Chemical Engineering Journal 238 (2014) 234–241

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

# Biodiesel production from biobutanol. Improvement of cold flow properties

Abderrahim Bouaid, Noureddine El boulifi, Kalid Hahati, Mercedes Martinez, Jose Aracil *

*Chemical Engineering Department, Faculty of Chemistry, University of Complutense, 28040 Madrid, Spain*

## HIGHLIGHTS

- Biodiesel production from a cheap raw material was optimized by factorial design.
- Catalyst concentration was the most significant factor on ester yield.
- The biodiesel produced using biobutanol improved cold flow properties.
- The biodiesel samples showed a good oxidative stability over time.
- The resulting butyl esters match the European Biodiesel Standard EN 14214.

## ARTICLE INFO

*Article history:*
Available online 17 October 2013

*Keywords:*
Biodiesel
Cold flow properties
Oxidation stability
Fatty acid butyl esters
Optimization

## ABSTRACT

Experimental design methods have been successfully applied to develop and optimize the process of synthesis of butyl esters from rapeseed oil (RSO), the most common oil feedstock for biodiesel production in Europe and used frying oil (UFO), as a cheaper raw material, using biobutanol, and potassium methoxide ($KOCH_3$) as catalyst. The optimum conditions were found to be a catalyst concentration of 1.1% and 0.9%, an operation temperature of 78 °C and 80 °C for rapeseed oil butyl esters (RSOBE) and used frying oil butyl esters (UFOBE), respectively, obtaining ester yields of 96.86% and 96.54% with 6:1 biobutanol/oil molar ratio. Results show that biodiesel produced using biobutanol as alcohol in the transesterification process improved cold flow properties in terms of cloud point (CP), pour point (PP) and cold filter plugging point (CFPP) without significantly affecting the other fuel properties.

In order to determine the effects of long storage on oxidation stability, the biodiesel samples were stored for a period of 12 months, the analysis of fuel properties: peroxide value (PV), acid value (AV), iodine value (IV) and viscosity (ν) have been applied in oxidation studies. According to the results obtained, the RSOBE and UFOBE samples showed a good oxidative stability during the storage period. The resulting butyl esters can be used as a diesel fuel substitute, since it matches the European Biodiesel Standard EN 14214.



## 1. Introduction

Meeting sustainable energy demand with minimum environmental impact is a major area of concern in the energy sector. Nowadays, biodiesel (fatty acid alkyl esters) is considered as an important alternative biofuel to satisfy these energy needs, due to its environmental benefits and simple production from renewable resources.

The biodiesel production feedstocks vary considerably with location according to climate and availability. In United States, soybean oil is the most common biodiesel feedstock, whereas in Europe and in tropical countries, rapeseed oil and palm oil are the most common source for biodiesel respectively [1]. However, there are no technical restrictions to the use of other types of vegetable oils.

Currently, the cost of this fuel is a primary factor that limits its use. One way to reduce the cost of biodiesel is to use a less expensive form of vegetable oil such as used frying oil. In this context, waste frying oil is a promising alternative for producing biodiesel because it is a cheaper raw material that also avoids the cost of waste product disposal and treatment. Besides, it reduces the need to use land for biodiesel-producing crops [2]. Spain is a major consumer of vegetable oils, mainly olive and sunflower oil. These oils are not reused many times and, therefore, the free fatty acid contents are usually lower than 3% [3].

Many researchers [4–6] have found that acid value of the feedstock for alkaline transesterification has to be less than 2 mg KOH/g (i.e.1%). They also reported that when waste cooking oil is used as feedstock, acid value of up to 4.0 mg KOH/g were found.

* Corresponding author.
*E-mail address:* jam1@quim.ucm.es (J. Aracil).

1385-8947/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cej.2013.10.022

In the biodiesel production process the alcohol employed is generally methanol because it is the least expensive alcohol. However, this alcohol presents several drawbacks, such as high toxicity, being synthesized from non renewable sources, can be absorbed through the skin and is 100% miscible with water, so any kind of spill presents a serious problem. Ecological aspects are gaining a lot of recognition in our society.

Biobutanol is derived from agricultural products; it is renewable and is biologically less objectionable in the environment [7]. Compared to methanol, biobutanol is safer to handle because toxic effects to humans from exposure to fumes are reduced. Producing butyl esters rather than methyl esters is of considerable interest since it allows the production of an entirely agricultural fuel and the extra carbons brought by the biobutanol molecule slightly increases the heat content and the cetane number [8]. On the other hand, the butanolysis reaction has rarely been studied, especially in comparison to the intensive studies undertaken by numerous researchers on the methanolysis and ethanolysis reactions [9–11].

Hence, there is a constant demand to search cost-effective raw materials for economic biobutanol production. In such scenario, cheaper and readily available lignocellulosic materials such as agriculture waste (corn stover, wheat straw, corn fiber, barley straw, Carob pod, and switch grass), and wood residues, can be used for economical production of biobutanol.

In order to ensure customer's acceptance, standardization and quality assurance are key factors for the market introduction of biodiesel as fuel for transport and heating. One of the major problems associated with the use of biodiesel as supply for diesel engines is poor low-temperature flow properties. Pure biodiesel can solidify in fuel lines or clog filters when utilized in cold ambient conditions [12,13]. Other important criterion for the quality of a biofuel is its storage stability. Resistance to oxidative degradation during storage is an increasingly important issue for the successful development and viability of alternative fuels [14].

The objective of the present work is to evaluate the different variables affecting the alkaline butanolysis of rapeseed and used frying oils using biobutanol as alcohol. The optimum values for the variables affecting the process were determined by application of factorial design and response surface methodology. To date, the butanolysis reaction has not been optimized by response surface methodology (RSM).

Biobutanol was used as alcohol in order to meet the challenging requirement of low temperature properties. In addition, the storage stability of the two biodiesel samples was investigated over a storage time of 12 months. The goal was to provide a better understanding of the influence of long storage on biodiesel quality.

## 2. Experimental section

### 2.1. Equipment

Experiments were carried out in a stirred batch reactor of 500 $cm^3$ volume. This reactor was provided with temperature and speed control, and immersed in a thermostatic bath capable of maintaining the reaction temperature to within ±0.1 °C by means of an electrical device connected to a PID controller. The impeller speed between 500 and 1200 rpm were tested; a stirring speed of 600 rpm was found appropriate [15].

### 2.2. Materials

Rapeseed oil was supplied by Gracomsa Alimentaria (Valencia, Spain). Used frying oil (basically derived from sunflower and olive oils) was kindly provided from Faculty of Science and Technology Tangier (FSTT, Morocco). The fatty acids composition and physicochemical properties of the oils are summarized in Table 1. Biobutanol, of 99.8% purity was supplied by Cathay industrial Biotech (China).The catalyst used was potassium methoxide (32% purity) purchased from BASF (Spain).

### 2.3. Procedure

Experiments were performed according to the following procedure: 300 $cm^3$ of the vegetable oils (RSO or UFO) was added to the reactor and fitted with a reflux condenser. When the set temperature was reached, the $KOCH_3$ catalyst diluted in biobutanol was introduced in the reactor. Samples were taken at regular intervals and analyzed by gas chromatography. The total reaction time was 60 min. In order to separate the two layers butyl esters and glycerol, the excess of biobutanol in the reaction mixture was removed by simple evaporation under vacuum pump (70 mm Hg) and recovered to be reused. This step resulted in the separation of the two phases; the upper phase consisted of butyl esters, and the lower phase, glycerol, the butyl one was purified by gentle washing with distilled water to remove residual catalyst, glycerol and soaps. Initially, the pH of washing water was relatively high 10.3 due to the dissolved catalyst. After 3 successive rinses with water, the washing water became clear and its pH was 7.6. The washing process was continued until a pH of about 7 was achieved. Finally, the butyl ester phase was distilled to remove the residual water. The final water content of the RSOBE and UFOBE samples were less than 0.03%. Water in the sample can promote microbial growth, lead to tank corrosion, participate in the formation of emulsions, as well as cause hydrolysis or hydrolytic oxidation [16]. The methyl and ethyl ester samples used for cold flow properties and rancimat test comparison were produced by the transesterification reaction of RSO and UFO optimized in previous work [10,11].

### 2.4. Analytical method

Reaction products were monitored by capillary column gas chromatography, using a Hewlett–Packard 5890 series II equipped with a flame ionization detector (FID). The injection system was split-splitless. The carrier gas was helium at a flow rate of 1 mL/min. The separation program consisted of an initial oven temperature of 110 °C was increased at 4 °C/min to 160 °C for 1 min followed by a ramp of 30 °C/min to 320 °C and maintained for 20 min to complete the program. The other analysis operating conditions have been described in detail by Garcia et al. [17], in a previous work. The internal standard technique has been used in

**Table 1**
Characteristics of rapeseed oil and used frying oil used in this study and fatty acids composition.

| Characteristics | Rapeseed oil | Used frying oil |
|---|---|---|
| Acid number (mg kOH/g) | 0.10 | 0.14 |
| Iodine number ($I_2$/100 g) | 104 | 115 |
| Peroxide number (meq Per/kg) | 0.87 | 6.9 |
| Viscosity (40 °C) ($mm^2$/s) | 41.62 | 55.81 |
| Water content (%) | 225 | 235 |
| *Fatty acid compositions (%)* | | |
| Capric (C10:0) | 0.6 | – |
| Myristic (C14:0) | 0.1 | – |
| Palmitic (C16:0) | 5.1 | 2.95 |
| Stearic (C18:0) | 2.1 | 8.89 |
| Oleic (C18:1) | 57.9 | 19.09 |
| Linoleic (C18:2) | 24.7 | 63.15 |
| Linolenic (C18:3) | 7.9 | 3.57 |
| Eicosanoic (C20:0) | 0.2 | – |
| Henicosanoic (C20:1) | 1.0 | – |
| Other minor components | Rest to 100 | Rest to 100 |