

# Production of biodiesel from mixed waste vegetable oils using Ferric hydrogen sulphate as an effective reusable heterogeneous solid acid catalyst



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## ABSTRACT

Biodiesel production by simultaneous esterification and transesterification of waste oil with methanol has been studied in a heterogeneous system using solid ferric hydrogen sulphate [Fe(HSO<sub>4</sub>)<sub>3</sub>] acid catalyst. The catalyst was prepared by displacement reaction followed by calcination at 400 °C for 3 h. The prepared catalyst was characterized using X-ray diffraction (XRD), Fourier transform infrared spectrometer (FT-IR), Brunner-Emmett-Teller surface area measurement (BET), thermal gravimetric analyzer (TGA) and temperature-programmed desorption of NH<sub>3</sub> (TPD - NH<sub>3</sub>). Furthermore, the dependence of the conversion of mixed waste oil on the reactions variables such as the molar ratio of methanol/oil, the amount of catalysts used, reaction temperatures, reusability were also investigated. The catalyst was reused many times with slight loss in activity and the maximum yield of 94.5% was achieved at the optimized conditions of reaction temperature of 205 °C; stirring speed of 350 rpm, 1:15 molar ratio of oil to alcohol and 1% w/w catalyst loading.

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## 1. Introduction

Due to the potential depletion of petroleum and environmental concerns about air pollution caused by the combustion of fossil fuel, the search for alternative fuel has gained much attention [1]. Waste cooking oil can be another cheap feedstock for biodiesel production. In most cases, waste oil is being used at restaurants for cooking and process of food. The number of times of re-use cooking oil could have significant impact on human health. Therefore, biodiesel production from the waste cooking oil could be suitable alternative to avoid their adverse effect on human health and environment.

Homogeneous catalysts, although effective, lead to serious environmental and corrosion related problems make their use non-practical for biodiesel production [2]. The use of heterogeneous catalysts to replace homogenous ones can be expected to overcome the problem associated with homogenous catalysts. The solid base

catalyst are easily regenerated and have a less corrosive nature, leading to safer, cheaper and more environment friendly operations. However, they can only be directly used as catalysts to prepare biodiesel when the FFA contents in the range of (0.5–1.0% feedstocks). Hence, the catalyst is not suitable for the waste cooking oils. Heterogeneous acid catalysts can simultaneously catalyze the transesterification of triglycerides and esterification of FFA. So, the use of heterogeneous acid catalysts to produce methyl ester is becoming more popular. It will also be reduced the environmental contamination, awful impact on human health and further reduced the biodiesel production costs. There are several reports about the use of heterogeneous acid catalysts to produce biodiesel, including zeolites [3] La/zeolite beta [4], Amberlyst-15 [5], Nafion [6], sulphonated solids [7], sulphated metal oxides [8] and supported heteropolyacids [9]. A survey of literature showed that no work has been done so far on the production of biodiesel using Fe(HSO<sub>4</sub>)<sub>3</sub> acid catalyst.

The main purpose of this study was to produce ferric hydrogen sulphate acid catalyst for the production of biodiesel over esterification and transesterification of mixed waste cooking oil (MWCO). The catalyst was prepared by displacement method and characterized by using X-ray diffraction (XRD), Fourier transform infrared spectrometer (FT-IR), Brunner-Emmett-Teller surface area

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measurement (BET), thermal gravimetric analyzer (TGA) and temperature-programmed desorption of  $\text{NH}_3$  (TPD -  $\text{NH}_3$ ). Moreover, the dependence of the conversion of waste oil on the reactions variables such as the molar ratio of methanol/oil, the amount of catalysts used, reaction temperatures, reusability were also appraised.

## 2. Experimental

### 2.1. Material

Different waste vegetable oil samples were obtained from various local markets. Waste palm oil sample was collected from restaurants inside University Putra Malaysia, Serdang Malaysia. Waste corn oil and sunflower oil samples were obtained from Arabian restaurants – south city area in Malaysia. The collected waste vegetable oils were mixed equally (by weight) to prepare mixed waste vegetable oils. A total of 3.0 kg of oil was used for the optimization of biodiesel production process. Anhydrous ferric chloride, concentrated sulfuric acid of (98%) and methanol of (99.5%) purity were obtained from (Sigma–Aldrich, Malaysia).

### 2.2. Pretreatment of mixed waste cooking oil

For a successful simultaneous reaction and high yield of FAME, the oil must be free of water and other impurities. Initially, the received mixed waste cooking oil was heated at  $105^\circ\text{C}$  to remove water by evaporation and food debris through filtration. Its free fatty acid (FFA) content was determined by a standard titration method [10].

### 2.3. Characterization of mixed waste cooking oil

Determinations of saponification value and acid value of the mixed waste oil were carried out according to the standard AOCS methods [11].

### 2.4. Catalyst Preparation

The replacement reaction (sulphation) was performed as follows. A 250 ml suction flask was equipped with a dropping funnel. A gas outlet was connected to a vacuum system through an alkaline solution trap. Anhydrous  $\text{FeCl}_3$  (10 mmol) was charged into the flask and concentrated sulfuric acid (30 mmol) was added dropwise over a period of 30 min at room temperature through dropping funnel. HCl gas evolved immediately (white fumes with ammonium hydroxide in glass rode). After completion of the addition, the mixture was shaken for 30 minutes at  $100^\circ\text{C}$ , while the residual HCl gas was eliminated by suction. Finally, a pale-brown to yellowish solid  $\text{Fe}(\text{HSO}_4)_3$  was obtained [12].

### 2.5. Catalyst characterization

The powder X-ray diffraction analysis was carried out using a Shimadzu diffractometer model XRD 6000. The diffractometer employing  $\text{Cu-K}\alpha$  radiation to generate diffraction patterns from powder crystalline samples at ambient temperature. The  $\text{Cu-K}\alpha$  radiation was generated by Philips glass diffraction X-ray tube broad focus 2.7 kW type.

The acidity of the catalyst was studied by temperature programmed desorption using  $\text{NH}_3$  as probe molecule. TPD- $\text{NH}_3$  experiment was performed using a Thermo Finnigan TPDRO 1100 apparatus equipped with a thermal conductivity detector. Catalyst approx 0.1 g of catalyst was placed in the reactor, treated under  $150^\circ\text{C}$  for 15 min in  $\text{N}_2$  ( $20\text{ ml min}^{-1}$ ). 10%  $\text{NH}_3$  in helium gas was ramped at  $1^\circ\text{C min}^{-1}$  for 60 min. the purging with  $\text{N}_2$  was done at room temperature for 45 min to remove  $\text{NH}_3$  in the gas phase. The

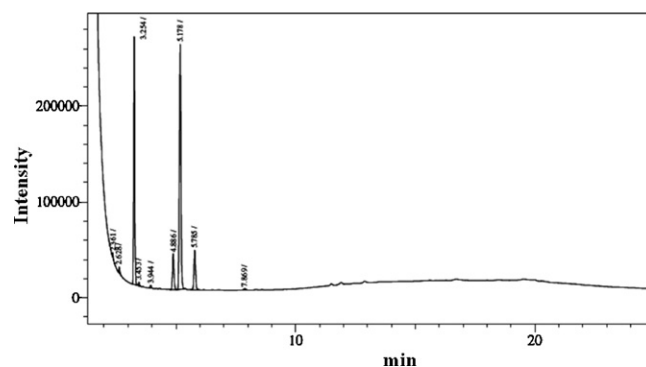


Fig. 1. The gas chromatogram of MWCO Biodiesel.

analysis of  $\text{NH}_3$  desorption was then carried out between  $50^\circ\text{C}$  and  $900^\circ\text{C}$  under helium flow ( $15^\circ\text{C min}^{-1}$ ,  $20\text{ mL min}^{-1}$ ) and detected by thermal conductivity detector.

The TGA analysis was carried out on a Mettler Toledo TG-SDTA apparatus (Pt crucibles, Pt/Pt–Rh thermocouple) with the purge gas (nitrogen) flow rate of  $30\text{ ml min}^{-1}$  and the heating rate of  $10^\circ\text{C min}^{-1}$  from 25 to  $1000^\circ\text{C}$ .

The Fourier transform Infrared analysis was carried out with PerkinElmer spectrometer model 100 series (sample preparation UATR). The quantitative chemical composition of the prepared ferric hydrogen sulphate acid catalyst was characterized using energy dispersive X-ray spectroscopy (EDS) for elemental chemical analysis.  $\text{Fe}(\text{HSO}_4)_3$  was characterized by the determination of its H<sup>+</sup> content using titration method [13].

The total surface area of the catalysts was obtained using Brunauer–Emmer–Teller (BET) method with nitrogen adsorption at  $-196^\circ\text{C}$ . Analysis was conducted using a Thermo Fisher Scientific S.p.A (model: SURFER ANALYZER) nitrogen adsorption-desorption analyzer.

### 2.6. Esterification and transesterification process

The simultaneous esterification and transesterification of mixed waste vegetable oils containing 14.7 wt. % free fatty acids was carried out using prepared ferric hydrogen sulphate acid catalyst in BERGHOF high pressure laboratory reactor. A certain amount of catalyst, methanol and oil were added to the reactor. The reaction was started by stirring at 350 rpm and heated to specified temperature and time. Then, the mixture was cooled to room temperature and separated by centrifuge (Kubota 4200) at rpm 350 for 20 min. Finally, the product was analyzed by gas chromatography using PerkinElmer with FID detector, equipped with BP-21 capillary column. Dichloromethane was used as an internal standard. The gas chromatogram of the biodiesel product was shown in Fig. 1 and the FAME's composition in Table 1. Yield of FAME's can be calculated as follow [14]:

$$\text{yield}(\%) = \frac{\text{total weight of methyl esters}}{\text{total weight of oil in the sample}} \times 100$$

Table 1  
Compositions of MWCOME's and their corresponding retention time.

| FAMEs compositions  | Carbon | Retention time (min) | % from GC |
|---------------------|--------|----------------------|-----------|
| Methyl myristate    | C14:0  | 2.361                | 1.85      |
| Methyl palmitate    | C16:0  | 3.254                | 42.19     |
| Methyl palmitoleate | C16:1  | 3.454                | 0.81      |
| Methyl stearate     | C18:0  | 4.886                | 5.97      |
| Methyl oleate       | C18:1  | 5.178                | 41.65     |
| Methyl linoleate    | C18:2  | 5.785                | 6.77      |
| Methyl arachidate   | C20:0  | 7.869                | 0.76      |

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