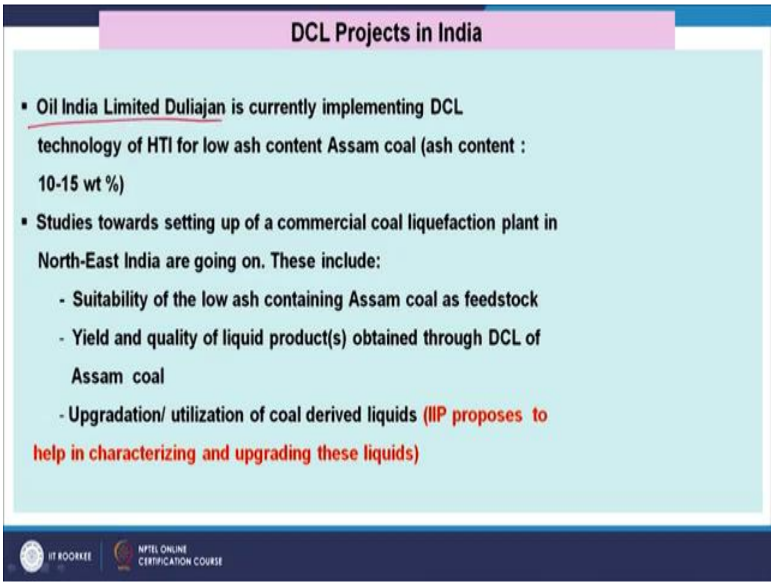

DCL Projects in India

- Oil India Limited Duliajan is currently implementing DCL technology of HTI for low ash content Assam coal (ash content : 10-15 wt %)
- Studies towards setting up of a commercial coal liquefaction plant in North-East India are going on. These include:
  - Suitability of the low ash containing Assam coal as feedstock
  - Yield and quality of liquid product(s) obtained through DCL of Assam coal
  - Upgradation/ utilization of coal derived liquids (IIP proposes to help in characterizing and upgrading these liquids)

But, this is Oil India Limited Duliajan, they are putting their effort to develop the technology and they are targeting to use the low ash content Assam coal for this purpose and one study was going on I am not aware about the latest status update and IIP Dehradun was contributing on the upgradations of the coal liquid. And the benefits of Liquefaction, the direct liquefaction technology has higher efficiency you see 70 to 75% just we have discussed that when we are involving more steps, obviously the efficiency will be less.

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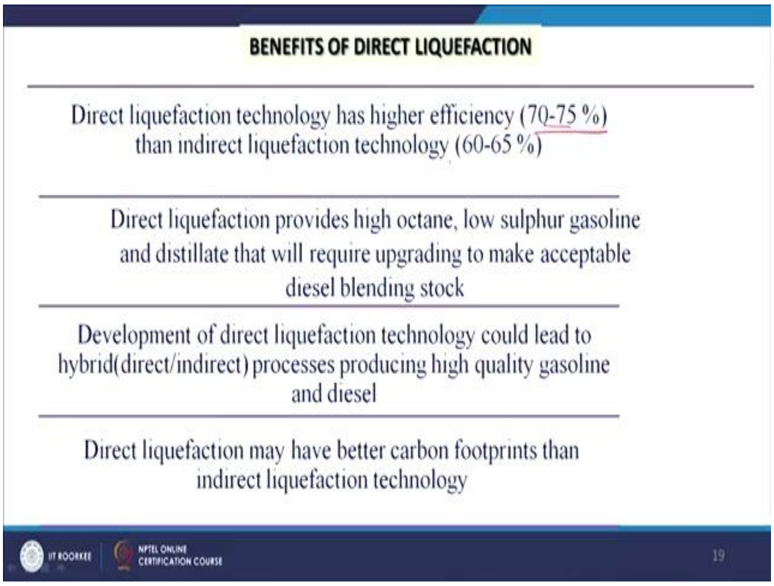

BENEFITS OF DIRECT LIQUEFACTION

Direct liquefaction technology has higher efficiency (70-75 %) than indirect liquefaction technology (60-65 %)

Direct liquefaction provides high octane, low sulphur gasoline and distillate that will require upgrading to make acceptable diesel blending stock

Development of direct liquefaction technology could lead to hybrid(direct/indirect) processes producing high quality gasoline and diesel

Direct liquefaction may have better carbon footprints than indirect liquefaction technology

So, in this case we can get higher efficiency with respect to other technology say IGCC like this indirect way 60 to 65% maximum we can achieve. And then direct liquefaction provides high octane, low sulphur gasoline and distillate that will require upgrading to make acceptable diesel blending stock. So, these are advantage and development of direct liquefaction technology could lead to hybrid processes producing high quality gasoline and diesel. And direct liquefaction may have better carbon footprints then indirect liquefaction process.

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Direct liquefaction challenges

- **Uncertainty in World Oil Prices (viable** when crude oil price > \$70–80 per barrel)
- **High Capital Costs**
- **Investment Risk**
- **Technical Challenges**

– First technology (since 2nd World War) is commercialized in China in 2008 – need other first-of-kind large scale operation (with carbon management) to verify baselines and economics

– R&D activity should focus on remaining process issues such as further improvement in efficiency, product cost and quality, reliability of materials and components and data needed to better define carbon life cycle

– Hybrid technology needs development including integrated demonstration

- **Environmental Challenges**

–CO_2 and criteria pollutants as well as water use

But what are challenges? Uncertainty in oil prices as you know, this method is not very cheap method, it will be costlier and will be feasible only when the crude price will be very high, it is feasible when the crude price is more than 70 to 80 \$ per barrel. And high capital cost as you see that high pressure systems are required. So, we high capital cost is also needed. And then investment risk is also there that the market what will be the value of crude oil it fluctuates.

So, what will be the stability of the market of these that is also uncertain and so, it is there is a risk for the investment on this and technical challenges. This is you know this process was discovered many years ago, but commercialization take only in 2008 because there are many technical challenges although there is one plant commercial plant in China, but still more research is required on this field and to make it to develop confidence on the technology.

LCA can be done. So, hybrid technology needs development including integrated demonstration and environmental challenges. It has some challenges also carbon dioxide and criteria pollutants as well as water use. So these are also related. These are not well addressed on this plant. Thank you very much for your patience.