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Studies on co-processing of jatropha oil with diesel fraction in hydrodesulfurization

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ABSTRACT

Hydrotreating of vegetable oils to hydrocarbon is one of the processes presently being considered for obtaining biofuel that can be blended with petroleum fuel as it provides chemically similar products i.e. hydrocarbons. In the present study hydrotreatment of jatropha oil and its mixture with straight run diesel fraction (DHDS feed) has been studied over commercial and a lab made hydrodesulfurization (HDS) catalysts. Jatropha oil has been co-processed with straight run diesel fraction in 10, 20, 30, 40 and 50% jatropha oil and its effect on the product and catalyst was examined. Both feeds and products are well characterized by SIMDIST analysis (D2887), distillation (D86), gas chromatography, density, viscosity, pour point and Fourier transform infrared spectroscopy (FT-IR). Products contain only hydrocarbons and are found to be in diesel range and no significant effect on sulfur content of the products was observed. But pour point of the product is higher when higher content of jatropha oil is processed. Catalyst was found to be stable as it didn't get deactivated for more than 150 h of operation.

1. Introduction

Depleting oil reserves, increasing demand and environmental concerns have led to various initiatives from both scientific and industrial scales for the use of renewable resources for energy production, especially for transportation [1,2]. More emphasis is being given to the use of biofuels in place of diesel and petrol for sustainable growth in the future. Currently ester based biodiesel (FAME—Fatty Acid Methyl Ester) obtained by transesterification of vegetable oils is used in blends with diesel but it has some issues such as it requires separate production facilities and glycerol formed as byproduct has low energy content and oxidative instability [3–5]. Another alternative is to convert vegetable oil directly into hydrocarbon which can be blended with petrodiesel or could be used as cetane booster. Oxygen is removed from vegetable oil to obtain hydrocarbon in diesel range by traditional refinery hydrodesulfurization process [4,6,7]. Vegetable oil can be hydroprocessed either in standalone unit or co-processed with petro-diesel fraction used in hydrotreating unit. Vegetable oil cannot replace fossil fuel but only can reduce its consumption [8] therefore it is better to use vegetable oil in small fraction along with petroleum feedstock in the existing refinery units, instead of installing new one. Co-processing of vegetable oil in DHDS unit can provide several advantages such as existing refinery facilities can be used and diesel product with better properties like cetane number can be obtained besides adding the green factor due to renewable vegetable oils [9].

Several studies towards the co-processing of vegetable oil have been attempted in hydrotreating [10–12] as well as in FCC units [13,14]. But most of the HVO is produced by Neste-oil. Many petroleum companies are also investigating processing of vegetable oils especially non-edible oils with the petroleum feedstock. In the present study, we have evaluated two catalysts one is commercial HDS catalyst and the other one is lab developed HDS catalyst for the hydroprocessing of jatropha oil and its mixture with straight run diesel fraction. Influence of jatropha oil amount over diesel products has been studied by characterization of products and feed with various techniques.

2. Experimental

2.1. Catalyst preparation

Two catalysts were used for the hydroprocessing of jatropha oil. CoMo based commercial catalyst and NiMo based catalyst were prepared by dry impregnation using alumina extrudates as support. First the extrudates were dried at 523 K for at least 2 h and pore volume was measured with water. Requisite amount of metal salt was dissolved in calculated amount of water and added to extrudates drop wise at slow rate. Then sample was left at room temperature for 2–3 h and dried at 373 K overnight. Finally the sample was calcined at 773 K for 5 h. Ammonium heptamolybdate hydrate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$] and nickel nitrate hexahydrate [$Ni(NO_3)_2\cdot 6H_2O$] were used as source of molybdenum and nickel.

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2.2. Activity evaluation

Custom made bench scale unit was used for performing catalyst evaluation studies. The bench scale unit has one tubular fixed bed reactor with a length of 55.7 cm, ID = 12.9 mm and OD = 18.9 mm. Catalysts in the form of extrudates having a diameter of about 1 mm and length from 1 to 2 mm were loaded along with 80 mesh (180 μm) silicon carbide particles (inert) in 1:1 ratio to make the flow uniform to avoid channeling of flow. Reactor bed thermocouple is inserted in place to measure the catalyst bed temperature.

2.3. Sulfidation of the catalyst

Both catalysts were sulfided using 2% SulfrZol in n-octane as a feed. The SulfrZol releases hydrogen sulfide (H_2S) in the reactor, which helps in the conversion of metal oxides in the catalyst to their sulfides. After attaining the sulfidation temperature of 350 °C, sulfidation feed was passed over catalyst at a flow rate of 0.2 cm^3/min under 40 bar hydrogen pressure for 5 h. Excess sulfur is taken to ensure the full conversion of metal oxides to sulfides.

2.4. Activity studies

To assess the activity of catalyst for jatropha oil hydroconversion to diesel, studies were carried out at various process conditions by varying the catalyst isothermal bed temperature, space velocity, reactor pressure, H_2/oil ratio and DMDS. After stabilization at each condition, reaction was carried out for longer durations and samples were collected for analysis. Feed containing different amounts of jatropha oil such as 0, 10, 20, 30, 40, 50 and 100% was used to see the effect of jatropha oil over desulfurization and final diesel products.

All the feed and products were analyzed by SIMDIST analysis (D2887), distillation (D86), gas chromatography, density, viscosity; pour point, Fourier transform infrared spectroscopy (FT-IR), CHNS and total N & S analyzer.

3. Result and discussions

Hydrotreatment of jatropha oil and its co-processing with DHDS feed (straight run diesel) was studied over lab made NiMo based catalyst and its activity was compared with a commercial catalyst. Various physical properties of these catalysts are presented in Table 1 and their N_2 adsorption–desorption isotherms are shown in Fig. 1. Average pore size (118 Å) and pore volume (0.68 cm^3/g) of the lab catalyst-1 were found to be higher than commercial catalyst but its bulk density (0.61 cm^3/g) is lower. Surface area of lab catalyst-1 (232 m^2/g) is slightly lower but still in similar range. Both catalysts (pore size 8 and 11 nm) have requisite pore size and can accommodate the triglyceride molecules without any diffusion limitations Fig. 1 showed that both possess type VI isotherm with clear hysteresis loops in the pressure range of 0.4–1.0, which indicates that both are mesoporous [15,16]. BJH pore size distribution reveals that commercial catalyst contains narrow pore size distribution peaking at 66 nm while lab catalyst-1 contains bimodal pore structure having average pore diameter of 82 and 122 nm.

Various feeds such as 100% jatropha oil, 10% JO + 90% DHDS feed, 20% JO + 80% DHDS feed, 30% JO + 70% DHDS feed, 40% JO + 60% DHDS feed, 50% JO + 50% DHDS feed and 100% DHDS feed were used for the study. Various properties such as sulfur content, pour point, density and viscosity are presented in Table 2. DHDS feed has 6377 ppm sulfur and jatropha oil itself contains negligible sulfur (19 ppm) therefore as the jatropha content in the feed increases feed's sulfur content decreases. Since the density and the viscosity of jatropha oil are higher than DHDS feed, density and viscosity of the feeds increase with the amount of jatropha oil. These feeds were hydroprocessed under similar reaction conditions of temperature (573 K), pressure (50 bar) and hydrogen flow (4 L h^{-1}) to study the influence of jatropha oil over desulfurization and other properties of the obtained product. To estimate how much vegetable oil was left, Fourier transform infrared (FTIR) spectroscopic method was used [17]. This FTIR method is also used for biodiesel blend analysis (ASTM D7371 and EN 14078) [18]. Fig. 2 shows the FTIR spectra of the feeds with different concentrations of jatropha oil and their product. Peak at 1747 cm^{-1} corresponding to carboxyl group (O–C═O) stretching vibration completely disappeared

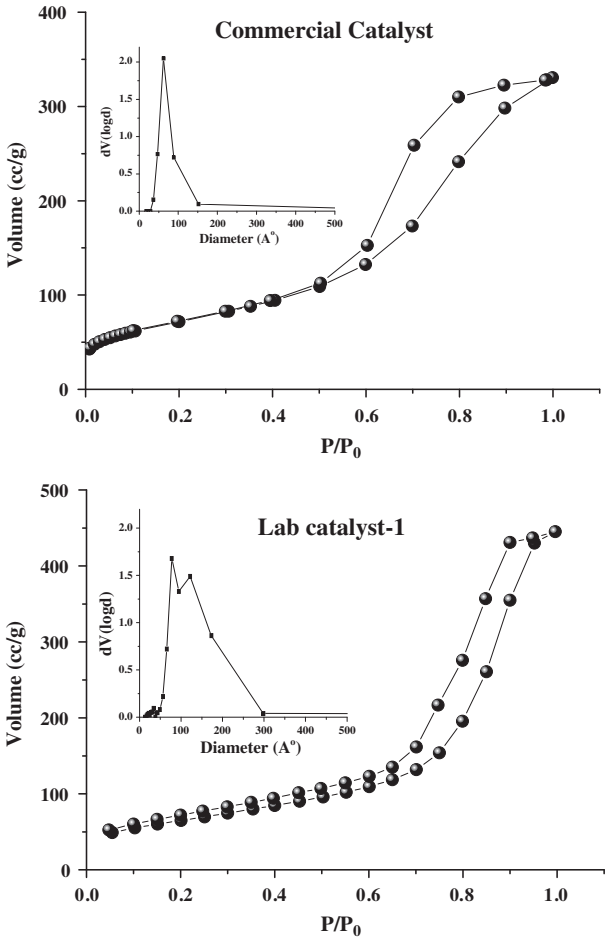

Fig. 1. N_2 adsorption–desorption isotherm of commercial and lab made hydroprocessing catalysts.

Table 1
Physical properties of catalysts.

Property	Commercial catalyst	Lab catalyst-1
Surface area (m^2/g)	254	232
Pore volume (cm^3/g)	0.51	0.68
Average pore size (Å)	80	118
Bulk density	0.87	0.61

Table 2
Properties of feedstock used for hydroprocessing and co-processing.

Feedstock	S content (ppm)	Pour point (°C)	Density @ 15 °C (g/cm^3)	API	KV @ 40 °C (mm^2/s)
100% DHDS	6377	−8	0.8585	33.18	3.477
10% JO + 90% DHDS	5490	−7	0.8616	32.59	4.741
20% JO + 80% DHDS	4835	−7	0.8747	30.12	5.872
30% JO + 70% DHDS	4310	−7	0.8808	29.00	7.554
40% JO + 60% DHDS	3730	−6	0.8826	28.68	9.459
50% JO + 50% DHDS	3166	−6	0.8920	26.99	11.632
100% JO	19	−6	0.9197	22.22	35.391

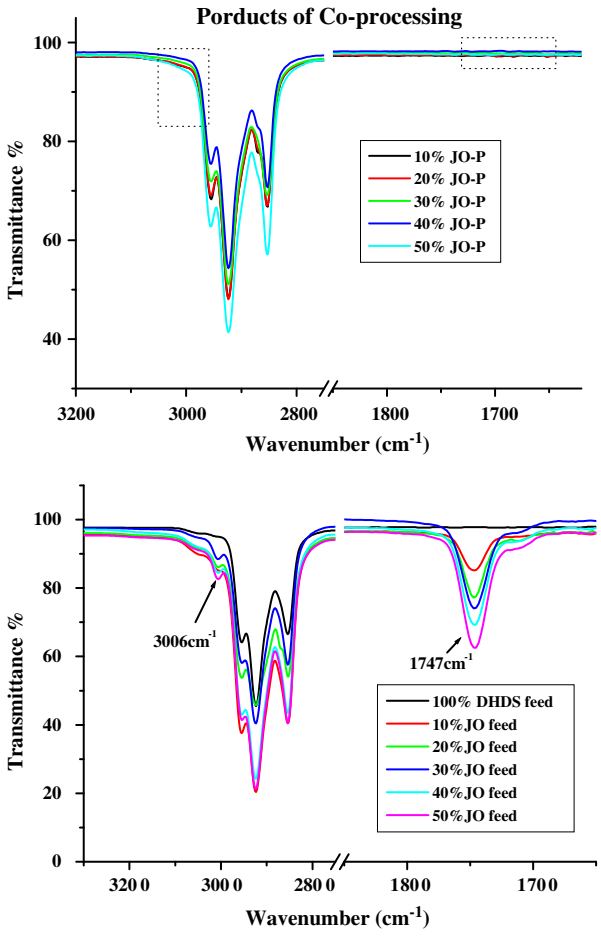

Fig. 2. FTIR spectra of feed and product.

(indicated by a horizontal dotted box in Fig. 2) in the products indicating complete removal of oxygen from the jatropha oil. In other words complete conversion of jatropha oil to hydrocarbons was obtained. To further confirm the presence of any impurities of glycerides present in the co-processed product, ^{1}H NMR of feed and products was recorded. Fig. 3 presents the ^{1}H NMR spectra of jatropha oil, 50% JO in HDS feed and co-processing product of 50% JO in HDS feed obtained over lab catalyst-1 & commercial catalyst. This showed the complete removal of glyceride peaks (−**CH$_2$**OCOR δ = 4.09–4.34 ppm & −**CH**OCOR 5.25 ppm (appears as hump as merging with olefinic protons)) along with the unsaturation (−**CH**=**CH**− olefinic protons δ = 5.3–5.4 ppm) [19]. Few samples were analyzed by CHNS analysis which gives the oxygen content by difference also supported near complete conversion of jatropha oil as oxygen content was almost negligible (<1 wt.%) in the products as compared to jatropha oil (10–11 wt.% oxygen content) (Table 3). Along with the removal of oxygen, unsaturation present in the jatropha oil is also removed by hydrogenation. This can be observed from the disappearance (indicated by a vertical dotted box in Fig. 2) of peak at 3006 cm^{-1} corresponding to the olefinic hydrocarbon stretching vibrations. Simulated distillation GC analysis of feed and products is presented in Fig. 4. This also showed that 95% fraction of the products distillated off below 380 °C indicating that the products are in the diesel range only except for 50% jatropha oil.

In co-processing, hydrodeoxygenation, hydrodecarboxylation, hydrogenation and hydrodesulfurization occur simultaneously. Jatropha oil contains mostly C16 and C18 fatty acids. Therefore, hydrodeoxygenation of jatropha oil results in hexadecane and octadecane while hydrodecarboxylation provides pentadecane and heptadecane, one carbon less which is lost as carbon dioxide/carbon monoxide. Ratio of C17/C18 tells us the relative extent of decarboxylation over hydrodeoxygenation. Analysis of products by gas chromatography is presented in Table 4 and Fig. 3. Hydroprocessing of jatropha oil over commercial catalyst as well as lab catalyst-1 results in more than 90% yield in the C15–C18 hydrocarbon range. But C17/C18 ratio was around 0.5 over commercial catalyst while over lab catalyst-1 C17/C18

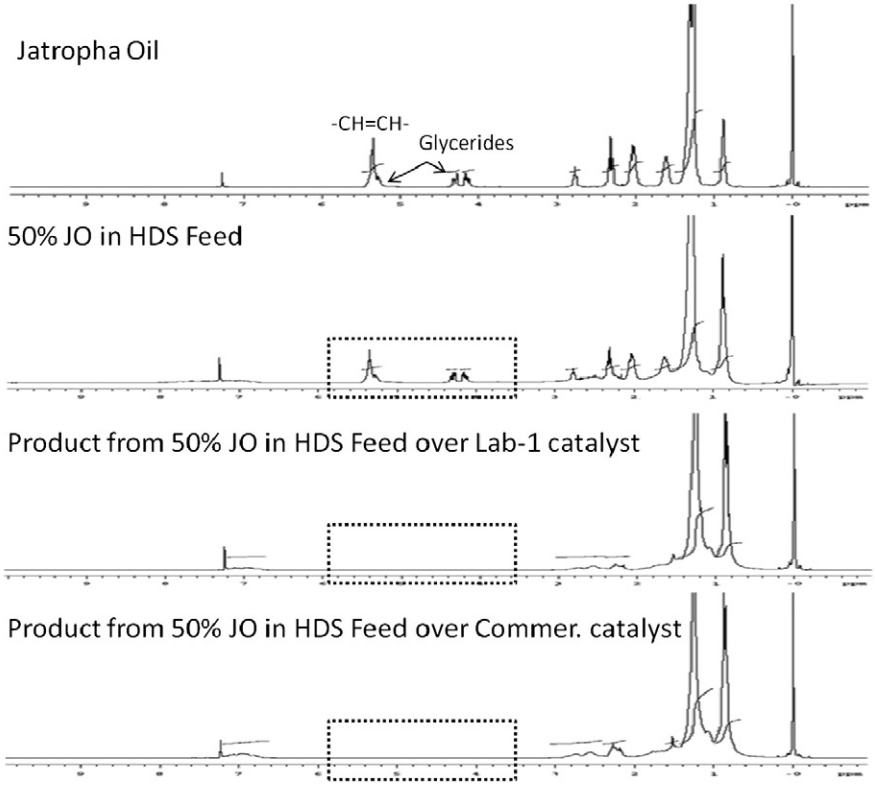

Fig. 3. ^{1}H NMR spectra of jatropha oil, 50% JO in HDS feed and co-processing product obtained over lab-1 catalyst & commercial catalyst.

Table 3
CHNS analysis of feed and products.

Sample	wt.%				
	C	H	N	S	O
Jatropha oil	76.4	12.2	N.D.	N.D.	11.4
100% DHDS	86.1	12.8	N.D.	0.6	0.5
Various feeds for co-processing					
10% JO + 90% DHDS	84.4	13.2	N.D.	0.6	1.8
20% JO + 80% DHDS	83.7	12.9	N.D.	0.5	2.9
30% JO + 70% DHDS	83.2	12.5	N.D.	0.4	3.9
40% JO + 60% DHDS	82.2	12.4	N.D.	0.4	5.0
50% JO + 50% DHDS	81.0	12.5	N.D.	0.3	6.2
Co-processed products from various feeds					
10% JO + 90% DHDS	86.2	13.3	N.D.	N.D.	0.5
20% JO + 80% DHDS	86.1	13.4	N.D.	N.D.	0.5
30% JO + 70% DHDS	85.7	13.9	N.D.	N.D.	0.4
40% JO + 60% DHDS	85.5	13.7	N.D.	N.D.	0.8
50% JO + 50% DHDS	85.6	13.7	N.D.	N.D.	0.7

Note: N.D. i.e. it is less than 0.1 wt.% (although in ppm level N & S are detected by N & S analyzer).

ratio is near 1.3 which indicates that hydrodeoxygenation is more prominent over commercial catalyst while over lab catalyst-1 hydrodecarboxylation was the main reaction. Gas chromatogram in Fig. 5 clearly showed the increase in the amount of C15–C18 hydrocarbons in the co-processed products with the jatropha oil in the feed. But in co-processing, over commercial catalyst also decarboxylation occurred more than deoxygenation. From Fig. 6 it is clear that lab catalyst-1 also promotes higher decarboxylation. Higher acidity for the lab catalyst-1 may be the reason for its higher decarboxylation activity.

Table 4
Distribution of hydrocarbons in the co-processed vegetable oil products.

Sample name	Distribution of hydrocarbons (%)									
	Commercial catalyst					Lab catalyst-1				
	C15	C16	C17	C18	Rest	C15	C16	C17	C18	Rest
Commercial diesel	4.0	4.7	4.5	4.2	82.6	4.8	5.3	5.1	4.4	80.4
10% JO	5.0	5.5	11.1	10.6	67.8	5.6	5.4	12.2	10.1	66.7
20% JO	6.0	6.0	15.7	13.7	58.6	6.3	6.0	16.3	12.3	59.1
30% JO	7.2	6.5	23.4	17.8	54.9	7.6	5.7	21.9	13.9	50.9
40% JO	7.3	6.4	27.5	17.8	41.0	8.6	6.1	28.0	15.3	42.0
50% JO	8.5	6.5	32.1	21.5	31.4	9.5	5.6	31.0	14.9	39.0
100% JO*	5.2	11.4	25.1	51.7	6.6	8.9	7.7	42.5	32.9	8.0

* H_2 flow - 21 L/h.

C17/C18 ratio is higher for lab catalyst-1 for all feeds as compared to commercial catalyst. But for both catalysts C17/C18 ratio increased with jatropha oil content in the feed. This could be due to the fact that as hydrogen flow was kept constant for all the feeds and when more jatropha oil was added to feed more hydrogen is required for the removal of oxygen while hydrogen remains the same resulting in higher decarboxylation as compared to deoxygenation which results in higher yields of heptadecane and C17/C18 ratio.

Sulfur content, pour point, density and kinematic viscosity of co-processed products are listed in Table 5. Density of the products was found to be decreasing over both catalysts with the increase in jatropha oil content in the feed while in viscosity no significant change was observed. This is due to the fact that C15–C18 straight hydrocarbons have lower density as compared to diesel. But their higher pour point

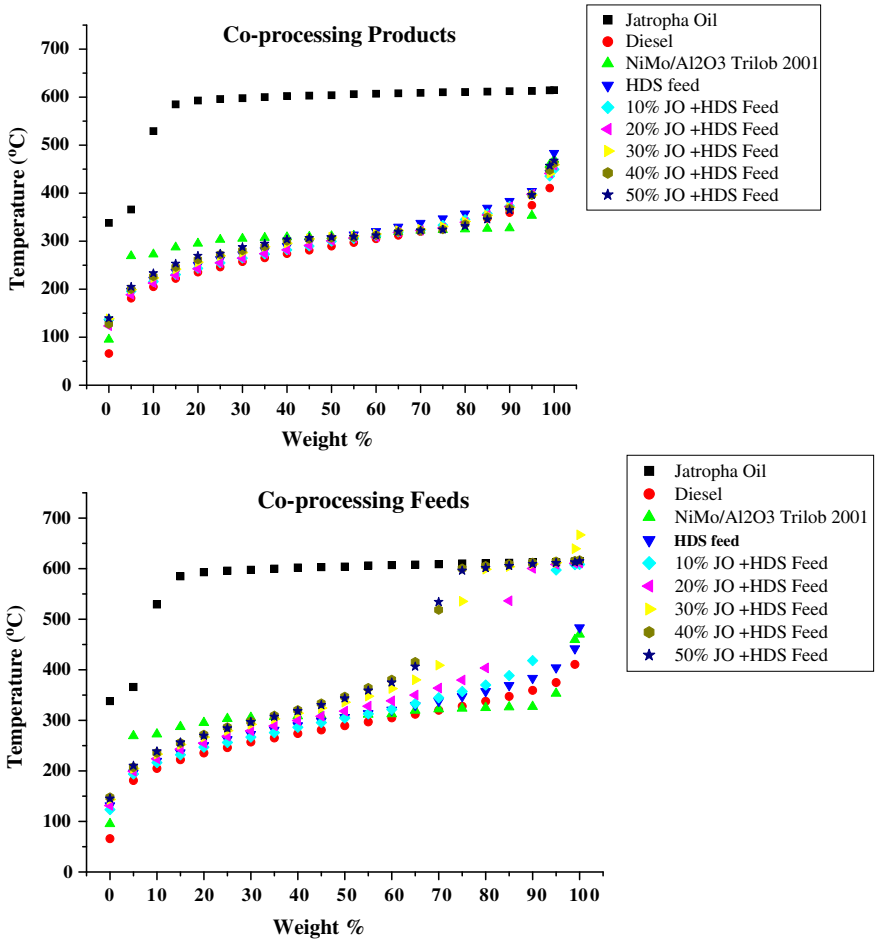

Fig. 4. SIMDIST analysis of various feeds and products.

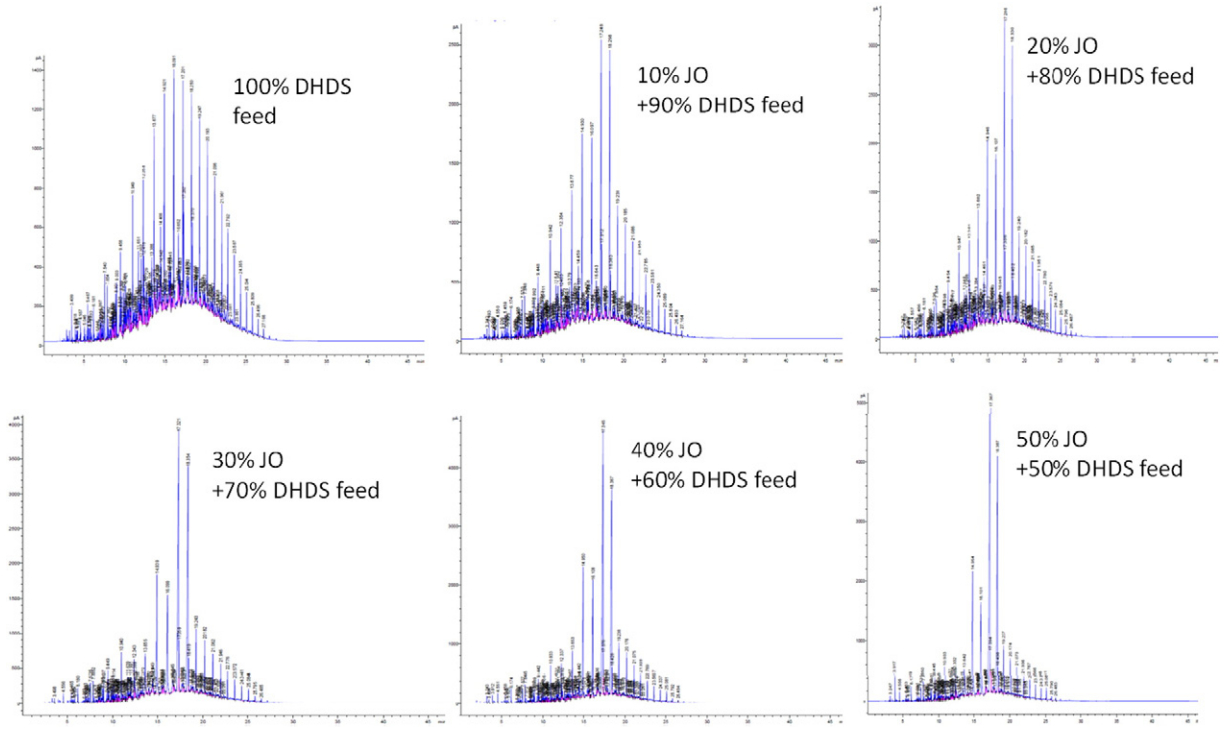

Fig. 5. GC chromatograms of products of co-processed jatropha oil products.

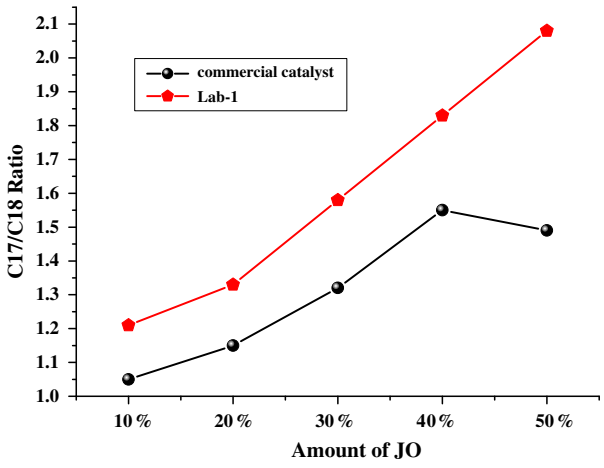

Fig. 6. Effect of JO content on C17/C18 ratio.

leads to increase in the overall pour point of the products (Table 5). Pour point of the products increases with the jatropha oil amount in the feed over both catalysts, but pour point of products over lab catalyst-1 was lower. This is due to more decarboxylation of the jatropha oil over lab made catalyst as compared to commercial catalyst which results in higher content of heptadecane (C17) and pentadecane (C15). This can also be co-related to the lower pour point of C17 & C15 as compared to C18 & C16 which are obtained by hydrodeoxygenation.

Sulfur content in the products slightly increased over commercial catalyst when jatropha oil is added to the feed and it remains more or less similar up to 40% jatropha oil (Table 5) in the DHDS feed but for 50% feed further increase was observed indicating a decrease in desulfurization activity of the commercial catalyst. But over lab catalyst-1 there is a decrease in the sulfur content of the products (from 308 to 219 ppm) as the jatropha oil in the feed increases up to 40% jatropha oil but for 50% jatropha oil feed an increase in sulfur content (310 ppm) was observed. Better desulfurization activity of lab catalyst-1 can be attributed to its higher acidity which leads to more decarboxylation i.e. less deoxygenation and water formation. This causes lesser deactivation of catalyst due to water and better activity. More decarboxylation though leads to lower yield but it leads to lesser deactivation of catalyst by water and carbon dioxide/carbon monoxide is easily removed as gaseous product as

Table 5
Processing of different amounts of jatropha oil with DHDS feed.

Feed	Commercial catalyst					Lab catalyst-1				
	S content (ppm)	Pour point (°C)	Density @ 15 °C (g/cm^3)	API	KV @ 40 °C (mm^2/s)	S content (ppm)	Pour point (°C)	Density @ 15 °C (g/cm^3)	API	KV @ 40 °C (mm^2/s)
100% DHDS	494	−3	0.8460	35.61	3.5446	308	−3	0.8269	39.48	3.603
10% JO + 90% DHDS	583	0	0.8409	36.61	3.546	309	−2	0.8369	37.41	3.384
20% JO + 80% DHDS	558	2	0.8346	37.88	3.332	275	0	0.8346	37.88	3.541
30% JO + 70% DHDS	588	5	0.8328	38.23	3.577	228	2	0.8297	37.90	3.483
40% JO + 60% DHDS	586	6	0.8274	39.35	3.569	219	2	0.8412	36.55	3.538
50% JO + 50% DHDS	610	6	0.8232	40.24	3.604	310	3	0.8253	39.81	3.692
100% JO[a]	19	21	0.7860	48.36	3.587	14	21	0.7873	48.06	3.515

Conditions: temp.—350 °C, pressure—50 bar, WHSV—1.2 h^{-1}, hydrogen flow—4 L h^{-1}.
[a] Hydrogen flow—21 L h^{-1}.

Table 6
Influence of flow rate of hydrogen with 10% JO and 90% DHDS feed.

Hydrogen flow ($L\ h^{-1}$)	Commercial catalyst		Lab-1 catalyst	
	S content (ppm)	Pour point (°C)	S content (ppm)	Pour point (°C)
4	583	0	321	−2
10	428	0	292	−2
21	437	0	281	−2

Conditions: temp.—350 °C, pressure—50 bar, WHSV—1.2 h^{-1}.

compared to water by deoxygenation. Jatropha oil contains 10–11% oxygen by weight while DHDS feed contains 0.5–2% sulfur by weight. As we add jatropha oil to the DHDS feed the amount of oxygen provided to catalyst is higher than the amount of sulfur decreased in feed by adding jatropha oil. As these are removed as H_2O and H_2S, more hydrogen is required. To see this effect 10% jatropha oil in DHDS feed was co-processed under different hydrogen flows over both catalysts. No significant change in the density, viscosity and pour point was observed but when hydrogen flow was increased from 4 L h^{-1} to 10 L h^{-1} there is a decrease in sulfur content. Over commercial catalyst it decreases from 583 ppm to 428 ppm while over lab catalyst-1, from 321 ppm to 292 ppm. Further increase in hydrogen flow from 10 to 21 L h^{-1}, no significant change in activity was observed (Table 6).

Primary reason for the deactivation of hydroprocessing catalysts is coking [20–23] and considerably depends upon reaction parameters and feed used. To study this, both spent catalysts were investigated by thermogravimetric analysis (TGA) in air flow up to 800 °C (Fig. 7). Spent lab catalyst-1 showed weight loss at 230 °C (9.1 wt.%) and 430 °C (15.8 wt.%) while spent commercial catalyst's weight loss was observed at 320 °C (9.3 wt.%) and 430 °C (13.9 wt.%). Hard coke above 350 °C was almost the same for both catalysts. Soft coke amount was also the same but for commercial catalyst soft coke was removed at significantly higher (90 °C) temperature as compared to lab catalyst-1. It can be seen in Fig. 7 where DTG peak for soft coke moves to higher temperature i.e. 320 °C in commercial catalyst when compared to lab catalyst-1 i.e. 230 °C. This may be responsible for lower activity of commercial catalyst. Lab made catalyst also has larger pore size (118 Å) and pore volume (0.68 cm^3/g) as compared to commercial catalyst (80 Å & 0.51 cm^3/g). Larger pore facilitates the transport for bigger triglyceride molecules to the active sites and better activity.

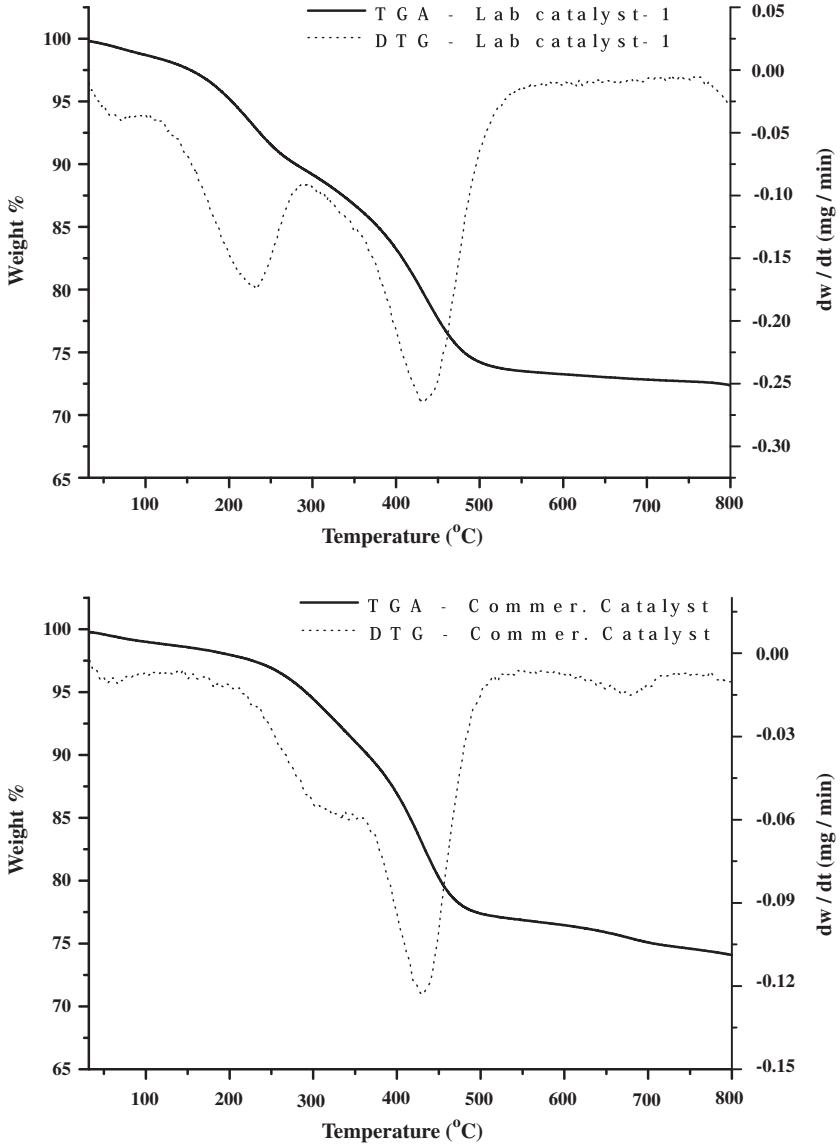

Fig. 7. TGA and DTG curves of spent commercial catalyst and spent lab catalyst-1.

4. Conclusions

Jatropha oil was co-processed with desulfurization diesel feed up to 50 wt.% over two catalysts; one is commercial hydrodesulfurization catalyst and second is laboratory formulated catalyst. Influence of jatropha oil over various properties of diesel product was studied. An increase in sulfur content was observed in co-processed products over commercial catalyst whereas it is decreasing in the case of lab catalyst-1. With the increment of jatropha oil concentration in diesel feed, slight decrease in density and increase in pour point were observed when compared with feed without jatropha oil. Based on the above mentioned studies it can be concluded that up to 30 wt.% jatropha oil can be processed without affecting final sulfur content of the DHDS product. Increase in hydrogen flow was found to be helpful in obtaining better desulfurization activity in co-processing.

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