# Catalytic conversion of waste cooking oil to fuel oil: Catalyst design and effect of solvent

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## ARTICLE INFO

## ABSTRACT

Waste cooking oil (WCO) is dispersed in tetralin or dodecane and hydrotreated in a batch reactor over a fabricated NiMo/γ-Al$_2$O$_3$-β-zeolite catalyst. The properties of catalysts are controlled by adjusting the mass fraction of β-zeolite in support ($x$), the mass fraction of NiO and MoO$_3$ ($m$) and Ni/(Ni + Mo) mol fraction ($y$) in catalysts. The effects of the catalytic properties, solvents and reaction conditions on the hydrodeoxygenation of WCO are investigated. The results showed that increasing $m$ and $y$ promoted WCO conversion and the formation of alkane hydrocarbons; the addition of Ni into Mo helped to promote the reducing ability of catalysts and enhanced deoxygenation via decarboxylation/decarbonylation pathway. An increase in β-zeolite was unfavourable for WCO conversion. A complete conversion of WCO to hydrocarbons was achieved at 350 °C under H$_2$ at 5 MPa for 3 h with dodecane as solvent. The isomerized compounds accounted for less than 10 wt%. A low H$_2$ pressure is suitable for tetralin exerting hydrogen-donating effect.

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## 1. Introduction

Diminishing fossil fuel reserve and increased greenhouse gas emission are driving an intensive research to find new and environmentally energy substitutes. Biomass and biomass-derived oil (biobased oil called below) are promising energy resources because of its renewable, abundance and carbon neutral [1–3]. Waste cooking oil (WCO), containing significant amounts of triglycerides, derives from biomass and is largely produced each year around the world. For instance, WCO production in the United States and China was approximately 10 and 5 million tons/year, respectively [4,5]. WCO is readily available in large quantity, do not contend with other food crops, and presents a cost effective resource for biofuel production. At present WCO was mainly used as feedstock to produce biodiesel through transesterification reaction [6]. Biodiesel shows cleaner combustion characteristics compared with petro diesel e.g. lower emissions of particulate matter, carbon monoxide and total hydrocarbons. However, biodiesel used for the hydrocarbon-based transport infrastructure may face serious energy-density and compatibility issues [7,8].

Recently, catalytic hydrogenation has been reported to show increased efficiency in converting biobased oil to diesel-like hydrocarbons (updated diesel) [8,9]. During the catalytic hydrogenation process, oxygen atoms in biobased oil are removed via two possible deoxygenation approaches: (i) hydrodeoxygenation (HDO) and (ii) decarboxylation/decarbonylation (HDC). In the first approach, oxygen is removed in the form of water while in the latter one it is removed as CO$_2$ or CO [7,10,11]. The updated diesel derives from renewable living organisms, has similar chemical composition and fuel properties to petro diesel such as high oxidation stability and high cetane number, furthermore, is more environmentally-friendly compared to biodiesel, and thus called as "green diesel" [1].

The most often used catalysts in the catalytic hydrodeoxygenation of biobased oil are nickel/cobalt-molybdenum catalysts supported on alumina or zeolite materials because of their low cost and high activity [12–14]. It is generally considered that the activity of catalysts and product distribution of fuel are significantly affected by the acidic properties, metal active sites, the pore structures of catalysts and process condition [15,16]. Most of previous research about hydrodeoxygenation of biobased oil was mainly carried out to evaluate the effect of different catalysts and process condition. However, little work has been done on

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investigating the influence of solvent on the hydrogenation process.

As a hydrogen donor, tetralin is widely used as solvent in the liquefaction of biomass and coal to produce liquid fuels. It can disperse and stabilize intermediate products from the liquefaction process by offering active hydrogen and consequently improves liquefaction efficiency and fuel quality [17–19]. In our last work, tetralin was used as solvent in the catalytic hydrogenation of stearic acid to produce fuel oil [20]. A nearly 90% conversion of stearic acid was achieved at 350 °C under $H_2$ at a pressure of 0.8 MPa (in other words, reactor was only replaced with 0.1 MPa $H_2$ at room temperature). The content of C16–C18 hydrocarbons in product was about 98%. These results indicated that tetralin improved hydrogenation efficiency by offering active hydrogen under a low $H_2$ pressure. Tetralin can be a promising hydrogen resource to substitute for the high-pressure hydrogen, which is currently used in catalytic hydrogenation process. However, little research has been carried out to investigate the effect of tetralin on catalytic HDO of other biobased feedstocks. Extensive research is desired to expand its application for production of oxygen-free fuels from biobased oils.

In this study, we prepared a serious of supported NiMo catalysts, and examined their catalytic activity on HDO of WCO in two solvents: tetralin (hydrogen donor) and dedocane (non-hydrogen donor). The effects of the properties of catalysts and solvents on the composition of product oils were investigated. This research could potentially provide a promising approach to develop an effective HDO technique for transforming WCO into oxygen-free fuel.

## 2. Experimental

### 2.1. Pretreatment of waste cooking oil

WCO was collected from a chophouse close to the student apartment of Guangxi University and pre-treated according to the method as reported in our last study [21]. In brief, WCO was washed with saturated salt water and distilled water, respectively. A certain amount of activated carbon was added into wash solution to decolorize WCO. The obtained WCO sample was evaporated under less pressure condition, dried, and used in the following experiments.

### 2.2. Synthesis of NiMo/Al₂O₃-Hβ catalysts

γ-Al₂O₃ (A) and H-type-β-zeolite (Si/Al = 25) (Z) were purchased from Nankai University Catalyst Co., Ltd. (Tianjin, China). All catalysts were prepared by a two-step method. The γ-Al₂O₃-β-zeolite (AZ) composite supports were firstly prepared by mechanically mixing β-zeolite and γ-Al₂O₃ with deionized water, and the mixture was then dried and calcined. Afterwards, nickel (Ni) and molybdenum (Mo) with desired amounts were loaded onto the AZ composite supports by impregnation method [20]. The obtained catalysts samples are denoted as $m$-$y$-NiMo/AZ-$x$, according to the different mass fraction of β-zeolite in AZ supports ($x$), the NiO + MoO₃ mass fractions in the catalysts ($m$), and the Ni/(Mo + Ni) molar fraction ($y$). $x$ was changed from 0 to 40%; $m$ was changed from 10% to 30%, and $y$ was changed from 10% to 30%.

### 2.3. Characterization of catalysts

X-ray diffraction (XRD) patterns were obtained on Rigaku MiniFlex600 diffractometer using CuKα radiation. Powder diffractograms of samples were recorded over a range of 2θ values from 5° to 70° at 40 kV and 100 mA with a scanning rate of 5°/min.

N₂ adsorption-desoption isotherms were measured using a Quantachrome NOVA 4000e instrument (Florida, UWCO) over samples evacuated at 250 °C for 4 h. The specific surface area ($S_{BET}$), the total pore volume ($V_{total}$), the volumes of the mesopores ($V_{meso}$) and micropores ($V_{micro}$) were determined according to the method as reported in our last study [20].

$H_2$ temperature-programmed reduction ($H_2$-TPR) and NH₃ temperature-programmed desorption (NH₃-TPD) were used to characterizing the reducibility of catalysts and the surface density of metal site and acid sites. The analysis was carried out in a quartz reactor equipped with an on-line mass spectrometer (RGA200, Agilent). The detail for NH₃-TPD had been described elsewhere [20]. $H_2$-TPR was performed as follows: 0.15 g samples were firstly treated at 350 °C in Ar for 1 h, cooled to 100 °C, and then shifted to 10% $H_2$–Ar and heated linearly at 10 °C/min up to 900 °C. $H_2$ ($m/e = 2$) and produced $H_2O$ ($m/e = 18$) in effluent were detected and recorded continuously as functions of temperature.

### 2.4. Catalytic hydrodeoxygenation of WCO

All experiments were carried out in a 20-ml stainless steel autoclave reactor. 0.1 g of catalysts was sulfided in situ prior to the hydrotreatment experiments by means of dimethyl disulfide (DMDS) [20]. 1.2 g of WCO and 4.8 g of solvents (tetralin and dodecane) were added into reactor, and reacted under various conditions: temperature (300–350 °C), $H_2$ pressure (2–5 MPa) and time (1–4 h).

### 2.5. Product analysis

It is considered that deoxygenation mechanism of triglyceride involves the following processes: triglyceride is firstly hydrocracked to fatty acids, and then the acids either ungergo further hydrogenation steps to yield fatty alcohols and ultimately saturated alkanes, or undergo decarboxylation to yield hydrocarbons directly [10]. The hydrogenated liquid products could contain the deoxygenated compounds such as hydrocarbons, intermediates such as alcohols, aldehydes and fatty acids as well as undecomposed triglycerides, which is strongly dependent on the used catalysts and reaction condition. In present study, liquid products were firstly methyl esterified according to the standard methods of GB/T 17376-2008. The components in the products were identified by GC-MS (GC 7820A, MS 5977E, Agilent) and quantified by GC-FID (GC-9792II, Fuli, China) [20].

The hydro-cracking ratio ($HC_r$), conversion (Con.) of WCO and isomerization ratio ($I_r$) of products were used to evaluate the efficiency of catalytic hydrogenation. Since tetralin will transfer into naphthalene after releasing the active hydrogen, naphthalene value ($Nv$) was used to evaluate the hydrogen-donating activity of tetralin. Conversion, $HC_r$, $I_r$ and $N_V$ were calculated using the following equations, respectively:

$$Con.(\%) = \left[ \frac{\varpi_1}{\varpi_1 + \varpi_e} \right] \times 100 \tag{1}$$

$$HCr(\%) = Con. + \frac{A}{56.11 \times 1000} \left( \frac{270 \times \varpi_{16e} + 298.5 \times \varpi_{18e}}{\varpi_{16e} + \varpi_{18e}} \right) \times 100 \tag{2}$$

$$Ir(\%) = \frac{\varpi_{iso}}{\varpi_1} \times 100 \tag{3}$$