Fuel 113 (2013) 323–330

Contents lists available at SciVerse ScienceDirect

Fuel

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

Optimization of biodiesel production process using sunflower oil and tetramethyl ammonium hydroxide as catalyst

B.S. Sánchez, G. Mendow, P.G. Levrand, C.A. Querini *

Research Institute on Catalysis and Petrochemistry – INCAPE (FIQ UNL-CONICET), Santiago del Estero 2654, 3000 Santa Fe, Argentina

HIGHLIGHTS

- Tetramethyl ammonium hydroxide (TMAH) is a good catalyst for the transesterification reaction.
- It is possible to obtain biodiesel with the quality specified in the EN 14214.
- The soap formation is similar to that observed with other hydroxides.
- The soap formation is considerably higher than that observed with sodium methoxide.
- TMAH favors the concentration of mono and diglycerides in the glycerin.

ARTICLE INFO

Article history:
Received 12 March 2013
Received in revised form 23 May 2013
Accepted 29 May 2013
Available online 11 June 2013

Keywords:
Transesterification
Tetramethyl ammonium hydroxide
Biodiesel

ABSTRACT

In this work, the biodiesel production process by transesterification of sunflower oil was investigated using tetramethyl ammonium hydroxide (TMAH) as catalyst. The reaction conditions, such as catalyst concentration, temperature and reaction time were optimized in order to obtain a product that fulfills the quality requirements of international standards. It was found that the optimum reaction conditions were: temperature 60 °C, 1.76 wt% TMAH catalyst and 2 h reaction time. High amount of soaps were formed when using this catalyst. Therefore, an alternative purification methodology was used, especially useful for samples with high soaps content. This procedure consists of a first extraction stage using neutral water, which efficiently remove soaps. TMAH increases the solubility of mono and di-glycerides in the glycerine phase, thus decreasing their concentration in the biodiesel phase. Consequently, for a given production of mono- and di-glycerides, lower amount of these compounds were found in the final biodiesel product, being this an important advantage of this catalyst.

1. Introduction

In recent years, increased attention has been given to biofuels, such as biodiesel, that can be used as an alternative fuel in compression–ignition engines. This fuel has many advantages with respect to petroleum-based fuel, namely, it is biodegradable, non-toxic, renewable, and it contributes to the reduction of CO_2 emissions, because it comprises a closed carbon cycle, and produces lower soot emissions in the tail-pipe exhaust gases [1,2].

Biodiesel is defined as fatty acid alkyl esters, which are typically produced by the transesterification of vegetable oils or animal fats with methanol or ethanol in the presence of a suitable catalyst. During the reaction, the triglyceride is sequentially converted into a diglyceride, monoglyceride and glycerine; 1 mol of ester being produced in each step.

Four groups of feedstock can be defined for biodiesel production [3]: edible and non-edible vegetable oils, animal fats, waste cooking oils and algal oils, which have been emerging in recent years as a feedstock of increasing interest because of their high oil content and rapid biomass production [4,5]. The vegetable edible oils such as soybean, rapeseed, sunflower or palm oil, are the main and more conventional feedstock for biodiesel production. However, their large demand as food and high prices has encouraged the use of non-edible oils as alternative feedstock. More than 26 plants species containing non-edible oil in their seeds were reported by Azam et al. [6] as potential sources for biodiesel synthesis. In addition to vegetable oils, animal fats can also be used for biodiesel production, having the advantage of a lower price. However, there exists the limitation of their availability, and consequently they will never be enough to replace vegetable oils. Another disadvantage is the higher melting point, and could complicate their processing and use [7]. Used cooking oils are priceless or at least cheaper than fresh vegetable oils, making them an interesting alternative as triglycerides source for biodiesel synthesis [8].

* Corresponding author. Tel.: +54 342 4533858; fax: +54 342 4531068.
E-mail address: querini@fiq.unl.edu.ar (C.A. Querini).

0016-2361/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.fuel.2013.05.085

However, these waste oils are usually contaminated by many types of impurities from the cooking process (polymers, free fatty acids) and their conversion to biodiesel could be complicated [9]. In recent years, biodiesel production from microalgae has received growing attention. Microalgae would offer various advantages such as: much higher biomass productivities than land plants, some species can accumulate up to 20–50% triglycerides; no agricultural land is required to grow the biomass and they required only sunlight and a few nutrients [10].

The transesterification reaction can be catalyzed both by homogeneous and heterogeneous catalysts. In general, the heterogeneous catalyzed biodiesel production processes have less number of unit operations; with simple product separation and purification steps [11]. The heterogeneous transesterification catalysts can be categorized into three main groups: acid, basic or bifunctional (acid-basic character) solids. In general, solid base catalysts are more active than solid acid catalysts, requiring relatively shorter reaction times and lower reaction temperatures [12]. However, solid acid catalysts have several advantages over solid base catalysts such as for example, that the reaction is less affected by the presence of water and free fatty acids [13]. New trends are oriented toward the search of new solid catalysts that can simultaneously carry out esterification and transesterification reaction steps, i.e., solid catalysts with combined acid and basic properties. Nevertheless, in general, heterogeneous catalysts for biodiesel synthesis are not able to achieve the conversion levels required, or need strong reaction conditions or extremely long reaction times, excluding them for their industrial application.

Currently, due to their simple usage and less time required for oil conversion, homogeneous catalysts dominate the biodiesel industry. These include alkalis and acids, being the basic catalysts the most commonly used, since the process is faster at mild reaction conditions [14]. However, their utilization in vegetable oil transesterification produces soaps due to the neutralization of the free fatty acids initially present in the oil and by triglyceride saponification that occurs when water is present in the reaction system [15]. In addition, the presence of water in the system generates further problems in the transesterification, because at high temperatures it can hydrolyze the triglycerides, producing fatty acids. Both, water and fatty acids produce a negative synergetic effect, because they partially consume the catalyst, decrease the biodiesel yield and generate soaps, complicating the separation and purification steps. Therefore, base catalyzed transesterification needs a high purity feedstock.

The most commonly used alkali catalysts are sodium and potassium hydroxides and methoxides. Many authors [15–17] have reported comparative studies between these four catalysts. However, such studies were performed using the same mass percentage of catalysts that have very different molar weights. Therefore, the results cannot be compared from a kinetic point of view. Pisarello [18] used the four alkali catalysts in the same molar concentration. The results showed that the sodium catalysts are more active than the potassium ones, and in turn, the methoxides are more active than the hydroxides [18]. From a large scale industrial production point of view, biodiesel manufacturing by homogeneously catalyzed transesterification reaction shows the disadvantages of high production costs, as the process involves washing and purification steps, and it is quite difficult to remove K and/or Na traces remaining in the biodiesel product [19]. Despite these drawbacks, currently, in large scale facilities, the sodium methoxide is exclusively used as catalyst, given its high activity at moderate reaction conditions.

The tetramethyl ammonium hydroxide (TMAH) is a strong base that constitutes an interesting alternative to the conventional alkaline homogeneous catalysts for biodiesel production. This would be specially useful in the eventual situation of a price raise or shortage of the sodium methoxide, which, as it was previously mentioned, is the main catalyst used in the biodiesel industry. Moreover, the methyl esters obtained in these conditions would be free from Na or K, which makes them especially interesting for their potential use in turbines as fuel for electric energy generation [20]. In this application, the limit established for sodium plus potassium is 0.5 ppm, i.e. one order of magnitude lower than in the case of using the biodiesel in diesel engines. Conventional processes based on sodium methoxide do not meet this specification; therefore, the use of a catalyst such as the TMAH is an interesting alternative. In addition, the glycerine would be also free from salts, if the catalyst could be eliminated by heating. The tetramethyl ammonium hydroxide has been used as catalyst for the transesterification of cottonseed oil and used frying oil as raw materials [21]. In this work [21], the effects of methanol:oil ratio and catalyst concentration on the transesterification reaction were addressed. The effect of the reaction temperature, and the study of the other process stages, such as phases separation and biodiesel purification were not addressed. It was found that high quality methyl esters could be obtained, especially when the semi-refined cottonseed oil was used as feedstock. Lower ester yields were achieved with waste oil, which were attributed to amide formation during the transesterification reaction. Almost all glycerides were converted into esters and remained below the EN 14214 limits with a catalyst amount of 2.5 wt% or higher for cottonseed oil, and a catalyst concentration higher than 3% for used oil. Non-ionic bases have been used for vegetable oil transesterification. The catalytic behavior of guanidines, amidines and triamino(imimo)phosphoranes has been reviewed by Schuchardt et al. [22]. The guanidines showed good activity with low soap formation, although the ester yield was 93% for a catalyst concentration of 3 mol%. Other guanidines displayed lower conversions. Different amines, including the TMAH were studied by Cerce et al. [23], and found that this catalyst displayed a better catalytic performance than the other amines (e.g. diethylamine, dimethylethanolamine, tetramethyldiaminoethane). However, Cerce et al. [23] showed only one experiment carried out with TMAH, using a 8.7:1 methanol:oil ratio, at 60 °C. Recently, a patent [24] reported in the use of TMAH but using co-solvents, such as tetrahydrofuran and acetone, being this an option that complicates the process design and the production costs. Tang et al. [25] also studied these amines, but in supercritical methanol and a continuous tubular-flow reactor, finding problems due to the poor mixing achieved in this configuration. Karavalakis et al. [26] studied the tetramethylguanidine as catalyst for transesterification of waste frying oil and semi-refined cottonseed oil, obtaining good results mainly with the latter.

TMAH was used to transesterify triglycerides with analytical purposes, but using reaction conditions different from those used in a commercial process [27,28]. In addition, it was considered as catalyst in order to analyze the economics of the biodiesel production process, but without including information regarding its catalytic behavior [29].

The objective of this work was to optimize the biodiesel production process using sunflower oil and tetramethyl ammonium hydroxide (TMAH) as catalyst, specially aiming to its application in the large scale industry. Therefore, the whole production process was analyzed, from the reaction stage to the quality of the final biodiesel obtained, in order to assess the possibility of using this catalyst at industrial level. The possibility of obtaining the glycerine free from salts was also explored.

2. Experimental

2.1. Materials

In order to avoid or minimize soaps formation, refined sunflower oil was used, with acidity lower than 0.02 wt% (g oleic