

## Research article

## Co-hydrotreatment of tire pyrolysis oil and vegetable oil for the production of transportation fuels



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## ARTICLE INFO

## Article history:

Received 24 November 2016

Received in revised form 28 January 2017

Accepted 29 January 2017

Available online xxx

## Keywords:

Co-hydrotreatment

Tire pyrolysis oil

Vegetable oil

Catalyst characterization

Catalytic behavior

Distillation

Fuel characterization

## ABSTRACT

Catalytic hydrotreatment followed by products isomerization is an effective technology to convert vegetable oil to a green fuel composed of straight and branched chain aliphatic hydrocarbons. The content of aromatics in this fuel is very low. In this paper we study the co-hydrotreatment of vegetable oil and tires oil in the presence of a CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst as a way of utilizing existing infrastructure created for vegetable oil processing for tire oil up-grading in order to obtain fuel cuts with aromatics. Hydrotreatment studies with different vegetable oil/tires oil blend ratios were conducted. The yield and composition of the resulting hydrotreated oils are reported. Aliphatic hydrocarbons ranging from C7 to C20 derived from vegetable oils and aromatics from C6 to C16 derived from the tire oil were identified as products. The resulting oils were then successfully distilled into naphtha, kerosene, diesel and gas oil cuts. The yield, chemical composition and the fuel properties of the transportation fuel cuts obtained are reported and compared with commercial petro derived fuels.

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## 1. Introduction

The growing environmental concerns associated with the use of petroleum derived fossil fuels has stimulated recent interest in alternative fuels [1]. Fuels derived from vegetable oils and tires oil show promising potential in replacing a fraction of the current petroleum based transportation fuels. Vegetable oils can be readily converted into biodiesel via transesterification with alcohols (methanol or ethanol). However, biodiesel suffers from drawbacks such as limited storage stability and poor cold flow properties [2]. The hydrocarbons resulting from the hydrotreatment (decarboxylation, decarbonylation and hydrodeoxygenation) and isomerization of vegetable oils (rapeseed, palm, soybean, sunflower, castor, jatropha and cooking oil) have better fuel properties [3–9]. The production of green diesel through hydrodeoxygenation (HDO) technology by various catalysts, (Pt/C, Pd/C, NiMo/Al<sub>2</sub>O<sub>3</sub> and CoMo/Al<sub>2</sub>O<sub>3</sub>) has received considerable attention in the last 10 years [10–14]. The expensive noble metals (Pt and Pd) typically show the highest HDO activity for vegetable oils [15,16]. Cheaper bifunctional catalysts, such as the NiMo/Al<sub>2</sub>O<sub>3</sub> has also been used for vegetable oil hydrotreatment [17]. Typically NiMo is responsible for the HDO while the acidic Al<sub>2</sub>O<sub>3</sub> support favors hydrocracking [18,19]. Studentschnig et al. [4] illustrated the importance of Mo in the NiMo/Al<sub>2</sub>O<sub>3</sub> system, and proved that the activity of catalysts decreased in the order NiMo/Al<sub>2</sub>O<sub>3</sub> > Mo/Al<sub>2</sub>O<sub>3</sub> > Ni/Al<sub>2</sub>O<sub>3</sub> [5]. Wang et al.

used three different types of acidic support to investigate the effect of supports on catalyst activity and selectivity during hydrotreatment of soybean oil [20]. The results demonstrated that NiMo/Al<sub>2</sub>O<sub>3</sub> selectively favored the production of diesel ranged hydrocarbons. Naptha cuts were favored with zeolite-supported NiMo. The mesoporous SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts are more acidic than Al<sub>2</sub>O<sub>3</sub> but less acidic than most of zeolites. SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> supported Ni is more selective for the kerosene range hydrocarbons than the less acidic Al<sub>2</sub>O<sub>3</sub> which favors diesel range hydrocarbons [21]. Similar results have been reported for Pt and Pb supported catalysts [22–24]. CoMo/Al<sub>2</sub>O<sub>3</sub> is another commercial catalyst for hydrocarbons production by HDO of various triglycerides. This catalyst is considered as a moderate acidic catalyst which favors hydrocracking of straight chain hydrocarbons [25,26].

The use of tire pyrolysis oil for the production of transportation fuels is much less studied than the vegetable oils. Pyrolysis converts between 40 and 60 wt.% of tires into oil [27]. Tires pyrolytic oil has a very high calorific value (44 MJ/kg), very low ash content (<0.05 wt.%) and a relatively low sulfur content (0.8–1.5 wt.%). Current jet fuel derived from fossil petroleum contains approximately 20 wt.% of paraffin, 40 wt.% isoparaffin, 20 wt.% naphthene and 20 wt.% aromatic compounds. The co-hydrotreatment of vegetable oil and tires oils offer an interesting opportunity to take advantage of existing infrastructure to process tires oil and to produce fuels with a content of aromatic comparable with its fossil fuel competitors.

In this study, the co-hydrotreatment on vegetable oil and pyrolysis oils derived from waste tires, were conducted using commercial CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts. The aim of co-hydrotreatment is to produce

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alternative fuels containing both aliphatic and aromatic hydrocarbons. The information collected will also be useful to understand the challenges and opportunities of co-processing tires oil in facilities built for the hydro-processing vegetable oils.

## 2. Materials and methods

### 2.1. Materials and reagents

The tire pyrolysis oil was provided by CONRAD Industries, Inc., Chehalis, WA. It was produced from shredded waste tires in a rotating kiln. The pyrolysis vapors were condensed using a spray condenser tower. The Canola oil studied was a commercial oil (Walmart Great Value: Canola Oil. 53,507-GRV). The chemical make-up of the vegetable oil studied was analyzed by transesterification with methanol and analysis of the resulting samples by GC/FID (FAMEWAX column, 30 m × 320 μm × 0.25 μm, Restek Corporation, Bellefonte, PA). The injector was kept at 260 °C, with an injection volume of 1 μL by split injection mode (ratio at 30:1). The initial oven temperature was set at 120 °C, then increased at a heating rate of 3 °C/min to 240 °C and held for 20 min. The detector temperature was set at 250 °C. Helium was used as carrier gas.

The CoMo/γ-Al<sub>2</sub>O<sub>3</sub> catalyst was purchased from Alfa Aesar (<http://www.alfa.com/>). Its nominal CoO-content was 2.9 wt.%, its MoO<sub>3</sub>-content was 13.5 wt.% and the BET surface area 193 m<sup>2</sup>/g [28]. The CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst was delivered as pellets, with particle length higher than 50 μm. The activity of such catalyst was low in our system, and therefore the pellets were ground into fine powder (between 0.1 and 0.5 mm). All the solvents (acetone, methanol) used for cleaning the reactor and collecting the products were reagent grade. Those used for analysis were HPLC grade.

### 2.2. Co-hydrotreatment tests

Fig. 1 shows a scheme with the tasks conducted. Different tire/canola oil mass ratio (4:1, 1:1, and 1:4) were preparing before hydrotreating. 100 g of the prepared blends were fed into reactor with 5 g of CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst in each test. Each blend was hydrotreated in duplicate and the average results reported. The tests were conducted in a 250 mL Parr reactor (Model# 4576A) with the stirring speed at 250 rpm. The initial pressure of hydrogen was 9.1 MPa at room temperature (25 °C) and it took 30–35 min to heat up to 350 °C. The final temperature was kept for another 4 h before the reactor was cooled down to room temperature (see scheme of installation and typical operational conditions in Fig. 2). Gaseous products were collected in gas sampling cylinders and analyzed by GC. The solid catalyst was separated from the liquid product by 30 min centrifugation followed by vacuum filtration. The filtrated liquid products were stored at 4 °C. The yield of gases was estimated as the difference of reactor weight with samples before and after each test. The yield of coke was calculated by subtracting the initial mass of catalyst added and the catalyst collected

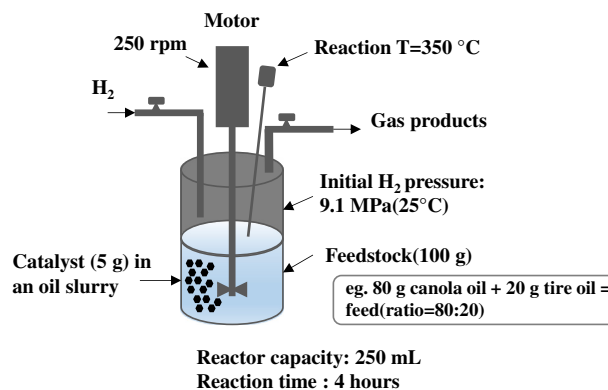


Fig. 2. Experimental set up and typical hydrotreatment conditions.

after filtering the oil and washing the catalyst with solvent. Finally, the yield of liquid was calculated by difference.

### 2.3. Distillation

A simple distillation setup (ASTM D86–12) was used. Briefly, a 20 g specimen was distilled in a laboratory batch distillation unit under ambient pressure. Systematic observations of temperature readings and mass of condensate are made. Hydrotreated liquid products were distilled to obtain the following fractions: <71 °C (lights), 71–182 °C (naphtha), 182–260 °C (kerosene), 260–338 °C (diesel), and 338–566 °C (gas oil). A solid residue was collected from the distillation unit and its yield was reported as heavies [29]. Distillation for each sample is conducted in duplicate and the average yield is reported.

### 2.4. Characterization on fresh and used CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts

Catalyst BET surface area and porosity was measured with micromeritics TriStar II PLUS (Norcross, GA, USA) using carbon dioxide and nitrogen adsorption isotherms at 273 K and 77.30 K respectively. Prior to each analysis samples were degassed at 200 °C for 18 h under vacuum (0.1–5 mbar). CO<sub>2</sub> adsorption isotherms were measured in the partial pressure range p/po = 10–5–0.03 using approximately 75 data points while nitrogen in a range of p/po 10–3–0.99. The micropore volumes were estimated for CO<sub>2</sub> adsorption using the Dubin-Radushkevich (DR) equation. BET equation was used to estimate the surface area for nitrogen adsorption. Density functional theory (DFT) calculations were also carried out from CO<sub>2</sub> adsorption isotherm using commercial software to calculate the micropore size distribution assuming a slit pore shape.

The topographic analysis of catalyst surface was carried out by scanning electron microscopy (SEM) with a Hitachi S-570 variable pressure instrumented. The samples were mounted on stub and later introduced into the instrument. Magnification ranged from 100× to 30,000×.

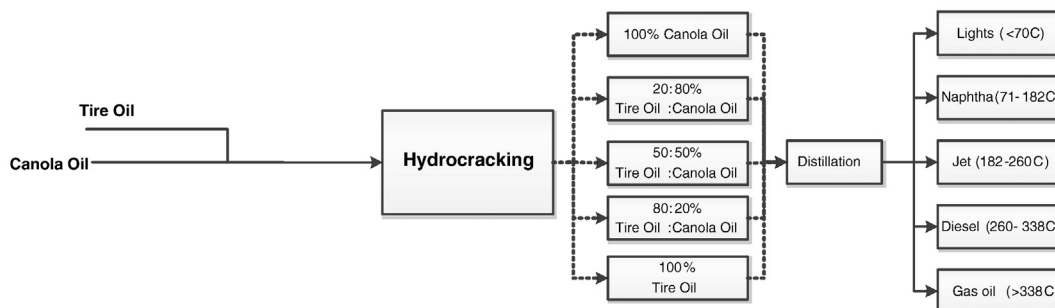


Fig. 1. Experimental workflow of co-hydrotreatment of tire pyrolysis oil and canola oil.

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