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The influence of reaction time to the characteristic of methyl ester sulfonate from ketapang seed oil

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Abstract

Methyl Ester Sulfonate had been prepared From Ketapang Seed Oil and was used as Surfactant. The optimum condition obtained by conducting preparation in various reaction time (3.5; 4.0; 4.5; 5.0; 5.5 hours). The methyl ester was analysis by GC-MS and sulfonate group was identified by using FTIR spectroscopy. GC-MS result showed the ester consisted of methyl palmitoleic, methyl linoleic, methyl palmitate, methyl stearate, methyl oleic, methyl palmitolenat and methyl eicosenoate. The optimum condition of methyl ester sulfonate achieved at reaction time 4.5 hours provided mass of methyl ester sulfonate obtained 34.85 g. FTIR spectra of sulfonate group indicated by shifting of wave number at 1118.71cm^{-1} to 1029.1 cm^{-1}. The methyl ester sulfonate has emulsion stability 71.684%, density 0.8714 g/mL, surface tension 36.232 dyne/cm^2, and maximum absorbance 1.428 at 660 nm wavelength.

Keywords: Surfactant, methyl ester sulfonate, reaction time, ketapang seed oil

Abstrak (Indonesian)

Telah dilakukan penelitian Pembuatan Metil Ester Sulfonat Dari Metil Ester Minyak Biji Ketapang Sebagai Surfaktan. Penelitian ini bertujuan untuk mengetahui kondisi optimum variasi waktu reaksi (3,5; 4,0; 4,5; 5,0; 5,5 jam) terhadap karakteristik metil ester sulfonat yang dihasilkan. Metil ester dari minyak biji ketapang diidentifikasi menggunakan GC-MS sedangkan gugus sulfonat pada metil ester menggunakan spektroskopi FT-IR. Hasil penelitian menunjukkan metil ester dari biji ketapang mengandung metil palmitoleat, metil linoleat, metil palmitat, metil stearat, metil oleat, metil palmitolenat dan metil eikosenat. Kondisi optimum waktu reaksi pembuatan metil ester sulfonat pada 4,5 jam dengan jumlah metil ester sulfonat yang dihasilkan 34,85 g. Terbentuknya gugus sulfonat diperlihatkan pada pergeseran bilangan gelombang 1118,71 cm^{-1} sampai 1029,1 cm^{-1}. Karakteristik metil ester sulfonat pada waktu reaksi optimum memiliki stabilitas emulsi 71,684%, massa jenis 0,8714 gram/mL, tegangan permukaan 36,232 dyne/cm^2, dan absorbansi maksimum 1,428 pada panjang gelombang maksimum 660 nm

Keywords: Surfactant, methyl ester sulfonate, reaction time, ketapang seed oil

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INTRODUCTION

Surface active agents known as surfactants are compounds used to lower the surface tension, interfacial tension and improve the stability of the emulsion system. The surfactants are main component in soap, shampoo, loundry powder and detergent. Linear Alkylbenzena Sulfonate (LAS) is the most extensively used surfactant nowadays. This surfactant was synthesized from petrochemicals, which are non renewable resources therefore alternative resources of surfactants is necessary. There are four types of surfactants, namely nonionic, anionic, cationic and amphoteric [1]. The anionic surfactants are type of surfactant widely used in many industries. Estimated the total product of surfactants to be 60% is anionic surfactant [2]. One of anionic surfactant is Methyl Ester Sulfonate (MES) which has a negative charge as surface active [3].

The raw material for MES synthesis can be obtained from vegetable and animal oils. Methyl ester acid from vegetable oils reacts with sulfate or sulfite group to produce surfactants [4]. The MES has advantages compared to LAS, i.e renewable natural resources, environmentally friendly, low production cost and can be used in water with high hardness levels [3]. In addition, this surfactant has a good solubility in the water and stable in high temperature [5]. Other natural resources that can be used as raw material in synthesis of surfactants are oil and grease. Utilization of MES surfactant as an active ingredient in detergents particularly has been developed due to the simple procedure of the synthesis, good dispersion in the water and clean power in hard water [6].

In this study, MES was synthesized using seed oil of Ketapang. Ketapang (*Terminalia catappa* Linn) is a plant with the potential to produce vegetable oil. In Indonesia, ketapang usually grown in the highland and hot climate region [7]. The oil content of Ketapang seed is approximately 40.15% [8]. In order to produce surfactant from seed oil, sulfonation reaction is the main stage that should be concerned. The optimization of MES synthesis from seed ketapang oil was conducted in various reaction time with the moles ratio of methyl ester and $NaHSO_3$ (1:1.5), at 100ºC. The parameters of analysis are emulsion stability, liquid density, surface tension, and maximum absorbance.

MATERIALS AND METHODS

Materials

Ketapang seed samples was taken from Indralaya, Ogan Ilir, South Sumatera. The chemical and reagent for surfactant synthesize include n-hexane, methanol, activated carbon, anhydrous Na_2SO_4, $NaHSO_3$, NaOH and HCl were purchased from Merck. The distillated water was used to make the reagents.

Extraction and Purification of Seed Ketapang Oil

The extraction of oil from Ketapang seed was conducted by soxhletation process. In a typical process, 50 grams of ketapang seeds are wrapped with filter paper and extracted using n-hexane 250 mL. The extraction is carried out at 70°C for 15 hours. After removing solvent using rotary evaporator, oil was purified through deposition (settling), separation of gumi (degumming) and bleaching. Finally, 1 g of anhydrous Na_2SO_4 is added to adsorp the water content.

Synthesis of Methyl Ester

Synthesis of methyl ester was conducted by reacting ketapang seed oil with methanol using NaOH catalyst. Volume ratio of methanol to ketapang seed oil is 80:20 and heated at 60°C. The amount of NaOH added is proportional to amount of ketapang seed oil. The mixture was heated for 2 hours and then cooled to form 2 layers. The top layer is an ester while the bottom layer is glycerol. These two layers were separated by a separating funnel. Ester layer was neutralized with 0.05 M HCl and washed with distilled water. Methyl ester product was determined by using Chromatography Gas-Mass Spectroscopy (GC-MS) QP2010S Shimadzu.

Synthesis of Methyl Ester Sulfonate (MES)

Methyl ester was added into sodium bisulfite using 1:1.5 (mole/mole) ratio and heated at 100ºC for 5 different reaction time (3, 3.5, 4, 4.5, and 5 hours). Futhermore, the mixture was centrifuged at 1500 rpm for 15 minutes to separate residual $NaHSO_3$. Methanol 30% (v/v) was added and then heated at 50°C for 1.5 hours. The synthesis was resumed by evaporating methanol excess and addition of NaOH (20% w/v) to neutralized the mixture. The volume and mass of methyl ester sulfonate resulted is measured. The functional groups of MES were confirmed using Fourier Transform Infra Red (FT-IR) 8400S Shimadzu.

Characterization of MES was carried out by measuring emulsion stability, density, surface tension and maximum absorbance. Emulsion stability was calculated from percentage of weight remaining after heated at 45°C for 1 hour. Density was determined by hydrometer; surface tension properties was measured using tensiometer at 25°C. Determination of absorbance using methylene blue carried out in accordance with SNI 06-6989.51.

RESULT AND DISCUSSION

Synthesis of Methyl Ester Sulfonate

Surfactants from vegetable oil is biodegradable and has good detergency. In this study, methyl ester sulfonate (MES) used as surfactant was synthesized from ketapang seed oil and sodium bisulfite. The seed ketapang was ilustrated in Figure 1. Oil from seed ketapang extracted using n hexane by sohxletation.

Chromatogram of methyl ester displayed in Figure 2. Some methyl esters contained in ketapang seed oil including methyl palmitoleic (0.04%), methyl linoleic (78.40%), methyl palmitate (0.31%), methyl stearate (6.67%), methyl oleic (14.03%), methyl palmitolenat (0.22%) and methyl eikosenoat (0.33%). Methyl linoleic was used as the basis for calculating mole of methyl ester due to its highest percentage in the oil.

Figure 1. Seed of Ketapang

Another product that can be formed is carboxy disodium sulfonate salt. The presence of salts can decrease the performance of methyl ester sulfonate. Therefore, methanol was added to reduce substitution of methyl groups on the structure of methyl ester sulfonate [9]. Methanol also binds the water and influence the viscosity of solution [10].

The mass of MES product showed in Figure 4 yield from methyl ester reactant 30 g. Reaction time 4.5 hours produced higher methyl ester sulfonate than other reaction time. After 5 and 5.5 hours, methanol evaporated into air and causing yield of methyl ester sulfonate reduced. pH of MES product is 6.53 whilst the appropriate value for surfactants are between 6.5−7.5.

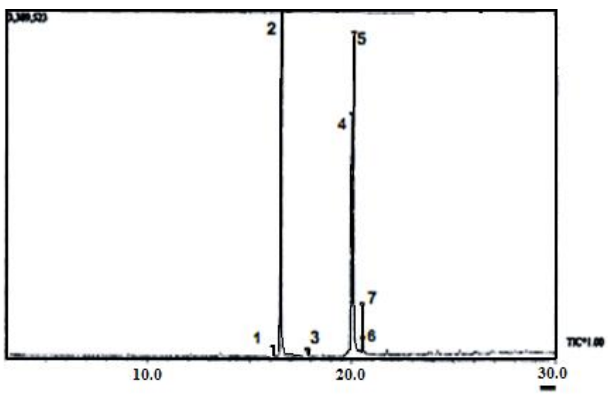

Figure 2. Chromatogram of methyl ester from seed ketapang oil

Infra red spectrum of MES at the optimum reaction time showed in Figure 5. The strong band at 1747.00 cm^{-1} is typical for carbonyl group C=O. The characteristic of ester appeared in region 1172.72 cm^{-1} indicate C-O bond. The broad vibration at 733.01 cm^{-1} assigned for alkene group (−CH=CH−) from unsaturated fatty acid chains. Peaks at 2924.09 cm^{-1} and 2854.65 cm^{-1} are absorption for C-H of the fatty acid chain. Absorbance at wave number 1118.71 cm^{-1} to 1029.1 cm^{-1} is credited to the sulfonate group [11]. The presence of sulfonate had been reported in MES derived from enhance oil recovery process exhibit strong peak at 1158 cm^{-1} [6].

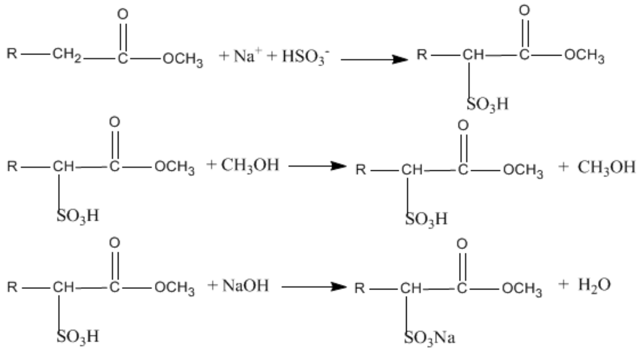

Figure 3. Reaction mechanism of methyl ester sulfonate formation

Influence of reaction time to characteristic of Methyl Ester Sulfonate

One of surfactant important properties is stabilizing emulsion. Emulsions is a system consist of two immiscible liquids. The liquids miscibility in emulsion is unstable hence need stabilizer in form of emulsifier. Emulsion stability of surfactant is related to its performance as emulsifier. The result of the emulsion stability of MES surfactants are shown in Figure 6.

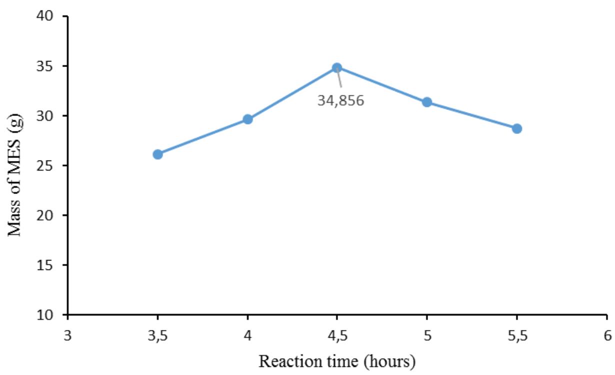

Figure 4. Mass of MES with variations of reaction times

Emulsion stability of MES was increased with increasing reaction time. Stabilization of emulsion depends on several factors such as drop size, polydispersity, drop volume fraction and solubility of the phase dispersed into the continuous one. Stability of emulsions can be last for a few minutes to several years depends on the surfactant and emulsion characteristics [12].

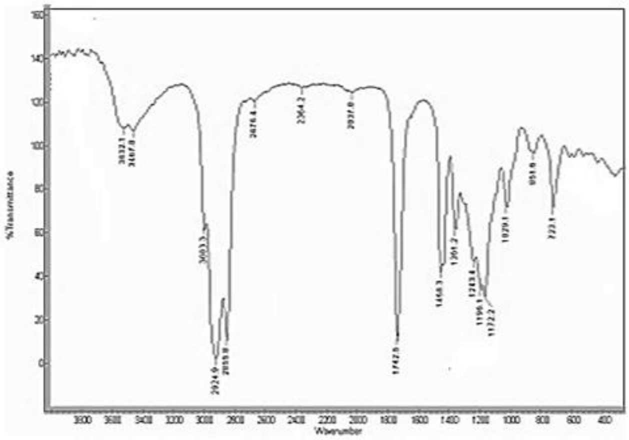

Figure 5. FTIR spectra of MES

The result of the MES density measurement displayed in Figure 7. Minimum standard for density of MES according to Chemiton Corporation Inc is 0.87 g/mL [13]. Figure 7 showed methyl ester sulfonate from oil ketapang seed at the reaction time of 4.5 hours has density 0.8714 g/mL. This result fulfills quality standard by Chemiton. Other studies which prepared methyl ester sulfonate from olein oil has higher density 0.98619 g/mL [14].

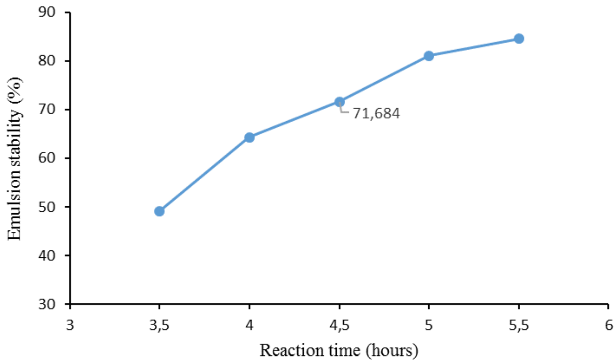

Figure 6. Emulsion stability of MES with variations of reaction times

One of distinctive properties of surfactant is its ability to reduce the surface tension of liquid. The surface tension is defined as the effort required to expand the liquid per unit area [15]. Surface tension occurs due to an imbalance of the forces by molecules on the surface. Surface tension of MES prepared in different of reaction time is represented in figure 8.

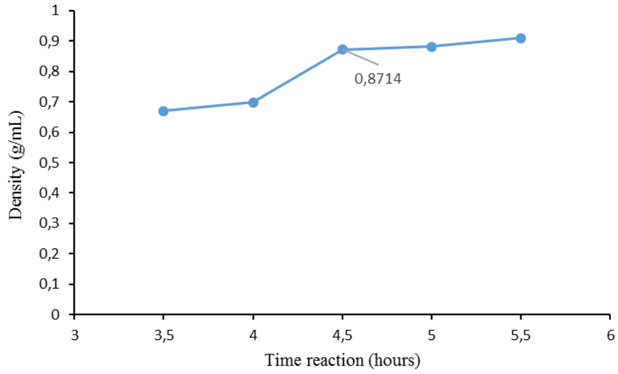

Figure 7. Density of MES with variations of reaction times

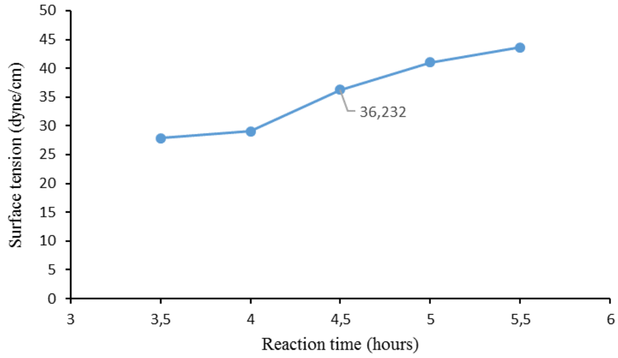

Figure 8. Surface tension of MES with variations of reaction times

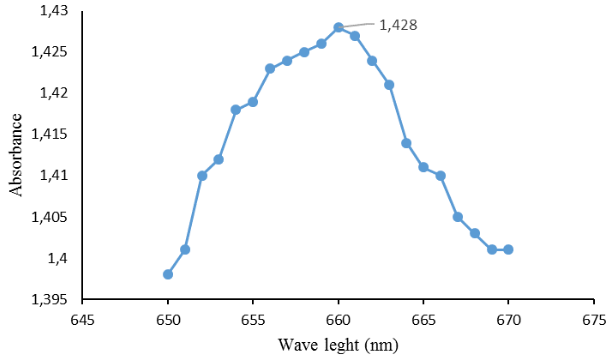

Figure 9. Absorbance of MES with variations of reaction times

The sulfonate group is an ionic hydrophilic which reduce the cohesive forces of the water molecules causing surface tension of water to decreased. The fewer layers of oil formed in surfactant formulations, the more good performance of the surfactant. Surface tension value therefore is affected by the concentration of MES. Increasing concentration of MES causes a decrease in value of surface tension recorded [6]. The surface tension of water is 72 dynes/cm^2 at 25^{o}C which will be reduced by adding MES to 30−40 dynes/cm^2 [15]. Methyl ester sulfonate prepared in 4.5 hours reaction time showed surface tension 36.232 dyne/cm^2. This surface tension value is similar to methyl ester sulfonate prepared from palm oil 32.6 dynes/cm and from castor oil of 38.4 dyne/cm [6,16].

UV-Vis spectrophotometer was used to determine anionic surface active agents on methylene blue in tap-water samples [17]. In this study, measurement was carried out at wavelength range of 650−670 nm to obtain the maximum absorbance of MES. The measurement of MES absorbance value for 4.5 hours reaction time represented in Figure 9. The maximum absorbance value of the MES is 1.428 at wavelength of 660 nm with 3.73% transmittance.

The absorbance of MES from ketapang seed oil is smaller than product by Chemiton Corporation Inc i.e 1.51. Smaller value of absorbance indicates that MES from ketapang seed oil has smaller ability to adsorb methylene blue than commercial products.

CONCLUSION

Synthesis of Methyl Ester Sulfonate (MES) from ketapang achieve optimum product using seed oil and sodium bisulfite mole ratio 1:1.5 at 100°C for 4.5 hours. Determination of characteristics of MES as surfactant anionic at the optimum time reaction obtained emulsion stability 71.684 %, density 0.8714 g/mL, surface tension 36.232 dyne/cm^2 and absorbance 1.428 at the maximum wavelength 660 nm.

REFERENCES

[1] M.A. Muherei, and R. Junin, "Mixing effect of anionic and nonioninc surfactant on micellization", *Mod. App. Sci.*, vol. 2 (3), pp 3–12, 2008

[2] A. Lavergne, Y. Zhu, A. Pizzino, V. Molinier and J. Aubrey,"Synthesize and foaming properties of new anionic surfactant based renewable building block sodium dodecyl isosorbite sulfates", *Journal of Colloids Interface*, vol 360(2), pp.645–653, 2011

[3] C. Watkin, All eyes are on Texas, *Inform*, vol 12, pp. 1152–1159, 2001

[4] D. Mansur, N. Astrini and Tasrif, "Sodium bisulfit as SO_3 source for synthesis of methyl ester sulfonate using RBD stearin as raw materials", *The Journal for Technology and Science*, vol.18 (4), pp. 116–122, 2007

[5] M. Puerto, J. Hirasaki, G. Miller, C.A. and J.R. Barner, "Surfactant system for EOR in high-temperature, High-Salinity Environments. *SPE*, vol 17 (1), pp.11-19, 2012

[6] E.M. Flores, *Species description terminalia catappa L*, Costa Rica: Academia, Naticional de Ciences de Costa Rica, Costa Rica, 1994

[7] A.M. Balogun, and B.L. Fetuga, "Fatty acid composition of seed oils of some membes of the meliaceae and combretaceae families*", J. Am. Oil Chem. Soc.*, vol. 62(3), pp. 529–531, 1985

[8] W. Adamsons, *Physical chemistry of surface*, A Wiley-Interscience Publication, United State of America, 1982

[9] K. Hovda, *The challenge of methyl ester sulfonation*, The Chemithon Corporation. USA, 2002

[10] R. M. Silverstein, F. X. Webster, and D.J. Kiemle, *Spectrometric identification of organic compounds*, John Wiley & Sons, New York, 2005.

[11] K. Babu, N. K, Maurya, A. Mandal and V.K. Saxena,"Synthesis and characterizaion of sodium methyl ester sulfonate for chemically-enhanced oil recovery", *Braz. J. Chem. Eng.*, vol 32 (3), pp.795–803, 2015

[12] J. Desbrieres, C. Bousquet and v. Babak," Surfactant-chitosan interactions and application to emulsion stabilization", *Cellulose Chem. Technol.*, vol 44(9), pp. 395–406, 2010

[13] Jorge, B.W. MacArthur, W.B. Sheats and B.J. Brooks, *MES-myths, misteries and prespectives and use*, The Chemithon Corporation, Seattle, USA, 2012

[14] F.S. Otto, *Preparation and Characterization Methyl Ester Sulfonate (MES) from Olein Methyl Ester*, Institut Pertanian, Bogor, 2011

[15] Shaw, D.J. "*Introduction to Colloid and Surface Chemistry*. Butterworths. Oxford, England, 1980

[16] P. D. Meshram, T. D. Patil, G. A. Usmani, H. V. Patil and N. B. Pawar, Novel Microwave Assisted Synthesis of Anionic Methyl Ester Sulfonate Based on Renewable Source, *International Journal of Engineering Sciences*, vol 4 (6), pp. 69–73, 2015

[17] E. Jurado, M. F. Serrano, J. N. Olea, G. Luzon and M. Luchega," Simplified spectrophotometric method using methylene blue for determining anionic surfactants: Applications to the study of primary biodegradation in aerobic screening tests", *Chemosphere*, vol 65, pp. 278–285, 2006