Energy 107 (2016) 165–171

Contents lists available at ScienceDirect

Energy

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

High-yield production of biodiesel by non-catalytic supercritical methanol transesterification of crude castor oil (*Ricinus communis*)

Celián Román-Figueroa [a], Pilar Olivares-Carrillo [b, *], Manuel Paneque [c], Francisco Javier Palacios-Nereo [b], Joaquín Quesada-Medina [b, **]

[a] Agroenergía Ingeniería Genética S.A., Almirante Lynch 1179, San Miguel, 8920033 Santiago, Chile
[b] Department of Chemical Engineering, Faculty of Chemistry, University of Murcia, Campus of Espinardo, 30071 Murcia, Spain
[c] Laboratory of Bioenergy and Environmental Biotechnology, Department of Environmental Sciences and Natural Resources, Faculty of Agricultural Sciences, University of Chile, Santa Rosa 11, 315, La Pintana, 8820808 Santiago, Chile

ARTICLE INFO

Article history:
Received 25 March 2015
Received in revised form
3 March 2016
Accepted 29 March 2016
Available online 26 April 2016

Keywords:
Biodiesel
Castor oil
Supercritical transesterification
Thermal decomposition

ABSTRACT

The synthesis of biodiesel from crude castor oil in a catalyst-free process using supercritical methanol in a batch reactor was investigated, studying the evolution of intermediate products as well as the conversion of triglycerides and the yield of FAMEs (fatty acid methyl esters) (biodiesel). Experiments were carried out in a temperature range of 250–350 °C (10–43 MPa) at reaction times of 15–90 min for a methanol-to-oil molar ratio of 43:1. Maintaining thermal stability of biodiesel is one of the most important concerns in high-yield supercritical biodiesel production. Hence, thermal decomposition degree of FAMEs was also investigated in different reaction conditions. The maximum yield of FAMEs (96.5%) was obtained at 300 °C (21 MPa) and 90 min. Under these conditions, the conversion of triglycerides was complete, the yield of intermediate products was low (3.29 and 1.41% for monoglycerides and diglycerides, respectively), and thermal decomposition of FAMEs did not occur. The maximum degree of thermal decomposition (80.9%) was produced at 350 °C (43 MPa) and 90 min. Methyl ricinoleate, whose fatty acid chain was the most abundant (88.09 mol%) in castor oil, was very unstable above 300 °C and 60 min, leading to low yields of FAMEs under these conditions.

1. Introduction

Biodiesel and other renewable fuels have garnered great interest in recent decades as a solution to various problems related to the use of fossil fuels (e.g. shortages of oil reserves, environmental consequences due to emissions of carbon dioxide and other greenhouse gases and energy dependence that some countries present on imports of these fuels [1,2]). Biodiesel and bioethanol fuels have clear advantages over fossil fuels because they are biodegradable and non-toxic and made from organic sources [3]. Bioethanol is obtained from simple sugars, starch and cellulose compounds [4], while animal fats and vegetable oils are the main raw materials used in the production of biodiesel, which are primarily composed of triglycerides [5].

Nowadays, 95% of the world biodiesel is produced from edible vegetable oils [6,7]. The main raw materials used for the production of biodiesel are palm, soybean, rapeseed and sunflower oils [4], species belonging to the first generation of biofuels. These feedstocks have major drawbacks due to negative externalities arising from its use [8]. Current levels of production of vegetable oils and animal fats for energy purposes would not be enough to replace all the liquid fossil fuels consumed today. Thus, biodiesel made from these raw materials could replace up to 25% of total diesel demand [9].

The traditional method for the production of biodiesel is the transesterification of triglycerides, a process where the oil reacts with a short-chain alcohol (such as ethanol or methanol), and glycerin and alkyl esters are obtained. This conventional method needs to use a homogeneous catalyst [3,5]: alkalis, such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) or sodium and potassium alkoxides; acids, for example sulfuric acid and hydrochloric acid; and enzymes such as lipases [3,7]. The price of NaOH and KOH are lower and the reaction is faster than when acids and enzyme catalysts are used, because of this, alkaline

* Corresponding author. Tel.: +34 868 88 4542.
** Corresponding author. Tel.: +34 868 88 7228.
E-mail addresses: pilar.olivares@um.es (P. Olivares-Carrillo), quesamed@um.es (J. Quesada-Medina).

http://dx.doi.org/10.1016/j.energy.2016.03.136
0360-5442/

transesterification is the most widely used industrially [7]. The main disadvantages of the traditional production process using homogeneous alkaline catalysts are directly related to the use of these catalysts: the need of using refined [FFA (free fatty acids) and water contents lower than 0.5 and 0.06%, respectively] vegetable oils or fats [3,10,11], and the neutralization and removal of the catalyst after the process.

Supercritical transesterification has been proposed as a solution to avoid the problems arising from the alkaline transesterification and the characteristics of the raw materials used for the reaction. In supercritical transesterification the water and FFA content of the oil or fat do not have a significant effect on the reaction; thus, transesterification of triglycerides and methyl esterification of FFA occur simultaneously [12,13]. Furthermore, the use of a catalyst is not necessary, since the mixture of alcohol and oil under supercritical conditions becomes a single homogeneous phase, reducing the mass transfer limitations [9]. Moreover, according to Medeiros et al. [14] and Mendoça et al. [15] the transesterification reaction with supercritical alcohols need less energy in the overall process. The high capital cost related to the high pressure and temperature operation of the supercritical process can be compensated by rapid reactions that implies in smaller reactors to obtain the same productivity [16].

Other advantages of the supercritical transesterification are that the separation of the biodiesel product and glycerol byproduct is simpler because the products are not miscible at ambient temperature, there is no catalyst in the mixture to be removed [2,9] and the reaction times are shorter (5 and 60 min, depending on the reaction temperature and pressure, the type of reactor and the fatty acid composition of the oil) [2,17] compared to alkaline transesterification (around 1 h) [2].

Castor (*Ricinus communis*) is considered as one of the most promising non-edible crops for biodiesel production due to its high annual seed production, high oil productivity of the seeds, high tolerance to drought and easy to grow on marginal lands and in semiarid climate [18]. The optimum average temperature for its development is between 24 and 27 °C [19], even though it is registered in zones with maximum temperatures of 30 °C (unpublished work). In the Northeast of Brazil, the soil planted with castor was increased in 180,000 ha between the years 2005 and 2011 [20], the production being increased by 122.8% between 2014 and 2015 [21]. The most important producers in the world (representing more than 90% of the international market) are India (54.0%), China (23.4%), Brazil (11.9%) and Mozambique (4.3%) [22].

The seeds of castor have an average of 48% oil by weight, but there are some varieties that can reach 55% [23]. Castor oil can be extracted from the seeds by mechanical pressing or using organic solvents, the most common method used being the cold or warm mechanical pressing [24,25]. Although the seeds could be shelled in order to optimize the process, the conventional method uses the whole seeds [25]. One of the disadvantages of mechanical pressing is that only around 45% of the oil is extracted and, hence, the remainder oil in the seeds needs to be extracted with organic solvents [24]. The main drawbacks of the solvent extraction process are its long duration and the large volume of solvent used [26]. Supercritical carbon dioxide extraction can also be used as an alternative method for oil extraction, leading to a lower environmental impact [25,26].

Castor oil, which is toxic for human and animal consumption because it contains ricin and ricinine (two highly toxic proteins [18,24]), has a wide range of applications due to its particular characteristics. It is primarily used in the chemical industry as a raw material for the manufacture of paints, varnishes, inks and lubricants [24]. However, its use as raw material for biodiesel production has been increasing over time. The kinematic viscosity of castor oil biodiesel is higher than that required by international standards, ASTM (American Society for Testing and Materials) D6751 and EN (European Norm) 14214 [1,18], while its cloud point and cold flow properties are highly positive [18,27].

Vieitez et al. [28] demonstrated that for the supercritical ethanolysis of castor oil, the production of ethyl esters was not affected by the presence of water in the oil, and that the ethyl esters production was boosted even with 5–10% water content. The content of water also favored the thermal stability of the fatty acid ethyl esters. Therefore, they concluded that water does not affect negatively the supercritical transesterification process; instead, the yield of ethyl esters increases steadily with increasing amount of water content [28].

The main parameters influencing the supercritical reaction are the temperature, the pressure, the methanol-to-oil molar ratio, the reaction time and the agitation speed of the medium. The optimum temperature and reaction time to reach maximum yields of biodiesel are in the ranges of 290–400 °C and 5–60 min, respectively, depending on the type of reactor and the oil used [29,30]. However, most of the authors reported an optimal methanol-to-oil molar ratio ranging from 40:1 to 45:1 [31–34] regardless of the kind of oil used. Focusing on the supercritical methanol and ethanol transesterification of castor oil to biodiesel in a batch reactor, Varma and Madras [17] and Rodríguez-Guerrero et al. [16] also obtained the highest conversion of TG (triglycerides) to esters for molar ratios between 40:1 and 45:1 (optimal value).

The effect of pressure on the supercritical methanol reaction depends largely on the kind of feedstock [35], the reaction temperature [36], the type of reactor (batch-type or flow-type) and the agitation speed of the medium [37]. Although the reaction pressure positively affected the yield of biodiesel, the effect of pressure was in general lower than that of temperature and reaction time [38]. In supercritical methanol reactions conducted without agitation and regardless of both the kind of reactor and feedstock, the pressure leading to the highest yield of biodiesel ranged from 30 to 35 MPa [32,39,40]. However, when the reaction was carried out in a batch-type reactor at optimal agitation speeds of 200–500 rpm and temperatures of 300–350 °C, the optimal operating pressure ranged from 18 to 21 MPa regardless of the kind of feedstock [35,37,38], the yield of biodiesel being hardly affected at higher operating pressures.

There are very few studies to date on the supercritical methanol transesterification of castor oil [17] to biodiesel and most of the existing investigations were conducted using supercritical ethanol [16,28]. In fact, methanol is the most used alcohol in the world for biodiesel production because it is cheaper and more reactive than ethanol. Therefore, in order to delve into this supercritical process from castor oil, the aim of the present study is to evaluate the synthesis of biodiesel from this crude oil in supercritical methanol in a batch reactor and without using catalyst. The variables tested were the reaction temperature (250–350 °C) and the reaction time (15–90 min) at endogenous pressures and a methanol-to-oil molar ratio of 43:1 (optimal value). The influence of these variables on the conversion of TG, the yield of individual and total FAMEs (fatty acid methyl esters) and the yield of intermediate products [MG (monoglycerides) and DG (diglycerides)] was studied. The degree of thermal decomposition of FAMEs was also evaluated under the conditions tested.

2. Materials and methods

2.1. Materials

Castor seeds were collected in Maipú, Región Metropolitana, Chile (latitude 33°29′S, longitude 070°40′O and altitude 240 m).