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A calcium oxide-based catalyst derived from palm kernel shell gasification residues for biodiesel production

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HIGHLIGHTS

- Palm kernel shell gasification residues were used for the first time to produce catalysts.
- Various analytical methods suggest that CaO is the catalyst's active component.
- The applicability/activity of the catalyst in transesterification reactions was verified by methanolysis of sunflower oil.
- Conversion ratios of approximately 99% were reached after 300 min.

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ABSTRACT

The fruit of oil-palm trees is used to extract millions of tons of palm oil annually across the globe. The extraction of palm oil leaves behind various residues such as empty fruit bunches, mill sludge and fibers, shells, and palm kernel cake. Considering the large amounts of solid organic wastes that are produced in oil palm mills, there is a need for their recovery and utilization. Palm kernel shells (PKS) are the most difficult fraction of the solid waste to decompose. In this work, PKS solid residues which had been subjected to thermal treatment in a gasifier were used as raw materials for the production of a calcium oxide (quicklime/burnt lime) catalyst. The produced catalyst was fully characterized by SEM–EDX, XRF, XRD, CHNS, TGA, and BET analyses. In addition, the basic strength and basicity of the catalyst were determined. The catalytic activity of the CaO-based catalyst was verified in transesterification of sunflower oil with methanol. The effect of the catalyst loading on the fatty acid methyl esters (FAME) formation at a methanol-to-sunflower oil ratio (9:1) at 60 °C was studied. The results show that the calcium carbonate contained in the palm kernel shell biochars is a promising source for calcium oxide catalyst production.
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1. Introduction

Palm oil is extracted from the fruit of what is known as the oil-palm tree. This particular tropical species of palm tree originated in West Africa, but now grows as a hybrid in many parts of the world. Palm oil is relatively cheap and can be used for a variety of purposes including for food or as raw material for biofuel production. Countries around the globe have injected millions of euros as subsidies and incentives to promote biodiesel production. This has in turn led to growth in the palm oil production sector. In addition, with the steady economic growth of China and India as the world's largest importers of palm oil, demand for palm oil is expected to continue to increase [1].

Both liquid and solid wastes are generated in large quantities in oil palm mills. The liquid wastewater generated from oil palm mills is referred to as palm oil mill effluent. This effluent comes from the oil extraction, washing, and cleaning steps of the process. The solid wastes from the process include leaves, tree trunks, decanter cake, empty fruit bunches, palm oil mill sludge (including fiber), shells, and palm kernel cake (PKC). The PKC is produced when white palm oil (palm kernel oil, also known as lauric oil) is extracted from the kernels (endocarp, also referred to as the endosperm). The PKC can be processed and used as animal feed or used as compost after nitrogen addition [2]. About 6% weight of the entering fresh fruit ends up as shell waste [3].

Considering the large amounts of solid waste that is produced in oil palm mills, there is a need for their recovery and/or recycling. These wastes are currently either disposed of in landfills or combusted for energy production. Palm kernel shells (PKS) do not

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decompose easily and substantial furnace modifications are usually required if they are to be used in boilers in place of firewood or fuel oil [4]. It has been reported that when burned in their raw form, PKS produce too much smoke and not enough energy [5].

On the other hand, biodiesel is a promising alternative to conventional fossil fuels which has gained massive support in recent years. One of the main advantages of biodiesel is that it is claimed to be 'carbon neutral'. This means that the carbon emissions released into the atmosphere while burning, are compensated by the amount of carbon that the plant has absorbed during its growth. Other advantages of biodiesel include its biodegradability, biorenewable nature and low toxicity [6]. A high flash point and good lubricity are other advantages [7]. In addition, the emissions of carbon monoxide and particulate matter have been reported to decrease when fueling automobiles with biodiesel [8,9]. Nearly 8 million metric tons of biodiesel are produced globally each year [10].

Although viscous straight vegetable oil can be used directly as fuel, it entails problems such as poor atomization, incomplete combustion, coking of the fuel injectors, ring carbonization, and accumulation of fuel in the lubricating oil. Hence, a transesterification process is needed to convert oils such as vegetable oil [11] and waste cooking oil [12] into biodiesel. Solid base catalysts are among the most popular candidates to be used for the transesterification reaction. They are cost effective and easy to separate from the final product.

CaO is an alkaline earth metal oxide with very weak Lewis acidity of the metal cation due to its small electronegativity. Hence, the conjugate anion (oxygen) displays strong basic properties [11].

Recently, CaO derived from wastes and natural resources have increasingly been tested as catalysts in transesterification reactions of vegetable oils for biodiesel production [13]. Advantages of waste-derived CaO catalysts include their low or no cost, and the reduction of wastes. Waste egg [14], oyster [15], shrimp [16], mullusk [17] and cockle [18] shells, as well as waste mud crab [19] and fish scale [20], have been used as resources for obtaining CaO-based catalysts. Also, tars and alkali ashes from biomass gasification processes are reported to be good waste resources for CaO-based catalysts for biodiesel production from vegetable oils [21]. A review of the catalyst preparation conditions and the reaction conditions of transesterification catalyzed by the obtained catalysts can be found elsewhere [22].

Solid fractions of oil-palm waste have previously been investigated for biodiesel catalyst production. Boey et al. [23] used empty fruit bunch ash for biodiesel production, obtaining a 90% conversion rate. Yaakob et al. [24] also attempted to use empty fruit bunches for this purpose, with the help of KOH doping. Loading palm oil mill ashes with CaO has also been attempted [25]. As far as the authors are aware, gasified palm kernel shell wastes have not been investigated for biodiesel catalyst production yet. Here, the PKS ash (biochar) residue after the gasification process is used for CaO-rich catalyst production, without the need for any additional doping and/or loading. Currently, the large amount of ash produced from gasification units (which is usually discarded as waste) is one of the problems associated with biomass gasification. Hence using gasification residues for catalyst production could potentially make biomass gasification processes more environmentally and economically attractive.

2. Materials and methods

2.1. Materials

2.1.1. Palm kernel shell biochars

Prior to being received, the PKS have undergone a type of gasification treatment to produce electricity from high calorific value gases (a combination of mainly hydrogen and carbon monoxide known as syngas). The remaining palm kernel shell biochars (PKSB) which are the solid residues coming out of the gasifier have been supplied to the research team for further utilization. PKSB is the abbreviation used to describe the PKS after it has been gasified. The received PKSB is in the form of a fine black powder.

2.1.2. Chemicals

Edible sunflower oil (Dijamant, Zrenjanin, Serbia) was purchased in a local shopping store. The acid value of the oil was 0.2 mg KOH/g. Certified methanol of 99.5% purity was purchased from Zorka Pharma (Šabac, Serbia). CaO (p.a.) was supplied by Kemika (Zagreb, Croatia). Methanol, 2-propanol and *n*-hexane, all of HPLC grade, were purchased from LAB-SCAN (Dublin, Ireland). Hydrochloric acid (36 wt%), was purchased from Centrohem (Belgrade, Serbia).

2.2. Methods

2.2.1. Catalyst preparation

The PKSB was calcined at 800 °C for 2 h under atmospheric pressure immediately before the use. The calcination temperature was chosen based on the results of the TGA and XRD analysis of the PKSB. The catalyst was used after cooling in a desiccator containing calcium chloride and potassium hydroxide pellets. For comparative purposes, CaO was calcined at the optimum temperature of 550 °C for 2 h, as suggested elsewhere [6], and used after cooling in the desiccator.

2.2.2. PKSB powder characterization

A JEOL 6300F Scanning Electron Microscope (SEM) with energy dispersive analysis by X-ray was used for viewing the surface of the powders. Energy dispersive X-ray analysis (EDX) was used for elemental analysis. In addition, the quantitative composition of the samples was determined by XRF spectroscopy (Philips PW 1480 spectrometer). Elemental Carbon, Hydrogen, Nitrogen, and Sulfur (CHNS) analysis was performed for determination of the absolute values for constituent elements. X-ray diffraction patterns were obtained at different temperatures using a Philips PW1825 diffractometer with Cu Kα radiation (40 kV and 50 mA). The angular scanning was performed in the range of $10° < 2\theta < 70°$ at a rate of $2° \text{ min}^{-1}$. The specific surface area of the materials was characterized by adsorption–desorption of N_2 (Brunauer–Emmett–Teller method, BET) at the temperature of liquid nitrogen (77 K) using an Autosorb1–Quantachrome instrument. The gas used for the analysis was 99.9% pure. The N_2 adsorption–desorption data showed no significant improvement in BET surface area due to the sample calcination.

Hammett indicators were used for determining the basic strength (H_) of raw and calcined PKSB and CaO [26]. Typically, 500 mg of the sample was shaken with 1 mL of Hammett indicators diluted in 20 mL of methanol and left to equilibrate for 2 h after which no further color change was observed. The following Hammett indicators were used: neutral red (H_ = 6,8), phenolphthalein (H_ = 9.3), thymolphthalein (H_ = 10.0), thymolviolet (H_ = 11.0) and 2,4-dinitroaniline (H_ = 15). To measure the basicity of raw and calcined PKSB and CaO, the method of Hammett indicator–benzene carboxylic acid (0.02 mol/L anhydrous ethanol solution) titration was used [26].

2.2.3. Equipment

The transesterification reaction was performed in a 250 mL three-neck glass flask, which was equipped with a reflux condenser and a magnetic stirrer. The flask was placed in a water tank keeping the temperature constant at 60 °C by circulating water from a thermostated bath.

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