Renewable Energy xxx (2017) 1–7

Contents lists available at ScienceDirect

Renewable Energy

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

Effect of *Crambe abyssinica* oil degumming in phosphorus concentration of refined oil and derived biodiesel

Emanuel Costa [a], Manuel Fonseca Almeida [a], Maria da Conceição Alvim-Ferraz [b], Joana Maia Dias [a,*]

[a] LEPABE, Departamento de Engenharia Metalúrgica e de Materiais, Faculdade de Engenharia, Universidade do Porto, R. Dr. Roberto Frias, 4200-465 Porto, Portugal

[b] LEPABE, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, R. Dr. Roberto Frias, 4200-465 Porto, Portugal

ARTICLE INFO

Article history:
Received 21 February 2017
Received in revised form
17 August 2017
Accepted 25 August 2017
Available online xxx

Keywords:
Crambe abyssinica
Phospholipids
Degumming
Non-edible oil
Biodiesel

ABSTRACT

In the present study, the effect of different degumming processes on the phosphorus content of *Crambe abyssinica* oil and resultant biodiesel was evaluated. The non-edible oil was submitted to water degumming and chemical degumming with different concentrations of phosphoric acid and varying the acid to oil volume percentages. Phosphorus content of the products was measured by UV spectroscopy after sample calcination, according to NP 1994:2000. Biodiesel was produced by transesterification using a 6:1 methanol to oil molar ratio and 1 wt% sodium hydroxide as catalyst at 65 °C, during 1 h. The biodiesel produced directly from the crude oil presented high phosphorus concentration (>20 ppm); consequently, a degumming process was required to fulfil the quality standard (<4 ppm according to EN 14214). Water degumming was not effective, leading to biodiesel with a phosphorus concentration of 12.2 ppm. Among the acid degumming processes evaluated and taking into account technical and operational variables, the best established conditions, which allowed the fulfilment of the quality standard regarding phosphorus concentration, was considered to be 25 wt% acid concentration and 0.80 vol% of acid to oil.

1. Introduction

Biofuels are extremely important for the diversification of energy sources in the transport sector [1]. Biodiesel is one type of biofuel which can be used in most of diesel engines without any modification [2]. The biodiesel might be produced from edible and non-edible oils (mostly from edible vegetable oils, such as rapeseed and soybean) and fats [1]. Currently, the research is focused on finding alternative non-edible raw materials, which might allow a greater sustainability of its production, taking into account the environmental, social and economic pillars. The main advantage of non-edible oils for biodiesel production is that they do not compete with the food market.

Non-edible oils such as *Jatropha curcas* oil, *Ricinus communis* oil and *Crambe abyssinica* oil can be used to obtain a more sustainable fuel [4,5]. One of the non-food crops with high potential for biodiesel production is the specie *Crambe abyssinica*, known as "Crambe". This specie had its origin in the Mediterranean region and it is able to adapt to diverse climatic conditions (cold and dry regions) [6,7]. Crambe has a high potential for biodiesel production due to its short annual cycle (90–120 days) and high content of oil in seeds (between 36 and 43 wt%); however, there are few studies using this non-edible oil for biodiesel production [8].

The direct use of non-edible oils for biodiesel production is not usually possible because typically they contain free fatty acids (FFA) and phospholipids as well as other undesirable compounds. Such impurities might, in particular: i) react or inactivate the transesterification (most used reaction) catalyst [9] and affect mass transfer; ii) difficult the separation of the biodiesel and glycerol products [10]; and iii) make more demanding the water washing purification step (conventionally used). In agreement, the degumming pre-treatment (to remove phospholipids, waxes, among others) together with the neutralization or esterification should be applied before biodiesel production. These procedures will therefore avoid problems concerning the biodiesel synthesis and purification aiming a proper product quality.

Since each oil might present different proportion of the mentioned contaminants, degumming should be studied for different raw materials, contributing to the economic viability of their use.

* Corresponding author.
E-mail address: jmdias@fe.up.pt (J.M. Dias).

http://dx.doi.org/10.1016/j.renene.2017.08.089
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The most common impurities in crude plant oils are phospholipids, sugars, acylglycerols, free fatty acids, steroids and trace metals [11–13]. Phospholipids are molecules constituted by glycerol with two fatty acids attached and a phosphoric molecule [9]. The presence of phosphorus in biodiesel is directly related with the degree of oil refining and it is regulated by the standard EN 14214 (<4 ppm). The phospholipids which can be found in the crude plants oil are mainly of two types: hydratable (HP) and non-hydratable (NHP).

The presence of phosphorus in biodiesel affects the catalytic conversion at the exhaust systems in diesel engines and increases the generation of several pollutants in the exhaust gases, such as particulate matter, carbon monoxide and sulfur dioxide [14,15].

The HP can be removed from the oil by adding hot water, which forms an insoluble water-phospholipid complex (hydrated the phospholipid), easily separated from the remaining phase by centrifugation [12,16]. The HP present in the crude oil are of two types: phosphatidyl choline (PC) and phosphatidyl inositol (PI). PC is easily hydrated because it contains a quaternary ammonium salt with positive charge for all range of pH and good affinity for water. PI charge balance depends on the pH but the presence of five hydroxyl groups (OH^-) makes it extremely hydratable by water for all pH range, presenting therefore a hydrophilic nature. After de degumming process it is possible to recover products with commercial value as a food supplement like lecithin phospholipid or phosphatidic acid [17].

In order to separate the NHP, chemical degumming is performed using mostly phosphoric acid (H_3PO_4), sulphuric acid (H_2SO_4), hydrochloric acid (HCl) and citric acid ($C_6H_8O_7$) [2,9,17,18]. These reagents promote their conversion into the hydratable form which can be more easily further removed [11]. The chemical degumming allows the removal of the two phospholipids types because usually combines the addition of acid and water. The main NHP found in vegetable oils are phosphatidyl ethanolamine (PE) and phosphatidic acid (PA). The PE shows a balance of charges equal to zero; and, therefore, it has no affinity with the polar water molecule, this characteristic is evidenced when the pH is close to neutral. For pH smaller than 3 or higher than 9, the phospholipid molecule can be hydratable. Sometimes it is possible to find PA in the form of calcium salts in the vegetable oils, which remain stable without charges regardless of the pH. For this reason, some degumming procedures include the addition of an alkali with objective to convert calcium salts in other salts (sodium salt or potassium salt) with higher water solubility [16,18].

From the literature review performed, few studies were founded regarding crude oil degumming, with focus in phosphorus content reduction [2,11,17–21] and none existed for crambe oil pre-treatment towards bioenergy production; from those found, although it is consistent the use of phosphoric acid and acid degumming as the best option, the conditions vary considerably making difficult the selection of the best route [2]. In addition, although studies mention the importance of degumming raw oil before biodiesel production [4,19], no studies exist on the effect of the pre-treatment on the biodiesel quality, as well as the combined effect of the crude oil pre-treatment and biodiesel post-purification procedures [16,22]. In agreement, the present study aims to evaluate the effect of different degumming pre-treatments of *Crambe abyssinica* raw oil on phosphorus concentration of oil and the resultant biodiesel, taking into account the quality standard EN 14214.

2. Materials and methods

2.1. Materials

Crambe abyssinica seeds were provided by B & T World Seeds (Czech Republic), and Fundação MS (Brazil). The use of two different seed suppliers was justified by the fact that the amount of seeds available for oil extraction from the European source (from which initial studies were developed) was not enough to complete the studies and no additional material was available. It should be highlighted that for the study of the degumming process both seeds were used, whereas for the biodiesel production using the refined oil only the oil obtained from the Brazilian seeds was used.

Petroleum ether (LabChem) was used for chemical extraction (soxhlet). Methanol 99.9% (analytical grade, Fischer Chemical) was used in the transesterification reaction and NaOH 97% powder (analytical grade, Aldrich) was used for transesterification and degumming processes. Phosphoric acid was prepared from concentrated acid (85%) supplied by Merck.

2.2. Preparation and extraction of Crambe abyssinica seed oil

The oil extraction was performed using a 1 L Soxhlet extractor. The procedure adopted was based in NP EN ISO 659 (2002). In a first phase, the seeds were crushed in a mortar and placed inside the thimble. Then the thimble was dipped in petroleum ether solvent for 6 h (equivalent to 14 turns of the solvent in the extractor). At the end of the extraction, the solvent was removed in a rotary evaporator at 73 °C. Several extraction cycles were conducted until the amount of oil necessary for the study was obtained.

2.3. Products characterization, oil degumming and transesterification

2.3.1. Crude oil properties

Crude oil was characterized in terms of phosphorus content, acid value, oxidation stability, density and fatty acid profile. The methodology used for phosphorus determination is described in Section 2.3.5. The acid value was determined according to EN 14104 (tritimetric method). The oxidation stability was measured in agreement with the EN 14112 by accelerated oxidation using a Rancimat equipment (Metrohm) and the density was determined at 15 °C using a pycnometer (standard NP 938 1988). The fatty acid profile was assessed through the fatty acid methyl esters content of Crambe abyssinica biodiesel using gas chromatography and following the standard EN 14103.

2.3.2. Water degumming

Water degumming experiments were conducted at different ratios of oil to water and at different temperatures (Fig. 1), in order to evaluate its impact on phosphorus content as well as to establish the best refining conditions.

The experiments were carried out by mixing raw oil (30 g per experiment) with water (3–5 wt%) at different temperatures (22 °C (ambient T), 35 °C, 40 °C, 45 °C and 50 °C) and stirring the mixture with magnetic stirrer (slow mix) during 30 min [18,22,23]. Finally, the mixture was submitted to centrifugation during 10 min at 3500 rpm.

2.3.3. Chemical degumming

To remove the maximum amount of phospholipids, chemical degumming is proposed by different authors [2,4,18,19] in order to convert NHP into HP and remove both. The most common acids employed are phosphoric acid or citric acid at doses between 0.05 and 2 wt%, relative to oil, depending on the acid concentration [17,24]. The addition of acid allows pH reduction and consequently the conversion of NHP into HP; the further use of an alkaline solution is sometimes required to neutralize the excess acid. The amount of alkaline solution should be the minimum possible to reduce the amount of soaps produced. The neutralization in the