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In-depth study of the transesterification reaction of *Pongamia pinnata* oil for biodiesel production using catalyst-free supercritical methanol process

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ABSTRACT

Non-edible vegetable oils are promising substitutes for traditional edible food crops used in the synthesis of biodiesel. Among them, *Pongamia pinnata* oil, also known as Karanja oil, is considered as a good candidate with potential availability of more than 135 Mtpa. The present work offers an in-depth study of the transesterification reaction of Karanja oil in supercritical methanol in one-step catalyst-free process. Triglyceride (TG) conversion and the yield of fatty acid methyl esters (FAMEs) are analyzed in the temperature and reaction time ranges of 250–350 °C (12–43 MPa) and 15–90 min, respectively, at an alcohol-to-oil molar ratio of 43:1. This study also covers the evolution of intermediate products such as monoglycerides (MG) and diglycerides (DG) and the thermal decomposition of fatty acid chains for the stated reaction conditions. Optimal reactions conditions were found at 300 °C and 90 min reaction with almost complete triglyceride conversion. Significant thermal decomposition was observed from 325 °C, mainly caused by the degradation of polyunsaturated fatty acid methyl esters. Maximum degree of thermal decomposition of 38% was determined at 350 °C after 90 min reaction time.

1. Introduction

The demand for fossil fuels has increased sharply in recent decades because of the global industrialization [1]. The search for alternative fuels is becoming increasingly pressing [2] due to the dwindling petroleum reserves and the stringent environmental standards [3,4]. In this context, biodiesel is seen as a promising renewable power source that could help to meet future energy demands, while mitigating the impact of the use of conventional fuels on the environment [5,6].

Biodiesel is defined as mono-alkyl esters of long chain fatty acids derived from triglycerides or free fatty acids [7–10]. Compared to diesel fuel, biodiesel offers several advantages such as no sulfur nor net carbon dioxide emissions, less carbon monoxide production, significant reduction in smoke and more free oxygen, which leads to complete combustion [11,12]. Biodiesel is typically produced through the reaction of a vegetable oil [13,14], including cooking/frying oils (UFO) [15], or animal fat [16,17] with an alcohol in the presence or the absence of a catalyst. Vegetable oils are regarded as promising feedstocks for biodiesel production since most of them are non-edible, renewable in nature and can be produced on a large scale in a sustainable way [18]. In this context, biofuel adoption would require non-edible feedstock supply from marginal land not destined for food cultivation, which would imply not only a source of renewable energy but also would alleviate the existing competitive situation between food and biodiesel feedstocks [19]. In this regard, *Pongamia* oil, also known as Karanja oil, is a strong candidate for sustainable biodiesel production [20] in line with other oil resources such as Castor, *Jatropha*, Rubber seed and Neem that are not suitable for human consumption since they contain toxic compounds.

Pongamia pinnata is a medium-sized fast growing leguminous tree native to humid, subtropical climate [21] that can grow under a wide range of agro-climatic conditions, ranging from stony to sandy and clayey soils, and that can be propagated either from seeds or from root suckers. Thus, its cultivation has been accepted over other non-edible oils in countries like India, Australia, USA, China, Japan

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or Malaysia, with a yield potential of 0.9–9 t seed/ha [22]. Moreover, fresh seeds normally have a moisture and oil content of approximately 10 and 35 wt%, respectively, according to previous studies [23–25]. Historically, this plant has been found to be originated in India and neighbor regions where it has been used as source of traditional medicines, animal fodder, green manure, timber and fuel. In India, *Pongamia* tree is available in more than 15 states with an oil potential of 135 Mtpa [23,26]. In addition, the Indian government is planning to grow suitable oilseed plants such as Karanja and *Jatropha* in cultivable wasteland areas totaling over 175 mha [24]. These figures show the significant potential impact of *P. Pinnata* oil as source for biodiesel production [27–30]. Regarding the advantages and limitations of biodiesel produced from this type of oil, some studies have succeeded in ensuring essential properties like oxidation stability up to 4 months through the addition of antioxidants [31], while other works point out the necessary of special storage precautions, such as limiting access to oxygen and exposure to light, metal and moisture [32]. Moreover, in comparison with other oils like *Jatropha* and Neem, some works have shown that Karanja oil biodiesel offers significantly higher brake thermal efficiency while producing fewer emissions [33–35].

The transesterification of Karanja oil for biodiesel production has been reported by using the well-known two-step process; i.e., conventional acid/alkaline esterification and transesterification process while analyzing the effects of alcohol-to-oil ratio, catalyst amount and reaction time on the conversion efficiency to produce Karanja oil biodiesel. This type of process usually requires high reaction times [36–38]. Several studies have suggested the use of supercritical methanol as a one of the most preferable options for the transesterification reaction of vegetable oils [39], studying operational parameters such as methanol concentration, temperature and reaction time. However, the in-depth study of the transesterification of Karanja oil is such conditions remain scarce in the literature. In the present paper, the transesterification reaction of Karanja oil in a one-step catalyst-free reaction process in supercritical methanol is fully investigated. The process is studied in the ranges of temperature and reaction time of 250–350 °C and 15–90 min, respectively, for a fixed methanol-to-oil molar ratio of 43:1. This work covers the conversion of triglycerides (TG) and the yield of fatty acid metyl esters (FAMEs) as well as the evolution of the intermediate products: monoglycerides (MG) and diglycerides (DG). Moreover, the thermal degradation of fatty acid chains for the mentioned reaction conditions is thoroughly analyzed. Finally, the results are compared with those obtained with other synthesis methods, showing the advantages and limitations of the process employed in the present work.

2. Materials and methods

2.1. Materials

The *Pongamia* oil used in this investigation was imported from India. *P. Pinnata* was grown in Delhi Technological University and its fatty acid profile was determined by gas chromatography (see Table 1). Anhydrous methanol was supplied by Panreac Química, S.A.U. (Castellar del Vallès, Barcelona, Spain) and methyl heptadecanoate, 1,2,4-butanetriol, 1,2,3-tricaproylglycerol (tricaprin), monoolein, diolein, triolein and glycerol, which were used as standards and supplied by Sigma–Aldrich (Tres Cantos, Madrid, Spain).

2.2. Working method

An 83 ml batch reactor of SS 316 was used to investigate the effect of reaction temperature (250–350 °C) and reaction time (15–90 min). For each biodiesel sample preparation, the reactor was filled with a total mixture of 50 g consisting of methanol and *Pongamia* oil at an alcohol-to-oil molar ratio of 43:1. The investigation of the influence of the molar ratio was not the focus of this study, and it was fixed according to the optimal methanol-to-oil ratio reported by other authors, 40:1–45:1, regardless the type of oil used [40–43].The reactor, which was tighten by a high torque spanner, was immersed in a pre-heated salt bath (an eutectic mixture of $NaNO_3$ and KNO_3) by a pneumatically controlled mechanical arm to reach the desired temperature in approximately 10–15 min. For all experiments, the reaction time was measured from the moment the reactor is introduced in the salt bath. The reactor has inner temperature and pressure sensors to monitor both parameters during the reaction. Pressure intrinsically changes depending on temperature, which was fixed at the desired value. The reactor was orbitally shaken at 70 rpm during the reaction to maintain uniform temperature. To stop the reaction, the reactor was immersed in a cold-water bath. Once the reaction is complete, the remaining methanol was removed in a rotatory vacuum evaporator at a constant temperature of 53 °C for approximately 45 min. Finally, the samples were stored in a refrigerator at below 8 °C before their analysis to prevent FAMEs from degradation. Reaction conditions were performed in duplicate.

Table 1
Fatty acid composition of Karanja oil used.

Name of Fatty acid	% By weight
Palmitic acid (C16:0)	11.79
Stearic acid (C18:0)	6.53
Oleic acid (C18:1)	52.57
Linoleic acid (C18:2)	19.53
Linolenic acid (C18:3)	3.88
Arachidic acid (C20:0)	1.35
Gadoleic acid (C20:1)	1.12
Behenic acid (C22:0)	3.23
Total	100

2.3. Analytical methods

A 3900 Varian gas chromatograph equipped with auto-sampler and attached to FID detector was used for the analysis of FAMEs, MG, DG, TG and glycerin in all biodiesel samples. The results obtained were stored in a personal computer for their offline analysis synchronized with the gas chromatograph.

2.3.1. Analysis of glycerides

The analysis of MG, DG and TG was carried out in accordance with the UNE-EN 14105:2003 standard. The analytical method of this standard lies on the conversion of glycerides into their respective silylated derivatives, which was performed by using *N*-methyl-*N*-(trimethylsilyl) trifluoroacetamide (MSTFA) and pyridine. This method also involves two internal standard solutions, (n° 1) dissolving 50 mg of 1,2,4-butanetriol in 50 ml of pyridine and (n° 2) dissolving 80 mg of 1,2,3-tricaproylglycerol in 10 ml of pyridine. 80 μl of standard solution n° 1, 100 μl of standard solution n° 2 and 100 μl of MTSFA were carefully added to 100 mg of sample in a 10 ml vial, trying to avoid moisture contact. The vials were properly shaken and then left to settle for 15 min at room temperature (RT), after which 8 ml heptane were added for further analysis in the chromatograph.

A FactorFour VF-5ht capillary column (10 m × 0.32 mm, 0.1-μm film) was installed in the chromatograph with a flow rate of 1 ml min^{-1} of helium (He) as carrier gas and a split ratio of 1:70. The temperature sequence in the oven was as followed: 1 min at 50 °C, 15 °C/min to 180 °C, 7 °C/min to 230 °C, 10 °C/min to 370 °C and finally, 5 min at 370 °C. The temperatures of the detector and injector were 380 °C and 280 °C, respectively.