

Characterization of Crude and Biodiesel Oils of *Jatropha curcas* and *Calophyllum inophyllum* in Guam *

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Abstract— Kernel oils of jatropha (*Jatropha curcas*) and da'ok (*Calophyllum inophyllum*) obtained in Guam were characterized for physio-chemical properties as potential biodiesels including calorific content, iodine value, peroxide value, saponification value, acid value, and moisture content. Jatropha oil had lower acid value, peroxide value and moisture content than da'ok crude oil. Additional pre-treatment of da'ok crude oil was necessary to prevent potential problems when converting to biodiesel. Crude oils of two species were converted to biodiesel using a supercritical methanol method. The composition of fatty acid methyl esters (FAMES) indicated that both crude oils and converted biodiesel of jatropha and da'ok contained palmitate (C16:0) with the range of 11.8-16.8% by weight, stearate (C18:0) with 6.5-8.6%, oleate (C18:1) with 40.5-52.6%, and linoleate (C18:2) with 22.0-34.2%. Based on FAMES, the cetane number was determined for jatropha and da'ok biodiesel as 52.7 and 54.1, respectively, indicating that both kernel oils were good source of feedstock to produce high quality biodiesel.

Introduction

Transportation fuels are the largest share of petroleum distillates consumed worldwide (US Energy Information Administration 2014), and account for an equal share of atmospheric emissions and other environmental effects (National Research Council 2011). Finding alternatives to distillate products such as diesel, gasoline, and kerosene is an important goal to meet growing projected demands (US Energy Information Administration 2011). Biofuel is a renewable energy to substitute petroleum-based energy to reduce global warming without the emissions of additional carbon dioxide. In Hawaii, two bio-energy forms, ethanol and biodiesel, have been studied, developed and utilized. Several oil-producing crops are summarized as biofuel plants in the insular tropics shown in Fig. 1 (Kinoshita 2006). An assessment of biomass-based ethanol production was reported based mainly on land availability, adaptability of crops to agroenvironments, and production of ethanol conversion technologies (Keffer et al. 2006). In their study, five tropical plants were considered as potential ethanol producing crops: sugarcane (*Saccharum officinarum*), napier grass (*Pennisetum purpureum*), two *Eucalyptus* spp. and giant leucaena (*Leucaena leucocephala*). For biodiesel, Oceanic Institute of Hawaii conducted a study on seed and nut processing and analysis for coconut (*Cocos nucifera*), kukui nut (*Aleurites moluccana*), and jatropha (*Jatropha curcas*) (Dominy et al. 2009). The extracted oils were further characterized for their quality, revealing that coconut oils appeared to be good feedstock while kukui and jatropha needed extra steps in the processing in

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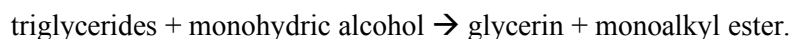
production of biodiesel (Litvin 2009). Coconut oil as biodiesel is being used in Pohnpei of the Federated States of Micronesia islands (Jim Currie, College of Micronesia, personal communication 2013), however since coconut is a valuable food crop in local cuisine, other non-edible crops have been searched for as biofuel crops. Examples of two non-edible crops on tropical islands are *J. curcas* and *C. inophyllum* (Ong et al. 2011). In Guam, the initial assessment of alternative energy was conducted in 2010-2011 and pointed out that Guam has limited agricultural land availability for production of commercial quantities of oils (Baring-Gould et al. 2011).

A collaborative study to develop low NO_x emitting biodiesel fuels from *Jatropha curcas*, *Calophyllum inophyllum*, and *Cocos nucifera* was performed earlier to enhance energy security and promote sustainable environments in Pacific islands with support of a SunGrant (the US Department of Transportation, Office of the Secretary, Grant No. DTOS59-07-G-00055). Participants of the project included University of Hawaii (UH), University of Alaska Fairbanks (UAF), University of Guam (UOG), College of Micronesia (COM), and Northern Marianas College (NMC). Oils of three species were collected from Pacific islands and were sent to UAF for chemical analysis. The result of the study indicated that oils collected from all locations were converted to biodiesel except *C. inophyllum* oil from Saipan. The study also suggested that chemical properties of crude oils varied due possibly to locality, agronomic environments, and oil extracting methods (Table 1). In Guam, two non-edible oil producing trees, *C. inophyllum* and *J. curcas* were selected to examine their potential as biodiesel sources in Guam.

Calophyllum inophyllum exists commonly in Guam as a landscape plant, windbreak, and coastal plant. It is a large evergreen tree in the family Calophyllaceae (formerly Clusiaceae) known commonly as da'ok in the Marianas islands, kamani in Hawaii, and tamanu in South Pacific islands (Fig. 2). This widely cultivated tree tolerates salt spray and strong wind. Seed oils are utilized for medicinal and cosmetic use as "tamanu oil" in other Pacific islands (Friday & Ogoshi 2010). A study in India indicated that the fatty-acid methyl ester of *C. inophyllum* seed oil met all of the major biodiesel requirements in the USA (ASTM D 6751-02, ASTM PS 121-99), Germany (DIN V 51606) and European Union (EN 14214), and the average oil yield was projected as 11.7 kg-oil/tree or 4680 kg-oil/ha (Azam et al. 2005).

Jatropha curcas, commonly known as jatropha, tuba-tuba (in Guam) and physic nut, belongs to the family Euphorbiaceae (Fig. 3). It is native to Tropical America and is now cultivated world-wide. This drought-resistant shrub or small tree can thrive in a wide range of environmental conditions. *Jatropha* oil-production is considered an option for rural development in the tropic and subtropic regions (Grass 2009). *Jatropha* is grown in Guam as an ornamental or a hedge plant (Stone 1970).

Biodiesel is the term used to describe the production of monoalkyl esters via transesterification. Transesterification is the process of taking a triglyceride molecule from plants and animal fats and oils, neutralizing the free fatty acids and producing an alcohol ester along with a glycerin molecule shown in the reaction of:



As an equilibrium reaction, excess monohydric alcohol, often methanol, must be added to maintain the reaction favoring the production of the monoalkyl ester. The reaction is aided by the addition of small quantities of either acid or base catalysts that speed up the reaction. The acid and base catalyzed reactions have been used at commercial scale in production of monoalkyl esters (US Energy Information Administration 2014), however the process requires the special storage, handling and disposal of acid and base chemicals. For islands like Guam, the transport of highly corrosive chemicals such as acids or bases by ship and air becomes a liability risk that potentially increases the cost of production and poses environmental risks to the island's fragile ecosystems.

An alternative approach is to perform the transesterification using supercritical fluids (Bernal et al. 2012, Tan & Lee 2011, Ilham & Saka 2010, Imahara et al. 2008, Demirbas 2005). This method

eliminates the need for acid or base catalysts, and the transesterification of the available triglycerides and the esterification of the fatty acids occurs simultaneously. Supercritical methanol has been used successfully to transesterify various plant derived triglycerides (Anitescu & Bruno 2012, Bernal et al. 2012, Tan & Lee 2011, Demirbas 2005). When a supercritical fluid has reached its critical temperature (T_c) and critical pressure (P_c), the characteristics of the fluid change dramatically from its state at room temperature and standard atmospheric pressure, exhibiting different solubility, polarity and diffusivity among many other properties (Soria et al. 2008a, 2008b). Reaction times are often relegated to seconds, and when the supercritical state is reversed back to a condition of room temperature and regular atmospheric pressure, most products are stable. For biodiesel, the most common aliphatic alcohols used are methanol ($T_c=512.2K$, $P_c=8.1$ MPa), ethanol ($T_c=615.2K$, $P_c=6.4$ MPa), iso-propanol ($T_c=537.2K$, $P_c=5.1$ MPa) and iso-butanol ($T_c=560.2K$, $P_c=4.9$ MPa).

In this study, we evaluated jatropha and da'ok kernel oils collected in Guam and converted oils to biodiesel with the supercritical methanol method. These biodiesels were characterized for their chemical properties to determine their potential bioenergy source for Guam.

Materials and Methods

OIL EXTRACTION

Fruits of jatropha and da'ok were collected from trees at Yigo Agricultural Experiment Station Farm in Yigo and University of Guam campus in Mangilao, respectively. Jatropha seeds were removed from the nuts by hand and dried in an oven at 37°C for five days. The dried seeds were ground using a food processor and the oil was extracted using an oil press (Model 70, AgOil Press Co. Eau Claire, WI). The extracted oil was stored in clear glass containers at room temperature. The kernels of da'ok were removed from the outer shell using a wooden nutcracker. The cream-colored kernels were dried in an oven at 37°C for 30 days. Kernels were then ground in a food processor and oil was extracted using the oil press. The extracted oil was stored in glass containers at room temperature. Upper layers of clear oil were collected for both jatropha and da'ok, leaving behind a layer of sediments on the bottom and sent to University of Alaska for chemical analysis.

OIL CHARACTERIZATION

(1) Preparation of Crude Oil for Chemical and Physical Analysis:

The oils were stored at room temperature and away from light until analysis. Some of the oils had fine solids, which required vacuum filtration before characterization analysis. All analyses were conducted in triplicates to present the average values.

(2) Calorific Content Determination:

The calorific content of jatropha and da'ok oils was determined using the procedure described in ASTM E711-87. An IKA Oxygen Bomb calorimeter was used, employing gel capsules to enclose the oils. Calculations were performed using IKA Software as per ASTM standards.

(3) Iodine Value:

To measure the degree of unsaturation of the oils, the iodine value was determined as the grams of iodine that are absorbed in 100g of oil samples based on ASTM D1959-97.

(4) Peroxide Value

The peroxide value of oil is indicative of the potential for that oil to become rancid or oxidize impeding its conversion and reducing its performance as a biofuel. Peroxide value was determined by titration as described in Ekop et al. (2007), and was expressed as the milliequivalents of peroxide per kg of oil.

(5) Saponification Value

Saponification is the process of treating a neutral fat with an alkali substance, breaking it down into glycerol and fatty acids. The saponification value is defined as the amount of alkali needed to saponify a given quantity of oil, as expressed in mg of KOH/g of sample as per ASTM D94-07. The analysis determined the total conversion potential of each oil based on biodiesel production via traditional transesterification methods.

(6) Acid Value

Acid value for biodiesel derived from oils are calculated based on the lower alkyl ester of fatty acids, as established by ASTM D974. The process involved a volumetric standard of KOH, used along with a titration solvent and an indicator solution as detailed in ASTM D974, using each oil sample. The basis for the reaction was to determine the total amount, as measured in milligrams of KOH that were needed to neutralize the free acids present in 1g of oil.

(7) Moisture Content

Moisture is defined for biodiesel production as water in the oil resulting in soap formation rather than biodiesel. The best procedure for determining water in oils involves the conversion of water into a gas, like hydrogen, and measuring the pressure generated by the gas within an enclosed vessel. The analysis was performed using a Sandy Brae Water Test Kit, which provides a measure of water as ppm (Sandy Brae Laboratories Inc., Newark, DE 19713).

SUPERCRITICAL METHANOL BIODIESEL PRODUCTION METHOD

J. curcas and *C. inophyllum* oils were converted into biodiesel using supercritical methanol. A Parr instruments 4740 reactor vessel was filled with 28mL of HPLC grade methanol and 6mL of oil, meeting a molar ratio of 40:1 methanol to oil. This ratio was stoichiometrically determined as the necessary methanol required to transesterify the oils in the reactor vessel and to achieve supercritical state ($T_c = 238^\circ\text{C}$, $P_c = 1178$ psig). The vessel was sealed and inserted in an electronically controlled heating chamber where the temperature was raised to 350°C , above the T_c . Given the batch nature of the reactor vessel, with every increase in temperature there was an increase in pressure. For the volumes of materials selected, the reactor pressure reached 3000 psig at the maximum temperature. A rotovap was used to remove any residual methanol from the mixture collected after each reaction.

BIODIESEL CHARACTERIZATION

(1) Preparation of Standards and Sample Oils:

The standards were prepared by dissolving 3.6mg of heneicosanoic acid (C21:0) in 25mL of n-hexane, 30.7mg of oleic acid, 13.9mg linoleic acid, 15.1mg palmitic acid and 14.7mg stearic acid. For jatropha crude oil and biodiesel, 26.6mg of the sample oil was dissolved in 1mL of heneicosanoic acid solution (4.1mg C21:0 in 10mL of n-hexane), while for da'ok 23.1mg of sample oil were dissolved in 1mL of the heneicosanoic acid solution prior to derivatization.

(2) Derivatization:

Derivatization is the process of substituting functional groups with more volatile species to aid the gas chromatography analysis. Derivatization of oils is necessary as the boiling point of some of the components of the oils do not readily volatilize or react under thermal conditions to yield unwanted products. We chose to use a standard BF_3 derivatization using boron trifluoride (BF_3) as the agent (Supelco, Sigma-Aldrich Co. 1998).

For analysis of jatropha and da'ok crude oil, after 1mL of the sample was added to 2mL of BF_3 and 1mL of water scavenger (2, 2-dimethoxypropane) in a 15mL test tube, the mixture was vortexed, and allowed to stand for 10min in a water bath heated to 60°C . Once the solution cooled, 1mL of distilled water and 1mL of n-hexane were added. When the phases were visually separated, the upper

layer was removed using a Pasteur pipet. The contents of the pipet were treated with anhydrous sodium sulfate in a 5mL test tube. A Pasteur pipet was used to transfer the liquid into a GC vial for analysis.

For jatropha and da'ok biodiesel, the same procedure used for crude oils were applied except an additional step of rotovaping to remove the remaining methanol from the mixture prior to injection of samples to GC. Quantification of fatty acid methyl ester (FAME) compositions was obtained from the triplicate runs.

(3) Cetane Number:

Cetane number (CN) is used for predicting the ignition quality of biodiesel as proxy to the ASTM D613 measurement, and is estimated by a multiple linear regression model from contribution of the fatty acid methyl ester (FAME) compositions (Tong et al. 2011). In this study, CN was estimated by an equation developed by Gopinath et al. (2009):

$$CN = 62.2 + 0.017L + 0.074M + 0.115P + 0.177S - 0.130O - 0.279LI - 0.366LL$$

where L, M, P, S, O, LI and LL are the weight percentage of methyl laurate (C12:0), myristate (C14:0), palmitate (C16:0), stearate (C18:0), oleate (C18:1), linoleate (C18:2) and linolenate (C18:3), respectively. Determination of these FAME compositions was performed by gas chromatography, using standards of the individual compounds, retention times and mass spectral data, along with NIST 05 libraries.

Results

OIL CHARACTERIZATION

Table 2 shows calorific value, iodine value, peroxide value, saponification value, acid value and moisture content of jatropha and da'ok oils collected from Guam. Jatropha oil had higher calorific content of 42,187 J g⁻¹ than da'ok of 40,910 J g⁻¹. Both iodine value (82.9 mg iodine g⁻¹ for jatropha and 84.9 mg iodine g⁻¹ for da'ok) and saponification value (183.9 mg KOH g⁻¹ for jatropha and 200.2 mg KOH g⁻¹ for da'ok) were not significantly different. However, peroxide value and acid value were significantly lower for jatropha oil than da'ok oil (p<0.0001). Peroxide value and acid value of jatropha oil were 2.59 and 0.07, respectively. Da'ok oil had 13.12 peroxide value and 28.1 acid value. Moisture content was also lower for jatropha (0.035%) than da'ok (0.061%) (p<0.05).

FATTY ACID METHYL ESTER COMPOSITION AND CETANE NUMBER OF OIL & BIODIESEL

The composition of fatty acid methyl esters (FAMES) for the crude oil and the biodiesel produced by supercritical methanol conversion method were compared by GC/MS derivatization. The resulting spectrums indicated the presence of FAMES that corresponded to 16 carbon chains (C16) to 18 carbon chains (C18), with a marked shift in their make up after the conversion. The data showed the percentage by weight of palmitate (C16:0), stearate (C18:0), oleate (C18:1) and linoleate (C18:2) (Table 3). Jatropha biodiesel had 52.6% oleate by weight while da'ok biodiesel had 43.5%. Oleate was the greatest in the weight % for both jatropha and da'ok biodiesel, which were increased from the crude oils by 7% for jatropha and 11% for da'ok. The weight % of palmitate, stearate, and oleate were also increased when oils were converted to biodiesel while the weight % of linoleate was decreased after conversion. The cetane number was calculated as 52.7 and 54.1 for jatropha biodiesel and da'ok biodiesel, respectively.

Discussion

The study showed that kernel oils from jatropha and da'ok obtained in Guam were potential sources of biodiesel. Calorific value is an important parameter that indicates the amount of fuel energy generated from oil. In this study jatropha oil had a calorific value of $42,187 \text{ J g}^{-1}$, and da'ok had $40,910 \text{ J g}^{-1}$. A study in literature showed that calorific number of biodiesel ranged from $39,000$ to $41,000 \text{ J g}^{-1}$ (Oliveira & De Silva 2013). Calorific value of jatropha oil was reported as $39,455 \text{ J g}^{-1}$ (Oliveira & De Silva 2013), $39,230 \text{ J g}^{-1}$ (Ong et al. 2011), and $38,500 \text{ J g}^{-1}$ (Sahoo & Das 2009). Our earlier work determined the calorific values of jatropha with range of $43,039 - 43,953 \text{ J g}^{-1}$ (Table 1). Similarly, da'ok was reported to have calorific values of $41,397 \text{ J g}^{-1}$ (Ong et al. 2011, Sanjid et al. 2013), $39,100 \text{ J g}^{-1}$ (Belagur & Chitimi 2013), $39,250 \text{ J g}^{-1}$ (Sahoo & Das 2009) and the range of $36,489 \text{ J g}^{-1} - 41,887 \text{ J g}^{-1}$ in our early work (Table 1). Calorific values of jatropha and da'ok oils in the present study were slightly lower than that of diesel shown as $45,843 \text{ J g}^{-1}$ (Oliveira & De Silva 2013), $43,000 \text{ J g}^{-1}$ (Belagur & Chitimi 2013) and $42,000 \text{ J g}^{-1} - 45,900 \text{ J g}^{-1}$ (Sanjid et al. 2013). It is suggested that higher calorific values of biodiesel contained greater amounts of ethyl esters with longer carbon chain (Oliveira & De Silva 2013).

The factors affecting the transesterification process, oil viscosity and operation of diesel engines were the iodine value, peroxide value, saponification value, acid value, and the moisture content and therefore indicate the quality of biodiesel (Crane et al. 2005, Murugesan et al. 2009a, 2009b). The iodine number is a measure of the degree of unsaturation as an indication of oxidative potential and as an overall indicator of the stability of the oil and biodiesel (Schober & Mittelbach, 2007). Low iodine number is indicative of better quality oil. The European biodiesel specifications EN14214 limits the maximum iodine value to 120 (Schober & Mittelbach 2007, Atadashi et al. 2010, Ong et al. 2011). The iodine values for jatropha and da'ok determined in this study were 82.9 mg iodine/g and 84.9 mg iodine/g , respectively, and they were much lower than the permitted maximum number according to EN14214. Other studies indicated the iodine values of jatropha as 103 (Toscano et al. 2012), 93 (Azam et al. 2005), $96 - 103$ (Naresh et al. 2012) and $91-109$ in our earlier work (Table 1). Iodine value of da'ok was reported as 71.5 (Azam et al. 2005), 90 (Crane et al. 2005), $82-98$ (Belague & Chitimi, 2013) and $87-104$ in our earlier study (Table 1).

The saponification value is an index of the total fatty acids present in oil (Toscano et al. 2012) as average molecular weight of triacylglycerols in the oil (Odoom & Edusei 2015). A higher saponification value suggests a higher incidence of corrosion problems to parts of the diesel engines (Belagur & Chitimi 2013). Saponification values of several seed oils reported earlier as the range of $168-202 \text{ mg KOHg}^{-1}$ (Belagur & Chitimi 2013), $173-200 \text{ mg KOHg}^{-1}$ (Toscano et al. 2012) and $169-312 \text{ mg KOHg}^{-1}$ (Azam et al. 2005). Four accessions of jatropha contained the saponification numbers ranged from $184 - 198$ (Naresh et al. 2012). Both saponification values of jatropha ($183.9 \text{ mg KOHg}^{-1}$) and da'ok ($200.2 \text{ mg KOHg}^{-1}$) oils in this study fell within the range of saponification values reported earlier from seed oils as biodiesel feedstock. Higher saponification values, $212 - 268$, from coconut (*Cocos nucifera*) oil originating from different Micronesian islands shown in Table 1 suggested that these oils were also good to use in production of soaps and shampoos, since the greater number of the saponification value, the better the soap making ability of the oil (Odoom & Edusei 2015).

The acid value of jatropha oil ($0.7 \text{ mg KOH g}^{-1}$) was much lower than da'ok oil ($28.1 \text{ mg KOH g}^{-1}$) in this study ($P < 0.0001$, Table 2). The acid number, an indicator of the acids present in oils generally as free fatty acids (FFAs) is defined as the amount of mg of KOH neutralized by FFAs in one gram of oil (Angelovie et al. 2014). FFAs are responsible for oxidation of the oils, resulting in a decrease of fuel stability (Atadashi et al. 2010, Angelovie et al. 2014). Reported acid number of jatropha oil was 28.0 (Tiwari et al. 2007), 13.8 (Feng et al. 2011), 3.8 (Sahoo & Das 2009), and $3.69-5.89$ (Naresh et al. 2012). In our earlier work, it ranged $0.7-3.9$ (Table 1). The acid value of da'ok was reported as 44 (Sahoo & Das, 2009), and 22.4 (Crane et al. 2005). Table 1 presents the range of

38.4-85.5 from four samples of da'ok oil collected from the Mariana islands. Two samples from Saipan were not transesterified into biodiesel due to high acid value and high contents of impurities (Soria, unpublished data).

The biodiesel property specification in American standards ASTM D6751 limits the acid number of biodiesel as 0.80 as maximum, and European Union EN14104 as 0.50 (Sanjid et al. 2013). The acid value was reduced during the transesterification process to convert crude oils to biodiesel (Ong et al. 2011, Tiwari et al. 2007). The acid value of jatropha biodiesel was reported as 0.21 (Oliveira & Da Silva 2013) and 0.40 (Tiwari et al. 2007). Sahoo et al. (2009) showed reduction of acid number from unrefined jatropha oil to biodiesel from 3.8 to 1.6 and from unrefined da'ok oil to biodiesel from 44 to 1.62.

To evaluate the potential rancidity directly, peroxide value was determined in both the jatropha and da'ok crude oils. The oils from jatropha showed a low peroxide value (Table 2), consistent with the acid value in the study, indicating that jatropha is a better quality oil. Da'ok, on the other hand showed elevated peroxide value, suggesting the potential for da'ok to polymerize, oxidize or transform into unwanted by-products as the result of storage, handling or exposure to oxidative atmospheres, light or other factors. However, Sahoo et al. (2009) demonstrated that after successfully converting to biodiesel from unrefined da'ok oil to meet the quality of the ASTM standards, da'ok biodiesel could be used as substitute fuel, either with or without blending with conventional diesel oil, for a water-cooled 3-cylinder tractor engine. They also noted that there was a reduction in smoke emission by addition of biodiesel.

The moisture content is also analyzed to assess the quality of the oil and ASTM D6751-02 Standards limit the moisture content of biodiesel to 0.030% and DIN EN14214 to 0.05% (Tiwari et al. 2007). The higher the moisture, the lower the quality of the fuel. When the moisture content is high, soaps can result from the conversion process. In our study the water content in jatropha oils was near trace amount levels (0.035%), an indicator of good feedstock quality. Da'ok oil had higher moisture with 0.061%. Pre-treatment with hexane followed by filtration removed the amount of moisture, solids and free fatty acids, resulting in adoption of da'ok oil as a biodiesel feedstock in this study. The amount of water content reduced greatly from 1.4% of jatropha oil to 0.025% in jatropha biodiesel in the study by Tiwari et al. (2007).

The supercritical methanol processing used in this study was very effective for conversion of the jatropha and da'ok oils into biodiesel, showing the conversion efficiencies higher than 92% on a volume basis in this study. Saka & Kusdiana demonstrated that, in a preheating temperature of 350°C and at a pressure of 45–65 MPa, 240 s of supercritical methanol treatment was sufficient to convert rapeseed oil to methyl esters. It was also found that this supercritical methanol process required shorter reaction time and simpler purification procedure without a catalyst. Kusdiana & Saka (2004) demonstrated that the presence of water did not have a significant effect on biodiesel yield when they used supercritical methanol treatment.

In our study jatropha oil was easily handled and visible solids were filtered. On the other hand, da'ok oil needed to have filtering and hexane cleaning process to remove fine particles before subjecting a process to produce biodiesel. The supercritical methanol method eliminated foaming or color change that indicates the presence of secondary compounds in oil, hampering the transesterification process. In a preliminary study, jatropha oil was transesterified using base catalysts and the resulting biodiesel foamed inside the injector system of a vehicle, resulting in hydrolocking or the process of air "locking" the pistons within the internal combustion engine, causing it to stop operating (Soria, unpublished data). Therefore, the supercritical methanol method was used in this experiment to avoid oxidation or some chemical change during storage, processing or use.

Table 3 shows composition analysis of fatty acid methyl esters (FAMES) in both jatropha and da'ok oils and their biodiesel after conversion. There was the highest concentration of oleate (C18:1) in all oils and biodiesel. Three other FAMES detected were palmitate (C16:0), stearate (C18:0), and

linoleate (C18:2), while laurate (C12:0), myristate (C14:0) and linolenate (C18:3) were not detected. The cetane number (CN) was estimated using a linear regression equation developed by Gopinath et al. (2009). CN is a measurement of ignition quality of diesel fuel. The standards of biodiesel have been set at a minimum of 47 (ASTM D6751) or 51 (EN14214) (Knothe 2005). The present study showed that CN of jatropha biodiesel was 52.7, which increased from 49.0 as crude jatropha oil after conversion. Similarly, da'ok biodiesel had CN of 54.1 compared to 51.6 of crude oil (Table 3). Azam et al. (2005) summarized physio-chemical properties of seed oils of 75 species from literatures and showed the CN range of 20.7 to 67.5, including jatropha of 52.3 and da'ok of 57.3. Our earlier study determined the range of 50.3 to 54.1 for jatropha oil and 55.0 to 60.4 for da'ok oil (Table 1). The present study showed both jatropha biodiesel with CN of 52.7 and da'ok biodiesel with 54.1 were greater than standards of biodiesel, ASTM D6751 and EN14214, indicating that both jatropha and da'ok oils collected in Guam are good feedstock to produce biodiesel.

Conclusions

1. The current study suggests both jatropha and da'ok oil as good feedstock for biodiesel production.
2. Da'ok needed extra steps for pre-treatment prior to transesterification process including the use of hexane and filtration to remove the free fatty acids, water and solids that were found in the crude oils.
3. Jatropha oil was of better quality as a feedstock than da'ok oil due to less moisture, a lower acid value, and lower iodine value.
4. Both jatropha and da'ok biodiesel, produced via supercritical methanol generated a large proportion of C18 fatty acid methyl esters.

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References

- Angelovie, M., Z. Tkae & J. Jablonicky. 2014. Determination model for cetane number of biodiesel at different fatty acid composition: a review. *Animal Science and Biotechnologies* 47:365-371.
- Anitescu, G. & Bruno, T.J. 2012. Fluid properties needed in supercritical transesterification of triglyceride feedstocks to biodiesel fuels for efficient and clean combustion: A review. *Journal of Supercritical Fluids* 63:133-149.
- Atadashi, L.M., M.K. Aroua & A.A. Aziz. 2010. High quality biodiesel and its diesel engine application: A review. *Renewable and Sustainable Energy Reviews* 14:1999-2008.
- ASTM D1959 – 97. Standard test method for iodine value of drying oil and fatty acids. *Annual Book of Standards*, Section 8.10. Pub: ASTM International, West Conshohocken, PA 19428 – 2959, USA.
- ASTM D94 – 07 Standard Test Methods for Saponification Number of Petroleum Products, Pub: ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428 – 2959, USA.
- ASTM D974 Standard Test Method for Acid and Base Number by Color-Indicator Titration, *Annual book of ASTM Standards*, vol. 08.15, American Society for Testing and Materials, West Conshohocken, PA, 2008, pp.1–7
- ASTM Standard E 711-87 Standard Test Method for Gross Calorific Value of Refuse-Derived Fuel by the Bomb Calorimeter. *ASTM Annual Book*. Conshohocken, PA, 2004, DOI: 10.1520/E0711-87R04
- Azam, M.M., A. Waris & N.M. Nahar. 2005. Prospects and potential of fatty acid methyl esters of some non-traditional seed oils for use as biodiesel in India. *Biomass and Bioenergy* 29:293-302.
- Baring-Gould, I., M. Conrad, S. Hasse, E. Hotchkiss & P. McNutt. 2011. Guam Initial Technical Assessment Report. National Renewable Energy Laboratory Technology Report NREL/TR-7A40-50580. 75p.
- Belagur, V.K. & V.R. Chitimi. 2013. Few physical, chemical and fuel related properties of *Calophyllum inophyllum* Linn (honne) oil and its blends with diesel fuel for their use in diesel engine. *Fuel* 109:356-361.
- Bernal, J.M., P. Lozano, E. Garcia-Verdugo, M.I. Burguete, M. Vaultier & V.L. Salntiago. 2012. Supercritical Synthesis of Biodiesel Molecules 17:8696-8719.
- Crane, S., G. Aurore, H. Joseph, Z. Mouloungui & P. Bourgeois. 2005. Composition of fatty acids triacylglycerols and unsaponifiable matter in *Calophyllum calaba* L. oil from Guadeloupe. *Phytochemistry* 66:1825-1831.
- Demirbas, A. 2005. Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods. *Progress in Energy and Combustion Science* 31:466-487.
- Dominy, W., W. Kashiwa, G. Nagaue & K. Chang. 2009. Oceanic Institute – Seed and Nut Processing & Analysis. In *Biodiesel from Fuel Crops in Hawaii*. A report to Environmental Protection Agency pp.6-17.
- Ekop, S.A., B.A. Etuk & N.O. Eddy. 2007. Effect of some local additives on the chemical constituent of palm oil. *Journal of Applied Sciences and Environmental Management*. 11:85-89.
- Feng, F.G., Z. Fang, X.F. Tian, Y.D. Long & L.Q. Jiang. 2011. One-step production of biodiesel from *Jatropha* oil with high-acid value in ionic liquids. *Bioresource Technology* 102:6469-6472.
- Friday, J. & R. Ogoshi. 2011. Farm and forestry production and marketing profile for tamanu (*Calophyllum inophyllum*). In: Elevitch, C.R. (ed.) *Specialty Crops for Pacific Island Agroforestry*. Permanent Agriculture Resources (PAR), Holualoa, Hawaii. <http://agroforestry.net/scps>.
- Gopinath, A., S. Puhan & G. Nagarajan. 2009. Relating the cetane number of biodiesel fuels to their fatty acid composition: a critical study. *Proceedings of the Institution of Mechanical Engineers, Part B: Journal of Engineering Manufacture* 223:565-583.
- Grass, M. 2009. *Jatropha curcas* L. Visions and Realities. *Journal of Agriculture and Rural Development in the Tropics and Subtropics* 110:29-38.
- Ilham, Z. & S. Saka. 2010. Two-step supercritical dimethyl carbonate method for biodiesel production from *Jatropha curcas* oil. *Bioresource Technology* 101:2735-2740.

- Imahara, H., E. Minami, S. Hari & S. Saka. 2008. Thermal stability of biodiesel in supercritical methanol. *Fuel*: 8, 1–6.
- Keffer, V., D. Evans, S. Turn & C. Kinoshita. 2006. Potential for ethanol production in Hawaii. Dept. of Business, Economic Development and Tourism, State of Hawaii. 58p.
- Kinoshita, C. 2006. *Ethanol Production Option*. Presented at Hawaii Agriculture Bioenergy Workshop, Panel on Hawaii Crop Production Opportunities. Oct. 27, 2006.
- Knothe, G. 2005. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. *Fuel Processing Technology* 86:1059-1070.
- Kusdiana, D. & S. Saka. 2004. Effects of water on biodiesel fuel production by supercritical methanol treatment. *Bioresource Technology* 91:289-295.
- Litvin, L. 2009. Pacific Biodiesel Technologies – Oil characterization, biodiesel processing & analysis. In *Biodiesel from Fuel Crops in Hawaii*. A report to Environmental Protection Agency pp.19-28.
- Murugesan, A., C. Umarani, T.R. Chinnusamy, M. Krishnan, R. Subramanian & N. Nedunchezian. 2009a. Production and analysis of bio-diesel from non-edible oils-A review. *Renewable and Sustainable Energy Review* 13:825-834.
- Murugesan, A., C. Umarani, R. Subramanian & N. Nedunchezian. 2009b. Bio-diesel as an alternative fuel for diesel engines – A review. *Renewable and Sustainable Energy Review*. 13:653-662.
- Naresh, B., M.S. Reddy, P. Vijayalakshmi, V. Reddy & P. Devi. 2012. Physio-chemical screening of accessions of *Jatropha curcas* for biodiesel production. *Biomass and Bioenergy* 40:155-161.
- National Research Council. 2011. *Renewable Fuel Standard: Potential Economic and Environmental Effects of U.S. Biofuel Policy*. Washington, DC: The National Academies Press, 2011. doi:10.17226/13105.
- Odoom, W. & V.O. Edusei. 2015. Evaluation of saponification value, iodine value and insoluble impurities in coconut oils from Jomoro district in the western region of Ghana. *Asian Journal of Agriculture and Food Sciences*. 3:494-499.
- Oliveira, L.E. & M.L.C.P. Da Silva. 2013. Comparative study of calorific value of rapeseed, soybean, jatropha, and crambe biodiesel. *International Conference on Renewable Energies and Power Quality, Bilbao (Spain)*, on 20-22 March 2013. 4p
- Ong, H.C., T.M.I. Mahlia, H.H. Masjuki & R.S. Norhasyima. 2011. Comparison of palm oil, *Jatropha curcas* and *Calophyllum inophyllum* for biodiesel: A review. *Renewable and Sustainable Energy Reviews* 15:3501-3515.
- Oliveira, L.E. & M.L.C.P. Da Silva. 2013. Comparative study of calorific value of rapeseed, soybean, jatropha curcas, and crambe biodiesel. *International Conference on Renewable Energies and Power Quality, Bilbao (Spain)*, on 20-22 March 2013. 4p.
- Sahoo, P.K. & L.M. Das. 2009. Process optimization for biodiesel production from Jatropha, Karanja and Polanga oils. *Fuel* 88:1588-1594.
- Sahoo P.K., L.M. Das, M.K.G. Babu, P. Arora, V.P. Singh, N.R. Kumar & T.S. Varyani. 2009. Comparative evaluation of performance and emission characteristics of jatropha, karanja and polanga based biodiesel as fuel in a tractor engine. *Fuel* 88:1698-1707.
- Sanjid, A., H.H. Masjuki, M.A. Kalam, S.M. Ashrafur Rahman, M.J. Abedin & S.M. Palash. 2013. Impact of palm, mustard, waste cooking oil and *Calophyllum inophyllum* biofuels on performance and emission of CI engine. *Renewable and Sustainable Energy Reviews* 27: 664-682.
- Schober, S. & M. Mittelbach. 2007. Iodine value and biodiesel: Is limitation still appropriate? *Lipid Technology* 19:1-4.
- Stone, B.C. 1970. *The Flora of Guam*. Micronesia, 6:658p.
- Soria, A.J., A.G. McDonald & S.R. Shook. 2008a. Wood solubilization and depolymerization using supercritical methanol. Part 1: Process optimization and analysis of methanol insoluble component (bio-char). *International Journal of the Biology, Chemistry, Physics, & Technology of Wood*. 62:402-408.
- Soria, A.J., A.G. McDonald & B.B. He. 2008b. Wood solubilization and depolymerization using supercritical methanol. Part 2: Analysis of methanol soluble compounds. *International Journal of the Biology, Chemistry, Physics, & Technology of Wood*. 62:409-416.

- Tan, K.T. & K.T. Lee. 2011. A review on supercritical fluids technology in sustainable biodiesel production. *Renewable and Sustainable Energy Reviews* 15:2452–2456.
- Tiwari A.K., A. Kumar & H. Raheman. 2007. Biodiesel production from jatropha oil (*Jatropha curcas*) with high free fatty acids: An optimized process. *Biomass and Bioenergy* 31:569–575.
- Tong, D., C. Hu, K. Jiang & Y. Li. 2011. Cetane number prediction of biodiesel from the composition of the fatty acid methyl esters. *Journal of the American Oil Chemist's Society* 88:415-423.
- Toscano, G., G. Riva, E. Foppa Pedretti & D. Duca. 2012. Vegetable oil and fat viscosity forecast models based on iodine number and saponification number. *Biomass and Bioenergy* 46:511-516.
- US Energy Information Administration. 2014. Assumptions to the Annual Energy Outlook 2014. Electronic link: <http://www.eia.gov/forecasts/aeo/assumptions/pdf/transportation.pdf>, accessed Sept 16, 2014.
- US Energy Information Administration. 2011. Monthly Biodiesel Production Report, Electronic link: <http://www.eia.gov/biofuels/biodiesel/production/>, accessed Sept 22, 2014.

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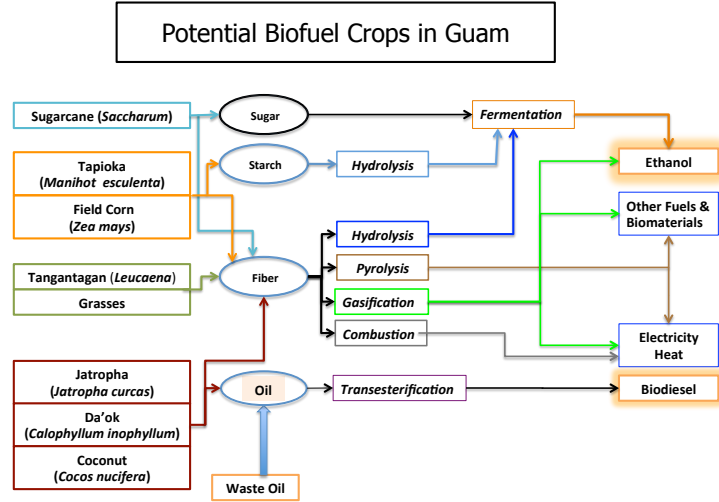


Fig. 1. Potential biofuel crops in Guam. Flow chart is indicating processing to produce biofuels. (from Marutani and Martinez, presented at the 5th Regional Conference of Island Sustainability on April 15, 2014)



Fig. 2. *Calophyllum inophyllum* showing: tree (2A), fruits on a tree (2B), harvested fruits (2C), cracked nuts (2D), fresh kernels (2E), ground dry kernels (2F), calophyllum oil and sediment (2G).

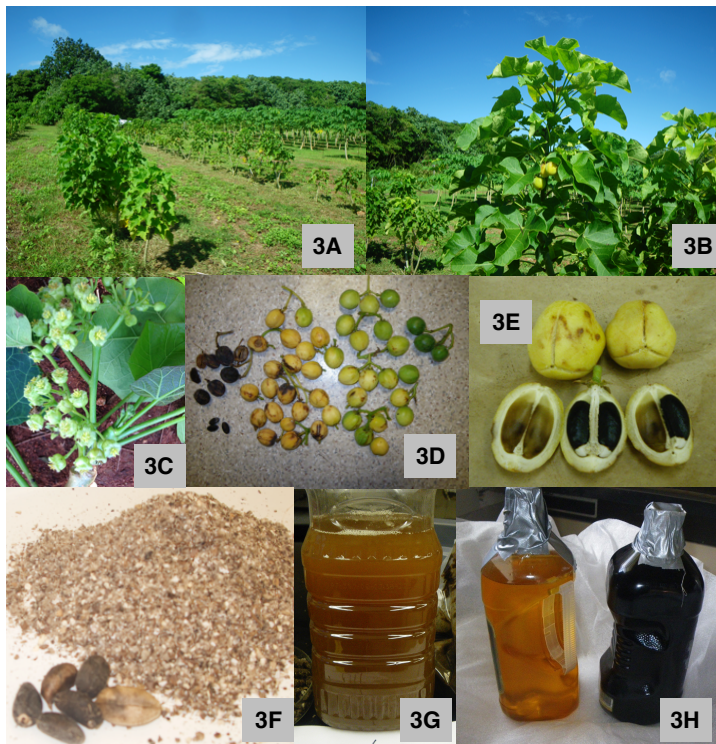


Fig. 3. *Jatropha curcas* showing: field planting in Guam (3A); a close-up tree (3B); inflorescences (3C), different stages of fruits (3D); open fruit with three seeds in each fruit (3E); dried seeds and ground seeds before extracted oil (3F); oil extracts (3G); and final product of crude oils of jatropa (left) and da'ok (right) after removing sediments (3H).

Table 1. Characterization of crude oils of *Jatropha curcas*, *Calophyllum inophyllum*, and *Cocos nucifera* from Hawaii, Mariana islands, and Micronesian islands. (Sortia, A., unpublished data, from a study supported by the US Department of Transportation, Office of the Secretary, Grant No. DTOS59-07-G-00055)

Feedstock	Location	Physical state at room temp.	Color	Heating content (J/g)	Saponification value mgKOH/g	Acid value mgKOH/g	Moisture content %	Iodine value mg iodine/g	Cetane number	Did it transesterify into biodiesel?	Emissions Test of biodiesel-IM240*	Emissions Test of biodiesel-Idel*
<i>Jatropha curcas</i>	Kula, Maui Hawaii	Liquid	Clear gold /yellow	43039.3	191.0	0.7	0.12	109	50.3	Yes	Yes	Yes
	Pearlho, Oahu, Hawaii	Liquid	Deep gold/yellow	43953.4	192.9	3.9	0.10	100	52.1	Yes	Yes	Yes
<i>Calophyllum inophyllum</i>	Guam, Mariana Is.	Liquid	Brown/gold	43276.1	192.7	1.8	0.10	91	54.1	Yes	Yes	Yes
	Saipan, Mariana Is.	Solid	Dark green	36489.5	153.3	85.5	0.10	104	58.6	No	No	No
	Saipan, Mariana Is.	Liquid	Dark green	38661.6	164.5	48.0	0.18	95	58.0	No	No	No
	Rota, Mariana Is.	Liquid	Dark green	38640.1	159.7	38.4	0.16	89	60.4	Yes	Yes	Yes
<i>Cocos nucifera</i>	Guam, Mariana Is.	Liquid	Dark green	41887.1	193.2	38.8	0.10	87	55.0	Yes	Yes	Yes
	Saipan, Mariana Is.	Solid/liquid	Tan/brown	37511.5	214.3	4.3	0.16	6	70.5	Yes	Yes	Yes
	Tinian, Mariana Is.	Solid	White	37628.2	212.3	4.1	0.10	6	70.6	Yes	Yes	Yes
	Rota, Mariana Is.	Solid	cream/ivory	37585.4	213.1	2.4	0.10	7	70.4	Yes	Yes	Yes
	Pohnpei, Sapwirik 1 Micronesia	Solid	White	41401.7	261.5	2.4	0.10	6	65.9	Yes	Yes	Yes
	Pohnpei, Sapwirik 2 Micronesia	Solid	White	37435.6	267.7	1.0	0.12	6	65.3	Yes	Yes	Yes
	Pohnpei, Pehleng Micronesia	Solid	White	37254.2	261.8	0.5	0.10	6	65.9	Yes	Yes	Yes
	Kosrae, Uwe Micronesia	Solid	White	41230.6	265.0	3.1	0.14	7	65.3	Yes	Yes	Yes
	Kosrae, Tafuna Micronesia	Solid	White	41277.9	267.7	1.5	0.14	7	65.3	Yes	Yes	Yes

Table 2. Characterization of *Jatropha curcas* (jatropha) and *Calophyllum inophyllum* (da'ok) crude oils in this experiment. Values are averages of triplicate runs.

	Crude oil of jatropha	Crude oil of da'ok	p-value (t-test)
Calorific value (J/g)	42187.5	40910.4	0.0045*
Iodine value (mg iodine/g)	82.9	84.9	0.525 ns
Peroxide value (ug/g)	2.59	13.12	<0.0001 ***
Saponification value (mg KOH/g)	183.9	200.2	0.1483ns
Acid value (mg KOH/g)	0.7	28.1	<0.0001 ***
Moisture (%)	0.035	0.061	0.0246 *

*, *** and ns mean significant at 0.05, 0.001 level and nonsignificant, respectively.

Table 3. Composition of fatty acid methyl esters (FAMES) of crude oil and biodiesel obtained from jatropha (*Jatropha curcas*) and da'ok (*Calophyllum inophyllum*) and cetane number.

Fatty acid methyl ester *	Jatropha		Da'ok	
	Crude Oil (Weight %)	Biodiesel (Weight %)	Crude Oil (Weight %)	Biodiesel (Weight %)
Palmitate (C16:0)	11.8	16.7	14.6	16.8
Stearate (C18:0)	6.5	8.6	12.0	14.6
Oleate (C18:1)	47.5	52.6	40.5	43.5
Linoleate (C18:2)	34.2	22.0	32.8	25.1
Cetane number	49.0	52.7	51.6	54.1

* Laurate (C12:0), myristate (C14:0), and linolenate (C18:3) were not detected from the samples.