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Biodiesel Production from a Novel Nonedible Feedstock, Soursop (*Annona muricata* L.) Seed Oil

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Abstract: This study investigated the optimal reaction conditions for biodiesel production from soursop (*Annona muricata*) seeds. A high oil yield of 29.6% (*w*/*w*) could be obtained from soursop seeds. Oil extracted from soursop seeds was then converted into biodiesel through two-step transesterification process. A highest biodiesel yield of 97.02% was achieved under optimal acid-catalyzed esterification conditions (temperature: 65 °C, 1% H_2SO_4, reaction time: 90 min, and a methanol:oil molar ratio: 10:1) and optimal alkali-catalyzed transesterification conditions (temperature: 65 °C, reaction time: 30 min, 0.6% NaOH, and a methanol:oil molar ratio: 8:1). The properties of soursop biodiesel were determined and most were found to meet the European standard EN 14214 and American Society for Testing and Materials standard D6751. This study suggests that soursop seed oil is a promising biodiesel feedstock and that soursop biodiesel is a viable alternative to petrodiesel.

Keywords: *Annona muricata*; biodiesel production; seed oil; soursop; two-step process

1. Introduction

Fossil fuel depletion and environmental concerns have stimulated the search for alternative fuels from renewable sources. Biodiesel, a biomass-derived fuel, is renewable, exhibits superior combustion properties, and is completely suitable for diesel engines [1,2]. Furthermore, the use of biodiesel results in relatively low environmental pollution because biodiesel is sulfur free and emits minimal carbon monoxide and hydrocarbons [3–5]. Because of these merits, biodiesel has been developed worldwide to replace petrodiesel.

Biodiesel has been mainly produced from edible oil using an acid, alkali, or enzyme catalyst [6,7]. Nevertheless, the use of edible oil as a feedstock increases the production cost of biodiesel [8], thus limiting the commercialization of biodiesel. Furthermore, the use of edible feedstock for fuel purpose may cause adverse effects on food supply [9–11]; therefore, alternative feedstocks must be identified for biodiesel synthesis. Numerous cheap and nonedible feedstocks, including microalgae oil [12–14], Jatropha oil [15,16], waste cooking oil [17–19], insect fat [20–22], Chinese tallow tree seed oil [23], tobacco seed oil [24], sweet basil seed oil [25], *Brucea javanica* seed oil [26], spent coffee grounds [27], and food waste [28] have been investigated as vital feedstocks for biodiesel synthesis. Two-step transesterification (acid-catalyzed esterification followed by alkali-catalyzed transesterification) is a promising method to produce biodiesel from high free fatty acid oils [29,30]. The acid oils (fatty acid content >1%, *w*/*w*) should be esterified using an acid catalyst to lower the oil acidity before applying an alkali catalyst to transesterify the oil into biodiesel [31–33]. This two-step process not only minimizes soap formation but also enhances biodiesel yield [31,34,35].

Soursop (*Annona muricata* L.), which belongs to the Annonaceae family, is an economically critical crop worldwide [36,37]. *A. muricata* is native to North and South America and is popularly distributed in the tropical and subtropical areas of Western Africa, Central America, the Caribbean, and the Asian continent [37–39]. The *A. muricata* tree is approximately 5–8-m tall with low branches [39], and the trees yield up to 10 tons of fruit per hectare [38]. The oval or heart-shaped fruit is 15–30-cm in length, 10–20-cm in width, and, on average, weighs up to 4.0 kg [36,39]. The edible white pulp of soursop fruit comprises about 80% water, 18% carbohydrate, 1% protein, and 1% fiber content and contains beneficial vitamins [40]. The mesocarp contains numerous black seeds, which are each approximately 2 cm long and 1 cm wide [36]. The soursop is mainly cultivated for its fruit, which is used in fresh and processed forms in the production of juice, ice cream, sherbet, beverages, and candy [37,41,42]. The use of soursop fruit in food production results in various waste materials, including seeds which account for 5–8.5% of the fruit [37,38,43]. The seeds are usually discarded and cannot be used as animal feed because they contain toxic substances such as annonacin and acetogenins [37,43,44]. Studies have shown that oil comprises up to 40% of the soursop seed [37]. The seed oil mainly comprises palmitic acid, oleic acid, and linoleic acid [37,45]. This composition is similar to that of other biodiesel feedstocks [24,29,31]. Therefore, the nonedible soursop seed oil is a promising and cheap biodiesel feedstock. In addition, the use of this seed for biodiesel synthesis can resolve the problematic surplus of the seed in the food industry. Only few studies have reported the potential use of this seed oil for biodiesel production [46,47]. However, no optimization study on reaction conditions has investigated for biodiesel production from *A. muricata* seed oil.

This study optimized the reaction factors for producing biodiesel from *A. muricata* seed oil. Because of the presence of a high level of free fatty acid (FFA) in the seed oil, a two-step process was used to convert FFAs and triglycerides into biodiesel. The effects of reaction factors (molar ratio of methanol to oil, temperature, catalyst amount, and reaction time) on esterification and transesterification were investigated to optimize the reaction conditions. The biodiesel's properties were finally characterized according to the American Society for Testing and Materials (ASTM) methods.

2. Materials and Methods

2.1. Materials

Ripe soursop fruits were purchased from Thu Duc Agromarket (Ho Chi Minh City, Vietnam). The seeds were removed from the fruit and air-dried at room temperature for 3 days. The soursop seed kernels were then separated from the hulls, ground with a blender (EUPA TSK-935BAP, Tsann Kuen Enterprise Co., Ltd., Taipei, Taiwan), and stored at room temperature. Methanol, sulfuric acid, sodium hydroxide, n-hexane, and other reagents used in this study were of analytical grade ($\geq$99.0% purity) and were obtained from Tedia Company, Inc. (Fairfield, CT, USA).

2.2. Extraction of Crude Oil

Soursop seed powder was immersed in n-hexane (1:4, w/v) at room temperature for 2 days, and stirred to extract the oil from soursop seed. After extraction, the hexane layer was separated from solid residue by filtration (Advantec No. 5C filter paper). The n-hexane was then removed using a R300 Buchi Rotary Evaporator (Büchi Labortechnik, Flawil, Switzerland), and the soursop seed crude oil was obtained. The crude oil's properties, such as acidity, saponification, and iodine values, were measured using the standard method [48,49].

2.3. Production of Biodiesel through Two-Step Process

2.3.1. Esterification Step

An H_2SO_4-catalyzed pretreatment was employed to reduce the oil's acidity and convert its FFAs into biodiesel. To study the influence of reaction factors on esterification, several experimental trials were conducted in a sealed reactor with stirring under different conditions: molar ratios of methanol to oil (4:1–12:1), temperatures (45–85 °C), catalyst amounts (0.25–2.0%), and reaction times (30–150 min). After each reaction, the samples were withdrawn to evaluate the FFA conversion.

2.3.2. Transesterification Step

The oil pretreated through H_2SO_4-catalyzed esterification was used for the transesterification step. The esterified reaction mixture was kept in a funnel for phase separation. After two phases were completely separated, the crude oil and biodiesel (upper layer) was poured into a sealed reactor and subsequently transesterified into biodiesel using NaOH as catalyst. A set of experiments with various methanol to oil molar ratios (4:1–12:1), temperatures (45–85 °C), catalyst amounts (0.4–1.2%), and reaction times (15–75 min) were studied for their effects on the conversion yield. After each reaction, the reactor was placed at room temperature for phase separation. The mixture's upper layer containing biodiesel was collected to determine the biodiesel yield.

2.4. Analysis

The acid value (AV) of the oil sample was measured using a titration method reported previously [50,51]. The FFA conversion was then calculated as follows:

$$\text{FFA conversion } (\%) = \frac{\text{AV}_1 - \text{AV}_2}{\text{AV}_1} \times 100 \quad (1)$$

where AV_1 is the initial acid value, and AV_2 is the acid value after the esterification reaction.

The composition of the biodiesel was quantified using a Shimadzu GC-2014 gas chromatograph system (Shimadzu Corp., Kyoto, Japan) equipped with a Stabilwax capillary column (Restek Corp., Bellefonte, PA, USA) and a flame ionization detector (Shimadzu Corp., Kyoto, Japan) according to the procedure reported in our previous study [10]. The fatty acid profiles of the soursop biodiesel were characterized based on Supelco 37 Component FAME Mix reference standards (Sigma-Aldrich Corp., St. Louis, MO, USA). The biodiesel content was quantified by comparing the peak areas of fatty acid methyl esters with those of the internal standard, methyl pentadecanoate. The soursop biodiesel yield was then calculated as follows [10]:

$$\text{Biodiesel yield } (\%) = \frac{A_{\text{sample}}}{A_{\text{standard}}} \times \frac{W_{\text{standard}}}{W_{\text{sample}}} \times \frac{W_{\text{biodiesel}}}{W_{\text{oil}}} \times 100 \quad (2)$$

where A_{sample} is peak area of biodiesel sample, A_{standard} is peak area of international standard, W_{sample} is weigh of biodiesel sample, W_{standard} is weight of internal standard, $W_{\text{biodiesel}}$ is weight of total biodiesel product, and W_{oil} is weight of oil used.

The acid value, viscosity, sulfur content, water content, ester content, cetane index, density, and flash point of the produced biodiesel were determined using the ASTM D664, D445, D5453, D95, D7371, D613, D1480, and D93 methods, respectively [52].

3. Results and Discussion

3.1. Properties of Soursop Seed Oil

Table 1 shows the characteristics of soursop seed oil. The oil extracted from soursop seeds reached the yield of 29.6%, demonstrating the soursop seed's high oil content and subsequent potential as

an oil source. The saponification value of soursop seed oil was 244.7 mg KOH/g, indicating that the average molecular weight of soursop seed oil was 884.4 g/mol. The acid value of the soursop seed oil was 54.4 mg KOH/g, indicating a high FFA content. Biodiesel production processes must be refined to maximize the value of materials and minimize costs [25,53,54]. To maximize the biodiesel yield from oils with high FFA levels, esterification must be performed to reduce the level of FFAs prior to transesterification [31,34,35]. Therefore, the two-step process of acid-catalyzed esterification followed by alkali-transesterification was selected for biodiesel synthesis from soursop seed oil in this study.

Table 1. Properties of crude soursop seed oil.

Fat Yield (%)	Acid Value (mg KOH/g)	Saponification Value (mg KOH/g)
29.6 ± 0.2	54.4 ± 0.4	244.7 ± 1.6

3.2. Conversion of FFAs into Biodiesel through Acid-Catalyzed Esterification

3.2.1. Effect of Methanol to Oil Molar Ratio

Esterification pretreatment enhances the biodiesel yield by reducing the oil's acidity and converting its FFAs into biodiesel [29,51]. To optimize reaction conditions, this study investigates the influences of methanol to oil molar ratio, temperature, H_2SO_4 amount, and reaction time on the FFAs conversion. First, esterification was performed at 75 °C with 1% H_2SO_4 (w/w) and various methanol to oil molar ratios (4:1–12:1) for 60 min. As shown in Figure 1a, FFA conversion was greater at higher methanol to oil molar ratios. This result corresponds with those of other studies [35,55]. The molar ratio of methanol to oil is a critical factor affecting the efficiency of esterification reactions. A high methanol to oil molar ratio is required to drive esterification reactions toward completion [55]. In this work, the highest FFA conversion occurred at the methanol:oil molar ratio of 12:1. However, the FFA conversion had insignificant differences between the methanol:oil molar ratios of 12:1 and 10:1. Therefore, the methanol:oil molar ratio of 10:1 was chosen for the next experiments.

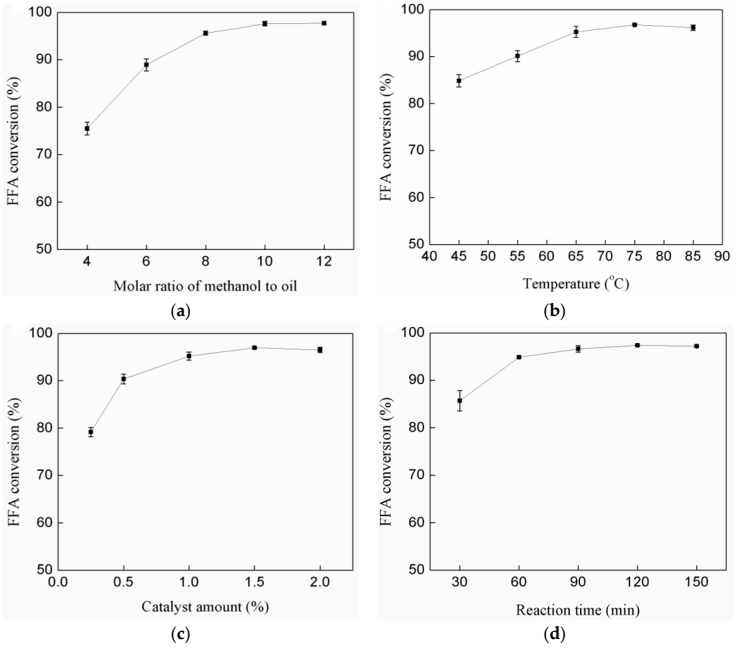

Figure 1. Effects of (**a**) molar ratio of methanol to oil (with a fixed temperature of 75 °C, 1% H_2SO_4, and a reaction time of 60 min); (**b**) temperature (with a fixed methanol:oil molar ratio of 10:1, 1% H_2SO_4, and a reaction time of 60 min); (**c**) catalyst amount (with a fixed methanol:oil molar ratio of 10:1, a temperature of 65 °C, and a reaction time of 60 min); and (**d**) reaction time (with a fixed methanol:oil molar ratio of 10:1, a temperature of 65 °C, and 1% H_2SO_4) on FFA conversion in soursop seed oil.

3.2.2. Effect of Temperature

To investigate the impact of temperature on the efficiency of esterification, the reaction was performed at various temperatures (45–85 °C), whilst keeping the other factors constant. As shown in Figure 1b, FFA conversion was enhanced from 84.86 to 96.16% when the temperature was increased from 45 to 85 °C. This result is reasonable because a high temperature enhances the reaction rate [51,56]. However, no significant differences were found in the proportion of FFA conversion at temperatures of 65, 75, and 85 °C. Therefore, to reduce energy consumption, 65 °C was selected as the optimal temperature for the esterification reaction.

3.2.3. Effect of Catalyst Amount

The results in Figure 1c reflect the effect of sulfuric acid amount on FFA conversion. FFA conversion significantly improved when the catalyst levels increased from 0.25 to 1.0%. Nevertheless, increasing the catalyst load to 1.5% resulted in only a slight increase in FFA conversion, and a 2% catalyst load caused a slight decrease in conversion efficiency. This slight decrease at a 2% catalyst load is similar to of the results of other studies [35,55]. Excess H_2SO_4 catalyst can activate the polymerization of unsaturated FFA, causing the product's darkened color due to the oxidation and decarboxylation of FFA [55]. Therefore, 1.0% H_2SO_4 was chosen as the optimal catalyst amount for further experiments.

3.2.4. Effect of Reaction Time

Various reaction times (30–150 min) were tested for esterification performed at 65 °C with a methanol:oil molar ratio of 10:1 and 1% H_2SO_4 (w/w). As shown in Figure 1d, FFA conversion increased from 85.71 to 96.61% when increasing reaction time from 30 to 90 min. Increases in reaction times beyond 90 min resulted in insignificant increases in FFA conversion, indicating that reactions reached equilibrium at 90 min. In conclusion, the optimal conditions for the H_2SO_4-catalyzed esterification were determined to be a methanol:oil molar ratio: 10:1, a temperature: 65 °C, 1% H_2SO_4 (w/w), and 90 min. These conditions were thus used in this study for the esterification step in biodiesel production.

3.3. Conversion of Triglyceride into Biodiesel through Alkali-Catalyzed Transesterification

3.3.1. Effect of Methanol to Oil Molar Ratio

The esterified oil was used as the material for producing biodiesel through alkali-catalyzed transesterification. To optimize transesterification conditions, the influences of methanol to oil molar ratio, temperature, NaOH amount, and reaction time on the biodiesel yield were examined. First, transesterification was performed at 65 °C with 0.8% NaOH (w/w) and various methanol to oil molar ratios (4:1–12:1) for 30 min. As can be seen from Figure 2a, the biodiesel yield increased from 81% to 96.37% when the molar ratio of methanol to oil was increased from 4:1 to 8:1. Nevertheless, a higher methanol to oil molar ratio caused a decrease in the biodiesel yield. This result is consistent with that reported in the study of biodiesel synthesis from *Jatropha curcus* seed oil [31] and *Croton megalocarpus* oil [57]. A high level of methanol may have increased the glycerol solubility in the solution, driving the equilibrium to a reverse reaction and thus lowering the biodiesel yield [57]. Therefore, this study selected the methanol:oil molar ratio of 8:1 as the optimal reactant ratio for transesterification.

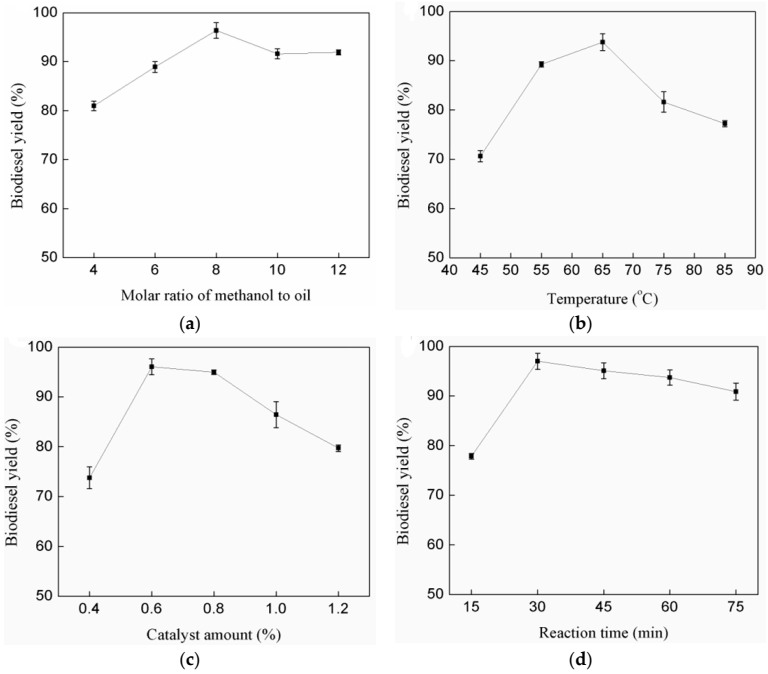

Figure 2. Effects of (**a**) molar ratio of methanol to oil (with a fixed temperature of 65 °C, 0.8% NaOH, and a reaction time of 30 min); (**b**) temperature (with a fixed methanol:oil molar ratio of 8:1, 0.8% NaOH, and a reaction time of 30 min); (**c**) catalyst amount (with a fixed methanol:oil molar ratio of 8:1, a temperature of 65 °C, and a reaction time of 30 min); and (**d**) reaction time (with a fixed methanol:oil molar ratio of 8:1, a temperature of 65 °C, and 0.6% NaOH) on transesterification of soursop seed oil.

3.3.2. Effect of Temperature

To investigate the influence of temperature on the biodiesel yield, transesterification was carried out at various temperatures (45–85 °C) with a methanol to oil molar ratio, NaOH amount, and reaction time maintained at 8:1, 0.8%, and 30 min, respectively. As can be seen from Figure 2b, the biodiesel yield increased when temperature was increased from 45 to 65 °C. Nevertheless, the biodiesel yield reduced at temperatures greater than 65 °C. This result is in agreement with those of other studies [57,58]. A high temperature may have enhanced side reactions, including saponification, thus resulting in a lower biodiesel yield [57]. Based on this result, 65 °C was chosen as the optimal temperature for the transesterification.

3.3.3. Effect of Catalyst Amount

Catalyst amount is a critical factor affecting the efficiency of transesterification. In this study, various NaOH amounts were tested with other factors maintained as constant to evaluate the influence of NaOH amount on the biodiesel yield. Results revealed that the biodiesel yield increased when the amount of catalyst increased from 0.4 to 0.6% (Figure 2c). However, when the catalyst amount is higher than 0.6%, the biodiesel yield reduced. Excess catalyst favored the saponification reaction, enhancing the formation of an emulsion and gel, thus lowering the biodiesel yield [31,55,57]. Therefore, 0.6% NaOH was selected for use in further experiments.

3.3.4. Effect of Reaction Time

Finally, the influence of reaction time on the biodiesel yield was examined using the optimal reaction conditions obtained in previous experiments. Transesterification was performed at 65 °C with a methanol:oil molar ratio of 8:1, 0.6% NaOH (*w*/*w*), and various reaction times (15–75 min). As indicated in Figure 2d, the biodiesel yield increased from 77.85 to 97.02% when the reaction time increased from 15 to 30 min. A reaction time longer than 30 min caused a slight decrease in the biodiesel yield. Therefore, a reaction time of 30 min was determined as sufficient for the transesterification reaction. In conclusion, the highest biodiesel yield of 97.02% was achieved under the following optimal transesterification conditions: 65°C, 0.6% NaOH (*w*/*w*), 30 min, and methanol:oil molar ratio of 8:1.

3.4. Fatty Acid Profiles of Soursop Biodiesel

Table 2 illustrates the fatty acid profiles of soursop biodiesel in comparison with rapeseed biodiesel. Nine fatty acid methyl esters were identified in the soursop biodiesel, among which oleic acid methyl ester (43.68%), linoleic acid methyl ester (32.45%), and palmitic acid methyl ester (18.14%) were present in the highest amounts. The synthesized biodiesel was found to comprise 78.07% unsaturated fatty acids and 21.93% saturated ones. The saturated fatty acid level in soursop biodiesel was higher than that of rapeseed biodiesel (4.3%) [51], indicating a higher cetane index for the soursop biodiesel. This is because the high level of saturated fatty acid increases the cetane index of a fuel [59]. In addition, because saturated fatty acid methyl esters exhibit higher oxidative stability than unsaturated ones [4,60], the soursop biodiesel can have more oxidative stability than rapeseed biodiesel. These results suggest that soursop seed oil is a suitable feedstock for biodiesel synthesis.

Table 2. Fatty acid methyl ester compositions of soursop biodiesel compared with rapeseed biodiesel.

Composition	Rapeseed Biodiesel [a] (%)	Soursop Biodiesel [b] (%)
Palmitic acid methyl ester (C16:0)	3.5	18.14
Palmitoleic acid methyl ester (C16:1)	na [c]	0.81
Stearic acid methyl ester (18:0)	0.8	3.79
Oleic acid methyl ester (C18:1)	64.4	43.68
Linoleic acid methyl ester (C18:2)	22.3	32.45
Linolenic acid methyl ester (C18:3)	8.2	1.13

[a] Data obtained from Reference [51]; [b] This study; [c] na = none reported.

3.5. Properties of Soursop Biodiesel

The soursop biodiesel's properties were characterized using ASTM standard methods and were compared with the corresponding properties of rapeseed biodiesel [51]. As indicated in Table 3, most soursop biodiesel's properties were similar to those of rapeseed biodiesel. Remarkably, most properties of synthesized biodiesel, sulfur content (0.04%), ester content (98.6%), viscosity (5.5 mm^2/s), water content (300 mg/kg), cetane number (53), density (868 kg/m^3), and flash point (123°C), met the standards ASTM D6751 [52] and EN 14,214 [61]. These results indicate that the synthesized biodiesel may serve as an alternative to petrodiesel. Moreover, the high ester content in the biodiesel indicates that the conditions identified in this study are optimal for the esterification and transesterification reactions. However, the acid value of synthesized biodiesel was 0.8, which was higher than the standards EN 14,214 and ASTM D6751: this could be due to the presence of free fatty acid in the biodiesel product. A further purification step is therefore required in order to reduce the acid value [62].

Table 3. Soursop biodiesel's properties compared with those of rapeseed biodiesel, the standards ASTM D6751, and EN 14214.

Properties	ASTM Method	ASTM D6751 [a]	EN 14214	Rapeseed Biodiesel [b]	This Study
Acid value (mg KOH/g)	D664	<0.5	<0.5	0.31	<0.8
Sulfur content (wt. %)	D5453	<0.05	<0.05	<0.01	0.04
Ester content (%)	D7371	na [c]	>96.5	na [c]	98.6
Viscosity at 40 °C (mm^2/s)	D445	1.9–6.0	3.5–5.0	6.35	5.5
Water content (mg/kg)	D95	na [c]	<500	300	300
Cetane number	D613	>47	>51	45	53
Density (kg/m^3)	D1480	na [c]	860–900	880	868
Flash point (closed cup) (°C)	D93	100–170	>120	na [c]	123

[a] Data obtained from Reference [52]; [b] Data were obtained from Reference [51]; [c] na = none reported.

3.6. The Feasibility of Soursop Seed Oil as Biodiesel Feedstock

With an increasing demand for renewable energy, biodiesel has been widely produced to replace petrodiesel. To reduce the production cost, various non-edible feedstocks including microbial oil [12–14], waste cooking oil [17–19], insect fat [20–22], and plant seed oil [23–25], have been studied for biodiesel production because of their low-price. However, the availability of those oils is still a major concern for large-scale production [10]. Therefore, efforts have been made to search for new low-cost biodiesel feedstocks. In recent years, the use of plant seed obtained from fruit production industry for biodiesel production has attracted much attention due to its low cost and availability [25,26]. In the state of Bahia (Brazil), approximately 20 thousand tons of soursop fruit are produced annually, thus producing about 1.7 thousand tons of soursop seed each year [37]. Since soursop is an economically important crop worldwide [37,41], the global food production from soursop fruit can cause a problematic surplus of this seed. To add value to the soursop seeds, the effective method of recycling these seeds is being investigated. In the present study, soursop seeds were used as a non-edible feedstock for biodiesel production—a solution to the soursop seed disposal problem. The results suggested that soursop seed can be a potential biodiesel feedstock along with other non-edible plant seed oils.

4. Conclusions

This paper investigates the use of soursop seed oil for biodiesel production. In the current study, the reaction conditions of acid-catalyzed esterification and alkali-catalyzed transesterification were optimized to maximize biodiesel yield. Under optimized conditions, 97.02% biodiesel yield was obtained. The properties of the soursop biodiesel were determined and were found to meet the ASTM D6751 and EN 14214. The results of this study suggest that soursop seed oil is a potential biodiesel feedstock and the soursop biodiesel can serve as an alternative for petrodiesel.

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