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RESEARCH ARTICLE

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## Effect of ZSM-5 catalyst on co-cracking of jatropha oil with bagasse

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**Abstract:** Co-cracking of Jatropha oil (JO) and bagasse (BA) in the presence of ZSM-5 catalyst was investigated in a fixed bed tubular batch reactor under atmospheric pressure. It was observed that ZSM-5 increases the gaseous product yield though the liquid yield is not much affected. From the GC-MS characterization of the liquid yield it was observed that liquid yield mainly consisted of compounds in the carbon number range of C<sub>12</sub>-C<sub>22</sub> as compared to thermally co-cracked liquid. This indicates that the presence of ZSM-5 catalyst leads to polycondensation, recombination and rearrangement reactions taking place during co-cracking process.

**Keywords:** Co-cracking, Jatropha oil, Bagasse, ZSM-5, liquid product

**1 Introduction:** Energy is the main stay of national economics. National economy is highly dependent on the means of transportation. The development of the transportation system depends on the efficient utilization of fuels. As our energy needs increases, the demand for transportation fuels also increases. The reserves of fossil fuels are depleting, the demand is increasing and to meet this demand the world is forced to look for alternate sources of fuels. Thus, the use of plant seed oils for generating fuels has come up as a lucrative option. Cracking of these plant seed oils such as edible oils [1-4] and non-edible oils [5-11] and waste oils [12] have been widely studied. These vegetable/ plant seed oils are basically triglycerides, which contain fatty acid chains connected via the carboxylic group to a glycerol backbone. These vegetable oils cannot be used directly as liquid fuels because of their high viscosity, instability, and formation of carbon deposits in parts of automobile engines (i.e. in diesel engines) [8]. Transesterification of these plant seed oils to obtain biodiesel has the disadvantage of requirement of large amounts of methanol for the process and production of glycerol as a by-product [8]. Thus, cracking, catalytic cracking, and hydrocracking for conversion of these plant seed oils to transportation fuels is a better method. Cracking of edible plant seed oils such as palm oil [3-4], soybean oil [1] etc. has been investigated by researchers. For avoiding competition of oil as food source, it is required to carry out cracking of non-edible vegetable oils such as Jatropha oil to generate transportation fuels. Catalytic cracking of Jatropha oil (JO) [2], thermal cracking [10], and hydroprocessing [8] have been investigated by researchers. But, the availability of these plant seed oils at the consumption scale required is a major issue. Generation of liquid fuels by thermal and catalytic cracking of another renewable source biomass has also been investigated [13-16]. Co-cracking/co-processing of biomass with vacuum residue, coal and plastic has been well studied [17-21]. Co-processing of plant seed oils with vacuum gas oil and vacuum residue has also been investigated by many researchers [22-27]. The present authors have carried out co-cracking of jatropha oil (JO) and biomass derived bagasse to derive liquid, gaseous and char products [28].

It was observed by researchers [29-30] that catalytic co-processing can generate lighter oils in diesel and gasoline range. Thus, it would be interesting to see the effect of catalyst on the co-cracking of jatropha oil and bagasse. Thus, in the present work an attempt was made to study the effect of ZSM-5 catalyst on the co-cracking of JO and bagasse in a batch reactor. The yield of the liquid, solid char and gaseous products obtained were quantified. The liquid product obtained was then characterized using GC-MS analysis to understand the effect of catalyst on the quality of the liquid product.

## 2. Experimental:

**2.1 Materials:** Jatropha oil (JO) was procured from Jatropha Vikas Sansthan, New Delhi. Bagasse was procured from the local market. The ultimate analysis Jatropha oil (JO) and Bagasse (BA) was presented in Table 1. ZSM-5 with Si/Al ratio 35 was procured from Sud Chemie India (P) Ltd. The ZSM-5 was calcined at 500 °C for 4 h to get the required catalyst.

Table (1): ultimate analysis of original sample.

Sample	C	H	N	S	O <sup>a</sup>	Atomic H/C	Atomic O/C
JO	70.84	10.85	0	0	18.31	1.84	0.19
Bagasse	45.76	6.30	0.42	0.07	47.44	1.65	0.78

**2.2 Catalytic Co-cracking in a batch reactor:** Cracking of JO+Bagasse in the presence of ZSM-5 was carried out using a batch reactor under nitrogen atmosphere and atmospheric pressure. The flow of nitrogen was maintained at 120mL/hr for the course of the reaction [10, 27-28]. The co-cracking reactions were studied at 350 oC, 375oC and 400oC. All the reactions were studied in triplicates. The reactions were followed by the quantitative measurement of the products formed i.e. liquid product and char. The amount of gaseous products formed was calculated by difference, i.e. by material balance.

**2.3 Characteriation of the liquid product:** The liquid product obtained from the co-cracking reaction of JO+Bagasse in the presence of ZSM-5 catalyst was characterized using GC-MS. The GC-MS was performed on the apparatus Thermo Trace GC ultra GC-MS. A column of 25 m X 0.25 mm (ID) fused silica capillary coated with DB-5 [10, 27] was used for the separation. The oven programming was as follows 35 °C hold for 4 min, heated at 10 °C /min to 200 °C and subsequently at a rate of 4 °C /min to 280 °C (and held at the temperature for 30 min). The injector temperature was 200 °C and the detector temperature was 280 °C. Injector type used was a split injector.

## 3. Results and discussion:

**3.1 Catalyst characterization:** The BET surface area, total pore volume and average pore distribution were determined from N<sub>2</sub> adsorption/desorption isotherms measured at -196 °C using Micromeritics ASAP 2010 apparatus. Prior to gas adsorption measurements the catalyst was degassed at 180 °C under high vacuum for a period of 6 h. The total pore volume was calculated at a relative pressure of approximately 0.99. The BET surface area for the calcined catalyst ZSM-5 was 51.7 m<sup>2</sup>/g. The pore volume and average pore diameter were 0.29 cm<sup>3</sup>/g and 6.5 Å respectively.

Figure 1 shows the XRD pattern of ZSM-5. The different peaks obtained from the XRD pattern clearly indicate the crystalline nature of the catalyst used. The peaks clearly indicate the presence of MFI structure. Peaks for Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> were also obtained.

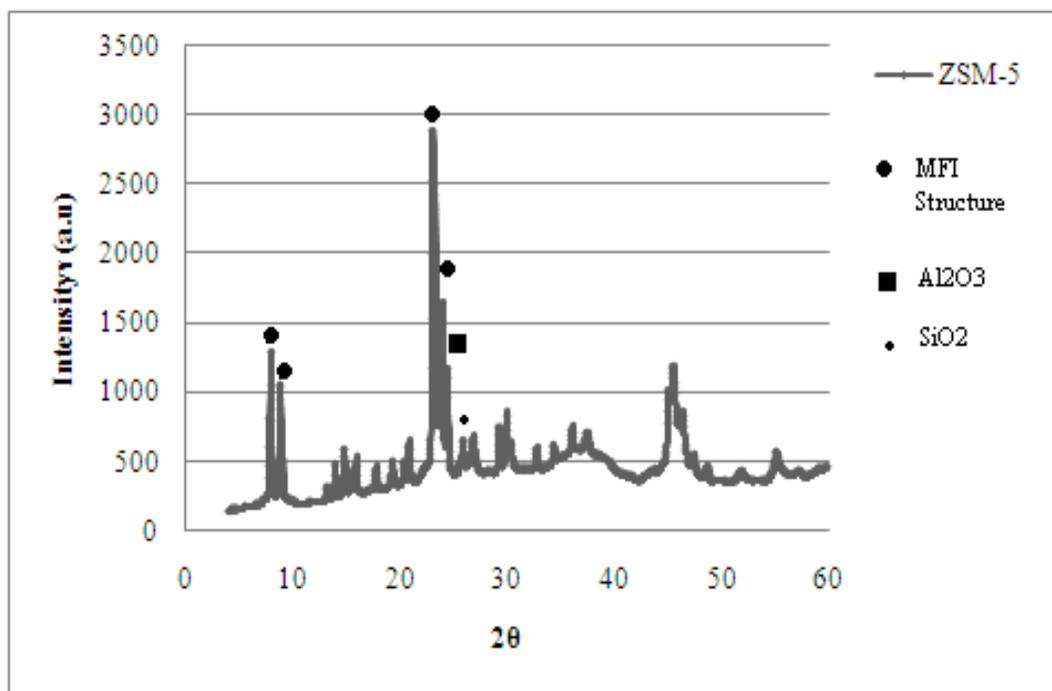


Figure (1): XRD pattern obtained for ZSM-5.

The TEM images obtained (Fig. 2) clearly show the crystalline nature of the catalyst used. TEM was performed using PHILIPS CM12 microscope operated at an accelerating voltage of 100 kV. Both fresh and post-reaction samples were grounded in a mortar subsequently ultrasonically dispersed in ethanol-water solution. A drop of the suspension was then deposited on a Cu grid covered with a perforated carbon membrane for TEM observation. The ZSM-5 catalyst showed the presence of needle/rod type crystals in the agglomerate structure.

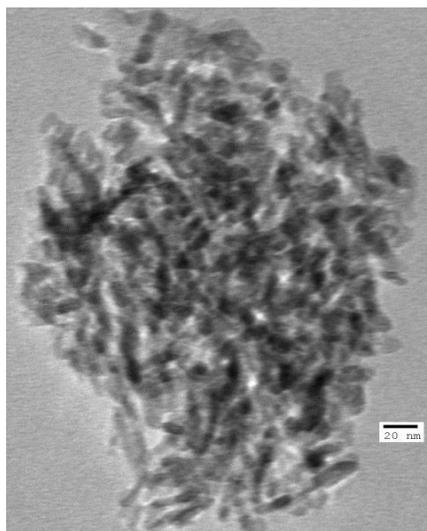


Figure (2): TEM images obtained for ZSM-5.

**3.2 Catalytic co-cracking of JO and Bagasse in a batch reactor:** The catalytic co-cracking reaction of JO and Bagasse was carried out in the batch reactor for the different temperatures of 350 °C, 375 °C and 400 °C for the conversion to liquid, gaseous and solid products. It was observed from previous experiments by the present authors that the co-cracking of JO+Bagasse is maximum at 375°C with a liquid yield of 43 % and char yield of about 9 % and gaseous yield of 47 % (Biswas et al, 2014) [28].

When catalyst ZSM-5 is used during co-cracking reaction, the liquid, char, gaseous product yields are obtained as follows 41.4% ,7.8 %, 50.8 % respectively. The presence of catalyst does not have much effect on the liquid yield though the gaseous yield increases with the decrease in char yield.

**3.3 Characterization of the liquid product obtained from the catalytic co-cracking reaction:** The GC-MS analysis of the liquid product obtained from co-cracking of JO and Bagasse in the presence of ZSM-5 catalyst is presented in Table 2. The Liquid product obtained from catalytically co-cracked liquid of JO+Bagasse consists of various components such as alkanes, aromatics, cycloalkanes, nitrogen compounds, ketones, alcohols, esters and carboxylic acids.

The carbon number distribution of the liquid products obtained from the catalytic co-cracking reactions of JO+Bagasse were characterized by using GC-MS analysis studies and is presented in Table 3.

It was observed that the liquid product obtained from catalytic co-cracking mainly contained compounds with carbon number C12-C22 (92%) as compared to the thermal co-cracking reactions where the liquid product consisted of 53 % C7-C11 hydrocarbons and 44% C12-C22 carbon number hydrocarbons. The increase in the yield of higher carbon number compounds indicates that ZSM-5 in co-cracking of JO+Bagasse facilitates polycondensation, recombination and rearrangement reactions.

Table (2): compounds present in the liquid product obtained from co-cracking of JO+Bagasse in the presence of ZSM-5 catalyst.

Compound	%
Heptane	1.3
CYCLOHEXANE, METHYL-	1.6
BENZENE, METHYL-	0.9
Octanoic Acid	0.9
NONANOIC ACID	0.7
n-Decanoic Acid	1.5
1-Tetradecene	0.8
TETRADECANE	1.3
1-Pentadecene	0.7
Pentadecane	5.2
Cyclohexene, 1-nonyl-	0.7
1-Heptadecene	0.9
Nonadecane	8.1
9-Eicosene, (E)-	3.7
3-Heptadecene, (Z)-	3.2
Cyclopentane, heneicosyl-	0.6
9,17-Octadecadienal, (Z)-	0.7
2-Nonadecanone	1.7
HEXADECANOIC ACID, METHYL ESTER	3.3
n-Hexadecanoic acid	13.6
EICOSANE	1.6
Octadecanoic acid, 2-propenyl ester	1.4
cis-11,12-Epoxytetradecen-1-ol	0.8

Z-2-Octadecen-1-ol acetate	0.8
9,12-OCTADECADIENOIC ACID (Z,Z)-, METHYL ESTER	0.9
9-Octadecenoic acid (Z)-, methyl ester	6.5
Oleic acid	29.2
Heneicosane	2.8
OXACYCLOHEXADECAN-2-ONE, 16-METHYL-13-NITRO	1.8
Cyclododecanemethanol	0.8
9-Octadecen-1-ol, (E)-	0.69
1-Nonadecene	0.19
9-Tricosene, (Z)-	0.27
Tetratetracontane	0.69

Table (3): carbon number distribution from GC-MS data observed in the liquid product obtained from co-cracking and catalytic co-cracking of JO+Bagasse.

Carbon number		JO+Bagasse	JO+Bagasse (ZSM-5)
<C <sub>7</sub>		<b>3.0</b>	-
C <sub>7</sub> -C <sub>11</sub>	Paraffins	23.0	1.3
	Cyclic compounds	-	1.6
	Mono-aromatics	3.8	0.9
	Acids	3.4	3.1
	Nitrogen compounds	22.7	-
	Total	<b>52.9</b>	<b>6.9</b>
C <sub>12</sub> -C <sub>22</sub>	Paraffins	25.2	19.0
	Olefins	-	9.6
	Cyclic compounds	12.9	1.3
	Acids	1.7	43.6
	Aldehydes	-	0.7
	Alcohols	-	2.3
	ketones	2.2	1.7
	Esters	-	12.1
	Nitrogen compounds	2.1	1.8
	Total	<b>44.1</b>	<b>92.1</b>
>C <sub>22</sub>		-	<b>1.0</b>

**4 Conclusions:** The presence of ZSM-5 catalyst does not affect the liquid yield though it increases the gaseous yield by about 3 %. The GC-MS analysis of the liquid product obtained from the catalytic co-cracking reactions of JO and Bagasse indicated the presence of C<sub>12</sub>-C<sub>22</sub> carbon number compounds. The increase in the higher carbon number range compounds in the liquid product indicates that catalyst ZSM-5 in the co-cracking of JO+Bagasse leads to polycondensation, rearrangement and recombination reactions during co-cracking process.

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