



Magnetically recyclable acidic polymeric ionic liquids decorated with hydrophobic regulators as highly efficient and stable catalysts for biodiesel production

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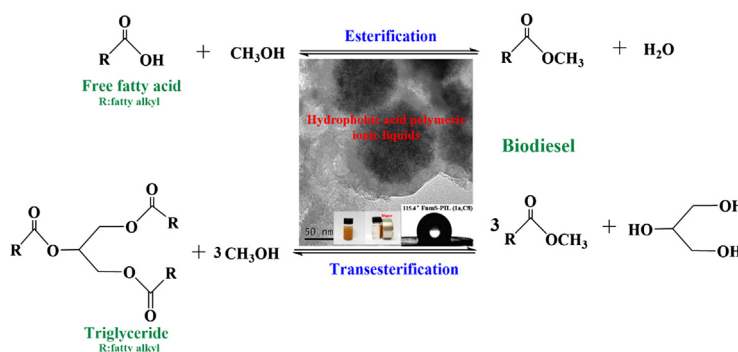
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HIGHLIGHTS

- Magnetically hydrophobic acidic polymeric ionic liquids were successfully prepared.
- 96.1% biodiesel yield for oleic acid esterification by response surface methodology.
- 91.7% biodiesel yield in (trans)esterification of crude *Euphorbia lathyris* L. oils.
- Stable for 5 cycles for both esterification and (trans)esterification.
- Water content effect, kinetic studies and reaction mechanism were investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

Biodiesel, typically produced from non-food crops with heterogeneous catalysts, seems to be a promising and sustainable alternative biofuel to petroleum-derived fuels. In this study, to improve biodiesel production process efficiency by acids, biodiesel production were successfully developed using a series of magnetically acidic poly(ionic liquid) catalysts with varying hydrophobicity and controllable acidity. The detailed characterization results demonstrated that the FnmS-PIL (1a, C8) core-shell structure catalyst had large Bruner Emmett and Teller (BET) surface area (128.1 m²/g), uniform mesoporous structure (4.2 nm), strong magnetism (12.4 emu/g), a high number of acid sites (2.14 mmol/g), strong acid strength (strong electron-withdrawing anion CF₃SO₃⁻ effect, -8.2 < H₀ < -5.6) and strong hydrophobicity (water contact angle, 115.4°). For the biodiesel production, high biodiesel yields could be achieved by the esterification of oleic acid (by response surface methodology, RSM) and (trans)esterification of crude *Euphorbia lathyris* L. oils with an acid value of 24.59 mg KOH/g (by single factor optimization). Furthermore, a relative kinetic study was conducted wherein the activation energy was calculated as 39.2 kJ/mol and a pseudo-first-order model was determined for esterification. More importantly, the FnmS-PIL (1a, C8) catalyst was separated simply using a magnet and exhibited constant activity with biodiesel yield of 87.5% after five cycles in (trans)esterification. In addition, the biodiesel yield was maintained above 90% even with a water content of 6 wt% with respect to crude *Euphorbia lathyris* L. oils, and the fuel properties of *Euphorbia lathyris* L. biodiesel were found to satisfy the EN 14212 and ASTM D6751

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standards, highlighting its potential in industrial biodiesel production as derived from crude non-food oil resources.

1. Introduction

Due to the low carbon footprint of renewable non-petrochemical resources, biomass, sustainable biofuels and value-added chemicals derived from biomass can somewhat satisfy and alleviate the increasing global energy demands [1]. Biodiesel, a mixture of mono-alkyl esters of long-chain fatty acids, owning renewability, biodegradability, local availability and environmental friendliness, has been deemed a state-of-the-art sustainable biofuel that can be prepared directly from non-edible, renewable and sustainable feedstocks [2,3]. Compared with traditional diesel fuels, the utilization of biodiesel can reduce 70% hydrocarbons and 50% particulate matters on exhaust emissions [United States Environmental Protection Agency (US EPA)], and net 78% CO₂ emissions because of its relative sustainability [4,5]. These properties make biodiesel a class of promising biofuels.

In general, biodiesel is commercially manufactured from vegetable oils, animal fats, and waste grease *via* transesterification or esterification of free fatty acids (FFAs) with a short-chain alcohol typically methanol [6–8]. Industrially, biodiesel production is usually performed by employing strong basic catalysts such as KOH and NaOH, which should require refined triglyceride (TG) feedstocks with FFAs < 0.5 wt% and free of moisture [9]. Otherwise, unavoidable problems including saponification and hydrolysis will occur. Alternatively, economic assessment and sensitivity analysis indicated that the acid-catalysed one-step process (simultaneous esterification and transesterification) using non-edible feedstocks with high FFAs proved to be technically feasible with less complexity (*i.e.*, no need of pre-treatment unit for esterification reactor, glycerol washing tower and methanol recovery process) than the two-step process. Therefore, one-step process is a competitive alternative to commercial biodiesel production using the alkali-catalysed processes (*i.e.*, 644 vs. 884 \$/tonne of break-even price of biodiesel) [10]. However, homogeneous acids such as H₂SO₄ are difficult to reuse, and request additional neutralization process. As promising alternatives to homogeneous acids for biodiesel production, heterogeneous acid catalysts are typically reusable, equipment non-corrosive, and environmentally friendly [11]. As a consequence, biodiesel production using heterogeneous acidic catalysts for esterification of FFAs and (trans)esterification of low purity raw oils is preferable.

It is worth noting that non-edible and sustainable crude oils such as waste cooking oils and non-food crops would be better feedstocks to be used for biodiesel production, especially based on the governmental policies of developing countries with large populations [12]. As one of the sustainable and non-edible feedstocks, *Euphorbia lathyris* L., discovered by our research group towards the biodiesel production employing non-food oils, an erect biennial herb, is native to southern Europe, north-western Africa, southwest Asia and western China. More importantly, *Euphorbia lathyris* L. can thrive in drought, frost and arid soils. The seed yield ranges from 1.5 to 2.5 tons/ha/year along with a 48 wt% high oil content. Taking the aforementioned properties along with its high acid value (24.59 mg KOH/g) into consideration, we selected *Euphorbia lathyris* L. as the raw material for the one-pot process in this study.

On the other hand, a variety of solid acid catalysts for the esterification and (trans)esterification using different feedstocks to prepare biodiesel have been reported, such as transesterification of soybean oil with zinc aluminate [13], transesterification of soybean oil with CaO–MoO₃–SBA-15 catalysts [14], transesterification of yellow horn seed oil with Nafion resin [15], transesterification of rape seed oil with calcined scallop shell [16], esterification reaction of oleic acid with ionic liquid functionalized polymers [17], transesterification of *Jatropha* oil with sulfonic acid-functionalized platelet SBA-15 [18], and

esterification of rapeseed oil fatty acids with sulfonated carbon materials [19]. However, some of the aforementioned biodiesel process used the edible feedstocks, which somewhat increased the biodiesel production costs accordingly. In addition, prolonged reaction time or high temperature (*i.e.*, 200 °C) is required to achieve relatively high yields. As a result, serious catalyst leaching and poor recyclability are always encountered when using the aforementioned catalysts. More importantly, the biodiesel yield is compromised by esterification/hydrolysis equilibrium in the presence of significant amounts of water, and the acid catalysts will also be somewhat poisoned by the water [20]. Therefore, it is of great interest to develop a highly active (*i.e.*, strong acidity) and stable (*i.e.*, hydrophobic) solid acidic catalyst to prepare biodiesel *via* esterification of FFAs and (trans)esterification of low quality feedstocks in a one-pot process.

Ionic liquids (ILs) have attracted considerable interest as green materials, alternative reaction media and promising catalysts [21]. In addition, poly(ionic liquid)s (PILs), which are ionic polymers comprising a polymeric backbone and IL units, can serve the twin functions of IL and polymer, with high thermal stability, corrosion resistance and easily variable structures [22]. For biomass conversions, some PILs catalysts have been reported for the preparation of biodiesel and biofuel 5-ethoxymethylfurfural, with highly catalytic activities [23–25]. However, although the used PILs in the above context exhibited high activities, they are mono-functionalized, which somewhat limits their broad applications. Ideally, for the development of solid acid catalysts, the fabrication of heterogeneous catalysts with tuneable acidity and surface polarity is the ultimate objective [26]. On the basis of viewpoints derived from previous research in the above context, for the biodiesel production *via* a one-pot process from crude non-food oil resources, heterogeneous catalysts with multifunctional physicochemical properties such as appropriate acidities and a certain hydrophobicity are preferable. Furthermore, in order to cut down the energy consumption and cost in the separation of products and catalysts by tedious procedures such as centrifugation or filtration, endowing appropriate magnetism to the solid catalysts should be beneficial for their separation and recovery from the reaction mixture. Of particular interest is the immobilization of active acidic PILs on magnetic supports with appropriate hydrophobicity to fabricate such catalysts, namely, magnetically recyclable acidic polymeric ionic liquids decorated with hydrophobic regulators. It can be speculated that these catalysts will have good activity and recyclability in the production of biodiesel *via* esterification and (trans)esterification.

Inspired by these aforementioned findings, to continue our group's efforts towards biodiesel production from non-edible feedstocks [2,9,12,23,27–32], we herein design and prepare magnetically acidic PILs with the hydrophobic regulator catalyst Fnm-PILs *via* radical polymerization and anion exchange for biodiesel production by the esterification of oleic acid and (trans)esterification of real raw feedstocks from *Euphorbia lathyris* L., in high efficiency. In addition, the relative biodiesel reaction parameter optimization (response surface methodology (RSM) and single factor optimization), structure-activity relationships, catalyst reusability, fuel properties and the reaction mechanism, along with relative kinetic studies, were investigated.

2. Materials and methods

2.1. Materials

Euphorbia lathyris L. seeds were purchased from Luodian County, Guizhou Province, China. Oleic acid (AV = 188.5 mg KOH/g), iron chloride hexahydrate (FeCl₃·6H₂O, 99%), tetraethyl orthosilicate

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