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Co-cracking of jatropha oil, vacuum residue and HDPE and characterization of liquid, gaseous and char products obtained

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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 with a nitrogen flow of 120 ml/h. Higher conversion of the reactant mixture was observed with the formation of liquid, gases and residual char. The co-cracking/co-processing of the JO, VR and HDPE showed synergism in their co-cracking reaction. The liquid products obtained from the co-cracking of JO, VR and HDPE were mostly aliphatic in nature. The cracked liquid obtained from the co-cracking reactions showed the presence of mainly diesel range hydrocarbons, though cracked liquid of VR + HDPE and JO + VR + HDPE showed the presence of about 22% gasoline range hydrocarbons. The gaseous products obtained consisted of methane, n-pentane, n-butane, iso-butane, 2-methyl butane and certain uncondensed components. The chars obtained indicated the presence of metals such as Ni, Fe, V, Mg and K. The overall results indicate the existence of interactive reactions between the reactive moieties generated, when JO, VR and HDPE were co-cracked together.

1. Introduction

With the growing demand of transportation fuel and depleting petroleum reserves, a situation has arisen when the world is forced to look for alternate sources of fuels. Thus, the utilization of plant seed oils has come up as a lucrative option for generation of liquid fuels. Cracking of these plant seed oils have been widely studied [1–6], but the availability of these seed oils at the consumption scale required is a major issue. With the modernization and urbanization the use of plastics has increased and although there are biodegradable plastics appearing on the market increasingly, many of the plastics being used around the world are still nonbiodegradable. Even recycling has limitation of the number of times recycling can be done without effecting its quality and environment [7,8]. Thus, utilization of these plastic wastes by cracking these along with other fuel sources seems to offer an attractive option. Even refineries utilizing heavy crude oils generate about 30–40% vacuum residue. With the depletion of lighter crudes reliance on heavy crudes is increasing however the refining of heavy crudes results in an increased amount of vacuum residue. This leads to reduction in 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 [9–13]. The main problem associated with its cracking is the formation of coke which is a bottle neck in the processing of vacuum residue in residue fluid cokers or cracking and upgrading units. Thus, the utilization of these fuel sources by co-cracking these fuels 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 [14–22]. Cracking and utilization of plant seed oils by incorporating or blending it into co-processing unit with vacuum gas oil has also been studied [23–27]. Kinetic studies on the co-cracking of jatropha oil with vacuum residue and high density polyethylene under non-isothermal conditions have been carried out [28,29]. Plastics such as HDPE are aliphatic, plant seed oils such as JO are lipids, which are glycerides and contain aliphatic side chains whereas VR is predominantly aromatic but contains aliphatic compounds as well. Therefore, the processing of these fuels through co-cracking may lead to an interesting interplay of plethora of different free radical moieties. The stabilized products formed after a series of thermochemical reactions may afford the production of lighter oils. Thus, in the present work an attempt has been made to study the cracking of these samples alone as well as co-cracking of these samples to generate different liquid, gaseous and solid char products. The kinetic studies using Arrhenius model fitting were carried out to understand the synergism of the co-cracking reactions in the batch reactor and gaining an insight into the mechanism and order of

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Table 1
Ultimate 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	70.8	10.8	0	0	18.4	1.84	0.19	0	46.91
VR	84.6	10.9	0.5	1.1	2.9	1.55	0.02	0.005	43.26
HDPE	84.9	14.4	0	0	0.7	2.04	0.006	0	49.54

[a] By difference.

the reactions involved. The liquid, solid char and gaseous products obtained were characterized. The liquid products obtained were characterized using ^{1}H NMR and ^{13}C NMR spectral studies, gas chromatography mass spectroscopy (GC–MS), FTIR spectral studies, ultimate analysis and liquid column chromatographic separation. The chars obtained were characterized using scanning electron microscope (SEM), energy-dispersive X-ray spectroscopy (EDX), and ultimate analysis. The calorific values of the liquid products and solid chars were obtained using a bomb calorimeter. The gaseous products were analyzed by GC. The calorific value of the gaseous product was calculated considering the calorific values of the individual components and the percentage composition of each component.

2. Experimental

2.1. Materials

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 ultimate analysis and calorific value of JO, VR and HDPE is shown in Table 1. The calorific value of a fuel is the quantity of heat produced by its combustion. The calorific values obtained for JO was about 47 MJ/kg, whereas for VR it was 43 MJ/kg and HDPE it was 49 MJ/kg using a bomb calorimeter.

2.2. Cracking/co-cracking in a batch reactor

Cracking of single components and co-cracking of the mixtures were carried out using a fixed bed tubular batch reactor under nitrogen atmosphere and atmospheric pressure. The flow of nitrogen was maintained at 120 ml/h for the course of the reaction. About 5–7 g of the sample was used for the cracking/co-cracking reactions under shock heating conditions to maximize the liquid yield. Shock heating would avoid the secondary reactions which could take place during slow heating.

The reactor assembly is shown in Fig. 1. The feedstock material was introduced into the reactor as soon as the reactor reached the desired temperature and kept at this temperature for different time intervals. The products formed during cracking are swept out of the reactor and the condensable liquids are condensed using a condenser and then collected in the liquid sample vial as shown in Fig. 1. The gaseous products formed are collected in a gas bag and analyzed using GC. The residue left in the reactor vessel is scraped out, which is, the char obtained in the process. The temperature range studied for the cracking and co-cracking reactions was from 350 to 550 °C. The co-cracking mixtures studied are JO + VR (1:1), JO + HDPE (1:1), VR + HDPE (1:1), JO + VR + HDPE (1:1:1). For the effect of residence time of reaction, 10 min to 1 h span of reaction was used. 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 product formed was calculated by difference i.e. by material balance. The structure of the liquid products obtained from cracking and co-cracking reactions were studied using IR (Thermo Scientific Nicolet 6700) spectral studies and the peaks were defined (only after 120 scans by the instrument). For FTIR analysis KBr pellets were made and the sample was tested on the KBr pellets.

The liquid samples obtained were also characterized by NMR spectral studies using Bruker Spectrospin 300 NMR spectrometer. $CDCl_3$ (TMS as internal reference) was the solvent used for carrying out the NMR spectral studies.

The cracked liquid was separated into different fractions by liquid column chromatographic technique [6]. The hexane fraction of the liquid products obtained from the cracking and co-cracking reactions were characterized using GC–MS. The GC–MS was performed on the apparatus Thermo Trace GC ultra GC–MS. The separation was conducted on a column of 25 m × 0.25 mm (ID) fused silica capillary coated with DB-5 [6]. 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. The ash content of the cracked and co-cracked liquid products were obtained in the electric muffle furnace.

The gaseous samples were collected in a gas bag and analyzed by Gas Chromatograph (Nucon GC) with split-less injector and flame ionization detector (FID). The metal analysis of the char/solid residue was carried out by using scanning electron microscope–energy-dispersive X-ray spectroscopy (SEM–EDX) analysis using ZEISS EVO Series Scanning Electron Microscope EVO 50. The morphology of the char samples was investigated using SEM (ZEISS EVO Series Scanning Electron Microscope EVO 50) [6]. The ultimate analysis of the initial reactants, cracked liquids and solid

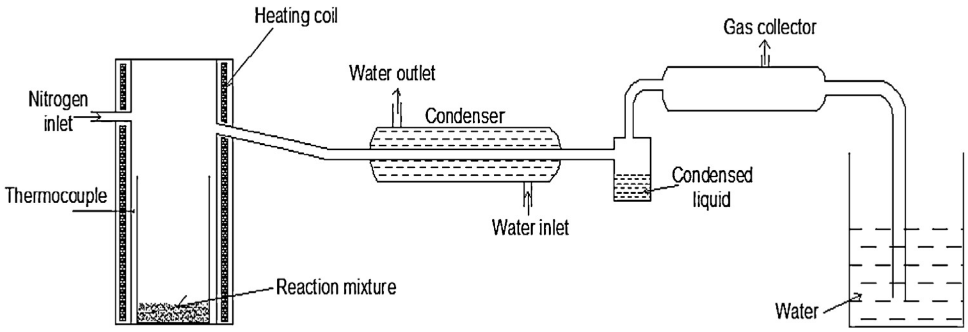

Fig. 1. Cracking reactor assembly.