Utilization of waste cooking oil as raw material for synthesis of Methyl Ester Sulfonates (MES) surfactant

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Abstract. In this study, MES surfactant was synthesized from waste cooking oil (WCO) which can lower the synthesis cost and represent efficient utilization of waste. MES is an eco-friendly anionic surfactant, which can be used for our detergent application. The purpose of this study was to obtain optimum MES surfactant from purification of WCO. WCO is purified first to reduce high impurities and free fatty acid (FFA). Purification steps of WCO consist of filtration to separate food residues, neutralization with various concentrations of NaOH solution 13%; 14%; 15%; 16% and bleaching with activated carbon 7.5% (wt. % of oil). After purification followed by transesterification process with variation of mole ratio oil and methanol 1:8; 1:9; 1:10 then synthesized MES surfactant with sodium bisulfite (NaHSO₃) as sulfonating agent. Neutralization results showed high reduction percentage of FFA was 31.31% for 15% NaOH solution; bleaching results showed reduction percentage of FFA was 20.27% and WCO color was originally dark brown to be light yellow. The results of transesterification showed highest yields 94.15% for mole ratio of oil and methanol 1:9 and sulfonation results will be described further in this paper.

1. Introduction
Waste cooking oils (WCO) are generated from cooking and frying food with edible vegetable oils, which is usually disposed into the environment [1, 2]. In Indonesia, most of waste cooking oil (WCO) from households is being disposed to drainage and soil causing environmental pollution [3]. WCO cannot be consumed again due to presence of toxic components which can damage cytochrome enzymes and other enzymes in human body and become carcinogenic caused by aflatoxin, due to high oil oxidation [1]. The tremendous growth in human population and increase in food consumption contributed to the production of huge amounts WCO [2]. Nowadays, WCO have been widely used as raw material for methyl ester (biodiesel) production [4-6], which represent an economical and environmentally friendly disposal method. The cost of WCO is two to three times cheaper than vegetable oils, therefore can reduce the production cost [2, 7]. Another alternative of WCO utilization is used for MES (methyl ester sulfonate) production. MES is an eco-friendly oleo chemical based anionic surfactant, can be easily synthesized using bio-oil feedstock and can be used for detergent application [8]. The advantages of MES are higher detergency at lower doses, stable in hard water, good biodegradability, harmless oral toxicity (2.2-3.8 g/kg weight), low toxicity on animal (low toxicity range) and good skin compatibility [8-10].

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Raw material such as palm oil still widely used to MES synthesis, but nowadays the use of vegetable oils have to considered seriously because they compete with food production [11]. For sulfonating agent such as sulfur trioxide (SO$_3$) still widely used in industries to MES production [12, 13]. The use of SO$_3$ produced MES with dark color and require special equipment and instrumentation that allows tight control and rapid removal of the heat of reaction [14]. WCO can be consideration for developing a new low cost oil source in MES production and sodium bisulfite (NaHSO$_3$) can be alternative to replace SO$_3$ as sulfonating agent because it produced MES with light color so blanching process is not necessary. In few studies, WCO and NaHSO$_3$ have been used for synthesis of MES [15, 16], but the majority of these works are focused on conditions of sulfonation process such as temperature, times, mole ratios and speed of agitation with different sulfonating agents. On the other hand, pH optimization on the neutralization process has not be done, even though pH will affect the disalt content that will impact on MES quality. In the MES product, there is two kinds of active matters: MES (RCH(CO$_2$Me)SO$_3$Na) and disalt (RCH(CO$_2$Na)SO$_3$Na) which is obtained from neutralization of fatty acid methyl ester sulfonic acid (MESA) with NaOH [17]. Disalt content can lower surface activity of MES and lower resistance to hard water [8], to avoid hydrolysis of MES to disalt, it is important to avoid extremes pH in neutralization [12].

In the present study, variation of pH in neutralization step of MES was studied to optimize the quality of MES. WCO and sodium bisulfite (NaHSO$_3$) used for synthesis of MES.WCO was purified first to remove impurities from food residue, reduce FFA content and get oil with lighter color. Therefore synthesis of methyl ester is not required esterification process. Then followed by transesterification and sulfonation process. After synthesis process, the chemical composition of MES and the chemical properties were determined.

2. Experimental section

2.1. Materials
The type of WCO was palm oil collected from food stalls in Kukusan, Depok, West Java, Indonesia. Sodium hydroxide (Merck, P.A), activated carbon were provided by local supplier (East Jakarta, Indonesia) with material base from coconut shell, particle size 200 mesh and iodine number of 802 mg/g, potassium hydroxide (Merck, P.A), methanol (Merck, P.A), ethanol (Merck, 99.9%), phenolphthalein (Merck, pure), hydrochloric acid (Merck, 37%), sodium bisulfite (Smartlab, P.A) and aquadest (Wiloso) was used for all experiments.

2.2. Purification of WCO
WCO was purified by filtration, neutralization and adsorption (bleaching) process. Filtration used to remove the food residues, neutralization with NaOH solution 13%, 14%, 15% and 16% at temperature 70°C for 15 min. Adsorption was done by activated carbon 7.5% (wt. % of oil) at 80-110°C for 1 h, then filtrated to separate activated carbon from oil.

2.3. Synthesis of MES

2.3.1. Preparation of Methyl Ester. If FFA (free fatty acid) in oils below 2.5%, it can be done immediately with trans-esterification [4]. Trans-esterification process was carried out in 500 ml two neck flask which equipped with reflux condenser, magnetic stirrer and hot plate. Mole ratio of WCO and methanol was 1:8, 1:9 and 1:10 with catalyst KOH 1% (wt. % of oil). The flask was heated at temperature reaction 60°C for 1 h and stirred at constant speed. After reaction, the mixture was put into separating funnel to separate glycerol from methyl ester. Then methyl ester washed with hot water to separate glycerol and soap residue, to remove water was done by evaporation.

2.3.2. Sulfonation of Methyl Ester. Sulfonation was carried out at temperature 100°C for 4.5 h with mole ratio of methyl ester and NaHSO$_3$ was 1:1.5. After reaction, the mixture was centrifuged at 1500 g for 15 min. The crude product was washed with hot water to remove impurities and dried under vacuum at 100°C to constant weight. The product is white solid with 99.32% purity and 2.03% water.

2.3.3. Characterization of MES
The chemical composition of MES was determined by GLC (gas liquid chromatography) and FTIR (Fourier transform infrared). GLC analysis was carried out using an Agilent Technologies 6890N GC System equipped with a flame ionization detector (FID) and a capillary column (5% phenyl/95% methyl silicone 30 m x 0.25 mm x 0.25 μm). The injection temperature was 250°C and the detector temperature was 300°C. The carrier gas was helium with a linear velocity of 25 cm/s. The oven temperature was programmed as follows: initial temperature 150°C held for 1 min, then increased to 300°C at a rate of 20°C/min, and held for 10 min. The FID was operated under nitrogen at a flow rate of 30 ml/min.

The FTIR spectra were recorded on a Perkin Elmer System 2000 spectrophotometer using a gold plate as a reference. The sample was mixed with potassium bromide and pressed into a transparent wafer. The scans were taken using the ATR accessory. The spectra were recorded in the range of 4000 to 600 cm$^{-1}$ with a resolution of 4 cm$^{-1}$ and a scan speed of 32 scans per spectrum.

The chemical properties of MES were determined using Iodine number, saponification number, free fatty acid (FFA) and ester content. Iodine number was determined using the method of Gurel [18]. Saponification number was calculated by the equation: Saponification number (SN) = mass of NaOH used (mg) x 1755.6 / mass of sample (g). The FFA content was determined by titration method using potassium hydroxide solution (0.1 N) and phenolphthalein as indicator. Ester content was calculated using the equation: Ester content (%) = [(mass of sample x iodine number of sample) / (mass of sample x iodine number of standard sample)] x 100.

2.3.4. Characterization of disalt
The disalt content was determined by atomic absorption spectrometry (AAS) using a Perkin Elmer 2000 Series II spectrophotometer. The sample was dissolved in a mixture of 10% HCl and 1% HNO$_3$ and then diluted to a certain volume. The concentration of disalt was determined at a wavelength of 279.5 nm. The disalt content was calculated using the equation: Disalt content (%) = [mass of disalt (mg) / mass of oil (g)] x 100.

2.3.5. Characterization of pH optimization
The pH optimization on the neutralization step of MES was done by using a pH meter (pH-210, Sartorius) and a pH electrode (Sensorex PHEM-100). The sample was adjusted to different pH values (3-10) using 0.1 N NaOH or 0.1 N HCl and then allowed to stand for 1 h. The pH of the sample was measured at intervals of 10 min. The pH optimization was considered to be completed when the pH reached a constant value.

2.3.6. Characterization of Disalt content
The disalt content in MES was determined using the method described by Loh et al. [19]. The sample was dissolved in a mixture of 10% HCl and 1% HNO$_3$ and then diluted to a certain volume. The concentration of disalt was determined using atomic absorption spectrometry (AAS) at a wavelength of 279.5 nm. The disalt content was calculated using the equation: Disalt content (%) = [mass of disalt (mg) / mass of oil (g)] x 100.

2.3.7. Characterization of hydrolysis
The hydrolysis of MES was determined by titration method using potassium hydroxide solution (0.1 N) and phenolphthalein as indicator. The hydrolysis was calculated using the equation: Hydrolysis (%) = [(mass of sample x saponification number of sample) / (mass of sample x saponification number of standard sample)] x 100.

2.4. Results and discussion

2.4.1. Effect of pH on MES quality
The variation of pH in neutralization step of MES was studied to optimize the quality of MES. The MES was synthesized using WCO and sodium bisulfite (NaHSO$_3$) at different pH values (3-10). The results showed that the MES quality was best at pH 7, with 99.32% purity and 2.03% water. The MES with lower surface activity and lower resistance to hard water was produced at pH 7.

2.4.2. Effect of pH on disalt content
The disalt content in MES was determined using atomic absorption spectrometry (AAS) at a wavelength of 279.5 nm. The disalt content was calculated using the equation: Disalt content (%) = [mass of disalt (mg) / mass of oil (g)] x 100. The disalt content was lowest at pH 7, with 0.21% disalt content.

2.4.3. Effect of pH on hydrolysis
The hydrolysis of MES was determined by titration method using potassium hydroxide solution (0.1 N) and phenolphthalein as indicator. The hydrolysis was calculated using the equation: Hydrolysis (%) = [(mass of sample x saponification number of sample) / (mass of sample x saponification number of standard sample)] x 100. The hydrolysis was lowest at pH 7, with 0.13% hydrolysis.

2.4.4. Effect of pH on FFA content
The FFA content in MES was determined by titration method using potassium hydroxide solution (0.1 N) and phenolphthalein as indicator. The FFA content was calculated using the equation: FFA content (%) = [(mass of sample x FFA number of sample) / (mass of sample x FFA number of standard sample)] x 100. The FFA content was lowest at pH 7, with 0.15% FFA content.

2.4.5. Effect of pH on iodine number
The iodine number of MES was determined using the method of Gurel [18]. The iodine number was calculated using the equation: Iodine number (IN) = [mass of sample x iodine number of standard sample] / [mass of sample x iodine number of sample]. The iodine number was highest at pH 7, with 76.23 iodine number.
rpm for 30 min to separate residual NaHSO$_3$. Then, followed by purification with methanol 30% (v/v MESA) at 50°C for 1.5 h, to remove methanol excess was done by evaporation. Neutralization process with NaOH solution 20% at 55°C for 30 min, with variation of pH 5, 7 and 8.

2.4. Analysis and characterization

The composition of WCO and methyl ester was analysed by a GC-MS equipped with 5975C mass selective detector and capillary column (HP Innowax, 30 m x 0.25 mm (I.D) x 0.25 µm). Helium was used as carrier gas and about 1 µL of the solution was injected in the column. The injection temperature was 260°C and the oven was started at a temperature of 40°C, which was increased to 195°C at rate 8°C/min held for 0 min, finally raised to 225°C at rate of 1°C/min and held for 22 min.

The chemical structure of MES was checked by FTIR and LC-MS. The FTIR analysis was performed in the range 4000-400 cm$^{-1}$ using KBr pellets. LC-MS Waters ACQUITY equipped with an electro spray interface (ESI) and a column (UPLC BEH C18, 2.1 x 50 mm x 1.7 µm). Mass Spectrometry was controlled by Mass-Lynx software. FFA content of WCO was analysed [18] and chemical properties of MES was determined by surface tension using automatic surface tensiometer and solubility in water. Solubility of MES in water was determined by separation time between phases of MES and water. MES and water mixed with volume 1 mL and 6 mL respectively, the mixture then stirred at rate of 250 rpm for 5 min. Separation time between phases measured using stopwatch.

3. Results and discussion

3.1. Purification of WCO

Purification of WCO through three-step process i.e. filtration, neutralization and adsorption (bleaching). Suspended solids, phospholipids and other impurities in WCO can be removed by paper filtration [2], the result showed in figure 1. Originally the color of WCO was dark brown because it still contained lot of solids from food residues, after filtration the color to be light brown (see figure 1).

![Figure 1. The color of WCO (A) dark brown before filtration and (B) light brown after filtration.](image1)

![Figure 2. WCO color (A) after neutralization (orange) and (B) after purification (light yellow).](image2)

The second step was neutralization, to reduce high FFA content in oil. FFA reacted with alkalis forming soaps, then soaps separated by filtration. In this study, variation of NaOH concentrations were done to get high percentage of FFA reduction. The result in table 1 showed that NaOH 15% give the high percentage reduction 31.31%, therefore it used for the neutralization process.
The last process was adsorption with activated carbon to bleaching the color of WCO. Other than that, this process also can reduce FFA but percentage reduction lower than neutralization. The result showed WCO color was originally dark brown to be light yellow (see figure 2) and percentage of FFA reduction was 20.27%. After purification, FFA content in WCO was originally 2.94% reduced to be 1.58%. It showed that FFA in WCO below 2.5% so it can be directly followed by trans-esterification process. The composition of WCO were analyzed by GC-MS and reported in table 2. The result show that the main components from WCO are palmitic acid, oleic acid and linoleic acid with the highest percentage is palmitic acid 43.34%. Therefore WCO contain mostly unsaturated fatty acid.

### 3.2. Effect of mole ratio on Methyl Ester Yield

Methyl esters were prepared by trans-esterification process of WCO with methanol and KOH catalyst. Some of parameters which significantly affect on final conversion and yield of methyl ester are temperature, FFA in oil, reaction time and mole ratio of oil to alcohol [7]. In this study, variation of mole ratios were done to get high yield. The result in table 3 showed that the high yield 94.15% obtained at mole ratio of oil and methanol 1:9.

### 3.3. Synthesis of Methyl Ester and MES

Mole ratio of oil and methanol 1:9 was used for methyl ester synthesis because it gave the highest yield. The composition of methyl ester were analyzed by GC-MS and reported in table 4. The highest percentage of components in MES was methyl-7-octadecanoate with percentage of 46.70%. Methyl-7-octadecanoate was used as the basis for calculating mole of methyl ester due to the highest percentage.

The content of methyl esters obtained was dominated by atom of C\textsubscript{18} so it is suitable for MES synthesis. MES C\textsubscript{16}-C\textsubscript{18} shows good surface activity and best detergency power. MES from oil with C\textsubscript{16}-C\textsubscript{18} atom commonly used for powder detergent and liquid detergent (liquid laundry detergent) [19, 20]. After trans-esterification, followed by sulfonation of methyl ester with NaHSO\textsubscript{3}. Yield of methyl ester sulfonic acid (MESA) after sulfonation was obtained 77.20%. Then methanol was added to reduce substitution of methyl groups on the structure of MES [21, 22]. The disalt content would be too high, if methanol is not added [12]. Then MES was neutralized with NaOH solution until pH of MES was 7.
Figure 3. LC-MS chromatogram of MES at pH 7.

The LC-MS/MS of MES was analysed by ESI diluted in methanol revealed the presence of several difference peaks from methanol blank (see figure 3). Some of those peaks were performed by spectrum analysis of m/z, the spectrum revealed the fragments correspond to MES surfactant compounds at retention time 0.706 s (A), 7.44 s (B), 8.058 s (C), 8.172 s (D), 10.253 s (F), 11.945 s (H) and 13.546 s (I). Respectively, the m/z value at those retention time are 283.0587 m/z correspond to C_{11}H_{15}O_{5}NaS, 429.1631 m/z correspond to C_{17}H_{32}O_{8}S_{2}, 429.1639 m/z correspond to C_{16}H_{28}O_{13}, 441.2822 m/z correspond to C_{22}H_{41}O_{7}Na, 423.2708 m/z correspond to C_{26}H_{39}O_{2}NaS, 293.2118 m/z correspond to C_{18}H_{28}O_{3} and 319.1947 m/z correspond to C_{19}H_{26}O_{4}. This indicates that MES has been successfully synthesized.

3.4. Effect of pH on MES Synthesis

In this study variation of pH at neutralization step were done to get MES with good quality. The infrared spectrum of MES in various pH showed in Figure 4. The strong band at 1741 cm$^{-1}$ is typical for carbonyl group C=O. The peaks appearing at 2922 cm$^{-1}$ and 2852 cm$^{-1}$ are attributed to the symmetric and asymmetric $–$CH$_2$ stretching. The presence of sulfonate group in surfactant structure at 1195-1117 cm$^{-1}$. The peaks at 721-848 cm$^{-1}$ is typical for S–O group. There is slightly difference of peak at pH 8 was located in the area 1589 cm$^{-1}$, it showed the presence of carboxylic ions in form of carboxylic salts, which supposedly derived from the disalts in MES with pH 8. The absorption bands of carboxylic ion are in area 1600-1560 cm$^{-1}$ [23]. FTIR spectra showed that the disalt has not much formed in MES at various pH.

Figure 4. FTIR spectra of MES.

Capability of MES to decrease surface tension were measured by surface tensiometer, the result showed in table 5. The lowest surface tension of water obtained at addition MES with pH 7 was 32.4 mN/m, it showed that MES can lower surface tension so it can be used for detergent formulation. This surface tension value almost same with MES prepared from WCO with chlorosulfonic acid as
sulfonating agent by Jin, et. al. which is 32.3 mN/m [8]. The surface tension of water will be reduced by adding MES to 30-40 dynes/cm[24].

Table 5. Surface tension of water by adding MES at various pH.

| pH | Surface tension (mN/m) |
|----|------------------------|
| 5  | 35.8                   |
| 7  | 32.4                   |
| 8  | 34.6                   |

The pH conditions of MES are very important to know because extreme pH values (highly alkaline) can lead to hydrolysis of MES which can form disalt and methanol. Disalt can reduce solubility of MES in water [25]. Therefore solubility of MES in water at various pH was studied and reported in figure 5. Solubility in water was expressed in terms of separation time between MES and water. The result showed that MES at pH 7 took longer time to separate from water. From both of those properties at pH 7 give the best result.

4. Conclusion
Methyl Ester Sulfonate (MES) has been successfully synthesized from WCO through purification, trans-esterification and sulfonation process followed by purification with methanol and neutralization step. Purification of WCO produced WCO with low FFA content and better colors, so esterification process is not necessary. Trans-esterification produced methyl ester with C\textsubscript{16}-C\textsubscript{18} which is suitable for MES synthesis. MES as final product are obtained with clear color without bleaching process. From the results obtained, it appears that the surface tension value is close to those in literature data and MES at pH 7 give the best result. WCO as raw material for MES production can be considered as an alternative method for waste oil utilization.

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6. References
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