Science and Technology Indonesia
e-ISSN:2580-4391 *p*-ISSN:2580-4405
Vol. 9, No. 4, October 2024

Research Paper

Methyl Ester Sulfonate (MES) Surfactant Production from Waste Cooking Oil (WCO) with Microwave Technology

Lailatul Qadariyah[1*], Dhea Septyanonie Ryvalda[1], Narendra Yudha Aditama[1], Viqhi Aswie[2], Mahfud Mahfud[1]

[1]*Department of Chemical Engineering, Institut Teknologi Sepuluh Nopember, Surabaya, 60111, Indonesia*
[2]*Madrasah Aliyah Negeri 1 Kota Sukabumi, Sukabumi, 43144, Indonesia*
***Corresponding author**: lqadariyah@chem-eng.its.ac.id

Abstract
Traction Energy Asia 2020 reported that 3 million kilolitres of WCO were collected in Indonesia in 2019, 1.6 million kilolitres from urban households. WCO poses risks due to common reuse or disposal. Repurposing for MES surfactant is vital. Hence, this study aims to produce an MES surfactant from WCO feedstock using $NaHSO_3$ as a microwave-assisted reactant by observing the influence of variables such as reactant mole ratio, catalyst concentration, sulfonation reaction time, and microwave power. The adsorption method involves vacuum filtration of WCO to remove impurities, mixing with activated carbon, and settling before a second filtration. Transesterification transforms WCO into methyl ester through mixing with methoxide solution with a molar ratio of methanol to WCO of 1:9 and a 1 wet% NaOH catalyst based on WCO, followed by washing and drying. Sulfonation involves reacting methyl ester with $NaHSO_3$ (1:1, 1:2, 1:3, 1:4) and CaO catalyst (1%, 1.5%, 2%, 2.5%). The reaction occurs in a microwave at power variations of 300, 450, 600, and 750 Watts, as well as with variations in time of 20, 30, 40, 50, and 60 minutes. After that, it ends with purifying and neutralizing to produce MES. The optimal conditions for MES production are a 1:2 molar ratio of reactants, 1.5% CaO catalyst concentration, 20 minutes, and 450 W, yielding 48.06%. MES characteristics: pale yellow color, density of 0.859 g/cm^3, viscosity of 1.780 cSt, and surface tension of 32.62 dyne/cm. FTIR analysis confirms sulfonic acid groups at 1195.27 cm^{-1} and 1169.1 cm^{-1} wavelengths.

Keywords
Methyl Ester Sulfonate, Microwave, Surfactant, Transesterification, Waste Cooking Oil

Received: 6 June 2024, Accepted: 2 August 2024
https://doi.org/10.26554/sti.2024.9.4.929-940

1. INTRODUCTION

Surfactants are dual-purpose, amphipathic molecules, which can be described as polar and non-polar compounds because they have two distinct parts (Ivankovic et al., 2009). First, there are polar groups containing elements such as oxygen, phosphorus, nitrogen, and functional groups such as alcohols, sulphates, sulfonates, and others (Alwadani and Fatehi, 2018). The non-polar part consists of long hydrocarbon chains, such as alkyl or alkyl benzene. Surfactants have a hydrophilic head that has a higher affinity for polar solvents and a long hydrophobic tail, which Favors non-polar compounds (Sorhie et al., 2022).

Surfactants have been widely used in various applications including detergents (Scott and Jones, 2000), wetting agents (Panda et al., 2020), emulsifiers (Marti-Mestres and Nielloud, 2002), health products (Johnson et al., 2021), paint and printing processes (Kulkarni and Jaspal, 2023; Pan et al., 2018). Surfactant production reached 14.1 million tons in 2017 and has increased by 18% in 2022 (Johnson et al., 2021). This increase occurred due to demand for health-related products during the COVID-19 pandemic (Jesus et al., 2021).

Most of the surfactants currently produced are derived from petroleum. However, these synthetic surfactants tend to be toxic and difficult to break down by microorganisms (Masakorala et al., 2011) and most have negative impacts due to their corrosive (Alwadani and Fatehi, 2018). In addition, their use leads to a greater shortage of fossil resources and global warming issues (Jahan et al., 2020).

Therefore, the scientific community is now looking for surfactants produced directly from plants such as saponins and lecithin (Auliya Putri et al., 2023), or generated (Liu et al., 2020). Various industries have started to use these types due to their various benefits, including diverse structures, reduced toxicity, increased biodegradability, improved selectivity, the capacity to function in a variety of pH, temperature, and salinity conditions, as well as a lower CMC and higher pH (Da Rosa et al., 2015).

One of the natural materials that can be used as surfactants is coconut or palm oil sulfonate-based surfactants (Hill, 2001). These-based surfactants are more stable and more tolerant to pH hydrolysis than surfactants from other plants (Perkins, 1998). Even Masuda et al. (1993) stated that MES being carbon neutral is more environmentally friendly than synthetic surfactants, produces less organic waste due to lower washing doses, and exhibits higher biodegradability. Therefore, MES seems suitable as surfactant precipitation due to its good biodegradability (Maurad et al., 2006; Tobori et al., 2023).

Slamet et al. (2017) developed surfactants from crude palm oil, achieving a 99% conversion rate in a two-hour esterification and transesterification process, with a surface tension of 36 dyne/cm. However, utilizing vegetable oils like coconut or palm oil may compete with the food sector (Aswie et al., 2021; Mahfud et al., 2020). So, it is necessary to develop waste-based surfactants or use materials sourced from waste by-products (Drakontis and Amin, 2020). One of them is waste cooking oil. Currently, used cooking oil is still a problem because its annual production reaches 190 million metric tons (Lin et al., 2013). Currently, WCO's primary use is limited to green diesel production, which is economically unattractive due to falling oil prices (Sharma et al., 2021). Thus, there's a need to synthesize WCO into high-value materials, such as surfactant raw materials (Yuarini et al., 2021).

Jin et al. (2016) produced MES by sulfonating methyl esters with reactants such as chlorosulfonic acid for 3 hours at 60°C using soybean oil and waste cooking oil (WCO). The best yield was obtained for soybean oil at 82% compared to 78% for WCO. However, the best surface tension was obtained from WCO at 32.3 mN/m compared to soybean oil (Jin et al., 2016). Sharma et al. (2021) also synthesized WCO into a surfactant using an epoxidation technique for 5.5 hours at 65°C with conventional heating and continuous stirring. The best yield was obtained at 68.52% with an interfacial tension of 31.35 dyne/cm. Based on these studies, surfactant production still requires a long time because it uses conventional heating.

One promising technology is the microwave for the transesterification process (Anggraini et al., 2019). A microwave is an artificial heating device that utilizes microwave propagation, which can accelerate heating and make it more effective than conventional heating (Mahfud et al., 2020) Microwaves can enhance the reaction up to 1000 times compared to conventional heating (Karami et al., 2015). "Microwave irradiation" transfers energy as electromagnetic waves instead of thermal reflux. This makes the polar ions vibrate, generating heat that directly increases the reaction yield by touching the reaction medium (Huang et al., 2020; Qadariyah et al., 2022). Referring to this, some researchers have used this heating such as Qadariyah et al. (2022) who converted virgin coconut oil by transesterification process for 1 hour and obtained the best power at 450 watts. Mi et al. (2024) also used this heating to convert wheat bran into alkyl glycoside-based biosurfactants. Yield was 53% with a 72% reduction in reaction time compared to conventional heating (Mi et al., 2024). This proves the potential of microwave heating in converting biomass into surfactants.

Therefore, it is necessary to develop WCO as surfactants. So far, the utilization of waste cooking oil is limited to fuel substitution (Hingu et al., 2010; Kumar et al., 2020; Lam et al., 2019). No study reports the use of WCO as a surfactant using microwave technology. Therefore, this study aims to utilize WCO to produce environmentally friendly MES surfactants, replacing petroleum-derived surfactants known for environmental pollution.

2. EXPERIMENTAL SECTION

2.1 Materials

Materials used in this research are Waste Cooking Oil (WCO) from CV. Pradana Berkah Energi, Lamongan Regency, East Java with the characteristics as Table 1.

Table 1. The Characteristics of Waste Cooking Oil

Parameter	Value
Free fatty acid (FFA)	2.970 %
Density	0.896 gr/mL (at 25°C)
Viscosity	5.132 cSt (at 25°C)
Absorbance	2526 Å
Color	Blackish-brown

Supporting materials are activated carbon in granule form, sodium hydroxide (NaOH) ≥ 99% Merck 1.06498.1000 as transesterification catalyst, methanol (CH_3OH) 99.9% Merck 106498 as transesterification reactant, sodium bisulfite ($NaHSO_3$) 98-100.5% Merck, calcium oxide (CaO) 99.995% sigma-Aldrich as a catalyst for sulfonation process, phenolphthalein, and aquadest.

2.2 Adsorption Equipment

The equipment used for the adsorption process of raw materials WCO using a vacuum pump ARUKI VP-1C-2 with a vacuum strength of 10 Pa and oil capacity of 220 mL. The vacuum pump is equipped with a 500 mL PYREX Filter Flask, a Buchner funner, a rubber cone, and filter paper Whatman No.93.

2.3 Transesterification & Sulfonation Equipment

Microwave is the main equipment of the process. The SHARP R-21D0(S)-IN microwave (maximum power 750 watts and voltage of 220 V) is equipped with a batch reactor system consisting of a 2-neck Pyrex-flask, reflux condenser, magnetic stirrer, thermocouple, and temperature controller.

2.4 Experimental Methods

2.4.1 Adsorption

The adsorption method is carried out by passing WCO through vacuum filtration to remove suspended solid impurities. After the initial filtration, WCO is heated to 90°C before being mixed with 10% w/w activated carbon adsorbent. Adsorption is conducted for 90 minutes at the same temperature. After that,

the mixture is allowed to settle to precipitate the adsorbent. Subsequently, a second filtration is performed using vacuum filtration to separate the adsorbent from WCO. WCO that has been separated with adsorbent then analyzed FFA through 0.1 N NaOH titration and PP indicator. GC-MS analysis and absorbance using spectrophotometry were also conducted.

2.4.2 Transesterification

WCO is trans-esterified into methyl ester by combining it with a solution of methoxide. The methoxide solution is a mixture of methanol with a molar ratio of methanol to WCO of 1:9 and a 1 wt% NaOH catalyst based on WCO. The solution is reacted in a two-neck flask inside a microwave at 300 watts and a temperature of 60°C for 10 minutes. The reaction results in two layers in a separating funnel, with methyl ester on the upper layer and glycerol on the lower layer. Only the methyl ester will be used for the subsequent process. The methyl ester is washed using distilled water at 60°C until it reaches a neutral pH, approximately through three repetitions. Subsequently, the methyl ester is heated in an oven at 110°C to reduce the water and methanol content.

2.4.3 Sulfonation

The methyl ester reacts with the NaHSO3 reagent and CaO catalyst to complete the sulfonation reaction. The use of the reagent is done with variations in molar ratios of 1:1, 1:2, 1:3, and 1:4 methyl ester to $NaHSO_3$. The use of the catalyst is also done with variations of 1%, 1.5%, 2%, and 2.5% wt%. Previously, the $NaHSO_3$ reagent was dissolved in distilled water to form a 35% v/v NaHSO3 solution. The reaction takes place in a microwave at power variations of 300, 450, 600, and 750 watts, as well as with variations in time of 20, 30, 40, 50, and 60 minutes. Afterward, two layers will form, with the MES layer on top and the remaining unreacted catalyst and reagent at the bottom in a separating funnel. The next step is to purify the MES by adding 35% v/v methanol and conducting it in the microwave at 300 watts for 10 minutes at a temperature of 55°C. The purified MES is then heated in an oven at 110°C to reduce the water and methanol content. The final step is to neutralize the MES by adding 2% NaOH until it reaches a neutral pH.

2.5 Characteristics Product

2.5.1 Physical Characteristics of MES Surfactant

The mass balance of methyl ester sulfonate was used to compute conversion, and the Ostwald viscometer, Du-Nuoy Tensiometer, pH meter, and pycnometer were used to calculate physical parameters including viscosity, surface tension, and density, respectively. Meanwhile, the Hydrophile-Lipophile Balance (HLB) was measured using the Griffin equation (Nollet et al., 2019). The HLB calculation obtained can be used as an indicator to select surfactants for certain applications.

2.5.2 UV-Vis Spectrophotometer Analysis

Absorbance measurements of waste cooking oil samples were carried out using a UV-Vis spectrophotometer with the Thermoscientific GENESYS 30 Visible Spectrophotometer brand and were carried out at a wavelength of 465 nm.

2.5.3 Gas Chromatography-Mass Spectrometry (GC-MS) Analysis

Using an Agilent Technologies 7890B/5977B MSD, 2 μL of the solution from the inlet sample was injected into the injection site to conduct a Gas Chromatography-Mass Spectrometry analysis.

2.5.4 Fourier-Transform Infrared Spectroscopy (FTIR) Analysis

The functional groups of the surfactant (sample) are analyzed using Thermo Scientific FT-IR spectrum, Nicolet IS10, which has a spectral range of 7800-350 cm^{-1}. The device's plate receives one drop of the sample, which is subsequently compressed by a mechanical mechanism. The plate is then put in the FT-IR sample holder after this pressure is sustained for a few minutes.

3. RESULTS AND DISCUSSION

3.1 Adsorption Process

When the adsorption process is complete, the color changes and the Free Fatty Acid (FFA) value decreases. The FFA content in the oil can lead to saponification, which can interfere with the transesterification process and therefore needs to be reduced. The FFA content, initially at 2.97%, decreased to 0.81% after adsorption. As for the color change, there was a transition from the initial dark brown to a light brownish-yellow. Hence, the addition of activated carbon as an adsorbent has proven to be effective in binding the color substances in WCO and reducing the FFA content in the oil (Buchori et al., 2018).

Before proceeding to the transesterification stage, GC-MS analysis was conducted to determine the content and composition of the oil. The GC-MS analysis results in Table 3 indicate that the dominant fatty acid in WCO is Oleic Acid at 40.92% and also Palmitic Acid at 35.8%. Both of these compound components confirm that the majority of the used WCO is palm oil waste, which is dominated by oleic acid and palmitic acid (Azman et al., 2021).

Data on the composition of fatty acid of WCO, which is shown in Table 2, is collected based on Figure 1.

The analysis results also reveal the presence of other fatty acid components, allowing for the calculation of the molecular weight of WCO. The calculated molecular weight of WCO obtained is 848.44 g/mol.

Based on Table 3, it can be seen that there is no significant change in the density and viscosity values of WCO before (Table 1) and after adsorption. However, there are changes in FFA content and color after adsorption on WCO. The FFA content contained in the raw material was 2.97%. This can trigger a saponification reaction so it needs to be lowered. After adsorption, there was a decrease in FFA levels by 2.160% from the initial raw material of 2.970% to 0.810%. As for the color difference of WCO before and after adsorption, it also

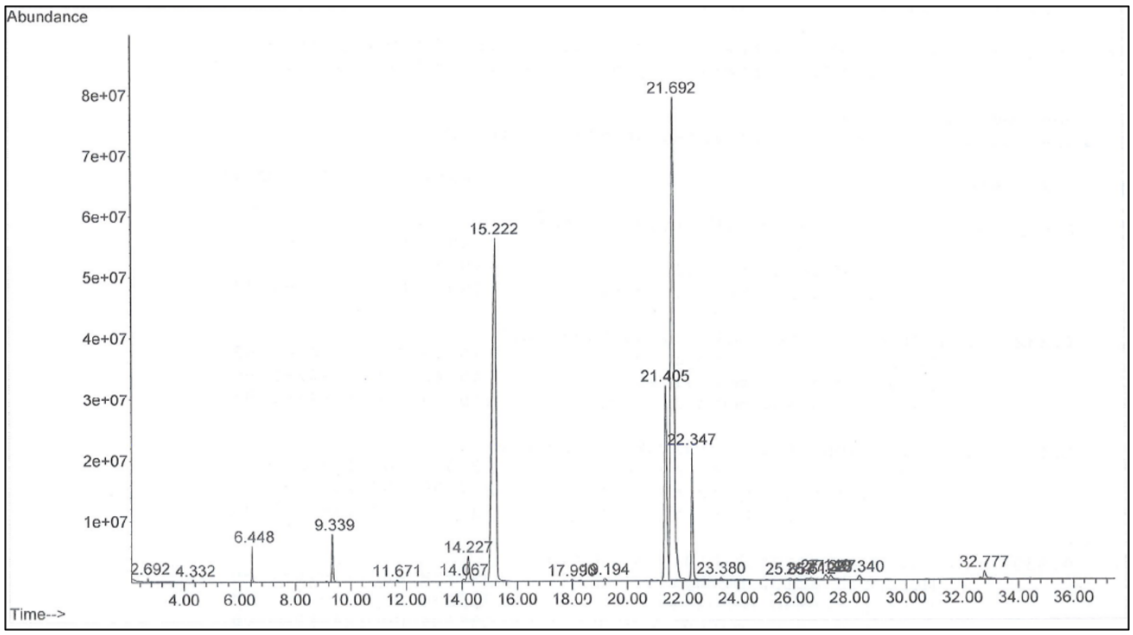

Figure 1. GC-MS Result of Waste Cooking Oil

Table 2. Fatty Acid Composition of WCO

RT (second)	% Area	Fatty Acid
2.692	0.05	Caprylic
4.32	0.04	Capric
6.448	0.63	Lauric
9.339	1.37	Myristic
14.227	1.58	Palmitoleic
15.222	35.80	Palmitic
21.405	12.53	Linoleic
21.692	40.92	Oleic
22.347	6.04	Stearic

Table 3. WCO Characteristics After Adsorption

Parameter	Value
Density	0,896 gr/mL (at 25°C)
Viscosity	5,136 cSt (at 25°C)
Color	Yellowish-brown
Absorbance	1,618 Å
FFA	0,810 %

changed from blackish brown to brownish yellow. This is also supported by the results of color absorbance analysis using the help of a UV-Vis spectrophotometer at a wavelength of 465 nm where the original absorbance value of 2.526 Ådropped to 1.618 Å. Therefore, the addition of activated carbon as an adsorbent proved effective in binding the blackish dye in WCO and reducing the FFA content in the oil. This is to the study conducted by Sashikesh et al. (2023) that activated carbon is effective in absorbing phenol compounds in the oil. Phenol compounds are one type of organic compound that can be found in used cooking oil that has been oxidized or degraded.

3.2 Transesterification Process

In the transesterification process, the yield of methyl ester produced can reach 95% with a kinematic viscosity of 4.024 Cst and a density of 855 kg/m^3. GC-MS analysis was also performed on the methyl esters produced from transesterification and the chromatograms are presented in Figure 2. Based on the figure, the methyl ester composition obtained is 98.88%, given in Table 4. From the GC-MS results, it can also be determined that the dominant fatty acid composition in the methyl ester is methyl oleate at 45.12% and methyl palmitate at 35.65%. Furthermore, based on the known components of the methyl ester, the calculated molecular weight of the methyl ester obtained is 284.29 g/mol.

Table 4. Methyl Ester Composition

Retention Time (min)	% Area	Methyl ester
2.698	0.09	Methyl Caprylate
4.341	0.06	Methyl Caprate
6.444	0.58	Methyl Laurate
9.326	1.42	Methyl Myristate
14.226	1.52	Methyl Palmitoleate
15.428	35.65	Methyl Palmitate
21.428	7.57	Methyl Linoleate
21.911	45.12	Methyl Oleate
22.443	6.87	Methyl Stearate

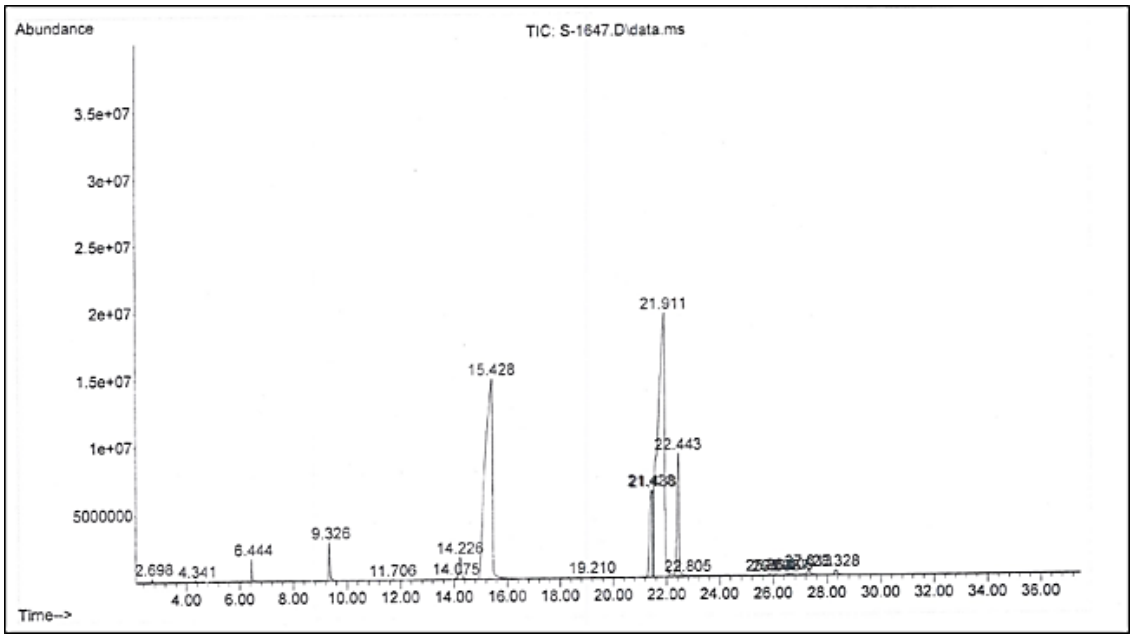

Figure 2. GC-MS Result of Methyl Ester

3.3 Sulfonation Process

3.3.1 The Effect of Reactant Mole Ratio on Yield of MES

In Figure 3, it is shown that there is an increase followed by a decrease in yield at a reactant mole ratio of 1:2. At a 1:2 reactant mole ratio, the highest yield obtained is 47.28% at 90°C and 48.06% at 100°C, 450 watts and 20 minutes. In the 1:4 ratio, a lower yield is produced. Sulfonation is an equilibrium reaction, and achieving a higher product yield requires more reactants than the feedstock to shift the reaction toward the right or the product side (Dolganova et al., 2024). On the other hand, an increased use of reactants can also lead to the formation of more by-products (Ghaedrahmati et al., 2023). Consequently, the decrease in yield at reactant mole ratios of 1:3 and 1:4 can be attributed to the excessive formation of by-products, such as disodium carboxy sulfonate (disalt), which hinder the contact between methyl ester and the reactant.

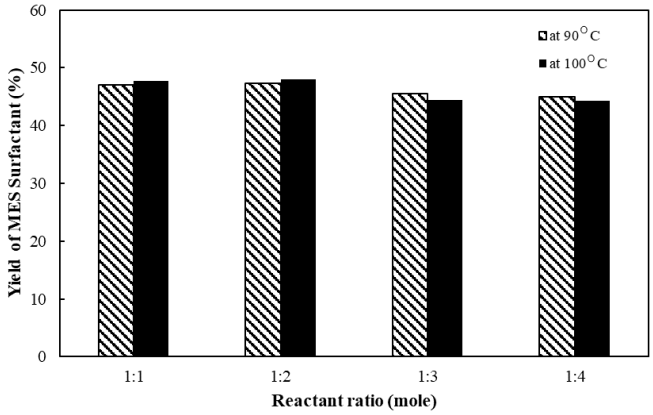

Figure 3. Effect of Reactant Mole Ratio on the Yield of MES

3.3.2 The Effect of Catalyst Concentration on Yield of MES

The use of a catalyst is employed to speed up the sulfonation reaction. The use of a catalyst can lower the activation energy, thereby increasing the reaction rate and reducing the sulfonation time (Efiyanti et al., 2020).

Based on Figure 4, results indicate that the best MES yield, at a catalyst concentration of 1.5%, was 48.06%. In theory, the greater the amount of catalyst used, the greater the reduction in the activation energy of the reaction, resulting in a higher product yield (Roduner, 2014). However, as seen in Figure 4, the use of 2% and 2.5% catalysts led to a decreasing yield. This is attributed to excessive use of the catalyst, which increases the production of unwanted byproducts in the form of undesired results, consequently reducing the purity of MES.

3.3.3 The Effect of Reaction Time on Yield of MES

This differs from the previous study. Sahila et al. (2021), investigated the effect of reaction time on yield and found an increase in the yield percentage from the 20-minute variation to 40 minutes, but it decreased after variations longer than 40 minutes. According to Qadariyah et al. (2022), as the reaction time increases, the contact time between methyl ester and $NaHSO_3$ reactant also increases, leading to an increase in MES product yield. However, if the reaction is carried out for an extended period, not only MES will be produced, but also by-products in the form of disalt, which can reduce the purity of MES itself. In this research, as the reaction time increased, the production of disodium carboxy sulfonate also increased. The decrease in yield can also be attributed to the microwave used as an energy

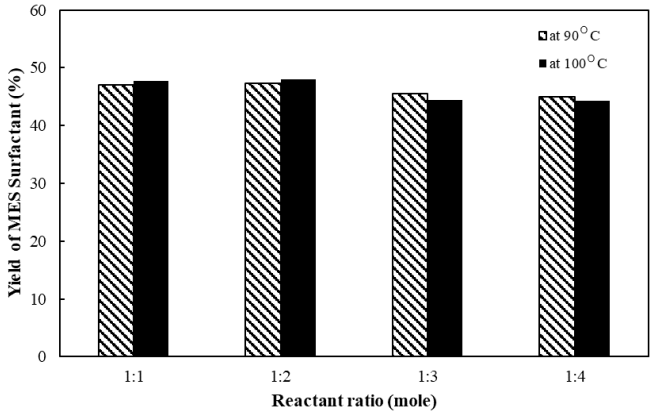

Figure 4. Effect of Catalyst Concentration on the Yield of MES

source. Microwaves rapidly agitate particles in the substance, which can increase product yield quickly. However, at certain times, it can decrease yield because increased and prolonged agitation disrupts the orderly movement of molecules and can damage the organic content in the substance Qadariyah et al. (2022).

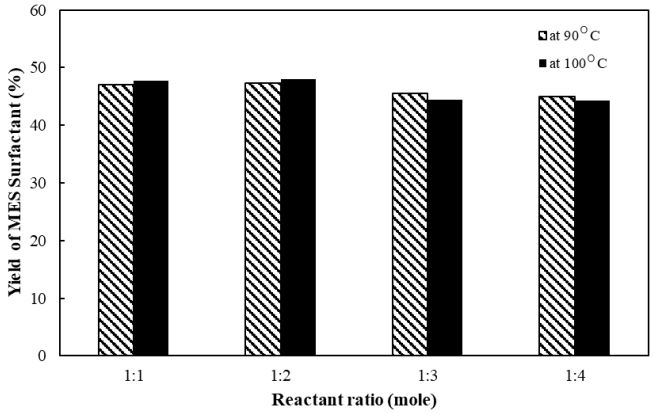

Figure 5. Effect of Reaction Time on the Yield of MES

Based on Figure 5 shows that The highest yield was obtained at the 20 minute reaction, which was 46.34% at 300 watts and 48.06% at 450 watts. The yield continuously decreased as the reaction time extended.

3.3.4 The Effect of Microwave Power on Yield of MES

In a microwave, several factors affect the reaction in methyl ester synthesis. One of them is the power used to operate the microwave. The microwave power affects the reaction temperature and the formation of MES (Methyl Ester Sulfonate).

Based on Figure 6, when using a microwave power of 300 W, the maximum solution temperature that can be achieved is 102°C. However, with microwave powers of 450 W, 600 W, and 750 W, the maximum solution temperature achievable is

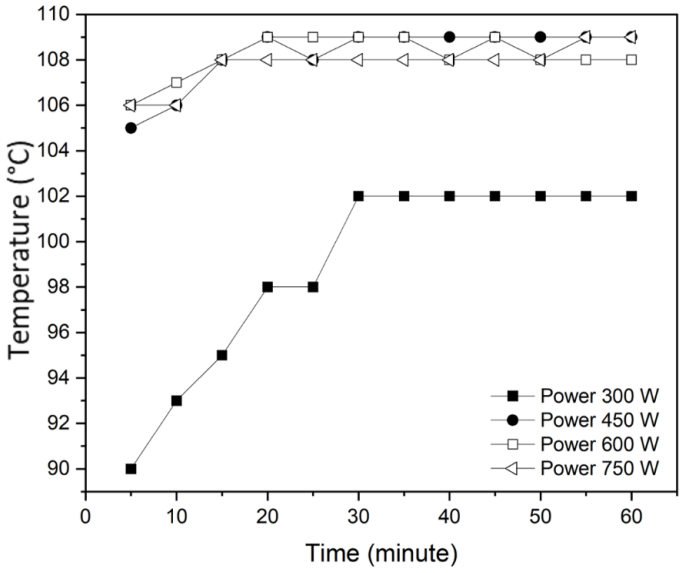

Figure 6. Effect of Microwave Power on Temperature Profile

109°C. Additionally, the rate of temperature increase varies at each power level. Using a 90°C reference temperature, it takes around 4 minutes and 45 seconds to reach this temperature at 300 W. Meanwhile, at 450 W, it takes around 2 minutes and 44 seconds. At 600 W, it requires 1 minute and 34 seconds, and the fastest time to reach 90°C is achieved when using 750 W, which is 45 seconds. This demonstrates that the higher the power used, the faster the reaction temperature can be reached (Aswie et al., 2022).

In Figure 7, the highest yield was obtained at 450 W power for 20 minutes, which amounted to 48.06%. The lowest yield was achieved at 750 W power for 50 minutes, yielding 36.22%. Research on the effect of power usage on MES yield is very minimal or has not been conducted yet, so concluding the following variables is based on possibilities and some related studies. In theory, the use of high power can result in high reaction temperatures, leading to increased yield (Qadariyah, 2021). However, Figure 6 displays contradicting results, which are thought to be caused using increased microwave power, which may cause molecules to collide too quickly, potentially lowering purity. Dudley et al. (2015) concluded that in the synthesis process of Methyl ortho-Methoxycinnamate (MOMS), relaxation must be given in the middle of the reaction because the use of microwave causes a very fast reaction so if relaxation is not given to the reaction, it will damage the resulting compound (Dudley).

3.3.5 The Physical Characteristics of MES Surfactant

MES Surfactant at the most optimal condition (450 watts, reactant ratio 0f 1:2, 1.5% of catalyst concentration at 20 minutes) was analyzed for its physical characteristics. Some of the physical characteristics measured include density, viscosity, color test, surface tension, and Hydrophilic Lipophilic Balance.

Based on Table 5, the color of the MES surfactant is a pale

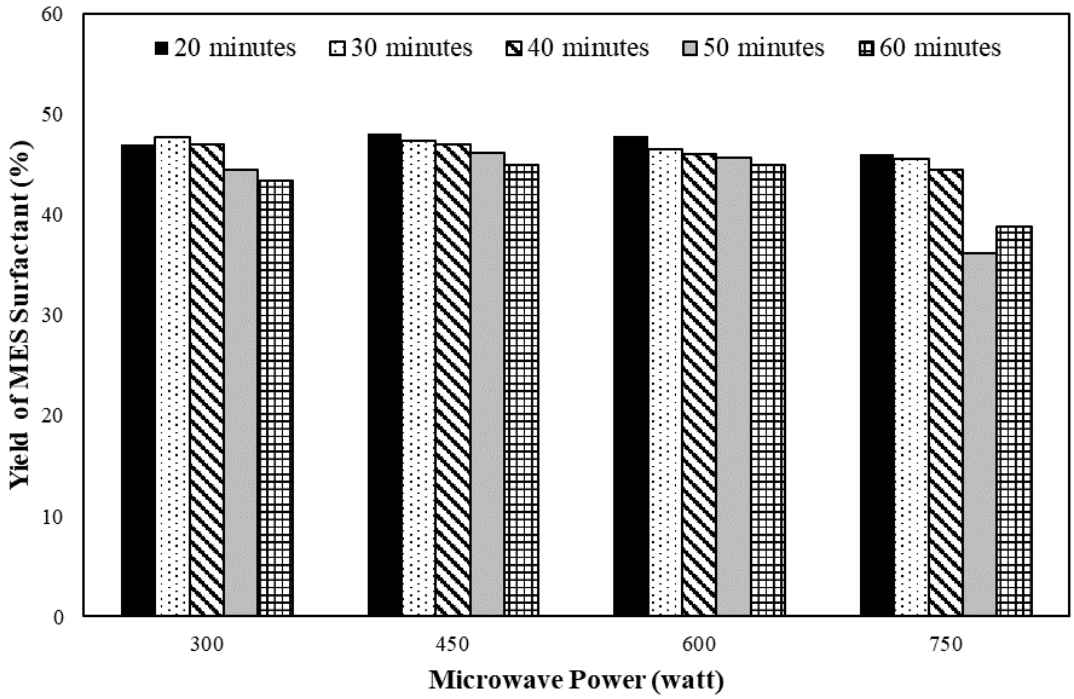

Figure 7. Effect of Microwave Power on Yield of MES

Table 5. The Physical Characteristics of MES Surfactant

Parameter	Value
Color	Pale yellow
Density	0.859 gr/ml (at 25°C)
Viscosity	1.780 cSt
Surface tension	32.26 dyne/cm
Hydrophilic Lipophilic Balance	6-8

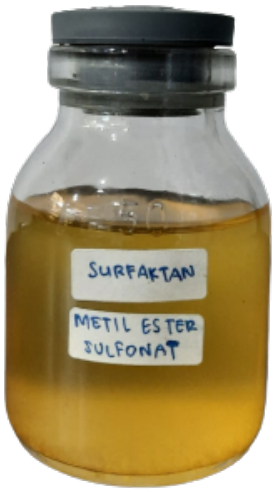

Figure 8. The MES Surfactant Product

yellow color (32 – 45 Klett) and can be seen in Figure 8. This color meets the parameter requirement for MES flake products from PT. Wilmar, with a maximum color (Klett) of 70. Color analysis was conducted using a UV-Vis spectrophotometer at a wavelength of 420 nm (Mansur et al., 2007). In addition, color analysis was also performed on commercial MES, yielding a result of 70 Klett at the same wavelength.

Density is an important parameter to observe as it is used in yield analysis. In the best conditions for each observed variable, the density of the MES is analyzed. Density analysis is performed using a pycnometer. After analysis, it is fou;nd that the density of MES under the best conditions is 0.859 gr/ml. Density is measured based on conditions at 300 W power, a reactant ratio of 1:2, 1.5% wt catalyst concentration, and a temperature of 100°C, resulting in a yield of 51.5%.

Viscosity, commonly referred to as thickness, is a property of fluids influenced by the size of molecules and the forces between molecules. The viscosity of a solution is measured using a viscometer, where the fluid to be measured is placed inside a tube within the viscometer. The MES under the best observed conditions, its viscosity was analyzed. After viscosity analysis, it was found that the viscosity of MES under the optimal conditions is 1.780 cSt, measured at room temperature. The viscosity value is obtained from the measurement of the time it takes for the substance to pass between two specified

Table 6. GC-MS of MES Surfactant

Retention Time (min)	%Area	Compound
6,481	0.41	Dodecanoic acid, methyl ester
8,739	0,03	1-Tetradecanol (CAS)
8,964	1,12	Methyl tetradecanoate
11,504	1.54	9-Hexadecenoic acid, methyl ester, (Z)-
11,981	26,80	Pentadecanoic acid, methyl ester
16,448	52,93	9-Octadecenoic acid (Z)-, methyl ester
17,079	7.21	Octadecanoic acid, methyl ester
20,833	0,87	Eicosanoic acid, methyl ester

points. Surface tension is the force pulling downward or the force that causes the contraction of a liquid's surface, making it appear elastic and taut. The decrease or increase in surface tension can occur due to the attractive forces among molecules at the surface. Surface tension is measured using a capillary tube by measuring the rise of the liquid inside the capillary tube (Sahila et al., 2021). The surface tension values in MES range from 65.25 to a minimum of 22.84 dyne/cm, calculated based on the influence of variables such as power, mole ratio of reactants, catalyst concentration, and reaction time. Under optimal conditions, the surface tension of MES was found to be 32.26 dyne/cm. A low surface tension value indicates that sulfonation reactions occur in the surfactant. The results obtained are by the data submitted by Hariani et al. (2016) that the surface tension of MES surfactant is in the range of 30-40 dyne/cm.

Hydrophilic Lipophilic Balance (HLB) can be used to determine the appropriate application of a surfactant type based on its functional groups. To determine the HLB value of a surfactant, the analysis involves theoretical calculations and experimental analysis of the surfactant (Corin and O'Connor, 2014). Through theoretical calculations using the William Griffin equation, the saponification number of MES surfactant was found to be 126.207 mg KOH/g, while its acid number was 0.56 mg KOH/g. The saponification number obtained is higher than the acid number, making theoretical calculations unfeasible. The HLB value was then tested using trials that involved combining the surfactant with water. The obtained HLB value falls within the range of 6-8, with the result that the solution becomes turbid after vigorous stirring. Therefore, MES surfactant is classified as a surfactant that can be used as a wetting agent or Water in Oil (W/O) emulsifier (Sakamoto et al., 2017).

3.3.6 GC-MS Analysis of MES Surfactant

The results of GC-MS analysis of MES surfactant products were conducted to determine the components of the forming compounds that make up the MES surfactant products. From the results of the analysis that has been done, obtained components of supporting compounds with 8 highest peak in Table 6.

Based on Table 6. it can be seen that the content of MES Surfactant compounds is mostly a methyl ester as a constituent compound of MES manufacturing raw materials. Such as Dodecanoic acid, methyl ester which is Methyl Laurate; Methyl tetradecanoate or can also be called Methyl Myristate; 9-Hexadecenoic acid, methyl ester, (Z)- as Methyl Palmitoleate; Pentadecanoic acid, methyl ester or Methyl Palmitate; 9-Octadecenoic acid (Z)-, methyl ester and Octadecanoic acid, methyl ester as Methyl Oleate. In addition, 1-Tetradecanol (CAS) was also found which is a compound that can be used as one of the intermediate raw materials in the chemical synthesis of products such as surfactants (Masyithah et al., 2020; Ohbu Fujiwara et al., 1998). As for the Eicosanoic acid compound, the methyl ester found is a compound that can be used for the production of detergents and lubricants. The methyl ester compounds read in the GC-MS results are valuable components in methyl ester sulfonate from a fuel application point of view. In outline, methyl ester sulfonate compounds can only be read through liquid chromatography-mass spectrometry (LC-MS) analysis (Permadani et al., 2018). Analysis of MES surfactant using LC-MS (Liquid Chromatography-Mass Spectrometry) is preferred over GC-MS (Gas Chromatography-Mass Spectrometry) due to the chemical nature of the surfactant. LC-MS is more suitable for polar compounds and compounds soluble in organic solvents, such as the anionic surfactants present in MES. In contrast, GC-MS is more suitable for non-polar and volatile compounds, which may not be suitable for the analysis of anionic surfactants such as MES (Soy et al., 2020). Therefore, to support the results of this analysis, FTIR analysis was carried out to identify the formation of sulfonate functional groups in the surfactant.

3.3.7 The FT-IR Analysis of MES Surfactant

One of the analyses that can be conducted to prove the formation of MES surfactant is by performing FTIR functional group analysis. The working principle of FTIR is to identify the functional groups of a compound by measuring the infrared absorbance of that compound. The absorption patterns vary for each compound, allowing for the differentiation and quantification of compounds (Liu et al., 2019). FTIR analysis is conducted to detect the presence of sulfonate groups in the MES sample. In Figure 9, the FTIR spectrum shows strong intensity absorption peaks for the carbonyl group C=O at a

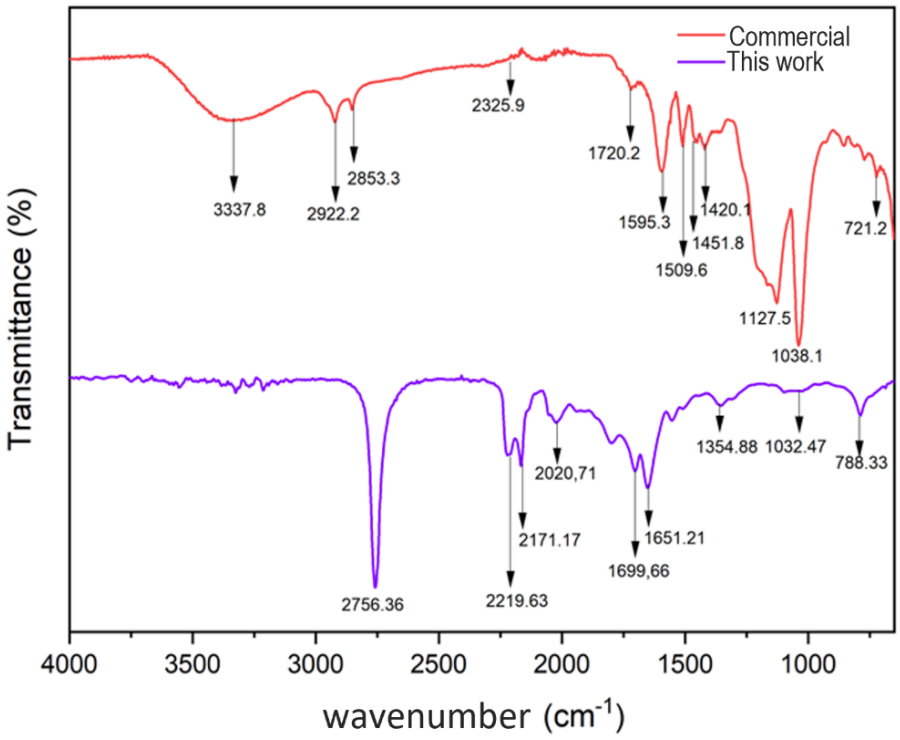

Figure 9. FTIR Analysis of Methyl Ester Sulfonate

wavelength of 1699.66 cm^{-1}. The existing C=O group is one of the characteristic bonds of the ester group. At the absorption peak of 2756.36 cm^{-1}, there is evidence of C–H groups. Both of these groups are consistent with previous research, where Iman et al. (2016) investigated the FTIR spectrum of MES and found absorption peaks of C–H functional groups in the range of 2924.01-2721.32 cm^{-1}. Additionally, they also found the C=O functional group at an absorption peak of 1742.44 cm^{-1}. The FTIR test results also revealed sulfonate groups, as indicated by wave numbers ranging from 1354.88 to 1032.47 cm^{-1}. The S=O group is found at a wave number of 1354.88 cm^{-1}, and the S–O group is observed at an absorption peak of 788.33 cm^{-1}. With the presence of sulfonate groups, it can be proven that the conversion from methyl ester to MES has occurred. In the FTIR analysis results, there is no broad vibration region in the wave number > 3600 cm^{-1}, indicating that there are no hydroxyl (−OH) groups from alcohol constituents that have not separated during drying. Therefore, it can be concluded that residual alcohol has been minimized in the produced MES product (Qadariyah et al., 2022).

As for the FTIR analysis results of MES products available in the market, as shown in Figure 9, it can be seen that the absorption results for both samples are different. This indicates that the MES from the research did not convert well, resulting in high absorption peaks for C–H groups and low absorption peaks for sulfonate groups. This could be attributed to the small amount of SO_3 groups produced by the reactant, possibly due to $NaHSO_3$ not being conditioned in an acidic environment.

4. CONCLUSIONS

Waste Cooking Oil (WCO) can be the main raw material to produce Methyl Ester Sulfonate (MES) surfactant with the assistance of a microwave and the reactants $NaHSO_3$ and CaO catalyst. The best molar ratio of reactants is achieved at a 1:2 molar ratio reactant, CaO catalyst concentration of 1.5%, reaction time of 20 minutes, and microwave power of 450 W, yielding 48.06%. The characteristics of Methyl Ester Sulfonate (MES) surfactant include a pale-yellow color, a density of 0.859 g/cm^3, a viscosity of 1.780 cSt, and a surface tension value of 32.62 dyne/cm. The analysis of Methyl Ester Sulfonate (MES) surfactant was further confirmed by the presence of sulfonic acid ($-SO_3H$) groups observed through FTIR analysis at the wavelengths of 1195.27 cm^{-1} and 1169.1 cm^{-1}.

5. ACKNOWLEDGMENT

Firstly, the authors would like to express their gratitude to the Institut Teknologi Sepuluh Nopember for the financial support provided through their research fund, as well as to the Process Laboratory within the Department of Chemical Engineering at the same institution for providing access to the required research facilities. Furthermore, the authors thank CV. Pradana Berkah Energi for providing Waste Cooking Oil (WCO) as the raw material, Bea&Cukai's Laboratory for conducting the GCMS Analysis, and the materials characterization laboratories under the Department of Materials and Metallurgy at Institut Teknologi Sepuluh Nopember for their assistance in carrying

out the FTIR analysis.

REFERENCES

Alwadani, N. and P. Fatehi (2018). Synthetic and Lignin-Based Surfactants: Challenges and Opportunities. *Carbon Resources Conversion*, **1**(2); 126–138

Anggraini, I. F., M. Said, and M. Faizal (2019). Production Methyl Ester Sulfonate (MES) Based Rubber Seeds as One of Chemical Injection Solution in Enhanced Oil Recovery (EOR) Process. *Science and Technology Indonesia*, **4**(2); 52–56

Aswie, V., L. Qadariyah, and M. Mahfud (2021). Pyrolysis of Microalgae Chlorella sp. Using Activated Carbon as Catalyst for Biofuel Production. *Bulletin of Chemical Reaction Engineering & Catalysis*, **16**(1); 205–213

Aswie, V., L. Qadariyah, and M. Mahfud (2022). Kinetics and Characterization of Microalgae Biofuel by Microwave-Assisted Pyrolysis Using Activated Carbon. *Journal of Engineering and Technological Sciences*, **54**(2); 318–331

Auliya Putri, E. F., E. Indahyanti, D. Mardiana, M. L. A. D. Lestari, and Z. Ningsih (2023). Okra Mucilage Extract as a Co-Surfactant Increased the Curcumin Nanoemulsion Stability and Encapsulation Efficiency. *Science and Technology Indonesia*, **8**(3); 509–515

Azman, N. S., T. S. Marliza, N. Asikin-Mijan, T. Y. Y. Hin, and N. Khairuddin (2021). Production of Biodiesel from Waste Cooking Oil via Deoxygenation Using Ni-Mo/AC Catalyst. *Processes*, **9**(5)

Buchori, L., D. Labibah Ubay, and K. Syahidah (2018). Biodiesel Production from Waste Cooking Oil Purified with Activated Charcoal of Salak Peel. *Reaktor*, **18**(3); 149–154

Corin, K. C. and C. T. O'Connor (2014). A Proposal to Use Excess Gibbs Energy Rather than HLB Number as an Indicator of the Hydrophilic-Liphophilic Behavior of Surfactants. *Minerals Engineering*, **58**; 17–21

Da Rosa, C. F. C., D. M. G. Freire, and H. C. Ferraz (2015). Biosurfactant Microfoam: Application in the Removal of Pollutants from Soil. *Journal of Environmental Chemical Engineering*, **3**(1); 89–94

Dolganova, I., I. Dolganov, E. Ivashkina, A. Zykova, and D. Sladkov (2024). Studying the Alkylbenzenes Sulfonation Process Using the Mathematical Model Considering the Mass Transfer. *South African Journal of Chemical Engineering*, **48**; 196–203

Drakontis, C. E. and S. Amin (2020). Biosurfactants: Formulations, Properties, and Applications. *Current Opinion in Colloid and Interface Science*, **48**; 77–90

Dudley, G. B., R. Richert, and A. E. Stiegman (2015). On the Existence of and Mechanism for Microwave-Specific Reaction Rate Enhancement. *Chemical Science*, **6**; 2144–2152

Efiyanti, L., D. A. Indrawan, Z. Arif, D. Hutapea, and A. D. Septina (2020). Synthesis and Application of a Sulfonated Carbon Catalyst for a Hydrolisis Reaction. *Indonesian Journal of Science and Technology*, **5**(3); 410–420

Ghaedrahmati, A., H. Jafarian, S. Khani Moghanaki, and A. R. Eivani (2023). On the Normal and Inverse Portevin–Le Chatelier Behavior in Hot Rolled Inconel 617 Superalloy. *Journal of Materials Research and Technology*, **26**; 445–461

Hariani, P. L., F. Riyanti, and A. Fadilah (2016). The Influence of Time Reaction to Characteristic of Methyl Ester Sulfonate from Seed Oil Ketapang. *Indonesian Journal of Fundamental and Applied Chemistry*, **1**(1); 14–18

Hill, K. (2001). Fats and Oils as Oleochemical Raw Materials. *Journal of Oleo Science*, **50**(5); 433–444

Hingu, S. M., P. R. Gogate, and V. K. Rathod (2010). Synthesis of Biodiesel from Waste Cooking Oil Using Sonochemical Reactors. *Ultrasonics Sonochemistry*, **17**(5); 827–832

Huang, D., H. Xu, B. Jacob, R. Ma, S. Yuan, L. Zhang, and Z. Cheng (2020). Microwave-Assisted Preparation of Two-Dimensional Amphiphilic Nanoplate Herding Surfactants for Offshore Oil Spill Treatment. *Journal of Loss Prevention in the Process Industries*, **66**; 104213

Iman, N., A. Rahman, and D. Nurhaeni (2016). Synthetis of Methyl Ester Sulfonic (MES) from Methyl Laurate. *Kovalen*, **2**(2); 54–66

Ivankovic, T., J. Hrenovic, and I. Gudelj (2009). Toxicity of Commercial Surfactants to Phosphate-Accumulating Bacterium. *Acta Chimica Slovenica*, **56**(4); 888–895

Jahan, R., A. M. Bodratti, M. Tsianou, and P. Alexandridis (2020). Biosurfactants, Natural Alternatives to Synthetic Surfactants: Physicochemical Properties and Applications. *Advances in Colloid and Interface Science*, **275**; 102061

Jesus, C. F., A. A. S. Alves, S. M. Fiuza, D. Murtinho, and F. E. Antunes (2021). Mini-Review: Synthetic Methods for the Production of Cationic Sugar-Based Surfactants. *Journal of Molecular Liquids*, **342**; 117389

Jin, Y., S. Tian, J. Guo, X. Ren, X. Li, and S. Gao (2016). Synthesis, Characterization and Exploratory Application of Anionic Surfactant Fatty Acid Methyl Ester Sulfonate from Waste Cooking Oil. *Journal of Surfactants and Detergents*, **19**(3); 467–475

Johnson, P., A. Trybala, V. Starov, and V. J. Pinfield (2021). Effect of Synthetic Surfactants on the Environment and the Potential for Substitution by Biosurfactants. *Advances in Colloid and Interface Science*, **288**; 102340

Karami, Z., Z. Emam-Djomeh, H. A. Mirzaee, M. Khomeiri, A. S. Mahoonak, and E. Aydani (2015). Optimization of Microwave Assisted Extraction (MAE) and Soxhlet Extraction of Phenolic Compound from Licorice Root. *Journal of Food Science and Technology*, **52**(6); 3242–3253

Kulkarni, D. and D. Jaspal (2023). Surfactants in Waste Water: Development, Current Status and Associated Challenges. *Materials Today: Proceedings*

Kumar, S., M. R. Shamsuddin, M. S. A. Farabi, M. I. Saiman, Z. Zainal, and Y. H. Taufiq-Yap (2020). Production of Methyl Esters from Waste Cooking Oil and Chicken Fat Oil via Simultaneous Esterification and Transesterification Using Acid Catalyst. *Energy Conversion and Management*, **226**; 113366

Lam, S. S., W. A. Wan Mahari, Y. S. Ok, W. Peng, C. T.

Chong, N. L. Ma, and D. C. W. Tsang (2019). Microwave Vacuum Pyrolysis of Waste Plastic and Used Cooking Oil for Simultaneous Waste Reduction and Sustainable Energy Conversion: Recovery of Cleaner Liquid Fuel and Techno-Economic Analysis. *Renewable and Sustainable Energy Reviews*, **115**; 109359

Lin, C. S. K., L. A. Pfaltzgraff, L. Herrero-Davila, E. B. Mubofu, S. Abderrahim, J. H. Clark, and R. Luque (2013). Food Waste as a Valuable Resource for the Production of Chemicals, Materials and Fuels: Current Situation and Global Perspective. *Energy and Environmental Science*, **6**(2); 426–464

Liu, C., X. Duan, Q. Chen, C. Chao, Z. Lu, Q. Lai, and M. Megharaj (2019). Investigations on Pyrolysis of Microalgae Diplosphaera sp. MM1 by TG-FTIR and Py-GC/MS: Products and Kinetics. *Bioresource Technology*, **294**; 122126

Liu, K., Y. Sun, M. Cao, J. Wang, J. R. Lu, and H. Xu (2020). Rational Design, Properties, and Applications of Biosurfactants: A Short Review of Recent Advances. *Current Opinion in Colloid and Interface Science*, **45**; 57–67

Mahfud, M., U. Kalsum, and V. Aswie (2020). Biodiesel Production through Catalytic Microwave In-Situ Transesterification of Microalgae (Chlorella sp.). *International Journal of Renewable Energy Development*, **9**(1); 113–117

Mansur, D., N. Astrini, and T. Tasrif (2007). Sodium Bisulfite as SO3 Source for Synthesis of Methyl Ester Sulfonate Using RBD Stearin as Raw Material. *IPTEK The Journal for Technology and Science*, **18**(4); 161–167

Marti-Mestres, G. and F. Nielloud (2002). Emulsions in Health Care Applications - An Overview. *Journal of Dispersion Science and Technology*, **23**(1-3); 419–439

Masakorala, K., A. Turner, and M. T. Brown (2011). Toxicity of Synthetic Surfactants to the Marine Macroalga, Ulva lactuca. *Water, Air, & Soil Pollution*, **218**(1); 283–291

Masuda, M., H. Odake, K. Miura, K. Ito, K. Yamada, and K. Oba (1993). Biodegradation of 2-Sulfonatofatty Acid Methyl Ester (α-SFMe). II. Biodegradation Pathways of α-SFMe. *Progress in Colloid and Polymer Science*, **42**; 206–213

Masyithah, Z., E. K. Sinaga, P. A. Gultom, and A. Ginting (2020). Synthesis of N-Acyl Arginine Surfactants from Tetradecanol and Arginine Using Tert-Amyl Alcohol. *ARPN Journal of Engineering and Applied Sciences*, **15**(23); 2770–2777. Retrieved from www.arpnjournals.com

Maurad, Z. A., R. Ghazali, P. Siwayanan, Z. Ismail, and S. Ahmad (2006). Alpha-Sulfonated Methyl Ester as an Active Ingredient in Palm-Based Powder Detergents. *Journal of Surfactants and Detergents*, **9**(2); 161–167

Mi, J., J. Cheng, K. H. Ng, and N. Yan (2024). Biomass to Green Surfactants: Microwave-Assisted Transglycosylation of Wheat Bran for Alkyl Glycosides Production. *Bioresource Technology*, **401**; 130738

Nollet, M., H. Boulghobra, E. Calligaro, and J. D. Rodier (2019). An Efficient Method to Determine the Hydrophile-Lipophile Balance of Surfactants Using the Phase Inversion Temperature Deviation of CiEj/n-Octane/Water Emulsions. *International Journal of Cosmetic Science*, **41**(1); 99–108

Ohbu Fujiwara, Y., K. M. Abe, K. M. Ohbu Fujiwara, and Y. Abe (1998). Physicochemical Properties of α-Sulfonated Fatty Acid Esters. *Progress in Colloid and Polymer Science*, **109**; 206–213

Pan, F., Z. Li, H. Gong, J. T. Petkov, and J. R. Lu (2018). Membrane-Lytic Actions of Sulphonated Methyl Ester Surfactants and Implications to Bactericidal Effect and Cytotoxicity. *Journal of Colloid and Interface Science*, **531**; 18–27

Panda, A., A. Kumar, S. Mishra, and S. S. Mohapatra (2020). Soapnut: A Replacement of Synthetic Surfactant for Cosmetic and Biomedical Applications. *Sustainable Chemistry and Pharmacy*, **17**; 100297

Perkins, W. S. (1998). Surfactants - A Primer. *ATI - Dyeing, Printing and Finishing*, **27**; 51–54

Permadani, R. L., M. Ibadurrohman, and Slamet (2018). Utilization of Waste Cooking Oil as Raw Material for Synthesis of Methyl Ester Sulfonates (MES) Surfactant. *IOP Conference Series: Earth and Environmental Science*, **105**(1); 012036

Qadariyah, L. (2021). The Effect of Reaction Time and Temperature on the Synthesis of Methyl Ester Sulfonate Surfactant from Palm Oil as a Feedstock Using Microwave-Assisted Heating. *AJCHE*, **16**(6); e63786

Qadariyah, L., S. Sahila, C. Sirait, C. P. E. Purba, D. S. Bhuana, and M. Mahfud (2022). Surfactant Production of Methyl Ester Sulfonate from Virgin Coconut Oil Using Aluminum Oxide with Microwave Assistance. *International Journal of Technology*, **13**(2); 378–388

Roduner, E. (2014). Understanding Catalysis. *Chemical Society Reviews*, **43**(24); 8226–8239

Sahila, S., L. Qadariyah, and M. Mahfud (2021). The Study on Factors Affecting the Synthesis of Methyl Ester Sulfonate from Palm Oil Using CaO Catalyst with Microwave-Assisted. *Journal of Physics: Conference Series*, **1845**(1); 012004

Sakamoto, K., R. Y. Lochhead, H. I. Maibach, and Y. Yamashita (2017). *Cosmetic Science and Technology: Theoretical Principles and Applications*. Elsevier, second edition

Sashikesh, G., P. Anushkkaran, Y. Praveena, M. Arumukham, V. Kugamoorthy, and V. Kandasamy (2023). A Comparison Study of the Efficacy of Different Activated Charcoals Derived from Palmyra Kernel Shell in Removing Phenolic Compounds. *Current Research in Green and Sustainable Chemistry*, **6**; 100355

Scott, M. J. and M. N. Jones (2000). The Biodegradation of Surfactants in the Environment. *Biochimica et Biophysica Acta*, **1508**(1); 235–251. Retrieved from www.elsevier.com/locate/bba

Sharma, K., S. S. Toor, J. Brandão, T. H. Pedersen, and L. A. Rosendahl (2021). Optimized Conversion of Waste Cooking Oil into Ecofriendly Bio-Based Polymeric Surfactant - A Solution for Enhanced Oil Recovery and Green Fuel Compatibility. *Journal of Cleaner Production*, **294**; 126214

Slamet, M. Ibadurrohman, and P. P. Wulandari (2017). Synthesis of Methyl Ester Sulfonate Surfactant from Crude Palm Oil as an Active Substance of Laundry Liquid Detergent.

AIP Conference Proceedings, **1904**(1); 020058

Sorhie, V., Alemtoshi, B. Gogoi, B. Walling, S. A. Acharjee, and P. Bharali (2022). Role of Micellar Nanoreactors in Organic Chemistry: Green and Synthetic Surfactant Review. *Sustainable Chemistry and Pharmacy*, **30**; 100875

Soy, R., P. K. Kipkemboi, and K. Rop (2020). Synthesis, Characterization, and Evaluation of Solution Properties of Sesame Fatty Methyl Ester Sulfonate Surfactant. *ACS Omega*, **5**(44); 28643–28655

Tobori, A., K. Yamamoto, and H. Suzuki (2023). Recent Advances in Surfactant Technology for Environmental Applications. *Environmental Science and Technology*, **57**(4); 1456–1472

Yuarini, D. A. A., G. Ganda Putra, A. Suryawan Wiranatha, and L. Putu Wrasiati (2021). Production and Added Value of Waste Cooking Oil Product Derivatives in the Bali Province. *Advances in Food Science, Sustainable Agriculture and Agroindustrial Engineering*, **4**(1); 56–62

