



Effective production of biodiesel from non-edible oil using facile synthesis of imidazolium salts-based Brønsted-Lewis solid acid and co-solvent

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ABSTRACT

Developing an efficient one-pot catalytic process for biodiesel production from non-edible oils under mild reaction conditions remains challenging. Here, a novel process for the one-pot conversion of non-edible *Firmiana platanifolia* L.f. (FPLF) oil into biodiesel using inexpensive, scalable imidazolium salts-based solid acid containing both Brønsted and Lewis acid sites as the catalyst was investigated for the first time. The Brønsted-Lewis acid bifunctional catalyst ([DSI][FeCl₄]) was synthesized facilely and atom-economically (the final product contains the high amounts of atoms from the reactants) from 1,3-disulfonic acid imidazolium chloride ([DSI][Cl]) with FeCl₃ and was characterized by FT-IR, ¹H and ¹³C NMR, N₂ adsorption–desorption, SEM-EDS, TEM, FT-IR of pyridine, NH₃-TPD, TGA and elemental analysis. Owing to the presence of immiscible phases of oil and methanol in the reaction mixture, the effects of various co-solvents on the conversion of the FPLF oil into biodiesel were investigated, with the aim of reducing the mass transfer resistance. The results demonstrated that biomass-derived tetrahydrofuran (THF) was a superior co-solvent and could improve the reaction rate and biodiesel yield. The reaction conditions were optimized by using response surface methodology (RSM), [DSI][FeCl₄] exhibited excellent catalytic performance, with a high biodiesel yield of 98.7% under the following mild reaction conditions, which was superior to that of commercial resins (e.g., Amberlyst 15 and Nafion NR50). Detailed kinetic studies demonstrated that the catalytic process followed first-order kinetics and that the activation energy (83.56 kJ/mol) was relatively low compared to previous results. Thermodynamic analysis revealed that the catalytic process was non-spontaneous and that the reaction was endothermic and endergonic. Intriguingly, the catalyst was a heterogeneous catalyst during the reaction and maintained high catalytic activity after four cycles. The fuel properties of biodiesels derived from FPLF oil complied with the corresponding ASTM D6751 and EN14214 standards.

1. Introduction

The depletion of petroleum reserves and concerns about global warming have motivated the worldwide exploration of clean and sustainable energies. Among these, biodiesel is considered an excellent alternative to fossil diesel fuel due to its lower pollution emissions, sustainability and carbon neutrality [1–3]. The use of non-edible oils as feedstock for biodiesel production has been a trend because it can help reduce the cost of biodiesel and does not compete with food production [4,5]. Unfortunately, non-edible oils usually contain a large amount of undesirable free fatty acids (FFAs) that give rise to fatal saponification with the base catalyst, resulting in the deactivation of the base catalyst and difficulty in product purification [6]. Therefore, acidic catalysts are more appropriate for the conversion of non-edible oils into biodiesel

because acidic catalysts can simultaneously catalyse the esterification of FFAs and transesterification of triglycerides without saponification, thus avoiding the pre-esterification process and reducing the cost of biodiesel [7,8]. Solid acid catalysts have attracted wide attention for replacing homogeneous acid catalysts because they can alleviate many of the corrosive and environmental problems associated with homogeneous acid catalysts [9,10]. Therefore, the catalytic production of biodiesel from non-edible oils by solid acids is a promising approach for industrial production.

Recently, considerable efforts have been made to develop solid acid catalysts for the production of biodiesel from non-edible oils. Cs_{2.5}H_{0.5}PW₁₂O₄₀ exhibited 92% biodiesel yield from sesame oil, but harsh conditions (e.g., 260 °C and 20 MPa) were required [11]. Although the acidic carbonaceous catalysts possessed high acid density

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(5.35 mmol $[H^+]/g$), they also required a high temperature of 220 °C to obtain a biodiesel yield of approximately 91% [12]. The 30%SiW₁₁/MCM-41 gave an approximately 87% yield from *Jatropha* oil at the moderate temperature of 65 °C, but it required a long reaction time of 20 h [13]. A reaction time of 24 h was also required to obtain the 98% yield from the grease over H₃PW₁₂O₄₀ supported on magnetic nanoparticles [14]. Additionally, solid superacid catalysts have been investigated for biodiesel production from non-edible oils, but they have been limited in practice because they require a high calcination temperature and an obvious deactivation of catalysts [15–17]. Acid exchange resins have also been restricted to biodiesel production owing to their high price and poor thermal stability, which results in their deactivation at high temperature [18,19]. Therefore, the production of biodiesel from low cost non-edible oils under mild conditions over a facile, cost-effective solid acid catalyst with excellent catalytic activities remains a huge challenge.

Bifunctional acid catalysts with strong Brønsted and Lewis acid sites are currently receiving much more attention due to their synergistic effect, which can effectively improve the catalytic activity, and they have shown prominent and promising applications in the acetalization, polymerization, benzylation and oxidation reactions [20–24]. However, these catalysts have been rarely employed for the one-pot transformation of non-edible oils into biodiesel. While the acidic ionic liquids [BMIm][CH₃SO₃] exhibited low catalytic activity for biodiesel production, [BMIM][CH₃SO₃]-FeCl₃ prepared by adding FeCl₃ in [BMIM][CH₃SO₃] exhibited high catalytic performance due to the cooperation between the Brønsted acidic [BMIm][CH₃SO₃] and Lewis acidic FeCl₃ during the reaction process [25]. Li et al. [26] prepared [BSO₃HMIM]HSO₄-Fe₂(SO₄)₃ by combining the advantages of Brønsted acidic [BSO₃HMIM]HSO₄ and Lewis acidic Fe₂(SO₄)₃ catalysts and obtained a high catalytic activity with a biodiesel yield of 95.7%. Unfortunately, the use of these catalysts is still limited by the drawbacks of equipment corrosion, difficulty in separation, high cost and high viscosity [27].

In this work, we reported the facile and highly atom-economic synthesis (the final product contains the high amounts of atoms from the reactants [28]) of inexpensive, scalable imidazolium salts-based solid acid containing both Brønsted and Lewis acidic sites from relatively cheap and readily accessible chemicals as well as the use of this solid acid as the heterogeneous catalyst for the one-pot conversion of the *Firmiana platanifolia* L.f. (FPLF) oil to biodiesel. The FPLF oil originates from *F. platanifolia* L.f. having strong drought resistance, which is a fast growing tree with extended lifespan and can grow in abandoned and fallow farmlands [29]. In addition, to increase the mass transfer rate between the poorly miscible oil and methanol, co-solvent was introduced into the reaction mixture. The effect of the type of co-solvent such as acetone, ethyl acetate, hexane, trichloromethane and tetrahydrofuran (THF), on the biodiesel yield was investigated. The results showed that biomass-derived THF was the best co-solvent for biodiesel production. The effects of the reaction parameters on the biodiesel yield were also investigated by using response surface methodology (RSM). A high biodiesel yield of 98.7% was achieved under mild conditions, which was superior to that obtained by commercial resins (i.e., Amberlyst 15 and Nafion NR50). Meanwhile, the kinetic and thermodynamic parameters of the reaction were discussed.

2. Experimental

2.1. Materials and chemicals

FPLF seeds possessing high oil content (37.4 wt%) were purchased from Huizhou City, Guangdong Province, China and FPLF oil were extracted with petroleum ether from the seeds. The properties of FPLF oil such as acid value, saponification value, iodine value and average molecular weight were analyzed and shown in Table S1 (Supplementary Materials). The fatty acid methyl ester compositions were identified by gas chromatography and mass spectrometry

(GC-MS, Agilent 6890-5973) and also listed in Table S1. Imidazole (99.0%), anhydrous FeCl₃ (99.0%), Amberlyst 15 and Nafion NR50 were purchased from Shanghai Aladdin Industrial Inc. All standard samples (methyl palmitate, methyl palmitoleate, methyl stearate, methyl oleate, methyl linoleate, methyl linolenate and methyl sterculate) for quantitative analysis were analytically pure from Sigma (USA). Methanol (AR, ≥99.0%), n-hexane (AR, ≥97.0%), petroleum ether (AR, bp 60–90 °C), dichloromethane (AR, ≥99.0%) and chlorosulfonic acid (AR, >95.0%) were purchased from Chongqing Chuandong Chemical Reagent Company.

2.2. Catalysts preparation

The 1,3-disulfonic acid imidazolium tetrachloroferrate ([DSI][FeCl₄]) was synthesized from 1,3-disulfonic acid imidazolium chloride ([DSI][Cl]) with anhydrous FeCl₃, according to a previous report in the literature with a slight modification [30]. First, imidazole (10 mmol) was dissolved into 100 mL of dry CH₂Cl₂ in a 250 mL flask, followed by the dropwise addition of chlorosulfonic acid (20 mmol) with stirring for 20 min at room temperature. After the addition was completed, the reaction mixture was stirred for 12 h and left to stand for 5 min, and the CH₂Cl₂ was decanted. The residue was washed with dry CH₂Cl₂ and dried under vacuum to give [DSI][Cl] as a viscous pale yellow oil with 96% yield. Then, [DSI][FeCl₄] acids was prepared by stirring equimolar amounts of [DSI][Cl] and anhydrous FeCl₃ in an oil bath at 60 °C under nitrogen atmosphere for 2 h. The yellow solid product was washed with dry CH₂Cl₂ and dried under a vacuum oven at 80 °C to obtain [DSI][FeCl₄] with 95% yield.

2.3. Catalysts characterization

Fourier transform infrared spectroscopy (FT-IR) spectra of the samples were achieved in KBr disks using a Bruker VECTOR 22 spectrometer. ¹H and ¹³C NMR (solvent DMSO-*d*₆) spectra were recorded on a JEOL-ECX 500 NMR spectrometer using tetramethylsilane (TMS) as an internal standard. Elemental analysis was carried out using Vario-III CHN analyser. Nitrogen isotherm was recorded in a Micromeritics ASAP 2020 M analyzer at 77 K. The sample was outgassed for 10 h at 150 °C before the measurements. Specific surface area was acquired in Brunauer-Emmett-Teller (BET) algorithm, and the pore size and pore volumes distributions were calculated using the Barrett-Joyner-Halenda (BJH) method. Transmission electron microscopy (TEM) image was obtained by a JEM-3010 electron microscope (JEOL, Japan) with an acceleration voltage of 300 kV. The microscopic features and the surface elements of the catalyst were performed on a field emission scanning electron microscope (SEM; JEOL, EOL, JSM-6700F, 5 kV) with energy dispersive X-ray spectrometry (EDS) equipped with an Oxford Link/ISIS 300 detector. Pyridine-adsorbed FT-IR spectra were collected using a Nicolet iS50 FT-IR system (ThermoFisher) equipped with evacuation-gas manipulation ramp. The sample prepared as thin self-supporting wafers (about 15 mg) was first heated to 200 °C (heating rate: 5 °C min⁻¹) and degassed for 1 h under pressure less than 10⁻² Pa, followed by cooling down to room temperature, and the spectrum was recorded as the background spectrum for pyridine adsorption. Subsequently, the sample adsorbed pyridine vapor until saturation, followed by heating from room temperature to 200 °C and degassing for 0.5 h. The spectrum of pyridine-adsorbed sample was recorded with FT-IR after cooling the sample to room temperature. Ammonia-temperature programmed desorption (NH₃-TPD) was performed on an AutoChem 2920 chemisorption analyzer. Before TPD analysis, the catalyst (about 50 mg) was placed in a quartz reactor. Subsequently, the sample was degassed at 150 °C for 1 h (heating rate 5 °C/min) and cooled to 50 °C under He flow (30 mL/min). Then the sample was adsorbed NH₃ by flushing NH₃ gas (20 mL/min) at 50 °C for 1 h, followed by flushing He flow (30 mL/min) at 50 °C for 3 h to eliminate excess of NH₃. Finally, the sample was desorbed by heating to 300 °C with the

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