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Research article

Selective adsorption of fatty acid methyl esters onto a commercial molecular sieve or activated charcoal prepared from the *Acrocomia aculeata* cake remaining from press-extracting the fruit kernel oil

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Abstract: Mixing light biodiesel at low concentrations (not exceeding 5% by volume) with mineral kerosene is thought to be an interesting alternative to aviation fossil fuels without the need for engine adjustments. From the environmental point of view, this addition would mean significantly minimizing the impacts of conventional fuel emissions. The adsorption of relatively short molecular chain (C8, C10 and C12) fatty acid methyl esters (FAME), constituents of the biodiesel produced from the macaúba oil, was investigated using two types of adsorbents: A commercial molecular sieve 13X and the activated charcoal prepared from the macaúba cake remaining after press-defatting the macaúba fruit kernel. The adsorption experiments were performed on a glass column filled with the adsorbent. The activated charcoal is more efficient than the molecular sieve for selectively adsorbing FAME with C8, C10 and C12 carbon chains. The process of separating shorter chains from biodiesel by adsorption was proven to be adequate and does not compromise the energy balance. This study indicates that the charcoal obtained from the macaúba cake remaining after extracting the oil might be suitable for the selective separation of fatty acid esters, which could potentially lead to the preparation of lighter biodiesel (of lower average molecular weight) than that produced from the crude oil.

Keywords: biodiesel; oil; transesterification; fatty acids; adsorption; activated charcoal

1. Introduction

With the rise in the price of oil and the devaluation of the Brazilian currency relative to the US dollar, the world economic scenario has impacted demand and a considerable portion of the total cost of the transport sector, in particular that of the aviation sector, such as fuel and aircraft maintenance. The fuel used in aviation, the aviation kerosene (designated QAV-1, by the Brazilian Petroleum Agency [1]), is a petroleum derivative and accounts for about 40% of the operating costs of Brazilian airlines and for about 2% of global CO_2 emissions. This contribution is indeed significant, especially when the fact that the emission of pollutants occurs directly in the troposphere and the stratosphere is taken into account. The emissions tend to increase with the growth of the air-transport sector at a rate of 5% per year [2]. The growing trend in the aeronautical industry and concerns about the environmental impact of CO_2 emissions have led the International Air Transport Association [3] to require associated airlines to optimize fuel use and reduce CO_2 emissions by 50% by 2050 (compared to 2005).

Aviation kerosene derived from fossil fuels, denominated QAV-1 by the ANP [1], is composed of 35–60% (mass) of paraffin chains with 11–12 carbon atoms, containing at most 26.5% (mass) of aromatic compounds and 25–50% of naphthenic compounds [4]. Control of the occurrence of aromatic compounds must be rigorous to avoid the formation and deposition of soot and problems with reactions with the rubber components of the fuel system. Because of its low freezing point (−47 ℃), density, viscosity and flash point (between 38 ℃ and 60 ℃), it is a suitable fuel for turbine-driven engines, and it is the most widely used fuel in civil aviation in the world [4].

The transport sector, particularly the airline industry, has been under pressure by the global effort to reduce greenhouse gas emissions and the dependence on mineral oil. Investment in the development of drop-in biofuels from biomass as a sustainable alternative to reduce the carbon emissions generated by aircrafts is necessary to more rationally meet the growing global demand by civil aviation [5]. Drop-in biofuels are defined by the International Civil Aviation Organization (ICAO) as alternative biofuels for conventional jet fuel that are fully compatible and miscible with conventional fuel without requiring any adjustment to the aircraft engine or airport infrastructure and without any restriction with respect to their use by aircraft [6].

The methods developed for producing synthetic kerosene (SPK—Synthesized Paraffinic Kerosene) mainly involve the paraffinic kerosene synthesized by the Fischer-Tropsch method of synthesis (SPK-FT) and paraffinic kerosene synthesized from hydroprocessed esters and fatty acids (SPK-HEFA). Both products are intended for use in mixtures with conventional mineral kerosene up to the maximum limit of 50% [1]. However, an interesting alternative consists of mixing biodiesel at low concentrations (not exceeding 5% by volume) with mineral kerosene without the need to modify the engines [7]. Such a preferably lighter biofuel should have low concentrations of long-chain, saturated fatty acid methyl esters (FAME) for good performance at low temperatures and good oxidative stability [8]. Llamas et al. separated the short-chain fatty acid esters obtained from transesterified vegetable oils by vacuum distillation and mixed them with conventional fossil fuel [9,10]. However, this process implies a high consumption of energy, which can compromise the energy balance in industrial fuel production. An alternative to distillation for the separation of fatty acids and fatty acid esters is selective adsorption, followed by a desorption process with a desorbent material such as an aromatic hydrocarbons under the same conditions as the adsorption process [11]. According to Cleary et al. [12], the use of a non-zeolitic hydrophobic crystalline silica molecular sieve lead to separation of the esters of rosin acids found in tall oil from the esters of fatty acids. Üstün [13] studied the separation of fatty acid methyl esters (FAME) by selective adsorption using commercial type 13X molecular sieve, and their results showed that the separation of FAME from resin acids (RA) was effective and nearly complete. The objective of this work was to evaluate the efficiency of the commercial molecular sieve 13X and activated charcoal as adsorbents for separating shorter FAME chains (methyl octanoate, C8:0; methyl decanoate, C10:0 and methyl laurate, C12:0) obtained through transesterification of the macaúba kernel oil. An exploratory work on a first evaluation of the adsorption efficiency of a new activated charcoal prepared from the macaúba cake for selectively separating the lighter esters of biodiesel produced from the macaúba oil is also reported.

2. Materials and method

2.1. Biodiesel preparation and characterization

The commercial macaúba (*Acrocomia aculeata* (Jacq.) Lodd. ex Mart.) kernel oil was submitted to transesterification using homogeneous basic catalysis under reflux with magnetic stirring. The sodium methoxide reagent was first prepared from 0.5 g NaOH and 20 g of methanol. The reagent was then mixed with 100 g of oil in a glass flask coupled to a reflux condenser. The operating temperature was maintained at 60 ℃ with magnetic stirring, and the formation of the reaction product was monitored by TLC using a mixture of 9:1 hexane:ethyl acetate as the eluent. The TLC plates were developed in a sublimated iodine chamber. At the end of the reaction, the mixture was placed in a separatory funnel, and the glycerin (bottom portion) was separated. The biodiesel was washed with sodium chloride solution, and the pH was determined. The biodiesel was washed again with water and dried with anhydrous magnesium sulfate.

The kinematic viscosity was determined from the dynamic viscosity measured on a Brookfield DV III—Ultra Rheometer viscometer at 40 ℃ and the specific mass of the biodiesel. The acidity index of the biodiesel produced was determined by the potentiometric titration of a solution of the sample in a mixture of 2:1 ethyl ether:ethyl alcohol with 0.1 mol L^{-1} sodium or potassium hydroxide standardized to the turning point using the phenolphthalein indicator. The viscosity and the acidity index were compared with the data specified by the ANP [1].

2.2. Adsorbent preparation

The commercially purchased 13X molecular sieve (Sigma-Aldrich, pore diameter 13 Å) was dehydrated in an oven at 120 ℃ for 48 h. An activated charcoal was produced by the dehydration of *in natura* macaúba cake obtained as a residue from the press-extraction of the oil from the macaúba kernel, followed by carbonization and activation. The objective of the chemical activation of charcoal is the increase in its adsorbent properties by increasing its internal porosity. The chemical agent is impregnated within the particles of the charcoal, and, after washing, the microporosity is generated and the surface area of the material increases. The activated charcoal was prepared from the fruit kernel. The cake was washed with distilled water and oven-dried for 4 h at 105 ℃. The dried material was carbonized in a muffle furnace for 2 h at 500 ℃. The charcoal was activated with 85% phosphoric acid using 1.7 g acid per gram of charcoal with stirring for 24 h. The charcoal was washed with distilled water to remove the excess acid until the pH reached 7.0, and it was oven-dried at 110 °C for 12 h, according to the method described by Alves et al. [14].

2.3. Adsorption experiments

The separation was performed on a 20 cm-long and 2.0-cm-diameter glass column filled with the adsorbent to form a fixed bed of about 15 cm. The biodiesel flowed through the bed at a flow rate of approximately 1.3 mL min^{-1}. The samples were collected at different times and analyzed on a high-resolution Agilent 7820A gas chromatograph equipped with a flame ionization detector. An HP-INNOWAX (HP), 15 m × 0.25 mm × 0.25 μm column was used with a temperature gradient from 120 °C to 220 °C at 7 °C/min; injector (split ratio of 1/50) temperature at 250 °C and detector temperature at 250 °C. Hydrogen was the carrier gas (3 mL/min), and the software EZChrom Elite Compact (Agilent) was used for data acquisition. The injected volume was 1 μL. All the tests were performed in triplicate at 20 °C. The amount of C8, C10 and C12 FAME per unit mass of adsorbent (mg g^{-1}) was determined using Eq 1 [15,16]:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where C_0 and C_e (mg mL^{-1}) correspond to the concentrations of FAME at initial and sampling times, respectively; q_e is the amount adsorbed (mg g^{-1}); V is the volume (mL) of the solution; and W is the mass (g) of adsorbent used. A reference biodiesel sample was used as a blank sample in each series of experiments.

3. Results and discussion

3.1. Characterization of the biodiesel

The viscosity, acidity and specific mass data of the biodiesel produced from the macaúba kernel oil were within the limits specified by the ANP [1], as can be seen in Table 1.

Table 1. Result of the characterization of the biodiesel produced.

Parameters	Biodiesel	ANP Standard
Acidity Index (mg KOH g^{-1})	0.26	0.5
Viscosity at 40 °C (mm^2 s^{-1})	4.2	3.0–6.0
Specific mass (kg m^{-3})	917	850–900

3.2. Parameters of the adsorption isotherms

The composition of biodiesel before and after passage through the adsorbent is shown in Tables 2 and 3 for the samples collected at different times.

Table 2. Composition of biodiesel before (BD1) and after passage through the molecular sieve.

Sample	Concentration (mg mL^{-1})							
	C8:0	C10:0	C12:0	C14:0	C16:0	C18:0	C18:1	C18:2
BD1	0.61	0.45	4.05	1.10	0.88	0.35	2.83	0.41
1	0.54	0.41	3.77	1.04	0.84	0.31	2.68	0.43
2	0.55	0.43	3.93	1.07	0.84	0.33	2.74	0.41
3	0.52	0.42	3.77	1.03	0.82	0.31	2.58	0.39
4	0.54	0.43	3.92	1.08	0.86	0.33	2.75	0.42
5	0.53	0.42	3.85	1.06	0.84	0.32	2.65	0.40
6	0.55	0.41	3.97	1.09	0.87	0.33	2.77	0.39
7	0.47	0.39	3.59	0.99	0.79	0.30	2.52	0.37
8	0.47	0.39	3.71	0.99	0.80	0.30	2.59	0.37

Table 3. Composition of biodiesel before (BD2) and after flowed through the activated charcoal.

Sample	Concentration (mg mL^{-1})							
	C8:0	C10:0	C12:0	C14:0	C16:0	C18:0	C18:1	C18:2
BD2	0.43	0.35	2.96	0.79	0.66	0.30	2.04	0.28
1	0.24	0.23	2.34	1.14	0.84	0.47	2.80	0.54
2	0.17	0.18	2.34	0.98	0.76	0.41	2.64	0.34
3	0.22	0.24	2.49	0.76	0.64	0.34	2.22	0.29
4	0.19	0.20	2.35	0.74	0.72	0.41	2.64	0.35
5	0.18	0.19	2.26	0.79	0.67	0.41	2.67	0.34
6	0.20	0.20	2.02	0.63	0.62	0.77	2.65	0.93
7	0.17	0.17	1.80	0.55	0.60	0.37	2.55	0.32
8	0.17	0.16	1.94	0.68	0.67	0.37	2.49	0.31

To optimize the adsorption process for selectively separating the FAME. The experimental data were tested using the Langmuir isothermal model. The adsorption isotherms are theoretical relationships graphically represented by curves that measure the adsorption efficiency and describe the relationship between the amount of adsorbate adsorbed by the adsorbent and the amount remaining in the medium. The statistical reliability of the isothermal equations was evaluated by their corresponding correlation coefficients, R^2.

The Langmuir model is the simplest model and assumes that (a) there is a specific number of sites; (b) all the sites have the same adsorptive energy; (c) there is no interaction between adsorbed molecules and neighboring sites; (d) the adsorption is reversible; and (e) the adsorption occurs in a monolayer. This model is described by Eq 2:

$$q_e = \frac{q_m k_\alpha C_e}{1 + k_\alpha C_e} \tag{2}$$

where q_m is the maximum adsorption capacity (mg g^{-1}) and k_α is the Langmuir constant related to the adsorption energy. Eq 2 is arranged in a linear form (Eq 3) for testing the experimental data [14,15].

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m k_\alpha} \tag{3}$$

Plotting $1/q_e$ against $1/Ce$ furnishes the slope of the line $1/(k_\alpha\ q_m)$ with the linear coefficient $1/q_m$. The adsorption obeys the Langmuir isotherm model for the adsorbents studied, as is shown in Figures 1–3.

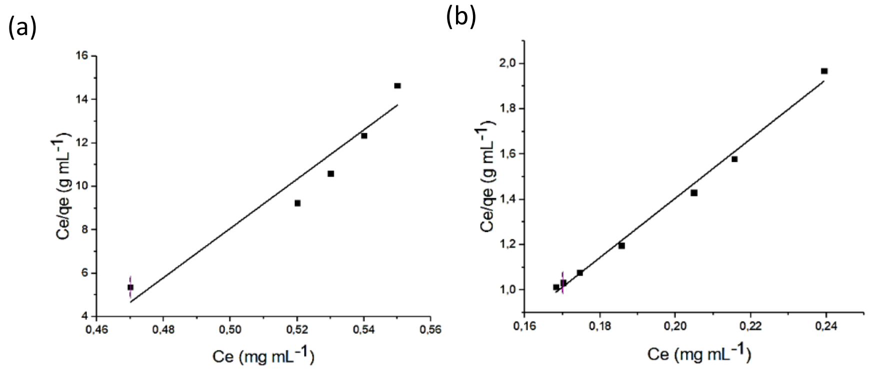

Figure 1. Langmuir adsorption isotherm for methyl octanoate (C8): (a) 13X molecular sieve; (b) activated charcoal.

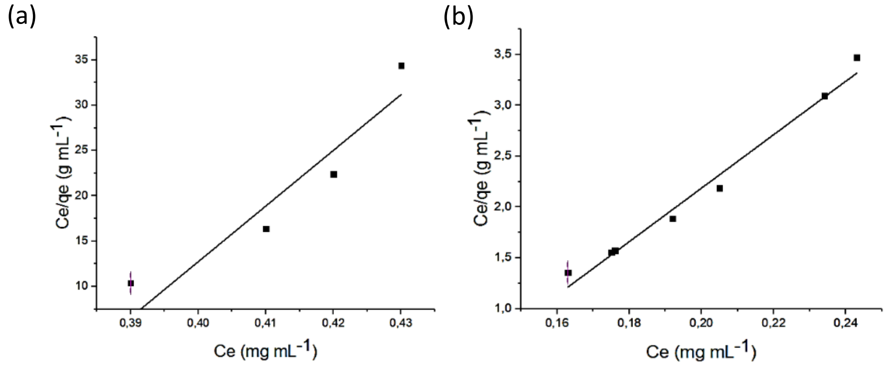

Figure 2. Langmuir adsorption isotherm for methyl decanoate (C10): (a) 13X molecular sieve; (b) activated charcoal.

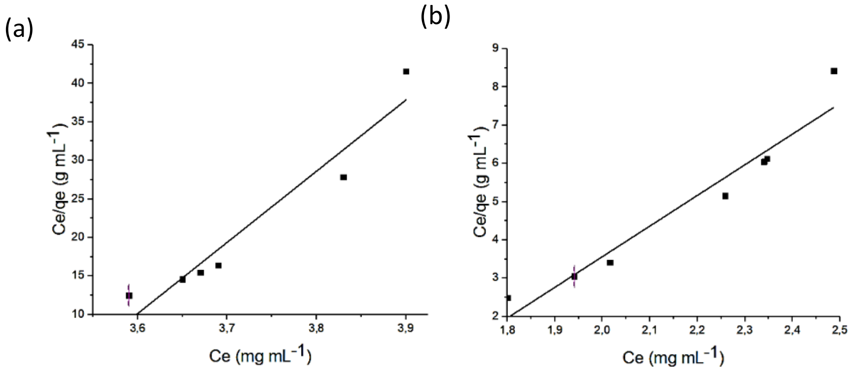

Figure 3. Langmuir adsorption isotherm for methyl laurate (C12): (a) 13X molecular sieve; (b) activated charcoal.

The viability of the adsorption process can be evaluated in terms of the dimensionless equilibrium parameter R_L, which describes the adsorption process (Table 4) [16]. The R_L-value can be estimated through the use of Eq 4:

$$R_L = \frac{1}{1 + k_\alpha C_0} \quad (4)$$

where the value of k_α was derived from the Langmuir isotherm.

Table 4. Values of the parameter R_L and its relationship with the type of adsorption.

R_L value	Type of adsorption
$R_L = 0$	Irreversible
$0 < R_L < 1$	Favorable
$R_L = 1$	Linear
$R_L > 1$	Unfavorable

The Langmuir parameters for the adsorption of short chain FAME on the 13X molecular sieve and on activated charcoal are presented in Table 5.

Table 5. Langmuir parameters for FAME adsorption on 13X molecular sieve and activated charcoal.

	13X molecular sieve			Activated charcoal		
	C8	C10	C12	C8	C10	C12
R^2	0.933	0.878	0.937	0.993	0.978	0.941
Maximum adsorption, q_m (mg g^{-1})	0.020	0.004	0.003	0.822	0.325	0.078
Binding energy constant, k_α (mg mL^{-1})	0.429	0.379	3.490	0.093	0.117	1.565
R_L parameter	0.792	0.854	0.066	0.961	0.960	0.177

The value of the dimensionless parameter, R_L, for all the samples indicated favorable adsorption ($0 < R_L < 1$) on both the adsorbents tested. The fit of the experimental data and the correlation coefficient, R^2, were better for the adsorption on activated charcoal than those for the molecular sieve. The best results were observed for esters of fatty acids with carbon chains of 8 and 10 carbon atoms. The amounts of C8 and C10 FAME adsorbed were 0.822 mg g^{-1} and 0.325 mg g^{-1}, respectively.

The maximum adsorption capacity for lighter acid methyl esters from biodiesel was greater on activated charcoal, and this fact can be explained in terms of polarity and the high degree of porosity and extended interparticulate surface area. Activated charcoal is classified as a hydrophobic solid, whereas the molecular sieve has a hydrophilic character. Because of the lack of polarity of the carbon chain, the fatty acid esters have a higher affinity for these adsorbents. However, reactions and chemical adsorption can affect the hydrophobic nature on the surface and reduce the hydrophobic properties of the activated charcoal. Activated charcoal has a surface area on the order of 800 to 1500 m^2 g^{-1} contained in micropores with effective diameters smaller than 2 nm [17]. The adsorption capacity decreased with the increase in the length of the ester chain because smaller chains more easily access the pores of the adsorbent, which, in this case, acts as a filter to exclude larger molecules.

The Langmuir model predicts the formation of an adsorbate monolayer on the surface of the adsorbent. The amount of adsorbate necessary to form the monolayer decreases as the number of carbon atoms in the FAME chain increases from C8 to C12. This variation occurs because the higher molecular weight and, consequently, lower mobility, make it difficult for the longer chains to access the pores of the adsorbent [18]. Although the adsorption of organic compounds on activated charcoal is very efficient, few studies have been published on the use of activated charcoal as an adsorbent to separate fatty acids or esters of fatty acids.

4. Conclusion

The isothermal adsorption model of Langmuir is proposed to describe the adsorption of methyl esters of fatty acids with medium-size chains on activated charcoal produced from macaúba cake, a residue from the extraction of macaúba oil, and on the commercial molecular sieve 13X. The maximum adsorption capacity was observed for the activated charcoal/C8 FAME system. These results open real perspectives for the production of biodiesel with a lower molecular weight than that of the biofuel produced from the whole crude macaúba oil. This fact can be understood as a step favoring further chemical transformations using lighter fractions of biodiesel as precursors to produce biokerosene or even blending these fractions with conventional mineral kerosene for as aviation fuel.

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Conflict of interest

The authors declare no conflict of interest in this paper.

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