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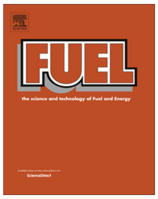

Effect of different catalyst on the co-cracking of Jatropha oil, vacuum residue and high density polyethylene

Shelly Biswas [a,c,*], Sachchit Majhi [b], Pravakar Mohanty [b], K.K. Pant [b], D.K. Sharma [a]

[a] *Centre for Energy Studies, Indian Institute of Technology Delhi, New Delhi 110016, India*
[b] *Department of Chemical Engineering, Indian Institute of Technology Delhi, New Delhi 110016, India*
[c] *Department of Chemistry, Vel Tech Dr. RR & Dr. SR Technical University, Avadi, Chennai 600062, India*

HIGHLIGHTS

- Catalytic co-cracking of Jatropha oil, vacuum residue and high density polyethylene.
- Formation of 45% gasoline components from JO + HDPE cracking with CAT-R.
- 37% gasoline, 35% diesel components formed from co-cracking of JO + VR with CAT-Z.
- Positive effect on pH content with the use of catalyst.

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ABSTRACT

Co-processing of Jatropha oil (JO), vacuum residue (VR) and high density polyethylene (HDPE) were investigated to determine the behavior of the individual and blended mixture under atmospheric pressure and thermal heating conditions. A fixed bed tubular batch reactor was used for the experimental study under nitrogen atmosphere. The activity of the four catalysts CAT-A (Ni–Mo/SiAl), CAT-R (ZSM-5 + SiAl), CAT-Z (ZSM-5) and FCC catalyst CAT-N on the co-cracking of binary and ternary mixture has been studied. CAT-R was the best catalyst used for JO + HDPE co-cracking as it leads to the formation of 45%, gasoline range hydrocarbons (C_7–C_{11}) and 49% diesel range hydrocarbons in the cracked liquid. CAT-Z was the best catalyst for VR + HDPE co-cracking as it lead to the formation of 33% olefins which were absent in the thermally cracked liquid. In case of JO + VR co-cracking CAT-Z was found to show increase in the liquid yield and it also lead to the formation of 37% gasoline range hydrocarbons and 35% diesel range hydrocarbons. It was also observed that the use of catalyst had a positive effect on the pH content of the catalytically cracked liquid products.

1. Introduction

The petroleum reserves are depleting and the demand of transportation fuels is ever increasing. Thus, a situation has arisen where alternate sources of fuels such as plant seed oils, plastic wastes for generation of liquid fuels need to be discovered. It is well known that the production of biofuels may have to be increased to match the scale of use of fossil fuels. Developments in fossil fuels have taken place over the last almost 100 years. Therefore, it may take at least two decades before biofuels based bioeconomy matches fossil fuel scales. Therefore the intervening period of transition, co-processing of biomass or biomass derived oil with residual oils such as petroleum, vacuum residue or organic waste. may be required to generate enough fuels.

Cracking of the plant seed oils have been widely studied in literature [1–3]. The main problems associated with the use of these plant seed oils as liquid fuels directly are their instability, high viscosity and formation of carbon deposits in parts of automobile engines (i.e. in diesel engines) [3]. The use of large amounts of methanol and formation of glycerol as a by-product are bottlenecks to the process of transesterification of these vegetable oils to derive biodiesel [4]. Thus, cracking, catalytic cracking, and hydrocracking of these plant seed oils to transportation fuels are a better alternative.

The use of plastics has increased manifold with the modernization and urbanization of the society. Consequently its disposal has resulted in many environmental problems as these are mostly

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* Corresponding author at: Centre for Energy Studies, Indian Institute of Technology Delhi, New Delhi 110016, India. Tel.: +91 9958067120; fax: +91 11 26581121.
E-mail address: shelly.biswas@gmail.com (S. Biswas).

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nonbiodegradable. Thus, utilization of these plastic wastes by cracking these along with other fuels sources seems to offer an effective and good alternative [5]. With the depletion of lighter crudes, refineries are using heavy crudes which generate large amounts of vacuum residue (30–40%). This leads to reduction in the margin of refineries. Therefore, there is a need to crack the vacuum residue to obtain lighter products. Several workers have reported the cracking of vacuum residue under thermal and catalytic conditions to generate lighter liquid products [6–8]. The main problem associated with its cracking is the formation of coke which makes its utilization as a feedstock for cracking a less practical choice [9]. Thus, utilization of these fuel sources by co-cracking these together appears to be a feasible and valuable option.

Co-cracking/co-processing of vacuum residue with coal, plastic and biomass has been widely studied [10–13]. Cracking and utilization of plant seed oils by incorporating or blending it into co-processing unit with vacuum gas oil has been widely studied [14–17]. Thus, the co-cracking of these fuel sources together could generate new fuels for transportation. The isothermal and non-isothermal kinetics of the cracking and co-cracking of JO with VR and HDPE under nitrogen atmosphere in a batch reactor and TGA conditions respectively has been studied by the present authors [11–13].

Recently, Ali et al. [18] have reported that the use of zeolite catalyst in the co-cracking of waste plastic, vacuum residue and coal enhances the yield of the hexane soluble liquid products. Effect of catalyst on the cracking of vacuum residue with coal and plastics has been studied by various researchers to enhance the liquid yield [18–20]. Therefore, presently attempts were made to study the effect of different catalysts in the co-cracking of JO, VR and HDPE blended mixtures. In fact, authors had also studied the cracking of Jatropha oil with petroleum vacuum residue and waste plastic such as high density polyethylene and this had resulted in the production of biodiesel mainly [11]. The fuel produced also had low pH values which could affect the engine life. Therefore, further attempts were made to use catalyst for cracking reaction for exploring the possibility of producing biogasoline along with biodiesel firstly and secondly, for increasing the pH of the biofuels produced so as to reduce the corrosion effects on IC engines.

2. Material and methods

2.1. Material

The Jatropha oil was procured from Jatropha Vikas Sansthan, New Delhi. Vacuum residue used in this study was procured from the local refinery. HDPE was procured from Indian Petrochemicals Corporation Limited (IPCL-Dahej). The elemental analysis and calorific value of JO, VR and HDPE has been presented in Table 1.

2.2. Experimental preparation of the catalysts

Four catalysts have been used for studying the effect of catalyst on the co-cracking reaction. Of the four catalysts a commercial FCC catalyst was taken from the refinery and calcined at 400 ± 5 °C for 4 h and this catalyst was denoted as CAT-N.

ZSM-5 with Si/Al ratio 35 was procured from Sud Chemie India (P) Ltd. The ZSM-5 was calcined at 520 ± 5 °C for 4 h to get the catalyst CAT-Z. The third catalyst CAT-R was prepared by physical mixing of ZSM-5 and Silica alumina support. The silica alumina support (for Si/Al ratio 45) was prepared from Aluminium secondary butoxide (Fluka analytical) tetraethyl ortho silicate (Acros organics) by co-precipitation method [21,22]. The required amount of aluminium secondary butoxide was dissolved in ethanol and thoroughly mixed with tetraethyl ortho silicate and then the mixture was stirred for 1 h, NH_4OH was added drop wise to precipitate out the mixture. The precipitated mixture dried at room temperature and then at 60 °C for 2 h, the dried support was then calcined at 700 °C for 3 h and then crushed to get the prepared support. CAT-R was prepared by physical mixing of the prepared support with ZSM-5 in deionised water solution under overnight stirring conditions. The obtained mixture was filtered, dried overnight at room temperature and then at 160 °C for 2 h. The dried catalyst was then calcined at 510 ± 5 °C for 4 h to get the CAT-R.

The fourth catalyst CAT-A was prepared by impregnating silica alumina support with 4% Ni and 15% Mo loading [23]. The required weight of nickel nitrate was dissolved in deionised water and then under stirring condition, required amount of ammonium molybdate solution was added and thoroughly mixed. To this solution the silica alumina support was added under stirring condition and stirring continued for 1 h. The resultant mixture was then dried in a rotatory evaporator and dried overnight at 120 °C. The prepared catalyst was calcined at 500 °C for 4 h. The prepared CAT-A was reduced by chemical method. 4 g of the calcined catalyst was dissolved in 120 mL of deionised water and 0.4 g of $NaBH_4$ in aqueous solution was added to it. The mixture was then stirred overnight, filtered, washed copiously with deionised water and dried under vacuum conditions to get the reduced catalyst CAT-A.

2.3. Characterization of the catalysts

The surface areas and pore volumes of the catalyst (CAT-A, CAT-R, CAT-Z and CAT-N) were analyzed using N_2 adsorption. The BET surface area, total pore volume and pore size distribution were determined from N_2 adsorption/desorption isotherms measured at −196 °C using Micromeritics ASAP 2010 apparatus [23,24]. 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. XRD pattern was obtained using a Bruker-model operated at 40 kV and 20 mA using Cu Kα radiation with a wavelength of 1.54 Å. The diffraction angle was varied from 4° to 60° at a scan rate of 0.02°/s. The average particle size of the catalysts was estimated from Scherrer's equation using the most intense reflection obtained at the different 2θ values. TEM was performed using PHILIPS CM12 microscope operated at an accelerating voltage of 100 kV [25,26]. The morphology of the catalyst sample was investigated using SEM (ZEISS EVO Series Scanning Electron Microscope EVO50). The ZEISS EVO 50 is a versatile analytical microscope with a large specimen chamber. Scanning Electron Microscope EVO 50 having the resolution of 2.0 nm at 30 kV (SE withLaB6 option) with magnification range up to 1,000,000×. The structures of the

Table 1
Elemental analysis of Jatropha oil, vacuum residue and HDPE.

Sample	C	H	N	S	O[a]	Atomic H/C	Atomic O/C	Atomic S/C	CV (MJ/kg)
JO	82	13.6	0	0	4.4	1.99	0.04	–	46.91
VR	83.4	10.5	0.5	–	–	1.51	–	–	43.26
HDPE	85.5	14.2	0	0.3	0	1.99	–	0.0006	49.54

[a] By difference.

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