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Effect of Moisture Content on Roselle Seed Oils Properties and its Biodiesel Properties for Renewable Fuel

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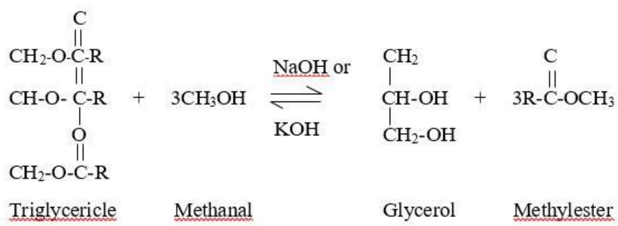
ABSTRACT

Roselle seeds were obtained after harvesting the roselle flower. These seeds contain an oil content of about 10-20% w/w that indicates the possibility for using as raw material for biodiesel production. In this study, the effect of moisture content on roselle seed (8%, 10%, 12%) obtained after frying combined with oven drying are studied on the properties of oil content, volatile matter, fix carbon, ash content, and fatty acid composition, The results showed that roselle seed contained 8 to 12% of moisture content have 1274-1323 ml per 0.0468 g of Oil contained, 69.83-73.01% of volatile matter, 16.07-17.82% of fixed carbon, 6.92-8.47% of ash content. The results on fatty acid composition found that roselle seed contained 8 to 12% of moisture content contained 20.81-22.46% of palmitic acid, 4.83-5.04% of stearic acid, 38.80-47.73% of oleic acid, 21.69-33.33% of linoleic acid and 2.16-2.71% of linoleic acid. After that, the combined oil from three different moisture content was further produced biodiesel and its properties were analyzed. The result showed that all properties in terms of pour point, acidity, viscosity, flash point, density met the properties of biodiesel standard that revealed roselle seed oil can make renewable fuel.

1. INTRODUCTION

The consumption and demand for petroleum products are increasing yearly due to the increase in population. Coal and electricity are the main energy sources around the world [1]. However, the scarcity of fossil fuel resources and their negative impact on the environment [2] has called for the demand for finding an alternative feedstock for energy needs. Among alternative transport fuels for the transport sector, biofuels have received much consideration as a substitute product for diesel fuel due to it is biodegradable, non-toxic and can considerably decrease exhaust emissions and overall life cycle emission of carbon oxides from the diesel engine when utilized as a fuel [3] [4]. One of the biofuels is biodiesel. Biodiesel is an oxygenated fuel made from vegetable oils and animal fats offering the benefits of a greener synthesis route for obtaining diesel fuel [5]. Biodiesel can be produced by the conversion of the triglycerides to esters (primarily methyl esters) via various esterification processes [6]. Biodiesel can be synthesized on a laboratory scale; then scaled up to pilot and industrial scale [7]. P. Chandrasekar [8] has converted pumpkin seeds oil into methyl ester (biodiesel) and used it as an alternative fuel for CI engines. The test performed showed that the combustion characteristics of the fuels and their diesel blends closely followed the diesel fuel operation. Ali et al. [9] performed the biodiesel production from neem oil and found that the density of neem oil could be reduced and the calorific value was improved with the transesterification process. Biodiesel is defined as a mono-alkyl ester of fatty acids derived from vegetable oils or animal fat. Biodiesel can be produced by a transesterification reaction between triglyceride (or vegetable oils) with alcohol mainly methanol in the presence of an alkaline catalyst to produce fatty acid methyl ester (or biodiesel) There are three stepwise reactions with intermediate resulting in the production of three moles of methyl esters and one mole of glycerol. The overall reaction is:



Many types of alcohol such as methanol, ethanol, propanol, and butanol are used in the transesterification reaction. But methanol and ethanol are used most frequently, especially methanol due to their few price, and chemical and physical advantages. They can quickly react with triglycerides and sodium hydroxide is easily dissolved in then alcohol [10] Roselle (*Hibiscus sabdariffa* L.) is an important crop in the tropics and subtropics countries and it is generally considered as a

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medicinal plant. The calyces or petals of the flower are extensively used to prepare herbal drinks, cold and warm beverages, as well as making jams and jellies. The brilliant red color and unique flavor coupled with other organoleptic attributes make them valuable food products. In addition, Roselle seeds are usually harvested ten days after the flower blooms. The large flowers fade and fall off, leaving behind their bright red, fleshy lotus-shaped calyces. Inside each calyx is a pod of seeds. These calyces are harvested carefully snipping them off the steam with sharp pruners or scissors. The seeds grow within the calyces in a velvety capsule similar to how seeds grow in peppers. After they have been harvested, the seed pod is pushed out of the calyx with a small hollow metal tube. The Roselle flower seeds are there dried to be planted later and the fleshy red calyces are dried or eaten fresh. The small, brown, kidney-shaped seeds themselves, are only actually used to grow more plants. Due to its high content of oil in Roselle seed, it is possible to use it as raw material for biodiesel production. Roselle seed usually is extracted from the oil by using solvent extraction or pressing extraction. The drawback of solvent extraction is environmental pollution that limits the use of Roselle oil in food and biofuel application [11] pressing refers to oils are extracted by pressing or squeezing oily materials with a screw press or hydraulic press. Pressing technology is commonly used to squeeze oil from oilseed materials (like Roselle) with relatively high oil content. The moisture content of Roselle seed can significantly affect the oil yield and the properties of oil that obtain after pressing. So, the objective of this research is to study the effect of different moisture content on the properties of extracted Roselle oil obtained after pressing by screw press. The obtained oil is further mode biodiesel are further evaluated, too.

2. MATERIALS AND METHODS

2.1 Material

In this research sample of Roselle, seeds were collected from Doembang Nangbuat District, Suphanburi Province, Thailand. The cultivated plantation area for Roselle is 2,400,000 m^2. The Roselle seeds were dried in over to remove the moisture content until their moisture content reached 8, 10, 12%. The Roselle seeds were further pressed by a screw extractor to obtain Roselle oils. All chemicals used in the experiment such as methyl alcohol, sodium hydroxide were purchased from Merck (Germany).

2.2 Oil Extraction

Each Roselle seeds with three different moisture content [8% (M8), 10% (M10), 12% (M12)] was placed in a cylindrical container that had 0.0468 m^3 of volume. The Roselle seeds were extracted with a screw-type oil expeller powered by a three-horsepower motor, which forced the fluid through a circular grooved steel plate placed on a belt in front of the motor. The seed oil under compression passed from the screw plate through the filter with a filter paper.

2.3 Transesterification process

The transesterification of crude Roselle oil with methanol by using sodium hydroxide (NaOH) as a catalyst was carried out in a laboratory scale. The reaction was performed at the amount of NaOH catalyst equal to 2%, the amount of oil per methanol volume ratio was 100 ml:23 ml, the reaction time was 1 hour, and the reaction temperature was 60ºC. After the reaction was completed, the mixture was transferred into a separation funnel that could separate the mixture into two-layer that the top layer was biodiesel and the bottom layer was glycerol. The obtained biodiesel was further washed with a dilute acid solution followed by two times warm water. In the final step, the purified biodiesel was further dried at 110ºC to remove the remained water in biodiesel. The obtained purified biodiesel was investigated for its properties.

2.4 Analytical Method

Roselle seeds of M8, M10, M12 were analyzed moisture content, the percentage of oil content, volatile matter, fix carbon, and ash content the methods for this analysis can be briefly explained follow these details.

Moisture content was measure by placing 1 g of ground Roselle seeds into a pre-dried glass tube (six replicates). The sample-loaded tubes were placed into the oven for 6 h. The moisture content of each seed sample was calculated based on the difference in weight of the seed sample before and after drying divided by the weight of the wet seed sample.

Percentage of oil content was measure by using 26.6 kg of each M8, M10, and M12 sample. Each Roselle seed sample was extracted by screw press. The percentage oil content was calculated using the following equation.

$$\%\text{ oil content} = \frac{\text{volum of oil (Liter)}}{\text{weight of sample (kg)}} \times 100 \quad (1)$$

Ash content was determined by placing 5g of ground Roselle seeds into crucible after that put the sample into muffle furnace. The muffle furnace has maintained a temperature between 500 to 600℃ and the sample was elated for 6 hours. The % ash content was determined following this equation.

$$\%\text{ ash (net basis)} = \frac{\text{weight of ash}}{\text{weight of wet seed}} \times 100 \quad (2)$$

Fix carbon was a measure of the amount of non-volatile carbon remaining in the seed sample. It was a calculated value determined from other parameters measured follow this equation.

$$\%\text{ fix carbon} = 100\text{-}60\ \%\text{ moisture content} + \%\text{ volentile matter} + \%\text{ ash} \quad (3)$$

The volatile matter was determined by putting 5g of ground Roselle seed into the crucible. The crucible was put into furnaces that maintain the temperature at 950℃ for 7 min. After completing 7 min the sample was kept out from the furnace and then cooled the crucible in the desiccator. The weight loss of the sample represents volatile matter content.

Roselle seeds oils were analyzed fatty acid composition by gas chromatography (GC), pour point, acid value, viscosity, iodine value, flash point, and density. These analysis methods were briefly explained follow these details.

The fatty acid composition was analyzed in this study. Fatty acid methyl 1 ester (FAME) was prepared by esterifying with the alcoholic sulfuric acid reagent. A Hewlett Packard GC equipped with an FID was used for GC analysis of the methyl esters. Methyl esters were analyzed on a Hewlett Packard Free Acid Phase column (30 m x 0.53 mm x 1.0 µm). The injection and detector temperatures were maintained at 250 and 300°C, respectively. The flow rate of the carrier gas (nitrogen) was 20 ml/min. The oven temperature was programmed from 100 to 180°C at the rate of 5°C/min. FAME were identified by using authentic standards, and the peaks area were quantified by using digital integration. The percentage area of each fatty acid was reported as relative proportions of the total peak area.

Pour point was measured by cooling the roselle oil at the specified rate and examined at intervals of 3°C for flow characteristics, The lowest temperature at which movement of the specimen is observed is recorded as the pour point.

The acid value was determined through the direct titration method of roselle oil in an alcoholic medium against standard potassium hydroxide. The acid value was calculated according to the following equation.

$$\text{Acid value} = \frac{56.1(\text{ml of KOH})\ (\text{Molarity of KOH})}{\text{weight of oil sample(g)}} \quad (4)$$

The viscosity of the Roselle oil sample was measured by a capillary viscometer at 40°C. The flow time of the oil sample measured with a stopwatch.

Iodine value (IV) measured by titration oil sample with an excess of iodothyronine (IBr) in glacial acetic acid. Unreacted iodothyronine is reacted with iodide which converts it to iodine. The iodine concentration is then determined by titration with standard sodium thiosulphate. IV is determined using this equation:

$$IV = \frac{(b-v) \times N \times 126.9 \times 100}{w \times 1000} \quad (5)$$

Roselle seed oil biodiesel was analyzed methyl ester composition, pour point, acid value, viscosity, flash point, and density.

3. RESULTS AND DISCUSSION

3.1 Results of Moisture Content and Oil Contents

The moisture contents for M8, M10, and M12 are shown in Figure 1. The x-axis represents the number of experiments and the y-axis show the moisture content.

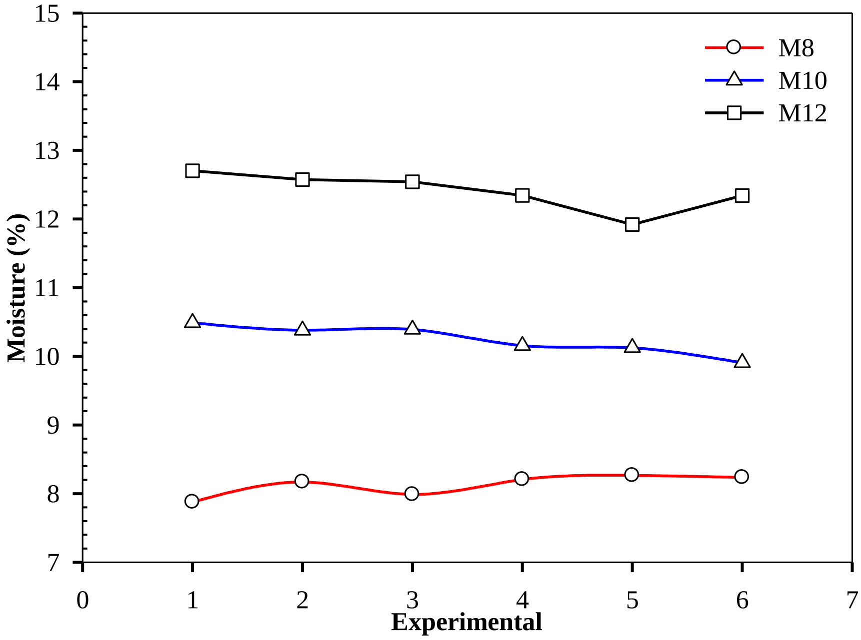

Fig. 1. The moisture content of six experiments for average moisture content determination.

From Figure 1, there is 6 experiment to determine the moisture content of M8, M10, and M12. M8 is the average moisture content that calculates from the summation of six moisture between 7.87 to 8.20 divided by 6. M10 is the average moisture content that calculates from the summation of six moisture content between 9.00 to 10.49 divided by 6. and M12 is the average moisture content that calculates from the summation of six moisture content between 11.91 to 12.70 divided by 6. The crude extracted Roselle seed oil is a yellow and viscous liquid.

The amount of extracted oil for three different moisture contents was determined by using the same amount of Roselle seed weight at 26.60 kg. the result of the amount of extracted oil is revealed in Table 1.

From Table 1, it shows that the trend of the amount of extracted oil at M8 and M10 that give the amount of oil at 1.300 Liter and 1.323 Liter is higher than M12 that give 1.274 Liter, the reason for M12 gives the lower amount of oil is M12 contain the higher amount of water in the seed than M8 and M10. So it needs to dry the Roselle seeds to reach the moisture content of less than 10% before screw pressing.

3.2 Results of Organic Compound contained in Roselle Seeds

The three different moisture content of Roselle seeds were brought to determine the different types of organic compounds that contain in Roselle seed. These organic compounds are volatile matter fixed carbon and ash content. The results of the analysis are shown in Table 2.

From Table 2, it shows the relationship between moisture content with the volatile matter, fixed carbon, and ash content. For moisture content 8% (M8), it contained 72.47% of volatile matter, 16.39% of fixed carbon, and 7.14% of ash content. For 10% (M10), it contained 73.01% of volatile matter, 16.07% of fixed carbon, and 6.92% of ash content. For 12% (M12), it contained 69.83% of volatile matter, 17.82% of fixed carbon, and 8.47% of ash content. The results showed that three organic compounds (volatile matter, fixed carbon, ash content) contained in Roselle seed with moisture content 8, 10, 12% are nearly the same amount.

3.3 Results of Fatty Acid Compositions of Roselle Seed Oil with Moisture Content 8, 10, 12%

The Roselle seed oils with different moisture content were determined their fatty acid composition by using GC-FID. The result of the chromatograph of M8, M10, and M12% was shown in Figures 2, 3, and 4.

Table 1. Oil amount of Roselle seeds at different moisture content.

Sample of Roselle seeds	Volume of Roselle Seed (kg)	Oil amount (Liter)
M8	26.60	1.300
M10	26.60	1.323
M12	26.60	1.274

Table 2. Organic compounds contained in Roselle seeds.

Sample of Roselle seeds	Volatile Matter (%)	Fixed Carbon (%)	Ash (%)
M8	72.47	16.39	7.14
M10	73.01	16.07	6.92
M12	69.83	17.82	8.47

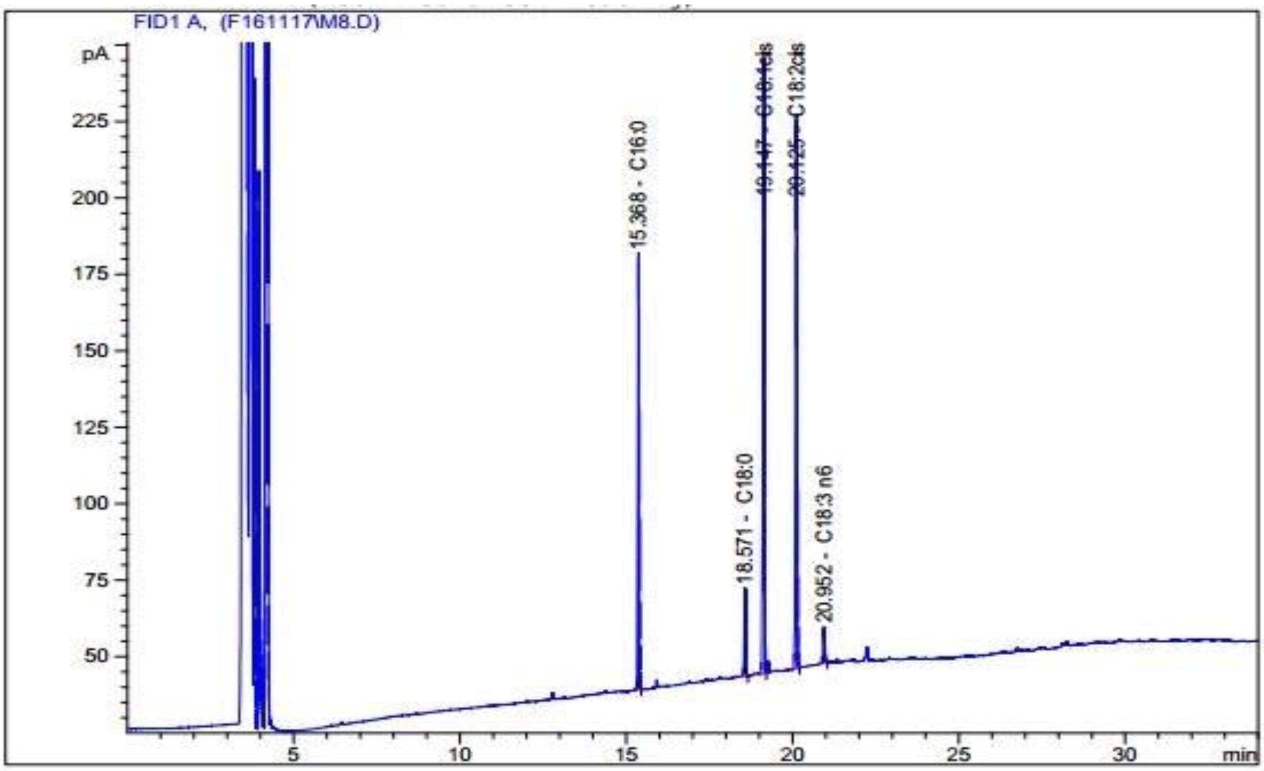

Fig. 2. GC-FID Chromatogram of M8.

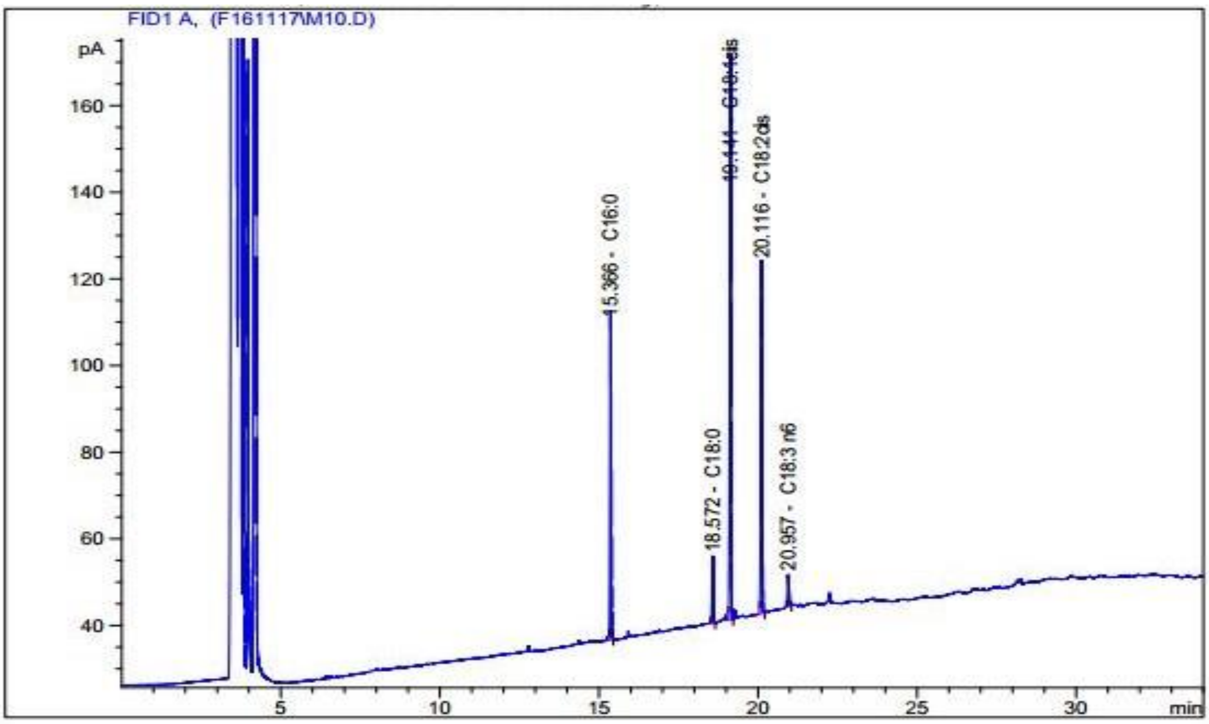

Fig. 3. GC-FID Chromatogram of M10.

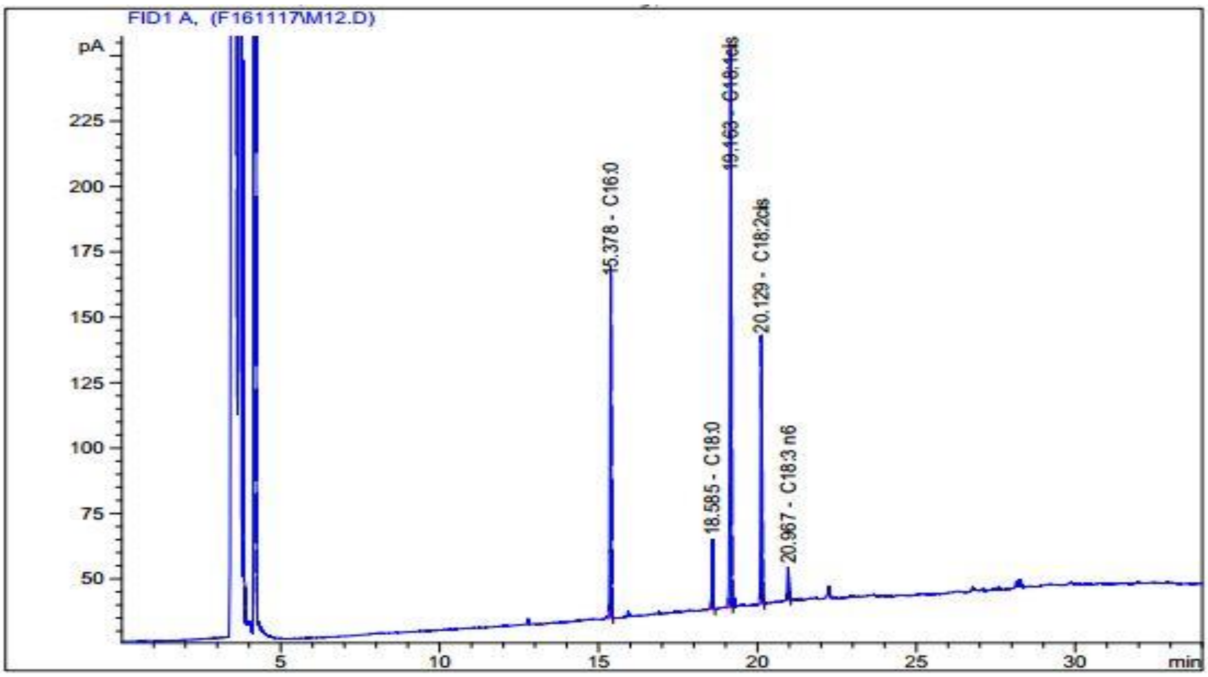

Fig. 4. GC-FID Chromatogram of M12.

Table 3. Fatty acids composition of Roselle seed oil with moisture content 8, 10, 12% (M8, M10, M12).

Fatty acid	Amount (% Area)		
	M8	M10	M12
Palmitic acid (C16)	20.88	20.81	22.46
Stearic acid (C18)	4.83	4.99	5.04
Oleic acid (C18:1)	38.80	43.92	47.73
Linoleic acid (C18:2)	33.33	27.62	21.69
Linoleic acid (C18:3)	2.16	2.66	2.71
Total	100	100	100

The fatty acids composition of M8, M10, and M12 is shown in Table 3. From Table 3, Roselle seed oil contained all of these fatty acids; palmitic acid (C16), stearic acid (C18), oleic acid (C18:1), Linoleic acid (C18:2), and Linolenic acid (C18:3) but the variation of the amount of oleic acid (C18:1) and Linoleic acid (C18:2) is higher about 10% than another fatty acids due to oleic acid (C18:1) and Linoleic acid(C18:2) are unsaturated fatty acids that eazy to occur hydrolysis reaction with water contained in Roselle seed when compare with palmitic acid (C16) and stearic acid (C18). Both are saturated fatty acid, so the variation in the amount of fatty acid in three different moisture content of both acids are less than oleic acid (C18:2) and Linoleic acid (C18:2)

Result in chemical properties of Roselle seed oils due to the slight difference of organic compound and fatty acid composition that contain in Roselle seeds with three different moisture content. So, we combined the extracted oils from M8, M10, and M12 together after that it was brought to analyze chemical properties. These chemical properties are pour point-that analyzed followed ASTM D5950, acidity that analyzed followed ASTM D664, viscosity that analyzed followed ASTM D445, iodine value that analyzed followed EN14111, a flashpoint that analyzed followed ASTM D93 and density that analyzed followed ASTM D4052. The result is shown in Table 4.

From Table 4, it found that the acidity value of Roselle seed oil was higher than 4 mg KOH/g. That means this oil was the need to neutralize by a base such as sodium hydroxide (NaOH) to decrease the acidity from 32.45 to 4 mg KOH/g. when this acid reaches 4 mg KOH/g, this oil can make biodiesel by transesterification reaction. So, this study makes biodiesel from 100 g of neoterized Roselle seed oil with 23 ml of methanol using 1g of NaOH under 60ºC for 1hr. of the transesterification reaction. Another property such as pour point, viscosity, iodine value, flash point, and density was nearly the same as the properties of Jatropha oil [12].

3.4 Result on Biodiesel Properties

The properties of Roselle seed oil biodiesel were compared with methyl ester standards that follow the USA (ASTM standard) and German and Europe (DIN.EN standard). The results were exhibited in Table 5.

The results from Table 5 revealed that all properties of the produce biodiesel meet well with both biodiesel standards. In addition, this result implied that Roselle seed oil can be used as feedstock to produce high-quality biodiesel that meets well with biodiesel standards.

Table 4. Chemical properties of Roselle seed oil.

Properties	Amount
Pour point (°C)	3.5
Acidity (mg KOH/g)	32.45
Viscosity (c St)	41.05
Iodine (g I_2/100 g)	40.05
Flash point (°C)	278
Density (15°C, kg/m^3)	910

Table 5. Properties of Roselle seed oil biodiesel.

Properties	This biodiesel	Biodiesel ASTM D 6751- 02	Standard DIN EN 14214
Pour point (°C)	-1	-	-
Acidity (mg KOH/g)	0.43	< 0.80	< 0.50
Viscosity (c St)	4.5	1.9 –6.0	3.5 –5.0
Flash point (°C)	285	>130	>120
Density at (15°C, kg/m^3)	860	-	860 -900

4. CONCLUSION

In this study, the effect of moisture content on the properties of extracted seed oil was determined. The result showed these details:

The result on oil content, showed that lower moisture content (8%, 10%) gave the higher amount of oil content than higher moisture content (12%).

The result on the volatile matter, fixed carbon, and ash content, showed that all of these moisture content (8%, 10%, 12%) gave the near value of the volatile matter, fix carbon and ash content value.

The result on fatty acid composition from GC. It showed that different moisture content (8%, 10%, 12%) had more effect on oleic acid and linoleic acid than palmitic acid, stearic acid, and linolenic acid. The variation of the amount of oleic acid, linoleic acid is higher than palmitic acid, stearic acid, and linolenic acid.

The combined extracted seed oil from different moisture content has a higher acid value than 4 mg KOH/g. So it needs to neoterize this oil with the base to below 4 mg KOH/g of acid value. The obtained oil will further make biodiesel by using a transesterification reaction to produce biodiesel.

The obtain roselle seed oil biodiesel had every property (pour point, acidity, viscosity, flash point, density) met well with ASTM and DIN EN standard.

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NOMENCLATURE

ASTM	=	American Society for Testing and Materials
DIN EN	=	European sStandard
FAME	=	Fatty acid methyl esters
ISTA	=	International Seed Testing Association
M8	=	The moisture content of roselle seeds at 8 percent
M10	=	The moisture content of roselle seeds at 10 percent
M12	=	The moisture content of roselle seeds at 12 percent
GC-FID	=	Gas Chromatography - Flame Ionization Detector

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