Synthesis of Methyl Ester Sulphonate Surfactant from Palm Oil Methyl Ester by Using UV or Ozone as an Initiator

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Methyl ester sulphonate (MES) derived from palm oil is environmental friendly and offers good detergent properties. Although Alpha methyl ester sulphonate (α-MES) has been produced by many producers in detergent industries, it has some problems such as disalt formation and low water solubility. In order to overcome these drawbacks, MES is synthesized via sulphoxidation by using different initiators. Ozone is one of the most interesting agents because of its highly oxidizing power, which can react with organic compound rapidly under mild conditions. In this work, ozone and UV are used as an initiator in order to generate radicals along carbon chain to react with sulphur dioxide and oxygen. The reaction is performed in a photochemical reactor with UVC lamps (253.7 nm). The outlet product is transferred to separation and purification steps by liquid extraction techniques. The obtained products are analysed by FT-IR and ESI-MS to confirm MES products. When reaction time is fixed at 4 h, conversions are around 7.5, 6.9 and 13.5 wt% for UV, ozone and UV/ozone systems, respectively.

1. Introduction

At present, there has been an increased focus by global detergent producers on oleo based raw materials, such as surfactant made from the bio-degradable vegetable oil and used in enhanced oil recovery (Nagy et al, 2014). In addition, methyl ester sulphonate (MES) is interesting because it can be derived from palm and coconut (Norman et al., 2008). A number of research on MES surface properties, detergency and environment behaviour (Satsuki et al., 1992) have been investigated in the last decade. Several companies, such as Lion Coporation, Stepan Company and Chemithon Corporation, have produced alpha methyl ester sulphonate (α-MES) conducted in a film-falling reactor (Ortega, 2012) via the sulphonation reaction of methyl ester and sulphur trioxide (SO_3). Although α-MES production has already been produced in commercial scale, there are some limitations, which are low water soluability and hydrolytic stability. Aparicio et al. (2012) studied the effect of Krafft point temperatures or T_k, which is the minimum temperature at which surfactants form micelles. It was found that T_k of pure MES aqueous solutions (C16 and C18) are higher than other common anionic surfactants, such as LAS and AS, resulting in the limitation of solubility, especially in cold water washing. Another drawback of the traditional production is disalt formation, causing poor detergency. In order to minimize disalt, several processes need to be performed at sufficient temperature for a sufficient time (Xie et al., 2013).

To overcome these disadvantages, Platz et al. (1943) were the first German group to discover photosulphoxidation under UV light. Photochemical sulphoxidation or photosulphoxidation is an exothermic reaction that alkanes or cycloalkanes are induced by a mixture of SO_2 and O_2 in the presence of the UV light to form sulfonic acids.
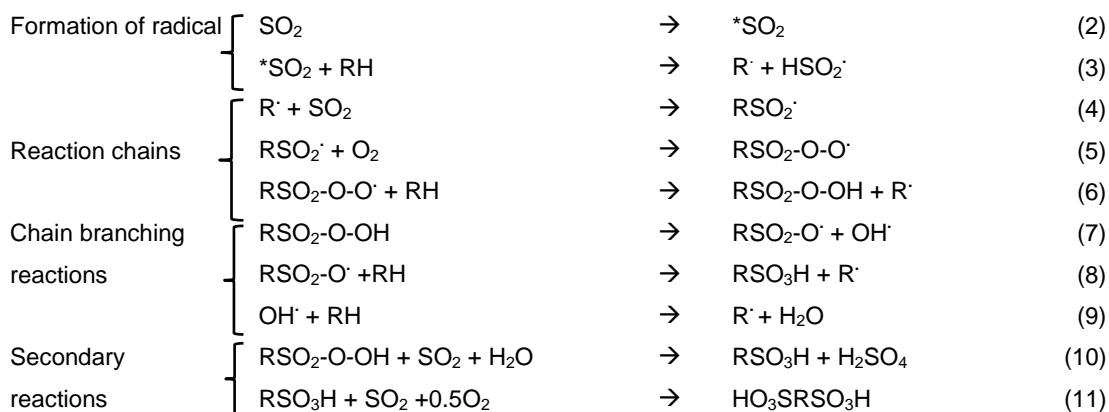
$$RH + SO_2 + 0.5O_2 \xrightarrow{h v} RSO_3H \tag{1}$$

According to Eq(1) (Denisov et al., 2005), the sulphoxidation is normally performed by the ratio of gaseous reactions $SO_2:O_2$ = 2:1 at an atmospheric pressure. Regarding the temperature of sulphoxidation, it relies on the source of initiation. For example, UV light, γ-radiation and ozone occur at room temperature, but

peroxide and organic peroxides are initiated at elevated temperatures (320-360 K). The primary products of alkane sulphoxidation are alkylsulphonic acids, sulphuric acid and alkylpolysulphonic acids.

From 1998 to 2010, Cohen et al. have studied about the synthesis MES by reacting methyl ester with SO_2 and O_2 (in the excess amount) via the Rayonnet photochemical reactor consisting of 16 lamps. UV wave length at 253.7 nm and temperature at 40 °C were the suitable condition to synthesize MES. In addition, Cohen et al. (2001) studied the separation and extraction of MES by using liquid-liquid extraction techniques.

The mechanism of sulphoxidation is different from that of conventional sulphonation. α-MES is produced via an electrophilic substitution mechanism (Holmberg, 2003) resulting in the α position of the long chain, whereas MES via the sulphoxidation reaction is proceeded through a radical mechanism. Gref's studies help to clarify the mechanism of alkane sulphoxidation (Gref R., 1952). UV sulphoxidation occurs via free radicals (Nagayama et al., 1972), which SO_2 absorbs light and initiates the reaction. To form radicals, SO_2 is excited by UV light to be in the triplet state ($*SO_2$), which then abstracts hydrogen from hydrocarbon to produce an alkyl radical as shown in Eq(2) and (3). Subsequent chain reactions with SO_2 and O_2 create an alkylpersulphonyl radical in Eq(4) and (5), which produces another starter radical and a persulphonic acid in Eq(6). Then, an alkylpersulphonyl radical continuously fragments and abstracts hydrogen in Eq(7) and (8) to generate the alkanesulphonic acid. In addition, Eq(9) shows the presence of water formed by the reaction of RH and OH radical. According to Eq(10), the alkanesulphonic acid can also be occurred by the reaction of persulphonic acid, water and SO_2. Besides main products (mono-sulphonic acid), polysulphunic acid in Eq(11) can be occurred as well.

Formation of radical	SO_2	$\rightarrow$	$*SO_2$	(2)
	$*SO_2 + RH$	$\rightarrow$	$R^. + HSO_2^.$	(3)
Reaction chains	$R^. + SO_2$	$\rightarrow$	$RSO_2^.$	(4)
	$RSO_2^. + O_2$	$\rightarrow$	$RSO_2\text{-O-O}^.$	(5)
	$RSO_2\text{-O-O}^. + RH$	$\rightarrow$	$RSO_2\text{-O-OH} + R^.$	(6)
Chain branching reactions	$RSO_2\text{-O-OH}$	$\rightarrow$	$RSO_2\text{-O}^. + OH^.$	(7)
	$RSO_2\text{-O}^. + RH$	$\rightarrow$	$RSO_3H + R^.$	(8)
	$OH^. + RH$	$\rightarrow$	$R^. + H_2O$	(9)
Secondary reactions	$RSO_2\text{-O-OH} + SO_2 + H_2O$	$\rightarrow$	$RSO_3H + H_2SO_4$	(10)
	$RSO_3H + SO_2 + 0.5O_2$	$\rightarrow$	HO_3SRSO_3H	(11)

In this work, the study focused on using another initiator to help generate free radicals, which is more economical and stable than using only UV light. Ozone (O_3) is a well-known initiator, produced by introducing O_2 to an ozoniser, can be used in sulphoxidation. Galimova et al. (1973) proposed the limiting step of cyclohexane oxidation as shown in Eq(12) and (13). The purpose of this work was to synthesize MES via the sulphoxidation reaction by using UV, ozone and UV/ozone as an initiator. MES was synthesized, separated, purified and characterized.

$$RH + O_3 \rightarrow R^. + HO_3^. \tag{12}$$

$$RH + O_3 \rightarrow R^. + HO^. + O_2 \tag{13}$$

2. Materials and Methods

2.1 Materials

Methyl ester (white grade) was obtained from Thai Oleochemicals Co., Ltd., Thailand. For surfactant synthesis, gas reactants were oxygen, nitrogen, sulphur dioxide. For separation and purification steps, all chemicals including methanol (99.9 %), n-Hexane (99.0 %) and n-butanol (99.4 %) were of analytical reagent (AR) grade. Sodium hydroxide (NaOH) was used to neutralise MES products. Water was deionized.

2.2 Synthesis Method

Methyl ester (200 mL) was added into a photochemical reactor, which consists of 16 UVC lamps (253.7 nm). All experiments were performed in the batch reactor at 40 °C in anhydrous medium. SO_2, O_2 (100 mL/min) and O_3 (0.5 L/min) were flowed into a reactor continuously for 4 h. After reaction was done, N_2 was used to purge into the reactor for an hour so as to remove residual SO_2 in the system.

2.3 Separation Method

The undesired products were separated from reactor outlet by liquid extraction techniques. Reactor outlet was mixed with hot water in a separatory funnel. Water (125 mL) was heated to 70 °C before mixing with the product outlet. Mixture solution was left over night in the oven set 60 °C. There were two phases separated in the funnel: the upper layer (organic phase) and lower layer (aqueous phase). After the water phase was separated out, 125 mL of hot water was mixed again with the organic phase and left in the oven. All aqueous phase was blended with 200 mL of methanol. For the organic phase which contained the unreacted methyl ester, a small amount of fatty acid and water, it was transferred to a rotary evaporator (80 to 100 °C for 2 h) in order to remove the small amount of water in methyl ester and the unreacted methyl ester was weighed to calculate conversion. For water-methanol solution, it contained methyl ester sulphonic acid, sulphuric acids and the small amount of fatty acid. Fatty acids were extracted out by using n-hexane as a solvent in a liquid-liquid extractor (for solvents lighter than water). The bottom flask filled with 500 mL of n-hexane was heated to reflux for 8 h at 100 °C. The free fatty acid solution remained in the extractor, while unreacted methyl ester, fatty acids and n-hexane were recovered in the bottom flask. Free fatty acid solution was continuously transferred to the rotary evaporator. Methanol was evaporated out by slightly reducing pressure from 280 to 160 mbar at 50 °C for 2 h.

2.4 Purification Method

n-butanol was used as a solvent to extract the desirable product from the water phase. In this step, the neutralized solution was sent to the liquid-liquid extractor with 500 ml of n-butanol. The extraction condition was set at 150 to 160 °C and heated to reflux for 10 h. The MES was recovered with n-butanol in the bottom flask, while the impurities were left in the aqueous phase. The n-butanol phase was distilled under vacuum in a rotary evaporator set at 100 °C for 2 h. The recovered n-butanol phase could be used again. Finally, the acid solution was neutralized with a 30 % sodium hydroxide solution until pH was equal to 7.

2.5 Measurements

- Conversion was calculated based on mass balance of methyl ester.
- A Fourier transform infrared (FT-IR) spectrophotometer was performed to identify the functional group of products. A thermo Nicolet (Nexus 670) was operated in the transmittance mode with 128 scans, a resolution of 8 cm^{-1} and wave number ranges of 4,000-650 cm^{-1}. A ZnSe disc was used as the background materials of a liquid sample.
- A Gas Chromatography equipped with a Mass Spectrometry of Time of Flight type (GC-TOF), Agilent$^{©}$7890, was used to identify carbon distribution of methyl ester. Helium and nitrogen were used as a carried gas and a cooling gas, respectively. GC conditions were set as follows: Initial temperature of 120 °C, time at initial temperature of 1 minute, 2 °C/min heating rate to 200 °C, held 3 minutes at 200 °C, 3 °C/min to 280 °C, and final temperature of 280 °C, held for 10 minutes.
- Electrospray Ionization Mass Spectrometry (ESI-MS) was used to analyse sample by direct infusion ESI at a flow rate of 180 μL/h. ESI-MS fingerprints were obtained in the negative ion modes in a Q-TOF mass spectrometer (micrOTOP II, Bruker Daltonics). Typical ESI-MS conditions were as follow: source temperature 100 °C, desolvation temperature 100 °C, capillary voltage 3.8 kV and cone voltage 40 V. Fingerprint mass spectra were acquired in the range between m/z 50 and 1,000.

3. Results and Discussion

3.1 Palm Oil Methyl Ester Composition

Gas chromatographic-mass spectrometry (GC-MS) was used to find the contribution of chain length in palm oil methyl ester. The contribution and composition of each component are concluded in Table 1. Methyl ester used in this experiment consists of 36.0 % of C16 and 64.0 % of C18.

Table 1: Fatty acid composition present in palm oil methyl ester

Fatty acid		Formula	Molecular weight	Area (%)
Palmitic acid methyl ester	C16:0	$C_{17}H_{34}O_2$	270	36.0
Octadecenoic acid methyl ester	C18:1	$C_{19}H_{36}O_2$	296	45.4
Linoleic acid methyl ester	C18:2	$C_{19}H_{34}O_2$	294	0.5
Stearic acid methyl ester	C18:3	$C_{19}H_{38}O_2$	298	18.1

Table 2: Conversion percentage of three different systems

Systems	Conversion (%w/w)
UV	7.5
O_3	6.9
UV/O_3	13.5

3.2 Conversion

Conversion percentages are calculated and concluded in Table 2. The UV and O_3 systems are studied so as to investigate the effect of different initiators. UV and O_3 are individually used as an initiator for the first and second systems, respectively. The conversion of these two systems is 7.5 % and 6.9 % which are not significant different. However, when UV light and O_3 are used together in the third system, conversion increases to be approximately 13.5 %, which is improved by 6.0 % and 6.6 % for the first and second systems, respectively.

3.3 Infrared spectra

As shown in Figure 1, the spectra of unreacted methyl ester from four systems (b-d) show mostly the same functional groups as palm oil methyl ester (a). As the palm oil methyl ester is mainly mono-alkyl ester, the high intensity of carbonyl stretching band of ester appears at 1,170 and 1,742 cm^{-1}. Moreover, CH_2- symmetric and asymmetric stretching frequencies of linear alkane range from 2,852 to 2,929 cm^{-1}, while CH_2- bending frequency appears at 1,460 cm^{-1}. Furthermore, it can be noticed that there is a peak at 1,710 cm^{-1} of -C=O of saturated carboxylic acids in unreacted methyl ester (b-d). This may be due to methyl ester groups are hydroysed by water and then become carboxylic groups. However, carboxylic groups of fatty acids can be recovered by esterification with a large excess of anhydrous methanol and an acidic reagent as catalyst as shown in Eq(14). Therefore, the unreacted methyl ester can be reused.

$$RCOOH + CH_3OH \xrightarrow{\quad H^+ \quad} RCOOCH_3 + H_2O \tag{14}$$
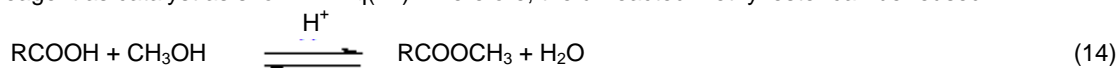
Figure 2 shows IR spectra of α-MES C18 compared to synthesized MES of each system. It is found that all synthesized MES show the same frequencies as α-MES C18, which are 3,456 cm^{-1} (OH stretching), 2,859-2,928 cm^{-1} (CH_2- symmetric and asymmetric stretching), 1,742 cm^{-1} (-C=O stretching of ester), 1,457 cm^{-1} (CH_2- bending), 1,200 cm^{-1} (SO_3 asymmetric stretching) and 1,040 cm^{-1} (SO_3 symmetric stretching in R-SO_3). These results indicate that this sodium methyl ester sulphonate is sulphonated via the sulphoxidation reaction.

3.4 Electrospray Ionization Mass Spectrometry

MES products were analyzed by direct infusion negative ion mode electrospray ionization mass spectrometry (ESI-MS). Figure 3 shows fingerprints from three different initiators, which display ions of m/z 361, 379, 393, 443, 459, 473 and 491 with variable intensities. The ions of m/z 361, 379 and 393 represent mono-sulphonate of C18, whereas 443, 459, 473 and 491 refer to di-sulphonates of C18. According to the suphoxidation mechanism in Eq(2-11), there are a number of intermediates happening during the reaction, such as RSO_2^-, RSO_3 and RSO_4. It can be noted that the three large peaks at 361, 379 and 393 mass units correspond to mono-sulphonates in the forms of RSO_2H, RSO_3H, and RSO_4H, respectively. In addition, there are four peaks of di-sulphonates C18 such as the masses at 443 (-SO_2H and –SO_3H), 459 (two groups of –SO_3H), 473 (-SO_3H and -SO_4H) and 491 (two groups of -SO_4H). The height of peaks does not reflect the abundances of the different sulphonated species. Therefore, ESI-MS only confirm the presence of mono- and di-sulphonates of C18.
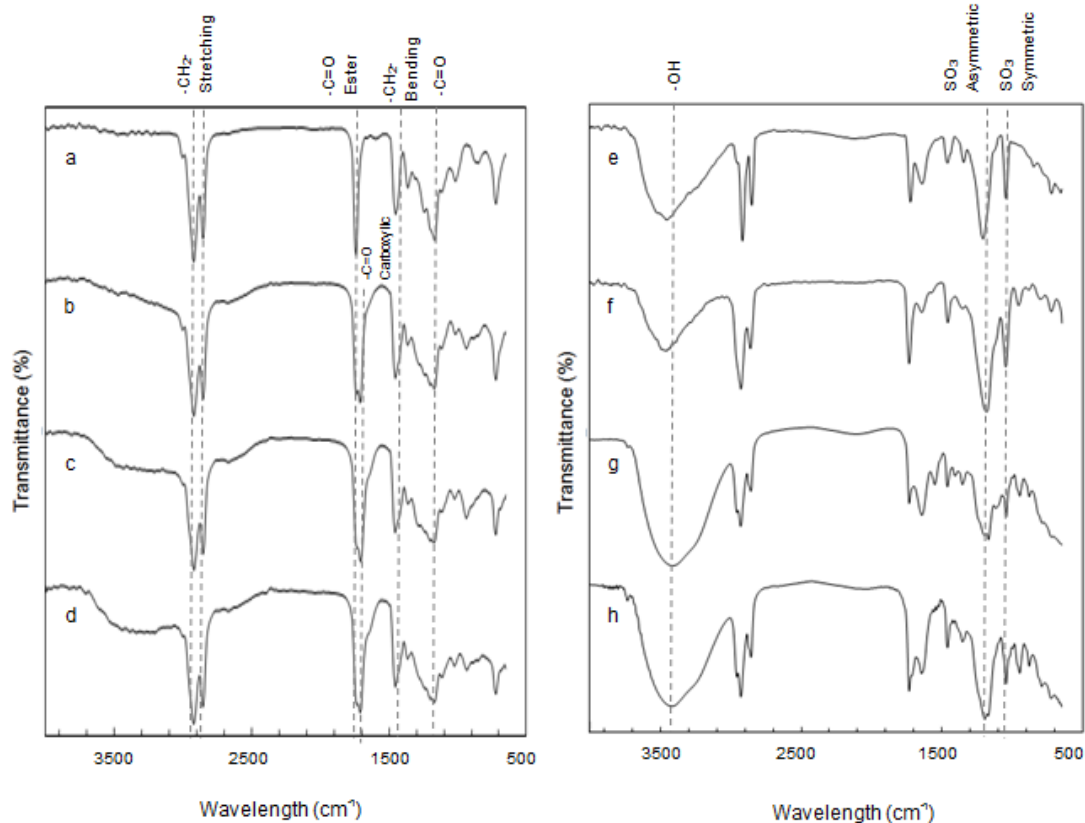
Figure 1: Infrared spectra of a) methyl ester compared to unreacted methyl ester b) UV c) O_3 d) UV/O_3 systems

Figure 2: Infrared spectra of e) α-MES C18 compared to neutralized MES from f) UV g) O_3 h) UV/O3 systems
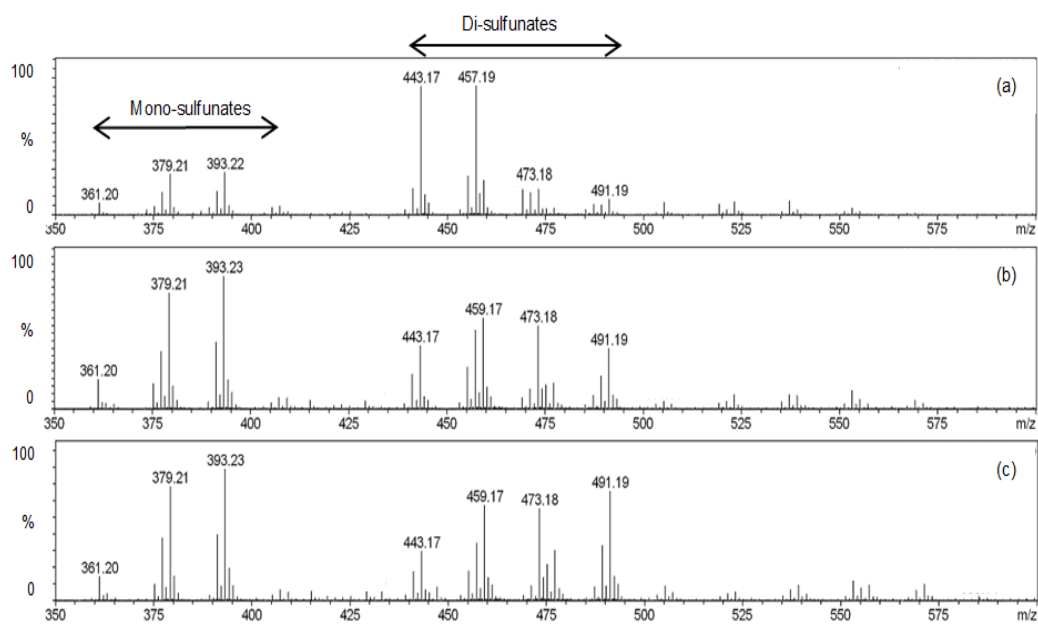

Figure 3: ESI-MS fingerprints in the negative ion mode of a) UV b) O_3 c) UV/O_3 systems

4. Conclusion

MES was successfully synthesized by using UV and O_3 as an initiator and SO_2 and O_2 as a reactant. The conversion percentage of UV/ozone is up to 13.5 %wt, which is about two times of using only UV and O_3 in each system. The FT-IR results confirm that there are sulphonate groups in the synthesized compounds. Additionally, ESI-MS results indicate that not only mono-sulphonates are generated but also di-sulphulnates of C18 are present.

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