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Biodiesel production from raw castor oil

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ABSTRACT

A preliminary assessment of castor plant adaptability at Northern Portugal was performed, together with the evaluation of the extracted raw oil, without any refinement, for biodiesel production. Castor was seeded, plants grew and seeds were manually harvested after 2 years. Mechanical and chemical oil extraction procedures were evaluated. Biodiesel was produced by homogenous alkaline transesterification and experimental planning was conducted to evaluate the influence of temperature and reaction time in product yield and quality; 20 experiments were performed. A 54.1% (*w*/*w*) oil yield was obtained by Soxhlet extraction with methanol after grinding the seeds. Product yield ranged from 43.3 to 74.1% (*w*/*w*), biodiesel quality varied and the conditions that lead to the best product were established. Results indicate that, to achieve higher product yields and quality using raw oil, longer reaction times are required compared to what is generally reported for refined oil. Statistically significant predictive models were obtained to estimate product yield and quality as function of the studied reaction variables. The best temperature and reaction time to produce biodiesel from raw castor oil were 65 °C and 8 h, where models predict a product yield of 73.62% (*w*/*w*) and a purity of 83.41% (*w*/*w*).

1. Introduction

Biodiesel is a biofuel that might be produced from different raw materials, categorized into three main groups according to Banković-Ilić [1]: vegetable oils (edible and non-edible), animal fats and waste cooking oils. A fourth group of increasing interest are the algal oils, with very high oil productivities; however, their application in the short term is still limited due to high associated costs [2].

Currently, edible oils account to more than 95% of the world biodiesel production [3]. This is due to the fact that they are easily available from large scale agricultural production activities; however, this is not a desirable situation due to the potential impacts on food supply leading to the so called "food versus fuel dispute" [4]. In fact, considering that 60% of the population in the world is currently malnourished, the use of food crops, which play an essential role in overcoming such fundamental social aspect, should be avoided [4,5].

In addition to the social aspects, it is known that the cost of the raw-materials can account for 70–95% of total biodiesel production cost [4]; therefore, alternative low cost raw materials are also essential to overcome economic constraints to its production.

The production of biodiesel using non-edible crops, inappropriate for human consumption due to the presence of toxic compounds, has been investigated in the last few years. Amongst the most studied crops are: jatropha (*Jatropha curcas* L.), karanja (*Pongamia pinnata*), castor (*Ricinus comunis* L.), rice bran, linseed, coriander (*Coriandrum sativum* L.), tobacco seed (*Nicotiana tabacum* L.), cotton, rubber and wild mustard (*Brassica juncea* L.) [3,4,6].

The comparison of plantation costs and oil yields of the mentioned crops [3] place castor clearly on the top of the most interesting non-edible crops. Castor (also called castor bean and ricin) is originally a tree or shrub that, depending on the cultivated variety, can grow from around 1 m, to several meters in perennial cultivation [7]. The castor oil seeds usually contain 40–55% of oil, a very high potential as compared to other most commonly used oil crops (soybean: 15–20% (*w*/*w*), sunflower: 25–35% (*w*/*w*), rapeseed: 38–46% (*w*/*w*), and palm: 30–60% (*w*/*w*) [8]). In addition, the cost of plantation can be 50% of the cost of planting rapeseed and 25% of the cost of planting jatropha [3].

Castor oil presents between 80 and 90% of ricinoleic acid (12-hydroxy-9-*cis*-octadecenoic acid). Such unique composition brings a disadvantage for its use for biodiesel production, since its viscosity is about 7 times higher than the one of other vegetable oils [1]. Because castor oil is highly hygroscopic, water content might also be higher than desirable. To overcome such issues, its use in

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mixture with petrodiesel has proven effective, namely in a 10% blend, to ensure specifications in standards [9]. In fact, Canoira et al. [10] evaluated castor oil transesterification and also the resulting FAME (Fatty Acid Methyl Esters) in mixture with reference diesel concluding that until around 40% incorporation, the obtained fuel met most quality specifications. The use of vegetable oil mixtures might also be done. Plentz Meneghetti et al. [11] evaluated biodiesel production using soybean oil and cotton seed oil mixed with castor oil. The authors found that it was possible to obtain the same biodiesel yield using the oils alone or mixed with castor oil. In addition, the purification process of biodiesel was improved when mixtures were used, compared to the use of castor oil alone.

Due to its unique referred properties, castor oil is used for a wide range of other applications, such as lubricants, coating, plastics, other polymers and cosmetics [7,11]. This should be taken into account, namely within the context of the implementation of biorefineries.

India produces around 60% of the world castor oil production [1]. However, castor plant grows uncultivated (in most tropical and sub-tropical countries) tolerating variable weather conditions and soil types [12], also, it provides soil support (perennial crop), reducing erosion effects.

Land abandonment has been a central problem in many rural areas of Mediterranean Europe, especially in those at periphery or with more difficult natural conditions like Portugal. Land abandonment might lead to fire events and consequently to soil degradation. Soil erosion is the main cause of agricultural soil degradation in Portugal, leading to the loss of the surface layer with higher organic matter content and reduction of soil thickness and fertility [13].

Despite the fact that castor is not an autochthonous Portuguese plant, the soil and climate characteristics of Portugal makes it interesting as a complementary oilseed crop, namely in abandoned or poorly managed lands, for their restoration (erosion problems) along with the production of one or more valuable products. The lack of related studies led to the development of the present work.

To study castor oil for biodiesel production, namely in Portugal, it is important to assess the production process. Biodiesel is conventionally produced through a homogenous alkaline transesterification reaction, consisting on a sequence of 3 reversible reactions where triglycerides (main constituents of oils and fats), in the presence of an alcohol, are converted into a mixture of fatty acid esters and glycerol. Due to its low cost, high availability and easier production process, methanol is usually used; reason why the common name for biodiesel is FAME (Fatty Acid Methyl Esters). During alkaline transesterification, the most important variables to be considered are: reaction time, temperature, type and amount of catalyst, and, alcohol to oil molar ratio [14–16]. Regarding the raw-material processing, usually refined oils are used; however, it would be interesting to evaluate the production of biodiesel using raw castor oil, as means of additionally reducing production costs and process complexity.

The information dedicated to the castor oil biodiesel production is rather scarce compared with the general literature of biodiesel using different raw materials. This fact is probably related with the specific oil characteristics, but also due to the fact that studies are mostly developed by specific climate adapted countries, presenting available land and also national incentives for its growth (such as Brazil). An evaluation of scientific literature has shown no studies on the evaluation of biodiesel production and influence of reaction parameters using raw castor oil; studies found, and described below, were dedicated to the use of refined oils [1,4,6,9,12,17–21].

De Oliveira et al. [19] studied the influence of temperature (30–70 °C), reaction time (1–3 h), catalyst concentration (0.5–1.5% (*w*/*w*), NaOH) and alcohol to oil molar ratio (3:1–9:1) using a Taguchi experimental design on the ethanolysis of commercial refined castor oil, concluding that the increase of all parameters, except for catalyst concentration, led to an enhancement in reaction conversion.

Da Silva et al. [17] evaluated the transesterification of castor oil (from an oil company) with ethanol and sodium ethoxide as catalyst. The authors studied temperature (30–80 °C), catalyst concentration (0.5–1.5% (*w*/*w*)) and alcohol to oil molar ratio (12:1–20:1), during up to 90 min reaction time and used response surface methodology (RSM) to optimize selected parameters. Good results were achieved with the lowest temperature; a high ethanol:oil ratio was needed (20:1) and maximum ethyl ester conversions (93.78%) were obtained using 0.8–1.3% (*w*/*w*) catalyst.

Cavalcante et al. [21] studied the ethanolysis of refined castor oil and the effects of reaction time (40–140.45 min), catalyst amount (1.33%–2.17% (*w*/*w*) KOH) and ethanol to oil molar ratio (9.65:1–12.35:1) at around 30 °C, on biodiesel yield, using a composite rotatable design [21]. The optimum conditions were obtained at 1.5 h, 1.75% (*w*/*w*) KOH and 11:1 methanol to oil molar ratio. The catalyst concentration was considered to mostly influence biodiesel yield and maximum yield was around 85%.

Plentz Meneghetti et al. [20] evaluated biodiesel synthesis from commercial castor oil, through ethanolic and methanolic route and using different homogenous catalysts. The authors evaluated the progression of the reaction from 1 to 10 h; the yield of FAME was higher than the one of FAEE (fatty acid ethyl ester) at lower temperatures and reaction times; the highest yields, obtained using homogenous alkali catalysts, were around 85%.

Jeong and Park [22] evaluated the optimization of biodiesel production using RSM and a refined, bleached castor oil as raw material. The optimal reaction conditions were as follows: 35.5 °C, 8.24:1 methanol:oil molar ratio, 1.45% *w*/*w* KOH and a reaction time of 40 min, to obtain a product with a purity of around 92% (*w*/*w*).

Albuquerque et al. [12] studied biodiesel production and quality obtained using different raw materials including castor oil; reaction was performed at 25 °C, using a 6:1 molar ratio of methanol to oil and sodium methylate ($NaOCH_3$) as catalyst; the authors do not present conversion percentages but evaluated product quality and castor oil biodiesel produced showed a viscosity of 13.5 $mm^2\ s^{-1}$, a density of 920 $kg\ m^{-3}$, an iodine value of 85.2 g I_2/100 g and an acid value of 0.42 mg KOH g^{-1}.

Ramezani et al. [6] evaluated methyl ester synthesis from refined castor oil, studying different basic catalysts ($NaOCH_3$, $KOCH_3$, NaOH, KOH), reaction temperatures (25 °C–80 °C), catalyst concentrations (0.25–0.5% (*w*/*w*)), alcohol to oil molar ratios (4:1–8:1) and mixing intensities (250–600 rpm) using a Tagushi experimental design. The optimal results led to around 87% purity, using 0.5% (*w*/*w*) $KOCH_3$, 65 °C, 400 rpm, 8:1 methanol to oil and a reaction period of 2 h.

The wide range of results regarding the best reaction conditions, even within the same alcohol route (ethanolysis/methanolysis), shows that it remains important to evaluate their influence on castor oil biodiesel yield and quality.

In agreement with what has been stated, the main objective of the present work was to provide novel information on biodiesel production from raw castor oil (since no studies are reported so far). The specific objectives were to: i) harvest castor seeds and extract the oil using different procedures; and, ii) study biodiesel production through alkali transesterification of the extracted raw oil, considering the influence of reaction conditions in product yield and quality, by using response surface methodology. A preliminary evaluation of castor adaptability in Northern Portugal was also conducted.

2. Materials

Brazilian castor seeds were used for seeding activities (Section 3.1), being collected randomly, directly from castor trees located at