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Purification of biodiesel by dry washing, employing starch and cellulose as natural adsorbents

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HIGHLIGHTS

- Biodiesel from sunflower oil was successfully purified with natural adsorbents.
- Starch from different sources and cellulose fibers were used as adsorbents.
- Dry washing has removed more impurities than the wet washing.
- Was reduced the acidity index, alkalinity, free glycerine and turbidity of biodiesel.

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ABSTRACT

This work describes a study of the purification of biodiesel produced from sunflower oil by dry cold washing using natural adsorbents as cellulose and starch from different sources (corn, potato, cassava and rice), and the comparison with dry cold washing with a commercial adsorbent Select 450® and with the conventional wet washing with hot water. The purification by dry washing was carried out by varying the amount of adsorbents in 1%, 2%, 5% and 10% (w/v) at 25 °C for 10 min. For the purification by wet washing, the biodiesel was successively washed with acidified water and pure water at 85 °C until neutralisation. The efficiency of the processes for the removal of biodiesel impurities was evaluated by determining the acidity index, combined alkalinity, free glycerine and turbidity of the biodiesel. All adsorbents studied presented good efficiency in the removal of the impurities and showed similar behaviour independent of the kind or amount of adsorbent employed. The use of natural adsorbents for the purification of biodiesel have been shown to be a promissory process to be applied as an industrial stage of the purification of biodiesel during their production.

1. Introduction

The most common way to produce biodiesel is by transesterification. Transesterification is the general term used to describe a class of important organic reactions in which an ester is transformed into another by the exchange of alkoxide groups. Among all of the alternatives, the transesterification can be considered the best choice because this process is relatively simple [1]. Additionally, depending on oil origin (ester) used, it is possible to obtain biodiesel with physicochemical characteristics similar to diesel. The resulting products of this reaction are divided into two phases, the first one composed mainly of esters (biodiesel), fatty acids and certain amounts of glycerides, and the second phase, the denser, constituted mainly by glycerol and residues of transesterified triglycerides. Phase separation is by settling and/or centrifugation [2]. After the removal of glycerine, biodiesel may present traces of alcohol, catalyst, free fatty acids, glycerine, water, etc. However, it is essential to use the purification and drying processes so that biodiesel becomes acceptable in the market; i.e., it is essential that certain specifications are complied with to ensure the quality of biodiesel. In this way, it is necessary to establish quality standards, aiming to set limits for the levels of contaminants that will not harm the quality of emissions from burning, as well as performance, integrity and security of the engine [2–4].

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The reduction of impurities in the biodiesel can be achieved by applying further purification steps, subsequent to decantation. Traditionally, the most widely used method is wet scrubbing (wet washing), which consists of using hot water due to the high solubility of these contaminants in water, coupled with the low cost, simplicity, efficiency and abundance. The disadvantage of the method, besides the formation of the emulsion, preventing the separation of esters and allow the formation of free fatty acids and soap, is the large volume of wastewater generated. In this last case, it can be circumvented by applying dry purification methods which do not use water to wash the biodiesel.

The technique of dry washing is promising for removing the contaminants present in the biodiesel because of its low cost, simplicity of design and operation, and because of the selectivity of some adsorbents [2–5]. Adsorption is a physical–chemical phenomenon of great importance due to the multiple applications in industry. The liquid phase adsorption is one of the most well used and effective methods for the removal of impurities. The process of solid–liquid adsorption exploits the ability which certain solids have in attracting substances present in the liquid phase to their surface. Thus, the components of the liquid phase can be separated.

Several studies in the literature report different adsorbents having been used for biodiesel purification. Faccini used commercial adsorbents such as Magnesol®, Amberlite BD10 DRY®, Purolite PD 206® and silica [6]. Manique carried out the purification process using agroindustrial residue (ash from rice hulls) and compared this with the acidic aqueous washing and Magnesol® [7]. Manuale and co-workers elected a commercial silica, Trysil 3000, as a good adsorbent material for biodiesel purification [8]. Berrios and Skelton shown purification using magnesium silicate [1]. Cavallari evaluated the biodiesel purification processes for dry cleaning, including adsorption methods in different materials and filtration membranes, making a comparative critical analysis of purification processes studied and tested by several authors, using, as a basis, published articles and dissertations [5]. Silva and co-workers tested the removal of free glycerol into biodiesel using smectite clay, diatomaceous earth, amorphous silica and specific commercial resin for biodiesel purification in order to have a pattern for adsorption tests [9]. Leeruang and Pengprecha studied the biodiesel purification with silica from natural bentonite [10]. Atadashi and co-workers conducted a study related to biodiesel refining technologies and also made a critical review of the latest research findings related to biodiesel refining technologies, both conventional purification as the latest technology with membranes [11,12]. Costa carried out the study with three alternative adsorbents: bentonite clay, diatomite A and B; the commercial resin Purolite® PD206 was used as a standard [13]. Paula and co-workers evaluated the effectiveness of treating biodiesel prepared from discarded frying soybean oil, using the techniques of washing with distilled water, distillation and adsorption with bauxite, bentonite and attapulgite [14].

In short, there are many biodiesel purification studies with adsorbents via dry washing, but no work was found concerning the studies employing starch and cellulose as adsorbents. The cellulose and starch are cheap materials, abundant, from renewable sources, biodegradable, non-toxic, biocompatible and have great potential to be employed as natural adsorbents in the purification of biodiesel.

In this way, this study aims to perform the study of the adsorption of biodiesel contaminants after the production process of biodiesel from sunflower oil, using natural adsorbents, such as potato starch, corn starch, rice starch, cassava starch, eucalyptus bleached kraft cellulose, along with an industrial adsorbent, Select® 450, and to compare this with the use of water in the purification of biodiesel, using techniques and analysis methodologies established by the National Agency of Petroleum, Natural Gas and Biofuels (ANP) standards.

2. Materials and methods

2.1. Biodiesel preparation

The biodiesel employed in this study was obtained from commercial sunflower oil (LIZA) by alkaline transesterification via the methyl route. In the method employed for obtaining biodiesel from sunflower, 20% methanol (v/v) and 0.6% NaOH (w/v) were employed as catalysts, with respect to the sunflower oil. Initially, sodium methoxide was obtained by mixing methanol and sodium hydroxide under constant agitation until complete homogenisation. Then, the sodium methoxide was added to the sunflower oil, and the mixture was kept under constant stirring for 30 min, at a temperature of 60 °C. At the end of the reaction, the mixture was transferred to a separatory funnel in order to separate the phases. After resting, we observed two distinct phases: one containing esters, which was less dense and lighter, and the other rich in glycerine, which was denser and darker. After standing for 24 h, glycerine was removed and the resulting biodiesel was employed in the different purification processes studied here [11,12,15].

2.2. Purification processes

2.2.1. Wet washing

The purification process of biodiesel with water was performed in the separatory funnel, with successive washes with acidified water (HCl 1 N – 1: 4, 85 °C) and distilled water (85 °C), until neutralisation. Then, the biodiesel was dried in an oven at 105 °C by 1 h. After this, the resulting sample was stored for later analyses [4,7].

2.2.2. Dry washing

The purification process of biodiesel via dry washing was carried out employing different natural adsorbents (potato starch (YOKI), corn starch (CARGILL), cassava starch (AMAFIL), rice starch (MAIZENA) and eucalyptus bleached Kraft cellulose) and a commercial adsorbent Select 450®. The process was carried out by adding 1%, 2%, 5% and 10% (w/v) of adsorbents with respect to the biodiesel, and the mixture remained under constant stirring for 10 min at 25 °C and 150 rpm. Then, the samples were filtered in a simple funnel with filter paper to remove the adsorbents and the purified biodiesel was stored for later analyses.

Select 450® is a selective adsorbent developed from Oil-Dri® Company. Select 450® is prepared from natural aluminium silicate and magnesium, which is modified through a special process for producing an adsorbent with affinity to soaps, metals and phospholipids.

2.3. Biodiesel characterisation

The samples of biodiesel before and after the dry and wet purification processes were characterised with respect to the acidity index (EN 14104), combined alkalinity (AOCS method Cc 17-19), free glycerine and turbidity. The efficiency of the different processes was assessed by analysis of variance (ANOVA) double factor without repetition, and those considered significant were those which presented $p \leqslant 0.05$ [16,17].

2.3.1. Acidity index

The method used in this work follows the standard EN 14104, using an alcoholic solution of KOH as the titrant and phenolphthalein as indicator. The acidity index, based on standard EN 14104, is given by mass of sodium hydroxide required to neutralise free fatty acids contained in one gram of sample. Acidity is the percentage of free fatty acids in a fat or oil. According to the proposed