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Liquid hydrocarbon fuels obtained by the pyrolysis of soybean oils

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ABSTRACT

The pyrolysis reactions of soybean oils have been studied. The pyrolytic products were analyzed by GC–MS and FTIR and show the formation of olefins, paraffins, carboxylic acids and aldehydes. Several kinds of catalysts were compared. It was found that the amounts of carboxylic acids and aldehydes were significantly decreased by using base catalysts such as Na_2CO_3 and K_2CO_3. The low acid value pyrolytic products showed good cold flow properties and good solubility in diesel oil at low temperature. The results presented in this work have shown that the pyrolysis of soybean oils generates fuels that have chemical composition similar to petroleum based fuels.

1. Introduction

The production of biofuels as an alternative fuel from natural oils or fats is environmentally friendly because they are free of nitrogen and sulfur compounds. Biofuels can be used as fuel or fuel additives to reduce vehicle emissions. Vegetable oils and animal fats can be transesterified to produce what is commonly referred to as bio-diesel. The term bio-diesel is formally defined as a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats (Knothe and Steidley, 2005; ASTM D 6751-03a, 2005). Although bio-diesel shows great promise as a renewable, alternative fuel it is important to note that there are still disadvantages associated with its production and use. Bio-diesel exhibits poor cold flow properties, which can be a problem for engine performance. Moreover, the presence of oxygen lowers the heat content, as shown by the heating values of bio-diesel, which are 9–13% lower than those of conventional diesel fuels on a mass basis (Demirbas, 2003; Maher and Bressler, 2007). There are also stability problems, since it is well known that vegetable oil derivatives are prone to deterioration through hydrolytic and oxidative reactions.

Pyrolysis or thermal cracking of triglyceride materials represents an alternative method of producing renewable bio-based products suitable for use in fuel and chemical applications. This option is especially promising in areas where the hydroprocessing industry is well established because the technology is very similar to that of conventional petroleum refining. There are significant advantages in this type of technology over transesterification including lower processing costs, compatibility with infrastructure, engines and fuel standards, and feedstock flexibility (Stumborg et al., 1996). More importantly, the final products are similar in composition to diesel fuel.

Studies of pyrolysis in the absence of a catalyst have been reported previously (Schwab et al., 1988; Fortes and Baugh, 1994; Idem et al., 1996). In these papers, the characterization of pyrolysis gas and liquid products was reported and some reaction pathways were proposed. In recent years, some new types of catalyst such as HZSM-5 (Twaiq et al., 2003a,b) and MCM-41 (Sang et al., 2003, 2004) have been developed and used in a pyrolysis reaction. It was observed that the product in this case has lower viscosity (2–3 mm^2/s) and a higher cetane number (>50) compared to pure vegetable Soybean oil (Lima et al., 2004). It is worthwhile mentioning that the pyrolytic oils exhibited high carboxylic acid content (acid number $\approx$ 116–133). These undesired products have great effects on the corrosion value, cold filter plugging point and freezing point of the biofuel.

In this paper, we wish to report a study using soybean oil as the raw material for liquid hydrocarbon fuel preparation by a pyrolysis reaction. We aim to find a suitable methodology to obtain pyrolytic oils with low carboxylic acid content. Different kinds of catalysts have been prepared and tested in the pyrolysis process. The resulting pyrolytic oils have been characterized by FTIR and GC–MS and their fuel properties also tested.

2. Methods

2.1. General

Refined soybean oil was obtained from commercial sources and used without further purification. Other materials used were of technical grade. Gas chromatography–mass spectrometry

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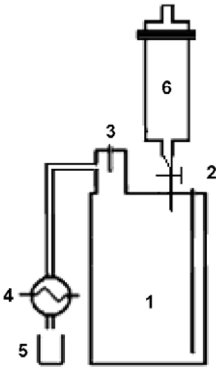

Fig. 1. Apparatus (250 mL) used for vegetable oil pyrolysis experiments: (1) Pyrolysis reactor; (2) and (3) thermocouple probes; (4) heat exchanger; (5) liquid collector and (6) dropping funnel.

(Agilent 6890N/5973N) measurements were used to analyze the composition of the product. The separation was realized on a column of HP-5, 30 m × 0.25 mm × 0.25 μm, working between 50 and 250 °C at a heating rate of 5 °C/min. The presence of different classes of compound present in the pyrolysates was confirmed using the total ion chromatogram (TIC) and selected ion mass chromatogram analyses, in addition to fragmentation patterns and library matching (NIST). Identification was carried out according to pre-established criteria for the analysis of the data. IR 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). Cold filter plugging point and freezing point were tested by SYP 2007-2 and SYP 1008-5, respectively.

2.2. Apparatus and method

Pyrolysis experiments were carried out at temperatures ranging from 350 to 400 °C using the 250 mL glass vessel shown in Fig. 1. The soybean oil was introduced into the pyrolysis reactor (1 of Fig. 1) with a dropping funnel (6 of Fig. 1) and then heated by an external electrical resistance. The temperature was measured at two positions using calibrated thermocouples (see 2 and 3 in Fig. 1). When the temperature inside the reactor had reached 300 °C, the vegetable oil was pyrolyzed and vaporized. The vapor left the reactor through the top at temperatures ranging from 200 to 280 °C. The vapor feed then enters a water cooled heat exchanger (4 of Fig. 1). As a result, two liquid fractions were obtained in the collector (5 of Fig. 1), an aqueous fraction and an organic fraction. The organic phase was weighed to give the yield of organic liquid product (yield of OLP) and analyzed by gas chromatography and FTIR. The residue in the reactor was weighed to give the coke yield.

3. Results and discussion

3.1. Pyrolysis of soybean oil using different catalysts

The activities of different catalysts were investigated for the cracking of soybean oil. The performance of the catalysts was evaluated in terms of the yield of organic liquid product (OLP), coke yield and other fuel properties such as acid value, cold filter plugging point and freezing point. The detailed results are shown in Table 1.

From Table 1, it can be seen that as the acid value increased, the cold filter plugging point and freezing point of the pyrolytic oil also increased. That is to say, the acid value had a close relationship to the cold flow properties. We tried to use the high acid value product, catalyzed by Al_2O_3, to blend with diesel and discovered that it was difficult to dissolve in diesel because the carboxylic acid compounds had a great effect on the hydrophobic properties of the product. Compared with high acid value pyrolytic oil, using Na_2CO_3, K_2CO_3 as the base catalyst gave pyrolytic oils with low acid value and the product showed good solubility in diesel at low temperature.

However, when the soybean oil was introduced to reactor using the dropping funnel, the pyrolysis produced oils with low acid value. The acid value decreased from 120 to 89 by adding soybean oil slowly, drop by drop, to the reactor. Accordingly, we have adopted this methodology for the study of the pyrolysis process using other catalysts.

3.2. Fractions characterization

In order to identify the pyrolysis products a CG–MS analysis was carried out. Among the classes of compounds formed, hydrocarbons and oxygenated organic compounds such as alkanes, alkenes, alkadienes, and carboxylic acids were identified. Fig. 2 shows chromatograms for the products with different acid values obtained in the pyrolysis (Table 1). These results show that the products obtained were changed by using a basic catalyst. Peaks of several kinds of carboxylic acids (*n*-hexadecanoic acid, octadec-9-enoic acid and octadecanoic acid) identified in Fig. 2a were significantly decreased by using Na_2CO_3 as catalyst.

We tried to use FTIR spectra to analysis the pyrolysis product obtained from soybean oils (Table 1) with different acid values. Each spectrum was normalized by the intensity of the absorption band centered at 2930 cm^{-1} (the strongest band). Characteristic vibrational modes are observed at 3080 cm^{-1} (CH stretching, olefinic), 2850–2980 cm^{-1} (CH stretching, aliphatic), 1710 cm^{-1} ($C{=}O$ stretching), and 1642 cm^{-1} ($C{=}C$ stretching, olefinic).

It was found that the products with high acid value present some absorption features that are not observed in the low acidic products, e.g. the absorption at 2713 cm^{-1}, characteristic of aldehydes. A very broad absorption centered at 3500–3000 cm^{-1} is observed in the spectra of the pyrolytic oils with high acid value. This

Table 1
The results of pyrolysis catalyzed by different catalysts.

Catalyst	Yield of OLP (%)	Coke yield (%)	Acid value (mg KOH/g)	Cold filter plugging point (°C)	Freezing point (°C)
Al_2O_3[a]	75.3	8.5	120	11	8
Al_2O_3[b]	80.6	6.9	89	3	−15
Na_2CO_3[b]	73.3	8.4	21	−2.5	−33
K_2CO_3[b]	75.6	7.3	28	−2.0	−29
MCM-41[c]	81.3	6.5	70	0.5	−18

The amount of catalyst used in all experiments was 2.5%.

[a] All reactants (include soybean oil and catalyst) were charged into the reactor before pyrolysis.

[b] Soybean oil was introduced into reactor over a period of 2 h using a dropping funnel and at temperatures ranging from 350 to 400 °C.

[c] MCM-41 was prepared according to the literature (Xu et al., 2008). Other reaction conditions were the same as b.