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Book of Abstracts

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This volume contains the extended abstracts presented at the 14th International Chemical and Biological Engineering Conference (CHEMPOR 2023), held in Bragança - Portugal, from the 12th to the 15th of September, 2023.

Instituto Politécnico de Bragança & Ordem dos Engenheiros

**14th International Chemical and Biological Engineering
Conference
(CHEMPOR-2023)**

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Edited by:

Ana Maria Alves Queiroz da Silva
António Manuel Coelho Lino Peres
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Title

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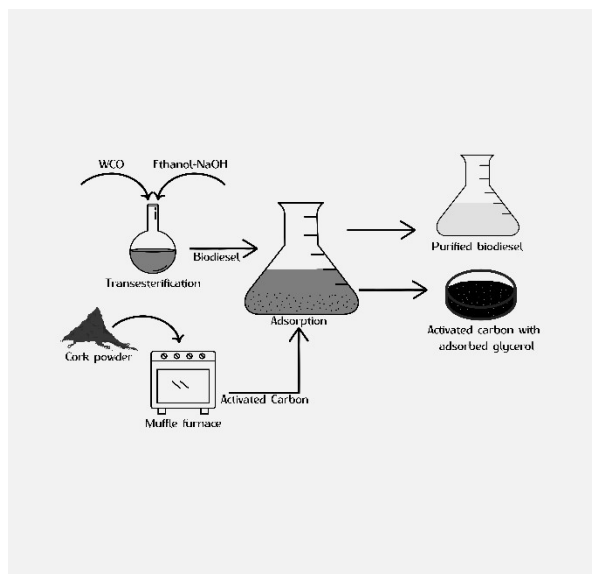
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Biodiesel production from residual cooking oils and its purification through adsorption processes using activated carbon prepared from cork waste

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Biodiesel is a renewable fuel that can be produced from waste cooking oil mainly through transesterification. However, from its production results a contaminant called glycerol, which must be removed. Wet washing is the most common method for biodiesel purification, but it has several drawbacks, including high costs and the generation of large amounts of aqueous effluent. This study proposes using activated carbon obtained from industrial cork waste in adsorption as an alternative method for glycerol removal. This approach could potentially reduce the environmental impact and cost of producing biodiesel, while also providing an alternative for the valorization of industrial cork waste. The highest value of removal of 89% of glycerol occurred with a cork chemically activated carbon with KOH at a load of 2%wt at 25°C for 6 hours of contact. After the biodiesel washing using adsorption process, the remaining glycerol content was 0.016%wt, below the maximum value of 0.02%wt specified by the EN14214:2012 standard.

Introduction

Global energy consumption has increased in recent decades, and the International Energy Agency predicts a 50% increase in demand for energy by 2030. As the supply of fossil fuels is limited and has environmental problems, researchers are exploring alternative energy sources. Biofuels, such as biodiesel, are promising renewable energy sources with lower carbon emissions that can be made from a variety of resources, including waste cooking oil, oily sludge from factories, and discarded animal fats [1].

Biodiesel is renewable, biodegradable, non-toxic, sulfur-free, and aromatic carcinogen-free, making it a more environmentally friendly option compared to petroleum-derived diesel. The cost of biodiesel is currently higher than petroleum diesel, but using waste cooking oil as a feedstock can reduce the cost since it is 25% to 40% of the price of edible oil. Biodiesel is produced mainly through transesterification, a process that converts oils or free fatty acids into alkyl esters and glycerol [2].

The properties of biodiesel depend on the feedstock used, and it must meet certain standards, such as the European Biodiesel Standard EN 14214:2012, which defines characteristics that determine the behavior of biodiesel combustion in an engine and the methods used to determine those parameters. To meet these specifications, the biodiesel produced must undergo a purification process to remove impurities such as glycerol, which, according to the standard, must be a maximum of 0.02%wt [3].

Several studies related to the purification of biodiesel by adsorption have been carried out. Materials such as silicates, clays, and polymers, among others, are widely used as adsorbents. In this work, activated carbon from cork residue was investigated as a potential adsorbent due to the high porosity and large surface area of the material [4].

Materials and methods

The first stage of the work was to optimize biodiesel production, using temperatures of 30, 45 and 60°C and oil:alcohol molar ratios of 1:6, 1:7.5 and 1:9. The catalyst used was NaOH and its load was fixed in 1%wt, since it is a concentration suitable for obtaining high ester yield in biodiesel.

After biodiesel production, four types of activated carbon were produced to be used as adsorbent in purification using a two-step carbonization process with chemical activation with solid KOH. Cork powder was first carbonized at 550°C for 1 and 2 hours, resulting in CC1 and CC2, respectively. These materials were then mixed with solid KOH in a weight proportion of 1:5 and carbonized again at 750°C for 2 hours, resulting in the final products CCB1 and CCB2. These materials were washed with HCl (0.1M) and distilled water until neutral pH and dried in an oven at 100°C. Posteriorly, all materials, including cork powder, were characterized by their surface area at 77 K using Quantachrome NOVATOUGH LX², elemental composition with a CHNS analyzer Flash 2000 (Thermo Fisher Scientific, Massachusetts, USA), pH_{PZC} using the methodology from Rovani (2015) [5] and thermogravimetric analysis using a TGA-50 Shimadzu equipment.

The last experimental stage was the adsorption process. First, a preliminary study was made to determine which materials had the highest potential in glycerol removal, and then the selected ones were used to study adsorption kinetics and equilibrium in the temperatures of 25, 35, and 45°C and adsorbent load from 0.1 to 3%wt. The experimental data was fitted to kinetic and equilibrium models.

Results and discussion

The studies showed that the best Fatty Acid Ethyl Ester's yield of 88.26%, was achieved with a reaction temperature of 30°C,

1%wt catalyst load, and 1:9 oil:alcohol molar ratio. The activated carbon production resulted in a carbonization process yield of approximately 20% and the activation process yielded around 50%. Some results are shown in Table 1.

Table 1. Adsorbents characterization results.

Material	S_{BET} (m ² /g)	C/H ^a	pH _{PZC}
Cork	5.16	0.65	4.64±0.15
CC1	203.65	3.07	10.47±0.05
CC2	64.41	3.18	10.40±0.02
CCB1	2057.25	11.21	9.76±0.00
CCB2	1687.22	11.40	8.71±0.02

^aC/H molar ratio obtained from the elemental composition analysis.

The surface area of the prepared cork activated carbon materials was similar to those reported in the literature, with the highest surface area (S_{BET}) of 2057.25 m²/g observed for CCB1. The analysis of the elemental composition and the increase of the calculated ratios (C/H) indicated the high efficiency of the carbonization process. Thermogravimetric analysis showed that the most significant weight variation is the loss of moisture, except for cork, which showed significant losses during the degradation of cellulose and suberin.

The pH_{PZC} value for cork was consistent with the literature, being an acid pH value. Other materials had a basic PZC due to decreased oxygen content from carbonization and the strong base used in chemical activation. The chemically activated materials were washed until neutral pH, decreasing PZC.

In the preliminary adsorption studies, it was shown that the best materials for glycerol removal were original cork and CCB1. The first was effective because of its acid pH_{PZC}, which increases the affinity with glycerol, and CCB1, despite its basic pH_{PZC}, has a very high surface area, increasing the removal efficiency.

The adsorption kinetics was studied using 2 and 3%wt adsorbent concentrations. It was shown that the increase in the temperature decreased adsorption capacity, disfavoring the washing process. Due to the low density of the materials, causing relatively large sample volumes to be handled, the increase in adsorbent load also negatively impacted the adsorption, generating agglomerations of adsorbent and reducing its contact area with the adsorbate.

The equilibrium time was similar for all kinetic studies, around 6 hours, and using 2%wt of CCB1 at 25°C the biodiesel was purified until the amount required in the European standard. The obtained adsorption profile and glycerol content are presented in Figure 1.

The data were fitted to pseudo-first order and pseudo-second order models. The second one represented better the experimental profile in most of the cases, and the highest adsorption capacity reached was 66.25 mg/g using 2%wt of CCB1 at 25°C.

Lastly, the equilibrium adsorption was studied. The tests were made with concentrations from 0.1 to 3%wt of adsorbent at the

temperatures of 25, 35, and 45°C. The adsorption profile presented an unfavorable behavior, which indicates that the adsorption is more significant in higher adsorbate concentrations.

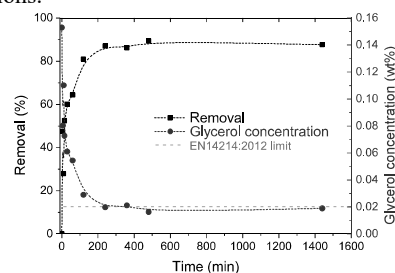


Figure 1. Adsorption profile of glycerol in biodiesel using 2% CCB1 as adsorbent at 25°C

The data were fitted to the Freundlich and Langmuir models, but only the first one could represent the adsorption. The estimated parameters confirmed the unfavorable adsorption behavior.

As in kinetic studies, the highest removal value was obtained with CCB1 at 25°C. The variation of glycerol removal and its content in relation to the adsorbent concentration is shown in Figure 2.

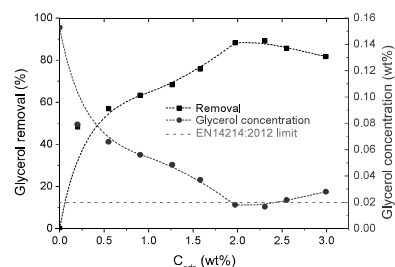


Figure 2. Glycerol removal and content for biodiesel purified with CCB1.

It is possible to confirm that the glycerol removal decreases with the increase of adsorbent concentrations when it is above 2.3%wt. In both kinetics and equilibrium studies, it was possible to remove more than 89% of glycerol from biodiesel, achieving a final concentration of approximately 0.016%wt, below the requirements of EN14214:2012.

Conclusions

Based on the objectives of this work, the optimization of biodiesel production and its purification through adsorption using cork waste, and its activated carbons as an alternative method to washing with water, were studied. Therefore, it can be concluded that the carbon in cork residues chemically activated with KOH has great potential in removing glycerol. This process can replace the water washing process, contributing to the reduction of effluent generation and to the reuse of a large-scale residue produced by Portuguese cork industry.

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