Energy Conversion Technologies (Biomass and Coal)

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Lecture 26

Green diesel synthesis from bio-based feedstocks

Good morning everyone.

Welcome to this third lecture of module 6. In this lecture, we will discuss another chemical conversion process that is Green Diesel synthesis from bio-based feedstock and its application.

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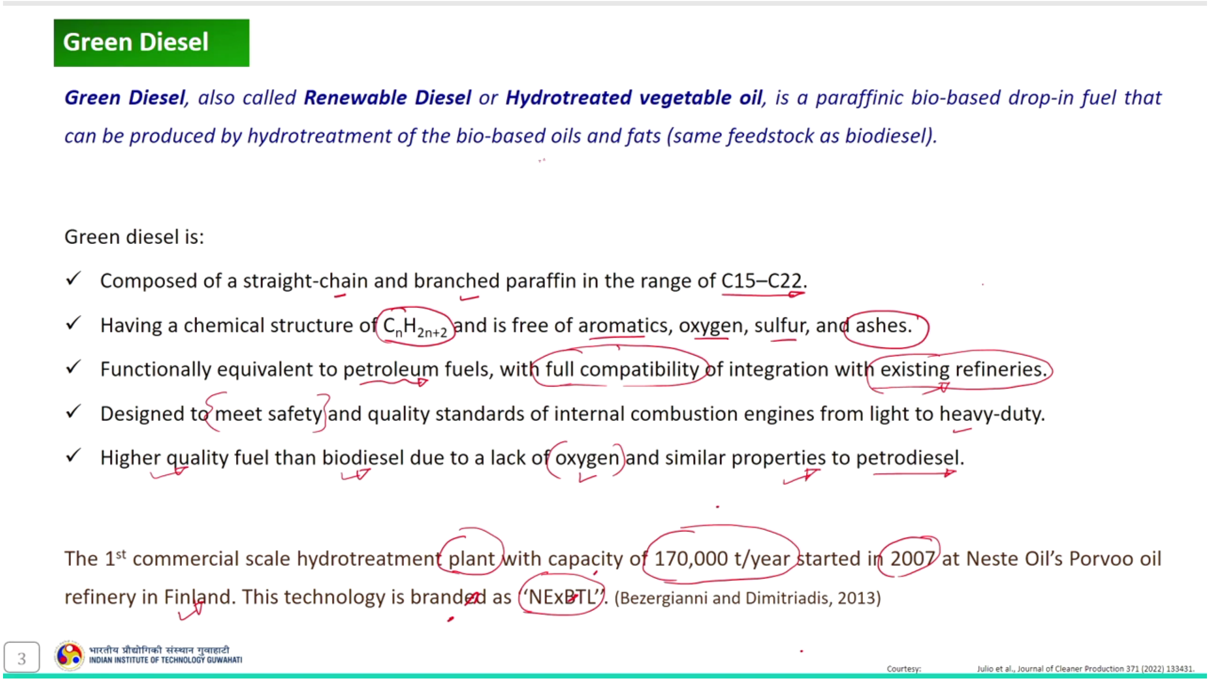

Green Diesel

***Green Diesel**, also called **Renewable Diesel** or **Hydrotreated vegetable oil**, is a paraffinic bio-based drop-in fuel that can be produced by hydrotreatment of the bio-based oils and fats (same feedstock as biodiesel).*

Green diesel is:

- ✓ Composed of a straight-chain and branched paraffin in the range of C15–C22.
- ✓ Having a chemical structure of C_nH_{2n+2} and is free of aromatics, oxygen, sulfur, and ashes.
- ✓ Functionally equivalent to petroleum fuels, with full compatibility of integration with existing refineries.
- ✓ Designed to meet safety and quality standards of internal combustion engines from light to heavy-duty.
- ✓ Higher quality fuel than biodiesel due to a lack of oxygen and similar properties to petrodiesel.

The 1st commercial scale hydrotreatment plant with capacity of 170,000 t/year started in 2007 at Neste Oil's Porvoo oil refinery in Finland. This technology is branded as 'NExBTL'. (Bezergianni and Dimitriadis, 2013)

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Courtesy: Julio et al., Journal of Cleaner Production 371 (2022) 133431.

Green Diesel also called as renewable diesel or hydrotreated vegetable oil, is a paraffinic bio-based drop-in fuel that can be produced by hydrotreatment of bio-based oils and fats. And the feedstock used in the hydrotreatment process is same as that of the feedstock used in the bio-diesel synthesis process. Green Diesel is composed of straight chain and branch paraffin in the range of C15 to C22, having a chemical structure of C_nH_{2n+2} and is free of aromatics, oxygen, sulphur and ashes.

The produced Green Diesel is functionally equivalent to petroleum fuels and the process used for the synthesis of Green Diesel is fully compatible with existing refineries. So, that means the process which is used for the Green Diesel synthesis is compatible for integration with the existing refineries. So, the produced Green Diesel meet the safety and quality standards of internal combustion engine from light to heavy duty.

And the produced Green Diesel has higher quality than bio-diesel and that is mainly due to lack of oxygen in its composition. And also it possesses properties similar to that of the petrol diesel. And the first commercial scale hydrotreatment plant with capacity of this much ton per year it is started in 2007 at Finland. And this technology is branded as NExBTL technology and this is very popular technology for the conversion of bio-based oils and fats into Green Diesel.

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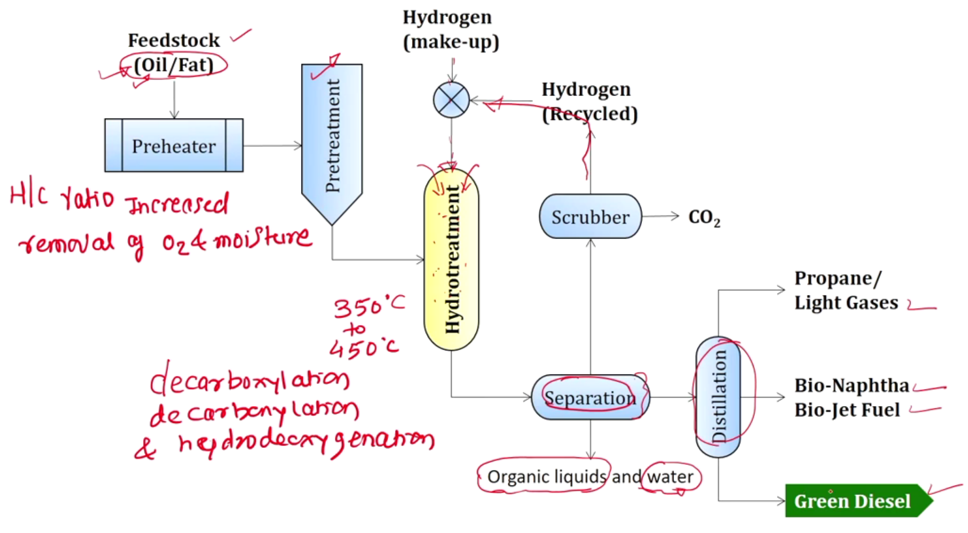
Hydrotreatment Process to obtain Green Diesel



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Courtesy: Kalnes et al., International Journal of Chemical Reactor Engineering, 2007, 5, A48

And this schematic here it represents the hydrotreatment process to obtain Green Diesel. The hydrotreatment of liquid bio-based feedstock is a common refinery technique and as we know the feedstock used in this process is a liquid feedstock. And the only technology that has overcome all the limitation of liquid bio-based material as a feedstock for the fuel production. And this is the only technology which overcomes this limitation of conversion of this liquid bio-based feedstock to fuel. And the H/C ratio in this process is increased with removal of moisture and oxygen. In the hydrotreatment process the first step is the pre-treatment step.

And it is generally used for the removal of impurities from the liquid sample followed by hydrogenation through the contact between the triglycerides and hydrogen. And the hydrogen used in this process is in excess and it is generally carried out at temperature range of 350 to 450 °C and pressure around 4 to 15 MPa using a heterogeneous catalyst. And the feedstock which is used in this process mostly contains the triglycerides because the feedstocks used in this process are mostly oil and fats. So, the oil and fats are mostly consists of the triglyceride and FFA. So, the triglyceride which is present in the liquid feedstock reacts with the hydrogen and the hydrogen which is used in this process it is in the excess.

And this is the hydrogen feed line to the reactor here. And this entire reaction is carried out at relatively higher temperature and pressure between 4 to 15 mega Pascal with the help of heterogeneous catalyst, and followed by that the hydrogen analysis step that is also called as a propane cleave is performed by inserting more hydrogen to break this glycerol compound and resulting in the propane and chain of free fatty acids, followed by that three reactions are performed simultaneously in this process that is called as a decarboxylation reaction. And hydro deoxygenation reaction and these reactions are performed simultaneously to form the desired straight chain alkanes during this process. And after the hydrotreatment reaction the product enters a gas liquid separation chamber here where the gases in these sections are separated out.

And the gases are mostly consists of hydrogen, H_2S, carbon monoxide, CO_2, C_3H_8, and CH_4 along with the NH_3. And there are also liquid byproduct mainly consist of the organic liquids and water. And the production of this liquid product mainly varies with the process and the feedstock used for the hydrotreatment process. Recycling some gaseous product is a common technique to improve the yield and the efficiency of this particular process. The liquid product obtained here in the separation chamber follows the last stage that is a fractionation where it is fractionated and yield hydrocarbons of different ranges such as light gas, bio naphtha, biojet fuel and green diesel.

So, here the light gases range from C1 to C4, naphtha range from C5 to C11, biojet fuels range from C8 to C15 and the diesel like fuel range from C12 to C22.

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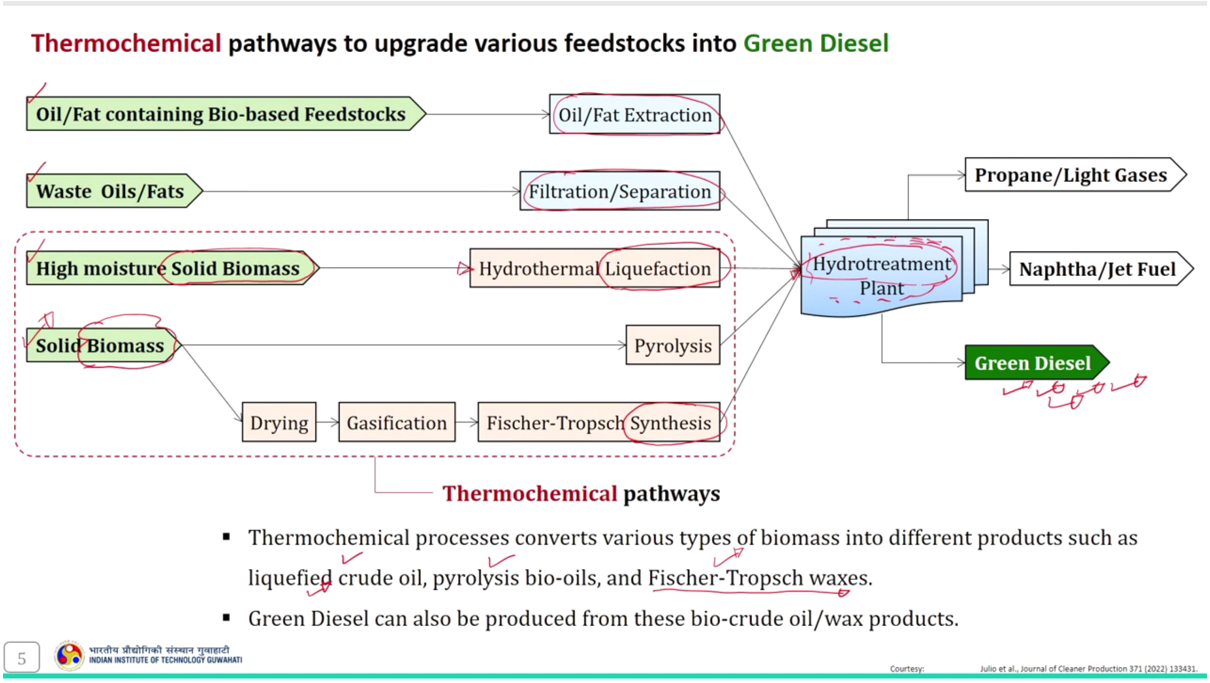

Thermochemical pathways to upgrade various feedstocks into Green Diesel

Oil/Fat containing Bio-based Feedstocks → Oil/Fat Extraction

Waste Oils/Fats → Filtration/Separation

High moisture Solid Biomass → Hydrothermal Liquefaction

Solid Biomass → Pyrolysis

Solid Biomass → Drying → Gasification → Fischer-Tropsch Synthesis

Hydrotreatment Plant → Propane/Light Gases; Naphtha/Jet Fuel; Green Diesel

Thermochemical pathways

- Thermochemical processes converts various types of biomass into different products such as liquefied crude oil, pyrolysis bio-oils, and Fischer-Tropsch waxes.
- Green Diesel can also be produced from these bio-crude oil/wax products.

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Courtesy: Julio et al., Journal of Cleaner Production 371 (2022) 133431.

And this schematic here it shows the different thermochemical routes that are available to reach paraffinic green diesel and the different biomass class suitable for the each conversion pathway. So, if you see here these are the different biomass classes suitable for the conversion to produce paraffinic diesel. And this schematic also it provides information on the different thermochemical processes to upgrade the different biomass liquid samples such as liquefied crude oil, pyrolysis biooil and the liquid fuel produced through Fischer-Tropsch synthesis process that is Fischer-Tropsch waxes. So, if you look at this particular chart the oils and fats containing bio-based feedstock after pretreatment can be hydrated to produce green diesel.

Similarly the waste oils and the fats after pretreatment operation that means after removing the impurities can be hydrated to produce green diesel. However, when the high moisture containing solid biomass is used as a feedstock then this particular biomass first converted using the hydrothermal liquefaction process which produces liquefied crude oil as a product. And this liquefied crude oil can further be upgraded using this hydrotreatment process to produce green diesel. So, this is another advantage of this particular process here, the liquefied crude oil obtained after the hydrothermal liquefaction process can further be upgraded using this hydro treatment process to produce green diesel. And hence this particular process can also be considered as an upgradation process to convert the various feedstocks into green diesel.

Similarly, solid biomass with relatively low moisture content feedstock, if it is being used for the conversion operation then it can first be pyrolyzed to produce the pyrolysis bio oils. And the produced bio oil can be upgraded using this hydrothermal process. Or this biomass can be gasified first and can convert into a liquid fuel through Fischer-Tropsch synthesis process. And then produce liquid fuel other Fischer-Tropsch process can be upgraded using this hydro treatment process to produce green diesel. Likewise different routes are available to reach paraffinic renewable diesel.

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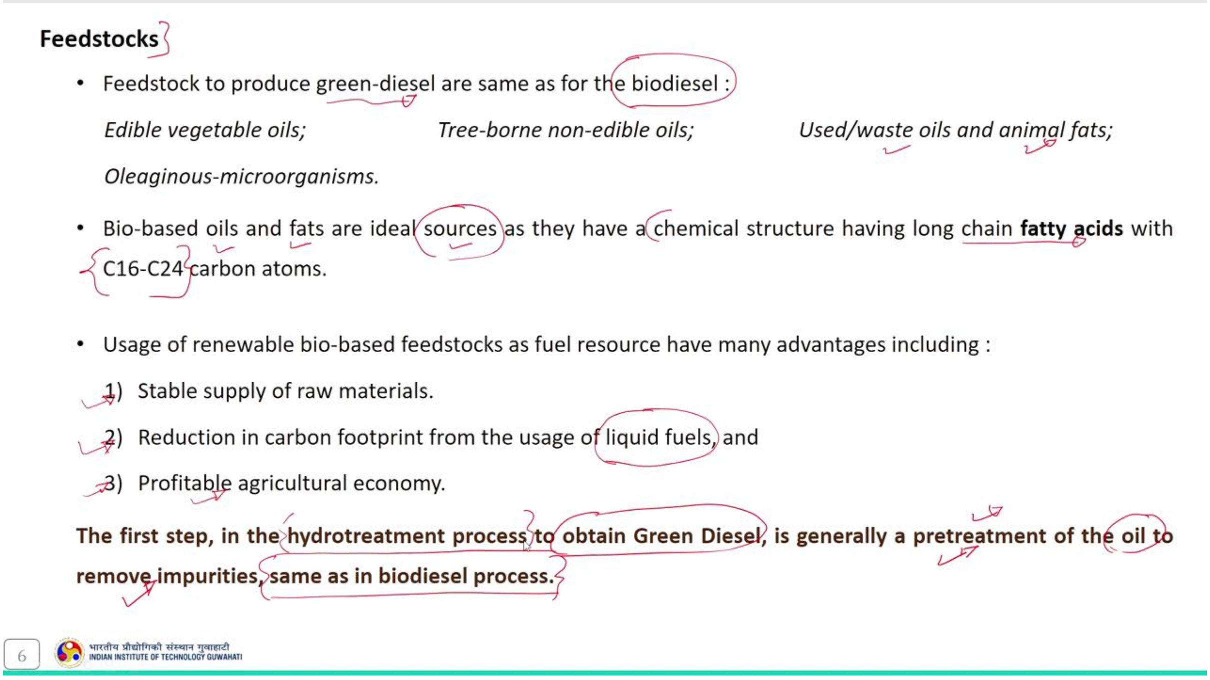

Feedstocks

- Feedstock to produce green-diesel are same as for the biodiesel :

  Edible vegetable oils; *Tree-borne non-edible oils;* *Used/waste oils and animal fats;*

  Oleaginous-microorganisms.
- Bio-based oils and fats are ideal sources as they have a chemical structure having long chain **fatty acids** with C16-C24 carbon atoms.
- Usage of renewable bio-based feedstocks as fuel resource have many advantages including :
  1) Stable supply of raw materials.
  2) Reduction in carbon footprint from the usage of liquid fuels, and
  3) Profitable agricultural economy.

The first step, in the hydrotreatment process to obtain Green Diesel, is generally a pretreatment of the oil to remove impurities, same as in biodiesel process.

So, as discussed in the previous slide, the feedstock used to produce green-diesel are same as used for the biodiesel synthesis process, and it includes edible, vegetable oils, tree born non edible oils, waste oils and fats, and olegenous microorganisms. Olegenous microorganism in the sense the microorganisms which contains lipids so the lipid produced from this olegenous microorganism can also be used as a feedstock for the green diesel synthesis. The reason for selection this kind of feedstock material for the green diesel synthesis is the bio-based oils and fats are ideal sources as they have chemical structure having long chain fatty acids with C16 to C24 carbon atom in its composition. And the uses of such renewable bio-based feedstock as a fuel source have many advantages in the sense stable supply of raw material, reduction in the carbon footprint from the uses of this liquid fuels and also profitable agriculture economy.

And as we discussed before the first step in the hydro treatment process to obtain this green diesel is generally a pre-treatment step that is basically the pre-treatment of the oil to remove the impurities. So, if the oil contains certain impurities because as we mentioned earlier, the waste oils as well as the animal fats are also used as a feed material for this particular process. So, the waste which is present in the oil can be removed using this pre-treatment operation and this pre-treatment operations are same as out of the operation used in the bio diesel synthesis process. And after this pre-treatment the pre-treated oil can be used as a feed for the hydro treatment process.

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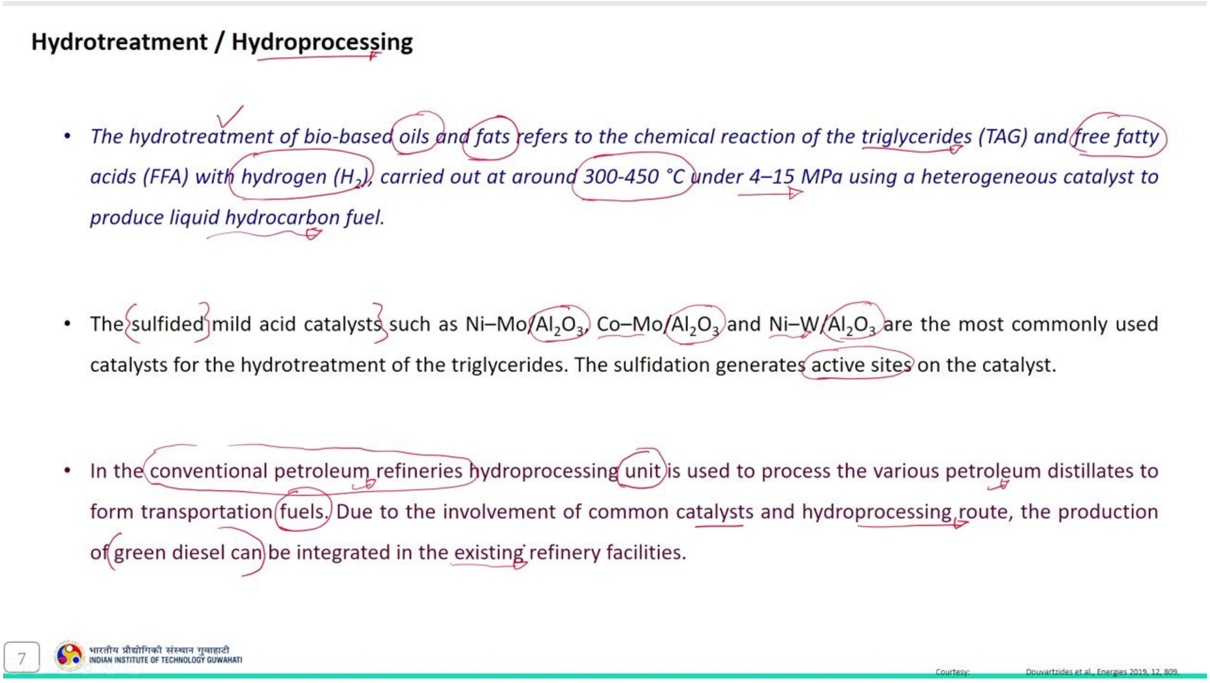

Hydrotreatment / Hydroprocessing

- *The hydrotreatment of bio-based oils and fats refers to the chemical reaction of the triglycerides (TAG) and free fatty acids (FFA) with hydrogen (H_2), carried out at around 300-450 °C under 4–15 MPa using a heterogeneous catalyst to produce liquid hydrocarbon fuel.*
- The sulfided mild acid catalysts such as Ni–Mo/Al_2O_3, Co–Mo/Al_2O_3 and Ni–W/Al_2O_3 are the most commonly used catalysts for the hydrotreatment of the triglycerides. The sulfidation generates active sites on the catalyst.
- In the conventional petroleum refineries hydroprocessing unit is used to process the various petroleum distillates to form transportation fuels. Due to the involvement of common catalysts and hydroprocessing route, the production of green diesel can be integrated in the existing refinery facilities.

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Courtesy: Douvartzides et al., Energies 2019, 12, 809.

So, what is hydrotreatment? That is also termed as hydro-processing. So, the hydrotreatment of the bio based oils and fats it refers to the chemical reaction of triglycerides. So, as we are discussing mostly on the feed materials as oils and fats, so these oils and fats contain triglycerides and free fatty acids. So, during this hydro treatment process these oils and fats that means the triglycerides and free fatty acids reacts with hydrogen. And the hydrogen also used in this process it is in excess. And this reaction is carried out at around 300 to 450 °C and pressure 4 to 15 MPa using a heterogeneous catalyst to produce liquid hydrocarbon fuel.

And the advantage of this process is it produces liquid hydrocarbon fuel which has properties similar to that of the petrol diesel. And the catalyst used in this process is a sulfided mild acid catalyst such as nickel molybdenum, aluminum oxide so this is support, cobalt molybdenum this is also support here or nickel tungsten with alumina oxide. And these are the most commonly used catalysts for the hydrotreatment process. And this sulfidation this is required because then it generates the active sites on the catalyst. And another advantage of this hydrotreatment process is- it has lot of similarities with the existing process used in the petroleum refineries.

In the conventional petroleum refineries hydroprocessing unit is used to process the various petroleum distillates to form transportation fuels. And due to involvement of the common catalysts as well as the hydro-processing route the production of this green diesel this can be integrated in the existing refinery facilities. And that is what the advantage of this process is. As I mentioned that it has lot of similarities with the existing hydro-processing unit in the conventional petroleum refineries. So, it can be easily integrated in the existing refinery facility.

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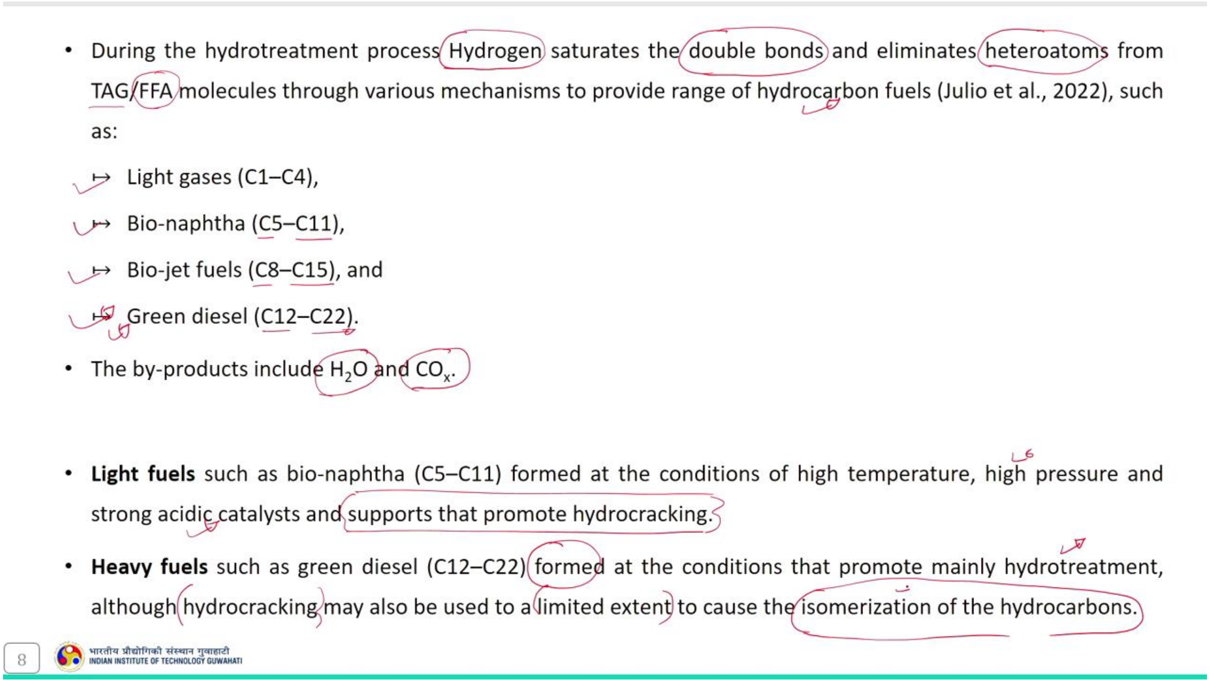

- During the hydrotreatment process Hydrogen saturates the double bonds and eliminates heteroatoms from TAG/FFA molecules through various mechanisms to provide range of hydrocarbon fuels (Julio et al., 2022), such as:
    - ↦ Light gases (C1–C4),
    - ↦ Bio-naphtha (C5–C11),
    - ↦ Bio-jet fuels (C8–C15), and
    - ↦ Green diesel (C12–C22).
- The by-products include H_2O and CO_x.

- **Light fuels** such as bio-naphtha (C5–C11) formed at the conditions of high temperature, high pressure and strong acidic catalysts and supports that promote hydrocracking.
- **Heavy fuels** such as green diesel (C12–C22) formed at the conditions that promote mainly hydrotreatment, although hydrocracking may also be used to a limited extent to cause the isomerization of the hydrocarbons.

So, during this hydro treatment process as mentioned earlier as well it uses excess amount of hydrogen. And it saturates the double bonds present in the feedstock, and also eliminates hetero atoms from triglycerides or free fatty acid molecule through various mechanisms to provide range of hydrocarbon fuels. And it produces hydrocarbon fuel such as light gases, bio naphtha in the range of C5 to C11, bio jet fuels C8 to C15, and green diesel that is in the range of C12 to C22. Along with this it also produces the byproduct which includes water and COx that is carbon monoxide or CO_2. And this bio naphtha which is termed as a light fuel, it formed at the condition of high temperature and high pressure and strong acidic catalyst and the support that promote the hydro caking reaction.

Similarly the green diesel that is termed as a heavy fuel formed at the condition that promotes mainly hydrotreatment. Although the hydro caking may also be used to a limited extent to cause the isomerization of the hydrocarbon that is called as a branching of the paraffin. So, during this isomerization operation it produces branched paraffin.

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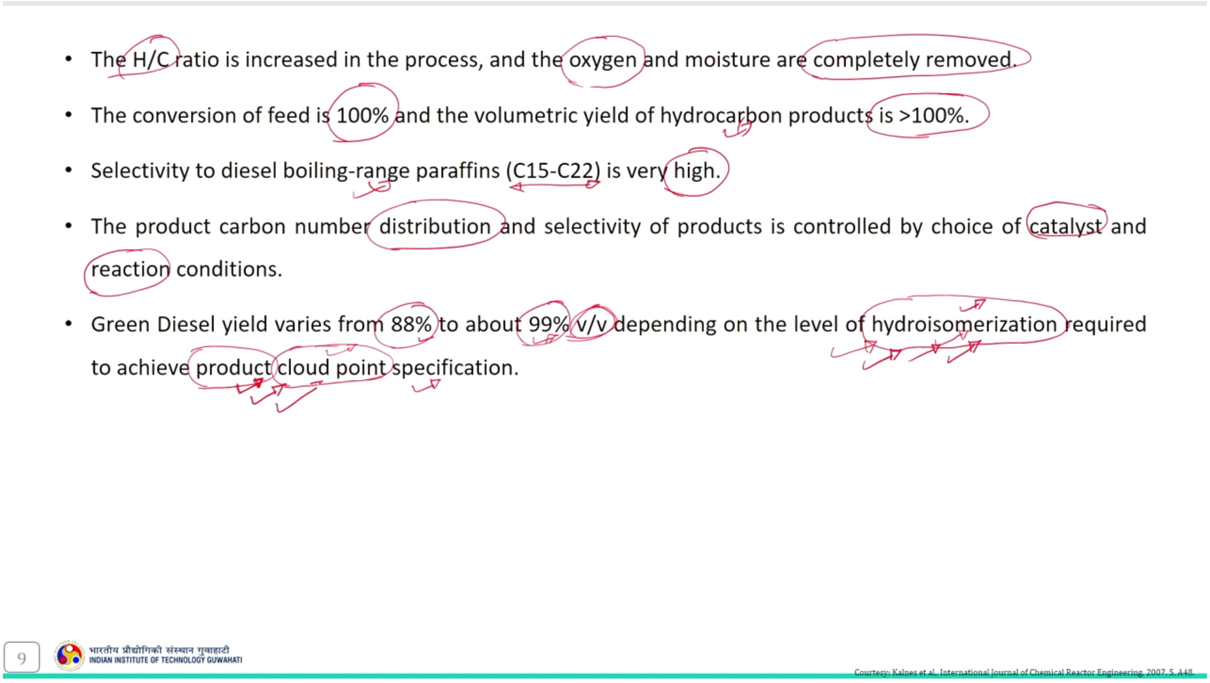

- The H/C ratio is increased in the process, and the oxygen and moisture are completely removed.
- The conversion of feed is 100% and the volumetric yield of hydrocarbon products is >100%.
- Selectivity to diesel boiling-range paraffins (C15-C22) is very high.
- The product carbon number distribution and selectivity of products is controlled by choice of catalyst and reaction conditions.
- Green Diesel yield varies from 88% to about 99% v/v depending on the level of hydroisomerization required to achieve product cloud point specification.

Courtesy: Kalnes et al., International Journal of Chemical Reactor Engineering, 2007, 5, A48.

So, during this process the H/C ratio increased and the oxygen and the moisture are completely removed. So, as we mentioned earlier the oxygens are completely removed during this particular hydrotreatment process.

And here the conversion of the feed is around 100% and the volumetric yield of the hydrocarbon product is significantly high. However, the selectivity to diesel boiling range paraffin is also very high during the hydro treatment process. And the paraffin range here is C15 to C22 as we mentioned earlier. And the product carbon number distribution and the selectivity of the product are controlled by choice of the catalyst as well as the reaction conditions. Even this green diesel yield also varies from 88% to about 99% that is on the carbon volume basis.

And it all depends on the level of the hydro isomerization reaction which is required to achieve product cloud point specification. If the product cloud point specification needs to be of specific value then the level of isomerization need to be controlled during the reaction so that it can achieve product cloud point of certain specification. And that is the another advantage of the hydro isomerization process where it can lead to a production of specific quality fuel.

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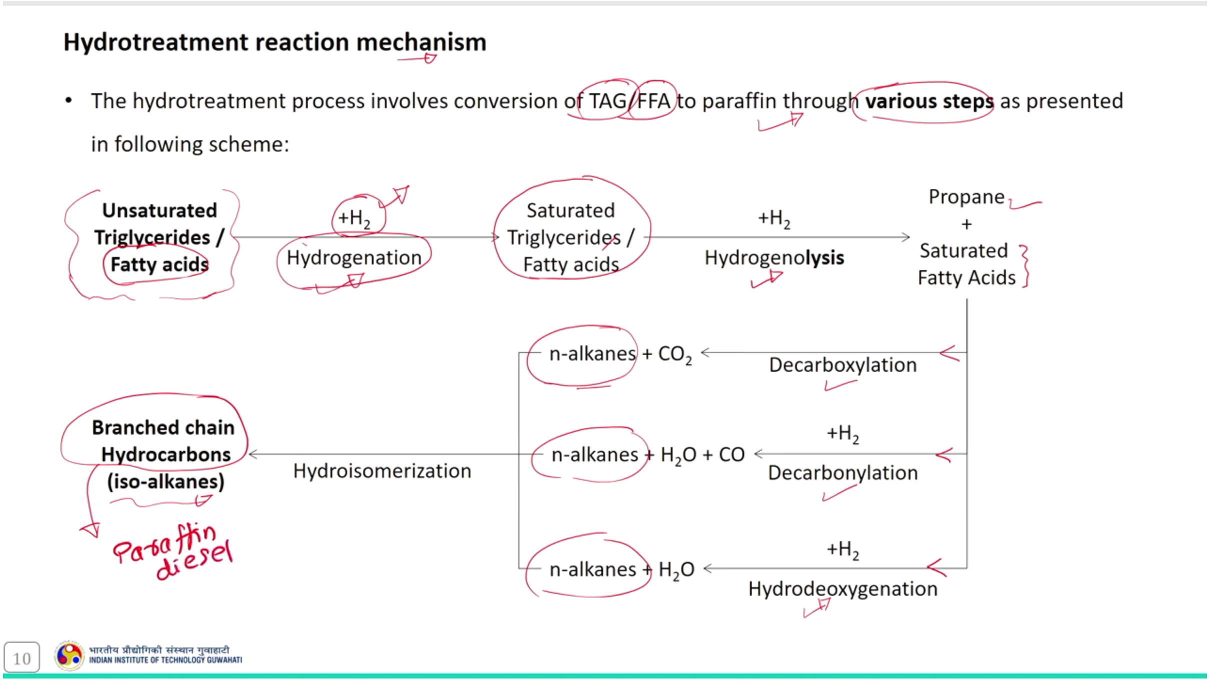

Hydrotreatment reaction mechanism

- The hydrotreatment process involves conversion of TAG/FFA to paraffin through **various steps** as presented in following scheme:

Unsaturated Triglycerides / Fatty acids

$+H_2$

Hydrogenation

Saturated Triglycerides / Fatty acids

$+H_2$

Hydrogenolysis

Propane + Saturated Fatty Acids

n-alkanes + CO_2

Decarboxylation

n-alkanes + H_2O + CO

$+H_2$

Decarbonylation

n-alkanes + H_2O

$+H_2$

Hydrodeoxygenation

Hydroisomerization

Branched chain Hydrocarbons (iso-alkanes)

Paraffin diesel

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So now, let us move on to the hydrotreatment reaction mechanism. So, as we discussed earlier this hydrotreatment process it involves the conversion of triglycerides and free fatty acids to paraffinic diesel through various step as presented in the following scheme.

In hydrotreatment process the first step is generally the pretreatment of the oil to remove the impurities. And once the impurities are removed the pretreated oil is used for the hydrotreatment process in which the hydrogenation of the pretreated oil is carried out in presence of excess hydrogen at relatively high pressure and the temperature and it gives saturated triglycerides and fatty acids. Similarly hydrogenolysis is performed by inserting more hydrogen to break this glycerol compounds and resulting in propane and a chain of free fatty acids. So, this particular process is also called as propane cleave process and followed by that three reactions are performed simultaneously to form a desired straight chain alkanes that is decarboxylation reaction, decarboxylation reaction and hydro deoxygenation reaction. And it forms straight chain alkanes as a product.

And all these three reactions are performed simultaneously in the process. And followed by that is a hydrocaking it also be used to a limited extent to cause the isomerization of the product to form the branch chain hydrocarbon that is isoalkanes and that is also called as paraffin diesel.

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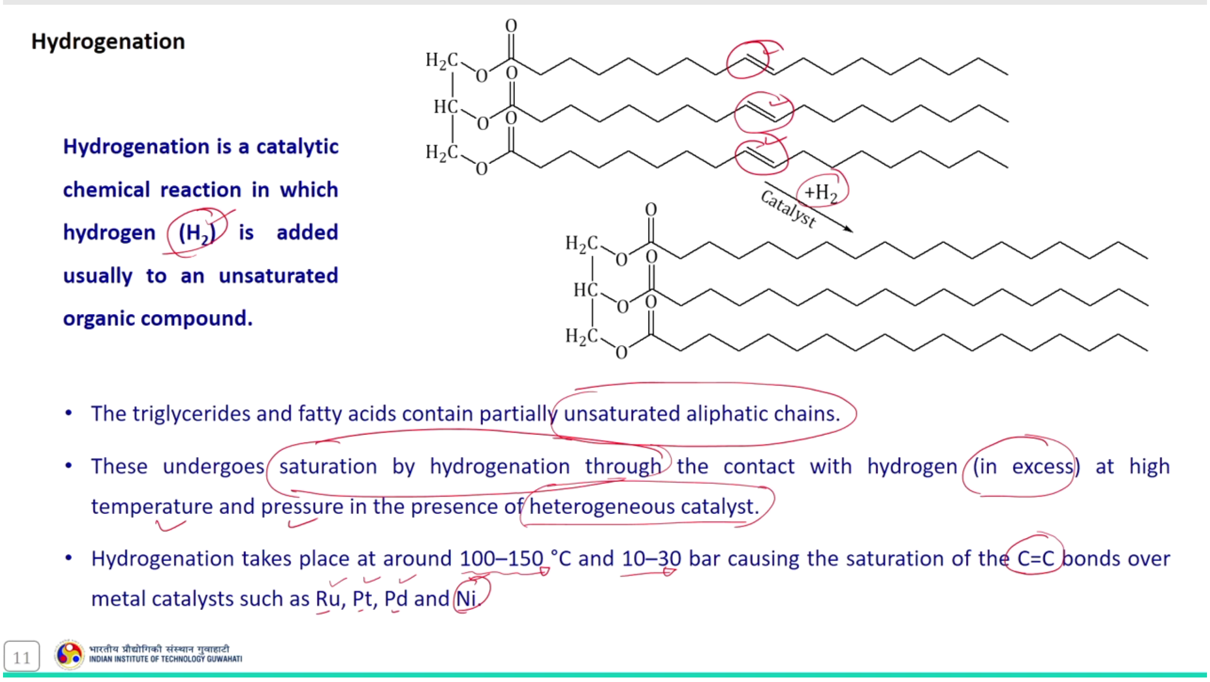

Hydrogenation

Hydrogenation is a catalytic chemical reaction in which hydrogen (H_2) is added usually to an unsaturated organic compound.

- The triglycerides and fatty acids contain partially unsaturated aliphatic chains.
- These undergoes saturation by hydrogenation through the contact with hydrogen (in excess) at high temperature and pressure in the presence of heterogeneous catalyst.
- Hydrogenation takes place at around 100–150 °C and 10–30 bar causing the saturation of the C=C bonds over metal catalysts such as Ru, Pt, Pd and Ni.

So, in this case now if you look at this hydrogenation reaction, so hydrogenation is a catalytic chemical reaction in which the hydrogen is added usually to an unsaturated organic compound. So, during this reaction the triglycerides and the fatty acids containing partially unsaturated aliphatic chains converts into a saturated aliphatic chains. And this undergoes the saturation by the hydrogenation through the contact with hydrogen and hydrogen use here it is in excess at relatively high temperature and pressure in the presence of heterogeneous catalyst, as we discussed earlier.

And this hydrogenation it takes place at around 100 to 150 °C, pressure around 10 to 30 bar and causing the saturation of the double bonds over the metal catalyst such as ruthenium, platinum, palladium and nickel. So, specific catalyst of choice needs to be selected for this operation to achieve product cloud point specification.

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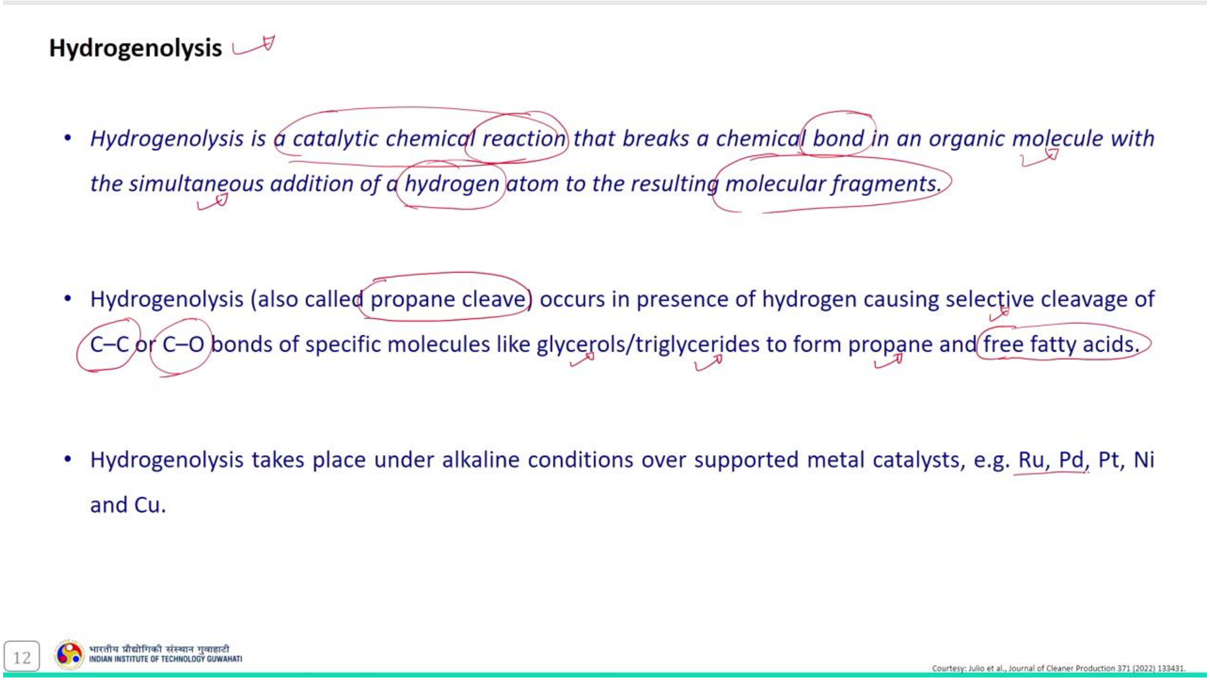

Hydrogenolysis

- *Hydrogenolysis is a catalytic chemical reaction that breaks a chemical bond in an organic molecule with the simultaneous addition of a hydrogen atom to the resulting molecular fragments.*
- Hydrogenolysis (also called propane cleave) occurs in presence of hydrogen causing selective cleavage of C–C or C–O bonds of specific molecules like glycerols/triglycerides to form propane and free fatty acids.
- Hydrogenolysis takes place under alkaline conditions over supported metal catalysts, e.g. Ru, Pd, Pt, Ni and Cu.

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Courtesy: Julio et al., Journal of Cleaner Production 371 (2022) 133431.

So, next is the hydrogenolysis reaction. So, it is a catalytic chemical reaction that breaks chemical bond in the organic molecule. So, in the previous reaction so in this case the unsaturation in the aliphatic undergoes the hydrogenation reaction to produce saturated compounds.

Whereas in this case it breaks the chemical bond in the organic molecule with the simultaneous addition of more hydrogen atom and resulting in the formation of molecular fragments. And this hydrogenolysis also called as a propane cleave as we discussed just one slide before. It occurs in the presence of hydrogen causing the selective cleavage of these bonds of specific molecules like glycerols, triglycerides to form propane and free fatty acids. And this process takes place under alkaline condition or supported metal catalyst. The catalyst as mentioned before the same catalyst can be used during this process.

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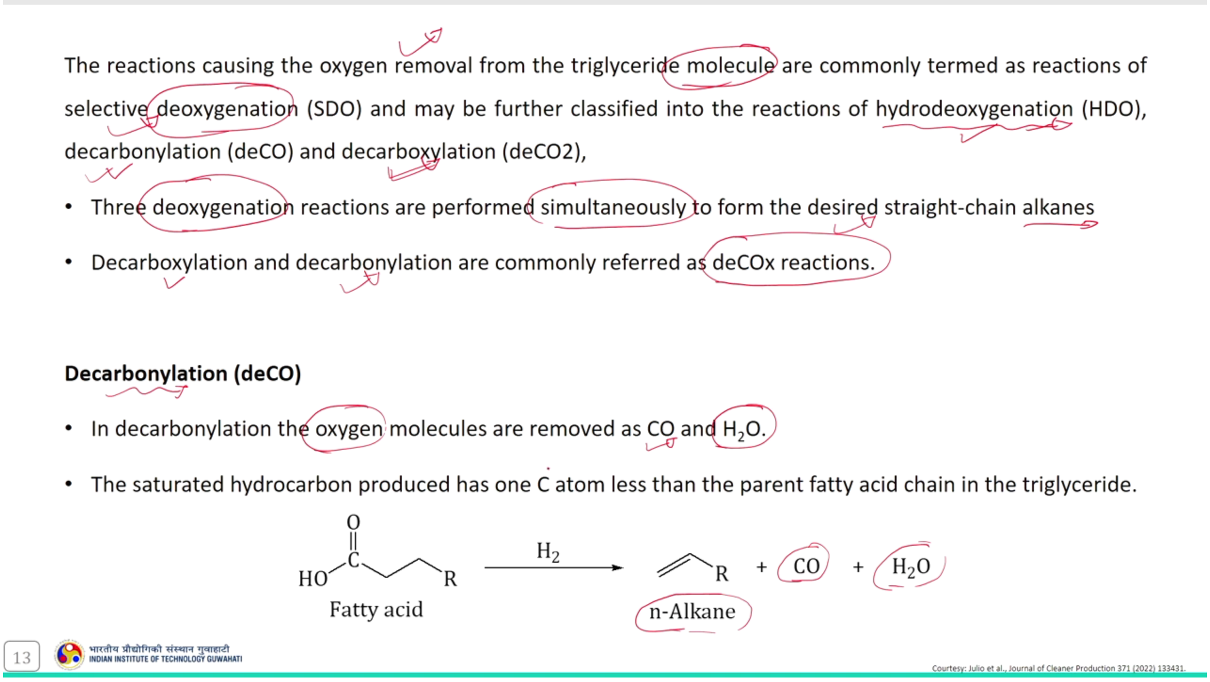

The reactions causing the oxygen removal from the triglyceride molecule are commonly termed as reactions of selective deoxygenation (SDO) and may be further classified into the reactions of hydrodeoxygenation (HDO), decarbonylation (deCO) and decarboxylation (deCO2),

- Three deoxygenation reactions are performed simultaneously to form the desired straight-chain alkanes
- Decarboxylation and decarbonylation are commonly referred as deCOx reactions.

Decarbonylation (deCO)

- In decarbonylation the oxygen molecules are removed as CO and H_2O.
- The saturated hydrocarbon produced has one C atom less than the parent fatty acid chain in the triglyceride.

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Courtesy: Julio et al., Journal of Cleaner Production 371 (2022) 133431.

And followed by that is the deoxygenation reaction in which the oxygen is removed from the triglyceride molecule. And this reaction is commonly termed as selective deoxygenation reaction and further be classified into the reaction of hydrodeoxygenation, decarboxylation and decarboxylation. Three deoxygenation reactions that are hydrodeoxygenation, decarboxylation and decarboxylation reaction, these reactions are performed simultaneously to form the desired straight chain alkanes. And if you recollect we just discussed this in the hydro treatment reaction mechanism, so these three reactions are performed simultaneously to produce desired alkanes. And here this decarboxylation and decarboxylation reactions are commonly referred as deCOx reaction.

Now let us see this decarboxylation reaction, first in decarboxylation reaction the oxygen molecules are removed as CO and H_2O. If you see this reaction here during this reaction the oxygen molecules are removed in the form of carbon monoxide and H_2O and it forms desired alkane as a product. And the saturated hydrocarbon produced as one carbon atom less than the parent fatty acid chain in the triglyceride.

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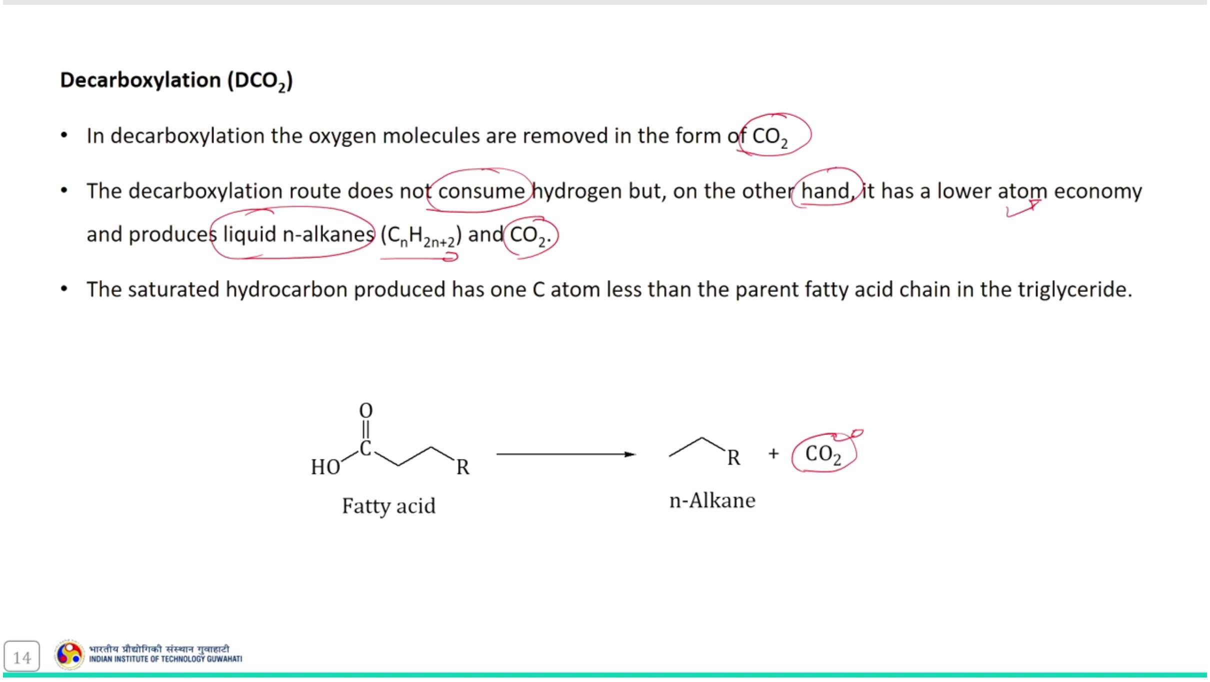

Decarboxylation (DCO_2)

- In decarboxylation the oxygen molecules are removed in the form of CO_2
- The decarboxylation route does not consume hydrogen but, on the other hand, it has a lower atom economy and produces liquid n-alkanes (C_nH_{2n+2}) and CO_2.
- The saturated hydrocarbon produced has one C atom less than the parent fatty acid chain in the triglyceride.

Similarly, in the decarboxylation reaction the oxygen molecules are removed but it is removed in the form of carbon dioxide. And in this process the decarboxylation route does not consume hydrogen. But on the other hand it has a lower atom economy and produces liquid n-alkanes and CO_2 as a product where it removes the oxygen from the feed material. And here in this case also the saturated hydrocarbon produced as one carbon atom which is less than the parent fatty acid chain in the triglyceride.

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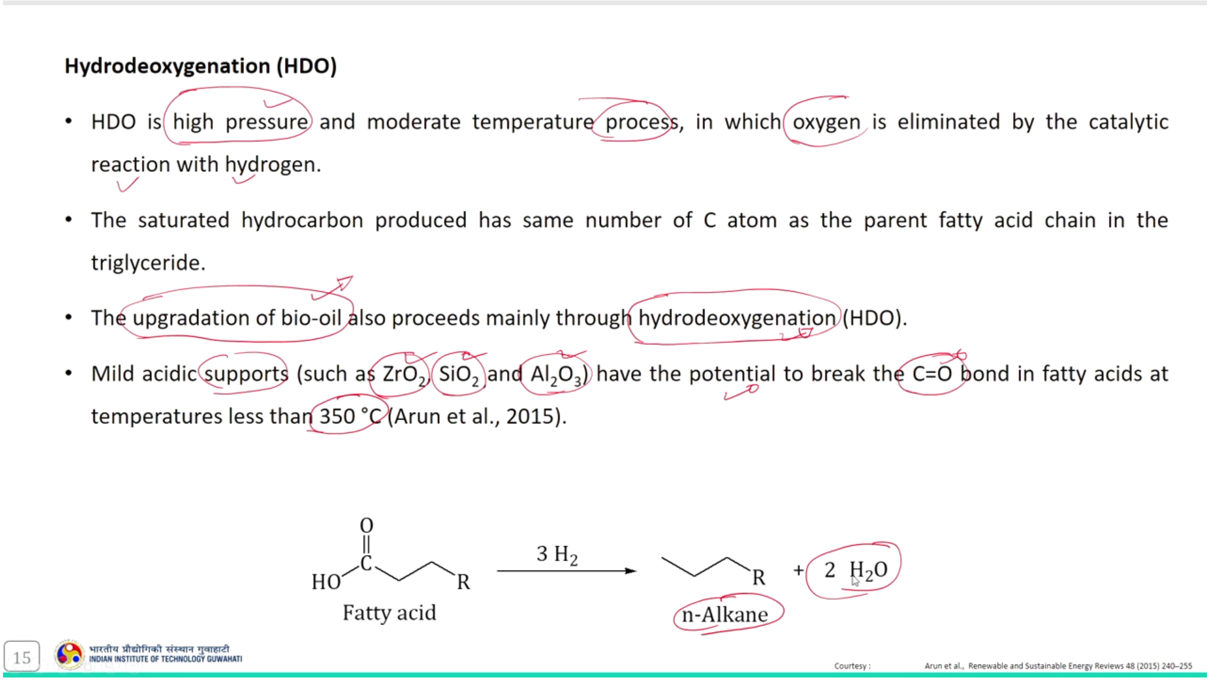

Hydrodeoxygenation (HDO)

- HDO is high pressure and moderate temperature process, in which oxygen is eliminated by the catalytic reaction with hydrogen.
- The saturated hydrocarbon produced has same number of C atom as the parent fatty acid chain in the triglyceride.
- The upgradation of bio-oil also proceeds mainly through hydrodeoxygenation (HDO).
- Mild acidic supports (such as ZrO_2, SiO_2 and Al_2O_3) have the potential to break the C=O bond in fatty acids at temperatures less than 350 °C (Arun et al., 2015).

Fatty acid $\xrightarrow{3\ H_2}$ n-Alkane + $2\ H_2O$

Courtesy : Arun et al., Renewable and Sustainable Energy Reviews 48 (2015) 240–255

So, next is the hydro deoxygenation reaction and it is performed at high pressure and temperature in which the oxygen is eliminated by the catalytic reaction with hydrogen. As we discussed before the up gradation of the bio oil also proceeds mainly through hydro deoxygenation process, in which the oxygen in the feed is eliminated by the catalytic reaction with hydrogen. And as we know bio oil contains significant amount of the oxygen.

So, once this oxygen is removed from the bio oil through this hydro-deoxygenation reaction then it produces relatively a high quality product. And the mild acidic supports have the potential to break this bond in the fatty acids at temperature even less than 350 degree Celsius. And these are basically act as a support in the catalyst and even the mild acidic support have this potential to break this bond in the fatty acid. And then it produces the desired alkane and releases oxygen in the form of water.

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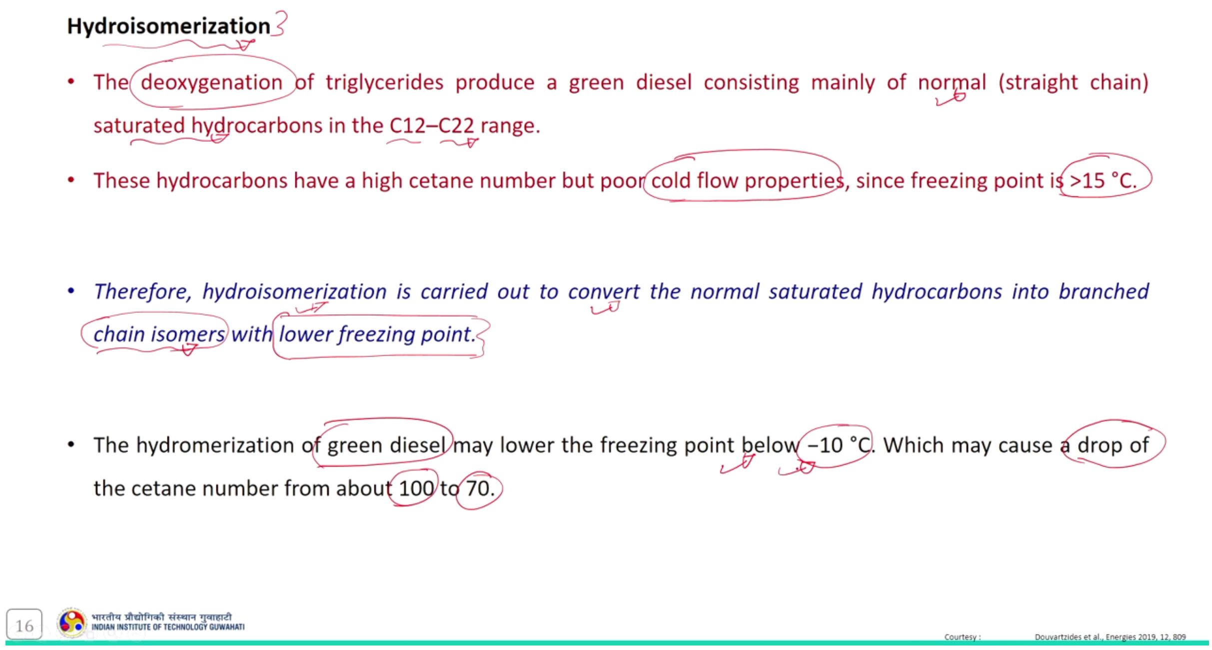

Hydroisomerization

- The deoxygenation of triglycerides produce a green diesel consisting mainly of normal (straight chain) saturated hydrocarbons in the C12–C22 range.
- These hydrocarbons have a high cetane number but poor cold flow properties, since freezing point is >15 °C.
- *Therefore, hydroisomerization is carried out to convert the normal saturated hydrocarbons into branched chain isomers with lower freezing point.*
- The hydromerization of green diesel may lower the freezing point below −10 °C. Which may cause a drop of the cetane number from about 100 to 70.

Courtesy : Douvartzides et al., Energies 2019, 12, 809

Followed by the deoxygenation reaction is the hydroisomerization of the produce alkanes. Because the deoxygenation of triglyceride it produces the green diesel consisting mainly of the normal saturated hydrocarbons in the range of C12 to C22. And these hydrocarbons they have high cetane number but possesses poor cold flow properties. And the freezing point is even greater than 15 degree Celsius. And because of that reason the hydro isomerization is carried out to convert these normal saturated hydrocarbons into branch chain isomers with lower freezing point. And that is what is termed as branch chain paraffins.

The hydroisomerization of this green diesel may lower the freezing point below even minus 10 degree Celsius, but during this process it may decrease the cetane number from 100 to 70. But in case if the product of specific quality or the specification need to be produced then such small alternate arrangement need to be performed to produce this green diesel.

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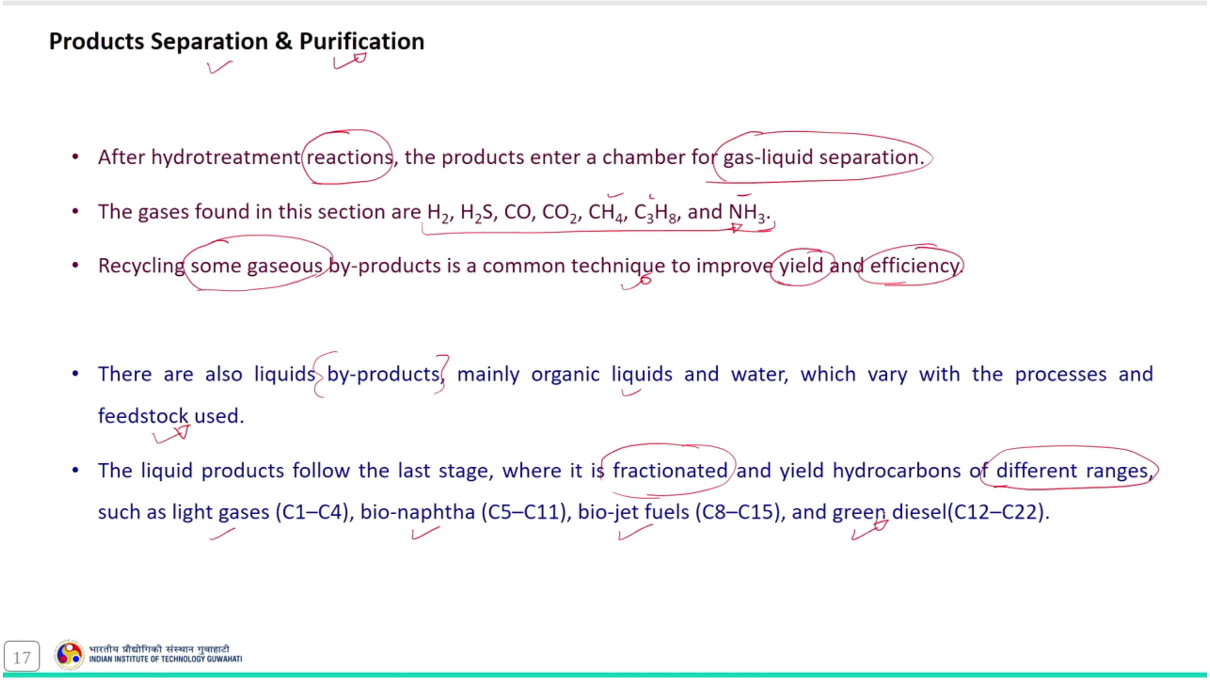

Products Separation & Purification

- After hydrotreatment reactions, the products enter a chamber for gas-liquid separation.
- The gases found in this section are H_2, H_2S, CO, CO_2, CH_4, C_3H_8, and NH_3.
- Recycling some gaseous by-products is a common technique to improve yield and efficiency.

- There are also liquids by-products, mainly organic liquids and water, which vary with the processes and feedstock used.
- The liquid products follow the last stage, where it is fractionated and yield hydrocarbons of different ranges, such as light gases (C1–C4), bio-naphtha (C5–C11), bio-jet fuels (C8–C15), and green diesel(C12–C22).

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Followed by that is the product separation and the purification operation as we discussed in the schematic of hydro treatment process. Then the products enter the chamber of gas liquid separation and the gases found in this section are mostly the gases as listed here. And recycling of some of this gaseous byproduct is common technique to improve the process yield and its efficiency.

And it also produces liquid byproduct mainly organic acids and water which vary with the processes and the feedstock used during the hydrotreatment operation. And the last stage in the process is fractionation where it yield hydrocarbon of different ranges such as light gases, bio naphtha, biojet fuels and green diesel.

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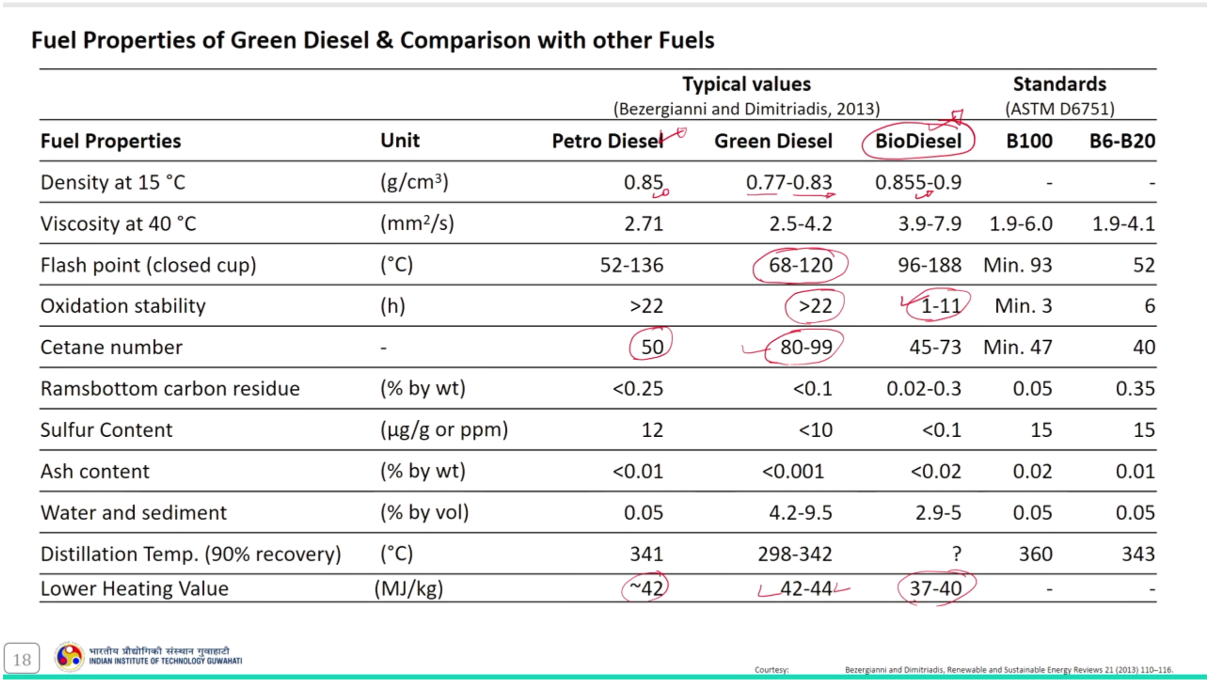

Fuel Properties of Green Diesel & Comparison with other Fuels

		Typical values (Bezergianni and Dimitriadis, 2013)			Standards (ASTM D6751)	
Fuel Properties	**Unit**	**Petro Diesel**	**Green Diesel**	**BioDiesel**	**B100**	**B6-B20**
Density at 15 °C	(g/cm³)	0.85	0.77-0.83	0.855-0.9	-	-
Viscosity at 40 °C	(mm²/s)	2.71	2.5-4.2	3.9-7.9	1.9-6.0	1.9-4.1
Flash point (closed cup)	(°C)	52-136	68-120	96-188	Min. 93	52
Oxidation stability	(h)	>22	>22	1-11	Min. 3	6
Cetane number	-	50	80-99	45-73	Min. 47	40
Ramsbottom carbon residue	(% by wt)	<0.25	<0.1	0.02-0.3	0.05	0.35
Sulfur Content	(µg/g or ppm)	12	<10	<0.1	15	15
Ash content	(% by wt)	<0.01	<0.001	<0.02	0.02	0.01
Water and sediment	(% by vol)	0.05	4.2-9.5	2.9-5	0.05	0.05
Distillation Temp. (90% recovery)	(°C)	341	298-342	?	360	343
Lower Heating Value	(MJ/kg)	~42	42-44	37-40	-	-

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Courtesy: Bezergianni and Dimitriadis, Renewable and Sustainable Energy Reviews 21 (2013) 110–116.

And this table here it depicts the fuel properties of the green diesel and its comparison with the other fuels including bio diesel. So, in this case the density range of the green diesel is between 0.77 to 0.83, which is in acceptable range with that of the diesel and even bio diesel. Green diesel has a flash point of 68 to 120 degree Celsius thus it is safe for handling and storage. Green diesel is a new biofuel which however is currently produced in industrial scale. Similarly the oxidation stability of the green diesel is greater than even 22 hours which is much better than the bio diesel. The cetane number of green diesel ranges between 80 to 99 which is much high compared to even standard diesel.

And hence it is rendering it a competitive diesel substitute. Even its net heating value is between 42 to 44, which is almost similar to that of the conventional diesel and even higher than the bio diesel. Overall these fuel characteristics of the green diesel are compatible with the fossil diesel and even superior to that of the bio diesel and hence rendering it a competitive diesel substitute. So, these are the references which you can refer to know more in detail about the green diesel synthesis process. So, this is all about green diesel synthesis from the bio based feed stock.

So, the next lecture, that will be the first lecture of module 7. We will discuss origin and composition of solid fuels properties of coal, coal classification, properties and storage of coal, coal carbonization, gasification and liquefaction processes.

Thank you.