Biofuel Synthesis by Jatropha Oil Cracking using Solid Acid Catalyst

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Abstract— **Vegetable oils and fats are potential feed stocks for development of renewable biofuels. Catalytic cracking of triglycerides in presence of solid acid catalyst gives rise to the liquid and gaseous hydrocarbon fuels.[1] In the present work we carried out Jatropha oil cracking in a fixed bed reactor by using transition metal oxide (TiO2, ZrO2 and CeO2) impregnated aluminosilicate catalysts; at 380°C temperature; 1.1 hr^{-1} LHSV. The study reveals the maxium liquid biofuel yield of 70% by volume could be achieved through zirconia impregnated catalyst. Products of reaction mainly consisted of liquid and gaseous hydrocarbons in addition to carbon dioxide and water. The distilled liquid biofuel product was characterized for physical properties like density, viscosity, flash point, calorific value etc. and shows resembles with petrol and diesel. Samples are also analyzed by IR and GC.**

Keywords- Jatropha oil, biofuel, cracking, fixed bed reactor

I. INTRODUCTION

Catalytic cracking of non edible oils has been proposed as an alternate method for the preparation of liquid hydrocarbon fuels. These liquid biofuel have chemical components similar to conventional petroleum fuels and can be directly used in the internal combustion engines [2]. Worldwide research is on going to maximise the yield of biofuel and establish the techno-economic viability of process. The present study summarises the cracking reaction of Jatropha oil and its conversion into hydrocarbon fuel by utilising transition metal oxide impregnated aluminosilicate catalyst.

Vegetable and animal oils and fats are esters of tri, di, or mono glyceride of different aliphatic fatty acids having 6 to 24 carbons. Thermolytic cracking of oils and fats in presence of a solid acid catalyst can yield saturated / unsaturated, aliphatic / aromatic hydrocarbons in addition to carbon dioxide, water vapor and olefins [3]. Since the cracking reaction is carried out at higher temperatures, it may be accompanied with thermolysis of the hydrocarbon chains as well. The reaction is carried out in fixed bed reactor under normal atmospheric pressure. The reaction can in general be represented as below.

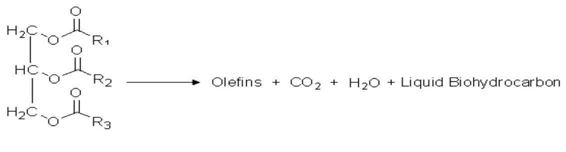
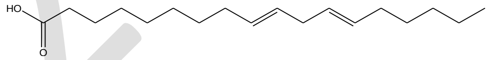


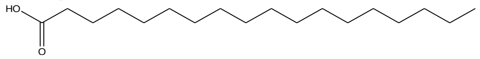
Figure 1. Triglyceride cracking reaction

Here R_1, R_2 and R_3 represent the hydrocarbon chain residues of corresponding fatty acid forming part of the oils / fats.

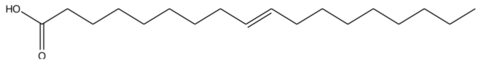
Oil of Jatropha curcas, grown in the tropical regions in India, is reported as efficient raw material for production of diesel like fuels. Toxicity of Jatropha curcas makes it unwanted by animals and men for other uses. Its draught resistant characteristic makes its economic cultivation viable and hence Jatropha curcas is considered as an alternate renewable energy source for future [4]. This oil contains saturated, monounsaturated and polyunsaturated fatty acids. The chemical structure of major fatty acids of jatropha oil is given below [5].



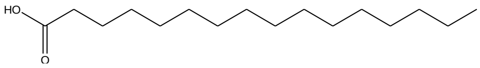
34.3 % Linoleic Acid



6.9 % Stearic Acid



43.0 % Oleic Acid



4.2 % Palmetic Acid

Figure 2.Structure and % of major fatty acids in Jatropha oil

Thermal cracking of oil through mesoporous catalytic materials has been attempted by many researchers. Porous aluminosilicate catalyst is found to be efficient catalyst to obtain middle distillate fuel as major fraction [6,7]. Amorphous aluminosilicate has been used by Takkai isoda and co-workers in Polyethylene-Liquefied Oil cracking [8]. Dessy and group has utilised the MCM-41 in Palm oil cracking reaction [9]. Over the time wide range of catalytic material like ZSM-5 [10, 11], AlMCM-41, SBA-15 [12] , have been utilised for cracking reaction The variation in terms of oils have included both edible and non edible variety like sunflower oil, cotton seed oil, rubber seed oil, pongamia pinnata etc.[13]. However, use of edible oil for biofuel raises conflict over the most prudent issue of food vs fuel and hence non edible varieties like Jatropha oil, used/ waste cooking oil, vegetable sludge are gaining more importance [14].

II. EXPERIMENTAL

Purified commercial grade Jatropha oil procured from Ms VP Enterprises, Pune was used in the cracking studies. The cracking was carried out using a fixed bed tubular reactor Three different silica alumina (97.5%) based catalysts impregnated with the transition metal oxides (concentration ~ 0.7 %) - titanium, zirconium and cerium were synthesized by procedure mentioned in US patent 4102938 by KVC rao.[1] The catalyst samples were characterized for morphological and surface parameters namely surface area, average pore width and total pore volume, average true density.

The cracking reaction was carried out by passing the Jatropha oil at predetermined flow rate measured as LHSV through the reaction column packed with catalyst pellets preheated to the reaction temperature. The reaction products were condensed by passing through condensation coils and the uncondensed gases were collected after passing through NaOH bubblers for trapping carbon dioxide. The liquid portion was subjected to fractional distillation and these fractions compared with petrol, diesel and biodiesel samples for physical parameters, Further they were anlyzed by IR and GCMS methods. Gaseous hydrocarbon were quantified and burnt through a laboratory bunsen burner.

The specific surface area of the catalysts used was measured by N_2 physisorption at liquid nitrogen temperature using Micromeritics Tristar II 3020 surface area analyzer with standard multi point BET analysis method after degassing at 250° C in N_2 flow for 4 hrs. The density of samples was determined by pycnometer Micromeritics AccuPyc 1330 instrument with Helium purging. The IR spectra of Jatropha oil, distilled biofuel fractions & normal petrol, diesel sample were taken on Shimadzu FTIR 8400 model instrument. GCMS analysis was carried over perkinelmer Clarus 560 GCMS using capillary column. Viscosity of fuel samples was determined by Saybolt Viscometer. The flash point of samples was analyzed Cleveland open-cup method. The calorific value of samples wase determined by using Parr 6300 bomb calorimeter.

III. RESULTS AND DISCUSSIONS

The physical parameters of the all three catalysts used in the present study are shown in Table 1. Catalyst were synthesized from batch composition of SiO_2- 85-87%, Al_2O_3- 14-12 %, *TMO- 0.5 %.

Table 1.Physical properties of Catalyst

Catalyst	**TMO used**	**Surface area m^2/g**	**Avg. pore width Å**	**Total pore volume cm^3 /g**	**Average True Density g /cm^3**
SAT	TiO_2	226	127	0.643	2.2635
SAZ	ZrO_2	283	95	0.6762	2.3417
SAC	CeO_2	194	145	0.7064	2.2572

*TMO-transition metal oxide

The effectiveness of above catalysts for cracking of Jatropha oil was studied and the results are presented in Table 2. The reaction was carried out in 250ml batch size at 380° C temperature and 1.1hr^{-1} LHSV. The catalyst is activated at 110°C for 2hr. prior to reaction to remove the residual moisture.

Table 2. Experimetal results of Jatropha oil cracking
Temp. 380 °C, LHSV 1.1 hr^{-1}

Catalyst	**% Crude liquid product (by volume)**	**Gaseous product lit at NTP / lit of oil**	**% of distilled liquid biofuel (by volume)**	**% of Residual tar (by mass)**
SAT	77	90	53	16
SAZ	79	102	68	10
SAC	72	105	59	12

The above result shows that the yield of desired product i.e distilled liquid biofuel varies in the range of 50-70 %. In the present studies under the given conditions of temperatures and LHSV;zirconia based catalyst has given the maximum conversion (68%). The cracking is brought about by the acidic sites – Bronsted as well as Lewis- provided by the matrix in addition to the delocalisation of vacant d orbital provided by the transition metal oxides .The surface area, pore volume and pore width of the catalyst also play a critical role in effecting the catalytic decomposition of the ester linkages. In the cracking reaction the reactants are adsorbed in the micro, meso and macro pores of the catalyst and the products get desorbed. The large surface area provided by the catalyst and the suiting average pore diameter might have contributed to the improved yield in the case of catalyst with zirconium as the active component. It is reported that zirconia provides amphoteric surface hydroxyl group which acts as active acidic sites for the reaction [15]. The distilled biofuel obtained from reaction of Jatropha oil with SAZ (zirconium based catalyst) was fractionated into two fractions of boiling point below 100° C and above 100 ° C and analyzed further for its physical properties and results were compared with those of biodiesel and standard petrol and diesel. These results are presented in Table 3.

The absence of sulphur component as anticipated in distilled biofuel fractions is an added advantage as it reduces harmful automobile emissions. High viscosity of biodiesel is pointed out as a disadvantage as it leads to operational problems such as engine deposits [16]. The distilled biofuel fractions are nearly free from –COOH, -OH, -O- and –CO- containing compounds as evidenced from IR graph Fig 3(B) and (C). The absence of such oxygenated compounds also is responsible for its lower viscosity comparable to that of petrol and diesel.

Table 3. Comparative evaluation of physical properties of distilled biofuel fractions with petrol, diesel and biodiesel

Physical parameter	***Distilled biofuel F 1***	***Distilled biofuel F2***	***Biodiesel***	***petrol***	***diesel***
Boiling range (o C)	< 100	>100	330-357	*60-80*	180-220
Flash point (o C)	< 40	< 60	>100	< 30	< 80
Specific gravity (^{o}API)	52.26	34.97	33.03	62.33	36.95
Viscosity cST	1.27	5.67	6.8	1.31	3.64
Calorific value Cal /g	9895	9407	9456	10894	9861

Distilled biofuel fractions were also subjected to IR and GC-MS analysis. The effectiveness of cracking reaction is monitored by IR spectroscopy for absence of carboxyl peaks in the product, while its composition wise comparison with petrol or diesel type fuels is possible with the help of retention time from GC technique. The typical IR spectra are presented in Fig 3 (A), (B), (C) and (D).

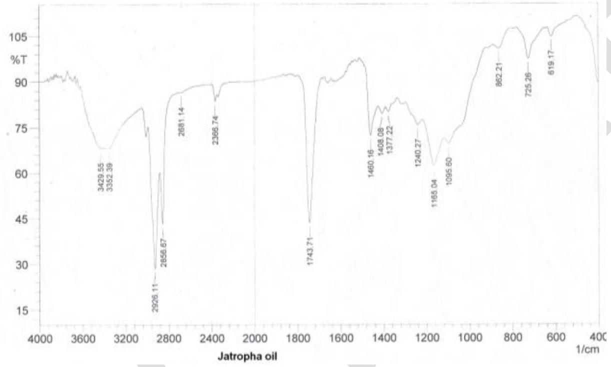


Fig 3 (A) IR spectra of Jatropha Oil

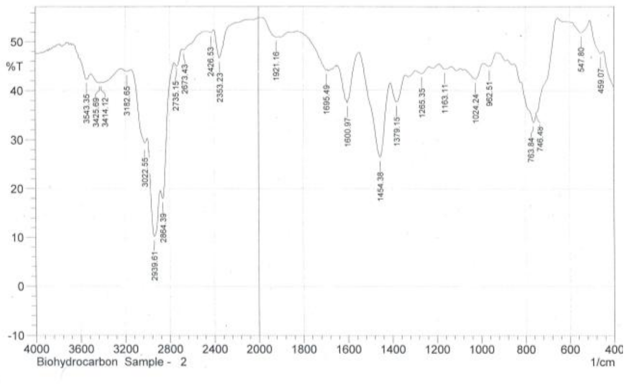


Fig 3 (B) IR Spectra of distilled biofuel fraction I (BP < 100^O C)

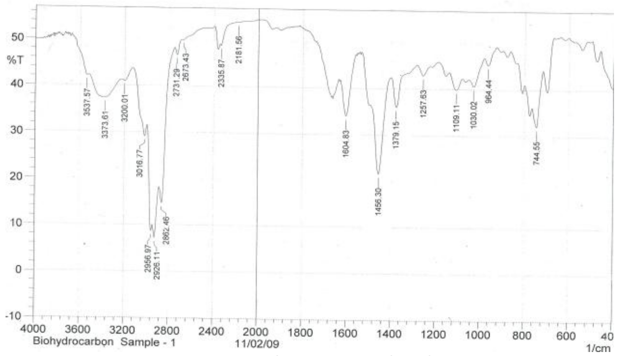


Fig 3 (C) IR Spectra of distilled biofuel fraction II (BP > 100^O C)

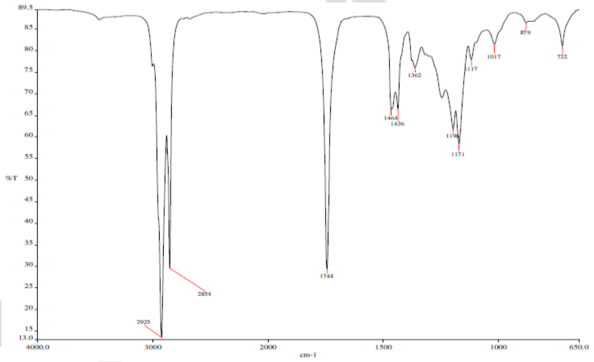


Fig 3 (D) IR Spectra of Biodiesel

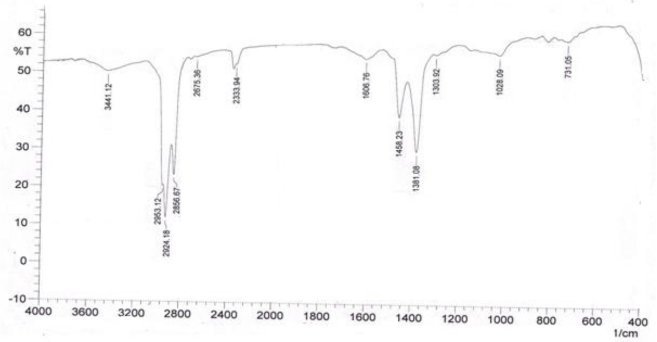


Fig 3 (E) IR Spectra of diesel

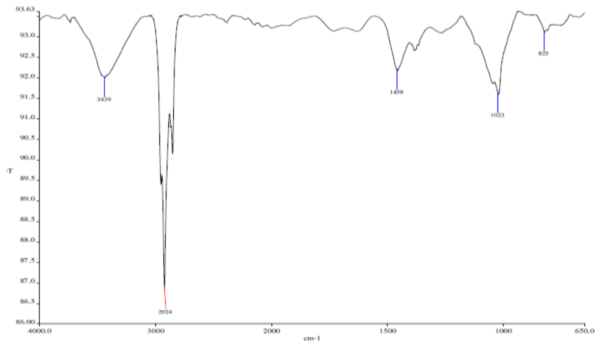


Fig 3 (F) IR Spectra of petrol

IR spectra of biofuel samples show absence of ester carboxyl peak at 1743cm^{-1} which is prominent in IR of Jatropha oil as well as in biodiesel sample, indicating effective cracking. The strong absorption band in the region 2850-3000 cm^{-1} (characteristic band at 2925 cm^{-1}) is due to the C- H stretching frequency of alkane which is prominent in IR of Biofuel samples. It is further supported by the symmetrical and asymmetrical C- H bending vibrations of methylene & methyl group which shows absorption at 1380 and 1460cm^{-1}[17]. On comparison with the IR spectra of distilled biofuel fractions with that of normal petrol and diesel, similarity in absorption band can be seen.

The results of IR analysis are further supported by GC MS analysis. GC spectra of distilled biofuel fraction II (Boiling point >100) is presented in Fig 4. Distilled biofuel fractions being mixture of different compounds, shows multiple peaks (near about 60) pattern similar to that of petroleum fuels. Further the mass spectroscopic analysis has shown that 90-95 % mass fragmentation pattern matches with aliphatic hydrocarbons, which also clearly indicate effective cracking. The detailed analysis is being attempted.

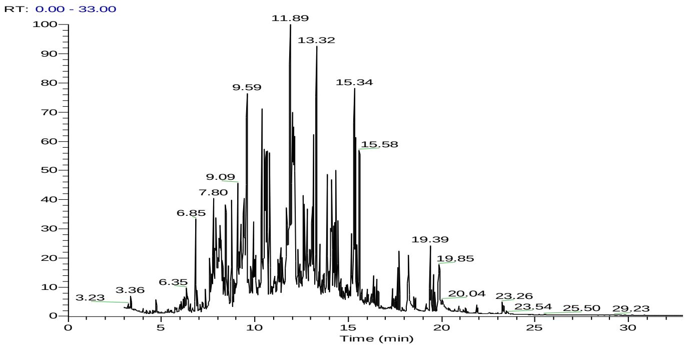


Fig 4 Gas chromatogram of distilled Biofuel fraction II (BP > 100o C)

IV. CONCLUSION

The feasibility of converting Jatropha oil into liquid biofuels with properties similar to that of petrol, diesel using solid acid catalysts and reaction conditions has been established. The studies indicate that in the present reaction condition and catalyst concentration zirconia based catalyst is more effective. As compared to biodiesel the distilled biofuel fractions have lower viscosity, lower density and flash point and higher calorific value. IR and GC analysis of distilled fractions also shows its compositional similarity to normal petrol, diesel. The biofuel developed through this technology from Jatropha oil can emerge as an effective alternate engine fuel, and the gaseous hydrocarbons may turn out to be a suitable substitute for LPG.

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