



Biodiesel production from acid oils using sulfonated carbon catalyst derived from oil-cake waste



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ABSTRACT

The utilization of oil-cake waste (OCW) derived catalysts in biodiesel production was demonstrated. The sulfonated carbon materials were utilized as catalysts for pretreatment of acid oils (oils containing 8.17–43.73 wt% of free fatty acids). The catalysts could be used to convert free fatty acids (FFA) present in acid oils into corresponding methyl esters within 6–8 h at 80 °C, thus reducing the FFA content to desirable levels below 2 wt%. The esterification activity was found to be dependent on the initial FFA concentration found in the acid oil as well as methanol-to-oil molar ratio. High methanol-to-oil molar ratios and the presence of higher initial FFA concentrations resulted in enhanced esterification rates. Acid oil containing 43.7 wt% FFA was easily converted into mixtures containing up to 71% methyl esters (FAME). The reported catalyst was successfully recycled in five consecutive experiments and exhibited high thermal stability. Most importantly, the catalytic activity of the solid acid was found to outperform homogeneous case when equivalent amount of H₂SO₄ under similar conditions was applied. Therefore, the OCW derived sulfonated carbon catalyst reported herein could be used as a potential substitute for corrosive, concentrated H₂SO₄ currently employed for acid oil pretreatment.

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1. Introduction

Biodiesel is a renewable fuel typically comprised of fatty acid methyl esters (FAMES) derived from vegetable oils or animal fats. Several papers comparing biodiesel and petroleum-based diesel have shown that biodiesel can be attractive in terms of reducing exhaust emissions of carbon monoxide, hydrocarbons, particulate matter, and sulfur dioxide. While there are advantages of biodiesel over the traditional petroleum based 'fossil' diesel, biodiesel commercialization is limited by production costs: the cost of biodiesel is dominated by the price of the feedstock (refined vegetable oil) [1] [2]. Acid oils (AOs) such as crude vegetable oils, waste cooking oils and yellow grease have the potential to serve as an attractive feedstock due to their lower cost. However, the chemical

composition of these oils is variable depending on the source of origin and, moreover, these oils possess a composition that is different from that of virgin oil due to the presence of large amounts of free fatty acids (FFA) and moisture [3]. Due to the presence of FFAs in such oils, the oils cannot be subjected to transesterification because this would lead to soap forming side reactions. Therefore, it is necessary to reduce the FFAs levels to ≤2 wt% prior to transesterification by a pretreatment step [4]. Conventional vegetable oil refining is not a viable option because it will drastically increase the cost of final product (biodiesel). Esterification has been previously demonstrated to reduce the FFA levels of AOs. However, large quantities of methanol are required to drive the reaction to considerable yields. Large quantities of methanol and elevated FFA contents are the main factors affecting the economics of FAME production from AOs. Currently, concentrated H₂SO₄ is employed in acid oil pretreatment, at commercial scale, due to its proven activity and low cost. However, the use of mineral acids comes along with many drawbacks such as the requirement of specialized acid resistant reactors to overcome corrosion problems and requirement of multiple washing steps after the reaction in order to remove the unreacted H₂SO₄ [5]. To overcome these limitations, the use of heterogeneous acid catalysts such as zeolites [6], heteropolyacids [7], Amberlyst-15 [8], H₃PW₁₂O₄₀·6H₂O [9], WO₃/ZrO₂ [10] and

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sulfonated carbon catalysts [5,11–14] have been suggested. Nevertheless, their industrial applicability has been limited by complex, expensive synthesis routes, low activity and poor reusability. Consequently, the sulfonated carbon catalysts could be considered as a viable alternative to H_2SO_4 owing to their low material cost and high catalytic activity.

Carbon-based solid acids are considered ideal catalysts for many reactions due to their chemical inertness and good mechanical and thermal stability. Sulfonated carbons are the most promising solid acids and their use have been demonstrated in many acid catalyzed reactions including that of FFAs esterification as well as cellulose hydrolysis [15,16]. Such catalysts are generally produced via sulfonation of incompletely pyrolysed biomass, such as sucrose [17], glucose [18], starch [19], glycerol [20] or biochar [13]. Carbon precursors are directly pyrolyzed and sulfonated in concentrated H_2SO_4 at high temperatures. However, this simple process usually produces sulfonated carbons with low specific surface area, low acid density and poor reusability. These carbon catalysts are difficult to disperse in liquid-phase reaction mixtures [18]. Other sulfonating agents include fuming H_2SO_4 , SO_3 , ClSO_3H and 4-benzenediazoniumsulfonate. Recently, it has been established that sulfonation is more efficient with 4-benzenediazoniumsulfonate instead of H_2SO_4 due to high degree of sulfonation and mild reaction conditions which preserves the structural integrity of the carbon surface upon sulfonation as well as improved reusability due to the high stability C– SO_3H bonds [22,23]. However, most of the studies reported in the literature deal with sulfonated carbons (prepared by H_2SO_4 treatment) targeted at either esterification of model oils containing very large amount of free fatty acids (usually $\geq 50\%$ or long chain fatty acids such as oleic acid) which in the real world scenario are non-existent as feedstocks. Moreover, sulfonated carbons prepared by direct sulfonation are prone to severe deactivation with a loss 30–40% loss of initial activity mainly due to leaching of $-\text{SO}_3\text{H}$ groups which limits their applicability [13,21]. Therefore, sulfonation of carbon materials with 4-benzenediazoniumsulfonate could be more beneficial in long term use as it could successfully address the reusability issues of sulfonated carbons prepared by direct sulfonation.

The present work was undertaken with the aim of transforming oil-cake waste (from non-edible oil seeds of *Mesua ferrea* L.), a by-product from biodiesel production, into carbon-based solid acids for pretreatment of acidic oils (AO). The porous carbonaceous material was prepared by chemical activation of OCW and it was subsequently sulfonated via covalent functionalization/grafting with 4-benzenediazoniumsulfonate to obtain the solid acid catalyst. In order to investigate the influence of the sulfonation conditions on catalyst activity, two different experimental conditions were adopted upon catalyst preparation: Method 1 introduces H_3PO_2 assisted synthesis [22] whereas method 2 depicts the spontaneous approach [23].

The catalytic activities of the resulting materials were studied in esterification/transesterification of various AOs containing 8.17–43.73 wt% FFAs with methanol. The influence of FFA concentration, MeOH-to-AO molar ratio, reaction temperature and catalyst loading were studied in order to determine the optimal reaction parameters (Scheme 2).

M. ferrea L. is a commonly found and slowly growing hardwood tree in the wet tropical parts of India and Asian subcontinent. *M. ferrea* L. oil has significant potential as a feedstock for biodiesel production owing to its oleic acid rich seeds with high oil content (~75%). Currently the oil has no use due to its bitter taste and toxicity. With proper and careful planning, *M. ferrea* L. could emerge as a major non-edible oil crop similar to *Jatropha curcas*, *Pongamia pinnata* and, consequently, play a major role in meeting the feedstock demand for sustainable biodiesel production, especially in counties like India and other countries in Asian subcontinent [24].

The use of such non-edible vegetable oil as feedstock is expected to increase to meet the growing demands of biodiesel. The above mentioned environmental issues will result in production of large quantities of solid waste in the form of oil-cake waste (OCW) which creates disposal problems because conventionally used disposal methods such as conversion of waste into cattle feed or manure are not suitable owing to the toxic nature of OCW, resulting from the presence of anti-nutritional components. Moreover, direct burning is not efficient and appropriate flue-gas cleaning facilities will be needed to minimize pollution. Therefore, cost effective and eco-friendly methods are required for disposal of this waste which does not adversely affect the economy of biodiesel production. The presence of toxic compounds in OCWs from vegetable oils of non-edible origin such as *J. curcas* (phorbol ester) and *P. pinnata* (karanjin) are well known. However, more research is needed to determine the toxic components present in *M. ferrea* L. OCW can be converted into value added products such as activated carbon or activated charcoal. The use of OCW as starting material for catalyst production can partly address issues concerning waste disposal and it can simultaneously help to generate revenue from a potential waste. These products can have applications in several fields such as soil nutrition, water purification and catalysis in general.

2. Experimental

2.1. Materials

The acid oils (AOs) used in this study were extracted from non-edible seeds of *M. ferrea* L. and *J. curcas* via soxhlet extraction. The oil seeds were purchased from Kaliabor Nursery, Nagaon (Assam). The extracted oils were kept at 150–170 °C in an oven for 24 h in order to increase their FFA levels. The FFA content in crude *J. curcas* and *Mesua F.* Linn oil were found to be 8.17 and 14.4 wt% respectively. The acid oil containing 43.73 wt% of free fatty acid (FFA) was prepared by means of hydrolyzing a portion of *Mesua F.* Linn oil. Oil-cake wastes from *Mesua F.* Linn seeds were collected, ground and passed through Standard ASTM sieve (Mesh No. 60, 0.25 mm) and used as a precursor for the preparation of porous carbon. Ortho-phosphoric acid (88%), sulfanilic acid (99%), NaNO_2 (98%), anhydrous Na_2SO_4 (99.5%), H_2SO_4 (98%), HCl (35%), acetonitrile (99.5%) and acetone (99.5%) were purchased from Merck India Ltd. Mumbai and used as received. The H_3PO_2 (30–32%) aqueous solution was purchased from Sisco Research Laboratories Pvt. Ltd., India.

Seventy millilitres of *M. ferrea* L. oil was refluxed with 9 g NaOH for 3 h. The oil phase was treated with 50% (v/v) sulfuric acid at 60 °C for 2 h. The brown crude oil was further treated with active clay to adsorb the residues, and settled in separating funnel and washed to pH 4–5. The upper layer was collected and dried over anhydrous Na_2SO_4 . The concentration of FFAs in the obtained oil was 43.73% on weight basis.

2.2. Catalyst preparation

In the present study, chemical activation with phosphoric acid was applied in catalyst preparation since it facilitates high porosity and specific surface area development, at low temperatures (450–500 °C) under the self-generated atmospheres [25]. In a typical process, 20 g of powdered oil-cake waste was soaked in 50% ortho-phosphoric acid in 2:1 (w/w) impregnation ratio for 24 h. The resulting material was then transferred to a silica crucible and calcined in a muffle furnace at 500 °C for 1 h in the self-generated atmosphere. The black solid produced was consequently washed with 180–200 mL double distilled water, HCl (0.01 mol L^{-1}) and finally with 1000–1500 mL hot double distilled water until pH of

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