Industrial Crops and Products 95 (2017) 1–5

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Eucalyptus pulp as an adsorbent for metal removal from biodiesel

André L. Squissato, Alexandre F. Lima, Eduardo S. Almeida, Daniel Pasquini*, Eduardo M. Richter, Rodrigo A.A. Munoz

Instituto de Química, Universidade Federal de Uberlândia, Av. João Naves de Ávila, 2121, 38400-902, Uberlândia, Minas Gerais, Brazil

ARTICLE INFO

Article history:
Received 21 April 2016
Received in revised form
27 September 2016
Accepted 2 October 2016

Keywords:
Biodiesel
Metal removal
Cellulose
Eucalyptus pulp
Washing
Adsorption

ABSTRACT

This work reports the use of eucalyptus pulp as an adsorbent for metal removal from biodiesel. Fatty acid methyl esters produced from sunflower oil (SfMB) and recycled used cooking oil (RMB), which contained Fe, Mn, and Cu, were treated through filtration on a column filled with the cellulosic adsorbent, and washed with deionized water for comparison. The treatment with cellulose material resulted in the removal of 13–81%, 35–84%, and 40–74% of Fe, Mn, and Cu in biodiesels, while the water washing removed 4–40%, 10–47%, and 4–19%, respectively. In addition to the higher efficiency, the use of cellulose is a more environmentally friendly process than the purification with water, once the latter results in a considerable volume of effluent requiring treatment prior to disposal, besides the high consumption of water. Moreover, the regeneration of the cellulosic adsorbent is demonstrated.

1. Introduction

Biodiesel is an alternative fuel derived from vegetable oils, animal fats or waste cooking oils produced by transesterification of triglycerides with an alcohol in the presence of a catalyst (Rahimi et al., 2014; Serqueira et al., 2014). The transesterification is the most simple and conventional method to produce biodiesel. Short-chain alcohols are commonly used such as methanol and ethanol, in the presence of alkaline catalysts such as sodium and potassium hydroxides, ethoxides and methoxides, yielding a mixture of esters (biodiesel) and glycerol byproduct, which is separated by decanting (Squissato et al., 2015).

From all the contaminants that impair the performance of biodiesel in diesel engines (alkali metals, residual alcohol, soaps, free glycerol, and residual glycerides) (Atadashi et al., 2011; Gomes et al., 2010), metals have received special attention by researchers due to the acceleration of biodiesel degradation processes compromising the storage time of this biofuel (Jain and Sharma, 2014; Sarin et al., 2009).

Sarin et al. (2009) studied the oxidative stability of Jatropha biodiesel (*Jatropha curcas*) in the presence of metal contaminants, such as Fe, Ni, Mn, Co and Cu. The induction time (measure of oxidative stability) decreased due to the acceleration of biodiesel degradation processes. The induction time was improved upon addition of the antioxidant butylhydroxytoluene (BHT), however, the higher the content of metals in the biodiesel, the greater the added amount of antioxidant was required, which can burden the price of the final product. In addition, the presence of these metals can interfere with the proper functioning of engines, and moreover, metals can be released into the environment when the biofuel is burned, causing contamination of soils, rivers and atmosphere (Pillay et al., 2009). Metals are primarily responsible for the deterioration of biodiesel catalyzing the oxidation processes of carbon chains. The result is the formation of short chain organic acids, ketones, aldehydes, hydrocarbons, starches, polymers and dimers. These products cause clogging of nozzles and fuel filters, improper burning, corrosion of metal parts and other problems that interfere with the proper functioning of the engine (Fazal et al., 2014; Jain and Sharma, 2014; Yaakob et al., 2014; Zuleta et al., 2012).

The type of soil used for soybean plantations, exposure to fertilizers, the presence of industries and highways near plantations, refining processes, synthesis, transport and storage are the main contamination sources of metals in the vegetable oil or in the produced biodiesel (Dugo et al., 2004; Garrido et al., 1994; Quadros et al., 2011).

The most commonly used processes for the purification of biodiesel consist of washing with deionized water (Kafuku and Mbarawa, 2010; Thiruvengadaravi et al., 2012; Van Gerpen, 2005), mineral acids (Faccini et al., 2011; He et al., 2006) or organic solvents (He et al., 2006; Siler-Marinkovic and Tomasevic, 1998;

* Corresponding author.
E-mail addresses: daniel.pasquini@ufu.br, danielpasquini2005@yahoo.com.br (D. Pasquini).

http://dx.doi.org/10.1016/j.indcrop.2016.10.004
0926-6690/

Table 1
Operating instrumental conditions for metal determinations by MIP OES.

Parameters	Cu	Mn	Fe	Pb
Wavelength (nm)	324.75	403.08	259.94	405.78
Nebulizer pressure (kPa)	200	220	100	200
Viewing position (mm)	−10	−10	0	0
Analytical curve (mg L^{-1})	2.0–10.0	2.0–20.0	2.0–10.0	2.0–10.0
Nebulizer	Inert OneNeb			
Spray chamber	Cyclonic single-pass			
Speed peristaltic pump (rpm)	15			
Read time (s)	5			
Number of replicates	3			
Stabilization time (s)	7			
Uptake sample time (s)	7			
Nitrogen (L min^{-1})	22.5			
Sample flow rate (mL min^{-1})	6.0			

Soriano et al., 2009). The large amounts of wastewater generated after biodiesel purification and the incorrect disposal intensify environmental problems (Saleh et al., 2010).

Aiming the removal of metals from biodiesel without the generation of great volumes of wastewater or residual solvents, studies are being conducted in order to identify and apply biomaterials with high adsorbing properties combined with sustainable properties such as abundance, low cost, biodegradability, and low waste generation. The cellulosic pulp has great potential for metal adsorption due to the presence of active hydroxyl groups in its main chain, and also has other advantages, including non-toxicity, biocompatibility, biodegradability, abundance and renewability (Gemeiner et al., 1998).

Duong et al. (2006) evaluated the adsorption capacity of Cd^{2+}, Co^{2+} and Ni^{2+} using the extracted pulp from fibers of pine (*Pinus radiata*) and they verified that the adsorption capacity is directly correlated with the cation hydration radius, thus Ni^{2+} ions presented higher affinity for cellulose fibers, followed by Cd^{2+} and Co^{2+} ions.

Rezić (2013) evaluated pulp fibers of three different materials, including cotton, flax and hemp, for retention of metals from aqueous solutions containing Al^{+3}, As^{+3}, Be^{+2}, Bi^{+3}, Co^{+2}, Cd^{+2}, Cr^{+3}, Cu^{+2}, Fe^{+3}, K^{+}, Hg^{+2}, Mg^{+2}, Mn^{+2}, Mo^{+6}, Ni^{+2}, Pb^{+2}, Se^{+2}, Si^{+3}, Sn^{+2}, Sm^{3+}, Tl^{+3}, and Zn^{+2}. Most metals were satisfactorily adsorbed on flax fibers, with higher efficiency than hemp and cotton.

In view of these considerations, the aim of this study is to evaluate the retention of Fe, Mn, Cu and Pb present in biodiesels produced from sunflower oil (SfMB) and residual cooking oil (RMB) using columns containing Kraft pulp eucalyptus fibers and compare the results with conventional purification using deionized water.

2. Experimental

2.1. Production and characterization of biodiesels

Refined sunflower oil (Liza, Brazil) and waste frying oil collected from a local restaurant, methanol (99.8% Vetec) and KOH (90% Vetec) were used for biodiesel production. The biodiesels were synthesized by the transesterification reaction in a molar ratio of 5:1 oil/methanol with 1% KOH (w w^{-1}). The reagents were added in a reactor under constant stirring for 1 h at room temperature (27 °C). After the reaction period, glycerol (by-product) was separated from the mixture of methyl esters (biodiesel) by gravity (Serqueira et al., 2014). The biodiesel was collected and stored in amber vials for subsequent purification column tests using cellulosic pulp or washing with deionized water.

The fatty acid methyl ester composition of both biodiesels (SfMB and RMB) was determined equipped with a gas chromatograph (Model 7890A, Agilent Technologies, USA), using a CPWAX 52cb capillary column (30 m × 0.25 mm × 0.15 mm), 0.5 mL of injection volume, injector temperature at 250 °C, oven at 170 °C, flame ionization detector (FID) at 390 °C with pressure and hydrogen flow rate of 200 kPa and 2 mL min^{-1}, respectively. Analyses were performed in triplicate, following the standard method EN 14103.

2.2. Purification with deionized water

Approximately 20 g of crude biodiesel (SfMB and RMB) was transferred to a separatory funnel and washed 5 times with 10 mL portions of deionized water at 80 °C or until the scrubbing water was clear. Subsequently, the aqueous (lower) phase was separated from the organic (top) phase and removed (Squissato et al., 2015). The purified biodiesel with deionized water was stored in amber glass for subsequent analysis of the metals.

2.3. Purification cellulose column

Bleached eucalyptus pulp obtained by the Kraft process was acquired by Suzano industry (Salvador, Brazil) in sheets of 40 cm × 30 cm. The physicochemical characterization of the cellulosic material was discussed in a previous work developed by our research group, in which this material was evaluated for removal of ethanol, glycerol and moisture from biodiesel (Squissato et al., 2015). Cellulose fibers were sieved using a 500 μm sieve pore size and presented 85% of cristallinity index, moisture content of 1.0% w w^{-1}, viscosimetric molecular weight of 152.293 g mol^{-1}, α-cellulose and hemicellulose contents of 90.0% and 10.0% w w^{-1}, respectively, and the average length of the fibers was 0.490 mm length × 21.20 μm width.

About 20 g of each crude biodiesel (SfMB and RMB) was passed through two identical columns (48 cm height × 1.3 cm diameter) containing 1.0 g of cellulose in each corresponding to 10 cm height and 10 cm^3 in volume. A pump (Barnant 400-1902 CO) was connected onto the top of the column to generate pressure equivalent to 1.22 atm and then to promote the purification process, carried out at 27 °C. The pulp was subjected to four consecutive cycles of use in order to check the maximum removal capacity of the metal, i.e., at what point the material cannot adsorb metals requiring their replacement or regeneration. For this analysis four samples containing 20 g of SfMB were added and purified by column. It was also carried out a study on the regeneration of the cellulose after 4 cycles of use to verify the efficiency in the removal of metals. The material was treated with an 90:10 v v^{-1} ethanol:water solution containing 0.01 M HCl with stirring for 2 h. Thereafter the pulp was filtered and washed with aliquots of deionized water and dried at 105 °C for 24 h. The dry material was crushed, sieved and used in metal removal processes described above for SfMB. After passing the biodiesel through the column, the collected material was stored in amber glass for assessing the content of each metal.