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Evaluation of Indian milkweed (*Calotropis gigantea*) seed oil as alternative feedstock for biodiesel

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ABSTRACT

Calotropis gigantea (Indian milkweed) is a common plant in Asia that grows as a weed on open waste ground. Flowering and fruiting take place throughout the year. In this study, Indian milkweed oil was evaluated as a potential feedstock for biodiesel production. The oil was extracted from Indian milkweed seeds with hexane in a Soxhlet apparatus. The seeds were found to contain 33.3 wt% oil. The extracted oil was analyzed for the fatty acid profile and oil properties. Several previously unreported minor fatty acids were identified. Because the free fatty acid content in the oil was 27.5 wt%, acid-catalyzed esterification was conducted to esterify free fatty acids and alkali-catalyzed transesterification was performed to produce biodiesel. The triglyceride content, diglyceride content, monoglyceride content, free glycerol, methanol, ester content, carbon residue, acid value, oxidation stability, tocopherol, water content, kinematic viscosity, density, cloud point and flash point of the prepared biodiesel were determined. With the exception of oxidation stability, all fuel properties conformed to four standards (Philippine National Standard PNS2020:2003, Japanese Automotive Standards Organization JASO M360, European Standard EN 14214, American Society for Testing Materials ASTM D6751). However, it was found that this biodiesel can be only used in tropical countries due to the poor cold flow properties.

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1. Introduction

Biodiesel, the mono alkyl esters of long chain fatty acids, is a chemically modified fuel produced from plant oils (edible and non-edible), waste cooking oils and animal fats. This fuel is nontoxic (Lapinskiene et al., 2006) and biodegradable (Prince et al., 2008). The triacylglycerols which form the bulk of its feedstock come from renewable resources like vegetable and animal oils. Although both edible and non-edible oils can be used for biodiesel production, edible oils are widely used at the present time. It has been estimated that 95% of the biodiesel feedstock comes from edible oils (Gui et al., 2008). Converting edible oils into biodiesel may negatively affect the balance of demand between food and fuel and lead to higher food prices (Trostle, 2008; Sawangkeaw and Ngamprasertsith, 2013). Availability of feedstock is also a problem. Razon (2009) estimated that only about 18% of transport diesel fuel demand in 2006 would be met if the production of the top 12 vegetable oils in the world were used solely for diesel transport fuel. In order to avoid such problems, many researchers have studied a wide variety of plant oils to find new and possible alternative feedstocks for biodiesel production (Azam et al., 2005; Canakci and Sanli, 2008; Durrett et al., 2008; Haas and Foglia, 2005; Iiyama et al., 2008; Moser, 2009; Pinzi et al., 2009; Razon, 2009; Sawangkeaw and Ngamprasertsith, 2013). Among these alternative feedstocks, the most studied has been *Jatropha curcas* but commercial viability remains elusive (Contran et al., 2013) and the primary feedstocks around the world continue to be rapeseed oil, palm oil, soybean oil, sunflower oil and beef tallow (Hamelinck et al., 2012). It has been frequently pointed out that blending biodiesel obtained from different feedstocks may be the best

Abbreviations: AOCS, American Oil Chemists Society; ASTM, American Society for Testing Materials; EN, European Standards; FAME, fatty acid methyl esters; FFA, free fatty acids; JASO, Japanese Automotive Standards Organization; PNS, Philippine National Standards.

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strategy for producing biodiesel with optimal qualities (Knothe, 2008; Pinzi et al., 2009; Razon, 2009). Hence the prudent course of action would be to continue to identify and characterize as many alternative feedstocks as possible in order to give the blender flexibility in the formulation of an optimal biodiesel.

One possible candidate is *Calotropis gigantea* or Indian milkweed, a shrub of the genus *Calotropis* and the family *Asclepiadaceae*. It is commonly known as milkweed or swallow-wort. A related plant, *Asclepias syriaca* (common milkweed), a plant also in the Asclepiadaceae family, has been tested for its potential as a biodiesel feedstock (Holser and Harry-O'Kuru, 2006). However, while the two plants have similar common names, common milkweed is a temperate-zone plant (Holser and Harry-O'Kuru, 2006) while Indian milkweed is a tropical plant (Kumar et al., 2013). As will be discussed in the results below, the oils of the two plants are different from each other and thus their biodiesel fuel properties are also different.

Indian milkweed is native to China, India and Malaysia and has been found in most of Asia and large parts of Africa and South America (Kumar et al., 2013). The plant can be cultivated in large scale for biodiesel production as it can grow on many types of soils in different climates. Moreover, as its common name implies, Indian milkweed grows so easily and generates so much biomass that it is sometimes considered a weed (see, for example, Chamuah et al., 2013; Eapen et al., 2006). In addition, the flowering and fruiting can occur throughout the year and the seeds are easily propagated. With a spacing of 2 m × 2 m, the plant can grow 166 cm in one year (Kiew, 2001). Because of its wide distribution and fast growth, it has been studied extensively for possible practical uses. Kumar et al. (2013) reviewed all of these studies in general, while Kadiyala et al. (2013) reviewed possible phytochemical and pharmacological applications. Its strong, light floss has long been known as a potential fabric (Tuntawiroon et al., 1984) and it has more recently been studied as a possible raw material for use in manufacture of fiber-reinforced composites (Ashori and Bahreini, 2009). Its fast growth and hardy qualities have also made it an attractive candidate for phytoremediation of soil contaminated with radioactive elements (Eapen et al., 2006) and as a source of biomethane (Shilpkar et al., 2007).

Sundar Rao et al. (1983) indicated that the seeds contained 30.8 wt% pale-yellow oil. It may be useful to compare this oil content to jatropha seeds whose dehulled and dried seeds contain 52.9–57.4% oil (Foidl et al., 1996) and common milkweed whose seeds were reported to contain 25% oil (Harry-O'kuru et al., 2002). A more complete list for comparison may be found in Sawangkeaw and Ngamprasertsith (2013). Because it contains calotropin and flavonol glycosides, Indian milkweed oil is not acceptable as an edible oil (Sen et al., 1992). Therefore, the use of Indian milkweed oil as a feedstock is acceptable because it will not compete with the food supply. By analyzing fuel properties that are computable from the fatty acid profile obtained by Sundar Rao et al. (1983), Razon (2008) determined that Indian milkweed has the potential to be a feedstock for biodiesel. While the previous study (Razon, 2008) predicted the biodiesel fuel properties based on calculations, the present study reports actual conversion of *Calotropis gigantea* oils to fatty acid methyl esters and measurement of the biodiesel fuel properties.

2. Materials and methods

2.1. Gathering and preparation of seeds/oil extraction

The pods of Indian milkweed were picked from the tree when the pods started turning from green to brown in Kanbalu, Shwebo District, Sagaing Division, Myanmar in October, 2011. Seeds were separated from the floss manually then dried under the sun for 14 h. Photographs of the plant, seeds and floss may be seen in the Supplementary Data.

A Wonder® blender (WB-1) was used to grind the seeds. The ground seeds were oven-dried for 1 h at 105 °C and then extracted to get oil, using hexane in a Soxhlet apparatus at 60 °C for 8 h.

2.2. Determination of oil properties

Fatty acid profiles were determined by the United States Department of Agriculture/Agricultural Research Service. A Hewlett-Packard 6890 GC equipped with a flame ionization detector and a DB-88 (88% cyanopropyl methylarylpolysiloxane) column (30 m × 0.25 mm ID × 0.20 μm film thickness) was used. The oven temperature was programmed to start and hold at 150 °C for 15 min, increase to 210 °C at 2 °C/min then 50 °C/min to 220 °C and then hold at 200 °C for 5 min. Helium was used as the carrier gas at 9.6 mL/min. The injector and detector temperatures were 240 °C and 280 °C, respectively. Retention times were verified against authentic samples of individual pure FAME.

The heteroelements Na, K, Ca, Mg, P and S were determined with a Perkin Elmer (Waltham, MA, USA) Optima 7000 DV ICP OES spectrometer. Tocopherol concentration was analyzed using High Performance Liquid Chromatography (Shimadzu LC-10AT) equipped with Shodex Asahipak ODP-50 6D column and ultraviolent detector SPD-10A. Density was determined using an I-type hydrometer. Water content was checked by Karl Fischer moisture titrator MKC-520 (Kyoto Electronics MFG. Co. Ltd.) and Automatic Kinematic Viscosity Measuring System AKV-201 was used to test kinematic viscosity at 40 °C.

2.3. Experimental procedures for biodiesel production

The FFA content of the oils was 27.5 wt% and therefore, the biodiesel was produced through acid-catalyzed esterification with methanol followed by alkali-catalyzed transesterification. To select an appropriate methanol-to-oil molar ratio for the acid-catalyzed esterification, trials at the different molar ratios (6:1, 20:1, 40:1) were conducted with concentrated sulfuric acid at 5 wt% of oil. It was observed that the esterified products solidified when the lower ratios were used and therefore the 40:1 methanol-to-oil molar ratio was used. The reaction was conducted in a round bottom flask, mounted with a condenser, with a magnetic stirrer rotating at 400 rpm for 1 h. The flask was heated using an oil bath at 60–65 °C. The resulting mixture was transferred to a separatory funnel and allowed to settle for a minimum of 12 h to allow separation of the esterified oil (bottom layer) and the alcohol-water-acid (top layer). The esterified oil was separated and washed with distilled water. For each washing, 50 vol% distilled water of the oil was used and washings were done about 5 to 7 times. The esterified oil was filtered using anhydrous sodium sulfate to remove water.

The same reactor set up was used for alkali-catalyzed transesterification. Methanol (6:1 molar ratio to oil) and sodium hydroxide (1 wt% of oil) were mixed together until the sodium hydroxide was completely dissolved in methanol to form sodium methoxide solution. The prepared sodium methoxide solution was poured into the esterified oil and stirred for 1 h at 60–65 °C. After transesterification, the product mixture was transferred to the separatory funnel for a minimum of 12 h to separate the biodiesel (fatty acid methyl esters; FAME) and glycerol layer. The washing process was performed in the same way as washing after acid-catalyzed esterification. The biodiesel was then filtered and passed through anhydrous sodium sulfate to remove water.

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