

Evaluation of the synthesis routes for the preparation of heterogeneous catalysts obtained from coconut shell and its application in the biodiesel production

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The synthesis and characterization of coconut-based heterogeneous catalysts and its application in the biofuel production has been studied. Catalyst samples were prepared according to an orthogonal experimental design where the best synthesis conditions were identified. Specifically, the catalysts were obtained from a char-based support prepared from the pyrolysis of coconut endocarp, which was chemically treated with KOH and Ca(NO₃)₂. Catalysts were employed for the transesterification reaction of commercial safflower oil with methanol at 60 °C to produce fatty acid methyl esters (FAMES). Surface chemistry characterization of the char support and catalysts was carried out in order to understand the impact of the synthesis route on the FAMES yield. These catalysts showed a competitive performance for biofuel production where the maximum FAMES yield was 90.5%.

Key words: Heterogeneous catalysts, transesterification, biodiesel, coconut biomass.

INTRODUCTION

Biodiesel is an alternative energy source widely known for its friendly environmental properties. This biofuel is non-toxic and biodegradable, it also emits less pollutants including carbon dioxide emissions and contains less sulfur in comparison to fossil fuels [1]. There are four main methods to produce biodiesel that include a direct use and mixing, microemulsion, thermal cracking and transesterification [2]. In particular, the production of biodiesel via transesterification has received a significant attention during last years. This process is carried out by mixing vegetable oils or animal fats with short-chain alcohols in the presence of a catalyst to obtain fatty acid methyl esters (FAMES) [3]. The use of a homogeneous catalyst has been associated to operational drawbacks such as the difficulty in the separation of products that are present in a homogeneous phase, including the non-reusability and high cost of the wastewater treatment system to neutralize the catalyst before being discharged [4]. On the other hand, the heterogeneous catalysts are easily separable and recyclable thus offering operational advantages for biodiesel production. They have proven to be a promising alternative with a performance comparable to that obtained for the homogeneous catalysts [5].

Heterogeneous catalysts prepared from biomasses have been studied since these feedstocks have the potential to reduce the biofuel production cost due to its abundant availability and completely renewable character. Note that this type of biomass

is firstly converted into a carbonaceous material, which can be used as a catalytic support for the incorporation of active specie(s) [6]. The preparation route of the support and the modification of its surface chemistry determine the catalyst performance. Therefore, an optimization of the catalyst preparation route should be performed.

This article reports the use of coconut (*Cocos nucifera*) endocarp as a precursor to synthesize a heterogeneous catalysts for the production of biodiesel. A detailed analysis of the preparation conditions has been performed to optimize the catalytic performance in the transesterification reaction of a commercial safflower oil with methanol to produce FAMES.

EXPERIMENTAL

For the synthesis of heterogeneous catalysts, the coconut endocarp was utilized to obtain a carbonaceous support via pyrolysis. This biomass was dried and sieved to obtain a mean particle diameter of 0.105 mm. An experimental orthogonal design was utilized to identify the impact of the catalyst preparation conditions on the percentage of FAMES yield via the transesterification reaction of a commercial safflower oil with methanol. In particular, the lignocellulosic precursor was pyrolyzed at N₂ atmosphere using a tubular furnace. This carbonaceous support was submitted to a chemical activation with a solution of potassium hydroxide (KOH) with a concentration 4 M during 24 h at room temperature under constant stirring. The sample was separated from the solution and dried at 100 °C for 24 h. Then, this sample was impregnated with a solution of calcium nitrate at

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room temperature for 24 h at constant stirring. The solid material was washed and dried at 100 °C for 24 h and a final thermal treatment was performed in a tubular furnace for 2 h under N₂ atmosphere. The variables studied in the experimental design were: the pyrolysis temperature (600, 750 and 900 °C) and dwell time (1, 2 and 3 h) to obtain the coconut-based char, the concentration of calcium nitrate (0.1, 0.2 and 0.4 M) used to modify the surface chemistry of this char and the conditions of the thermal treatment (500, 700 and 900 °C) to activate the catalyst surface.

A transesterification reaction was carried out to determine the FAMES conversion and performance of this heterogeneous catalyst. These experiments were done with batch reactors mixing commercial safflower oil with methanol in a molar ratio of 15:1, with 20% wt of catalyst respect to oil, at 60 °C for 8 h under constant stirring. This commercial safflower oil showed an average molecular weight of 885.47 g/mol and a fatty acid profile that included 77 % Linoleic, 13.5 % Oleic, 7.3 % Palmitic, 0.1 % Palmitoleic, 1.9 % Stearic and 0.2 % others. After the reaction, the catalyst was separated by centrifugation and the non-reacted methanol was evaporated. FAMES amount was quantified by a Thermo Scientific Trace 1300 gas chromatograph equipped with a flame ionization detector (FID) and a TG-5 SILMS column. FAMES amount was calculated based on a methyl heptadecanoate internal standard. The response variable of the experimental design was the percentages of FAMES yield using the catalyst and support. Statistical analysis of the experimental design was performed using the signal-to-noise ratio (S/N) where the best conditions for the catalyst synthesis were identified with ANOVA considering the perspective “the higher, the better”.

Surface chemistry of selected samples of the support and catalysts was analyzed. The crystalline structure of the samples was determined by X-ray diffraction. XRD patterns were recorded on a Malvern-PANalytical Empyrean X-Ray diffractometer using the Bragg-Brentano configuration with CuK α radiation. FTIR spectra of these samples were recorded using a Thermo Scientific Nicolet iS10 FTIR spectrophotometer in the range of 4000 to 400 cm⁻¹ with a resolution of 4 cm⁻¹ using 32 scans. Samples were dispersed in KBr reactive to be measured as pellets.

RESULTS

Results of the transesterification reaction of safflower oil using the heterogeneous catalysts showed a FAMES yield from 0.4 to 90.5%. In particular, the best catalyst was obtained from the

coconut endocarp pyrolysis at 600 °C for 1 h, impregnated with KOH and Ca(NO₃)₂ 0.1 M and thermally treated at 700 °C. This material showed the highest FAMES yield (i.e., 90.5 %). Herein, it is important to remark that the FAMES yield obtained with the char support (i.e., with no further modification) was 0.25 %, which indicated that the activation stage with KOH and Ca(NO₃)₂ has a significant impact on the catalytic properties. On the other hand, it was identified that the final thermal treatment after the nitrate calcium impregnation played an important role to improve the catalyst performance. Some samples obtained after the KOH treatment also showed competitive catalytic properties. These results indicated the relevance of synthesis route conditions in the properties of heterogeneous catalysts for biodiesel production.

Figure 1 shows the results of the signal-to-noise ratio where the impact of tested catalyst synthesis variables on the transesterification reaction can be observed. Statistical analysis clearly demonstrated that the catalyst properties were totally dependent on the conditions used in the synthesis. ANOVA analysis indicated that the pyrolysis conditions of the catalytic support were the variables with the highest impact in the synthesis process. Low FAMES yields of the catalyst could be due to the degradation of the surface functionalities of the char support due to the increment of the pyrolysis temperature and time [7]. These results confirmed that it is paramount to analyze the synthesis procedure and its operating conditions in order to select the route that provides the best properties to the support and catalyst [8,9].

XRD diffractograms and FTIR spectra are shown in Figure 2. XRD spectrum of the char support showed the peaks corresponding to an ordered carbon structure in a graphitic form with low crystallinity [10-12]. The crystallinity of modified coconut chars showed a slight decrement after the treatment with KOH. This change could be attributed to the presence of potassium on the solid surface. This support modified with KOH and Ca(NO₃)₂ showed peaks at 28, 36, 39 and 48 ° related to calcium carbonate according to the database HighScore Plus. These results were similar to those reported for materials prepared by other authors [13]. FTIR spectra of char and catalyst samples contained some characteristic bands of the lignocellulosic precursor, see Figure 2b. Specifically, the stretching vibration of the OH-appeared in the region 3600-3000 cm⁻¹, which can be associated to phenols and alcohols in cellulose, hemicellulose and lignin [14]. The absorption bands located in the region of 2916-2840 and 1504-1236

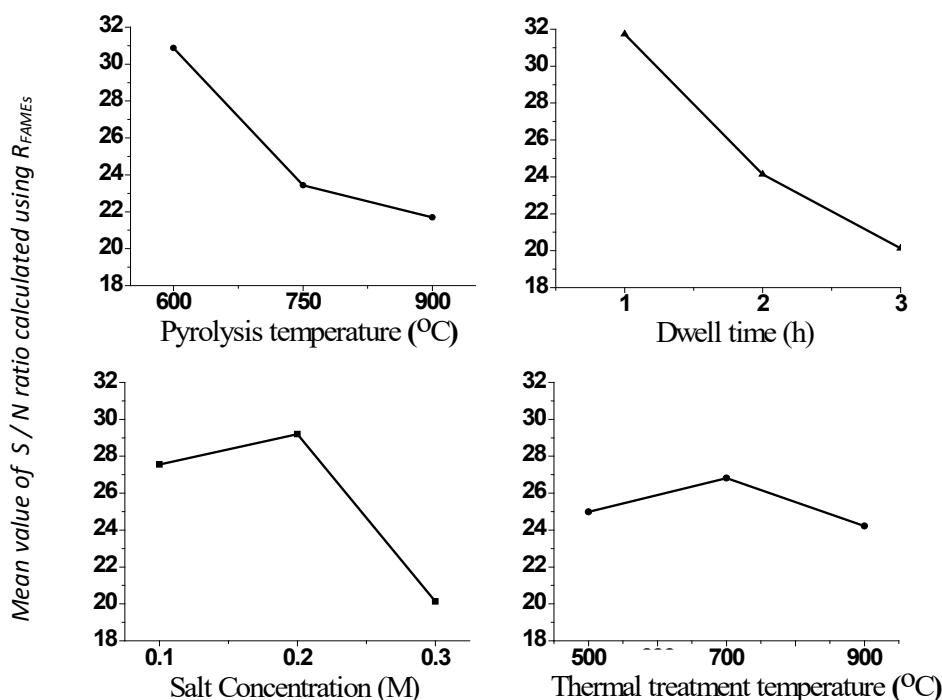


Fig. 1. Results of S/N ratio for the variables analyzed in the preparation of heterogeneous catalysts obtained from coconut biomass.

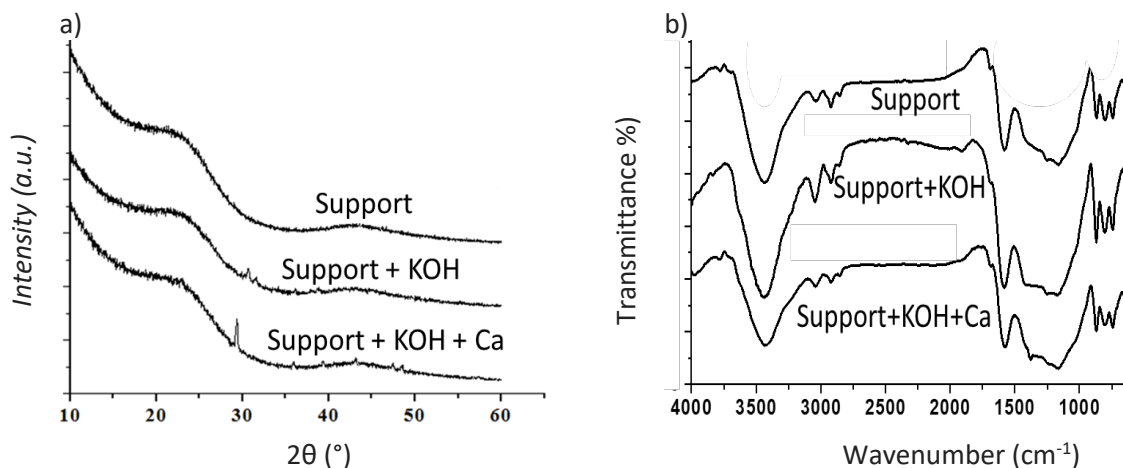


Fig. 2. a) XRD diffractograms and b) FTIR spectra of the coconut-based heterogeneous catalysts.

cm^{-1} corresponded to CH of aliphatic groups. The bands at 1734 and 1603 cm^{-1} were assigned to the C=O vibration in the form of ketone or carboxylic acid, while the bands at 1520 and 890 cm^{-1} indicated the presence of structural C=C of aromatic rings [11]. Finally, the band at 1160 cm^{-1} can be attributed to C-O vibrations indicating the presence of acids, alcohols, ethers and esters. Note that the FTIR spectrum of the coconut char modified with KOH did not show significant changes in the absorption bands. For the char treated with KOH and Ca, the band at 3400 cm^{-1} reduced and broadened, while the band at 1400 cm^{-1} increased its intensity. These changes could be related to the presence of calcium as Ca-OH and Ca-O thus suggesting the coordination of this metal with hydroxyl and carboxylic groups [15].

CONCLUSION

The preparation of catalytic supports obtained from coconut endocarp and its performance in FAMES production was analyzed and discussed. The highest FAMES yield was obtained with the catalyst prepared via pyrolysis of coconut biomass at $600 \text{ }^\circ\text{C}$ for 1 h, modified with KOH and $\text{Ca}(\text{NO}_3)_2$ 0.1 M and thermally treated at $750 \text{ }^\circ\text{C}$. This catalyst showed a 90.5 % FAMES yield in a transesterification reaction of commercial safflower oil with methanol at $60 \text{ }^\circ\text{C}$. These values were competitive and even higher than those reported in the literature for other heterogeneous catalysts. Statistical analysis allowed to identify the variables with a significant impact on the preparation of this heterogeneous catalyst, where the pyrolysis time and temperature showed the greatest influence on

the properties of coconut-based catalyst. Finally, it was concluded that the selection of the synthesis route was paramount to obtain a reliable heterogeneous catalyst with competitive properties to be used in the production of biodiesel.

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