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BIODIESEL SYNTHESIS OF CRUDE PALM OIL BY USING BIFUNCTIONAL CATALYST Sn/KAOLINITE AND K_2CO_3

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Abstract: The relatively high content of free fatty acids in crude palm oil inhibits the direct synthesis of biodiesel. The use of a bifunctional solid heterogeneous catalyst allows for simultaneous transesterification-esterification reactions and facilitates the purification of the final product from the reaction mixture. This study aimed to synthesize biodiesel from crude palm oil via the use of a Sn-K/metakaolinite catalyst in a simultaneous transesterification-esterification reaction. Biodiesel synthesis was carried out using crude palm oil before and after pretreatment. The optimum conditions were determined by the reaction time (1–5 hours), reactant molar ratio (1:2, 1:4, 1:6, 1:8, 1:10, 1:12), and catalyst concentration (1, 3, 5, 7 and 9%), and the resulting methyl esters were measured for density, viscosity, and free fatty acids and analyzed via GC–MS. The results obtained indicate that biodiesel synthesis was successfully carried out with completely converted methyl esters via treated crude palm oil. The optimum conditions for the reaction included a reaction time of 3 hours, a catalyst concentration of 5% and a reactant molar ratio of 1:10. The resulting methyl ester product has a density of 0.86 g/mL, a viscosity of 3.02 cSt and a free fatty acid content of 0.059%. The results of the GC–MS analysis revealed that the dominant methyl ester components were methyl oleate and methyl palmitate. The synthesis of biodiesel from crude palm oil with a Sn-K/metakaolinite catalyst has been proven to be carried out in simultaneous transesterification-esterification reactions with good catalytic activity.

Keywords: K_2CO_3, kaolinite, Sn, palm oil, simultaneous transesterification-esterification

Abstrak: Kandungan asam lemak bebas yang relatif tinggi dalam minyak sawit mentah menghambat sintesis langsung biodiesel pada minyak sawit mentah. Penggunaan katalis heterogen solid bifungsional memungkinkan terjadinya reaksi transesterifikasi-esterifikasi secara simultan dan memudahkan proses purifikasi produk akhir dari campuran reaksi. Penelitian ini bertujuan untuk mensintesis biodiesel dari minyak sawit mentah menggunakan katalis Sn-K/Metakaolinit pada reaksi transesterifikasi-esterifikasi secara simultan. Sintesis biodiesel dilakukan menggunakan minyak sawit mentah sebelum dan setelah dilakukan pretreatment. Kondisi optimum ditentukan melalui waktu reaksi (1-5 jam), rasio molar reaktan (1:2, 1:4, 1:6, 1:8, 1:10, 1:12), konsentrasi katalis (1,3,5,7 dan 9%) dan Metil ester yang dihasilkan diukur massa jenis, viskositas, asam lemak bebas, dan dianalisa dengan GC–MS. Hasil yang diperoleh menunjukkan bahwa synthesis biodiesel berhasil dilakukan dengan metil ester terkonversi secara total menggunakan minyak sawit mentah yang telah di-*pretereatment*. Kondisi optimum dalam reaksi tersebut didapatkan hasil yaitu waktu reaksi 3 jam, konsentrasi katalis 5% dan rasio molar reaktan 1:10. Produk metil ester yang dihasilkan memiliki massa jenis 0,86 g/mL, viskositas 3,02 cSt dan kadar asam lemak bebas sebesar 0,059%. Hasil analisa GC–MS menunjukkan bahwa komponen metil ester yang dominan adalah metil oleat dan metil palmitat. Sintesis biodiesel dari minyak sawit mentah dengan katalis Sn-K/Metakaolinit terbukti dapat dilakukan pada reaksi transesterifikasi-esterifikasi secara simultan dengan aktivitas katalitik yang baik.

Kata kunci: K_2CO_3, kaolin, Sn, Minyak sawit mentah, dan transesterifikasi-esterifikasi simultan.

INTRODUCTION

Palm oil has varying levels of free fatty acids (FFAs). To prevent catalyst deactivation during the biodiesel process, if the FFA content in vegetable oil is too high, an esterification process is necessary first to reduce the FFA level. The biodiesel production will then undergo a two-stage process (Arita et al. 2008; Pirouzmand et al. 2018). Therefore, to optimally produce biodiesel from palm oil, a catalyst capable of functioning simultaneously in both reactions is needed.

A commonly used heterogeneous catalyst is kaolinite as a support (Astar et al. 2015; Sari et al., 2016; Abukhadra & Sayed., 2018; Wahyuni et al., 2018). With respect to the enhancement of kaolinite performance, tin (Sn) compounds are of particular interest because they have the potential to be developed as heterogeneous catalysts in biodiesel production. In the +2 oxidation state, Sn has high Lewis acidity (Casas et al. 2013). Cardoso et al. (2008) used $SnCl_2$ as a catalyst in the esterification reaction of oleic acid, which resulted in a catalytic activity very similar to that of H_2SO_4. Roy et al. (2021) used $Sn(OH)_2$ as a catalyst in the esterification reaction of waste cooking oil, resulting in a FAME (Fatty Acid Methyl Ester) conversion of 99.5%, with a yield of 96%, but they could not be recovered because of their solubility in methanol and glycerol. Many researchers have focused on the use of heterogeneous base catalysts to solve these problems (Guldhe et al. 2017; Li et al. 2019). To reduce the disadvantages of homogeneous catalysts in esterification processes, research has focused on heterogeneous acidic or basic catalysts to develop a “green” approach for biodiesel production.

To increase the basicity of heterogeneous catalysts, K_2CO_3 (potassium carbonate) can be added. K_2CO_3 is widely found in coconut husk ash, empty palm fruit bunch ash, and coconut stem husk (Haryanto, 2005; Usman et al. 2007; Ritonga et al. 2013). K_2CO_3 can be utilized as a heterogeneous catalyst due to its alkali metal content, specifically potassium, which has a high level of basicity, making it a potential agent to increase the basicity of catalysts in biodiesel production. Dahlia et al. (2019) used K_2CO_3 impregnated into zeolite as a catalyst, which was able to reduce the free fatty acids in crude palm oil to 4.98%. Ritonga et al. (2013) used K_2CO_3 sourced from empty palm fruit bunch ash, producing methyl ester with the best yield of 81%, and the resulting methyl ester met the Indonesian National Standard (SNI) for biodiesel. Moreover, research by Jalalmanesh et al. (2021), who impregnated kaolin with K_2CO_3 as a catalyst in the production of biodiesel from sunflower oil, produced methyl esters with the best yield of 85.2%.

Therefore, in this study, the synthesis of a heterogeneous catalyst from kaolinite is conducted by impregnating it with Sn, followed by impregnation with K_2CO_3, with kaolinite as the support. The resulting catalyst will then be characterized via FTIR, XRF, and TPD techniques. After the catalyst is synthesized, it will be tested with palm oil, and the resulting product will be analyzed via TLC and GC–MS. The expected outcome is to increase the number of acid–base sites on the catalyst, leading to high conversion and yield.

METHOD

Materials and Equipment

The materials used in this research included oxalic acid ($C_2H_2O_4$, 99% Merck), sulfuric acid (H_2SO_4, 95–97%, Merck), dichloromethane (CH_2Cl_2), ethanol (C_2H_5OH, 95% Merck), phenolphthalein indicator, potassium hydroxide (KOH, 98%, Merck), tin(II) chloride ($SnCl_2$), potassium carbonate (K_2CO_3), anhydrous magnesium sulfate ($MgSO_4$), methanol (CH_3OH), n-hexane (C_6H_{14}), sodium chloride (NaCl), and silica gel G F254 plates, which were all procured from Merck. palm oil samples with FFA <5 (sample A) and FFA >5 (sample B), kaolinite obtained from the Capkala area of Bengkayang Regency.

The equipment used in this research included a 200 mesh sieve, Merck universal indicator, sieve shaker machine, Fourier transform infrared (FTIR, PerkinElmer Spectrum Version 10.400), X-ray fluorescence (XRF, PANalytical Epsilon 3), GC–MS Shimadzu QP2010 Ultra, vacuum pump, common laboratory glassware, a set of reflux apparatus, and a thermometer.

Kaolinite Preparation

The preparation of the clay followed the methods outlined by

Wahyuni et al. (2018). Kaolin was heated at a temperature of 80°C - 90°C for 3 hours, ground and washed with distilled water three times, followed by filtration. The wet kaolin was then dried at 80–90°C for 3 hours and sieved through a 200 mesh sieve. The prepared kaolin was calcined in a furnace at 600°C for 6 hours to produce metakaolin. The kaolin and metakaolin produced were analyzed via FTIR and X-ray fluorescence (XRF).

Catalyst Synthesis

The synthesis of kaolinite catalysts impregnated with Sn metal and K_2CO_3 was modified from the method of Yudistira et al. (2018) by dissolving $SnCl_2$ in H_2O and then adding metakaolin. In a reflux system, the catalyst mixture is prepared with a ratio of 1:4 based on metakaolin and $SnCl_2$ according to the cation exchange capacity (CEC) value at 70°C for 4 hours, left to stand for 24 hours, and then decanted to obtain a precipitate. The precipitate was dried for 20 hours at 100°C and then calcined at 450°C for 4 hours, resulting in a Sn/kaolinite catalyst. This Sn/kaolinite catalyst is then impregnated again with K_2CO_3. The impregnation was performed by mixing 5 grams of catalyst and K_2CO_3 solution with variations of 1.20, 2.00, and 2.80 grams in 60 mL of H_2O. The impregnation process of K_2CO_3 on the Sn/metakaolinite catalyst was carried out via the same procedure as the impregnation process of Sn onto metakaolinite, resulting in Sn-K/metakaolinite. The produced Sn-K/metakaolinite catalyst was then analyzed via X-ray fluorescence (XRF), Fourier transform infrared (FTIR), and acidity tests with temperature-programmed desorption (TPD).

Transesterification and esterification reactions of palm oil with a Sn-K/metakaolinite catalyst (Usman et al. 2009 and Yudistira, 2018)

The production of biodiesel through simultaneous transesterification-esterification reactions is carried out with a mixture of palm oil samples. The catalyst was then added to a three-necked flask and heated to a temperature of approximately 65°C while stirring with a magnetic stirrer. The reaction was monitored via thin-layer chromatography (TLC) with an appropriate eluent. The reaction product was then centrifuged and washed with a saturated NaCl solution, followed by the addition of anhydrous $MgSO_4$ to remove water. The product was then separated from anhydrous $MgSO_4$ by filtration, and the filtrate was collected. The free fatty acid content of the methyl ester produced was then determined via the following equation:

$$\text{FFA} = \frac{\text{mL KOH x N KOH x MW x 100\%}}{\text{sample weight (gram)x 1000}}$$

$$= \frac{\text{mL KOH x N KOH x BM}}{\text{sample weight (gram)x 10}}$$

MW = Sample weight

Analysis of Palm Oil Waste Esterification Products

The methyl ester product, which is solvent-free and residual catalyst-free, is then characterized for its physical properties (density and viscosity) and identified via GC–MS.

RESULTS AND DISCUSSION

Characterization of the Catalyst

Figure 1 shows the infrared spectral absorption of the four samples, which is quite sharp in the regions at approximately 600–1000 and 3400–3700 cm-1, with the kaolinite sample exhibiting sharp absorption peaks at 1000.31 cm-1, indicating the asymmetric stretching vibration of Si–O in tetrahedral layers (Tan, 1995). The peak at 914.80 cm-1 represents the vibration region of the Al-OH octahedron (Abdallah, 2006). The absorption peak at 758.41 cm-1 indicates the asymmetric vibration of Si-O-Si. Moreover, the absorption peak at 3677.52 cm-1 corresponds to the stretching vibration of Al-OH, which is a characteristic feature of kaolinite minerals. Overall, these functional groups are almost identical to the kaolin spectrum data presented by Rahmalia et al. (2018), Wahyuni et al. (2018) and Jalalmanesh et al. (2021)

These findings indicate that the structure of kaolin from Capkala village, Bengkayang Regency, West Kalimantan, can be classified into the alumina silicate mineral family, which specifically points toward kaolinite minerals (Sunardi et al. 2011).

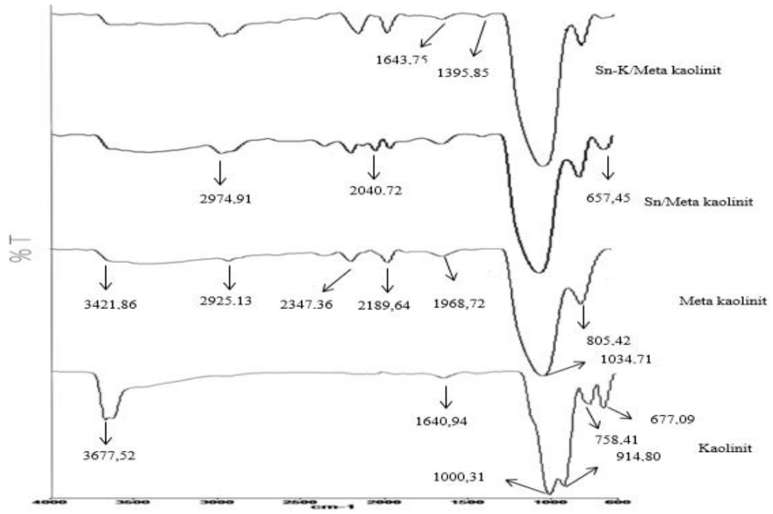

Figure 1. FTIR spectra of each catalyst

In the FTIR spectra of the metakaolinite (MK) sample, the peaks that were present in the kaolinite spectra before calcination disappeared. The disappearance of absorption peaks of -OH groups in the region of 914.80 and 3677.52 cm-1 after calcination is caused by dehydroxylation (release of -OH groups) (Ekosse, 2005). This indicates the alteration of the kaolinite structure, which consists of tetrahedral layers, during the calcination process and that the presence of silica or quartz structures is unaffected by the calcination process. Therefore, it can be concluded that structural changes occur in kaolinite after the calcination process, transforming it into metakaolinite.

The FTIR spectrum of the Sn/metakaolinite sample clearly reveals the influence of impregnation via $SnCl_2$ on the metakaolinite. This influence is observed by the appearance of new peaks, such as those in the regions of 2040.72 cm-1 and 657.45 cm-1, which were previously absent, indicating a structural change in metakaolinite, and there are absorptions maintaining the existing peaks in the region of 810–1050 cm-1. The absorption peaks at 810–1050 and 657.45 cm-1 indicate Si–O vibrations (Abdallah, 2006). The absorption peak in the region of 2040.72 cm-1 indicates O–H vibrations (Leanon *et al.*, 2015).

Moreover, in the Sn-K/metakaolinite sample, the influence of impregnation with K_2CO_3 on metakaolinite previously impregnated with $SnCl_2$ was also observed. This is evident from the disappearance and appearance of new absorption peaks, such as the disappearance of absorption peaks at 2347.66 and 2040.72 cm-1, which are attributed to -OH absorption peaks (Leanon *et al.*, 2015), and the appearance of new peaks at 1643.75 cm-1, indicating bending vibrations of -OH from H_2O trapped in the crystal lattice (Sunardi, 2010), and at 1395.85 cm-1 (Ekosse, 2005 and Jalalmanesh et al. 2021).

Tabel 1. Data characteristics via XRF

Sampel	**Composition Amount (%W/W)**						
	Si	**Al**	**Sn**	**K**	**Mg**	**Ca**	**Fe**
Kaolinite (K)	42,757	25,492	-	4,619	8,571	1,743	6,642
Metakaolinite (MK)	57,938	33,567	-	2,405	0,167	0,423	2,49
Sn/MK	32,069	23,02	32,264	-	0,396	0,656	4,995
Catalyst1	38,991	30,949	17,372	6,392	0,993	0,177	2,08
Catalyst 2	45,776	18,091	16,807	8,522	0,372	0,167	1,965
Catalyst 3	20,803	11,159	7,560	21,195	0,833	-	2,022

Tabel 2. Total Acidity of the Sn-K/Metakaolinite Catalyst

Sample Name	Description	Analyzed Area	Acidity (mmol/g)
Catalyst 1	Metakaolinite	0.07644	0.4192
Catalyst 2	Sn-Metakaolinite 4:1	0.09794	0.5197
Catalyst 3	Sn-K-Metakaolinite 1,2 g (K_2CO_3)	0.07525	0.3661
Catalyst 4	Sn-K-Metakaolinite 2 g (K_2CO_3)	0.12774	0.6414
Catalyst 5	Sn-K-Metakaolinite 2,8 g (K_2CO_3)	0.07012	0.3322

Table 1 shows that there are differences in composition before and after the addition of Sn and K_2O_3. Previously, kaolinite was shown to contain alkali and alkaline earth cations. After the impregnation of metakaolinite with Sn and K_2O_3, the chemical composition of the metakaolin changed, and there was an increase in the impregnated elements, namely, Sn and K, indicating the successful synthesis of the catalyst. XRF data are also used to determine the Si/Al ratio of kaolinite. The Si/Al ratios used in this study Kaolin is 1.67, the Si/Al ratio in metakaolin is 1.72, the Si/Al ratio in Sn/metakaolin is 2.31, the Si/Al ratio in catalyst 1 is 1.95, the Si/Al ratio in catalyst 2 is 2.53, and the Si/Al ratio in catalyst 3 is 1.86. On the basis of the XRF data, it can be concluded that there was a decrease in the Si/Al ratio in the Sn-K/metakaolinite catalyst, specifically in catalysts 1 and 3. This is because of the alkaline nature of the K ions in K_2CO_3, so the more K_2CO_3 added, the lower the Si/Al ratio of the catalyst.

Table 2 shows that the impregnation of Sn and K_2CO_3 is able to increase the acidity of metakaolinite, as evidenced by the increase in the total acidity of catalyst 4 to 0.6414 mmol/g. However, catalysts 3 and 5 instead experienced a decrease in total acidity. Overall, the total acidity of each Sn-K/metakaolinite catalyst tends to decrease. This occurred because of the alkaline nature of K_2CO_3; the more K_2CO_3 was impregnated, the less uniformly dispersed the potassium metal was, as evidenced by the decrease in the analyzed area of the catalyst.

Transesterification-Esterification Reaction of Crude Palm Oil via Sn-K/Metakaolinite Catalyst: Determination of the Reaction Time, Catalyst Concentration, and Reactant Molar Ratio

The optimal conditions were determined through reaction time (1–5 hours), reactant molar ratio (1:2, 1:4, 1:6, 1:8, 1:10, 1:12), and catalyst concentration (1, 3, 5, 7, and 9%) using Sn-K/metakaolinite catalyst 4 on the basis of the highest reduction in free fatty acids using crude palm oil with a moisture content of 0.28% and free fatty acid content of 18.17%.

Figure 2 shows that after 1 h of reaction, the crude palm oil sample was able to reduce free fatty acids, forming methyl esters, although the percentage was low at 8.96%. When the reaction time was increased to 2 h, there was a significant reduction in the percentage until the reaction time reached 3 h, with the reduction in free fatty acids down to 1.66%. This reduction occurred because the longer reaction time provided a greater opportunity for methanol and free fatty acids or triglycerides to collide and react to form methyl esters. Free fatty acids increased when the reaction proceeded for 4 h, and this increase continued when the reaction was conducted for 5 h, indicating that 3 h was the optimum reaction time. Extending the reaction time further would not be beneficial, as once the reaction reaches equilibrium, increasing the reaction time further would not increase the conversion yield. This proves that the simultaneous transesterification-esterification reaction that occurs is a reversible reaction.

Figure 3 shows that the optimum catalyst concentration in the reaction is 5% by weight, which can reduce free fatty acids to 1.66%. Generally, increasing the catalyst concentration increases the reaction rate, as the number of molecules and the chances of collisions increase (Hossain, 2010).

Using a higher catalyst concentration result in a decrease in the yield of methyl ester produced. This is due to the excessive reaction of the catalyst with triglycerides in palm oil, leading to the formation of more glycerol byproducts. Additionally, this may also be caused by the increased amount of methanol acting as a solvent for the catalyst rather than as a reactant, thus reducing product conversion since methanol can act as both a reactant and a protic solvent.

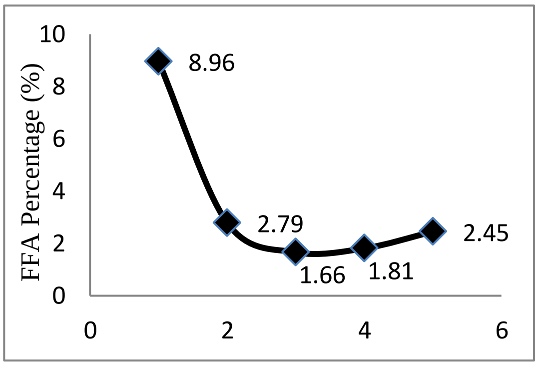

Figure 2. Percentage Reduction of FFA at Optimum Reaction Time

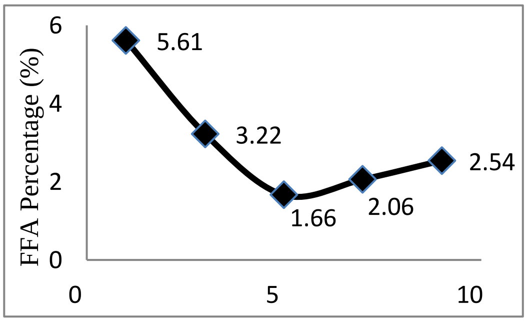

Figure 3. Percentage Reduction of FFA at Optimum Catalyst Concentration

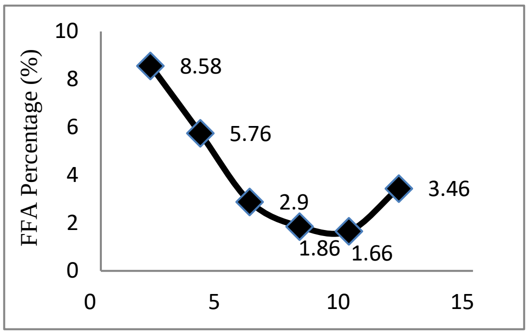

Figure 4. Percentage Reduction of FFA at Reactant Molar Ratio

Testing of the Sn-K/Metakaolinite Catalyst with CPO Pretreatment

The purpose of testing with CPO pretreatment is to observe the catalytic activity of the catalyst when palm oil (CPO) with an FFA content of <0.5% is used because when crude palm oil with an FFA content of 18.17% is used, the methyl ester is not completely converted, as evidenced by the presence of many oil stains in the synthesis product.

The testing was carried out by varying the Sn-K/metakaolinite catalyst (1.2 g K_2CO_3), Sn-K/metakaolinite catalyst (2.0 g K_2CO_3), and Sn-K/metakaolinite catalyst (2.8 g K_2CO_3) under optimum conditions, which included a reaction time of 3 hours, a catalyst concentration of 5%, and a reactant molar ratio of 1:10, with the crude palm oil having an FFA content of 0.43%.

Table 3 shows that with catalyst 5 Sn-K/metakaolinite (2.8 g K_2CO_3), the oil was completely converted to methyl ester, and no oil stains were present when the reaction proceeded for 3 hours. This proves that the catalyst has sufficiently high catalytic activity in the simultaneous transesterification-esterification reaction with CPO pretreatment with an FFA content of 0.43%. Reactions with CPO with <5% free fatty acids tend to undergo transesterification. However, the use of the Sn-K/metakaolinite catalyst with CPO pretreatment also significantly reduced the content of free fatty acids, with a reduction of 0.059%.

This research indicates that acidic active sites play a role in reducing free fatty acids, making the Sn-K/metakaolinite catalyst effective in the simultaneous transesterification-esterification reaction, with acidic active sites reducing free fatty acids and basic active sites converting triglycerides into methyl esters.

Table 3. Results of Methyl Ester Identification in CPO Pretreatment via Thin Layer Chromatography

Desciption	Reaction Time (Hour)	Catalyst Consentration (%)	Reactan Molar Ratio	TLC Result
Sn-K/Metakaolinite (1,2 g K_2CO_3)	3	5	1:10	Oil stains are still present
Sn-K/Metakaolinite (2,0 g K_2CO_3)	3	5	1:10	Oil stains are still present
Sn-K/Metakaolinite (2,8 g K_2CO_3)	3	5	1:10	Completely converted to Methyl Ester

Table 4. Methyl Ester Components in the Transesterification-Esterification Reaction Product of Crude Palm Oil with a Sn-K/Metakaolinite Catalyst

Methyl Ester	Peak	Area Coverage (%)
Methyl Laurat	1	0,11
Methyl Miristat	2	0,95
Methyl Oleat	3,7,13	45,58
Methyl Palmitat	4	45,49
Methyl Heksadekanoat	6	0,09
Methyl Stearat	8	6,26
Methyl Heksadekatrinoat	11	0,06
Methyl 6,9,12-Oktodekatrinoat	12	0,11
Methyl 10 0ksooktadekanoat	14	0,09
Methyl Araktat	15	0,40
Methyl Behenat	16	0,14
Methyl Lignoserat	17	0,09
Amount		**99,37**

Methyl Ester Characteristics

The characteristics of methyl esters, including density and viscosity, are determined physically and chemically through analysis via GC–MS. The results obtained are a density of 0.86 g/mL and a viscosity of 3.02 cSt. These results indicate that the methyl ester meets the fuel standard set (SNI-7182-2015). The GC–MS analysis results revealed that the major components present in palm oil are methyl oleate and methyl palmitate (Table 4).

CONCLUSION

The synthesis of biodiesel using the Sn-K/metakaolinite catalyst has been proven to be effective in the transesterification and esterification reactions of palm oil, with the oil being completely converted to methyl ester. The methyl ester product has a density of 0.86 g/mL, a viscosity of 3.02 cSt, and a final FFA content of 0.059%. GC–MS analysis revealed that the dominant components of the methyl ester are methyl oleate and methyl palmitate.

This study has several limitations, such as the excessive addition of K_2CO_3, which can reduce the acidity of the catalyst, and the absence of testing on the Sn-K/metakaolinite catalyst used after synthesis with crude palm oil. Therefore, further research is needed in the future to improve the efficiency of the catalyst by synthesizing the catalyst previously used in esterification and transesterification reactions simultaneously on palm oil.

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