DEVOTION
Journal of Research and Community Service
Volume 4, Number 3, March 2023
e-ISSN: 2797-6068 and p-ISSN: 2777-0915

SYNTHESIS AND CHARACTERIZATION OF BIODIESEL PRODUCTION FROM WOLFFIA USING HOMOGENEOUS KOH CATALYST BY IN SITU TRANSESTERIFICATION

S. Saifuddin, Nyakty Shalihah, N. Nahar, Ummi Habibah, Reza N
Politeknik Negeri Lhokseumawe, Indonesia
Email: drsaifuddinm@gmail.com, nyaktishalehah1999@gmail.com, nahar@pnl.ac.id, ummihabibah@pnl.ac.id, rnageubri@gmail.com

KEYWORDS
Biodiesel, Wolffia, In Situ Transesterification

ABSTRACT

This research aims to analyze the quality and characteristics contained in biodiesels produced using Wolffia as the raw material with variations in weight of 200, 250, and 300 grams, and temperatures of 50ºC, 55ºC, and 60ºC. Furthermore, the biodiesel utilized in this study was made with reactants (Wolffia oil and methanol), fat solvent (n-hexane), and a heterogeneous catalyst (potassium hydroxide (KOH)). The results show that biodiesel formation was significantly impacted by temperature. Its volume increases with an upsurge in temperature and/or in raw materials, and the highest biodiesel product volume obtained was 81 ml. Following this, the product's density value, which was 0.872 remained within the bounds of the SNI 04-7182:2015 standards, and the best calorific value was obtained from the biodiesel made with Wolffia, which was 9,754.70 cal/gr. Lastly, the maximum volume of Wolffia used was 300 grams, as this was the best composition to meet the SNI quality, and using the GC-MS analysis, the biodiesel's quality was tested and found to contain methyl ester.

INTRODUCTION

Indonesia is still dependent on fossil fuels, especially in its transportation and industrial sectors. Due to the escalation in population and the number of industries in the country, the need for these fuels will also increase (Rachmanita et al., 2018). Accordingly, biodiesel is one of the alternative energy sources that have emerged as a result of the depletion of petroleum reserves. It is a renewable fuel that is made from vegetable oils, animal fats, or recycled restaurant grease, and could act as a substitute for petroleum diesel. However, there is a drawback associated with the manufacturing process of this fuel using vegetable oils from crops such as corn, soybeans, jatropha, and palm oil. This drawback includes the crop's harvest time which is usually between 3 months – 5 years. Also, the process of producing biodiesel from animal fat is not expected to be optimal since fat can reduce the quality of biodiesel produced because it contains free fatty acids and high water contents (Feddern et al., 2011).

Therefore, it is important to look for alternative natural materials that could boost the production of biodiesel. Such an alternative should be preferably cheaper and unedible. The use of Wolffia as raw material, from an economical point of view, is cheaper and provides added value because it is a readily available resource. Fuels made up mostly of pure compounds in small amounts are referred to as substitute fuels because their behavior closely resembles that of an actual fuel, which contains many different compounds. Accordingly, the optimized substitute fuel's composition should closely resemble the essential physical and chemical properties of the actual fuel (Kerras, Outili, Loubar, & Meniai, 2020).

Indonesia is the third APEC member country with a sizeable potential for Wolffia production. Despite only having two seasons and being a tropical nation, Wolffia and other photosynthetic plants can thrive because they receive enough sunlight, which is an average of 12 hours per day.

Wolffia is a type of aquatic plant from the Lemnaceae family known as waterweed (Hounkpe, Aina, Crapper, Adjovi, & Mama, 2013). As a source of feed, its nutritional content is better than that of other plants, both in terms of protein content and plant productivity. Besides good protein content, this plant can be cultured at a low cost because it can grow in wastewaters containing high nutrients.

Furthermore, Wolffia is one of the world's fastest photosynthesizing organisms and it is a high oil content species capable of producing up to 200 times more oil yield than other food crops. When compared to soybeans and other legumes, which produce only 1.5 to 6 tons/year on an area of one hectare, the cultivation of Wolffia is 10–20 times more productive. Following this, extraction is the process of separating chemical compounds from plant or animal tissues using certain filters. The extracts are concentrated preparations obtained using a suitable solvent. The solvent is then evaporated and the remaining mass or powder is processed to conform to the Ministry of Health's standards (Rafi, 2019).

Transesterification is a conventional biodiesel production method that has been widely used in the biodiesel industry and has been considered the most efficient. The conventional biodiesel production process was carried out by extracting Wolffia lipids and followed by transesterification (Phromphithak, Meepowpan, Shimpalee, & Tippayawong, 2020).

Likewise, the study "In Situ Transesterification Process for Making Biodiesel from Wolffia Raw Materials" was conducted based on the description provided above. It is expected that the use of Wolffia as a biodiesel feedstock will encourage the investigation of greener alternative fuels. Therefore, it is important to observe the thermochemical conversion and degradation patterns of MLW when producing biofuels, bioenergy, and chemicals for the first time to assess their potential. In addition, different degradation stages and zones, which were based on temperature and mass loss, were identified to fully comprehend the pyrolytic behavior. Four different heating levels were used to perform the kinetic and thermodynamic analysis. To produce the most bioenergy products, pyrolysis was conducted at all heating levels between 200 °C and 430 °C (Ahmad et al., 2021).

RESEARCH METHOD

The tools used in this research were: a set of in situ transesterification equipment, a 3 neck flask, water bath, stirrer motor, beaker, thermometer, mass balance, spatula, propeller, a jack, separating funnel, and an adapter.

Research Stage

The Wolffia was sun-dried, mashed with a ±30 mesh sieve, and weighed following the ratio. Furthermore, the lipid fraction of the aqueous week can be used to make biodiesel at a Wolffia to methanol ratio of 1:5 (200 gr: 250 ml). Bio-methane and bio-hydrogen can also be developed from aquatic weed biomass through biological processes. Also, large-scale aquatic weeds production can be carried out using innovative and cost-effective methods of harvesting, drying, transporting to processing sites, and converting the dried aquatic weeds to their respective biofuels (Nawaja, 2021).

Following this, in accordance with the experimental variables, the solution was added with a KOH catalyst during the in situ transesterification method's biodiesel production process. The samples were stirred at room temperature with constant speed using a magnetic stirrer for 3 hours. Next, the stirred mixture was cooled for 30 minutes to stop the reaction, after which the reaction products, which were Wolffia precipitate and FAME, were separated. 50 mL of n-hexane was added, and stirring was performed for an hour to best remove the oil. After that, the mixture was distilled to separate the fame from the solvent (hexane), and the biodiesel was obtained by filtering, using a separating funnel. Then the processed biodiesel was analyzed.

Analysis Method

Density test

The biodiesel density was measured using a pycnometer which was filled with oil and calibrated to the specified limit and then weighed. Afterward, the pycnometer was then weighed empty, filled with biodiesel, weighed again, and recorded.

Calorie value test

An electric cooling water device was used to reduce the water's temperature to 20ºC. The thread was then fastened to the container's wire holder after the bomb calorimeter was turned on. The end of the thread was inserted into the sample and as much as 1 ml of distilled water was prepared to wet the vessel. The bomb calorimeter was then turned on and the vessel was inserted into the bomb calorimeter and left there to stabilize. The readiness to enter the sample weight data was indicated by the "ok for test" prompt on the screen.

Gas Chromatographic Analysis Test

Approximately 500 ml of the reaction sample was taken and diluted. About 20 ml of ethanol was used as a standard solution and 0.2 ml of the sample was injected into the GC-MS system. Furthermore, the column temperature, injection temperature, pressure, flow rate, column flow rate, and separation ratio were set to 80°C, 250°C, 12 kPa, 30.8 ml/min, 0.46 ml/min, and 59.1 respectively.

RESULT AND DISCUSSION

Biodiesel is an alternative fuel that can be produced from various raw materials such as vegetable oils, seeds, and animal fats. The oil was extracted from the seeds with the help of the expulsion process. Although chemical expulsion is a much more efficient method of extracting oil from seeds compared to mechanical expulsion, the mechanical method was majorly used because of its lower manufacturing costs (Jonnalagadda, Raj, Bharmal, & Balaji, 2020). Following this, The extraction step was skipped during the in situ transesterification process, which is a one-time procedure (Daryono, 2017). Table 1 outlines the characteristics of the biodiesel produced by in situ transesterifications in this study:

Table 1. Effect of Temperature Changes on Biodiesel Volume

Wolffia (gr)	Temperature (^{0}C)	Biodiesel Volume (ml)
200	50	13
	55	22
	60	51
250	50	14
	55	24
	60	65
300	50	21
	55	30
	60	81

Table 2. Characteristic Observation Data

Sample Code	Wolffia's Weight (gr)	Density (gr/ml)	Calorific Value(ml)	Biodiesel Volume (ml)	Result (%)
P_1	200	0,869	9.327,02	51	10,54
P_2	250	0,870	9.547,86	65	12,02
P_3	300	0,872	9.754,70	81	13,58

In this research, biodiesel was produced using a variety of raw materials, including Wolffia, methanol, n-hexane, and potassium hydroxide (KOH) to evaluate the qualities and traits of biodiesel oil made from Wolffia with weight variations of 200, 250, and 300. Furthermore, change in temperature has a direct effect on the volume of biodiesel produced. Figure 1 shows the effects of different temperatures on the amount of biodiesel obtained.

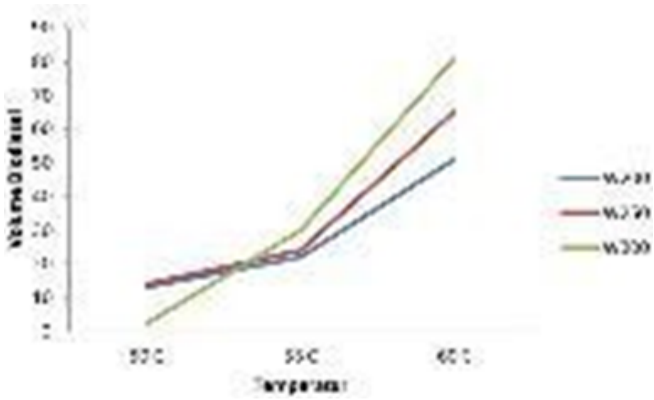

Figure 1. Effect of Temperature on Biodiesel Volume

Temperature significantly affects the biodiesel-forming reaction's success, both using conventional and in situ transesterification at 40-65°C with atmospheric pressure. The figure above shows that there is a directly proportional relationship between the temperature and the volume of biodiesel obtained, i.e. as the temperature increases, the volume of biodiesel increases. The highest biodiesel volume of 81 ml was obtained at a temperature of 60°C. However, an operating temperature of 65°C can cause the methanol, which was used as a solvent, to evaporate, hence affecting the biodiesel's production rate. Furthermore, an upsurge in temperature increases the kinetic energy of the reactants to overcome the energy barrier, which makes the collision between the triglyceride molecules and the solvent (methanol) more effective and speeds up the formation of the product over a given period. However, a higher process temperature can reduce the biodiesel yield, due to saponification reaction in the reactants which can hinder the fuel's formation, and a temperature higher than 65°C causes methanol to boil and evaporate (Pardal, Encinar, González, & Martinez, 2010). Following this, biodiesel yield is also affected by the amount of Wolffia used in its production as shown details in Figure 2.

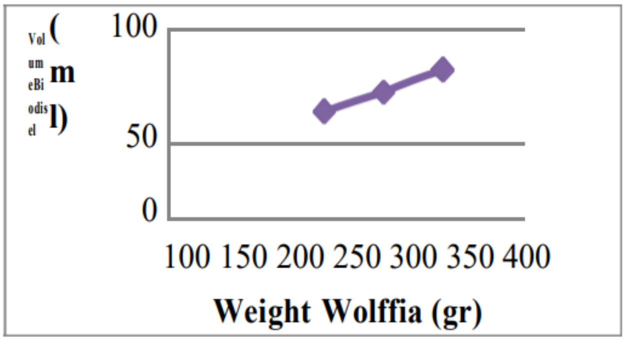

Figure 2. Effect of Wolffia's Weight on the Biodiesel Volume

As aforementioned, the volume of biodiesel produced was affected by the variation in Wolffia weight. Using 200 grams of Wolffia, the volume of biodiesel produced was significantly small due to the lack of raw materials needed for the oil extraction process.

However, when the Wolffia's weight was increased to 300 grams, a higher biofuel volume of 81 ml was produced. Indicating that the volume of raw materials determines the resulting biodiesel volume. The biodiesel product obtained has the characteristics of a good density in the SNI category and the results are shown in Table 3.

Table 3. Biodiesel Density

Sample	Density		
	Density (gr/ml)	Sni max (gr/ml)	Sni min (gr/ml)
P1	0.869	890	850
P2	0.87	890	850
P3	0.872	890	850

Based on the results outlined in table 3, the different compositions demonstrate that the biodiesel density increases with the weight of the Wolffia. The greater density was a result of insufficient washing and purification, because the glycerol in the product will not be completely removed. Also, the increase density of biodiesel is impacted by fatty acids that are not transesterified into methyl esters, KOH residue left over from the reaction, and residual methanol from the transesterification process (Ahmadi, Suyanti, Tikrahsari, & Aini, 2018).

The biodiesel produced has good quality density because its falls within the biodiesel standard quality density range specified by the Indonesian National Standard (INS). If biodiesel has a density exceeding these specified requirements, a defective reaction will occur during the conversion process from vegetable oil to biofuel, which will increase engine wear, emissions, and engine damage (Hasahatan, Sunaryo, & Komariah, 2012).

Subsequently, the calorific value or heating volume is the amount of energy released during the combustion process per unit volume or mass unit. The amount of fuel consumed per unit of time is based on the calorific value of the fuel.

Fajar TK, et al conducted a test on the calorific value of several pure fuels, and obtained calorific value of 9,381.11 cal/gr; 9,526.12 cal/gr CPO; 8,872.44 cal/gr distance; and 10,882.7 cal/gr diesel. Meanwhile, the best research finding's calorific value using Wolffia as the raw material was 9,754.70 cal/gr.

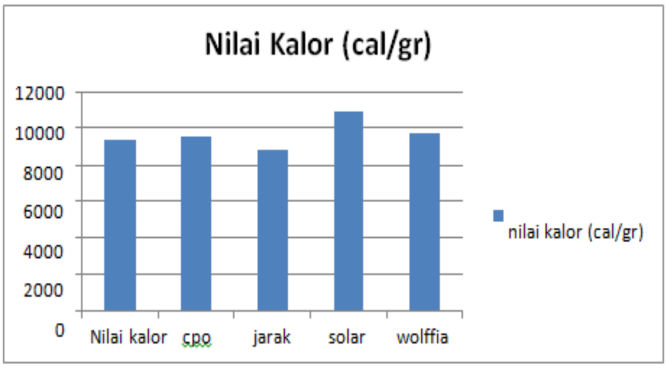

Figure 3. Calorific Value

The calorific value of Wolffia obtained was slightly higher than CPO, and jatropha, but lower than diesel fuel. This shows that Wolffia biodiesel's combustion rate is better than CPO and jatropha but still less than diesel fuel. However, the higher the calorific value, the less biodiesel there will be in the engine (Tazi & Sulistiana, 2011).

GC-MS Test On Wolffia Biodiesel

The constituent components of the material are identified using GC-MS (Gas Chromatography-Mass Spectrometry) (Majid, Prasetyo, & Danarto, 2012). In this research, the use of 300 grams of Wolffia at a temperature of 60°C led to an increased density, calorific value, volume, and yield. The components of the final product were then determined using the GC-MS analysis.

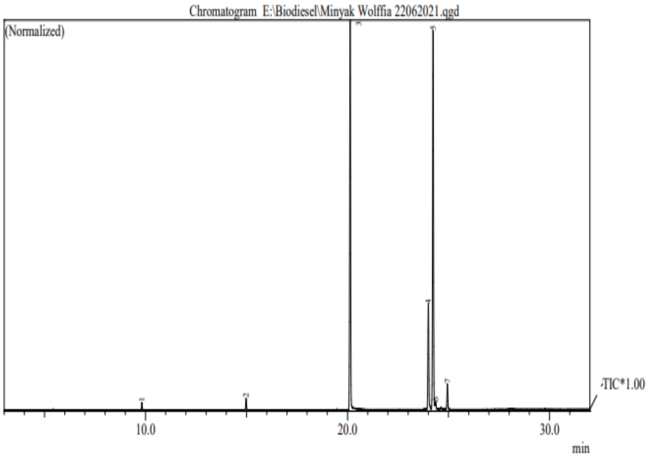

Figure 4. GC-MS Analysis

The GC-MS test results showed that the biodiesel is made up of 7 peaks. They are as follows: (1) 41.78% of methyl elaidat with a retention time of 24.237 minutes, (2) 41.55% of methyl palmitate with a retention time of 20.130 minutes, (3) 11.6% of methyl linoleate with a retention time of 23.999 minutes, (4) 2.59% of methyl stearate with a retention time of 24.947 minutes, (5) 1.03% of methyl myristate with a retention time of 14,983 minutes, (6) 0.82% of methyl oleate with a retention time of 24.362 minutes, and finally, the seventh peak was 0.62% of methyl margarate with a retention time of 9.822 minutes. From the outlined data, the predominant compound was methyl elaidat. Furthermore, the biodiesel content can be calculated by comparing the area of methyl ester contained in biodiesel with the total area analyzed in the GC test. However, the biodiesel's quality is not determined by the type of compounds contained, but by the characterization of their physical and chemical properties. The total peak area (%) of all the methyl ester components made up 100% of the fuel's components.

Table 4. Methyl Ester Content from GC-Ms Analysis

Asam Lemak	Nama Sistematik	Hasil Analisi (%)	Puncak ke-
Metil Elaidat	11-Octadecenoic acid, methyl ester	41,78	1
Metil Palmitat	Hexadecanoic acid, methyl ester	41,55	2
Metil Linoleat	9,12-Octadecadienoic acid, methyl ester	11,62	3
Metil Stearat	Octadecanoic acid, methyl ester	2,59	4
Metil Miristat	Tetradecanoic acid, methyl ester	1,03	5
Metil Oleat	9-Octadecenoic acid	0,82	6
Metil Margarat	Heptadecanoic acid, methyl ester	0,62	7

CONCLUSION

The results showed that; (1) the use of 300, 250, and 200 grams of Wolffia produced biodiesel in the volumes of 81, 65, and 51 ml respectively, (2) the use of 300 grams of Wolffia was the best composition to produce biodiesel with quality according to SNI, (3) in upsurge in the volume of raw materials led to a significant increase in biodiesel products, (4) temperature significantly influenced the success of the biodiesel-forming reaction. For example, the temperature increase followed by the biodiesel volume, and the highest volume obtained was 81 ml, (5) with the use of Wolffia, the biodiesel density obtained was 0.872, which was still within the range specified by the SNI 04-7182:2015 standards, (6) biodiesel with Wolffia as raw material produced the best calorific value of 9,754.70 cal/gr, and (7) the quality of biodiesel tested using GC-MS analysis found that biodiesel produced using Wolffia contained methyl ester.

REFERENCES

Ahmad, Muhammad Sajjad, Klemeš, Jiří Jaromír, Alhumade, Hesham, Elkamel, Ali, Mahmood, Abid, Shen, Boxiong, Ibrahim, Muhammad, Mukhtar, Ahmad, Saqib, Sidra, & Asif, Saira. (2021). Thermo-kinetic study to elucidate the bioenergy potential of Maple Leaf Waste (MLW) by pyrolysis, TGA and kinetic modelling. *Fuel*, *293*, 120349.

Ahmadi, Ahmadi, Suyanti, Ika, Tikrahsari, Sri Astuti, & Aini, Miftahul. (2018). Pengaruh Waktu Adsorpsi Minyak Jelantah Sebagai Bahan Pembuatan Biodiesel Dengan Tanah Liat Terhadap Kualitas Biodiesel. *Hydrogen: Jurnal Kependidikan Kimia*, *6*(2), 124–132.

Daryono, Elvianto Dwi. (2017). Biodiesel dari minyak biji pepaya dengan transesterifikasi insitu. *Jurnal Teknik Kimia*, *8*(1), 7–11.

Feddern, Vivian, Cunha Junior, A., Pra, M. C., de Abreu, Paulo Giovanni, dos Santos Filho, Jonas Irineu, Higarashi, Martha Mayumi, Sulenta, Mauro, & Coldebella, Arlei. (2011). *Animal fat wastes for biodiesel production.*

Hasahatan, Dennis, Sunaryo, Joko, & Komariah, Leily Nurul. (2012). Pengaruh ratio H2SO4 dan waktu reaksi terhadap kuantitas dan kualitas biodiesel dari minyak jarak pagar. *Jurnal Teknik Kimia*, *18*(2).

Hounkpe, Sena, Aina, Martin, Crapper, Martin, Adjovi, Edmond, & Mama, Daouda. (2013). Influence of salinity on duckweed growth and duckweed based wastewater treatment system. *Journal of Water Resource and Protection*, *5*(10), 993–999.

Jonnalagadda, M. Babu, Raj, N. V. Sai Deepak, Bharmal, Pruthviraj, & Balaji, M. (2020). Experimental investigation on the production of linseed biodiesel yielding and properties evaluation. *AIP Conference Proceedings*, *2311*(1), 20028. AIP Publishing LLC.

Kerras, H., Outili, N., Loubar, K., & Meniai, A. H. (2020). Surrogate Formulation optimization of diesel and Biodiesel blends. *2020 11th International Renewable Energy Congress (IREC)*, 1–6. IEEE.

Majid, Astsari Abdul, Prasetyo, Dhani, & Danarto, Y. C. (2012). *Pembuatan biodiesel dari minyak jelantah dengan menggunakan iradiasi gelombang mikro*.

Nawaja, A. (2021). *Aquating Weeds As a Biorethenery resources For Biofuels and Value added Products: Challenges and Recent Advan Comments*. (4).

Pardal, Ana Cristina, Encinar, J. M., González, J. F., & Martinez, G. (2010). *Transesterification of rapeseed oil with methanol in the presence of various co-solvents*.

Phromphithak, Sanphawat, Meepowpan, Puttinan, Shimpalee, Sirivatch, & Tippayawong, Nakorn. (2020). Transesterification of palm oil into biodiesel using ChOH ionic liquid in a microwave heated continuous flow reactor. *Renewable Energy*, *154*, 925–936.

Rachmanita, Risse Entikaria, Muntini, Melania Suweni, Thawankaew, Somphorn, Chao-Moo, Watchara, Vora-Ud, Athorn, & Seetawan, Tosawat. (2018). Fabrication and characterization of interdigital capacitors thin film by DC magnetron sputtering for measuring the permittivity of crude oil. *Materials Today: Proceedings*, *5*(7), 15192–15197.

Rafi, Ahmad. (2019). Analisis energi terbrukan pada proses pirolisis dengan memanfaatkan sampah plastik. *Jurnal Teknik Mesin*, *12*(01), 30.

Tazi, Imam, & Sulistiana, Sulistiana. (2011). Uji kalor bakar bahan bakar campuran bioetanol dan minyak goreng bekas. *Jurnal Neutrino*, *3*(2), 163–174.