Terbit *online* pada laman web jurnal : https://jes-tm.org/index.php/jestm/index

Journal of Engineering Science and Technology Management

| ISSN (Online) 2828-7886 |

Article

Synthesis of Methyl Ester Sulfonate from Crude Palm Oil Based on Aluminum Oxide Catalyst

Nur Asma Deli[1]✉, Razita Hariani[2], Rahma Sari Nasution[3]
Politeknik Kampar, Jl Tengku Muhammad Km. 2 Bangkinang, Indonesia(1,2,3)

E-mail: nur_asma@poltek-kampar.ac.id

ARTICLE INFORMATION

Volume 5 Issue 1
Received: 21 February 2025
Accepted: 28 March 2025
Published Online: 30 March 2025 *Online*: at https:JESTM.org/

A B S T R A C T

Surfactant is a surface active agent that reduces the surface tension of a medium, because it has the ability to combine parts between different phases such as air and water or phases that have different polarity such as oil and water. One of the vegetable oils that has great potential to be used as raw material for the manufacture of Methyl Ester Sulfonate (MES) is CPO. This Final Project aims to determine the manufacture of MES from CPO with $Na2S2O5$ as a sulfonation agent and understand the effect of $Al2O3$ (aluminum oxide) catalyst concentration on the characteristics of MES produced. The preparation of methyl esters was carried out by two-stage esterification and transesterification reactions using methanol as the alcohol source with $H2SO4$ as the acid catalyst and NaOH as the base catalyst. Sulfonation was carried out at temperature, ratio of methyl ester to $Na2S2O5$ 1:1, $Al2O3$ catalyst concentration of 0.5%, 0.75%, 1%, 1.25%, and 1.5% and reaction time of 5 hours. The best results were obtained from the treatment of 0.75% $Al2O3$ catalyst concentration with the quality of MES produced having a yield of 88.27%, pH 7.51, acid number 4.48 mgKOH/g, density 887 kg/m3 and sulfonate absorbance value 0.155.

Keywords

Methyl Ester Sulfonate
Sulfonation
Aluminum oxide
Methyl Ester

1. BACKGROUND

1.1 Introduction

Crude Palm Oil (CPO) is one of Indonesia's strategic commodities with abundant production and extensive utilization in both food and non-food sectors. Besides being used as a raw material for cooking oil, margarine, and biodiesel, CPO also has great potential as a base material for applied chemical products, including vegetable oil-based surfactants (Foo et al., 2022). The high triglyceride content in CPO makes it very suitable for conversion into methyl esters, which can then be processed into Methyl Ester Sulfonate (MES)-a type of environmentally friendly anionic surfactant (Amaliah et al., 2021).

MES surfactants are now an attractive alternative to synthetic surfactants such as linear alkyl benzene sulfonate (LAS), as they offer advantages in terms of biodegradability, low irritancy, and stable performance in hard water. MES also comes from renewable sources and has the potential to replace petrochemical-based surfactants in the long term (Kulkarni & Jaspal, 2023).

MES production from CPO consists of two main stages, namely transesterification and sulfonation (Amaliah et al., 2021). In the transesterification stage, triglycerides in CPO are converted into methyl esters through a reaction with methanol. This reaction is generally catalyzed by homogeneous bases such as NaOH or KOH, but the use of homogeneous catalysts produces by-products that are difficult to separate and pollute the environment. Therefore, the use of heterogeneous catalysts such as aluminum oxide (Al_2O_3) is a more sustainable alternative because it is stable, insoluble in the reaction phase, and can be reused.

1.2 Research Purposes

This study aims to investigate the synthesis of methyl ester sulfonate from crude palm oil using aluminum oxide catalyst, as well as to evaluate the effectiveness of the catalyst in the transesterification process and the quality of the MES product produced. This approach is expected to support the development of an efficient and environmentally friendly biomass-based surfactant industry**.**

2. LITERATURE RIVIEW

2.1 Surfactan

Surfactants are active compounds that reduce surface tension (surface active agents) and can be produced through chemical or biochemical synthesis. Surfactants have been used as coagulants, wetting agents, foaming agents, emulsifiers, and have been applied in the chemical, pharmaceutical, cosmetic, and food industries (Jahan et al., 2020).

The presence of hydrophobic and hydrophilic groups within a single molecule causes surfactants to tend to be found at the interface between phases with different degrees of polarity and hydrogen bonds, such as oil and water (Ghosh et al., 2020). The molecular structure of surfactants can be visualized as tadpoles or mini tennis balls consisting of a head and a tail (Fig. 1). The head and tail regions have different properties due to their unbalanced molecular structure (head-tail configuration). The head region, which is hydrophilic (water-loving), is highly polar and compatible with water. The tail region, which is hydrophobic (water-repelling), is nonpolar and more attracted to oil/fat.

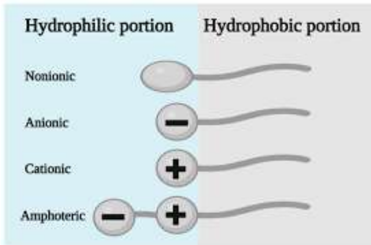

Fig. 1. Surfactant Molecular Structure

2.2 Surfactant Methyl Ester Sulfonate

MES is an anionic surfactant made from vegetable and animal oils and functions as an active ingredient that reduces surface tension. It is widely used in various industries such as food, beverage, soap, detergent, cosmetics, and petroleum (Kaur et al., 2023). The chemical structure of methyl ester sulfonate can be seen in Fig. 2.

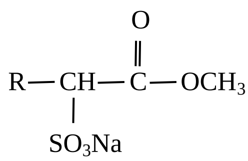

Fig. 2 Structure of methyl ester sulfonate

MES surfactants are produced through a sulfonation process, which involves reacting methyl ester with a sulfonating agent. The sulfonation agent used in the sulfonation process is a reactant containing a sulfonic group. Large industries use SO_3 gas as the reactant because it is highly reactive, produces high-yield products, generates no byproducts, and has lower waste treatment costs. However, its drawbacks include the high cost of the equipment required and the need for strict safety precautions due to the high reactivity of SO_3 gas (Yusuff & Bode-Olajide, 2023).

2.3 Sulfonation Agent

A sulfonation agent is defined as a component or material that can replace hydrogen bonds in a compound with a sulfonate group (SO_3H) (Akram et al., 2024). Sulfonation agents are used in sulfonation reactions, which are chemical reactions that add acid groups (SO_3H) to molecules. MES is produced through a sulfonation process, which involves reacting methyl ester with a sulfonation agent. The reagents that can be used in the sulfonation process include sulfuric acid (H_2SO_4), oleum (a solution of SO_3 in H_2SO_4), sulfur trioxide (SO_3), NH_2SO_3H, and $ClSO_3H$ (Sharghi et al., 2018).

3. METHODOLOGY

The materials used in the production of methyl ester are CPO as the raw material, methanol as the solvent, H2SO4 as the catalyst in the esterification process, and NaOH as the catalyst in the transesterification process. The materials used in the sulfonation process are methyl ester as the ester source, sodium metabisulfite ($Na_2S_2O_5$) as the sulfonation agent, aluminum oxide (Al_2O_3) as the catalyst, methanol, and NaOH. The materials used for analyzing the characteristics of CPO, methyl ester, and MES are 96% neutral alcohol, phenolphthalein indicator, 0.1 N NaOH, 0.1 N KOH, hexane, and butanol.

Methyl ester is produced through two reaction stages, namely esterification and transesterification. In the esterification stage, crude palm oil is reacted with methanol (ratio 6:1) and H_2SO_4 catalyst (1% oil mass) at a temperature of 65°C for 60 minutes with stirring at 400 rpm, then separated from the remaining methanol and water to reduce the free fatty acid content. In the subsequent stage, transesterification is carried out by adding methanol (ratio 6:1) and NaOH catalyst (1%) under the same conditions. The methyl ester was separated from glycerol using a separatory funnel, then purified by washing with hot water (70°C) until neutral, and dried at 120°C for 1 hour to remove residual water.

MES was synthesized through a sulfonation reaction between methyl ester and $Na_2S_2O_5$ with the aid of Al_2O_3 catalyst (0.5–1.5% w/w) at a temperature of 90 °C for 5 hours with stirring at 450 rpm. After the reaction, the mixture is allowed to settle for 24 hours to separate the remaining reactants and catalyst. Purification is carried out by adding 30% methanol (v/v) at 55°C for 1.5 hours, then the temperature is increased to 70–80°C to evaporate the methanol. After the methanol is condensed, the solution is neutralized with 20% NaOH to pH 6–8 and heated at 55°C for 30 minutes. The final MES is stored in glass containers and analyzed for its characteristics.

4. RESULTS AND DISCUSSION

4.1 CPO Characteristics

An analysis of the characteristics of crude palm oil (CPO) was conducted to determine the initial condition of the raw material before it was converted into methyl ester. The parameters tested included moisture content, free fatty acids (FFA), and impurities, which affect process efficiency and product quality. The results of the analysis are shown in Table 1.

The CPO moisture content of 0.3% meets the requirements for transesterification because it is below the maximum limit of 1%. However, the high free fatty acid (FFA) content of 3.07% exceeds the safe limit of 2%, so a preliminary esterification process is required to reduce the FFA before transesterification. High water and FFA content can trigger soap formation, reduce the effectiveness of the base catalyst, and complicate glycerol separation (Chanakaewsomboon et al., 2020). Therefore, the conversion of CPO into methyl ester is carried out through two reaction stages: acid-catalyzed esterification and base-catalyzed transesterification.

Table 1. Characteristics of CPO

Parameter	Value
Moisture content (%)	0.3
Free fatty acid content (%)	3.07
Impurity content (%)	0.05

4.2. Methyl ester

The characteristics of methyl esters produced from crude palm oil conversion were analyzed to evaluate the quality of the resulting products. The parameters tested included water content, acid value, viscosity, and yield, which are important indicators in assessing the success of the process and the suitability of the product to quality standards. The complete analysis results are presented in Table 2.

Tabel 2. Characteristics of Methyl Ester

Parameter	Value	SNI 7182-2015
Moisture Content (%)	0.09	0.05
Acid Value (mg KOH/g)	0.701	Max. 0.8
Viscosity (cSt)	5.949	2.3 - 6
Methyl Ester Yield (%)	91.63	-

The methyl ester produced exhibits characteristics indicative of successful CPO conversion, with a moisture content of 0.087%, slightly exceeding the SNI 7182-2015 standard (max. 0.05%), likely due to incomplete drying. The acid number of 0.701 mg KOH/g still meets the SNI limit (max. 0.8 mg KOH/g), although the high value may affect the performance of MES surfactants. The methyl ester viscosity of 5.949 cSt also meets quality standards. The methyl ester yield reached 91.6%, indicating high conversion efficiency and supporting previous findings that the use of a basic catalyst enhances ester formation from free fatty acids (Belousov et al., 2021).

4.3 Methyl Ester Sulfonate

MES yield is the amount of methyl ester sulfonate produced from the reaction to the amount of raw material used. In this study, the yield ranged from 71.92% to 83.27%. These results are in line with Isra's (2019) study, which reported a sulfonation yield of 83.47%. The effect of catalyst concentration on MES yield is shown in Fig. 3. The graph shows the effect of Al_2O_3 catalyst concentration on the yield of Methyl

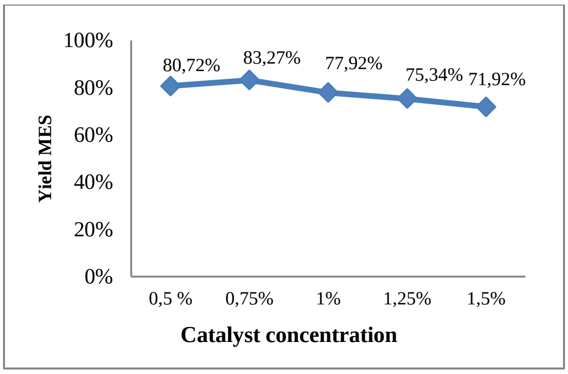

Fig. 3 Effect of catalyst concentration on MES yield

Sulfonate Ester (MES). It can be seen that the highest yield of 83.27% was achieved at a catalyst concentration of 0.75%, while lower concentrations (0.5%) and higher concentrations (1%, 1.25%, 1.5%) resulted in gradually decreasing yields, reaching the lowest value of 71.92% at a concentration of 1.5%. The increase in yield at a concentration of 0.75% indicates that at this point, the sulfonation reaction is most optimal, where the amount of catalyst is sufficient to accelerate the reaction without causing significant side effects. However, at concentrations above 0.75%, the decrease in yield is likely due to excess catalyst, which can cause side reactions, increased viscosity, or difficulties in product separation, thereby reducing reaction efficiency (Chowdhury et al., 2022).

4.4 Acidity

Acidity (pH) measurements were conducted to determine the acidity level of the Methyl Ester Sulfonate (MES) product produced at various catalyst concentrations. Appropriate pH values are very important because they affect the stability and effectiveness of surfactants in their application (Belhaj et al., 2020). The pH measurement results for each catalyst concentration variation are presented in Fig. 4.

Fig. 4 shows The pH values obtained from this study ranged from 6.51 to 7.65. This is consistent with the research conducted by The Chemiton Corporation, USA, which explains that the MES synthesis process carried out with an additional process that can increase the MES pH value, namely neutralization with the addition of NaOH. The effect of adding the neutralization process can be seen in the study conducted by Shakeel & Khan (2022), where the pH of MES before the neutralization process was 3.95–4.93 and after the neutralization process, the pH increased to 6.92–7.67. The pH value of MES produced in this study is higher than the pH value of commercial MES, which is 5.3 (Harti et al., 2016).

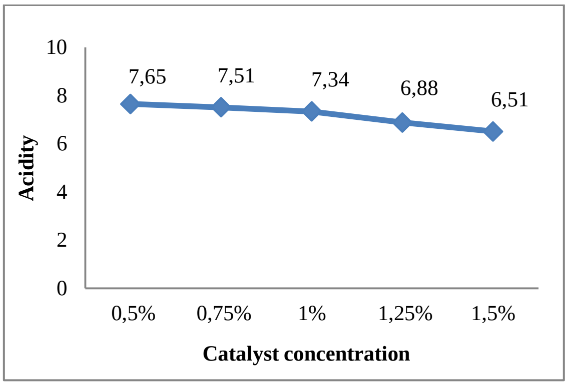

Fig. 4. Effect of catalyst concentration on acidity

4.5 Acid Value

Determining the acid value is necessary to determine the amount of KOH required to neutralize free fatty acids in MES. This value is also related to the sulfon content, where a higher acid number indicates excessive sulfon formation, which can reduce the solubility and effectiveness of MES as a surfactant. The analysis results show that the highest acid number of 6.45 mg KOH/g was obtained at a catalyst concentration of 1.5%, while the lowest value of 1.4 mg KOH/g was obtained at 0.5%. This trend indicates that increasing Al_2O_3 concentration enhances the reactivity of $Na_2S_2O_5$ with methyl ester, producing more sulfonate groups ($–SO_3$) that release hydrogen atoms and impart acidic properties to the product. This is consistent with Manggala et al. (2020), who stated that the better the contact between reactants, the higher the acid number formed. Additionally, according to Nur Iman et al. (2016), the purification process can also influence the acid number through the formation of di-salt compounds. The most significant increase occurred at a catalyst concentration of 0.75%, while at higher concentrations, the increase was more moderate. The graph showing the effect of catalyst concentration on MES acid number is presented in Fig. 5.

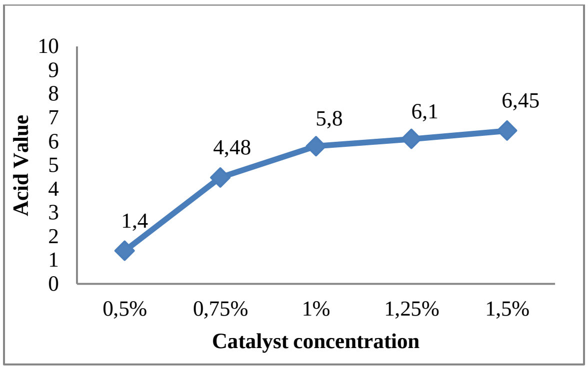

Fig. 5. Effect of catalyst concentration on acid value

4.5 Absorbance of MES Sulfonate

The absorbance of sulfonate content was measured using a UV-Visible spectrophotometer. The absorbance produced by the methyl ester sulfonation process in this final project ranged from 0.103 to 0.220. The highest value of 0.220 was obtained at a catalyst concentration of 1%. The graph showing the effect of catalyst concentration on sulfonate absorbance in MES can be seen in Fig. 6.

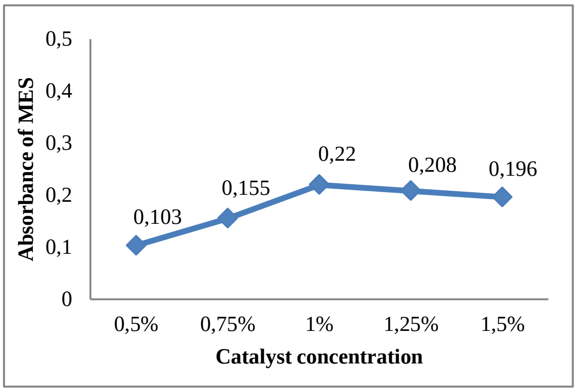

Fig. 6. Effect of catalyst concentration on absorbance of MES

Increasing the concentration of Al_2O_3 catalyst from 0.5% to 1% tends to increase the MES absorbance, indicating the formation of more sulfonate groups (Shi et al., 2025). However, when the catalyst concentration is increased to 1.5%, the absorbance decreases. This is likely due to increased collisions between $Na_2S_2O_5$ particles and methyl esters at high concentrations, which initially accelerate sulfonate formation. However, excess catalyst can lead to soap formation through side reactions, thereby reducing the number of effective sulfonate groups formed in the MES structure. This indicates that catalyst concentration directly influences the sulfonate absorbance value, which serves as an indicator of the success of the sulfonation reaction.

5. CONCLUSION

Based on the results of the study, it can be concluded that the production of Methyl Ester Sulfonate (MES) surfactant is carried out through several stages of processing, namely esterification, transesterification, sulfonation, purification, and neutralization of MES. The raw material used was Crude Palm Oil (CPO) with initial characteristics of free fatty acid content of 3.07%, moisture content of 0.30%, and impurity content of 0.05%. The esterification process successfully reduced the free fatty acid content to 1.50%, while the transesterification process produced methyl ester with a moisture content of 0.087%, acid number of 0.701 mg KOH/g, viscosity of 5.949 cSt, and methyl ester yield of 91.63%. The best MES product was obtained at a catalyst concentration of 0.75% Al_2O_3, with characteristics including a yield of 88.27%, pH of 7.51, acid number of 4.48 mg KOH/g, density of 887 kg/m^3, and sulfonate absorbance value of 0.155, indicating good surfactant quality.

Acknowledgement

The authors would like to express their sincere gratitude to **Politeknik Kampar** for the financial and institutional support provided during the completion of this research. The facilities and resources made available greatly contributed to the success of this study.

References

Akram, A., Iqbal, M., Yasin, A., Zhang, K., & Li, J. (2024). Sulfonated Molecules and Their Latest Applications in the Field of Biomaterials: A Review. Coatings, 14(2), 243. https://doi.org/10.3390/coatings14020243

Amaliah, D., Qadariyah, L., & Mahfud, M. (2021). The Production of Surfactant Anionic Methyl Ester Sulfonate (MES) from Virgin Coconut Oil (VCO) with Ultrasound-Assisted. Journal of Physics: Conference Series, 1845(1), 012005. https://doi.org/10.1088/1742-6596/1845/1/012005

Belhaj, A. F., Elraies, K. A., Mahmood, S. M., Zulkifli, N. N., Akbari, S., & Hussien, O. S. (2020). The effect of surfactant concentration, salinity, temperature, and pH on surfactant adsorption for chemical enhanced oil recovery: A review. Journal of Petroleum Exploration and Production Technology, 10(1), 125–137. https://doi.org/10.1007/s13202-019-0685-y

Belousov, A. S., Esipovich, A. L., Kanakov, E. A., & Otopkova, K. V. (2021). Recent advances in sustainable production and catalytic transformations of fatty acid methyl esters. Sustainable Energy & Fuels, 5(18), 4512–4545. https://doi.org/10.1039/D1SE00830G

Chanakaewsomboon, I., Tongurai, C., Photaworn, S., Kungsanant, S., & Nikhom, R. (2020).

Investigation of saponification mechanisms in biodiesel production: Microscopic visualization of the effects of FFA, water and the amount of alkaline catalyst. Journal of Environmental Chemical Engineering, 8(2), 103538. https://doi.org/10.1016/j.jece.2019.103538

Chowdhury, S., Shrivastava, S., Kakati, A., & Sangwai, J. S. (2022). Comprehensive Review on the Role of Surfactants in the Chemical Enhanced Oil Recovery Process. Industrial & Engineering Chemistry Research, 61(1), 21–64. https://doi.org/10.1021/acs.iecr.1c03301

Foo, W. H., Koay, S. S. N., Chia, S. R., Chia, W. Y., Tang, D. Y. Y., Nomanbhay, S., & Chew, K. W. (2022). Recent advances in the conversion of waste cooking oil into value-added products: A review. Fuel, 324, 124539.

Ghosh, S., Ray, A., & Pramanik, N. (2020). Self-assembly of surfactants: An overview on general aspects of amphiphiles. Biophysical Chemistry, 265, 106429. https://doi.org/10.1016/j.bpc.2020.106429

Jahan, R., Bodratti, A. M., Tsianou, M., & Alexandridis, P. (2020). Biosurfactants, natural alternatives to synthetic surfactants: Physicochemical properties and applications. Advances in Colloid and Interface Science, 275, 102061. https://doi.org/10.1016/j.cis.2019.102061

Jatikta Yuni Harti, Nirwana ’., & Irdoni ’. (2016). Sintesis Surfaktan Metil Ester Sulfonat dari Palm Oil Methyl Ester dan Natrium Metabisulfit dengan Penambahan Katalis Kalsium Oksida. Jurnal Online Mahasiswa Fakultas Teknik Universitas Riau, 3(1), 1–7.

Kaur, H., Kumar, P., Cheema, A., Kaur, S., Singh, S., & Dubey, R. C. (2023). Biosurfactants as Promising Surface-Active Agents: Current Understanding and Applications. In P. Kumar & R. C. Dubey (Eds.), Multifunctional Microbial Biosurfactants (pp. 271–306). Springer Nature Switzerland. https://doi.org/10.1007/978-3-031-31230-4_13

Kulkarni, D., & Jaspal, D. (2023). Surfactants in waste water: Development, current status and associated challenges. Materials Today: Proceedings, S2214785323050939. https://doi.org/10.1016/j.matpr.2023.11.022

Manggala, A., Ningsih, A. S., Hilmasari, J., Aliza, S. N., & Kusari, W. A. (2020). Pengaruh Variasi Suhu, Rasio Mol Reaktan Dan Persen Katalis Terhadap Metil Ester Sulfonat Menggunakan Reaktor Sulfonasi. 11(01).

Nur Iman, Abdul Rahman Razak, & Nurhaeni Nurhaeni. (2016). Sintesis Surfaktan Metil Ester Sulfonat (Mes) Dari Metil Laurat. Kovalen,2(2).https://doi.org/10.22487/j24775398.2016.v2.i2.6726

Shakeel, S., & Khan, M. Z. (2022). Enhanced production and utilization of biosynthesized acetate using a packed-fluidized bed cathode based MES system. Journal of Environmental Chemical Engineering, 10(4), 108067. https://doi.org/10.1016/j.jece.2022.108067

Sharghi, H., Shiri, P., & Aberi, M. (2018). An overview on recent advances in the synthesis of sulfonated organic materials, sulfonated silica materials, and sulfonated carbon materials and their catalytic applications in chemical processes. Beilstein Journal of Organic Chemistry,14,2745–2770. https://doi.org/10.3762/bjoc.14.253

Shi, N., Zhu, H., Qi, J., Li, B., & Zhang, J. (2025). Hydrolysis of carbonyl sulfide using non-ionic surfactant-modified mesoporous γ-Al2O3 catalysts with high efficiency. Separation and Purification Technology, 354, 129356. https://doi.org/10.1016/j.seppur.2024.129356

Yusuff, A. S., & Bode-Olajide, F. B. (2023). Comparing the performances of different sulfonating agents in sulfonation of methyl esters synthesized from used cooking oil. 60(4), 277–285. https://doi.org/10.1515/tsd-2023-2513