



Biodiesel synthesis over biochar-based catalyst from biomass waste pomelo peel



Che Zhao^{a,b,c,d}, Pengmei Lv^{a,b,c,e,*}, Lingmei Yang^{a,b,c}, Shiyong Xing^{a,b,c}, Wen Luo^{a,b,c}, Zhongming Wang^{a,b,c}

^a Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, China

^b CAS Key Laboratory of Renewable Energy, Guangzhou 510640, China

^c Guangdong Provincial Key Laboratory of New and Renewable Energy Research and Development, Guangzhou 510640, China

^d University of Chinese Academy of Sciences, Beijing 100049, China

^e Collaborative Innovation Center of Biomass Energy, Henan Province, Zhengzhou 450002, China

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ABSTRACT

In the present study, a novel solid carbon catalyst derived from pyrolytic pomelo peel was prepared for biodiesel synthesis. The composition, structure and texture of prepared catalysts were examined by X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), energy dispersive spectrometer (EDS), N₂ adsorption/desorption and the Hammett indicator method. The characterization results indicated that the surface area and pore volume of the biochar were increased significantly by chemical activation treatment with KOH. The best-performing catalyst was that loaded with 25 wt.% K₂CO₃ on the prepared biochar and calcined at 600 °C, due to it resulting in the highest conversion of the oil to FAME at 65 °C, reaction time of 2.5 h, 8:1 methanol/oil molar ratio and a catalyst amount of 6 wt.%. This extraordinary activity was identified owing to the strongest basic sites. Besides, after reusing for 8 cycles, the catalyst could exhibit a rather high biodiesel yield (above 82%). The deactivation of catalyst was mainly owing to K⁺ ions leaching to the product. These results indicated that the pomelo peel biochar supported catalyst demonstrated promise for biodiesel synthesis.

1. Introduction

Recently, as a result of the increase in energy demand, changing climate, and a rapid decline in accessible fossil fuel reserves, the development of green, renewable energy sources has gained great attentions [1,2]. Biodiesel, which is generated from the transesterification of vegetable oil feedstocks in the presence of alcohol, is a plant biomass-based alternative to diesel due to its renewable, sustainable and biodegradable features [3]. Generally, the commercial biodiesel production involves the use of homogeneous catalysts (KOH, NaOH and H₂SO₄) owing to their relatively high reaction rates and relatively mild reaction conditions [4–7]. However, those catalysts cannot be recycled and require a costly sequence of purification and removal steps which generate a large amount of wastewater, as well as equipment corrosion, operation costs and high energy consumption [8]. To circumvent these issues, the utility of heterogeneous base/acid catalyst for the transesterification reaction has been widely reported because they are less corrosive, easier to be separated and more eco-friendly [9]. Presently, many researchers have investigated a great deal of different

heterogeneous catalysts (such as alkali or alkaline earth oxides, supported alkali metals and basic zeolites) for biodiesel production [10–14].

Recently, in order to reduce the high cost of catalyst synthesis, a variety of solid waste materials (such as egg shells, fly ash and fish bones) have been used as feedstocks for the preparation of cost-effective catalysts [8,15–21]. Biochar, as a solid residue formed in the pyrolysis of biomass, can be produced on a scale ranging from large industrial facilities to individual farms [22]. Due to its low cost, contents of surface functional groups, relative high surface to volume ratios, biochar has a tremendous potential to be used as carbonaceous catalyst or support in biodiesel synthesis [23]. Specifically, Kostić et al. [24] have used palm kernel shell biochar as the catalyst to optimize sunflower oil methanolysis, and the optimization ensured the best FAME content reach 99%. Rafi et al. [25] have prepared a biochar catalyst derived from karanja seed shells to catalyze esterification of glycerol and it showed an excellent activity as the maximum conversion rate reached 95.6% under mild reaction conditions. Dehkoda et al. [26] have explored a biochar-based catalyst for simultaneous

* Corresponding author at: Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, China.
E-mail address: lvpm@ms.giec.ac.cn (P. Lv).

transesterification and esterification of canola oil and fatty acid and it exhibited high catalytic performance.

Pomelo is one of the characteristic fruit in China (approximately 3 million tons of pomelo are produced each year), and large amounts of waste materials (40% weight of pomelo) such as peels were discarded in landfills and would become an environmental menace in the country [27–29]. In previous work, pomelo peel have been exploited to fabricate conventional activated carbons for removal of organic pollutants or used as excellent anode materials for batteries. For instance, Zhu et al. [30] reported pomelo peels derived carbon aerogels for removal of organic pollutants/oils. After carbonization, the specific surface area of the carbon aerogel could reach up to 759.7 m²/g. Li et al. [31] have successfully used Fe₃O₄ nanoparticles loaded on the porous pomelo peel biochar as the sustainable alternative for anode materials of Li-ion batteries. Liu et al. [32] found that carbon derived from pomelo peel had a high catalytic performance for the vanadium redox flow battery due to its micro-mesoporous structure with high surface area of 882.7 m²/g. However, to date, pyrolysis pomelo peel, a carbonaceous support which has the similar features to activated carbon, has never been investigated as a catalyst carrier to prepare solid catalyst for biodiesel synthesis.

Currently, the use of activated carbon loading with different potassium salts has attracted great attention [33–36]. Since biochar used as a precursor for activated carbon has been studied, extending its application as a possible carbon precursor for catalyzing the transesterification reaction is of great interest [37]. Besides, utilization of biochar as a catalyst support would not only help the commercialization of biodiesel production, but also increase the environmental viability of the pyrolysis process [38].

Based on the facts above, in this study, a novel pyrolysis pomelo peel-supported alkaline catalyst was used for the first time to design and prepare cost-effective and stable catalytic systems for biodiesel production. The physico/chemical properties of the resulting catalysts were characterized by XRD, TGA, FTIR, SEM-EDS, N₂ adsorption/desorption and the Hammett indicator method. The effects of catalyst preparation conditions (*i.e.*, the loading of K₂CO₃ on the pomelo peel biochar and the active temperature), reaction conditions (*i.e.*, reaction time, methanol-to-oil molar ratio and catalyst loading) on the catalytic performance and the catalyst reusability were also carefully studied.

2. Experimental

2.1. Materials

Pomelo peel was obtained from a local fruit market. Vegetable oil (palm oil) was purchased from the local supermarket (Guangzhou, China) and the physicochemical properties of the selected oil were listed in Table 1. Potassium carbonate (99%), potassium hydroxide (99%), tetrahydrofuran (99.8%) and methanol of analytical grade (99.5%) were purchased from Fisher Scientific, UK.

Table 1
Physicochemical properties of palm oil.

Property	Analytical method	Unit	Value
Acid number	ASTM D-974	mg KOH/g	1.21
Saponification number	AOCs Cd 3a-94	mg KOH/g	190
Kinematic viscosity (40 °C)	ASTM D-445	mm ² /s	37.8
Cloud point	ASTM D-2500	°C	10
Density (15 °C)	EN ISO 3675	kg/m ³	915
Water content	ASTM D-1123	wt.%	0.02
Mean molecular mass	GB 5530-85	g/mol	887.27
Oxidation stability (110 °C)	EN 14112	h	3.02

2.2. Preparation of catalyst

The powdered pomelo peel was firstly washed by deionized water, and then dried in an oven overnight at 80 °C. The dried pomelo peel was subsequently calcined at 600 °C for 2 h within nitrogen atmosphere to generate the pomelo peel biochar. Based on the previous study, the obtained pomelo peel biochar (PB) was chemically activated [39]. Typically, 2 g of pomelo peel biochar with 500 ml of 2 M KOH solution was mixed and stirred for 2 h. And then the suspension was filtered and the biochar was recovered on VWR Qualitative Filter Paper (Model 28,321-077). Subsequently, the filtered biochar was washed by deionized water several times until the pH value was 7. The obtained biochar was finally dried overnight in an oven at 105 °C. The activated pomelo peel biochar samples, hereafter referred to as AP, were stored in air-tight container.

The pomelo peel biochar-supported catalysts were prepared using wet impregnation method. The AP was mixed with the K₂CO₃ impregnating solution which prepared with various concentrations (15 wt.%, 25 wt.% and 35 wt.%). In a typical process, to prepare 25 wt.% K₂CO₃ loaded catalyst, 2.5 g of K₂CO₃ powder was added slowly to 100 ml of water, followed by the addition of 7.5 g of dried AP. The suspension was stirred at 800 rpm. Subsequently, the suspension was dried at 105 °C for 24 h followed by activation for 3 h at 500–700 °C. The as-synthesized catalysts were designated as *a*K/pomelo peel-*T*, where *a* and *T* represented the K₂CO₃ loading (wt.%) and the calcination temperature, respectively.

2.3. Catalyst characterization

The thermogravimetric analysis (TGA) was performed using a Stanton Redcroft STA-780 thermal analyser between 30 and 850 °C. The morphology and surface elemental analysis of samples were recorded on a Quanta 200 SEM system equipped with EDS detector (FEI company, Netherlands). FTIR spectra (4000–400 cm⁻¹) of samples were obtained using a Shimadzu FTIR-8300. Powder samples were prepared by dispersing the samples in KBr (sample/KBr ratio of 1:150) and compressing the mixture to form disks. The XRD analysis was conducted by a Bruker D8 diffractometer using Cu K α radiation and a Lynx Eye detector. The surface area and pore structure of samples were characterized by N₂ physisorption using a Quantachrom Nova instrument. The surface area was calculated using the Brunauer, Emmett, and Teller (BET) equation over the pressure range $P/P_0 = 0.02-0.2$, where a linear relationship was maintained, while their pore volumes were calculated by the amount of nitrogen adsorbed at a relative pressure of 0.99. Base strength was determined by Hammett indicators. The total basicity of the catalysts was measured by the method of Hammett indicator-benzene carboxylic acid (0.02 M anhydrous methanol solution) titration [40]. The used indicators were as follows: neutral red ($H_- = 6.8$), bromothymol blue ($H_- = 7.2$), phenolphthalein ($H_- = 9.8$), 2,4-dinitroaniline ($H_- = 15.0$), and 4-nitroaniline ($H_- = 18.4$). The amount of metal ions was examined using the inductively coupled plasma optical emission spectrometer (ICP-OES), Perkin-Elmer Optima 3000 V. The operation conditions for ICP-OES analysis were as follows: the sample flow rate was 1.5 ml/min; plasma power was 1000 W; plasma, auxiliary and nebulizer gas flow rates were 10, 0.6 and 0.65 L/min, respectively.

2.4. Transesterification reaction

The pomelo peel biochar catalysts and methanol were used for the transesterification of palm oil in a three-neck, round-bottom flask equipped with a thermometer, condenser, and magnetic heating mantle. The transesterification reaction was represented as:

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