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Fuel properties of biodiesel from vegetable oils and oil mixtures. Influence of methyl esters distribution

G. Martínez [a], N. Sánchez [a], J.M. Encinar [a,*], J.F. González [b]

[a] Dpto. Ingeniería Química y Química Física, UEX, Avda. Elvas s/n, 06071 Badajoz, Spain
[b] Dpto. Física Aplicada, UEX, Avda Elvas s/n, 06071 Badajoz, Spain

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ABSTRACT

In this work, the quality of biodiesel produced by basic transesterification from several vegetable oils (soybean, rapeseed, sunflower, high oleic sunflower, *Cynara Cardunculus L.*, *Brassica Carinata* and *Jatropha Curca*) cultivated in Extremadura has been studied in detail. The influence of raw material composition on properties such as density, viscosity, cetane number, higher heating value, iodine and saponification values and cold filter plugging point has been verified. Other biodiesel properties such as acid value, water content and flash and combustion points were more dependent on characteristics of production process. Biodiesel produced by rapeseed, sunflower and high oleic sunflower oils transesterification have been biofuels with better properties according to Norm EN 14214. Finally, it has been tested that it is possible to use oils mixtures in biodiesel production in order to improve the biodiesel quality. In addition, with the same process conditions and knowing properties of biodiesel from pure oils; for biodiesel from oils mixtures, its methyl esters content, and therefore properties dependent this content can be predicted from a simple mathematical equation proposed in this work.

1. Introduction

Biodiesel, a biofuel comprised in general of long-chain fatty acid methyl esters (FAMEs) derived from vegetable oils or animal fats, is an alternative to fossil fuels and it can also be used as a fuel additive. The advantages of biodiesel fuels over diesel fuel are well known (less smoke and particulates production, higher cetane number, domestic origin, lower carbon monoxide and hydrocarbon emissions. They also are biodegradable and non-toxic, and provide engine lubricity to low sulfur diesel [1–3]).

The most common route to biodiesel production is the transesterification reaction, shown in equation (1). This process involves several critical parameters which strongly influence the final yield, such as reaction temperature, alcohol/oil molar ratio, type of catalyst, type/chemical structure of alcohol, amount/concentration of catalyst, reaction time and other technical aspects (heating system, super-critical and sub-critical conditions, bath or continuous flow processes, etc.) [4–6].

* *Corresponding author*. Tel.: +34 924 289672; fax: +34 924 289385.
E-mail address: jencinar@unex.es (J.M. Encinar).
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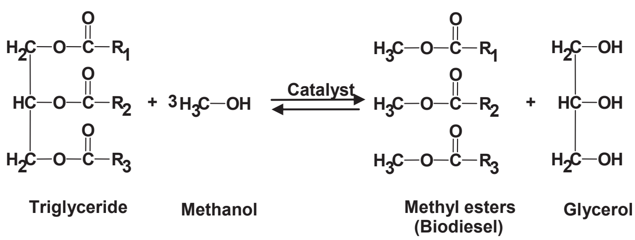

(1)

In addition to these factors, the selection of raw material is essential for the production of biofuel and this depends on local availability and corresponding affordability. Do not forget that the high production cost of biodiesel is largely attributed to the cost of feedstock. Traditionally, the use of edible vegetable oils and animal fats is the most widespread for biodiesel production. However, this use is controversial because edible vegetable oils compete with food materials – the food versus fuel dispute [7,8]. Therefore, recent focus about the use of non-edible plant oil source as the raw material for biodiesel production is on the rise: *Cynara Cardunculus L.* oil [9–11], *Jatropha Curcas L.* oil [12], *Brassica Carinata* oil [13,14], or *Pongamia Pinnata* oil [15]. Besides as European standard specification EN 14214 in 2004 defined the biodiesel as FAMEs from any kind of raw materials, including recycled frying oils, under fulfilling the given quality specifications; biodiesel production from used frying oils has also been studied in detail [3,16,17].

On the other hand, biodiesel quality depends on their fatty acid ester composition and therefore on fatty acid of raw materials (oils or fats). The main structural features that influence the physical fuel properties are chain length, degree of unsaturation and branching of the chain. Among the fuel specifications which depend on chemical composition are cetane number (CN), kinematic viscosity, density, oxidative stability, cold-flow properties in the form of cloud point (CP), pour point (PP), and cold filter plugging point (CFPP), iodine and saponification values (IV and SV), exhaust emissions, lubricity, and heat of combustion [7,18,19].

Therefore, the biodiesel production with full compliance with EN 14214 (or ASTM 6751-07) is a very challenging task. The search for new and low cost raw materials includes mixtures of different sources [20], as well as the development of simulation tools capable of predicting the properties of the final products [21].

According to these considerations, the main objective of this study is to determine the properties of different biofuels from vegetable oils (edible and not-edible) produced in the region of Extremadura (Spain) to check the influence of physical characteristics of these oils on the quality of biodiesel. The determined properties of biodiesel will be studied in detail. Also, different mixtures of oils with the best properties will be employed to improve the quality of biodiesel, as far as possible.

2. Materials and methods

2.1. Materials

Soybean (S), rapeseed (R), sunflower (SU), high oleic sunflower (HO), *Cynara Cardunculus L.* (CC), *Brassica Carinata* (BC), and *Jatropha Curca L.* (JC) oils were provided by Investigation Centre "*La Orden*" (Badajoz, Spain), Section of Non-Food Crops. Methanol (99.6 v/v%), potassium hydroxide (85 wt.%), sodium hydroxide (99 wt.%) and potassium methoxide (90 wt.%) were purchased from Sigma–Aldrich, Merck, Panreac and Alfa Aesar, respectively. Methyl esters of miristic, palmitic, palmitoleic, stearic, oleic, linoleic, linolenic, and erucic acids (employed as standards in the chromatographic determination) were purchased from Fluka and Sigma; and methyl heptadecanoate (used as internal standard) was purchased from Fluka. All reagents used in biodiesel characterization were of analytical grade. Moreover, mixtures of oils at different proportions by weight were also prepared for biodiesel production: rapeseed and soybean oils (50R50S; 75R25S; 25R75S), rapeseed and high oleic sunflower oils (50R50HO; 75R25HO; 25R75HO), and rapeseed, soybean and high oleic sunflower oils (33R33S33HO).

2.2. Experimental procedure

Transesterification reaction was carried out in a 500 mL spherical glass reactor, provided with a thermostat, magnetic stirring, condensation system, and sampling outlet. This installation was similar to that employed in previous works [9,22,23]. Before reactions, the material was washed and completely dried.

First, 250 g of vegetable oil or mixture were heated in the reactor at the reaction temperature, and when it was reached, methanol and dissolved catalyst were added and stirring started (zero time). At spaced intervals, samples of 2 mL were taken out from the reaction mixture and its methyl esters content was determined. Samples and reaction final mixture were placed in decantation funnels and allowed to stand overnight to ensure the complete phase separation (methyl esters and glycerol). The glycerol phase (bottom phase) was removed and the biodiesel phase (upper phase) was washed with deionizer water to reach neutral pH, to remove non-reacted methanol, homogeneous catalyst and possible glycerol remainders.

2.3. Analytical procedure

Biodiesel quality was evaluated according to biodiesel European Standard EN 14214. This organization specifies the criteria that should be satisfied by a biodiesel of high quality, or diesel and biodiesel mixtures, for its use in motor vehicles [24]. Similar methods were used to characterize the vegetable oils.

The content and the composition of FAMEs were analyzed by gas chromatography (GC) in a VARIAN 3900 chromatograph, provided with a flame ionization detector (FID), using a silica capillary column Agilent Technologies 1909-BD-113 of 30 m length, 0.32 mm inner diameter, and 0.25 μm film thickness. Helium was used as carrier gas at a flow rate of 0.7 mL min^{-1}. Injector temperature was kept at 270 °C, and FID temperature at 300 °C. The oven was maintained initially at 200 °C, during 21 min, and then it was elevated to 220 °C, at 20 °C min^{-1} and remained for 10 min up to 220 °C. The fatty acid profile in vegetable oils was determined by GC: oils were transesterified according to ISO 5509:2000, the FAMEs were