



Effective conversion of non-edible oil with high free fatty acid into biodiesel by sulphonated carbon catalyst



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HIGHLIGHTS

- Carbon-bearing materials were incompletely carbonized and sulphonated to obtain solid acid catalysts.
- The catalysts were characterized by SEM, XRD, NH₃-TPD, Raman, TGA, elemental analysis, FTIR.
- One step production of biodiesel from *Calophyllum inophyllum* oil with high FFA was performed on these catalysts.
- Catalytic performances of the sulphonated carbon materials were compared.
- Deactivation of the sulphonated carbon catalysts were partly caused by adsorption of chlorophylls.

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ABSTRACT

Interest in biodiesel research has increased over the years due to diminishing petroleum reserves but biodiesel has to be derived from non-edible oils in order to avoid the competition with food supply. Here, we report a one step catalytic conversion of non-edible seed oil, *Calophyllum inophyllum* with free fatty acid of 15% into biodiesel over biomass-derived catalysts. The effective catalysts were prepared by incomplete carbonization of carbon materials under inert atmosphere and then SO₃H groups were introduced to obtain catalysts whose activities are comparable to conventional acid catalysts. At the optimized conditions, high conversion (99%) was achieved. The stability of the catalysts was also investigated.

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1. Introduction

Currently, our energy sectors depend solely on fuels derived from fossil resources and thus there is growing concern about the current status of world's oil reserves and increasing environmental impacts of these fuels. There is a great expectation for alternative sources of energy from clean and renewable source. Biodiesel, which can be produced from plant oils or animal fats as a substitute for diesel compression ignition engines without the need for modification [1], has been regarded as a clean renewable fuel and attracted growing concern.

Biodiesel is mainly produced from refined edible oil such as sunflower [2], soybean [3], and rapeseed [4], but this practice is not sustainable because of its perceived competition with food thereby increasing both the cost of edible oils and biodiesel [5]. Recently, EU proposed a reduction in the use of food feedstock for fuel production [6] thereby stimulating research into the development of alternative non-food feedstock. Therefore, low grade vegetable oil is being employed for biodiesel production. These types of oils are cheaply available and generally termed as non-edible oil thereby ruling out any competition with food. Researchers have utilized various low grade vegetable oils for biodiesel production [7–11]. The free fatty acid (FFA) present in non-edible oil is first esterified to fatty acid methyl ester (FAME) in the presence of acid catalyst commonly sulphuric acid followed by transesterification of the triglyceride to biodiesel generally catalyzed by alkali such as potassium hydroxide and sodium hydroxide. However, these

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processes will lead to high production cost due to large energy consumption involved in the separation of the catalysts from the products [12].

One step production of biodiesel from non-edible oils would be desirable, attractive to investors and competitive with the current price of conventional diesel. A heterogeneous catalyst based on sulphonation of incompletely carbonized organic material was first introduced by Toda et al. [13] and applied in esterification of oleic acid and stearic acid to FAME. Since then, many researchers have synthesized robust solid catalysts from different organic materials for esterification of FFAs [14–19]. Also, the activities of these sulphonated carbon catalysts are either comparable or better than most conventional solid acid catalysts [12,14,18,19]. However, some reported works are centred on esterification of model FFAs such as palmitic acid and oleic acid present in low grade vegetable oils to FAME. The use of model fatty acids is not practicable in an industrial set-up since low-grade vegetable oil containing different types of FFA would be used for biodiesel production.

Here, we carried out one step catalytic conversion of vegetable oil with high FFA into biodiesel by synthesizing sulphonated amorphous carbon catalysts from biomass following the procedure in literature [13,14,18,20]. The activities of the catalysts were tested through simultaneous esterification and transesterification of *Calophyllum inophyllum* seed oil with high free fatty acids. *C. inophyllum* commonly known as polanga is a tropical seed found majorly in East Africa, Southern Coastal India to Malesia, Northern Australia and the Pacific Islands. It is also extensively found in the Philippines along its sea-shores [21]. Polanga kernels have very high oil content (75%), greenish yellow and a strong aromatic odour with an insipid taste [21]. The oil is classified as non-edible with very high FFA ranging from 14% to 22% [10]. A single tree is capable of producing 100 kg of fruits and 18 kg of oil [21]. A calculated oil yield of 4680 kg/ha (4175 lb/acre) under the assumption that 400 trees are planted per hectare (a tree producing 11.7 kg of oil) was proposed by Mohibbe Azam et al. [22]. The yield of *C. inophyllum* is comparable to the yield of most edible oils presently used for biodiesel production. At the optimized conditions, complete conversion to FAME was achieved with desirable fuel properties.

2. Experimental

2.1. Materials

C. inophyllum fruits were collected in the Botanical Garden, University of Ibadan, Nigeria. The seeds were removed mechanically, dried to the required moisture level, milled and the oil extracted by means of a soxhlet apparatus using analytical grade of hexane (Guangdong Xilong Chemical Co., Ltd.). The viscosity and average oil content are 21.2 mm²/s and 72.5% respectively. Furthermore, the physico-chemical analysis of *C. inophyllum* seed cake revealed the presence of carbohydrate 10.5%, protein 21.3%, ash 3.9% and crude fibre 3.1%. Prior to fatty acid determination by GC–MS, the oil was first derivatised into FAMES by using Sulphuric Acid–Methanol solution. 1 µL sample was then injected into the GC (Agilent 6890N, USA) with HP-5MS 5% phenyl methyl siloxane column (30 m × 0.25 mm × 0.25 µm) and Mass Spectrometer. The initial oven temperature was set at 120 °C. The temperature was then ramped at 5 °C/min to 180 °C (held for 10 min), at 5 °C to 200 °C and finally held for 4 min. Identification of the fatty acids were done with their respective standards; methyl palmitate (99.9 wt.%), methyl stearate (99.0 wt.%), methyl linoleate (99.4 wt.%) and methyl linolenate (99.0 wt.%) acquired from Accu-Standard while methyl oleate (99.0 wt.%) was purchased from J&K Chemicals. Fatty acid distributions as determined by GC–MS are;

palmitoleic acid 0.2%, palmitic acid 15.2%, stearic acid 17.4%, linoleic acid 27.3%, oleic acid 39.9%, heneicosanoic acid 0.1%. Glucose was obtained from Guangdong Xilong Chemical Co., Ltd., while *p*-toluenesulfonic acid (PTSA) (99.0 wt.%) from Sinopharm Chemical Reagent Co., Ltd., sulphuric acid (98.0 wt.%), methanol (99.5 wt.%) and isopropyl alcohol (99.7 wt.%) (Beijing Chemical Works), acetone (J.T. Baker, HPLC grade). All the reagents were of analytical grade and used as obtained.

2.2. Preparation of catalysts

About 200 g glucose or *C. inophyllum* seed cake (the residue obtained after oil extraction) was incompletely carbonized in a tubular furnace under constant nitrogen atmosphere at 400 °C. The heating rate was set at 2 °C/min and then kept at 400 °C for 1, 5 and 10 h respectively (*C. inophyllum* cake was only carbonized for 5 h). The solid obtained was made to pass through a 0.5 mm sieve to give a fine regular carbon powder. The carbon materials were then functionalized with concentrated H₂SO₄ (98 wt.%) and PTSA (99 wt.%) respectively following standard procedures with some modifications [13,20].

In a typical procedure, SO₃H groups were introduced into the polycyclic aromatic carbon sheets by heating 5 g of pyrolyzed carbon in 50 cm³ of concentrated H₂SO₄ at 150 °C under nitrogen for 10 h. After cooling at room temperature, 1 L of distilled water was added to the mixture and filtered. The solid was then washed repeatedly with hot distilled water (>80 °C) until impurities such as sulphate ions (SO₄²⁻) were no more detected. The catalysts were then dried at 60 °C in vacuum oven for 10 h. The catalysts were designated Cat-1 (glucose/H₂SO₄; 1 h), Cat-2 (glucose/H₂SO₄; 5 h), Cat-3 (glucose/H₂SO₄; 10 h) and Cat-4 (*C. inophyllum* cake/H₂SO₄; 5 h).

Functionalization with PTSA was carried out by mixing 5 g carbon material, 2.5 g *p*-toluenesulphonic acid (PTSA) and 20 cm³ of de-ionized water in a Teflon-lined autoclave at 150 °C for 5 h. The resulting product was filtered, washed with distilled water and methanol and dried in a vacuum oven at 100 °C for 4 h to obtain the catalyst. The catalysts were designated as follows; Cat-5 (glucose/PTSA; 1 h), Cat-6 (glucose/PTSA; 5 h), Cat-7 (glucose/PTSA; 10 h) and Cat-8 (*C. inophyllum* cake/PTSA; 5 h).

2.3. Catalysts characterization and screening

The surface area of the obtained carbon catalysts were determined by N₂ adsorption/desorption experiments conducted at –196 °C using Automatic Surface Analyzer and Porosity (Auto-sorb-1MP, Quantachrome). The samples were first degassed at 120 °C for 3 h. Structural information and amount of sulphur on the catalyst was obtained with SEM connected to Energy-Dispersive X-ray Spectroscopy (EDX). X-ray diffractometer (XRD) pattern was obtained using X'Pert PRO diffractometer employing Cu Kα₁ radiation (λ = 0.1540 nm), operated at 40 kV and 40 mA. Sample obtained by sulphonating with H₂SO₄ were scanned in the range of 2θ of 5–90° at a scanning speed of 0.05°/min. In the case of PTSA functionalized catalysts, the XRD patterns were obtained in the range of 2θ of 10–90° at a scanning speed of 0.05°/min. Functional groups attached to the catalysts were determined with FT-IR (Nicolet 380 spectrometer) using KBr pellets and Raman spectroscopy (LabRAM HR800).

Thermal stability was determined with DTA-TG Apparatus (Shimadzu DTA-60H). Sample weighing 10 mg was introduced into the system and the temperature was ramped from room temperature to 900 °C at a heating rate of 10 °C/min under nitrogen. Elemental composition of the catalyst was determined by elemental analysis (Vario EL cube elemental, Germany) which also gives information on the acid density of SO₃H attached to the catalyst.

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