CATALYTIC TRANSFORMATION OF BIODIESEL PRODUCTION WASTES TO MIDDLE DISTILLATE FUEL

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ABSTRACT: The transportation sector is relying on liquid fossil fuels. In order to mitigate future shortfalls of crude oil supply people all over the world are looking for technologies to replace fossil fuels with alternative fuels like rapeseed methyl esters, soybean methyl and ethyl esters, methanol and ethanol. Our method produces ready-to-use synthetic middle distillate fuel in one step by catalytic transformation. The used reactor for transformation of a wide variety of sources is Twin-Reactor Type OL 105/01. It includes electrical heating elements and can control the temperature, pressure, and time of the reaction. The process is environmentally friendly, producing no net greenhouse gases.

Key words: catalytic conversion, biomass to liquid, synthetic middle distillate fuel

1 INTRODUCTION

Biofuel production from vegetable oils is currently being studied [1-4], not only due to the depletion of fossil fuels but also the stringent regulations on the composition and quality of the transportation fuels. Biofuel is defined as liquid or gaseous fuel that can be produced from the utilization of biomass substrates and can serve as a (partial) substitute for fossil fuels. Liquid biofuel offers alternative fuel option in terms of environmental benefits since it is free from nitrogen and sulfur compounds. With biofuel, the greenhouse effect and air pollution can be minimized. Biodiesel is one of the alternative fuels produced from vegetable oils and being used in trucks and buses in western countries [5]. However, biodiesel can only be used in diesel engines, and not in gasoline engine [7].

The direct catalytic conversion of vegetable oils does not hold much promise since it will depend on the crop production and the market price of oil. Different reaction systems have been described for studying the catalytic cracking at the laboratory scale. Three different types of catalytic reactor are currently employed for the laboratory evaluation of cracking catalysts. The problems associated with cooking and limited feed/catalyst contact within the reactor make concurrent processing in fixed-bed reactors. Without good contact of feed and catalyst, the formation of large amounts of residue are likely, and scale-up to industrial scale is not feasible. In order to increase the yield of biofuel, and the same time, to reduce the yield of coke, many researchers found that short contact times between the catalyst and oil vapors and high temperatures are favorable. The fluid catalytic cracking in a transport riser reactor could provide a suitable solution for continuous production of liquid oil fraction and regeneration of coked catalyst [8]. In addition, the fluid catalytic cracking is the most widely process used to convert the heavy fraction of crude oil into gasoline and other hydrocarbons in the petroleum refinery [9].

In this direct catalytic conversion process, the choice of shape selective catalyst controls the type of fuel and its yield in the organic liquid product. The properties of the catalysts are governed by acidity, pore shape and size. Various types of zeolite catalysts are reported in the catalytic cracking for liquid fuel production from different raw materials. Zeolite can be more effective for larger reactant molecules by combining their microporous structure with mesoporous materials having higher adsorption capacity [10].

The operation and design of the reactor is one of the important issues to be considered in catalytic biorenewable processes. A number of catalytic process need multiphase reactor systems with catalyst geometries that accommodate these attributes of renewable feedstock: low volatility, thermal stability and multiple reaction phases. Besides the reaction that takes place within a single fluid phase, there are also multiphase reactions (liquid-gas-solid catalyst) which are affected by diffusional and thermal effects. These reactions need heterogeneous reactors like fluidized bed, entrained flow reactor, trickle bed, slurry phase, bubbling bed and fixed bed reactors to facilitate adequate contact between fluid phases and catalyst [11, 12].

In the present study, the oil-based fatty acid mixture residue obtained from biodiesel production is used as the raw material in catalytic conversion to fuel. The catalytic cracking process depends on the reaction operating conditions as well as the choice of the catalyst. In order to predict the optimum operating conditions in a process to obtain the highest yield of desired product, a statistical approach has been used.

The objectives in the present research are to study the catalytic conversion of oil-based fatty acid mixture to liquid hydrocarbon fuel at different operating conditions and to optimize these reaction-operating conditions.

2 EXPERIMENTAL

The oil-based fatty acid mixture residue obtained from biodiesel production is dark brown liquid, having mild smell, lighter than water and free of water and particles. The catalyst used for the experiments is zeolite type and was calcined in a muffle furnace for 6 h at 550 °C before it was used. The catalyst was characterized for its acidity, surface area and pore volume. The physical and chemical characteristics of catalyst are presented in Table I.

<table>
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<tr>
<th>Table I: Physical and chemical properties of the catalyst</th>
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<tr>
<td>Pore size (nm)</td>
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<td>Pore volume (cm³/g)</td>
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<td>Acidity (mmol NH₃/g)</td>
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The cracking of the oil-based fatty acid mixture was conducted at atmospheric pressure in a Twin-Reactor Type OL 105/01. The reaction temperature was in the range of 400-500°C and with a feed rate (weight hourly space velocity, WHSV) of 2.5-4.5 h⁻¹ while the feedstock to catalyst ratio was varied between 5 and 10. The catalyst was loaded in the reactor placed in the vertical tube furnace and the temperature was monitored by a thermocouple positioned in the center of the catalyst bed. Nitrogen gas was passed through the reactor for 1 h before the oil-based fatty acid mixture was fed. Once steady state had reached in the reactor, the liquid product (organic and aqueous fractions) was collected in a liquid sampler while the gaseous product was collected in a gas-sampling bulb. The process run time of each experiment varied from 2 to 4 h depending on the feed rate and oil-based fatty acid mixture/catalyst ratio. The unconverted raw material was separated from the liquid product in a laboratory vacuum distillation unit. The residue remaining after the vacuum distillation was termed as the residual oil-based fatty acid mixture. The gaseous product was analyzed by gas chromatograph. The organic liquid product was analyzed by ASTM D 86 (atmospheric distillation) and contains a large number of components of hydrocarbon compounds – middle distillate fraction. The spent catalyst was washed with acetone prior to the coke analysis. The amount of coke was determined by the difference before and after calcination in a muffle furnace.

### 3 RESULTS AND DISCUSSION

The important operating variables affecting the conversion and product distribution were reaction temperature, raw material to catalyst ratio and WHSV. The statistical method of factorial design eliminates the systematic errors with an estimate of the experimental error and minimizes the number of the experiments [13]. The conversion of the raw material and yield of middle distillate fraction were considered in the factorial design. A 2³ full factorial design with three process variables where each with two levels, namely low (-1) and high (+1) was used. Table II presents full factorial design with the operating range of each variable and the reaction conditions chosen in the design of experiments and responses.

<table>
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<th>Table II: Independent variables coded, real values used in the model and experimental matrix for 2³ full factorial design</th>
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<tr>
<td>Parameters</td>
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<tr>
<td>Reaction temperature (x₁), °C</td>
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<tr>
<td>Raw material/catalyst ratio (x₂), g/g cat.</td>
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<tr>
<td>WHSV (x₃), h⁻¹</td>
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The conversion and the yield of the middle distillate fraction are defined as:

\[
\text{Conversion} = \frac{\text{gas}(g) + \text{MDF}(g) + \text{water}(g) + \text{coke}(g)}{\text{rawmaterial}(g)} \times 100, \%
\]

\[
\text{Yield} = \frac{\text{MDF}(g)}{\text{rawmaterial}(g)} \times 100, \%
\]

where MDF represents middle distillate fuel and the total products are the sum of product gas, MDF, water and coke.

Table II shows that conversion of raw material was almost constant, which was above 90% at the feeding rate of 2.5 h⁻¹. These results indicated that at low space velocity, the conversion of the raw material was almost independent of the raw material to catalyst ratio and the reaction temperature. However, no significant trend in the conversion was observed when the space velocity was increased from 2.5 to 4.5 h⁻¹ for the reaction temperature higher than 400°C. The effect of space velocity was found significant at lower reaction temperature (400°C).

The results obtained from the eight experiments performed according to the full factorial design (Table II) were analyzed using the Statistical Analysis System (SAS) software version 9.1.3 to develop the following equations, which show the dependence of the conversion on reaction temperature, raw material to catalyst ratio, and WHSV:

\[
\text{Conv.} = 88.46 + 6.838X_1 + 2.012X_2 + 1.262X_3 - 6.312X_1X_2 + 2.188X_1X_3 + 4.062X_2X_3
\]

\[
\text{Yield} = 59.74 + 2.188X_1 + 2.012X_2 + 1.262X_3 + 4.062X_1X_3 + 55.5X_2X_3
\]

The test of the model adequacy was done through F-tests [13]. Equations (3) and (4) were chosen to fit the data after elimination of insignificant variables and their interactions.

In order to a model to be reliable, the results should be predicted with reasonable accuracy by the model and compared with the experimental results. A comparison between the experimental values with the simulated values of conversion and yield of middle distillate fraction are presented in Fig. 1 and Fig 2.
The values of correlation coefficient for the conversion and yield of middle distillate fraction were 0.9639 and 0.9404, respectively. Since these values are greater than 80%, it shows good agreement between experimental data and predicted values. Using the method of Box-Wilson we optimized the yield of middle distillate fraction, and obtained the optimal parameters for highest yield: 455°C, raw material to catalyst ratio 9.55, and WHSV of 3.46 h⁻¹. Then the yield of middle distillate fraction was 65.1%.

4 CONCLUSIONS

The yield of middle distillate fraction obtained from cracking process of oil-based fatty acid mixture residue can be adequately predicted using the proposed model. The most important process variables affecting the yield of middle distillate fraction were reaction temperature and WHSV. The optimum yield of middle distillate fraction was 65.1% at WHSV of 3.46 h⁻¹, reaction temperature of 455°C and raw material to catalyst ratio 9.55. The oil-based fatty acid mixture residue can be utilized to produce middle distillate fraction using catalytic process.

5 REFERENCES