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Valorization of walnut shell ash as a catalyst for biodiesel production

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ABSTRACT

The catalytic activity of the walnut shell ash was investigated in the biodiesel production by the sunflower oil methanolysis. The catalyst was characterized by the TG-DTA, XRD, Hg porosimetry, N_2 physisorption, SEM, and Hammett method. In addition, the effects of the catalyst loading and the methanol-to-oil molar ratio on the methyl esters synthesis were tested at the reaction temperature of 60 °C. The walnut shell ash provided a very fast reaction and a high FAME content (over 98%). As the reaction occurred in the absence of triacylglycerols mass transfer limitation, the pseudo-first-order model was employed for describing the kinetics of the reaction. The catalyst was successfully reused four times after the regeneration of the catalytic activity by recalcination at 800 °C.

1. Introduction

Biodiesel, a mixture of fatty acid alkyl esters, is obtained by the chemical reaction of oily raw materials (edible, non-edible, or waste vegetable oils, animal fats, or micro-algal lipids) with appropriate alcohol (usually methanol or ethanol). This reaction, named transesterification or alcoholysis, is usually realized in the presence of a suitable catalyst. The most commonly used catalysts are potassium and sodium hydroxide despite several problems associated with them. For instance, they cannot be recovered and reused after the reaction, must be neutralized at the end of the reaction by water washing, which generates a large amount of wastewater, and demand precautions for safe handling during operation and storage. A solution for these problems has been found in the application of heterogeneous catalysts such as alkali metal oxides as neat or loaded on the support. Their advantages over homogeneous catalysts refer to easy separation from the reaction mixture and the possibility to be reused. Moreover, since recently, the heterogeneous catalysts have been improved by loading the metals onto the catalyst surface to increase its hydrophobicity, which prevents the adsorption of water generated during the reaction and contributes to the catalyst stability [1,2]. On the other hand, the heterogeneously catalyzed reactions have a longer reaction time than homogenously catalyzed reactions. Besides that, some catalysts require a complex synthesis.

Since recently, to reduce the overall biodiesel production cost, appropriate solid catalysts have been prepared from waste materials such as agricultural wastes, sea materials, and biodegradable parts of industrial and municipal wastes. Special attention has been paid to biomass-derived solid catalysts, such as ashes obtained from coconut husk [3], empty fruit bunch [4], *Lemna perpusilla Torrey* [5], rice husk [6–8], tucumã peel [9] and “red” banana peduncle [10]. Generally, the preparation of these catalysts involves drying and combustion (in the range 350–900 °C) of biomass. In order to get more suitable catalysts, some ashes are used as a support for active components like the bamboo leaf and coal fly ashes for ZrO_2 [11] and calcined animal bone powder [12], respectively. Their preparation includes milling, impregnation of

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active components, drying and calcination. Although better stability of these catalysts is achieved by impregnation of the active component on the ash, the preparation method is more complex and requires the use of solvents. Therefore, simple combustion was used in the present work to get ash from waste walnuts shells, which may have practical applications.

The world productions of walnuts (in the shell) and walnut kernels are about 2,000,000 and 890,000 tons per year [13], respectively. Therefore, as a result of walnuts processing, a large amount of waste walnut shells is generated, which can be a valuable source of energy. The walnut shells (endocarp) contain lower contents of hygroscopic (cellulose and hemicellulose) and higher contents of hydrophobic (lignin) components [14], which result in an “energy content” comparable to that of coal [15] and more resistance to the moisture [16]. Besides energy (heat/electricity), combustion of walnut shells generates ash as a solid waste that could find some application as other ashes, for instance, as a catalyst, support for other catalytical species, or an adsorbent.

So far, the walnut shell has been used for the preparation of activated carbon, which was tested as an adsorbent for volatile organic compounds [17] and as a support for La and Ca employed in biodiesel production [18]. However, the catalytic activity of walnut shell ash has not been tested yet in transesterification reactions despite their chemical composition (with dominated alkali and alkali earth elements) indicates the possibility of its utilization as a catalyst. In addition, walnut shell ash has not been characterized completely as a solid catalyst.

This study deals with using ash, obtained by the air combustion of waste walnut shells, as a catalyst in the methanolysis of sunflower oil, which has not been reported yet. The obtained ash was characterized by the TG-DTA, XRD, Hg porosimetry, N_2 physisorption, SEM, and Hammett method. In addition, the effects of the reaction conditions (the initial methanol-to-oil molar ratio and catalyst loading) on methyl ester content were tested. Moreover, the kinetics of the methanolysis reaction was analyzed. The catalyst reusability was also studied to estimate the possibility of its commercial application. Therefore, the novelties of the present study are the first use of the waste walnut shells ash as a catalyst for biodiesel production, the complete characterization of the obtained ash including the evaluation of its reusability and the development of a simple mathematical model describing the kinetics of the tested reaction.

2. Materials and methods

2.1. Materials

In experimental work, the refined sunflower seed oil (Dijamant, Zrenjanin, Serbia) and methanol (purity of 99.5%; Zorka Pharma, Šabac, Serbia) were used. The oil consisted mainly of palmitic (6.20%), stearic (3.09%), oleic (30.79%) and linoleic (58.89%) acid, making up about 99% of the oil. The walnuts were obtained from a local market. Methanol, 2-propanol, and *n*-hexane, HPLC purity, were from LGC Promochem (Wesel, Germany).

2.2. Catalyst preparation

The walnut shell fraction remaining after crushing the walnuts and removing the kernels was combusted in the air, and the obtained biochar was cooled, ground, and calcined in a furnace at 800 °C in the air. The obtained walnut shell ash was used as the catalyst. The calcination temperature was selected based on the TGA/DTA analysis. The spent catalyst was recalcined in the same furnace at 800 °C for 2 h.

2.3. Catalyst characterization

The elemental analysis of walnut shell ash, spent and recalcined spent catalyst samples was performed by an Oxford Inca 3.2 energy dispersive spectroscopy (EDS) coupled with a Jeol JSM 5800 scanning electron microscope (SEM) operated at 20 keV. Before the analysis, the powders were affixed at the surface of graphite tape in the form of a thin layer. The thermal behavior was determined by simultaneous TG/DTA measurement (Setsys, SETARAM Instrumentation, Caluire, France) under a synthetic air flow in the temperature range from ambient temperature up to 1200 °C at a heating rate of 20 °C min^{-1}, using an alumina pan. The X-ray powder diffraction measurements were performed by a Philips PW 1050 X-ray powder diffractometer using Cu K$\alpha_{1,2}$ ($\lambda = 1.54178$ Å) radiation in the 2θ range of 10–90°, step-length of 0.01° and the scan time of 5 s. The morphology of the catalyst was observed by TESCAN MIRA 3 XMU field emission scanning electron microscope (FE-SEM), operated at 20 keV. A thin gold layer was deposited on the catalyst surface before analysis, in order to provide conductivity.

The textural properties of the walnut shell ash were determined by Hg intrusion porosimetry and N_2 physisorption at 77 K. The bulk density was measured on a Macropore Unit 120 (Fisons Instruments) using mercury as the displacing fluid. Prior to the analysis, the sample was dried in an oven at 110 °C during 16 h and additionally evacuated in a sample holder at the analytical position for 90 min. The Hg porosimetry measurement was performed on a high-pressure unit PASCAL 440 (Thermo Fisher) within the pressure range 0.1–200 MPa. Two subsequent intrusion–extrusion runs (Run1 and Run2) were conducted. An automatic data acquisition of intrusion–extrusion Hg volume *versus* applied pressure values was obtained through an interface SOL.I.D Software System collecting the data of the change in Hg volume with a resolution of 0.1 mm^3. Additionally, the SOLver Ver. 1.3.4 software was used for calculating the following parameters: total intruded Hg volume, specific surface area, bulk density, apparent density, and porosity.

Adsorption-desorption isotherm was obtained by N_2 adsorption at 77 K on a Sorptomatic 1990 Thermo Finnigan device. Prior to adsorption, the samples were outgassed for 2 h under vacuum at room temperature and afterward at 300 °C and the same residual pressure for 16 h. The sample of the spent catalyst was pretreated to remove the reaction products from the catalyst surface. The presence of the reaction products on the surface of the spent catalyst made the measurement of the specific surface area by N_2 physisorption at 77 K unmanageable in respect of accuracy of SSA determination and possible contamination of the instrument measuring line. The sample of the spent catalyst was transferred into a cellular tumble and 44 extractions were carried out in a Soxhlet apparatus using *n*-hexane. After extraction, the residual *n*-hexane was removed by heating in an oven at 110 °C. Finally, the sample was transferred in a sample holder and prepared for the N_2 measurement by the same procedure as the starting sample, i.e. outgassed for 2 h under vacuum at room temperature and afterward at 300 °C and the same residual pressure for 16 h.

The specific surface area of the samples was calculated from the linear part of the adsorption isotherm by applying the Brunauer-Emmett-Teller (BET) equation [19]. The micropore volume was estimated by the Dubinin-Radushkevich method [20]. The mesopore volume and the mesopore size distribution were estimated by the Barrett, Joyner, and Halenda (BJH) method [21] from the desorption branch using the Lecloux standard isotherm [22].

The base strength of the catalyst was determined by the Hammett indicators method. The following indicators were used: phenolphthalein ($H\_ = 9.3$), thymolphthalein ($H\_ = 10.0$), thymol violet ($H\_ = 11.0$), and 2,4-dinitroaniline ($H\_ = 15.0$).