



Optimization of catalytic cracking process for upgrading camelina oil to hydrocarbon biofuel



Xianhui Zhao, Lin Wei*, Shouyun Cheng, James Julson

Department of Agricultural and Biosystems Engineering, South Dakota State University, Brookings, SD 57007, USA

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ABSTRACT

Catalytic cracking of camelina oil over Zn/ZSM-5 catalyst in a fixed-bed tubular reactor was investigated. An optimization study on the catalytic cracking conditions based on nine well-planned orthogonal experiments was carried out. Three main operation conditions including reaction temperature, liquid hourly space velocity and oil extraction press frequency were studied to examine their effects on the yield and quality of hydrocarbon biofuel produced. Characterization of the catalyst, hydrocarbon biofuel and non-condensable gas was conducted. There was no significant difference between the bulk structures of fresh Zn/ZSM-5 and used Zn/ZSM-5. Small ZnO particles dispersed well on the parent ZSM-5. Hydrocarbon biofuel contained 65.18% hydrocarbons and its properties including dynamic viscosity, density and higher heating value were improved after upgrading, compared to camelina oil. It was found that the oil extraction press frequency was the most important factor and liquid hourly space velocity was the least important factor for the hydrocarbon biofuel production. In addition, the optimum conditions for camelina oil upgrading were a combination of reaction temperature of 550 °C, a liquid hourly space velocity of 1.0 h⁻¹ and an oil extraction press frequency of 15 Hz.

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1. Introduction

Conventional transportation fuel produced from petroleum has caused greenhouse gas emissions. Renewable fuel such as bio-jet fuel, biodiesel and ethanol is an effective alternative energy source. Exploring alternative energy sources, especially with the growing importance of bio-jet fuel in the aviation industries, has been paid attention to by researchers. It has been proved that renewable fuel can significantly reduce greenhouse gas emissions compared with conventional petroleum fuel. Under this situation, new crops such as camelina and jatropha have been studied as new feedstocks for renewable fuel production. In addition, camelina and jatropha are inedible plants, which do not compete with the food industry. Camelina is a low input oilseed crop that can provide sustainable biofuel. It has a high oil content, high tolerance to cold weather and drought conditions, short growth cycle, and resistance to common pathogens (Li and Mupondwa, 2014). Camelina is considered as an important renewable energy source due to its widespread production and high yield.

Well-known methods for biofuel production from vegetable oil mainly include thermal cracking, transesterification, hydroprocessing and catalytic cracking. Thermal cracking is a technique to

convert vegetable oil to biofuel at a high temperature and high pressure without catalyst. The thermal cracking process involves either a free radical mechanism or a carbonium ion mechanism. However, the cost is relatively higher and the gasoline yield is relatively lower compared with catalytic cracking (Li et al., 2009b). Transesterification of vegetable oil is a process in which solvents such as methanol and ethanol in the presence of catalyst are used to chemically break the molecules of vegetable oil into glycerol and esters of the renewable fuel. The product of this process is considered as biodiesel, but biodiesel is not suitable for future bio-jet fuel production because it exhibits some drawbacks such as low oxidative and storage stability, high density and viscosity, and water absorbency (Ribeiro et al., 2014; Zhao et al., 2015a,c; Habibullah et al., 2015). Hydroprocessing of vegetable oil requires severe conditions such as high catalyst activity and high hydrogen pressure. Although some noble metal catalysts possess a high activity, their high price and limitation of availability become an issue. During hydroprocessing, oxygen atoms are removed in the form of CO, CO₂ and H₂O with an introduction of hydrogen (Zhao et al., 2015c).

Catalytic cracking of vegetable oil has the potential to produce biofuel similar to petroleum based fuel. Triglycerides in vegetable oil are cracked into fatty acids through a decomposition. Then, fatty acids are converted into products such as gasoline, heavy hydrocarbons and light gaseous hydrocarbons (Rao et al., 2010). Catalysts with long lifetime and excellent selectivity can reduce the processing cost and improve the product yield. Distillation technology can

* Corresponding author. Fax: +1 6056886764.
E-mail address: lin.wei@sdstate.edu (L. Wei).

be used to separate an oil mixture with wide boiling ranges into products with narrower boiling ranges. The oil mixture is heated to vaporize the lighter components (Zhao et al., 2015c; Greg et al., 2006). After vegetable oil is upgraded into liquid hydrocarbons, the liquid hydrocarbons will be delivered to a petroleum refinery to produce bio-jet fuel.

Li et al. (2009a) used cottonseed oil to produce biofuel using a catalytic cracking method in a fixed-fluidized bed. The effect of residence time, catalyst-to-oil ratio and reaction temperature on the yield of bio-gasoline and light fuel oil was studied. It was found that catalyst-to-oil ratio and reaction temperature were important variables. In addition, the catalytic cracking method could be used to convert cottonseed oil to value added gasoline. Several studies in the literature have shown that the composition of vegetable oil had an influence on the yield and distribution of biofuel. For example, Ooi et al. (2004) found that the composition of feedstock including used palm oil and palm oil fatty acids mixture affected the conversion and liquid fuel distribution during the catalytic cracking process. Al-Sabawi et al. (2012) compared various vegetable oils for the biofuel production and found that the palm oil cracking produced more liquefied petroleum gas and light C₂–C₄ olefins than soybean oil and canola oil. Yang et al. (2013) studied that the concentration of the C₁₈ fatty acid mixture (including C_{18:0}, C_{18:1} and C_{18:2}) had a significant effect on the biofuel distribution. Morgan et al. (2012) studied the deoxygenation of soybean oil under nitrogen atmosphere over supported nickel catalysts. Oxygen atoms in the carboxyl group of the fatty acid structure were removed in the form of CO and CO₂. The catalytic cracking of the fatty acid chains produced liquid hydrocarbons (C₅–C₁₇). Unsaturated triglycerides as a feed led to the formation of lighter hydrocarbons and higher amounts of coke than using saturated triglycerides as a feed. However, only a few researchers have studied the catalytic cracking of inedible vegetable oil for biofuel production. In addition, it is important to optimize the catalytic cracking process conditions to produce biofuel with a high quality.

Zeolite catalyst includes ZSM-5, Beta, SBA-15, mordenite, Mor, FCC, etc. It was reported to be promising to convert biomass derived feedstocks into chemicals and biofuels. Among the zeolite catalysts, ZSM-5 has a high acidity and is effective to convert triglycerides into liquid fuel. ZSM-5 can increase the formation of aromatics and is widely used in the petroleum refinery process (Zhao et al., 2015c; Zhang et al., 2011). The loading of metals including Al, Ca, Cr, Cu, Li, Mg and Ni into ZSM-5 showed that they could enhance the active acid sites on the surface of ZSM-5 catalyst (Zakaria et al., 2012). However, the research on biofuel production using inedible vegetable oil over ZSM-5 catalyst doped with Zn is lacking. Actually, ZnCl₂ has a high activity and stereoselectivity and is easily available as well (Demirbas, 2003).

The objective of this work is to explore optimum operation conditions in which camelina oil underwent catalytic cracking over the Zn/ZSM-5 catalyst in a fixed-bed reactor. The effect of the operation conditions on the hydrocarbon biofuel yield and properties such as moisture content, density, dynamic viscosity and higher heating value (HHV) was discussed. The main compounds of hydrocarbon biofuel and non-condensable gas were determined.

2. Materials and methods

2.1. Feedstock and device preparation

Camelina (*sativa*) seeds were purchased from Hancock Seed Company, Dade, Florida, USA. The moisture content and bulk density of camelina seeds was 4.92% and 0.76 g/mL, respectively. The camelina seeds were used for oil extraction at the Advanced Bio-fuel Laboratory in the Department of Agricultural and Biosystems

Table 1
Main physicochemical properties of camelina oil.

Physicochemical properties	Camelina oil
Main constituents (area%)	Linolenic acid (C ₁₈ H ₃₀ O ₂): 78.67–84.47
Density (g/mL)	0.88–0.89
Moisture content (wt.%)	0.06–0.08
Dynamic viscosity (20 °C, cP)	58.85–59.65
HHV (MJ/kg)	39.41–39.65

Engineering, South Dakota State University (SDSU) using a cold press method. A M70 Oil Press, purchased from Oil Press Company (Eau Claire, Wisconsin, USA), was used for the oil extraction from camelina seeds and the nozzle size (inside diameter) of the Oil Press was 5.59 mm. The camelina seeds were pressed at three different frequencies (15 Hz, 20 Hz and 25 Hz), which were related to the screw rotation speed of Oil Press. The yield of camelina oil obtained from the cold press of camelina seeds at 15 Hz, 20 Hz and 25 Hz was 36.7%, 36.6% and 36.1%, respectively. The camelina oil produced at these three different frequencies was used for upgrading trials. Some physicochemical properties of the cold-pressed camelina oil are shown in Table 1 (Zhao et al., 2014b; Zhao et al., 2015b). The linolenic acid content of the cold-pressed camelina oil was higher than that of the camelina *sativa* oil (27.1–39.7%) reported by Abramovic and Abram (2005). Crowley and Frohlich (1998) have studied that the fatty acid composition of camelina oil was influenced by both variety and environment. For example, the linolenic acid content (percentage of total fatty acids) of a camelina *sativa* seed was between 12.3% and 32.0%. However, the linolenic acid content of a new transformed docosahexaenoic acid (DHA) producing camelina *sativa* seed was 38.6–54.1% due to the incorporation of microalgal genes (Mansour et al., 2014).

2.2. Catalyst preparation

The zeolite powders were purchased from Zeolyst International, Kansas City, Kansas, USA. The atomic ratio of silica-to-alumina of the zeolite was 15. The catalyst of ZSM-5 doped with 20 wt.% Zn (Zn/ZSM-5) was prepared using a wet impregnation method. Zinc chloride purchased from Fisher Scientific was used to provide Zn. The catalyst blended with boehmite and guar gum was pressed in a strip shape at about 6.9×10^4 Pa through a sieve in a hydraulic press (Owatonna Tool Company, Minnesota). The catalyst was sealed and stored at room temperature for 12 h and then calcined in the air at 550 °C for 4 h. The catalyst was stored in a sealed vial in a desiccator for upgrading use (Zhao et al., 2015b,c). In this study, the fresh Zn/ZSM-5 catalyst was used as a control compared to the used Zn/ZSM-5 catalyst (Zhao et al., 2015a). The used Zn/ZSM-5 catalyst was obtained after being used for a typical catalytic cracking of camelina oil.

2.3. Catalyst characterization

The bulk structure of fresh Zn/ZSM-5 and used Zn/ZSM-5 was examined using an automated multipurpose X-ray Diffractometer (XRD, SmartLab, Rigaku Corporation). The scan range was 5–50 degrees with a scan speed of 2°/min. The tube voltage and tube current were 40 kV and 44 mA, respectively. A Fourier transform infrared spectroscopy (FT-IR) analysis of the catalyst samples was performed on a Nicolet 6700 FT-IR spectrometer using KBr pellets. The surface area, pore volume and pore size of the catalysts were measured using a Micromeritics TriStar 3000 automated gas adsorption analyzer. The physisorption analysis with liquid nitrogen was carried out using an ASAP 2010 Micropore Analyzer at 77 K. The used Zn/ZSM-5 was pretreated in the air at 600 °C to remove the coke which could pollute the apparatus. The surface area was

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