Fuel 235 (2019) 277–287

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

In-situ transesterification of *Jatropha curcas* L. seeds using homogeneous and heterogeneous basic catalysts

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ARTICLE INFO

Keywords:
In-situ transesterification
Jatropha seeds
FAME
Heterogeneous catalyst
Homogeneous catalyst

ABSTRACT

The *in-situ* or direct transesterification from non-edible *Jatropha curcas* L. (Jatropha) seeds is a suitable alternative to produce fatty acid methyl esters (FAME) in one-step. The FAME production was investigated in presence of homogeneous (NaOH) or heterogeneous (Na_2ZrO_3) catalysts. Parameters, such as catalyst concentration (between 1 and 10 wt%), reaction time, temperature and methanol/oil molar ratio were analysed. The maximum heterogeneous direct transesterification of FAME yield was 99.9% using 5 wt% of Na_2ZrO_3 at 65 °C and 8 h. Results showed that no solvent for oil extraction is required. The resulting FAME shows good purity and composition. Moreover, no water is required to purify the FAME. Compositional analysis of FAME indicated that linoleic (C18:2), oleic (C18:1) and palmitic (C16:0) methyl esters were the major components. In addition, the reusability of the catalyst was also investigated. The basic heterogeneous catalyst exhibited stability in the direct transesterification reactions with yields of > 72.5% during five cycles. Finally, Green Metrics values were proposed as parameters to evaluate the FAME obtained in one-pot from seeds directly. The heterogeneous direct transesterification process resulted 55% greener as compared to conventional transesterification and 39.4% greener than homogenous direct transesterification. Heterogeneous direct transesterification is a promising alternative for more clean, efficient, scalable and cost-effective FAME production that has the potential to developing new technologies.

1. Introduction

Biodiesel is an alternative fuel for diesel engines that is made up of methyl esters of different fatty acids and is produced from chemical modification of edible and non-edible vegetable oils [1–5]. It is well known that the biodiesel is consider as sustainable alternative fuel and can be a substitute form petroleum-based diesel fuel. Due to biodiesel being a renewable, biodegradable, non-toxic, not contribute to a rise in the level of carbon dioxide in the atmosphere, sulphur-free and consequently mitigates the greenhouse gases compared to diesel fuel [6–8]. Both animal and vegetable feedstocks are promising renewable alternative diesel fuels in the view of energy security and environmental protection with great potential for carbon dioxide reduction from the entire cycle of biodiesel production [4–10]. In particular, > 95% of biodiesel feedstock comes from edible oil-seed crops such as soybean, rapeseed, groundnut, sunflower, etc. The use of edible oils for biodiesel production may create controversy [11]. Thus, the less expensive non-edible oils are the most promising feedstock for biodiesel production [11,12]. Non-edible oil-seed crops from *Jatropha curcas* L. may be a good choice for biodiesel or fatty acid methyl esters (FAME) production due to its hardiness, easy propagation, an adoption to wide agro-climatic condition, high oil content, low seed cost [11–16], and it provides commercially viable alternative to edible oils. The *Jatropha curcas* L. plants belonging to the *Euphorbiaceae* family and contain approximately 175 known species [16]. Jatropha is native of American tropics as Mexico, Central America, Brazil, Paraguay, and other counties, and it has spread beyond its original regions. These plants also are now found abundantly in tropical and subtropical regions such as Africa and Asia [15–18]. The main interest in using Jatropha oil for FAME production is because this oil is not suitable for human consumption, and therefore,

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https://doi.org/10.1016/j.fuel.2018.07.082
Received 23 January 2018; Received in revised form 18 June 2018; Accepted 19 July 2018
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its production does not interfere with the food industry or harvesting lands.

The most widely used method for the commercial production of biodiesel from vegetable oils/fats is a base catalysed transesterification process using KOH or NaOH as the homogeneous catalyst and MeOH. However, this conventional transesterification has drawbacks as long timespans, large amount of solvent for the oil extraction and large amount of water to neutralize the methyl esters to eliminate the catalyst, emulsions and soaps. Additionally, it causes an alkaline wastewater stream, which produces high corrosion on the equipment. Moreover, this process consists in two-steps: first, the oil extraction and then subsequently transesterification of triglycerides in presence of the catalyst [19,20]. Therefore, these disadvantages promote a more expensive biodiesel production. An alternative to the conventional method is the heterogeneous *in-situ* transesterification from the seeds (direct transesterification). The oil extraction and the transesterification reaction take place simultaneously in a one-vessel. The one-step process is more economical and efficient than conventional method. Few studies have demonstrated that the FAME production achieved from the *in-situ* transesterification of various oil seeds using a homogeneous catalyst [21–23]. However, no systematic studies were reported with base solid heterogeneous catalyst, including the reaction conditions optimization and the reusability of the catalysts. The heterogeneous *in-situ* or direct transesterification is expected to be an effective FAME production process with low cost and minimal environmental impact because of simplifying the production under mild reaction conditions.

Heterogeneous basic catalysts have many advantages, as they are cheap, high recyclability, environmentally friendly, reusability, simple recovery, easy separation, lower energy consumption, and cleaner operation conditions without employing water to wash the FAME production [24–29]. Moreover, the reaction usually results in pure glycerol as a by-product. Therefore, for the conventional transesterification, various heterogeneous catalysts have been developed for FAME production to overcome the problems encountered in homogeneous FAME technology [27–31]. Catalysts as CaO [29,32], MgO, BaO, TiO_2 and Mg-Al_2O_3 [30–33], SrO [34], ZrO_2 [24,35], hydrotalcites [36], ion-exchange resins [37] and heteropolyacids [38] have been reported in the conventional transesterification for FAME synthesis. However, some catalysts can be noxious and can be degraded in the presence of water or solvent (catalyst leaching) reducing their activity resulting in lower reaction rates [29]. Recently, it was also reported that Na_2ZrO_3 and Cs-Na_2ZrO_3 (cesium-modified zirconate) were used as conventional basic heterogeneous catalysts to produce FAME from soybean and Jatropha oils [39,40]. Both materials exhibited excellent catalytic activities, low solubility and good stabilities due to their basic character. Thus, motivated by these encouraging results, we present in this work the *in-situ* transesterification in one-pot from Jatropha curcas L. seeds using basic homogeneous (NaOH) and heterogeneous (Na_2ZrO_3) catalysts for FAME production. Additionally, the conventional (two-step process) and direct (one-step process) catalytic evaluation comparison was analysed for both catalysts. Moreover, the heterogeneous catalyst re-utilization in the *in-situ* transesterification reaction was evaluated. Finally, the Green Metrics values (Environmental factor, Process Mass Intensity, Environmental-Health-Safety Index and Transesterification Environmental Burden) were proposed as parameters to evaluate the obtained FAME. These parameters represent an important contribution in the quantification of biofuels synthesis process for potential technological applications.

2. Experimental

2.1. Materials

Heterogeneous catalyst, Na_2ZrO_3 was obtained by a procedure described in the literature as reference [39,40]. Na_2ZrO_3 was synthesized via a solid-state reaction. Sodium carbonate (Alfa Aesar, 98%) and zirconium oxide (powder, 5 μm, Aldrich Chemical Co., 99%) were used for the catalyst preparation. Sodium hydroxide (> 98%), hydrochloric acid (36–38%), *n*-hexane (> 98.5%) and methanol (> 99.8%) were purchased from Aldrich Chemical Co. and were used as received. *Jatropha curcas* L. seeds were provided by the State of Morelos in Mexico. The Jatropha seeds contain 54 wt% of lipids (NMX-F-615-NORMEX-2004), 26 wt% of proteins (NMX-F-608-NORMEX-2011), 9 wt% of fiber (NOM-051-SCFI/SSA1-2010) and 3 wt% of carbohydrates (NOM-086-SSA1-1994). All values were determined according to Mexican norms.

2.2. FAME characterization

The Jatropha oil and the fatty acid methyl esters (FAME) products were analysed by infrared spectroscopy (FT-IR). FT-IR spectra were obtained using a Perkin Elmer Frontier MIR FT-IR spectrometer fitted with a Frontier Universal Diamond/ZnSe ATR with single reflection top-plate and pressure arm. Data are presented as the frequency of absorption (cm^{-1}). The spectra were recorded in the region of 4000–500 cm^{-1}.

The oil conversion to FAME was determined using proton nuclear magnetic resonance (^1H NMR) analysis and labelled as yield FAME production. Samples (100 mg) were mixed in 0.6 ml of $CDCl_3$. ^1H NMR spectra were recorded at 298 K with a Bruker Ascend 400 spectrometer equipped with a cryoprobe at 400 MHz (1H). ^1H NMR spectra were recorded at 298 K. The chemical shifts are provided in parts per million from $SiMe_4$ (^1H) as internal reference.

The Jatropha triglycerides (TAG) and the FAME products obtained of the direct transesterification reactions were determined using the electrospray coupled with mass spectrometry (ESI-MS) technique. Samples spectra using ESI-MS analyses were acquired either in the positive or negative ion mode using a microOTOF-Q II (Bruker Daltonics, Bremen, Germany) instrument. Samples were injected directly to the spectrometer. TAG's and FAME's related peaks were found in positive ion mode (ESI (+)-MS) while the free fatty acids (FFA's) related peaks were found in negative ion mode (ESI (−)-MS). The capillary potential was 2.7 kV, the dry gas temperature was 180 °C and the drying gas flow was 4 L/min. Total ion chromatograms from m/z 50 to 3000 were obtained. MS data were processed using Compass TM software (Bruker Daltonics).

2.3. Transesterification reactions

2.3.1. Procedure for the extraction of Jatropha oil

Jatropha curcas L. seeds were broken separately using an agate mortar to achieve the optimum oil extraction from the core of the seeds. The broken seeds were dried under vacuum at 70 °C. *Jatropha curcas* L seeds (50 g) were mixed in *n*-hexane (350 ml). Then, the oil extraction was carried out using the Soxhlet extraction method in *n*-hexane for 3 h. The mixture was cooled, and the *n*-hexane was evaporated. The oil obtained was characterized using FT-IR, ^1H NMR and ESI-MS techniques.

2.3.2. Procedure for the conventional transesterification of Jatropha oil

The oil obtained in the first step (2.3.1) was transesterified in methanol using basic ($NaOH/CH_3OH$, 5 wt% that corresponds to NaOH/oil, 1 wt%) homogeneous catalysts. The oil transesterification was carried out at 65 °C for 3 h. At the end of the reaction, the products were cooled to room temperature and were washed with distillated water. Then, the two phases were separated. The oil transesterification reaction in the presence of a basic heterogeneous (Na_2ZrO_3/oil, 3 wt%) catalyst was performed. The transesterification proceeded at 65 °C for 3 h. The product was placed into a vial and centrifuged in a Clinical 428 (120 V, 50/60 Hz) at 1400 rpm for 15 min to separate the phases and recover the catalyst. No water was required to purify the FAME.

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