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Production of hydrocarbon fuels from pyrolysis of soybean oils

using a basic catalyst

XU Junming, JIANG Jianchun, SUN Yunjuan, CHEN Jie
(Institute of Chemical Industry of Forest Products, Research Institute of New technology CAF, Nanjing 210042, China)

Abstract: Triglycerides obtained from animals and plants have attracted great attention from researchers for developing an environmentally friendly and high-quality fuel, free of nitrogen and sulfur. In the present work, the production of biofuel by catalytic cracking of soybean oil over a basic catalyst in a continuous pyrolysis reactor at atmospheric pressure has been studied. Experiments were designed to study the effect of different type of catalysts on the yield and acid value of the diesel and gasoline fractions from the pyrolytic oil. It was found that basic catalyst gave a product with relatively low acid number. These pyrolytic oils were also further reacted with alcohol in order to decrease their acid value. After esterification, the physico-chemical properties of these biofuels were characterized, and compared with Chinese specifications for conventional diesel fuels. The results showed that esterification of pyrolytic oil from triglycerides represents an alternative technique for producing biofuels from soybean oils with characteristics similar to those of petroleum fuels.

Keywords: Biofuel; Soybean oils; Catalytic cracking; Basic catalyst; Esterification

1. Introduction

The increasing consumption of petroleum oil throughout the world is causing urgent
economic, security, and environmental problems. One of the best ways to reduce our dependence
on petroleum is to develop renewable fuels [Huber GW et al., 2006; Demirbas AH et al., 2007].
The main advantages of biofuels include renewability and low emission of pollutants. It is
important to note that biomass is the only renewable energy source that directly yields liquid fuels
[K.D. Maher et al, 2007]. The use of biomass is centered on the fact that it is composed of
lignocellulosic material [Luo, Z et al, 2004] and triglycerides [Demirbas, A, 2008]. The
well-known conventional biofuel that is currently used worldwide and is produced from biomass
is biodiesel, which is associated with fatty acid methyl esters produced by the transesterification of
triglyceride-containing feedstocks [Barakos N et al, 2008]. However, biodiesel exhibits poor
cold-flow properties, which can be a problem for engine performance. Moreover, the presence of
oxygen in biodiesel lowers its heat content, the heating values of biodiesel being 9–13% lower
than those of conventional diesel fuels on a mass basis [K.D. Maher et al, 2007; Demirbas, A.,
2003].
Catalytic cracking of triglycerides represents an alternative way of producing renewable
bio-based products suitable for use in fuel and chemical applications. This type of technology has
significant advantages over transesterification, including lower processing costs, compatibility
with engines and fuel standards, and feedstock flexibility. More importantly, the final products are
similar in composition to diesel fuel.
In most of the studies reported in the literature regarding triglyceride pyrolysis,
molecular-sieve catalysts, including ZSM-5, MCM-41 and Y zeolite [K.D. Maher et al, 2007] and
vegetable oils [K.V. Padmaja et al., 2009] and animal fat [AO Adebano et al. 2005] were used.
There are also some reports concerning thermal cracking of triglycerides without a catalyst.
However, the pyrolytic oils in these studies exhibited a high carboxylic acid content (acid number ≈17~142) [V.R. Wiggers et al. 2009]. These undesirable products have a large effect on the corrosion value, cold filter plugging point and freezing point of the biofuel.

In this paper, we choose soybean oil as raw material because soybeans grow on a variety of soils and has become naturalized in many tropical and subtropical areas, including China, India and North America. Therefore, soybean oil has great potential in sustainable oil production.

Thus, we report here a study on the catalytic cracking of soybean oils using basic catalysts in a continuous mode. The pyrolytic products in the boiling ranges of gasoline and diesel were separated out. The effects of different kinds of catalysts on the acid value and composition of the liquid product were studied. In order to decrease the acid value, the pyrolytic oils were further reacted with alcohol using a solid acid catalyst. After esterification, these two fractions were tested physically and chemically and their properties compared with those of biodiesel and diesel obtained from petroleum.

2. Experimental

2.1. General

Refined soybean oil was obtained from commercial sources and used without further purification. The compositions of soybean oil used in experiment are triglycerides. They are composed of different kinds of fatty acids, including pentadecanoic acid(10.9 wt%), octadecanoic acid(5.6 wt%), octadecenoic acid(25.2 wt%) and octadecaenoic acid(57.7 wt%). Other materials used were of technical grade. Gas chromatography – mass spectrometry (GC–MS, Agilent 6890N/5973N) measurements were used to analyze the composition of the product. The separation
was realized on an HP-5 column, 30 m × 0.25 mm × 0.25 μm, working between 50 and 280 °C at a heating rate of 5 °C/min. The MSD provided EI mass spectra at 70 eV, taking mass spectral scans from mass 50 to mass 550 (1.2 scans/s, electron multiplier, <2000 V). The products were identified according to pre-established criteria for data analysis. Size-exclusion chromatography (SEC) was performed at room temperature on a Waters 515 apparatus equipped with a Waters 2414 refractive-index detector. Styrage HR1, HR2 (300×7.8 mm) columns from Waters were used. High-purity liquid chromatography grade THF was used as eluent at a flow rate of 1 ml/min. The columns were calibrated by using polystyrene standards with molecular weights in the range 580 and 1.96×10^4 g/mol (with NMD for 1.1). Infrared spectra (max in cm⁻¹) were obtained on a MAGNA - IR 550 spectrophotometer. The dynamic viscosity was measured with SYP-IA viscometers (GB/T265-88), and the gross calorific value was measured using a IKA-C200 calorimetric bomb (ASTM D4809). The cold filter plugging point and freezing point were tested by SYP 2007-2 and SYP 1008-5 devices, respectively.

2.2 Description of the experimental apparatus

2.2.1 Pyrolysis of soybean oil

Pyrolysis experiments were carried out at temperatures ranging from 480 to 520 °C using the 250 mL glass vessel. The soybean oil was introduced into the pyrolysis reactor with a pump and it was then heated by an external electrical resistance. The temperature was measured at two positions (column temperature and bottom temperature) using calibrated thermocouples. When the temperature inside the reactor reached 400 °C, the vegetable oil was pyrolyzed and vaporized.

The vapor left the reactor through the rectification column at temperatures ranging from 300 to
340 °C. The vapor feed then entered two heat exchangers. The first held the temperature at 160 °C and the second was a water-cooled heat exchanger. As a result, two liquid fractions were obtained in the collector with different distillation temperature (DT) ranges: (a) DT <160 °C (gasoline fraction); (b) 160 °C < DT < 340 °C (diesel fraction). The different fractions were weighed and analyzed by gas chromatography and Fourier-transform infrared (FTIR) spectrometry.

The residue in the reactor was weighed to give the coke yield.

2.2.2 Esterification of diesel and gasoline fractions

Esterification of the diesel fraction: weighed amounts of the diesel fraction, methanol, and NaHSO₄ were added to a flask with a reflux condenser and magnetic stirrer. The esterification reaction was typically carried out for 2 h at the desired temperature with vigorous stirring. The unreacted methanol was then recovered by distillation. Then the reaction mixture was filtered to obtain the product (esterified diesel fraction). Esterification of the gasoline fraction: weighed amounts of the gasoline fraction, methanol, butanol, and NaHSO₄ were added to a flask with a reflux condenser and magnetic stirrer. The esterification reaction was typically carried out for 2 h at the desired temperature with vigorous stirring. The reaction mixture was then filtered to obtain the desired product (esterified gasoline fraction). The solid acid catalyst (NaHSO₄) could be used seven times without obvious decrease in catalytic activity. After the seventh run, the acid value of product can reach 7 mgKOH/g.

3. Results and discussion

3.1 Catalytic cracking of soybean oils using different kinds of catalysts

The activities of different catalysts for cracking soybean oil were investigated. The performance of the catalysts was evaluated in terms of the yield of organic liquid product
(including diesel and gasoline fractions), coke yield and acid value. The detailed results are shown in Table 1.

Table 1 shows that high yields of diesel-like fuel can be obtained from the catalytic cracking of soybean oils. These results also show that the acid value of the organic liquid product is greatly influenced by the type of catalyst. In earlier literatures, most studies are generally conducted at temperature ranges between 300-500 °C. The main products were found to be aldehydes, alkenes and carboxylic acids. Activated alumina(Al₂O₃) was one of the cracking catalyst used in pyrolysis reaction. It has been shown that activated alumina is an effective catalyst for decarboxylation of fatty acids at atmospheric pressure and 450 °C (Vonghia et al., 1995). In our experiment, we found that a basic catalyst gave a product with relatively low acid number. Compared with an Al₂O₃ catalyst, the acid number of the pyrolytic product decreased from 104.5 to 36.9 mg KOH/g using K₂CO₃ as the basic catalyst. It is likely that the basic catalyst reacts first with fatty acids to produce metal salts, which are then further decomposed into hydrocarbons [K.D. Maher et al, 2007]. In our previous research [XU Junming et al. 2009], the acid value was closely related to the cold-flow properties. In order to obtain a low acid number of the product, twice as much catalyst was used in the catalytic cracking process. With this increased amount of K₂CO₃, the acid number of the product (diesel and gasoline fractions) decreased further from 36.9 to 15.2 and 30.1 to 15.9, respectively. It can also be seen from Table 1 that the temperature of the rectification column influenced the yield of product. When this temperature decreased, the amount of diesel fraction decreased, while the amount of gasoline fraction, coke and gas yield increased. This indicates that the product compositions possibly vary at different column temperatures. More details about molecular weights and component analyses at different column temperatures are given below.
In order to identify the pyrolysis products, a GC–MS analysis was carried out. The distribution of the pyrolytic product was different when different types of catalysts, such as an acidic catalyst (Al₂O₃), basic catalyst (K₂CO₃), or neutral catalyst (MCM-41, CaCO₃) or thermal cracking (no catalyst) was used. It can also be analyzed from GC-MS that the basic catalysts gave similar product compositions compared to other types of catalyst because these compounds showed the same retention time in gas chromatography. Among the classes of compounds formed, hydrocarbons and oxygenated organic compounds, such as alkanes, alkenes, alkadienes, and carboxylic acids, were identified. However, the yield of carboxylic acids was relatively low when basic catalysts were used.

The molecular weight of the products is determined by SEC. It was found that the molecular weight of the product is related to the column temperature. In order to obtain suitably sized molecules comparable to those of diesel fuel, the column temperature should be kept at 320 °C.

We tried to use GC–MS to analyze the products from different column temperatures. It was also found that as the temperature increased, the non-volatile components in the pyrolytic oils increased. This is in good agreement with the observations from SEC studies. It is important to note that ketones such as 2-heptadecanone were characterized by GC-MS. This component arises from the decomposition of fatty acids [K.D. Maher et al, 2007].

3.2 Physico-chemical characterization of the products

We tried to use FTIR spectra to analyze the different kinds of products. Each spectrum was normalized by the intensity of the absorption band centered at 2930 cm⁻¹ (the strongest band).

Characteristic vibrational modes were observed at 3080 cm⁻¹ (CH stretching, olefinic), 2850–2980 cm⁻¹ (CH stretching, aliphatic), 1710 cm⁻¹ (C=O stretching), and 1450-1370 cm⁻¹ (CH, aliphatic).
The significant difference between diesel and pyrolytic products is the stretching of the carbonyl group (1710 cm⁻¹). This is in good agreement with the observations of the ketone component from the GC–MS studies.

In order to identify the products after esterification, a GC–MS analysis was carried out. Among the classes of compounds formed, hydrocarbons and oxygenated organic compounds, such as alkanes, alkenes, alkadienes, and ketone, were identified. It is worth mentioning that after esterification carboxylic acids disappeared and methyl esters were identified. This suggests that the acid value of the pyrolytic product can be efficiently reduced by reaction with alkanols.

3.3 Fuel properties of the products

The main properties of the diesel fuel obtained from soybean oil are shown in Table 2. For comparison purposes, Table 2 also gives the specified values for the petroleum-based fuel and biodiesel from transesterification reaction. After esterification, the pyrolytic products had a relatively low acid number. Therefore, the results show that the fuels derived from soybean oil possess acceptable values of the given properties when compared with those for the petroleum-based fuel.

4. Conclusions

The results presented here have shown that the catalytic cracking of woody oils generates fuels with a chemical composition similar to that of petroleum-based fuel. By using a basic catalyst, it is possible to obtain oils with good cold-flow properties and a high heat value. GC and FTIR analyses of the products have shown that the distribution of fractions in the product is modified by using a basic catalyst. Moreover, esterification of the pyrolytic oils has been carried
out using a solid acid catalyst. The results show that the fuels derived from soybean oil possess
acceptable fuel properties when compared with those of petroleum-based fuel. Further studies of
this reaction, such as a pilot experiment on catalytic cracking of soybean oils and the preparation
of an efficient solid acid catalyst, are needed and are currently under investigation in our research
group.

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References:
AO Adebanjo, AK Dalai, NN Bakhshi. 2005. Production of Diesel-Like Fuel and Other
quality oil feeds over an HT2 hydrotalcite catalyst. Bioresource Technology 99(11), 5037-5042.
Demirbas, A., 2003. Biodiesel fuels from vegetable oils via catalytic and non-catalytic
supercritical alcohol transesterifications and other methods: a survey. Energy Convers. Manage. 44
(13), 2093–2109.
Demirbas AH, Demirbas I. 2007. Importance of rural bioenergy for developing countries. Energy
Convers Manage 48, 2386-2398.
Demirbas, A., 2008. Relationships derived from physical properties from vegetable oil and
biodiesel fuels. Fuel 87, 1743-1748.

Huber GW, Iborra S, Corma A., 2006. Synthesis of transportation fuels from biomass: chemistry,

K.D. Maher, D.C. Bressler. 2007. Pyrolysis of triglyceride materials for the production of
renewable fuels and chemicals Bioresource Technology 98, 2351-2368.

fuels by fluid catalytic cracking. Biomass and Bioenergy 33, 1664-1669.

liquid fuel. Biomass and Bioenergy 26, 455-462.

Mordechay H. 2008. Reaction system for production of diesel fuel from vegetable and animals
oils. US 20080066374.

triglycerides to aliphatic-hydrocarbons over activated alumina. Energy Fuels 9 (6), 1090-1096.


Biofuels from continuous fast pyrolysis of soybean oil: A pilot study. Bioresource Technology 100,
6570-6577.

XU Junming, JIANG Jianchun, LU Yanju, CHEN Jie. 2009. Liquid hydrocarbon fuels obtained by
the pyrolysis of soybean oils. Bioresource Technology 100(20), 4867-4870.
Table 1  Results of cracking reactions using different catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Column temperature (°C)</th>
<th>Catalyst amount (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Yield(%)</th>
<th>Acid Number(mg KOH/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Diesel fraction</td>
<td>Gasoline fraction</td>
</tr>
<tr>
<td>Blank</td>
<td>340</td>
<td>-</td>
<td>70.7</td>
<td>7.7</td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>340</td>
<td>1.5</td>
<td>73.3</td>
<td>6.3</td>
</tr>
<tr>
<td>MCM-41</td>
<td>340</td>
<td>1.5</td>
<td>71.3</td>
<td>8.6</td>
</tr>
<tr>
<td>K&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>340</td>
<td>1.5</td>
<td>71.3</td>
<td>9.3</td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>340</td>
<td>1.5</td>
<td>70.7</td>
<td>8.7</td>
</tr>
<tr>
<td>NaOH</td>
<td>340</td>
<td>1.5</td>
<td>69.3</td>
<td>10.6</td>
</tr>
<tr>
<td>CaCO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>340</td>
<td>1.5</td>
<td>72.7</td>
<td>9.7</td>
</tr>
<tr>
<td>CaO</td>
<td>340</td>
<td>1.5</td>
<td>68.7</td>
<td>8.7</td>
</tr>
<tr>
<td>K&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>340</td>
<td>3.0</td>
<td>62.3</td>
<td>12</td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>340</td>
<td>3.0</td>
<td>71.6</td>
<td>8</td>
</tr>
<tr>
<td>CaO</td>
<td>340</td>
<td>3.0</td>
<td>54.2</td>
<td>9.7</td>
</tr>
<tr>
<td>K&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>320</td>
<td>1.5</td>
<td>68.3</td>
<td>10.6</td>
</tr>
<tr>
<td>K&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>300</td>
<td>1.5</td>
<td>69</td>
<td>11</td>
</tr>
</tbody>
</table>

<sup>a</sup> According to total amount of soybean oil

<sup>b</sup> Residue after the pyrolysis reaction is a mixture of coke and highly viscous black liquid
Table 2. Fuel properties of pyrolytic oil

<table>
<thead>
<tr>
<th>Fuel properties</th>
<th>Diesel fraction</th>
<th>Diesel fraction after esterification(^a)</th>
<th>Gasoline fraction</th>
<th>Gasoline fraction after esterification(^b)</th>
<th>Bio-diesel\cite{Mordechai2008}</th>
<th>Diesel used in China(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (kg/m(^3))</td>
<td>847</td>
<td>858</td>
<td>790</td>
<td>808</td>
<td>$\approx$885</td>
<td>840</td>
</tr>
<tr>
<td>Kinematic viscosity (20°C, mm(^2)/s)</td>
<td>4.09</td>
<td>4.37</td>
<td>4.32</td>
<td>1.45</td>
<td>$\approx$4.5(^c)</td>
<td>2.7</td>
</tr>
<tr>
<td>Calorific value (MJ/kg)</td>
<td>43</td>
<td>43</td>
<td>41</td>
<td>35</td>
<td>$\approx$38</td>
<td>44</td>
</tr>
<tr>
<td>Freezing point (°C)</td>
<td>-29</td>
<td>-17</td>
<td>-49</td>
<td>-39</td>
<td>$\approx$-5</td>
<td>-19</td>
</tr>
<tr>
<td>Cold filter plugging point (°C)</td>
<td>-10</td>
<td>-15</td>
<td>-35</td>
<td>-24</td>
<td>-5--10</td>
<td>0</td>
</tr>
<tr>
<td>Acid value (mg KOH/g)</td>
<td>36.9</td>
<td>3.2</td>
<td>30.1</td>
<td>3.3</td>
<td>1--2</td>
<td>No acid value</td>
</tr>
</tbody>
</table>

\(^{a}\) Optimum reaction conditions for esterification of diesel fraction: m(diesel fraction): m(methanol) : m(NaHSO\(_4\)) = 1:0.3:0.04, reaction time 2 h, reaction temperature 70 °C

\(^{b}\) Optimum reaction conditions for esterification of gasoline fraction: m(diesel fraction):

m(butanol):m(methanol):m(NaHSO\(_4\)) = 1:0.5:0.6:0.04, reaction time 2 h, reaction temperature 70 °C

\(^{c}\) Measured at 40 °C

\(^{d}\) Diesel used in China: number 0