Chemical Engineering Journal 256 (2014) 372–379

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Biodiesel purification in one single stage using silica as adsorbent

Debora L. Manuale [a,b], Elisabet Greco [a], Adriana Clementz [b], Gerardo C. Torres [a], Carlos R. Vera [a,b], Juan C. Yori [a,b,*]

[a] Facultad de Ingeniería Química, Universidad Nacional del Litoral, Santiago del Estero 2829, 3000 Santa Fe, Argentina
[b] Instituto de Investigaciones en Catálisis y Petroquímica (INCAPE) (FIQ-UNL, CONICET), Santiago del Estero 2654, 3000 Santa Fe, Argentina

HIGHLIGHTS

- We report a dry biodiesel purification method of one single stage treatment.
- The methodology is a solution for biodiesel refining saving money and process time.
- The treatment is made under conditions of vacuum and temperature.
- The selected adsorbent is silica Trisyl 3000.
- Silica behaves as a non-selective adsorbent of high capacity.

ARTICLE INFO

Article history:
Received 2 June 2014
Received in revised form 5 July 2014
Accepted 7 July 2014
Available online 14 July 2014

Keywords:
Biodiesel
Refining
Adsorption
Silica

ABSTRACT

In this paper a simple biodiesel purification method consisting of one single stage treatment with silica as adsorbent is described. The presented method seems a solution for biodiesel refining saving water, money and process time. The treatment is made under conditions of vacuum (0.2 bar) and mild temperature (65–90 °C). The method allows for the removal of the excess of methanol and water (present in the crude biodiesel and adsorbed on the adsorbent material) simultaneously with the adsorption of the impurities.

Silica Trisyl 3000 retains 23% of its weight when the process is conducted at atmospheric pressure and nearly 235% when performed under vacuum conditions. This greatly improves the utilization of the adsorbent and reduces the cost of the process.

Under these conditions, the silica behaves as a non-selective adsorbent of high capacity that is able to adsorb different types of impurities, which makes it an excellent adsorbent to purify biodiesel. On the other hand, the adsorption phenomenon is not limited to the formation of a theoretical "monolayer" of adsorbed impurities; it is more complex and includes the formation of multiple layers.

1. Introduction

Biodiesel is obtained from the transesterification of vegetable oils or animal fats with a short-chain alcohol, with or without the use of catalyst. After the reaction glycerol (the main by-product) is separated by settling or centrifuging and a crude biodiesel phase is thus obtained. Many contaminants can still be present in the crude biodiesel depending on the technology of transesterification used. Impurities such as residual methanol and traces of glycerol, soaps, catalyst, phospholipids, water and unreacted glycerides can be found, that can produce harmful effects on engine performance if not removed [1,2]. The crude biodiesel requires a subsequent refining process in order to meet the strict international biodiesel standard specifications (ASTM D6751 and EN 14214 Standards) [3,4].

The process of crude biodiesel refining is complex and it is usually achieved via two techniques; wet and dry washings. Conventionally wet washing is the most widely employed technique to remove these impurities.

The wet washing method employs multiple successive washing steps with water in order to remove major impurities such as soaps, catalyst, glycerol and methanol from biodiesel. This technique is based on the affinity of polar compounds with water. There are some disadvantages in the use of this method such as: (i) high cost (representing 60–80% of the total processing cost [5]), (ii) a substantial increase of total production time, since water

* Corresponding author at: INCAPE, Santiago del Estero 2654, 3000 Santa Fe, Argentina. Tel.: +54 342 4533858; fax: +54 342 4531068.
E-mail address: jyori@fiq.unl.edu.ar (J.C. Yori).

http://dx.doi.org/10.1016/j.cej.2014.07.022
1385-8947/

washing requires several cycles of washing and one stage of centrifugation and/or drying, which are time intensive processes, (iii) the difficulty of meeting normed specifications regarding final water content, (iv) product loss, because some of the biodiesel is lost with aqueous effluents, and, (v) the amount of waste water that is generated as process effluent, which must be treated before the final discharge, introducing an additional cost to the process.

In the wet washing process, for every 100 L of biodiesel produced some 20 L of wastewater are produced [5]. The water content of the biofuel after the washing step (mentioned in point iii), is around 0.15% [6,7]; this value is above the maximum set by the standards (0.05%) and it's therefore necessary to introduce a later stage of centrifugation and/or drying under vacuum conditions. The wastewater due to its physicochemical characteristics, should be treated before the final discharge in order to reduce the environmental impact. The washing water is characterized by high values of pH, COD (chemical oxygen demand), BOD (biological oxygen demand), fats and oils, needing a complicated and expensive biological treatment and thus increasing operating costs [5,8].

Problems associated with wet washing have led to the development of the dry washing process to purify crude biodiesel. This process involves the use of adsorbents such as carbon, silica, bleaching clay, and activated bleaching clay, zeolite, ion exchange resins (amberlite or purolite), cellulosics or sawdust, diatomaceous earth and magnesium silicate powder (magnesol) [9]. The process requires a mixing unit and the spent adsorbent must be generally discarded [10]. Cooke et al. [11] reported that water washing may be substituted in industrial plants by dry washing with Magnesol® (provided by Dallas Group of America, Inc.). However up to now the use of the dry washing technique has not spread much at industrial level, mainly due to the following disadvantages: (i) the cost of adsorbents, (ii) the difficulty of some adsorbents for adsorbing certain types of impurities such as glycerides and free fatty acids (FFA), and (iii) the difficulty of an adequate regeneration and reuse. For this reason the solid residue has to be disposed of in landfills or other applications (composting, use as a potential animal food additive) [2]. Therefore it is essential to find a cheap adsorbent, with high adsorption capacity and capable of adsorbing all biodiesel impurities.

Removal of glycerides from biodiesel is an important step of the process because key aspects of the quality of the fuel strongly depend on the content of bound glycerol. Main problem with these compounds is that when heated they tend to polymerize forming deposits. They also increase the cloud point of biodiesel and they complicate the operation of liquid–liquid phase splitting units due to their amphiphilic nature.

With respect to the ability to adsorb glycerides there are conflicting results in the literature. Berrios and Skelton [2] reported that magnesol and ion exchange resins do not retain glycerides (mono (MG), di (DG) and triglycerides (TG)) in a significant way; consequently, the refining process cannot comply with the limits set up in the EN 14214 standard. On the contrary, Faccini et al. [12] reported that Magnesol® and silica showed suitable results regarding free and bound glycerol removal.

It is known that silicas efficiently remove the main impurities of biodiesel, such as: methanol, residual metals, phospholipids and soaps [13]. It has been previously reported [14] that glycerol has a great affinity for the silica surface and is selectively adsorbed from biodiesel solutions. It was found that adsorption of glycerol is not influenced by the presence of small amounts of water and soaps. Conversely the presence of monoglycerides (MG) and/or methanol (MeOH) lowers the adsorption capacity of glycerol due to the competition for the adsorption sites on silica. Then, a necessary first step of methanol removal previous to the silica treatment is required.

The aim of this work was to develop a simple dry method for biodiesel refining, using silica as adsorbent material, involving the fewest possible steps in order to produce biodiesel that meets strict international quality standards. Refining operating conditions were sought to ensure: (i) adsorption of the main impurities of biodiesel, particularly glycerides, (ii) reduction of the refining costs, and (iii) optimization of the silica adsorption capacity.

2. Experimental section

2.1. Materials

The raw material employed to produce biodiesel was a degummed soy oil provided by a local producer. Methanol (99.9%) and pure glycerol (>99.5%) were supplied by Sintorgan SA. Sodium estearate (99%) was chosen as a model soap and was supplied by Serisa Química SRL. Glyceryl monoestearate (98%) was used as a model monoglyceride and was supplied by Cloretil SACIF. Silica samples were TriSyl 3000, 300B and 450 (provided by W.R. Grace Argentina SA).

2.2. Biodiesel preparation

Reference Methyl soyate was prepared according to the standard procedure (catalytic low-temperature method using NaOH as catalyst) described by Noureddini and Zhu [15].

Many batches of the solution of the biodiesel product and unreacted methanol were synthesized and mixed together in order to provide a common biodiesel stock. This biodiesel stock sample was spiked with contaminants such as monoglycerides and soaps, up to the values indicated in Table 1. Then it was kept in a dessicator for later use.

2.3. Bleaching experiments

The spiked biodiesel base sample was refined by performing bleaching tests at varying conditions and with different silica adsorbents. Bleaching was performed at different temperatures and contact times in a gas-tight stirred autoclave (stirring speed: 250 rpm). 100 cm^3 of spiked biodiesel were put in contact with the silica (adsorbent weight: 1.0 and 3.0 g) at the selected temperature (50, 65, 80 and 90 °C) for a conveniently chosen contact time (15–100 min) The influence of vacuum and temperature was assessed by performing the bleaching procedure at normal pressure and in vacuum (0.2 bar) and by varying the bleaching reactor temperature. After the treatment the adsorbents were decanted, filtered and the liquid phase was sampled for analysis. All experiments were performed in triplicates.

Table 1
Main properties of the spiked biodiesel.

Properties	Spiked crude biodiesel (%)	Normal limits[a] (%)
Free glycerol, %	0.20	0.02
Bound glicerol, %	0.84	0.24
Monoglycerides, %	2.41	0.80
Diglycerides, %	0.08	0.20
Triglycerides, %	0.04	0.20
Acidity, %	0.27	0.50
Soaps, %	0.25	0.02
Water, %	0.10	0.05
Methanol, %	5.00	0.20

[a] As specified by the ASTM D 6751 and EN 14214 quality standards.