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# Biofuel production from catalytic cracking of woody oils

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ABSTRACT

The catalytic cracking reactions of several kinds of woody oils have been studied. The products were analyzed by GC–MS and FTIR and show the formation of olefins, paraffins and carboxylic acids. Several kinds of catalysts were compared. It was found that the fraction distribution of product was modified by using base catalysts such as CaO. The products from woody oils showed good cold flow properties compared with diesel used in China. The results presented in this work have shown that the catalytic cracking of woody oils generates fuels that have physical and chemical properties comparable to those specified for petroleum based fuels.

## 1. Introduction

Biomass has been recognized as a sustainable replacement for its cleanness and substantial sources. Biomass, the only renewable resource to be converted to liquid fuel, despite containing the low carbon content, is clean, for biomass has a negligible content of sulfur, nitrogen and ash, which give a lower emission of $SO_2$, $NO_x$ and soot than that of conventional fossil fuels. Besides, zero emission of $CO_2$ can be achieved because $CO_2$ released from biomass will be incorporated into the plants by photosynthesis quantitatively.

Vegetable oils and animal fats are mainly triglyceride and 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 (Mittelbach and Gangl, 2001).

Catalytic 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 (Limaa et al., 2004).

It is worthwhile mentioning that almost all commercial triglyceride are from edible oils such as soybean oil and rapeseed oil. Therefore, biofuel is actually competing limited land availability with the food industry for the same oil crop. In order to overcome this issue, many researchers have begun searching for cheaper and non-edible oils to be used as alternative feedstock such as woody oils. Woody oil plants are widely distributed in south and center of subtropics in Asia in recent years. These plants have some characteristics such as wide distribution, strong adaptability and high yield. For example, Jatropha is a genus of approximately 175 succulent plants, shrubs and trees (some are deciduous, like *Jatropha curcas* L.), from the family Euphorbiaceae. It is proved to be a

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promising oil-bearing tree in the arid and semi-arid regions, and produces seeds containing 34.4% oil in average (Achten et al., 2008). Jatropha is native to Central America (Fairless, 2007) and has become naturalized in many tropical and subtropical areas, including India, Africa, and North America.

In this paper, we wish to report a study using several kinds of woody oils as the raw material for liquid hydrocarbon fuel preparation by a catalytic cracking reaction. We aim to find a suitable methodology to obtain products with desirable molecular weight comparable to petroleum based fuels. Different kinds of catalysts have been prepared and tested in the catalytic cracking process. The resulting oils have been characterized by FTIR, size exclusion chromatography (SEC) and GC–MS and their fuel properties also tested.

## 2. Methods

### 2.1. General

Woody oils such as Tong oil, Palm oil, Curcas oil and *Schisandra* wilsoniana Sojak oil were obtained from commercial sources and used without further purification. Other materials used were of technical grade. Gas chromatography–mass spectrometry (Agilent 6890N/5973N) measurements were used to analyze the composition of the product. The separation was conducted 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 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). IR spectra (max in $cm^{-1}$) were obtained on a MAGNA-IR 550 spectrophotometer. Size exclusion chromatography (SEC) was performed at room temperature on a Waters 515 equipped with a Waters 2414 Refractive Index Detector. The columns were Waters Styragel HR1, HR2 (300 × 7.8 mm) from Waters. HPLC 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 of 580 and $1.96 \times 10^4$ g/mol (with NMD for 1.1). 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

Catalytic cracking experiments were carried out at temperatures ranging from 450 to 500 °C using the 250 mL glass vessel shown in Fig. 1. 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 450–500 °C, the woody oil was introduced into the cracking reactor (1 of Fig. 1) with a constant flow pump (7 of Fig. 1) and then the woody oil was pyrolyzed and vaporized. The vapor left the reactor through the rectification column (4 of Fig. 1) with a conventional metal packing at temperatures ranging from 330 to 340 °C. The vapor feed then enters a water cooled heat exchanger (5 of Fig. 1). As a result, two liquid fractions were obtained in the collector (6 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, size exclusion chromatography (SEC) and FTIR. The residue in the reactor was weighed to give the coke yield.

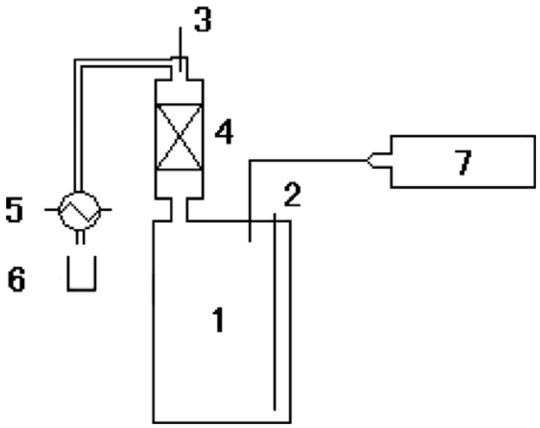

**Fig. 1.** Apparatus (250 mL) used for woody oils catalytic cracking experiments: (1) Cracking reactor, (2) and (3) thermocouple probes, (4) rectification column, (5) heat exchanger, (6) liquid collector, (7) pump.

## 3. Results and discussion

### 3.1. Catalytic cracking of different kinds of woody oil

The cracking reaction of different kinds of woody oils and activities of different catalysts were investigated. The reaction conditions such as reaction temperature, catalyst concentration and flow rate were also tested. The detailed results are shown in Tables 1 and 2.

From Table 1, it can be seen that the acid value of the product was decreased by using base catalyst such as CaO. Other catalysts gave similar results evaluated in terms of the yield of organic liquid product (OLP), coke yield and acid value. Compared with diesel used in China, these products showed good cold flow properties such as cold filter plugging point and freezing point. From Table 2, the suitable reaction conditions carried out in 250 mL glass ves-

**Table 1**
The results of cracking reactions using different woody oils.

| Different kinds of woody oils | Catalyst | Yield of OLP (%) | Coke yield (%) | Acid value (mg KOH/g) | Cold filter plugging point (°C) | Freezing point (°C) |
|---|---|---|---|---|---|---|
| Tong oil | Blank | 70.5 | 8 | 74 | −23 | −38 |
| Tong oil | $Al_2O_3$ | 75.5 | 8.5 | 78 | −18 | −27 |
| Tong oil | MCM-41[a] | 71 | 9 | 75 | −23 | −41 |
| Tong oil | CaO | 77 | 9 | 59 | −22 | −43 |
| *S. wilsoniana* Sojak oil | CaO | 69 | 13 | 77 | −23 | −30 |
| Curcas oil | CaO | 76 | 10 | 51 | −15 | −30 |
| Palm oil | CaO | 72.5 | 8.5 | 58 | −8 | −22 |

The amount of catalyst used in all experiments was 5%.

[a] MCM-41 was prepared according to the literature (Xu et al., 2008).

**Table 2**
Effect of reaction conditions on the products from Tong oil.

| Temperature (°C) | Amount of catalyst (%) | Flow rate (g/h) | Acid value (mg KOH/g) | Yield of OLP (%) | Coke yield (%) |
|---|---|---|---|---|---|
| 440 ± 15 | 5 | 50 | 48 | 53 | 33[a] |
| 480 ± 15 | 5 | 50 | 59 | 77 | 9 |
| 520 ± 15 | 5 | 50 | 55 | 78 | 13 |
| 480 ± 15 | 1 | 50 | 73 | 78 | 10 |
| 480 ± 15 | 3 | 50 | 56 | 81 | 7.5 |
| 480 ± 15 | 3 | 30 | 62 | 73 | 13.5 |
| 480 ± 15 | 3 | 70 | 53 | 79 | 8.5 |

[a] Residue after pyrolysis reaction is a mixture of coke and high viscous black liquid.