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Hydroprocessing Of Jatropha Oil To Produce Green Fuels

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1.Abstract: Mesoporous α - alumina used as a supports to prepare hydro treating(sulfideTMN/ α - Al_2O_3) catalyst. The hydroprocessing catalyst was used under typical hydroprocessing conditions to convert non- edible jatropha oil into saturated hydrocarbons. The Hydroprocessing catalyst was more selective for diesel range (250 -360°C) hydrocarbons.The hydrodeoxygenation pathway for oxygen removal from triglycerides seems to be favored over hydrotreating catalyst with yields Green Diesel.

KeywordsMesoporous, Hydrotreating, Hydrodeoxygenation, Triglycerides, Green Diesel.

2. Introduction

The production of biofuels is increasing rapidly due to sharply increasing in the petroleum prices, government regulations and environmental concern throughout the worldwide. The hydroprocessing of jatropha oil (plant derived oil) with refinery gas oil in the presence of hydrotreating catalyst namely Titanium, Molybdenum and Nickel (TMN/ α -alumina) in typical hydroprocessing conditions such as Temperature: 300-400 °C, Pressures ranges: 60-80 bar H_2/HC ratio: 1000-2000 lit/hr. and LHSV: 1-10 hr.

Hydroprocessing is used in the petroleum refinery to crack larger molecules and to remove sulfur, nitrogen and other metals from petroleum derived feed stocks such as gas-oil and heavy oil. Sulfided hydrocracking (such as Ni-W/ SiO_2 - Al_2O_3) and

hydrotreating (such as NiMo/ Al_2O_3 , Co-Mo/ Al_2O_3 ,) catalysts are typically used¹. Similar catalysts could also be used for deoxygenation of glycerides and fatty acid molecules from vegetable oil, waste restaurant oil, algae oil, jatropha oil etc. The process ends with fuels which would be desired viscosity, low atomization and lubricity. The following process is more suitable than Fatty Acid Methyl Esters (FAME) produced by transesterification of triglycerides. Since transesterification processes products requires some modification in engine with its poor performance in cold weather. For

bulky triglyceride molecules would require larger pore size catalysts to overcome diffusion limitations. Hydroprocessing has been reported to produce straight chain alkanes from fatty acid triglycerides of vegetable oil, tall oil and animal fat.

In general deoxygenation can refer to several reactions; mainly it contains decarboxylation, decarboxylation, dehydration, and hydro deoxygenation, and is often accompanied by hydrogenation of double bonds². It is generally accepted that mesoporous materials offer a great potential as support for the active species in the catalytic processes. Mesoporous alumina supports offer several advantages over conventional alumina, such as high specific surface area such as high specific surface area resulting in a possibility to achieve high dispersion and loading of active species on the support and narrow pore size distribution with pore size ranging from 2 to more than 10nm enabling the access of large organic molecules to the active sites situated inside the pores.

3. Experimental

Plant oils mainly consist of triglycerides with typically 1-2% free fatty acid content. The chemical structure of a triglyceride molecule is shown in (red= oxygen, white= hydrogen, grey= carbon atoms)

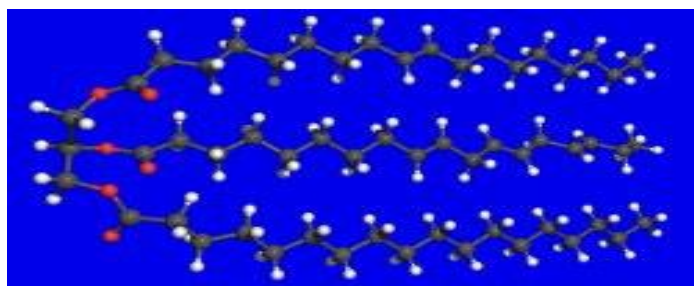


Fig. 1 Chemical Structure of Triglycerides

Triglycerides and fatty free acids both contain relatively long, linear aliphatic hydrocarbon chains. The aliphatic hydrocarbon always contains an even number of carbon atoms, is generally unsaturated, and also corresponds to the carbon number range typically found in diesel fuels. There is also a three carbon "backbone" in the triglyceride molecule. The *Jatropha* oil an ideal source for triglycerides which does not compete with arable for food and may yield more biofuel per hectare than Canola, Sunflower and Soybean. The *Jatropha* has 476 species and distributed throughout the world. Among them, 12 species are recorded in India³.

Typical hydrotreating catalysts are composed of molybdenum or tungsten as the active metal, nickel or cobalt as the promoter and the support material such as alumina, silica-alumina, silica or zeolites. The concentration of the metals on the support usually varies from 8 to 25 wt% for the active metal and from 1 to 4 wt% for the promoter.

Triglycerides molecules generally consist of condensation of glycerol (C_3 - backbone of the molecule) and three carboxylic acids (also termed as fatty acids). Although the triglycerides form is common to almost all the oils and fats, the chain lengths and degree of unsaturation vary significantly. Since the feedstocks is generally consists of small amount of impurities such as sulphur and nitrogen and therefore the required HDS conversion is lower when co-processing renewable feeds. The double bond hydrogenation reactions have saturated the fatty acids, the connection between fatty acids and C_3 backbone may be broken by one of at least two distinct reaction pathways^{4,5}.

The first pathway involves a complete hydrogenation to form six moles of water, one mole of propane and three moles of normal paraffin with the same chain length as the fatty acid chains ($n-C_{18}$ and $n-C_{22}$ in the case of rapeseed oil) per mole of triglyceride. This pathway is generally termed hydrodeoxygenation or simply HDO pathway. The other pathways involves a decarboxylation step, where three moles of CO_2 , one mole of propane and three moles of normal paraffins with a chain length, which is one carbon-atom shorter than the fatty acid chains ($n-C_{17}$ and $n-C_{21}$ in the case of rapeseed oil) are produced. Since the paraffins produced are in the diesel boiling range, this is the reason why the diesel hydrotreater unit is choice for the processing of such feeds⁵. As both carbon dioxide and carbon monoxide are produced, two additional reactions used to be taken into accounts. Hydrotreating catalysts are known to be active for both reverse water gas shift reaction.

The relative usage of decarboxylation and hydrodeoxygenation reaction routes is of major importance for hydrotreating process as these influences the hydrogen consumption, product yields, catalyst inhibition and heat balance. If all the triglycerides react by the decarboxylation

route, seven moles of hydrogen will be consumed as comparison to the sixteen moles of hydrogen consumed when all triglycerides are converted via the hydrodeoxygenation consumption. However, if when all the CO_2 produced is shifted to CO, and the entire CO formed is subsequently converted into CH_4 , a total 19 moles of H_2 will be consumed by the decarboxylation route. The liquid products were withdrawn after stabilization of reaction conditions (6h) in two hours intervals (at each temperature) and off gas-line gas chromatography after separation of water phase⁶.

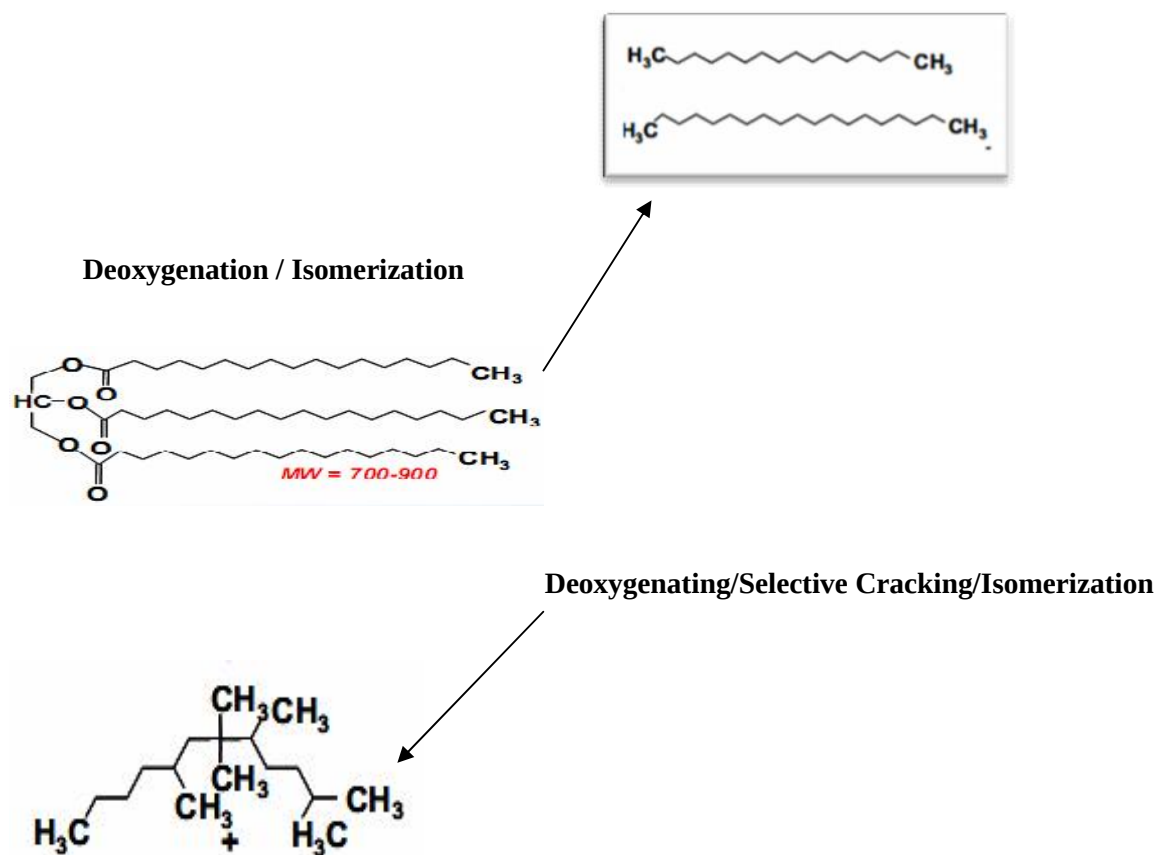


Figure 2. Reaction Mechanism

4. Results And Discussions

The loaded TMN catalyst has the following composition 4% Ti, 8% Mo, and 3% Co. The weight and volume of the catalyst is 1.7 ml and 0.707gm respectively. The catalyst is loaded in a tubular reactor. As seen from above figure 3, the >C15 yield is constant throughout the increase of temperature from 300 to 340°C. We also observe that the yield of C15-C18 fraction decreases up to 320°C from 60 % to 10 % and increases slightly up to 340°C for 30% yield. In the case of <C18 fraction the yield increase with respect to temperature up to 320°C and then there is some decrease in yield. When we compare the yield fractions of C15 –C18 products and the oligomerized products we observe that initially at lower temperature the triglycerides were being converted to <C18 products whereas at

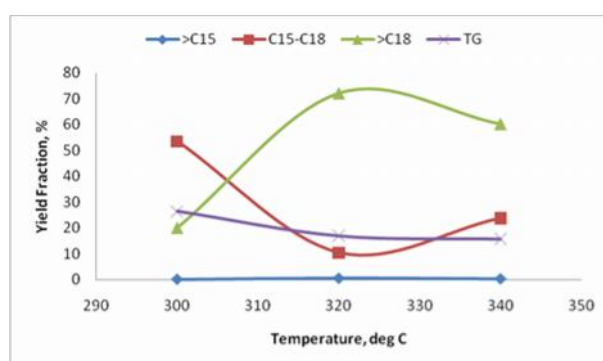
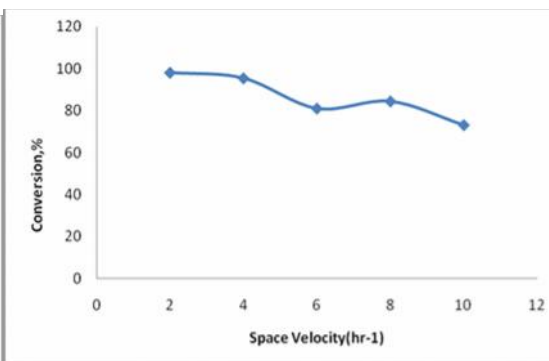
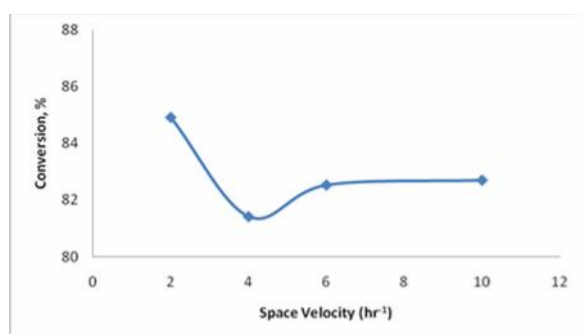
higher temperatures there is decrease in the oligomerization yield (<C18) and increase in the corresponding C15-C18 yield. Probably there is a change in the reaction pathway observed at these temperatures. The unconverted triglycerides decrease as increase in temperature which was very obvious. As seen from figure 4, the conversion slightly decreases as space velocity increases. Thus for better conversion of triglycerides we have to keep space velocity as lower as possible. But we see that there is some increase in conversion at 8 hr⁻¹ space velocity which shows that there is change in reaction pathways at this space velocity. In case in 320°C (Figure 5) the conversion decreases rapidly and slightly increases at 6 hr⁻¹ space velocity and then become constant as increase in space velocity. This shows that as increase in temperature is favorable up to a certain space velocity.

Table 1. Conversion at 300°C

Sr. No.	Catalyst	Temp(°C)	Space Velocity (h ⁻¹)	Pressure (bar)	H ₂ /HC (lit/hr)	>C15	C15-C18	<C18	TG	Conversion (%)
1	TMN	300	10	80	1200	0.18	53.508	19.923	26.389	73.1546287
2	TMN	300	6	80	1200	0.761	21.725	58.82	18.694	80.982706
3	TMN	300	4	80	1200	2.24	23.586	69.55	4.624	95.2960326
4	TMN	300	2	80	1200	0.091	14.48	83.404	2.025	97.9399797

Table 2. Conversion at 300°C

Sr. No.	Catalyst	Temp(°C)	Space Velocity (hr ⁻¹)	Pressure (bar)	H ₂ /HC (lit/hr.)	>C15	C15-C18	<C18	TG	Conversion (%)
1	TMN	320	10	80	1200	0.547	10.409	72.042	17.002	82.7039674
2	TMN	320	6	80	1200	0.154	19.2	63.475	17.171	82.5320448
3	TMN	320	4	80	1200	0.144	25.166	56.425	18.265	81.4191251
4	TMN	320	2	80	1200	0.713	34.054	50.404	14.829	84.9145473

**Fig-3**Yield as a function of various temperatures**Fig -4** Conversion as a function of space velocity (300°C T, 80bar P, 1200 H₂/HC)**Fig-5** Conversion as a function of space velocity (320°C T, 80bar P, 1200 H₂/HC)

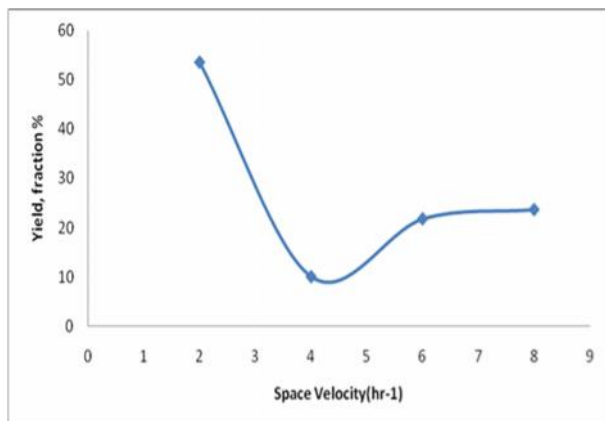


Figure-6 Yield (C15-C18) as a function of space velocity at (300°C, 80 bar P, 1200 H₂/HC)

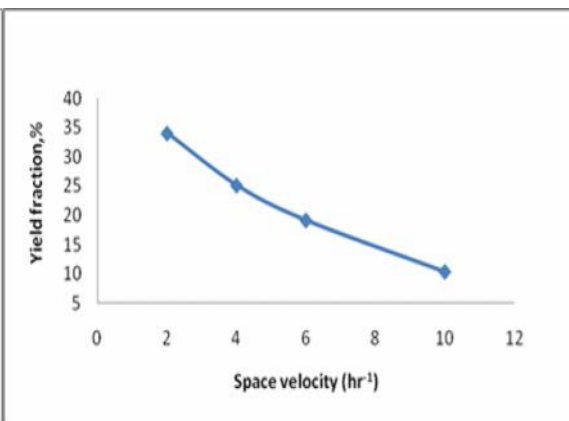


Figure-7 Yield C15-C18 as a function of space velocity at (320°C, 80 bar P, 1200 H₂/HC)

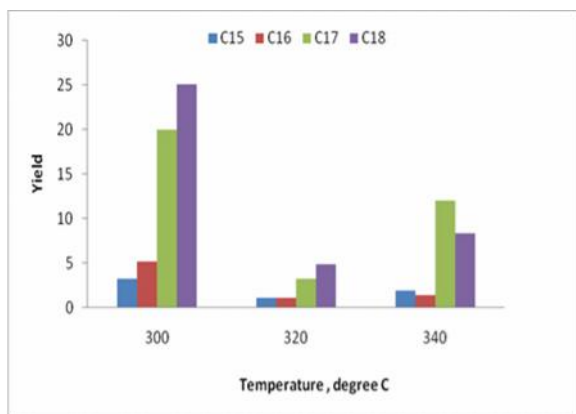


Figure- 8 Comparison of yields at various temperatures

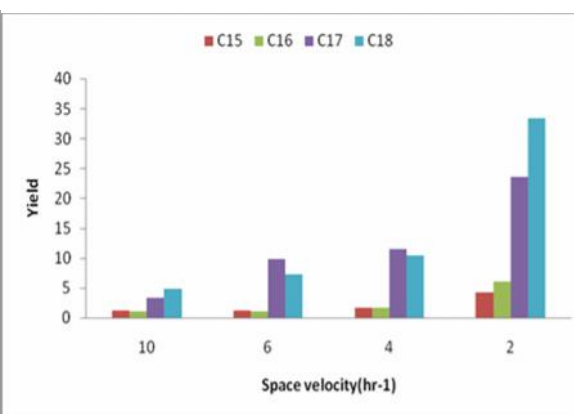


Figure-9 Comparison of yields at various space velocities

The C15-C18 yield is decreases rapidly up to 4 hr⁻¹ space velocity which is absolutely follow the reaction methodology but some increase in yield fraction and become constant this thing shows that reaction some other pathways as increase in space velocity. The unconverted triglycerides may be present in higher amount at these space velocities(Figure 6).At 320°C temperature and 80 bar pressure and 1200H₂/HC the yield fraction (C15-C18) is decreases as increases in space velocity. At these conditions the reaction pathways is more favorable since the fraction yield isdecreases. The conversion is obtained at these conditions is quite good(Figure 7).

5. Conclusion:

The mixtures of non-edible oil (Jatropha oil) and refinery gas- oil can be easily deoxygenated into

pure hydrocarbons under hydroprocessing conditions using typical hydroprocessing catalyst and mesoporous α - alumina. Plant – oils can be mixed with petroleum fractions and treated in a conventional hydrotreater with no adverse effect on hydrodesulphurization activity. TMN catalyst supported on mesoporous α - alumina could be used for selective cracking ability along with high selectivity for diesel range product due to deoxygenation of Jatropha oil into C15-C18 hydrocarbons. The study showing that hydrotreating and hydrocracking of vegetable oils with petroleum fractions is a viable process for production of liquid fuels with high cetane value and acceptable density using mesoporous catalyst supports.

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