J. of Supercritical Fluids 93 (2014) 130–137

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

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

Macauba oil as an alternative feedstock for biodiesel: Characterization and ester conversion by the supercritical method

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ARTICLE INFO

Article history:
Received 11 June 2013
Received in revised form 25 October 2013
Accepted 13 November 2013
Available online 21 November 2013

Keywords:
Macauba oil
Biodiesel production
Supercritical method
Catalyst-free continuous process

ABSTRACT

In this work different samples of Brazilian macauba oil obtained from mechanical pressing were characterized and production of esters of fatty acids using a catalyst-free continuous process under supercritical alcohols was assessed. Analysis of oil samples showed that the major fatty acid on pulp oil was oleic acid (mean value 62.8%), the amount of free fatty acid (FFA) was very high (37.4–65.4%), samples contained glycerides (7.4–16.5% TAG, 14.2–16.8% DAG and 1.0–3.4% MAG) and moisture was around 1.0%. Oil was processed in a continuous reactor using supercritical methanol or ethanol and the effects of temperature (573, 598, 623 and 648 K), pressure (10, 15 and 20 MPa), oil to alcohol molar ratio (1:20, 1:30 and 1:40), water concentration (0, 5 and 10 wt% added) and the flow rate of reaction mixture (1.0, 1.5, 2.0, 2.5 and 3.0 mL/min) on process efficiency were evaluated. The highest ester content achieved in reactions with supercritical methanol was 78.5% (648 K, 15 MPa, 1:30 oil:methanol molar ratio, 5 wt% water and 2.5 mL/min flow rate), while with supercritical ethanol was 69.6% (598 K, 15 MPa, 1:30 oil:ethanol molar ratio, 5 wt% water and 2.0 mL/min flow rate). The extent of the reaction was explored using a novel parameter, convertibility, which corresponds to the maximum ester content attainable from the feedstock. According to the convertibility of macauba pulp oil, the highest ester content corresponded to efficiencies of 98.0% and 86.9%, respectively. Results demonstrate that macauba oil might be a potential alternative for biodiesel production, though purification steps should be taken into account to achieve biodiesel specifications.

1. Introduction

Macauba (*Acrocomia aculeata*) is a palm native from South American tropical forests. An important amount of oil is obtained from the coconuts of this palm, its productivity yields between 1500 and 5000 kg of oil per hectare per year, which is the second largest productivity after palm oil (*Elaeis guineensis*). Macauba palm reaches a high productivity after 4 years of growth and keep producing for over 100 years. Other important characteristics of macauba palm are the high resistance to pests and temperature variations and the ability to grow in low-rainfall areas [1–3]. Because of these properties, most fruits that are being processed industrially come from unplanned crops of macauba without systematic domestication. It has been reported that if proper cultivation planning and oil extraction process were used, macauba oil productivity could easily reach 6000 kg of oil per hectare [2,4,5].

Several studies indicate that macauba coconuts present from 9 to 26 wt% oil content (wet basis) with a mean value of 19 wt%. In dry basis the pulp presents from 46 to 78 wt% oil with a mean value of 59 wt% and the kernel presents from 43 to 60 wt% oil with a mean value of 53 wt% [6–9]. Macauba oil has no tradition as food, though it presents a fatty acid profile comparable to olive oil and high content of bioactive compounds such as carotenoids and tocopherols [10,11]. This oil generally presents high acid value, which make it inappropriate for use as food or feedstock in conventional transesterification processes. Farias [8] indicated that the acid value of macauba oil increases during fruit storage reached 2% (maximum for crude oils) within 1 week and 20% after a month. He concluded that after macauba coconuts are collected, microorganisms penetrate into the fruits through the peduncle or skin cracks and the elevated water activity of the pulp favors a high enzymatic activity leading to lipid hydrolysis.

Macauba cultivation has to be planned carefully, but once established, it will offer opportunities for small-scale farmers and rural oil producers. The potential of macauba oil, especially as alternative feedstock for biodiesel production has been realized and significant

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http://dx.doi.org/10.1016/j.supflu.2013.11.008

research and development has been conducted showing environmental, economic and social benefits [1–11].

Biodiesel is defined as mono-alkyl esters of long chain fatty acids derived from vegetable oil or animal fats, a clean-burning biofuel that can be produced entirely from renewable sources [12]. Production of biodiesel has gained attention because of global environmental concerns and the fact that alternative renewable energy sources, such as vegetable oils, have become matter of great interest [13]. Large scale production of biodiesel is mainly performed through alkali-catalyzed transesterification of vegetable oils in the presence of a short chain alcohol to form fatty acid esters and glycerol [14,15]. Such conventional production technique presents negative effects on the transesterification reaction caused by the presence of free fatty acids or water in the feedstock [16–19].

The non-catalytic transesterification of vegetable oils in supercritical alcohols, so-called supercritical method, has received growing interest because the quality of the products generated and environmental benefits [20,21]. With such technique high yield of esters can be achieved and has been proved to be more tolerant to the presence of high contents of water and FFA, allowing the use of various types of vegetable oils, even waste oils [22–27] and animal fats [28], for which alkaline-catalyst transesterification is unsuitable [29,30]. The use of cheaper raw materials such as waste oils, raw vegetable oils and rectified alcohol for biodiesel production via the supercritical method is very important toward economic competitiveness of both, the biofuel and the process [31].

The Association for the Advancement of Cost Engineering International (AACEI) indicates that business plans for new industrial processes can be based on information from assessments of the cost of manufacturing (COM). The COM can be defined as the weighted sum of five factors, fixed cost of investment (FCI), cost of operating labor (COL), cost of raw material (CRM), cost of waste treatment (CWT) and cost of utilities (CUT) [32]. The International Energy Agency indicates that for conventional biofuels today, the main cost factor is CRM, which accounts for 45–70% of COM, whereas for advanced biofuels the main factor is FCI (35–50% of COM), followed by CRM (25–40% of COM) [33]. Some studies using computational simulation of the industrial processes for biodiesel production have found that CRM comprises for more than 80% of COM in conventional catalyzed transesterification of refined oils, while CRM accounts for 67–77% of COM in supercritical transesterification of waste vegetable oils [34–36].

The ethanol industry in Brazil is well developed and about 80% of biodiesel is produced from soybean oil [37]. Current price of soybean oil is around US$ 1100 per ton, while the price of macauba oil varies from US$ 600 to US$ 800 per ton [38]. This scenario would favor the use of the supercritical method and of entirely renewable raw materials for obtaining an affordable biofuel.

In this context, this work aims to establish the potential of macauba oil as a source for biodiesel production via the supercritical method. Different samples of macauba oil from Brazil obtained by pressing were characterized and production of methyl/ethyl esters using catalyst-free continuous process under supercritical alcohols was studied.

2. Experimental

2.1. Materials

Samples of macauba oil were obtained from the processing unit of macauba in Montes Claros (Minas Gerais, Brazil). The oils were obtained by pressing followed by filtration to separate rough impurities. After harvesting of macauba coconuts, these were stored about 3–6 months prior to oil extraction. Four different macauba pulp raw oils were analyzed together with one sample of unrefined oil from the kernel. Identification of oil samples is presented in Table 1. Methanol and ethanol were purchased from Merck with a purity of 99.9%. Other solvents, standards and reagents used in derivatization step, necessary for the analysis, were purchased from Sigma–Aldrich.

Table 1
Identification of macauba oils.

Sample	Description	Year of harvest
Pulp 1	Macauba pulp oil	2010
Pulp 2	Macauba pulp oil	2011
Pulp 3	Macauba pulp oil	2011
Pulp 4	Macauba pulp oil	2012
Kernel 1	Macauba kernel oil	2012

2.2. Oil characterization

Several analyses were performed for the characterization of macauba oils. The lipid classes were qualitatively determined by thin layer chromatography (TLC) on Silica Gel H using hexane/diethyl ether/acetic acid (80:20:1) as developing solvent. The lipid fractions were made visible by exposing the plates to iodine vapors [39]. Peroxide index (PI) was determined by titration according to method AOCS Cd 8-53. Moisture was determined by Karl Fischer titration, according to AOCS Ca 2e-84, using a DL 50 Mettler-Toledo titrator. The acid value was determined by titration according to AOCS Cd 3d-63 method.

The content of triacylglycerides (TAG), diacylglycerides (DAG) and monoacylglycerides (MAG) was determined by GC analysis according to [24]. A gas chromatograph Shimadzu GC-14B equipped with a capillary column Optima-1 TG (Machery-Naguel 10 m × 0.32 mm × 0.1 μm) was employed. The carrier gas was Nitrogen and column head pressure was 70 kPa. The temperature was programmed as previously described.

For the determination of fatty acid composition oil samples were previously derivatized to the corresponding methyl esters according to method AOCS Ce 2-66. Derivatized samples were analyzed using a GC Shimadzu 14B equipped with FID and a capillary column SGE BPX70 (25 m × 0.32 mm × 0.25 μm). The temperature program was set to heat from 433 K to 503 K at rate of 4 K/min and then holding for 10 min and nitrogen was used as the carrier gas at 50 kPa.

Considering that these crude vegetable oils could contain several compounds non-convertible to alkyl esters, the maximum theoretical ester content in the product may not correspond to 100% (wt/wt). Thus, in order to determine this maximum conversion, a parameter defined as the "Convertibility" was employed. For this purpose oil samples were quantitative transesterified using BF_3 as catalyst (as described in method AOCS Ce 2-66) and the ester content in the product determined by GC according to UNE-EN 14103, using methyl heptadecanoate as internal standard. Such ester content, corresponding to the maximum yield achievable from the raw material analyzed was defined as the "Convertibility".

2.3. Reactions

The equipment used for the reactions was the same reported in a previous work [40]. Briefly, the tubular reactor has a volume of 70 mL. All reactions were conducted in continuous mode and ester samples were collected after reaching the steady state. No catalyst was used. Reactions were conducted in supercritical methanol and supercritical ethanol to produced fatty acid methyl esters (FAME) and fatty acid ethyl esters (FAEE), respectively.

The process parameters studied were the reaction temperature (573, 598, 623 and 648 K), pressure (10, 15 and 20 MPa), oil:alcohol molar ratio (1:20, 1:30 and 1:40), water addition with respect to