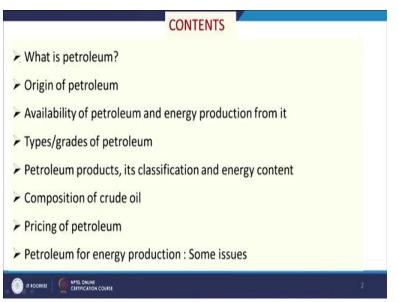
Technologies for Clean and Renewable Energy Production Prof. Prasenjit Mondal Department of Chemical Engineering Indian Institute of Technology-Roorkee

## Lecture-11 Petroleum as a Source of Energy

Hi friends now we will discuss on the topic petroleum as a source of energy. In the previous classes we have seen that after coal the petroleum is mostly used as energy resource around the world and this is also a fossil fuel. And now we will see what is petroleum? What is the composition of it and what is the heating value of it and what are the different forms of energy we can get from it and what are the issues, types of it etcetera.

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So, now the contents are here, what is petroleum? Origin of petroleum, availability of petroleum and energy production from it, types or grades of petroleum and petroleum products, its characterization, its classification and energy content, composition of crude oil, pricing of petroleum and petroleum for energy production: some issues. These are the contents of today's discussion.

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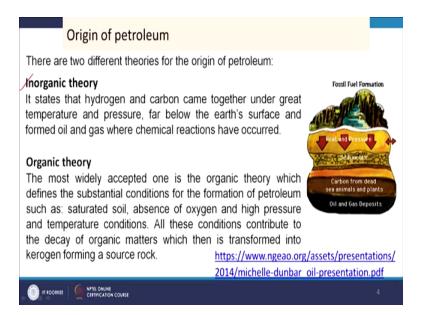
what is	petroleum?	
Petroleum: The word petroleum is "oleum" – oils. Hence it literally me occurring organic compounds from carbon and oxygen. Crude oils: Crude oil is a complex naphthenes and aromatics), brown	ans " <b>rock oil</b> ". It is n within the eartl mixture of hydro	basically a mix of naturally h that contain primarily hydrogen, carbons (i.e., paraffins,
	Carbon	83-87%
Petroleum is a broad category	Carbon Hydrogen	83-87% 10-14% (up to 5.5% in coal)
that includes both crude oil and		
	Hydrogen	10-14% (up to 5.5% in coal)
that includes both crude oil and	Hydrogen Nitrogen	10-14% (up to 5.5% in coal) 0.1-2%

Now let us see what is petroleum? so as the word says petroleum it is derived from the Petra and oleum so Petra means rock and oleum is oil. So, literally it means that rock oil and it is defined as a, it is basically a mix of naturally occurring organic compounds from within the earth that contain primarily hydrogen, carbon and oxygen. So, petroleum and crude oil these two terms are used widely and apparently both are similar and are used for the same purpose.

Where the crude oil is a complex mixture of hydrocarbons, different types of hydrocarbons paraffin's, naphthenes and aromatics and brownish black in colour and colloidal in nature petroleum is also similar, same. The only difference is that petroleum is a broad category that includes both crude oil as well as the petroleum products. And if we see the elemental composition of these it contains carbon, hydrogen, nitrogen, oxygen, sulphur and metals.

So, mostly carbon then hydrogen but here hydrogen is more with respect to coal and heating value is also higher in case of this. Now we will see the origin of petroleum, how the petroleum was originated? In case of coal we have seen that there are different thoughts who explain the formation of coal under the earth crust. Here also there are different thoughts, here some thoughts says that it is originated from animal sources and some thoughts says that it is from inorganic sources.

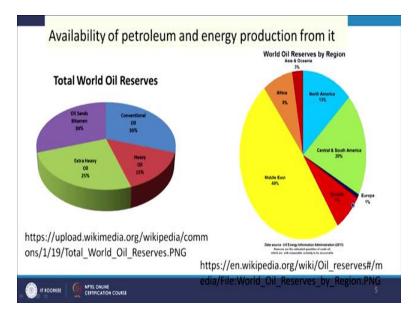
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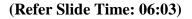
So, one is inorganic and organic theory, unlike coal this is suppose that petroleum is originated from animal sources but coal was from plant sources that is what this organic theory. Now if we see the inorganic theory then this theory says that carbon and hydrogen came together under high pressure and temperature below the earth's surface and formed oil and gas where chemical reactions took place.

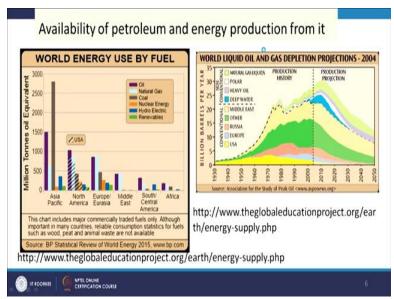
Organic theory says that the most that the substantial conditions for the formation of petroleum such as saturated soil, absence of oxygen and high pressure and temperature conditions, under these condition the decay of organic matters transformed into kerogen forming source rock. So, that is the source of the petroleum and it is assumed that the animal bodies are converted to this petroleum.

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Now what is the availability of petroleum and energy production from it? If we see the total world oil reserves then we get conventional oil 30%, heavy oil 15%, extra heavy 25%, and oil sand is 30%, so these are the different parts or the type of petroleum resources. And worldwide reserve by region wise if you see middle-east have around 49%, then America, North America 13% and Central and South America 20% then Africa is only 8% and Eurasia is 7% but we Asia has very less reserve. We also have some reserve but very limited.





Now if we see the world energy used by fuel then Asia Pacific region North America, Europe, Russia, Middle East, South Central America and Africa we see here now while oil is used everywhere in significant amount after coal. And the prediction says that we are here at say somewhere see prediction says that the world liquid oil and gas depletion has predicted in 2004 that in future the amount will be reduced, the availability of this oil may be reduced in near future.

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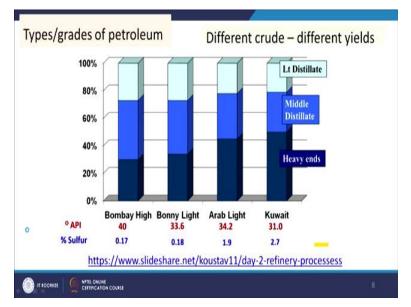
https://oilprice.com/Energy/Crude-Oil/A-Detailed-Types/grades of petroleum Guide-On-The-Many-Different-Types-Of-Crude-Oil.html Light crude oil is defined as having an API gravity higher than 31.1 °API Medium oil is defined as having an API gravity between 22.3 ° and 31.1 °API Heavy oil is defined as having an API gravity below 22.3 °API. Although over 160 different oils are traded on the market, the three primary oils that get most of the serious attention in the news and in the markets are: West Texas Intermediate (WTI) : An extremely high quality crude oil API Gravity" 39.6 degrees, Sulphur 0.24 % (sweet) Brent Blend : A combination of different oils from 15 fields throughout the Scottish Brent and Ninian systems located in the North Sea. "API Gravity" 38.3 degrees, Sulphur 0.37 % OPEC Reference Basket: A collective 11 different crude oils from Algeria, Iraq, Kuwait, Libya, Qatar, Iran, Saudi Arabia, Indonesia, Nigeria, Venezuela and the UAE. "API Gravity" 32.7 degrees, Sulphur 1.77 % https://www.opec.org/opec\_web/en/press\_ro IT ROORKEE CERTIFICATION COURSE

Now we will see the types and grades of petroleum. So, petroleum can be divided into different grades depending upon the degree API that is a specific gravity. So, light crude, heavy crude and medium crude oil. So, light crude means its degree API is higher more than 31.1 API and heavy is dense oil so it is having API below 22.3. So, in between these two 22.3 to 31.1 this is called medium oil. So, this is one way of classifications of the oil that is light, medium and heavy oil.

So, if we see the availability of the oil petroleum crude around the world we can get three major locations the one is your West Texas Intermediate in America another is your Brent blend, it is also located in the North Sea and then OPEC reference basket that is in Algeria, Iraq with Libya Qatar, Iran, Saudi Arabia, Indonesia, Nigeria, Venezuela and UAE. If we say this crude oil it's relatively of lower quality degree API is 32.7 whereas here we will get the highest quality 39.6 degree API and sulphur is also 0.24%.

And this is medium that a 38.3 lesser than 39.6 and sulphur is also higher than this 0.37% and here the sulphur is higher and this API gravity is also lower. So, in terms of these three this is of inferior quality crude oil.

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Now what we will see different crude oil will give us different yield. So, you see some example Bombay High, Bonny light and Arab light and Kuwait. So, these different sources crude oil if we take and if we want to refine it, we will not get the similar type of products. In India you see the Bombay High crude we are having very high amount of middle and light distillates also but heavy ends are also relatively less in this case.

So, the quality of the oil available in India in Bombay high it is good but Reserve is less but here you see Kuwait the heavy end is very higher amount then middle distillate and then light distillates. So, the origin of the petroleum will also can generate or can give different type of liquids after its refining or we need different types of technology to process this different type of feedstocks to get certain amount of liquid product.

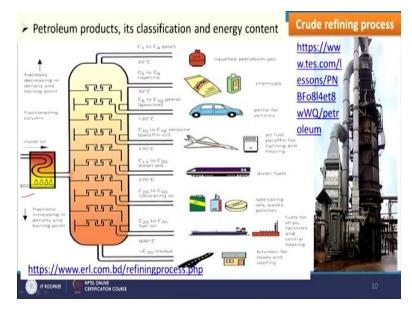
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PROPERTIES	UNIT	BH	KUWAIT	ARAB MIX	IRN LT.	IRN HY.
API Gravity @ 15°C		38.3	31.2	30.3	34.0	31.
Pour Point	°C	+30	-17	-15	-12	-6
Wax Content	% wt	14.7	4.5	5.6	5.7	4.4
Asphaltenes	% wt	0.05	1.3	2.7	0.9	2.0
Total Sulfur	% wi	0.2	2.54	2.65	1.4	1.65
Primary Yields						1
Light Distillates	% wt	24	14	16	17	16
Middle Distillates	% wi	46	36	36	43	36
Residue	% wt	30	50	48	40	48
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So, this slide gives us some comparison of middle-east crude quality that is Arab mix, Iran light Iran heavy and Kuwait and Bombay High so these are the properties like say gravity, pour point, wax content, asphaltenes, total sulphur and yields, light distillates, middle distillates, residue it is given. So, one thing it is clear that here it is having less residue higher the API lesser the residue obviously because it is lighter.

So, residual part will be less then what are the difference liquids we can get or different energy we can get from this, different form of liquids which can be used for energy source from the petroleum crude that we want to discuss. Now so crude will be refined first and different fractions we will get.

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So, here we are getting the crude it is heated, pretreated that is fractionated in this column, after fractionations we get different products as shown here  $C_1$  to  $C_4$  gases will get LPG here 220 degree centigrade and then here say  $C_5$  to  $C_9$  naphtha we will get 70 degree centigrade and  $C_5$  to  $C_{10}$  petrol or gasoline we can get at 120 degree centigrade  $C_{10}$  to  $C_{16}$  we can get kerosene and at 170 degree centigrade.

And  $C_4$  to  $C_{20}$  we can get diesel oil that is equal 270 degree centigrade and  $C_{22}$  to  $C_{50}$  that is lubricating oil and then  $C_{22}$  to  $C_{70}$  fuel oil and then the residual. So, these are the different fractions we can get from the crude oil and those fractions can be used in different applications like say LPG as a heat source and then naphtha is very, very important. Once naphtha can be converted to different types of chemicals that petrochemicals so we can get Petro chemicals from naphtha and as you know that diesel, petrol all those things are used to run vehicles.

And ATF aviation turbine fuel is also used that is the jet fuel there is a kerosene and ATF are having very similar properties and others are fuels that is lubricating oil is also used for the lubrications of machines. And residual part this is one issue that that can create a lot of pollution and we have a scope to improve the quality of residue so that we can reduce the loss and we can improve the economy of the process also.

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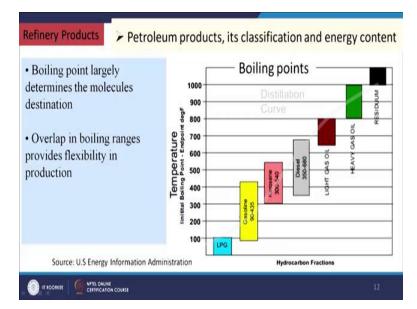
<ul> <li>PRIMARY PRODUCTS</li> <li>Gasoline – automobile, light truck, small engine fuel</li> <li>Diesel – automobile, heavy trucks, trains, heavy equipment</li> <li>Jet Fuel– Commercial and military aircraft</li> </ul>		<ul> <li>SECONDARY PRODUCTS</li> <li>Kerosene – Home heating, charcoal fluid</li> <li>Liquified Petroleum Gas (LPG) – Chemical feed, heating, commercial applications</li> <li>Fuel Oil – Home Heating, Ships, boilers, furnaces</li> <li>Asphalt – Roads, roofing material, sealants</li> <li>Carbon Black Oil – Carbon black manufacture, carbo composites, tires</li> <li>Lubricating Oil – Engine &amp; machinery lubrication</li> </ul>		
LPG Gasoline Kerosene Diesel Residue	46.1 MJ/kg 46.5 MJ/kg 46.2 MJ/kg 45.8 MJ/kg 42.2 MJ/kg	<ul> <li>Waxes - Candles, industrial sealants</li> <li>Petroleum Coke - Coal fired boilers, metals manufacture (anodes, fuel)</li> <li>Sulfur - Chemical and fertilizer manufacture</li> <li>NaHS (sodium hydrosulfide) - paper, copper mining, leather industries (Holly emphasis)</li> </ul>		

So, now we will see the different refined products so gasoline, diesel and jet fuel these are the major products which are produced through the refining of petroleum crude and used in different types of transport. And other secondary products are kerosene, LPG, fuel oil, asphalt, carbon black oil, lubricating oil, waxes, petroleum coke and those things and sulphur if you can recover then that can be used for chemical synthesis.

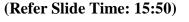
And NaHS that is used can be paper, copper mining and leather industries. So, these are the different refined products which you can get from petroleum refinery and that can be used for different applications. So, one way it is giving us energy other way it is also giving us different types of petrochemicals. Now we see the heating value of the different products which we can get from the petroleum crude refining.

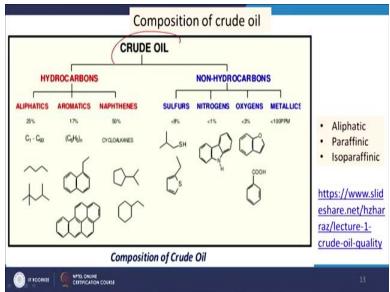
So, LPG, gasoline, kerosene, diesel and residue, heating value is this much for a LPG 46.1 mega Joule per kg then gasoline 46.5 mega Joule per kg, kerosene 46.2 mega Joule per kg, diesel 45.8 mega Joule per kg and residue 42.2 mega Joule per kg but in this case what we have discussed in the previous slide also that there is a specific temperature it is mentioned but we have some flexibility to vary this temperature and to maintain the or the control the quality of the products also.

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Then different petroleum products which we get that we have different boiling points we have discussed and that boiling point largely determines the size of the molecules and what type of product will get more. And overlap in boiling ranges provides flexibility in products and just we have discussed when you see LPG, gasoline, kerosene, diesel, light gas oil, heavy gas oil and the residual. So, this is the temperature at which we can get, these are the temperature we can get different types of product.





Now we will see what are the compositions of a petroleum crude or petroleum? So, petroleum crude oil if we see that is hydrocarbons basically. So, it will be mostly hydrocarbons and non hydrocarbons are also present those are called impurities. So, hydrocarbons may be aliphatic

naphthenic, naphthenes and aromatics so these three types of hydrocarbons basically present in crude oil and non hydrocarbons are like sulphurs, nitrogens, oxygens and metallics they are basically present in it.

And typical range is given say 25% asphaltic, 17% aromatics, 50% naphthenes and naphthenes is very important it is used for the production of different types of chemicals naphtha. And then sulphur is this one nitrogen is less and oxygen is also less and metals is also very less, less than 100 ppm. And these are the molecular structure of these different types of compounds which is present in it or hydrocarbons present in it.

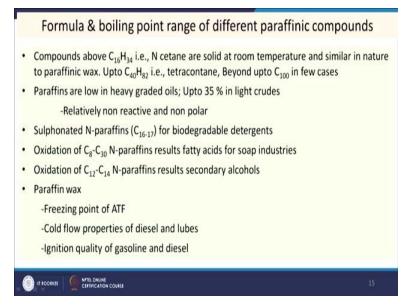
This is aromatic ring it has and it has some naphthenic rings, naphthenes. So, aliphatic and the paraffin are basically present in the crude oil and then isoparaffinic compounds are also present in largely in large amount. So, isoparaffinic and paraffinic both are present in asphaltic.

Compounds	Formula	Boiling point (°C)
Ethane	C <sub>2</sub> H <sub>6</sub>	-88.6
Propane	C <sub>3</sub> H <sub>8</sub>	-42.1
N Butane	C <sub>4</sub> H <sub>10</sub>	-0.5
N Hexane	C <sub>6</sub> H <sub>14</sub>	68.8
N Heptane	C <sub>7</sub> H <sub>16</sub>	98.4
N Octane	C <sub>8</sub> H <sub>18</sub>	125.7
N Nonane	C <sub>9</sub> H <sub>20</sub>	150.9
N Decane	C10H22	174.0
N Undecane	C <sub>11</sub> H <sub>24</sub>	195.8
N Dodecane	C <sub>12</sub> H <sub>26</sub>	216.3
N tridecane	C <sub>13</sub> H <sub>28</sub>	234.0

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Now we will see some example of this isoparaffin's that is propane, n-butane, n-hexane, n-heptane, n-octane, n-nonane, n-decane, n-undecane, n-dodecane, n-tridecane, so this is  $C_2$  to  $C_{13}$  some boiling range are given here. So, obviously the higher the carbon number more with the boiling range. So, upto  $C_3$ ,  $C_4$  basically we get it in LPG.

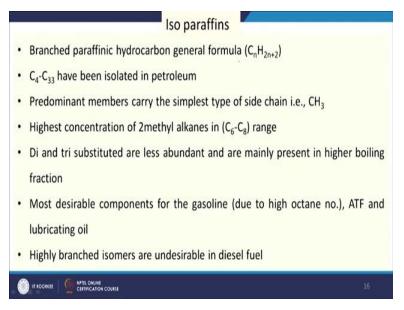
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Now the paraffin's which are available in petroleum crude basically they are having say  $C_nH_{2n+2}$  formula,  $C_nH_{2n+2}$  and the compounds which are higher carbon, which are having higher carbon that is say  $C_{16}H_{34}$  they are mostly in solid form and in some cases we get mostly we get  $C_{40}H_{82}$  and in some cases we can get  $C_{100}$  even mostly up to  $C_{80}$  we get, in some cases we can get more than that that is  $C_{100}$ .

And these paraffin's are low in heavy graded oils that is up to 35% in light Crudes and Sulphonated this paraffin's can be used for biodegradable detergent production and oxidation of  $C_8$  and  $C_{30}$  N-paraffin's results fatty acids and soap industries and oxidation of  $C_{12}$  to  $C_{14}$  normal paraffin's results secondary alcohols. And this paraffin wax which is available higher carbon number of paraffin's, they contribute on freezing point of ATF, Aviation Turbine Fuel. Cold flow properties of diesel and lubes and ignition quality of gasoline and diesel.

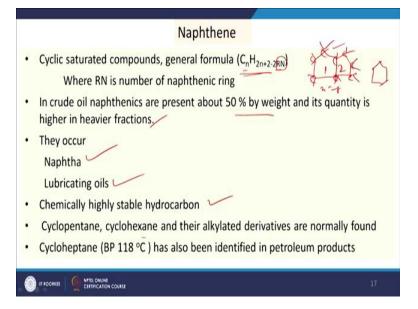
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And isoparaffin's which are available in this the general formula is  $C_nH_{2n+2}$  and  $C_4$  to  $C_{33}$  have been isolated in petroleum in higher extent and predominant form is here the CH<sub>3</sub>, CH<sub>3</sub> chain as a side chain is available in most of the cases and highest concentration of two methyl alkanes in  $C_6$  to  $C_8$  range it is available and di and tri substituted are less abundant and are mainly present in higher boiling fraction.

And most desirable components for the gasoline this one this isoparaffin's are desirable for gasoline, ATF and lubricating oil and these are the; if we have highly branched isomers then this is not undesirable.

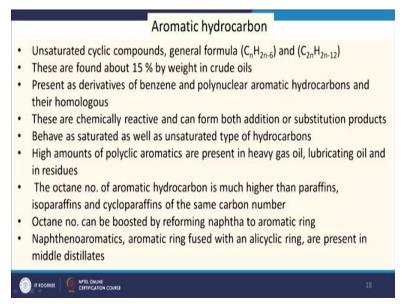
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The naphthene is  $C_nH_{2n+2-2RN}$  say this is one naphthene so how many this is C C C C C C C C C so how many moles num 1 2 3 4 5 6 7 8. So, 8 n equal to 8 so H we are having 2 H 2 H 2 H 2 H and then 2 H again here we will have 2 H and 2 H and here 1 H and 1 H, so these 2RN, RN means 1 and 2, 1 and 2 we have 2 rings 2 rings so RN is the number of naphthenic ring in this case if this one, we have one ring so RN equal to 1 so this is the general formula.

So here in this case n equal to 8 so that will be  $8 + C_8H_{2x8+2-2x2}$ . So, this is the formula of this naphthenic compound. Now in crude oil naphthenics are present about 50% by weight and its quantity is higher in heavier fractions, higher the heavier the crude more the naphthenic compounds. And if naphthenes are present then what will happen? They will give us more naphtha and lubricating oil and these are stable hydrocarbon and cyclopentane, cyclohexane and their alkylated derivatives are normally found.

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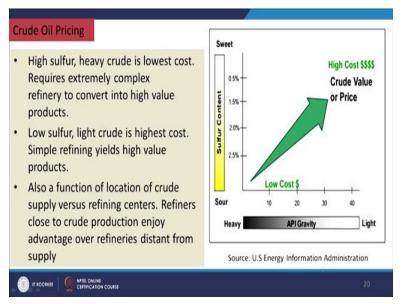
In aromatic hydrocarbons aromatic hydrocarbons means some benzene ring will be available or more number of rings may be available in this case. So, general formula is  $C_nH_{2n-6}$  or  $C_{2n}H_{2n-12}$  so this is the formula and these are already 15% of weight in crude oil it is and more the this aromatic present in it so what will be happen in this case octane number will be boosted. So, for gasoline it will be preferable so the octane number of aromatic hydrocarbon is much higher than the paraffins and Isoparaffins and these are chemically reactive and can form both addition or substitution products and high amounts of polycyclic aromatic are present in heavy gas oil lubricating oil and in residues.

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Hydrocarbor	ns: Compounds composed of C and H. Acc	count for 75 % of the material	
Carbon num	ber distribution in distillates		
	Carbon range		
LPG	Paraffins	C1 – C4	
Gasoline	Paraffins, aromatics and naphthenes	C5-C10	
Kerosene	DO	C11 – C18	
Gas oil	DO	C18-C28	
VGO	DO	C28 - C40	
Residue	Asphaltic	C40 onwards	

Now we will see main constituents of crude oil so basically carbon and hydrogen this is the main constituent and different fractions of this LPG, gasoline, gas oil, VGO and residue if we see basically the LPG paraffins then gasoline, paraffins, aromatics and naphthenes kerosene also same and the residue is mostly asphaltic and their carbon range is given here. These are the typical range.

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Now how we will price the crude? How the crude oil is priced? What is the cost is decided on which basis? Obviously it will be on its quality and degree API and sulphur content both are

considered for its pricing. In case of coal we have discussed that ash content and moisture content was also considered. So, in this case we have our sulphur and API they are used to fix the price. And then high sulphur heavy crude is obviously in low cost.

If you see we increase these if you go that way so degree API is increasing the quality is improved the light it is becoming lighter and lighter. And then sulphur content so sulphur content is also reducing so cost is higher, higher cost low sulphur and high API this is the basis the price is fixed.

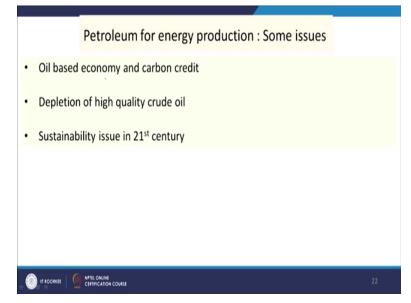
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Crude Oil Pricing		
used as a benchma Mercantile Exchan North American ne	ediate (WTI), also known as Texas light sweet, is a type of cruark in oil pricing and is the underlying commodity of New York ge's oil futures contracts. The price of WTI is often referenced ews reports on oil prices, alongside the price of North Sea Brewrant oil markers include the Dubai Crude and the OPEC referenced events and the OPEC referenced.	c d in e <b>nt</b>
OPEC policies     Original OPEC n	mand fundamentals [Organization of the Petroleum Exporting Countries (OPEC) - nembers include Iran, Iraq, Kuwait, Saudi Arabia ] mic developments in the exporting / consuming countries	
	une non course	21

But how the price will be fixed? There are benchmarks some benchmark one benchmark is your West Texas Intermediate, WTI, and then this is also called as Texas light sweet another is Brent crude and another is OPEC reference basket. So, in India we mostly dependent on OPEC reference basket and the price is dependent on many factors what would be the crude price today tomorrow it may change. So, that will be influenced by many factors those are supply and demand fundamentals.

Then we have OPEC policies, the organization's of the Petroleum Exporting Countries they have the members of this Iran, Iraq, Kuwait, Saudi Arabia etc so this country they have their policy and political issues also influence it. The political and economic developments in the exporting and consuming countries, so what is the relationship between India and Iran or Iraq or Kuwait so that will also influence the price of the crude. And weather conditions because how it will be transported and what is the weather conditions that will also influence our crude price.

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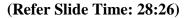
Then Petroleum for energy production: Some issues, we will be discussing some issues now. So, oil based economy and carbon credit that is one issue. You know we, our society is mostly dependent on oil utilization and it produces carbon dioxide. So, if we use more oil so we will be producing more carbon dioxide so carbon credit will be in consideration so that is one issue so you have to optimize the things that carbon emission will be reduced.

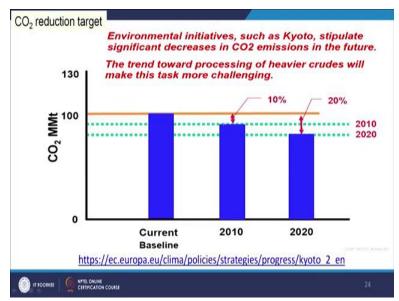
And depletion of high-quality crude oil, the high-quality crude oil is being reduced as you have seen in a one slide that it is projected that the supply of crude oil will be reduced and even the quality is also degraded day by day. So, lower the quality more the SOx emission and more the ash emission, so industrial emissions will be more with the degradation of the quality of the crude oil. And a sustainability issue, in 21st century sustainability is an issue where we have to ensure the energy supply, we have to environmental quality and social equity.

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So, under these situation if we see the carbon emissions from liquid fuels so here we have million tons  $CO_2$  released so total this much so year 2020 say 36834 million tons of  $CO_2$  is expected to come from different types of fuels and liquid fuel from it is expected to come 13582 million tons of  $CO_2$ . So, around one third of the total  $CO_2$  is coming from the liquid fuel so this is one concern that how to control the carbon dioxide emission from these fuel if we want to use more effectively this feedstocks for energy resource.





And then another target is that as per Kyoto protocol we have to reduce the carbon dioxide emission level in 1997 which we had and now 2010 we had some target that 10% will be reduced, the carbon dioxide emission will be reduced and 2020 it is targeted to reduce by 20% so

we are under pressure we have to reduce the carbon dioxide emission from all source of energy and other activities.

And this liquid fuel contributes on carbon dioxide emission so we have to take actions we have to develop cleaner technologies for its proper applications. So, upto this in this class thank you very much for your patience.