KARAKTERISASI SIFAT FISIK KIMIA METIL ESTER MINYAK BIJI WIJEN *(Sesamum indicum* L.) DAN KOMPOSISINYA

CHARACTERIZATION OF PHYSICAL AND CHEMICAL OF SESAME SEED OIL (S*esamum indicum* L.) METHYL ESTER AND COMPOSITION

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ABSTRACT

The methyl ester of sesame seed oil (Sesame seeds L.) was used to make diethanolamide. This process involved extraction, transesterification, and amidation. The research revealed that extraction by maceration yielded a sesame seed oil yield of 36.14 percent, an acid number of 1.1531 mg KOH/g, a FFA number of 0.5796 percent, and a saponification number of 51.287 mg KOH/g. In the process of converting sesame seed oil to methyl ester, the acid number was 0.5126 mg KOH/g, the FFA number decreased to 0.2704%, and the saponification number was 50.049 mg KOH/g. According to methyl ester GC-MS analysis, methyl oleate made up 39.13% of the methyl ester of sesame seed oil. The methyl ester FT-IR spectrum exhibits a specific absorption peak at 1743 cm-1 for C=O ester.

Keywords : sesame seed oil, transesterification, methyl ester

INTRODUCTION

Sesame plants are prevalent in Indonesia, and their seeds are utilized to produce oil. Sesame plants thrive in tropical and subtropical environments. Sesame seed oil can be used as a high-quality cooking oil because the saturated fatty acids it contains are low and non-cholesterol, which is advantageous for health. Furthermore, sesame seed oil is rich in vitamin E, which is also beneficial for health. The shelf life of sesame seed oil is high, so it has a relatively extended shelf life [1].

Oils derived from vegetation (seeds) are vegetable oils. Sesame seed oil is one of the vegetable oils that can be converted into methyl esters. Sesame seed oil is composed of 14% saturated fatty acids, 39% mono-chain unsaturated fatty acids, and 46% polyunsaturated fatty acids. Sesame oil contains the fatty acids oleic, linoleic, linolenic, palmitic, and stearic. These fatty acids can be converted into methyl esters through esterification and transesterification processes, where partial esterification can be achieved by adjusting the conditions of the reaction. because the formation of these esters depends heavily on the interaction between alcohol and fatty acids [3].

There are three methods for extracting sesame seed oil: cold pressing, heated pressing, and roasting. The presence of fatty acids and functional compounds in sesame seed oil can be altered by one of the processes involving heat in sesame oil processing. In addition, cold pressing can enhance the quality of the sesame seed oil produced [4].

On the basis of the preceding information, it is necessary to conduct research on synthesizing methyl esters from sesame seed oil via a transesterification reaction that was previously accomplished via a maceration extraction procedure, namely by immersing the sample in n-hexane solvent. [5] with the results of the characterization of its physical and chemical properties, including acid number, Free Fatty Acid (FFA) value, saponification number, Hydrophilic Lipophilic Balance (HLB) value, form, Thin Layer Chromatography (TLC), and solubility, as well as characterization using Fourier Transform -Infra Red (FT-IR) 8201 PC and Gas Chromatography-Mass Spectrometry (GC-MS) Agilent Technologies.

RESEARCH METHODOLOGY

Equipment

This study utilized a set of laboratory glassware, a set of reflux equipment, an analytical balance, a separating funnel, a rotary evaporator, a chamber, a TLC plate, FT-IR and GC-MS spectrophotometers, and an analytical balance.

Material

Sesame seeds (Sesame seeds L.), n-hexane, methanol, H_2SO4 (p) 4%, ethyl acetate, KOH 0.1015 N, distilled water, HCl 0.4901 N, PP indicator, $H_2C_2O_4$ 0.1 N, ethanol 95%, KOH-alcoholic 0.5 N, and Na_2SO_4 anhydrous were used in this investigation.

Research procedure

Sesame Seed Oil Extraction

The sesame seeds (*Sesamum indicum L.*) are cleaned and washed under flowing water, heated to 105 degrees Celsius in an oven, and then crushed. After that, it was extracted by maceration with n-hexane for 72 hours [5]. A rotary evaporator was used to purify and concentrate the maceration results.

Transesterification of Sesame Seed Oil

Seventy grams of sesame seed oil were placed in a three-neck, flat-bottom flask that was connected to a magnetic stirrer-equipped reflux apparatus. After that, 19.2 mL of methanol was added with an oil-to-methanol mole ratio of 1:6 while agitating with a magnetic stirrer. The flask is cooled with ice cubes, and up to 1.53 mL of H_2SO4 (p) at 4% w/w by weight of oil is steadily added as a catalyst. The mixture was then refluxed for four hours at 60 to 70 degrees Celsius. The results of this reflux are placed in a separatory funnel until two distinct phases form. The upper phase was extracted, rinsed with distilled water, and filtered with anhydrous Na_2SO_4. Then, evaporate using a rotary evaporator to obtain purer results [6].

Test the acid number and FFA level of sesame seed oil.

10 grams of sesame seed oil were added to a 250-mL Erlenmeyer flask, dissolved with 25 mL of ethanol, 3 drops of PP indicator were added, and the mixture was homogenized before being titrated with a standard solution of 0.1015 N KOH that had been standardized with solution $H_2C_2O_4$ 0.1 N until the color changed to violet red. The

KOH titration volume was documented, and the acid number (FFA level) was calculated using the following formula:

$$Acid\ Number\ = \frac{56{,}1\ \times\ V\ \times\ N\ KOH}{m}$$

$$Free\ Fatty\ Acid\ Content\ (\%)\ = \frac{282\ \times A \times N}{10\ \times m} \times 100\%$$

282 = Molecular weight of oleic acid
56.1 = Molecular weight of KOH

Saponification Number
Making Blanks

After adding 25 mL of 0.5 N KOH-alcoholic to the saponification vessel, 30 minutes of refluxing followed. After the solution has boiled, allow it to settle. Then, three droplets of PP indicator were added, and the solution was titrated with 0.4901 N HCl solution that had been standardized with 0.5 N KOH solution until it turned violet-red.

Sample Testing

10 grams of sesame seed oil may be added to the pumpkin. After meticulous heating, 25 mL of a 0.5 N KOH-alcoholic solution was added. After the solution had boiled, it was permitted to chill. Then, three droplets of PP indicator were added, and the solution was titrated with 0.4901 N HCl until a distinct color change was observed. The test was conducted in duplicate, the volume of HCl titration used was recorded, and the saponification number was calculated using the following formula:

$$Saponification\ Number\ (E)\ = \frac{56{,}1\ \times (B - C)\ \times\ N\ HCl}{m}$$

56.1 is the molecular weight of KOH.

Hydrophilic-Lipophilic Balance (HLB) Test

The Griffin method, which is the calculation of HLB for nonionic surfactants derived from fatty acid methyl ester, can be used to measure HLB. Theoretically, the HLB value can be calculated using the following equation:

$$\mathrm{HLB} = 20\ \mathrm{x} \frac{\mathrm{Mh}}{\mathrm{M}}$$

Mh = molecular weight of the hydrophilic component
M = overall molecular weight

Using the following formula, the HLB value can be determined based on the titration between the saponification number and the acid number.

$$\mathrm{HLB} = 20\left(1 - \frac{\mathrm{S}}{\mathrm{A}}\right)$$

S = saponification number of the surfactant
A is the acid number of the surfactant.

Solubility Test

Place the methyl ester sample in a test vial using a pipette. Then, solvents including methanol, ethyl acetate, and n-hexane were added. After shaking, each test tube was allowed to stand upright. The results were then observed.

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Thin-layer chromatography

In the thin-layer chromatography examination, a comparison of the eluent n-hexane:methanol (2:3) was used, and the sample was identified using a capillary tube on the TLC plate. After inserting the TLC plate into a chamber containing solvent, the plate is irradiated with a UV lamp emitting wavelengths of 254 and 365 nm, and the results are observed.

RESULTS AND DISCUSSION

Sesame Seed Oil Extraction

The maceration of sesame seeds with n-hexane solvent for at least 72 hours yielded a mixture of oil and solvent. A rotary evaporator was used to purify and concentrate the maceration results. The concentration procedure yielded a luminous yellow oil with a yield of 36.14 percent. Before transesterification, the acid number, FFA content, and saponification number of the produced sesame seed oil were evaluated.

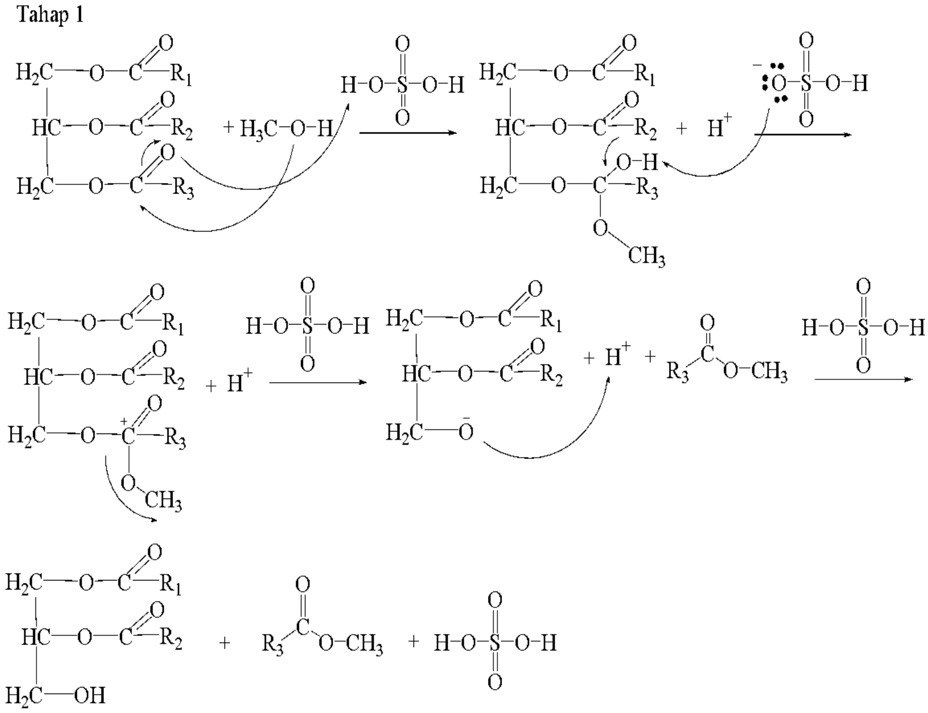
Table 1. Sesame seed oil test results

No.	Type of Analysis	Analysis results
1.	Acid Number (mg KOH/g)	1,1531
2.	FFA content (%)	0,5796
3.	Saponification Number (mg KOH/g)	51,287

Transesterification of Sesame Seed Oil

The transesterification procedure transforms triglycerides into methyl esters. At this point, sesame seed oil triglycerides are reacted with methanol, and the addition of the catalyst H_2SO_4 (p) produces methyl esters and then glycerol as a byproduct. Figure 1 depicts the formation of methyl esters during the transesterification reaction.

Tahap 1



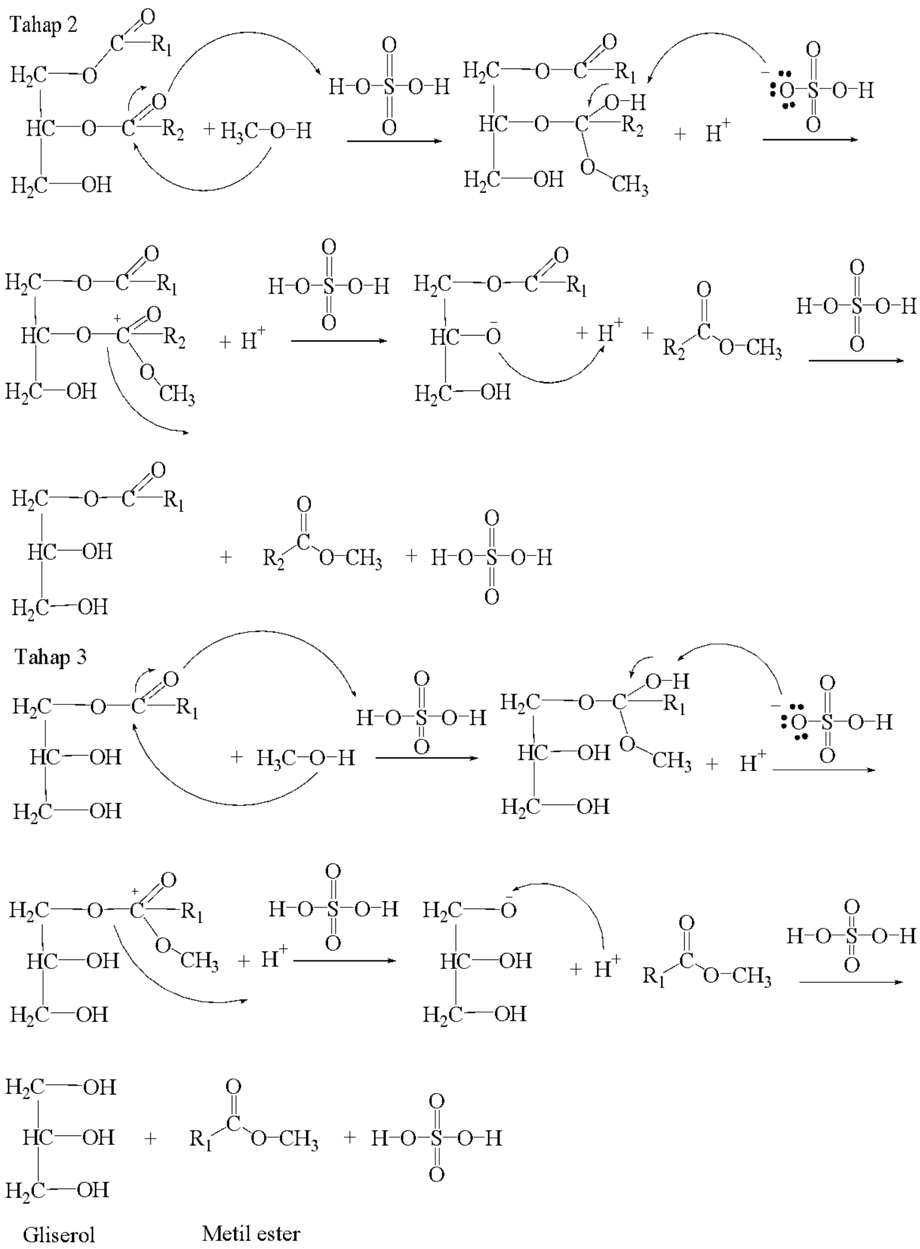


Figure 1. Transesterification reaction mechanism

At this point, 70 grams of sesame seed oil were combined with 19.2 milliliters of methanol (the ratio of oil moles to methanol moles was 1:6). The mole ratio of 1:6 is intended to shift the reaction to the right so that the conversion of triglycerides to methyl esters can operate optimally [7]. While stirring with a magnetic stirrer, 1.53 mL of 4% w/w catalyst H_2SO_4(p) sesame seed oil was steadily added. The catalyst is added prior to heating in order to slow down the catalyst's reaction rate; if the catalyst is added while reflux is occurring, the catalyst will react more quickly, and it is anticipated that this will cause a hydrolysis reaction [8]. Methanol serves as a methyl group donor, with the methyl group replacing the proton group (H^+) on the fatty acids in sesame seed oil to create methyl esters by bonding with ester groups. H_2SO_4(p) 4% by weight of sesame seed oil, specifically as a catalyst that can speed up the rate of the transesterification reaction because the reaction will run slowly without a catalyst, in addition to a catalyst concentration of 4% of the sample weight because it is the optimal condition for producing up to 90% methyl ester yields [9]. In addition, the addition of an acid catalyst to a completed reaction typically employs a catalyst concentration of 1% to 4% by weight of the sample [10]. The mixture was then refluxed for four hours at 60–70 °C methanol boiling point. The transesterification results were placed in a separatory receptacle and left to stand for 24 hours, at which point two phases formed. The upper phase is an opaque, yellow methyl ester, while the lower phase is a glycerol-based byproduct. The phase difference is caused by the polarity difference

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between methyl ester and glycerol; methyl ester is non-polar, whereas glycerol is polar. The upper phase, methyl ester, is repeatedly rinsed with distilled water to remove solvents and other impurities. The process is continued by purifying the methyl ester with anhydrous Na_2SO_4 to remove any remaining water and by evaporating the remaining solvent with a rotary evaporator to obtain a purer methyl ester. The evaporation of methyl ester resulted in the production of a yellow liquid with an 80% yield. Before proceeding with the amidation procedure, the methyl ester was evaluated for acid number, FFA content, saponification number, and HLB value, as well as analyzed by GC-MS and FT-IR to ascertain the fatty acid components and functional groups present in the methyl ester.

Table 2. Test results on sesame seed oil methyl ester

No.	Type of Analysis	Analysis results
1.	Acid Number (mg KOH/g)	0,5126
2.	FFA content (%)	0,2704
3.	Saponification Number (mg KOH/g)	50,049
4.	HLB value	2,0573

GC-MS analyses

On the basis of their molecular weight values, a GC-MS analysis of methyl esters was performed to ascertain the composition of the fatty acids present in the transesterified sesame seed oil methyl esters**.**

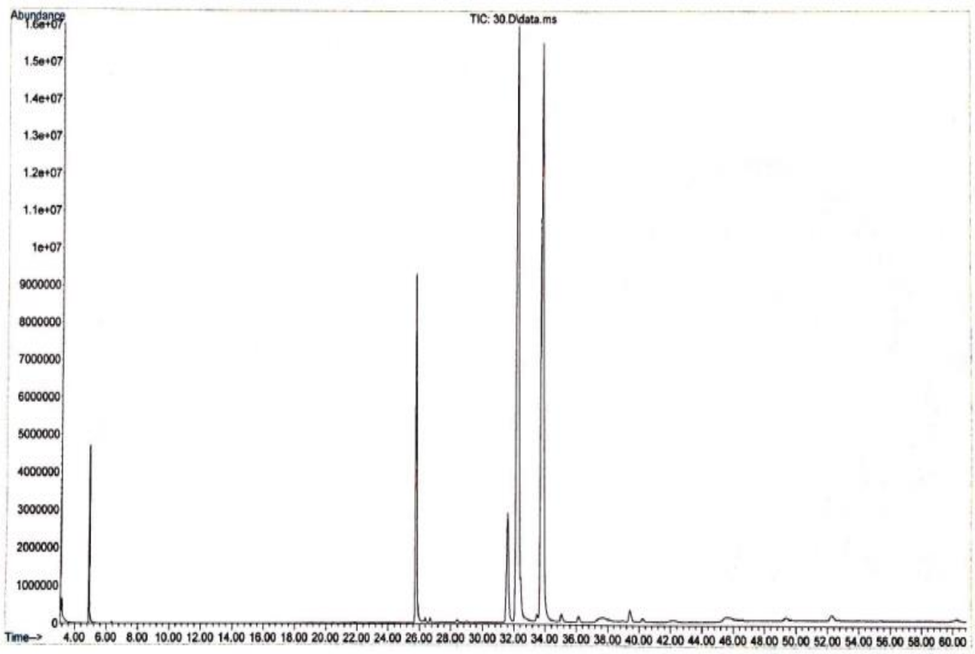

Figure 2. GC-MS Chromatogram of Sesame Seed Oil Methyl Esters

Table 3 displays the results of the GC-MS analysis of the methyl esters in sesame seed oil.

Methyl oleate, methyl linoleate, methyl palmitate, and methyl stearate made up 39.13%, 36.13%, 11.34%, and 6.14% of the dominant lactation components in sesame seed oil methyl esters, according to Table 3. Based on the GC-MS results, the compound is not only a methyl ester but also an ethyl ester; this is likely due to overheating and an inefficient reaction, as some fatty acids are not converted to methyl esters while others remain fatty acids. The conversion of lipids to ethyl esters The methyl ester with the highest concentration, 39.13%, was identified as the seventh peak in the GC-MS results. The following is the mass spectrum of methyl oleate, the most abundant methyl ester found in sesame seed oil.

Table 3. Fatty Acid Methyl Esters from Sesame Seed Oil

Peak	No	Retention Time	Area (%)
1	Methyl palmitate	25,828	11,34
2	(Z)-Methyl hexadec-11-enoate	26,235	0,07
3	Metil Palmitoleat	26,393	0,16
4	Hexadecanoic acid, ethyl ester	26,697	0,14
5	Heptadecanoic acid	28,379	0,08
6	Methyl stearate	31,640	6,14
7	Methyl Oleate	32,358	39,13
8	(E)-9-octadecenoic acid, ethyl ester oleate	33,502	0,36
9	Methyl linoleate	33,957	36,13
10	Linoleic acid ethyl ester	35,061	0,37
11	Methyl linoleate	36,157	0,27
12	9-octadecanoic acid	37,770	0,84
13	Eicosanoic acid	39,439	0,68
14	Cis-methyl 11-eicosenoate	40,246	0,18
15	9,12-octadecadienoic acid (Z,Z)	45,624	0,53
16	Methyl 20-methyl-heneicosanoate	49,396	0,21
17	n-Hexadecanoic acid	52,299	0,49
18	Octaethylene glycol monododecyl	60,256	0,23

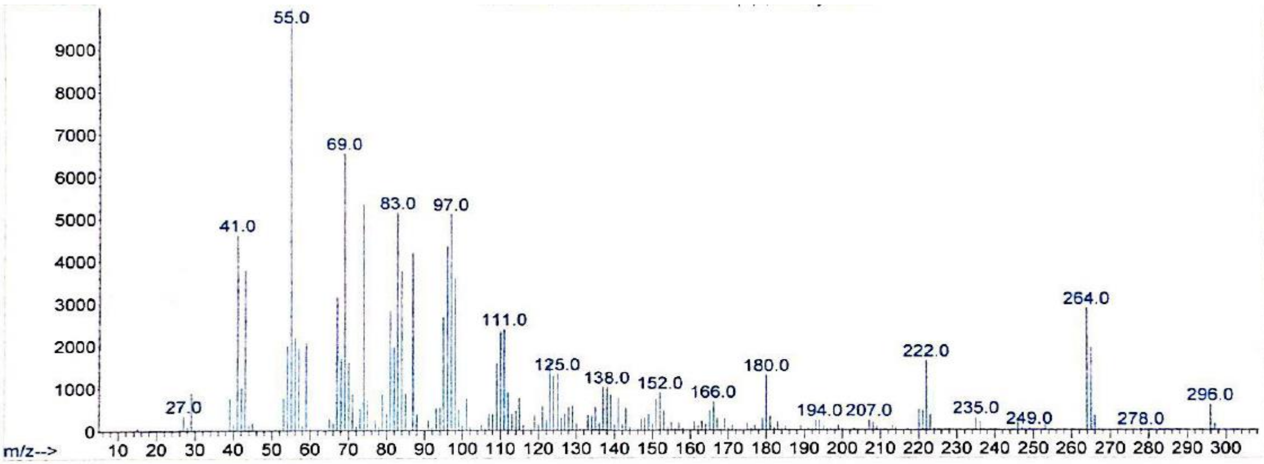

Figure 3. Methyl Oleate Mass Spectrum

The mass spectrum that appears on peak 7 in Figure 3 indicates a molecular weight of 296 and the molecular formula $C_{19}H_{36}O_2$ with a molecular weight of 296. Based on the molecular weight and molecular structure data acquired from the seventh peak, the spectrum is a methyl oleate compound with a 39.13% peak area, according to the data. Methyl oleate is the most abundant component of sesame seed oil's methyl ester, as determined by analysis.

Spectrophotometer FT-IR Analysis

Using the FT-IR spectrum, the functional groups of the obtained methyl ester were identified. An FT-IR analysis of sesame seed oil was not performed, but the acid number and FFA content of sesame seed oil with the resulting methyl ester were evaluated. If the value of the acid number and FFA methyl ester content is less than the value of the acid number and FFA content of sesame seed oil, then the compound resulting from transesterification

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is a methyl ester because some of the free fatty acids in sesame seed oil were converted to methyl ester, resulting in a decrease in the value of the acid number and content of FFA methyl ester. Figure 4 demonstrates the FT-IR results for methyl ester.

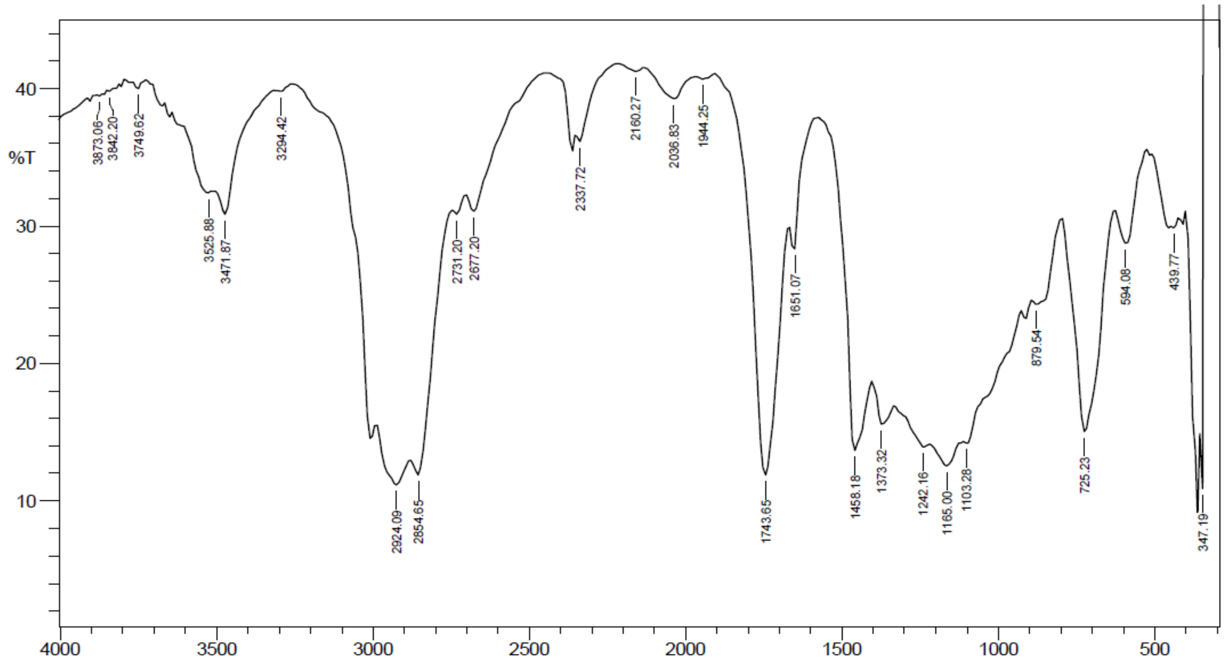

Figure 4. Spektrum FT-IR Methyl Ester

The FT-IR spectrum analysis of sesame seed oil methyl ester revealed absorption at wavenumber 2924 cm^{-1} and 2854 cm^{-1}, which is vibration stretching from the aliphatic C-H group, which is reinforced by the appearance of wavenumber 1458 cm^{-1} and 1373 cm^{-1}, which is vibration bending from the aliphatic C-H group. At wavenumber 1743 cm^{-1}, vibration extending from the C=O ester group is amplified, whereas at wavenumber 1165 cm^{-1}, vibration bending from the C-O group is amplified. Then absorption appears at wave number 1651 cm^{-1}, which is strengthened vibration stretching from the C=C group, which also appears at wavenumber >3000 cm^{-1}, and absorption appears at wavenumber 725 cm^{-1}, which is a chain of methyl ester compounds $-(CH_2)n-$. According to the results of the FT-IR spectrum analysis, the characterized compound is a methyl ester because it contains C=O ester, C=C, C-O, and aliphatic C-H groups.

Hydrophilic-Lipophilic Balance (HLB)

Value determination The Hydrophilic-Lipophilic Balance (HLB) of the methyl ester is derived from theoretical calculations, specifically the aggregate of the mixed HLB values of the hydrophilic and lipophilic groups in the methyl ester using the following formula:

$$HLB = 20 \text{ x} \frac{Mh}{M}$$

where Mh represents the relative molecular mass of the hydrophilic group and M represents the diethanolamide surfactant's relative molecular mass. The HLB value for sesame seed oil methyl ester is 2.0573 according to the above formula.

In addition, the HLB value of methyl ester can be calculated from the acid number and saponification number using the following formula:

$$HLB = 20\left(1 - \frac{S}{A}\right)$$

where S is the saponification number value and A is the acid number value of diethanolamide. Because the saponification number of sesame seed oil methyl ester is greater than the acid number, the HLB calculation of sesame seed oil methyl ester cannot be performed in practice.

Yield Characteristics of Methyl Esters

In addition to the FT-IR spectrum produced, the characteristics of the methyl ester were determined to acquire additional data, such as its form, solubility in various solvents, and TLC tests, in order to confirm that the synthesis product formed was a methyl ester. Table 4 displays the outcomes of the methyl ester's form, solubility, TLC test, and FFA value.

Table 4. Yield Characteristics of Methyl Esters

Sample	Phase	Solubility			KLT (2:3) (n-hexane : methanol)	FFA (%)
		N-hexane	Ethyl acetate	methanol		
Methyl Ester	Liquid	Soluble	Not Soluble	Soluble	Rf=0,48	0,2704

According to Table 4, methyl ester is non-polar, so it is completely soluble in n-hexane solvent, mildly soluble in ethyl acetate, and insoluble in methanol. As eluents for the TLC assay, n-hexane and methanol were used. According to the results, the ratio of n-hexane to methanol was 2:3, and methyl ester had an Rf value of 0.48 at one location. It can be concluded that the greater the Rf value, the closer the polarity of a sample is to the eluent used, so that methyl esters with low Rf values have non-polar properties in the TLC test. The FFA methyl ester test revealed a value of 0.2704%, which is lower than sesame seed oil's FFA content of 0.5796 percent. On the basis of the FFA from sesame seed oil and methyl ester, it can be concluded that the FFA value has decreased; this is due to the conversion of sesame seed oil's free fatty acids into methyl ester, so that the methyl ester contains relatively few free fatty acids.

CONCLUSION

Transesterification can produce sesame seed oil methyl esters with the addition of methanol and a 4% H_2SO_4(p) catalyst in the reaction process for four hours at 60-70 ^oC. According to GC-MS results, sesame seed oil methyl ester has a predominant methyl oleate content of 39.13% and yields 80%. Sesame seed oil methyl esters are a yellow liquid that is insoluble in methanol, faintly soluble in ethyl acetate, and soluble in n-hexane; it has an acid number of 0.5126 mg KOH/g, an FFA content of 0.2704%, and a saponification number of 50.049 mg KOH/g. The Rf value of sesame seed oil methyl esters in 2:3 eluents of n-hexane and methanol was 0.48, while the theoretical HLB value was 2.0573**.**

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REFERENCES

[1] Sunanto, Hatta. 2002. *Budidaya Wijen Manfaat dan Aspek Ekonominya.* Yogyakarta:Kanisius.
[2] Meisyahputri, B dan Martha A. 2017. Pengaruh Pemberian Kombinasi Minyak Rami dengan Minyak Wijen Terhadap Kadar Kolesterol *High Density Lipoprotein* (HDL) Tikus *Sprague Dawley Dislipidemia. Journal of Nutrition College Volume 6, Nomor 1, Halaman 35-42.*
[3] Daniel. 2009. Sintesis Surfaktan Dilauroil Maltosa Melalui Reaksi Asetilasi Terhadap Maltosa yang Diikuti Reaksi Transesterifikasi dengan Metil Laurat. *Indo. J. Chem., 2009 (3), 445-451.*
[4] Handajani, S., Godras J. M. dan Baskara K.A. 2010. Pengaruh Suhu Ekstraksi Terhadap Karakteristik Fisik, Kimia dan Sensoris Minyak Wijen (*Sesamum indicum* L.). *Jurnal AGRITECH, Vol. 30, No. 2.*
[5] Daniel. 2009. Pembuatan Senyawa Alkanolamida Tetrahidroksi Oktadekanoat yang Diturunkan dari Minyak Kemiri. *Indo.J. Chem., 2009, 9 (2), 271-277.*

[6] Daniel, Agustina R.M. dan Soerja K. 2018. Sintesis Surfaktan Turunan Amida yang Diperoleh Dari Reaksi Metil Risinoleat dan Etilendiamina. *Jurnal Kimia Mulawarman Volume 15 Nomor 2 Mei 2018.*
[7] Gunadi, F. 1999. Pemanfaatan Minyak Goreng Bekas Sebagai Bahan Baku Ester Metilat. *Skripsi fakultas Teknologi Pertanian Institut Pertanian Bogor.*
[8] Aziz, I., Siti N. dan Juwita S. 2013. Pembuatan Gliserol dengan Reaksi Hidrolisis Minyak Goreng Bekas. *Jurnal Chem. Prog. Vol. 6, No.1.*
[9] Sonntag, N. O. V. 1982. *Fat Splitting, Esterification and Interesterification. Dalam Daniel Swern. Bailey's Industrial Oil and Fat Products.* 4th ed.Vol 2. John Wiley and Sons, New York.
[10] Ketta, Mc., J.J. 1978. *Encyclopedia of Chemical Processing and Design. Vol. 1*. Marcel Dekker:New York.
[11] Makalalag, A. 2018. Pembuatan Metil Ester Dari Minyak Kelapa. *Jurnal Penelitian Teknologi Industri Vol. 10 No. 2 (67-74*).