



# Biodiesel production via esterification of oleic acid catalyzed by picolinic acid modified 12-tungstophosphoric acid



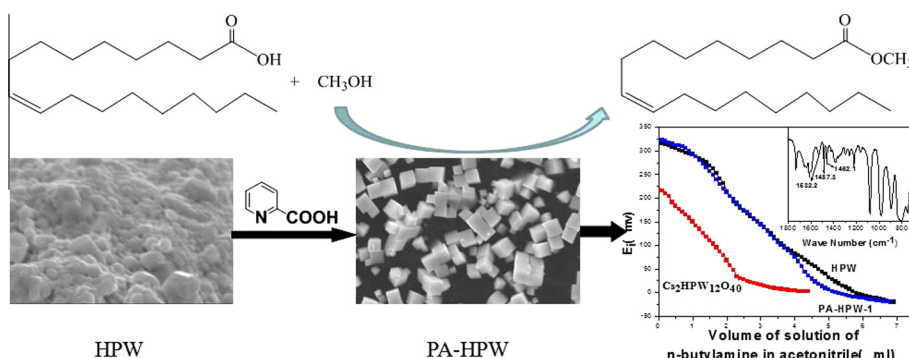
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## HIGHLIGHTS

- Esterification of oleic acid using modified HPW as heterogeneous catalyst.
- Picolinic acid was selected to modify HPW only via simple mixing reaction.
- Modified catalysts exhibited high acidity and good stability.
- High conversion was still obtained after reused several times.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Esterification of free fatty acids with alcohols catalytic by acid catalysts can synthesize sustainable production of biofuel. In this work, 12-tungstophosphoric acid was modified by picolinic acid to prepare solid acid catalyst (PA-HPW) and applied to the esterification, which was proved to be an efficient catalyst for the esterification of oleic acid and alcohols. For characterization of the catalysts, XRD, FT-IR, SEM and potentiometric titration method were employed. These analyses showed that there was no decomposition of the Keggin structure of 12-tungstophosphoric acid during preparation and esterification. The PA-HPW catalyst presented high acidity and good stability in esterification mixtures. Various reaction parameters, such as methanol/oleic acid molar ratio, catalyst dosage, reaction temperature and time were systematically examined. A quantitative conversion (100%) of oleic acid was achieved, using the most active modified catalyst at 80 °C with a 7 wt % catalyst/oleic acid ratio for 5 h, at a 10:1 of alcohol/acid mole ratio. The catalyst can be easily recovered and reused, which indicated that the PA-HPW catalyst is a promising new type of heterogeneous acid catalyst for conversion of free fatty acid feeds to biodiesel.

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## 1. Introduction

Biodiesel is usually defined as alkyl esters of long chain fatty acids that occur naturally in renewable resources such as vegetable oil or animal fats [1–3]. Compared with petroleum-based diesel, biodiesel has several advantages, such as being biodegradable

and clean burning. The nature of biodiesel, including high oxygen content, aromatic-free and lower CO<sub>2</sub> and sulfur emissions ensure it produces less environmentally harmful species [2–5]. Therefore, biodiesel is considered as a promising alternative of fossil fuel to ease these problems including global warming, environmental pollution and shortages of fossil resources, and more attentions have been devoted to the biodiesel production [6–8]. Biodiesel can be produced via transesterification of triglycerides or esterification of free fatty acids (FFAs) [1–13]. Triglycerides are usually derived

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from fatty acid sources, such as vegetable oils, waste oil or animal fats. In view of vegetable oils are expensive, some cheap feed stocks including non-edible and waste cooking oils are more used in transesterification to reduce the production costs of biodiesel [5,9,14]. However, the transesterification of waste oils is often accompanied by saponification reaction due to the fact that these waste oils generally have high levels of FFAs, which will increase the consumption of alkaline catalysts and lower the yield of esters, and the separation of esters also turn difficult due to the formation of soap. Therefore, a pretreatment step for the transesterification of waste oils is essentially required by converting FFAs to esters [1–4].

The esterification of FFAs such as oleic acid can be obtained through the catalysis of a homogeneous or heterogeneous acid catalyst [1–4,15–19]. Liquid inorganic or mineral acid, especially  $\text{H}_2\text{SO}_4$  has exhibited high catalytic activity in esterification of palm fatty acids [20,21]. However, these homogeneous catalysts are not environmental friendly, which includes corrosion to the equipment, generation of a larger amount of waste as well as difficulty to be separated from reaction medium and non-reusability [15–22]. Instead, heterogeneous acid catalyst can successfully solve these problems because the catalyst does not dissolve into the products, which means that it can easily be separated from the product by filtration after the reaction and can be reused [15–21,23,24]. Recently, several heterogeneous acid catalysts have been developed for esterification reaction, including chlorosulfonic acid modified zirconia [24], biomass carbon-based solid acid [15], heteropoly acids (HPAs) such as 12-tungstophosphoric supported in flint kaolin [25], and sulfated zirconia [26].

Among these above heterogeneous acid catalysts, HPAs with Keggin structures such as  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (HPW),  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  (HPMo), had been paid more attention due to their high thermal stability and strong acidity [27–30]. However, HPW and HPMo are difficult to be directly applied in esterification as heterogeneous catalyst because they are soluble in some alcohols, and they also suffer the disadvantage of low surface area ( $1\text{--}10\text{ m}^2\text{ g}^{-1}$ ) [31,32]. Therefore, HPAs were usually immobilized on porous carrier with high surface area and then applied in catalytic reaction [25,27]. Additionally, HPAs salts with high surface areas were prepared via partial or total proton exchange of the parent HPAs with large inorganic cations such as  $\text{Cs}^{2+}$  cation and  $\text{NH}_4^+$  cation, which had been proved that these salts obviously enhanced the stability of raw in polar systems [31,33–37]. Although some supported HPAs or HPAs salts catalyst had been reported and used in esterification, there are still some problems need to improve, which includes the leaching of HPAs active species in polar reaction media for supported catalyst. The acidity of some HPAs salts was lower than parent acid and their small particles could make the operation difficult in reactors [38]. Therefore, it is much desirable to design and prepare new HPAs catalysts.

In this present work, picolinic acid modified HPW catalyst was prepared only through simple method. The original design was to improve the stability of HPW via the formation of hybrid material based on the interaction between inorganic cluster of HPW and the lone pair electrons of nitrogen atom. The introduced carboxyl group shall maintain or improve acidity at the same time. As solid acid catalyst, the modified HPW was evaluated for esterification of oleic acid with methanol.

## 2. Experiments

### 2.1. Synthesis of catalysts

All chemicals were purchased commercially and used as received without any treatment. The equimolar picolinic acid and

HPW was dissolved in distilled water, respectively. Then the solution of picolinic acid was slowly dropped to the solution of HPW under vigorous stirring at room temperature. After stirring for 2 h, the resulting white precipitate was filtered. The prepared sample was dried at  $110\text{ }^\circ\text{C}$  and collected. Similarly modified catalysts were prepared via adjusting the amount of picolinic acid, which were referred to as PA-HPW-X representing the molar ratio of picolinic acid and HPW.

$\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$  was prepared by adding the  $\text{Cs}_2\text{CO}_3$  solution dropwise to the HPW solution under vigorous stirring according to the literature method [35].

### 2.2. Characterization

The crystallinity and the phase purity of modified samples were analyzed by X-ray diffraction (XRD) patterns by using X-ray diffractometer (Bruker D8 ADVANCE, Germany), and  $\text{Cu K}\alpha$  ( $1.54\text{ \AA}$ ) radiation. XRD was performed within  $2\theta$  range of  $5\text{--}80^\circ$ .

Fourier transform infrared (FT-IR) spectra of the samples pressed in KBr pellets were collected in a Thermo Nicolet 6700 FTIR spectrometer in the region  $4000\text{--}400\text{ cm}^{-1}$ .

Scanning electron microscopy images (SEM) were obtained with a JSM6380LV instrument to observe the morphology of the prepared samples.

The BET surface areas of catalysts were determined through  $\text{N}_2$  adsorption-desorption study performed at  $-196\text{ }^\circ\text{C}$  using a Quantachrome Autosorb IQ-C instrument. Before the measurement, the samples were evacuated at  $200\text{ }^\circ\text{C}$  for 2 h.

The acidity of the solid samples in aqueous solution was measured by the potentiometric titration method with an automatic potentiometric titrator using a PH composite electrode [39,40]. The solid ( $0.05\text{ g}$ ) was suspended in  $15\text{ ml}$  distilled water, and agitated for 3 h. Then, the suspension was titrated with a solution of  $0.05\text{ N}$  n-butylamine in acetonitrile.

### 2.3. Catalytic tests

The esterification reaction was carried out in a  $50\text{ mL}$  gas-tight batch reactor with a magnetic stirrer, and oil bath was used to maintain the reaction temperature. A typical reaction mixture in the reactor contained  $0.005\text{ mol}$  oleic acid,  $0.05\text{ mol}$  methanol and  $5\text{ wt}\%$  catalyst/oleic acid. After stirred for a certain reaction time at reaction temperature ( $40, 60, 80$  or  $100\text{ }^\circ\text{C}$ ), the catalyst was recovered by centrifugation and washed with methanol and then dried at  $110\text{ }^\circ\text{C}$  for reuse. The reaction products were identified by comparison with the authentic samples and finally by Gas Chromatography–Mass Spectroscopy (GC–MS). The conversion of oleic acid was determined using an Agilent 6890 gas chromatography equipped with a HP-5MS capillary column and FID detector, and methyl caprylate was selected as internal standard.

## 3. Results and discussion

### 3.1. Catalysts characterization

Fig. 1 shows the XRD patterns of PA-HPW-X catalyst. For comparison, the XRD patterns of raw HPW and picolinic acid are also displayed. The XRD pattern of parent HPW is similar to the reference pattern for  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  taken from the JCPDS powder diffraction file (card 50-0657), which confirms that the parent HPW exhibits typical cubic secondary structure of Keggin anion. The modified PA-HPW-1 sample exhibits new X-ray diffraction peaks different from those of raw HPW and picolinic acid, and there are no diffraction peaks of picolinic acid are detected, which revealed that new PA-HPW phase with good crystallinity was formed. The

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