BIODIESEL PRODUCTION FROM *Swietenia macrophylla* (MAHOGANY) SEEDS

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Abstract

Extraction of oil from the seeds of Swietenia macrophylla was carried out to determine its potential for bio-oil production and the eventual making of liquid biodiesel products. Central composite design of the response surface methodology was the experimental design employed considering reaction time, catalyst loading and amount of methanol as operating variables in the production of biodiesel. The biodiesel production, produced via transesterification process using the extracted oil from the seed, was catalyzed by potassium hydroxide and methanol. Hexane was used as the solvent in the extraction of oil from the seed. Essential characteristics of the seed, the extracted oil from the seed, and the produced biodiesel were all determined. The result showed that the seed has a moisture content of 10.6%. About 48.44% by weight of seed was elevated as bio-oil with 0.86 g/cm3 density and 6.25 pH. After refining, 36.10% by weight of the extracted oil constituted the final biodiesel product. The FTIR analysis identified the possible presence of alkanes, esters, aromatics, hydroxyl, and carbonyl in the biodiesel, compounds which are similar to the other biodiesel profile. Calorific analysis revealed biodiesel's high heating value of 39.87 MJ/kg, generally equal to 40 MJ/kg of the commercial heavy fuel. This work demonstrated that seeds from S. macrophylla are useful biomass in the production of high-energy biodiesel, a finding with huge implications for the biofuel industry.

Keywords: *biodiesel production; mahogany seed oil; transesterification; biofuel, Swietenia macrophylla seed*

1.0 Introduction

The imminent depletion of oil reserves around the world is becoming a major problem facing a world hungry for energy. Already, the high dependence on the energy of the transportation sector creates a volatile market with ever increasing prices of petroleum-derived fuels (Jacobson, Maheria, Dalai, & Kumar Dalai, 2013). This havoc prompts many concerned individuals to find alternative energy sources that could substitute the need for fuel, particularly liquid fuel, needed for transportation. The abundance of biomass worldwide is seen as one promising alternative source of energy. Exploitation of various biomass sources has been explored in the production of biofuels. First generation biofuels from food-based products such as bioethanol from corn, wheat or sugar beets sources and biodiesel from rapeseed and sunflowers have been commercially produced in biorefineries (Demirbas, 2011). However, the debate of food security versus biofuel production continues to be a challenge carrying social implications from first generation biofuel sources. Second generation biofuel from lignocellulosic feedstocks (like agricultural wastes), non-food crops and forest products are likewise used in bio-refineries.

Swietenia macrophylla is one of the tropical trees that could potentially provide biofuel products. Among the less utilized parts during fruiting stage are the matured discarded. Particularly, more than 50% of the components of the seed of the S. macrophylla are carbon (48.14%) and hydrogen (6.4%), the elements composing the biofuel products (Kader, Joardder, Islam, Das, & Hasan, 2012). With appropriate extraction method, compounds comprising carbon and hydrogen present in the seeds could become the elemental composition of a biofuel product either solid biochar, liquid bio-oil, or biogas.

Among the biofuels that needs intensive research considering its infancy stage is the production of liquid biofuel in the form of bioethanol, bio-oil, biogasoline and biodiesel. In this work, the oil of the S. *macrophylla* seeds was extracted and processed with the ultimate goal of producing high-quality biodiesel. Response surface methodology was employed to carefully study the interactive and overlapping effects of all the operating variables and got the best conditions that would optimize biodiesel production.

2.0 Materials and Methods

2.1 Preparation of S. Macrophylla Seeds

The S. *macrophylla* capsules were collected from Claveria, Misamis Oriental, Philippines. The seeds were manually taken from the capsules and sundried in 10 h (Aliyu, Lomsahaka, & Hamza, 2012). The moisture content of the sundried seeds was calculated following ASTM E1756, and using Eqs 1&2.

$$MC = \left[\left(\frac{M_i - M_f}{M_i}\right) x100\right] \quad \text{[Eq 1]}$$

$$MC_{Average} = \frac{MC_1 + MC_2 + MC_3}{3} \quad \text{[Eq 2]}$$

where MC is the moisture content of the seeds, M_i is the initial mass of the seeds and M_f is the mass of the seeds after oven drying.

2.2 Oil Extraction from S. macrophylla Seeds

Oil extraction adopted the methods reported elsewhere in extracting oils from seeds (Liauw et al., 2008). Sundried seeds were pulverized manually using mortar and pestle. For 24 h, the 25 g of ground seeds were soaked in 40 mL n-hexane in the closed 100 mL beaker. After 24 h, the mixture was filtered separating the residues from the filtrate. The filtrate was then heated on a hot plate at 60 ^oC for 5 min. The final product was allowed to cool and weighed to constitute the extracted oil. The oil yield was calculated using Eq 3.

$$\%Y = \left[\left(\frac{m_2}{m_1}\right) x\ 100\right] \quad \text{[Eq 3]}$$

where %Y is the percent yield of the oil extracted, m_1 is the initial mass of the S. *macrophylla* seed, and m_2 is the mass of the extracted oil.

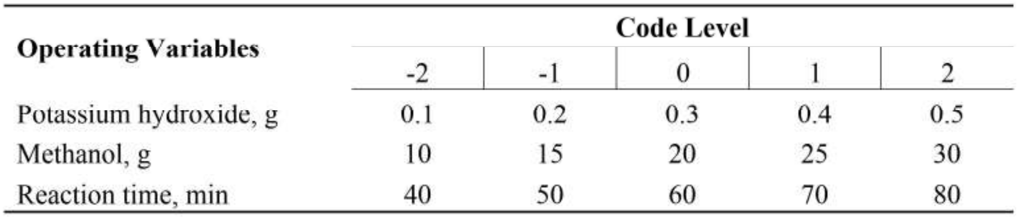
2.3 Experimental Design of Biodiesel Production

The Central Composite Design (CCD) of the Response Surface Methodology using Design Expert 7.0 software was employed as the statistical tool of the study. Response surface methodology (RSM) consists of a group of mathematical and statistical techniques used in the development of an adequate functional relationship between a response of interest, y, and some associated control (or input) variables denoted by x1,x2, ... ,xk (Gunst, 1996).

The main objective of RSM is to determine the optimum operational conditions of the system or to determine a region that satisfies the operating specifications. The application of statistical experimental design techniques in transesterification process development can result in improved product yields, reduced process variability, closer confirmation on the output response to the nominal target requirements, and reduced development time and overall costs.

The CCD was initializing how many grams of potassium hydroxide and methanol are to be added, and how long it would be stirred in the reaction container. The ranges and levels of operating variables used in the experiment of biodiesel production were given in Table 1.

Table 1. Experimental Range and Levels of Independent Variables



Operating Variables	**Code Level**				
	-2	-1	0	1	2
Potassium hydroxide, g	0.1	0.2	0.3	0.4	0.5
Methanol, g	10	15	20	25	30
Reaction time, min	40	50	60	70	80

With the values of independent variables in Table 1, there were 20 runs generated and was conducted for experimentation.

2.4 Biodiesel Production through Transesterification

The laboratory grade potassium hydroxide and methanol were all purchased from Harnwell Marketing, Cagayan de Oro City, Philippines. Potassium hydroxide (KOH), used as a catalyst, is in pellet form with ≥ 85% of total alkali calculated as KOH while methanol has 99.8% purity. About 20 mL of extracted seed oil was mixed to appropriate amount of methanol and KOH into the beaker. The mixture was heated and continuously stirred at 65 ^{o}C in a hot plate at predetermined reaction time. After 24 hours cooling, the glycerin and the biodiesel were separated by decantation. The final product was left exposed in an ambient atmosphere for 30 min to allow excess alcohol to escape from the product through volatilization.

2.5 Modeling and Optimization

The effect of the amount of potassium hydroxide and methanol, and the reaction time to biodiesel yield was determined and analyzed via 3D models generated using RSM. Analyses include the determination of best-fitted model, Analysis of Variance (ANOVA), diagnostics and 3D model graphs generation.

Numerical optimization was conducted to determine the Design Expert software's suggested solutions for the best conditions to have optimum yield of biodiesel. Solutions with high desirability were tested via actual verification runs. The result of the verification run with lowest error relative to the predicted/theoretical value was considered as the best condition to achieve optimum biodiesel yield.

2.6 Product Analysis

Percent yields of produced biodiesel were determined using analytical balance. The pH values of the yields were determined using the pH meter. The densities of the yields were computed using the standard ratio of mass and volume of a given sample. Bomb Calorimeter following ASTM D4809 determined the high heating value (HHV) of the product. FTIR analysis identified the functional groups found in the product yields.

The experimental set-ups of oil seed extraction and transesterification process are illustrated in Figures 1 and 2.

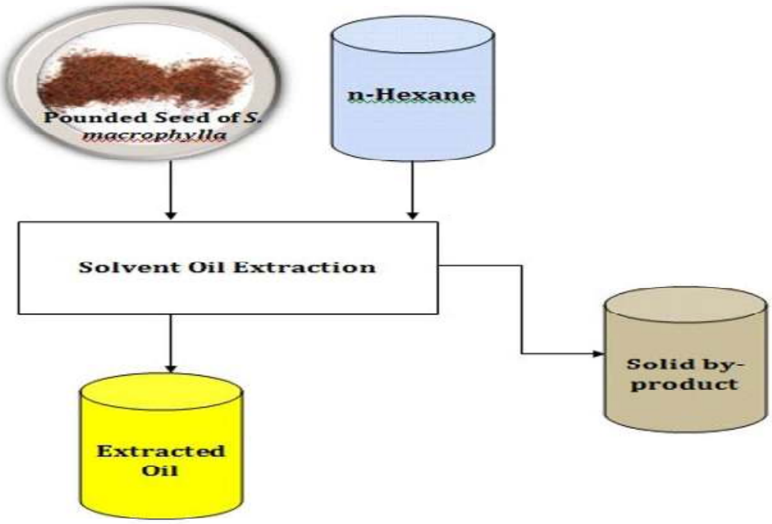


Figure 1. Schematic Flow of *S. macrophylla* Seed Oil Extraction

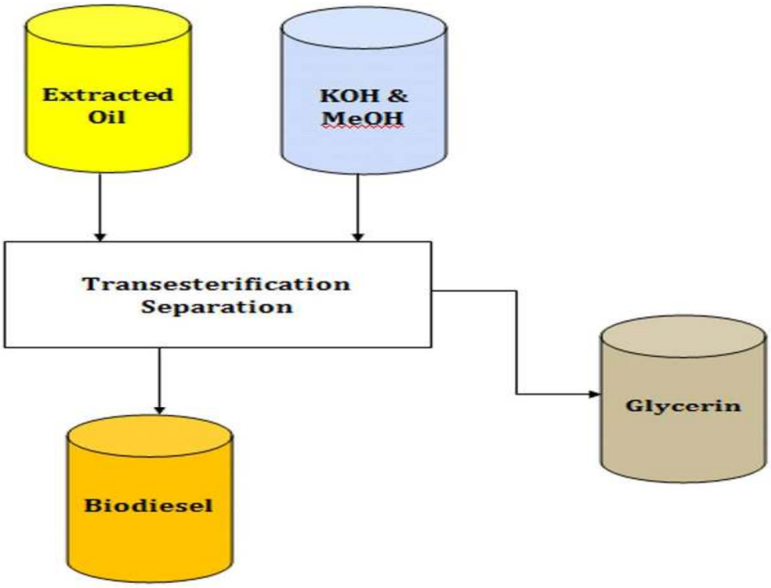


Figure 2. Schematic Flow of Trans esterification Process of *S. macrophylla* Seed Oil

3.0 Results and Discussion

3.1 Moisture Content of S. macrophylla Seeds

The moisture content of the S. *macrophylla* seeds after drying was determined in three (3) trials as shown in Table 2. The highest and least moisture contents of the seeds were recorded at 10.30% to 11.0%, respectively. The moisture content of S. *macrophylla* is somehow closer to the results of some studies in biodiesel production using Jatropha curcas L seed oil which is between 7.4%–10.7% (Moulana, Satriana, Supardan, & Aina, 2013).

Table 2. Moisture Content of *S. macrophylla* seeds

Trial	Initial Mass (g)	Final Mass (g)	Moisture Content (%)
1	200	179.09	10.5
2	200	179.49	10.3
3	200	178.20	11.0
Average		178.93±0.66	10.6±0.36

The presence of moisture content in seeds helped the reaction both the polar and non-polar compounds. The polar compounds which were not good in biodiesel production remained in the water while the nonpolar compounds of the S. *macrophylla* seeds reacted the methanol which is also nonpolar and the process of transesterification occurred. High moisture content in the seeds affected the amount of free fatty acids as well as esterification and transesterification process. High water levels caused hydrolysis, fatty acids in biodiesel is converted into free fatty acids, thereby increasing the acid number that can corrode engine parts and injection system (Vicente, Martínez, & Aracil, 2004). Other study reported maximum oil recovery at 6% moisture content and found that the increased of the moisture content to 14% resulted in a decrease in the oil recovery by 16% (Olayanju, Akinoso, & Oresanya, 2006). Besides, the water in the seed may be elevated to the liquid oil product during extraction which caused saponification and hydrolysis in the biodiesel production (Joseph, Chidozie, Obioma, Christopher, & Emeka, 2014).

3.2 Percentage Yield of Oil Extracted from S. macrophylla Seeds

The seed of S. macrophylla gave crude oil yield of 30.36%–48.44% by mass (Figure 3). This result is similar to findings of previous studies with oil yield from S. *macrophylla* seed between 33%–53% using boiling and skimming extraction method (Aliyu et al., 2012; Kim, 2013).

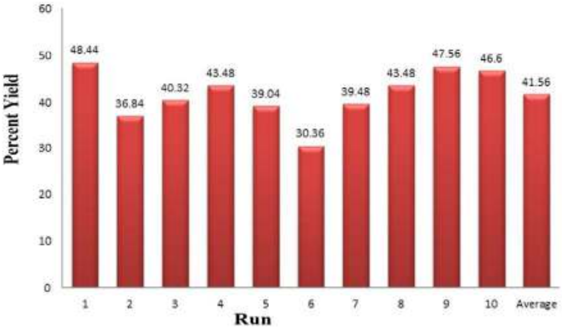


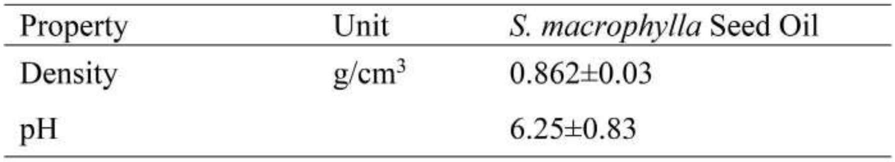
Figure 3. Percentage yield of oil extracted from *S.*

The high percentage of oil that can be extracted from S. *macrophylla* seed using n-hexane was further confirmed by the same literature (Vicente et al., 2004). The n-hexane is widely used solvent in oil extraction because of its ideal functionality for maximum extraction (Swanson, 2009). It is nonpolar and apparently dissolved nonpolar compounds in the seeds following the chemistry rule that "like dissolves like." It means nonpolar compounds in the seeds were dissolved by n-hexane and became part of the filtrate after the solid residues were separated.

The density and pH of bio-oil from S. *macrophylla* seed were determined (Table 3). The density of the bio-oil from S. *macrophylla* seed is 0.862 g/cm3 which meet the density specification for engine use (Valente, Pasa, Belchior, & Sodre, 2011). The relative density of the oil from S. *macrophylla* was found to be within the limits of biodiesel fuel standard (Joseph et al., 2014). The lower the density, the heavier the fuel and the harder it is to burn. Conversely, the higher density, the lighter the fuel and the poorer the fuel mileage (Janka, 2000).

3.3 Properties of S. macrophylla Seed Oil

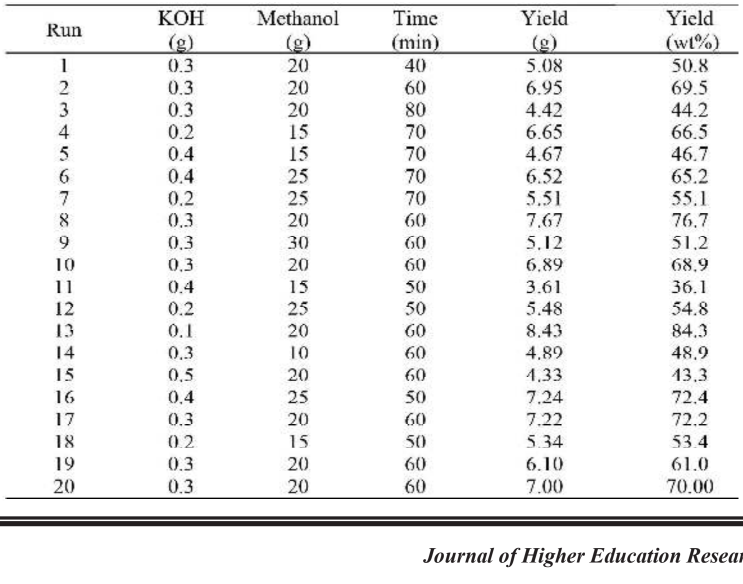
Table 3. Density and pH of *S. macrophylla* Seed Oil



Property	Unit	*S. macrophylla* Seed Oil
Density	g/cm^3	0.862±0.03
pH		6.25±0.83

The pH level of extracted oil is 6.25±0.83 which is nearly neutral, a desirable result considering that this would not trigger corrosion problem in pipelines and vessels of engines (Arazo, 2014). The acidic bio-oils are corrosive to common metals such as carbon steel and aluminum, and it can affect the engine, especially with elevated temperature and with the increase in water content (Yu et al., 2007).

Table 4. Percentage Yield of the Biodiesel from S. macrophylla Seed Extract



Run	KOH (g)	Methanol (g)	Time (min)	Yield (g)	Yield (wt%)
1	0.3	20	40	5.08	50.8
2	0.3	20	60	6.95	69.5
3	0.3	20	80	4.42	44.2
4	0.2	15	70	6.65	66.5
5	0.4	15	70	4.67	46.7
6	0.4	25	70	6.52	65.2
7	0.2	25	70	5.51	55.1
8	0.3	20	60	7.67	76.7
9	0.3	30	60	5.12	51.2
10	0.3	20	60	6.89	68.9
11	0.4	15	50	3.61	36.1
12	0.2	25	50	5.48	54.8
13	0.1	20	60	8.43	84.3
14	0.3	10	60	4.89	48.9
15	0.5	20	60	4.33	43.3
16	0.4	25	50	7.24	72.4
17	0.3	20	60	7.22	72.2
18	0.2	15	50	5.34	53.4
19	0.3	20	60	6.10	61.0
20	0.3	20	60	7.00	70.00

The yield of biodiesel from S. *macrophylla* seed oil after the transesterification process ranges from 36.10%–84.30% (Table 4). This finding is much higher compared to J. curcas seed oil, the widely used non-edible biodiesel feedstock with extracted oil content from 30% to 50% by weight (Aliyu et al., 2012). This result is also much higher compared to the previous study of extracting oil from S. *macrophylla* seed with 53% recovery (Aliyu et al., 2012).

3.5 Effects of the Chosen Parameters to the Yield of the Biodiesel

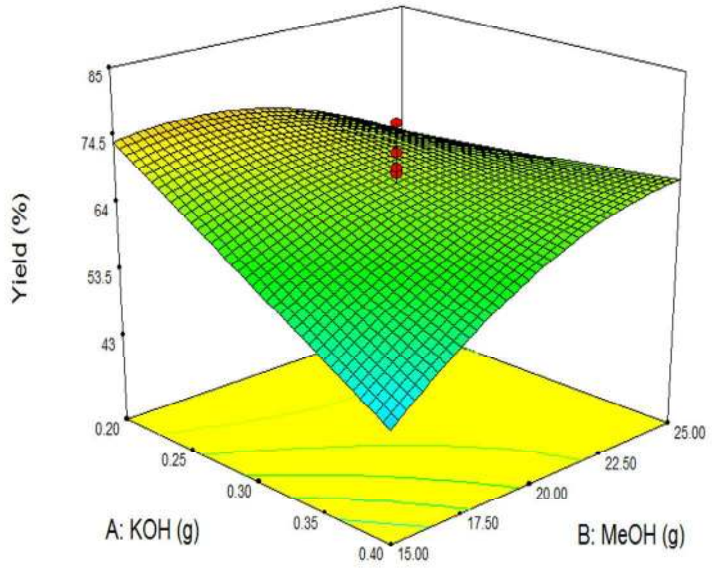


Figure 4. 3D Response Surface on the Yield of Oil Extracted from S. macrophylla Seeds

Figure 4 shows the effect of potassium hydroxide and methanol on the yield of biodiesel from S. macrophylla seed oil. It indicates that significant amount of KOH resulted in a substantial decrease of biodiesel yield. On the other hand, the increase of methanol led to an increase in the yield of the biodiesel. Increasing the amount of alcohol at minimum catalyst in the transesterification process predominantly leads to the increase of yield (Khurshid, 2014).

3.6 Model Befitting Biodiesel Yield from S. macrophylla Seed Oil

The quadratic model equation generated by CCD using the Design Expert 7.0 software was found well fitted and can predict the biodiesel percentage yield (Eq 4).

$$\%Yield = -9.94375 - 38.1125\,A + 0.32875\,B + 0.6435\,C - 1.62\,AB - 0.01883\,B^2 - 0.0054\,C^2 \qquad \text{[Eq 4]}$$

where %Yield is the predicted percentage yield of biodiesel, KOH that was used during the extraction process, B is the methanol that was added during the reaction, and C is the reaction time.

Table 5. ANOVA of the Yield of Biodiesel from S. macrophylla

Source	Sum of Squares	df	Mean Square	F Value	P-Value Prob> F
Model	23.38066	6	3.896776	6.130547	0.0031[a]
A-KOH	5.221225	1	5.221225	8.214217	0.0132[a]
B-McOH	1.525225	1	1.525225	2.399538	0.1454[b]
C-Reaction Time	0.0081	1	0.0081	0.012743	0.9118[b]
AB	5.2488	1	5.2488	8.257599	0.0131[a]
B^2	5.836857	1	5.836857	9.182752	0.0097[a]
C^2	7.525257	1	7.525257	11.839	0.0044[a]
Residual	8.263225	13	0.635633		
Lack of Fit	6.946142	8	0.868268	3.296176	0.1024[b]
Pure Error	1.317083	5	0.263417		
Cor Total	31.64388	19			

a= significant; b=not significant

Based on the predicted model, there is an expected decrease in the biodiesel yield when the amount of KOH is increased. The biodiesel yield can also be reduced with the interactive effect of AB (KOH and methanol), and quadratic values of B (methanol) and C (reaction time). This result is further supported by the result of the analysis of variance (ANOVA) shown in Table 5. The p-value of 0.0031 implies that the model has only 0.31% chance of committing an error in predicting the percentage yield of biodiesel. This outcome means that there is an assurance of 99.69% that the biodiesel can be correctly calculated using Eq 4. The reliability of the model is further strengthened by the not significant lack of fit with p-value of 0.1024 indicating that the model is well suited and can appropriately estimate the yield of biodiesel from the S. *macrophylla* seed extract.

The term A, AB and B2 and C2 are significant terms with p-values less than 0.05 implying that these conditions significantly affect the yield of biodiesel from the S. macrophylla seed extract. Not significant model terms greater than 0.05 were excluded in the model except the independent variables, to improve the accuracy of the model. Overall, the result implied that the yield of the biodiesel from seed extracts could be appropriately modeled with high reliability.

3.7 Properties of the Produced Biodiesel

The functional groups present in the biodiesel extracted from the S. *macrophylla* seeds were identified via FTIR analysis in the wavelength between 952–3989 $cm^{-}1$ wave numbers (Figure 5). The possible compounds and the identified possible functional groups were tabulated in Table 6.

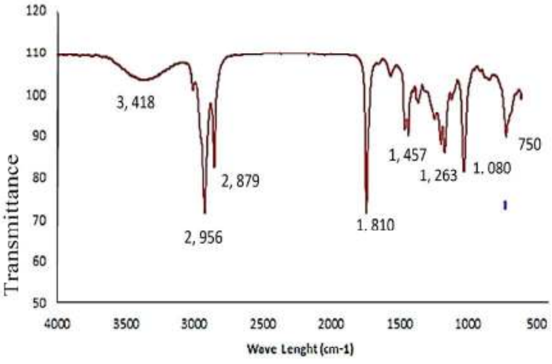


Figure 5. Fourier Transform Infrared Radiation (FTIR) Spectrum of Biodiesel from S. *macrophylla* Seed Extract

A broad absorption band observed between 3500–3000 cm-1 is attributed to the OH stretching of hydroxyl groups from phenols, alcohols, carboxylic groups and NH stretching of amines and amide groups. The observed peak between 2850–3000 cm-1 is caused by C–H stretch suggesting the presence of alkanes. The presence of C=C stretch in 1400–1600 cm-1 indicates the presence of aromatic compounds. Another band observed between 1670–1820 cm-1 are possibly caused by C=O stretching vibrations suggesting the presence of ketones, aldehydes, and esters (Arazo, 2014). The spectra at 1000–1300 cm-1 indicates the possible presence of esters in the C–O stretch group. The C=O stretching and OH bending group between 1300–950 cm-1 indicated the presence of alcohols in the product. Another group of aromatic compounds is possibly present considering the band between 900–675 cm-1 of the C–H stretch group (Arazo, 2014).

Table 6. The FTIR Functional Groups of Biodiesel from S. macrophylla Seed Extract

Compound	Wavelength Peak, cm^{-1}		Functional Group
	Range	Actual	
Hydroxyls	3200-3600	3418	O–H stretch
Alkanes	2850-3000	2956	C–H stretch
Carbonyls	1670-1820	1810	C=O stretch
Aromatics	1400-1600	1457	C=C stretch
Esters	1000-1300	1263	C–O stretch
Alcohols	1300-950	1080	C=O stretch & OH bend
Aromatics	675-900	750	C–H stretch

The calorific analysis of the produced biodiesel resulted to 39.87 MJ/kg high heating value which passes the 39.80 MJ/kg requirement of commercial biodiesel products (Gerpen, Shanks, Pruszko, & Clements, 2004). This result means that the biodiesel from the S. *macrophylla* seed oil can be used commercially considering that the product possessed the required energy of a commercial biodiesel. Moreover, analysis result revealed 0.12% sulfur content of the product, a little higher value to the maximum limit of 0.05% (Strong, Erickson, & Shukla, 2004). With employment of appropriate measures to further reduce the sulfur content of the product, the biodiesel from S. macrophylla seed is a very promising liquid fuel to substitute the petroleum-based diesel.

4.0 Conclusions

This work explored the potential of using the seeds of S. macrophylla in the production of biodiesel. The following are the major conclusions drawn from this investigation:

1. The S. *macrophylla* seeds, after sun drying, contains acceptable moisture content ready for oil extraction.
2. The S. *macrophylla* seeds have abundant oil that can be extracted with equivalent yield, density, and pH from those of other seed-based crude oil from other plants.
3. The percent recovery of biodiesel from the S. *macrophylla* seed oil is much higher compared to that of the widely used non-edible J. curcas seed oil.

4. Response surface methodology can model the biodiesel yield with high reliability. Notably, the reduced quadratic model best fit in predicting the biodiesel yield from S. *macrophylla* seed oil and found significant with 99.69% accuracy.

5. The biodiesel from S. *macrophylla* seeds indicated the presence of esters (C–0 stretch), alkanes (C–H stretch), aromatic (C=C stretch) carbonyl (C=O stretch), hydroxyls (O–H stretch), and alcohol (C=O stretch).

6. The biodiesel product has the needed energy to run engines with a high heating value of 39.87 MJ/kg, a value higher than the 39.80 MJ/kg requirement of commercial biodiesel products.

7. A ton of S. *macrophylla* (mahogany) seeds can produce 420 L bio-oil and 352 L biodiesel.

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