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การสังเคราะห์และผลิตสารลดแรงตึงผิวประเภทเมทิลเอสเทอร์ซัลโฟเนตจากน้ำมันปาล์ม

Synthesis and Production of Methyl Ester Sulfonate Surfactant from Palm Oil Methyl Ester

โดย

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เมทิลเอสเทอร์ซัลโฟเนตเป็นสารลดแรงตึงผิวซัลฟอนที่ได้น้ำมันปาล์มเมทิลเอสเทอร์สารลดแรงตึงผิวชนิดนี้มีข้อดีหลายประการเช่นสมบัติการทำความสะอาดที่ดีเยี่ยมความสามารถในการสลายตัวทางชีวภาพที่ดีและความสามารถในการทนต่อน้ำกระด้างเป็นต้นแม้ว่าแอลฟาเมทิลเอสเทอร์มีจำหน่ายตามท้องตลาดโดยทั่วไปแต่ก็ยังมีข้อเสียสองประการเช่นการเกิดโคซอลท์และข้อจำกัดในการละลายน้ำดังนั้นเพื่อหลีกเลี่ยงปัญหาเหล่านี้การสังเคราะห์เมทิลเอสเทอร์โดยผ่านปฏิกิริยาซัลฟอกซิเดชันด้วยตัวริเริ่มปฏิกิริยาเป็นสิ่งที่น่าสนใจอย่างยิ่ง โอโซนเป็นสารริเริ่มปฏิกิริยาที่มีราคาถูกและมีอำนาจในการออกซิไดซ์สูงจึงสามารถทำปฏิกิริยากับสารประกอบอินทรีย์ได้อย่างรวดเร็วภายใต้สภาวะปกติสำหรับงานวิจัยนี้การสังเคราะห์เมทิลเอสเทอร์ซัลโฟเนตโดยใช้ปฏิกิริยาซัลฟอกซิเดชันนั้นถูกแบ่งออกเป็นสามส่วนส่วนที่หนึ่งการพิสูจน์เอกลักษณ์ของสารตั้งต้นเมทิลเอสเทอร์และแอลฟาเมทิลเอสเทอร์ซัลโฟเนตส่วนที่สองการศึกษาผลของการใช้สารตั้งต้นและตัวริเริ่มปฏิกิริยาที่แตกต่างกันและส่วนที่สามการศึกษาผลของเวลาในการทำปฏิกิริยาในการทดลองนี้ปฏิกิริยาเกิดที่อุณหภูมิ 40 องศาเซลเซียสภายใต้ความดันบรรยากาศภายในเครื่องปฏิกรณ์แสงซึ่งประกอบด้วยหลอดยูวี 16 หลอดที่มีความยาวคลื่น 253.7 นาโนเมตรหลังจากเสร็จสิ้นปฏิกิริยาผลิตภัณฑ์ผ่านกระบวนการแยกและทำให้บริสุทธิ์โดยใช้เทคนิคการสกัดด้วยของเหลวสำหรับส่วนที่หนึ่งสารตั้งต้นเมทิลเอสเทอร์ประกอบด้วย 36 และ 64 เปอร์เซ็นต์ของคาร์บอน 16 และ 18 ตามลำดับเมทิลเอสเทอร์และแอลฟาเมทิลเอสเทอร์ถูกนำมาทดสอบเพื่อใช้เป็นสารมาตรฐานสำหรับส่วนที่สองเป็นผลการศึกษาผลของการใช้สารตั้งต้น(ก๊าซออกซิเจนและก๊าซซัลเฟอร์ไดออกไซด์) และตัวริเริ่มปฏิกิริยา(ยูวีและก๊าซ โอโซน) เครื่องวิเคราะห์สารด้วยอินฟราเรด (FT-IR) และเครื่องวิเคราะห์มวลสาร (ESI-MS) ถูกใช้เพื่อยืนยันโครงสร้างของผลิตภัณฑ์เมทิลเอสเทอร์ซัลโฟเนตค่าการเปลี่ยนรูปเรียงจากมากไปน้อยดังนี้ $UV/O_3/O_2$, UV/O_2 , O_3/O_2 และ UV/O_3 สำหรับส่วนที่สามการศึกษาผลของเวลาในการทำปฏิกิริยาเนื่องจากระบบ $UV/O_3/O_2$ ให้ค่าการเปลี่ยนรูปมากที่สุดระบบนี้จึงถูกนำมาศึกษาผลของเวลาจากการทดลองพบว่าเมื่อเวลาในการทำปฏิกิริยาเพิ่มขึ้นค่าการเปลี่ยนรูปเพิ่มขึ้นแต่อย่างไรก็ตามค่าการเลือกทำปฏิกิริยาลดลง

ABSTRACT

Methyl ester sulfonate (MES) is a potential anionic surfactant derived from palm oil methyl ester. MES shows several advantages, such as excellent cleaning properties, good biodegradability, and tolerance to hard water. Although alpha methyl ester sulfonate (α -MES) is commercially available, it still has some drawbacks, such as disalt formation and low water solubility. Since ozone possesses high oxidizing power, it can react with organic compounds rapidly under mild conditions. In this work, the investigation on the sulfoxidation reaction of methyl ester to methyl ester sulfonate was divided into three parts; (1) characterization of starting methyl ester and α -MES, (2) the effect of different reactants and initiators, and (3) the effect of reaction time. The reaction was performed at 40 °C under atmospheric pressure in a photochemical reactor with 16 UV lamps (253.7 nm). The outlet product was transferred to separation and purification processes by using liquid extraction techniques. For the first part, the starting methyl ester was comprised of 36.0 % C16 and 64.0 % C18. Methyl ester and α -MES were characterized and used as a standard. For the second part, there were four different systems aiming to study the influence of reactants (O_2 and SO_2) and initiators (UV and O_3). The presence of sulfonate groups and molecular weight of MES solution was confirmed by using FT-IR (Fourier Transform Infrared Spectrometer) and ESI-MS (Electrospray Ionization Mass Spectrometry). Conversion increased as follows: $UV/O_3/O_2 > UV/O_2 > O_3/O_2 > UV/O_3$. For the third part, since MES could be synthesized and yield the highest conversion on the $UV/O_3/O_2$ system, this system was chosen to study the effect of reaction time. It was found that when the reaction time inclined, conversion increased, but selectivity slightly decreased.

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CHAPTER I

INTRODUCTION

1.1 Introduction

Nowadays, a number of widely-used surfactants are synthesized from petroleum and natural gas. However, some difficult problems facing surfactant industries today are a lack of raw materials and an environmental issue. These are due to a high demand in a lot of applications such as detergent, personal care, fabric softening and industrial areas. These major issues force surfactant producers to change some traditional products, to meet environmental requirements, and to give the required performance of synthesized surfactants at the same time.

There has recently been an increased focus by global detergent producers in formulating MES-based products because methyl ester sulfonate (MES) derived from palm and coconut offers an environment friendly and has good detergent properties. Many companies, such as Lion Corporation (Lion), Stepan Company (Stepan), and Chemithon Corporation (Chemithon), have produced alpha methyl ester sulfonate (α -MES) conducted in a film-falling reactor via the sulfonation reaction of methyl ester and sulfur trioxide (SO_3). Although α -MES production has already been produced in commercial scale, there are some limitations, which are disalt formation and low water solubility (Norman *et al.*, 2008). To overcome these drawback, Cohen *et al.* (1998) proposed the use of sulfur dioxide/oxygen (SO_2/O_2) and ultraviolet (UV) irradiation via sulfoxidation reaction, providing a random of sulfonated group in alkyl chain (Φ -MES).

In this work, the study focused on using another initiator to help generate free radicals which is cheaper than using only UV light. Ozone is one of the most interest chemicals because it is an effective oxidizing agent, which is capable of reacting rapidly under mild conditions with organic compounds (Galimova *et al.*, 1973). The purpose of this work was to synthesize MES via the sulfoxidation reaction by using UV, ozone and UV/ozone as an initiator. The effect of reaction time was also evaluated.

1.2 Objective

1. To synthesize methyl ester sulfonates from methyl esters via the sulfoxidation reaction by using different initiators: UV light and UV light/ozone.
2. To study the effect of reaction time by choosing the suitable system from the first objective.

1.3 Scope of research

The scope of this research covers the following:

Scope 1: Effect of different reactants and initiators

Table 1.1 Systems to study the effect of different reactants and initiators for the first scope

	System	Reactant		Initiator	
		SO ₂	O ₂	UV	O ₃
1	UV/O ₂	✓	✓	✓	
2	O ₃ /O ₂	✓	✓		✓
3	UV/O ₃ /O ₂	✓	✓	✓	✓
4	UV/O ₃	✓		✓	✓

Controlled parameters

- The photochemical reactor with 16 lamps (253.7 nm) under atmospheric pressure.
- The amount of methyl ester was fixed at 200 mL.
- The reaction took place at 40 °C.
- SO₂ and O₂ flow rate were fixed at 100 ml/min.
- O₃ flow rate was fixed at 0.5 l/h.
- Nitrogen is used to remove sulfur dioxide residue for 1 h.
- Reaction time was fixed at 4 h.

In this scope, there are four different systems as shown in Table 1.1. The first system consisted of UV and O₂. The first system consisted of O₃ and O₂. The third system consisted of UV, O₃, and O₂. Finally, the fourth system consisted of UV and O₃.

Scope 2: Effect of reaction time

Table 1.2 Systems to study the effect of reaction time for the first scope

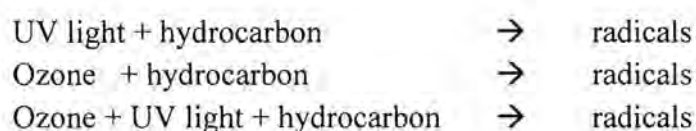
Reaction Time (h)
1
2
4
6

Controlled parameters

- The photochemical reactor with 16 lamps (253.7 nm) under atmospheric pressure.
- The amount of methyl ester was fixed at 200 mL.
- The reaction took place at 40 °C.
- SO₂ and O₂ flow rate were fixed at 100 ml/min.
- O₃ flow rate was fixed at 0.5 l/h.
- Nitrogen is used to remove sulfur dioxide residue for 1 h.
- The suitable system from the first scope was chosen to vary reaction time

In this scope, reaction time of suitable system which yields the highest conversion from the first scope is chosen to study the influence of reaction time. Reaction time was set for 1, 2, 4, and 6 h.

1.4 Hypothesis



In summary, the sulfoxidation reaction from methyl ester to MES for this work can be proposed as follows: First, uv t was be used to generate radicals. Second, ozone was be used to generate radicals as well. Last, the combination of uv and ozone were employed to generate radical easily. It is because the wave length between 220 nm and 280 nm was the most effective for ozone in UV.

1.5 Literature review

1.5.1 Background on surfactants

Nowadays, the demand of surfactants has increased continuously every year. In 2006, more than 1.3 million metric tons of surfactants were produced and the United States and Europe were the largest regions that played an important role in manufacturing and consuming surfactants (Figure 1.1). In addition, surfactants are used in various applications such as detergent, personal care, fabric softening and industrial areas, as shown in Figure 1.2 (Matthew, 2008).

A surfactant (surface-active agent) is a substance that can adsorb onto the surfaces or interfaces and change degree the surface or interfacial free energies of those surfaces when it presents at low concentration in a system (Rosen, 2012). Generally, a surfactant contains a hydrophobic part with little affinity for the bulk aqueous medium and a hydrophilic part attracted to the bulk aqueous medium, as shown in Figure 1.3.

Surfactant can be classified into four main types (Rosen, 2012)

1. Anionic surfactants e.g. LAS (linear alkylbenzenesulfonate)
2. Cationic surfactants e.g. CTAB (cetyltrimethylammonium bromide)
3. Nonionic surfactants e.g. AE (alcohol ethoxylate)
4. Amphoteric surfactants e.g. dodecyl dimethyl sulfobetaine and dodecyl dimethyl amine oxide

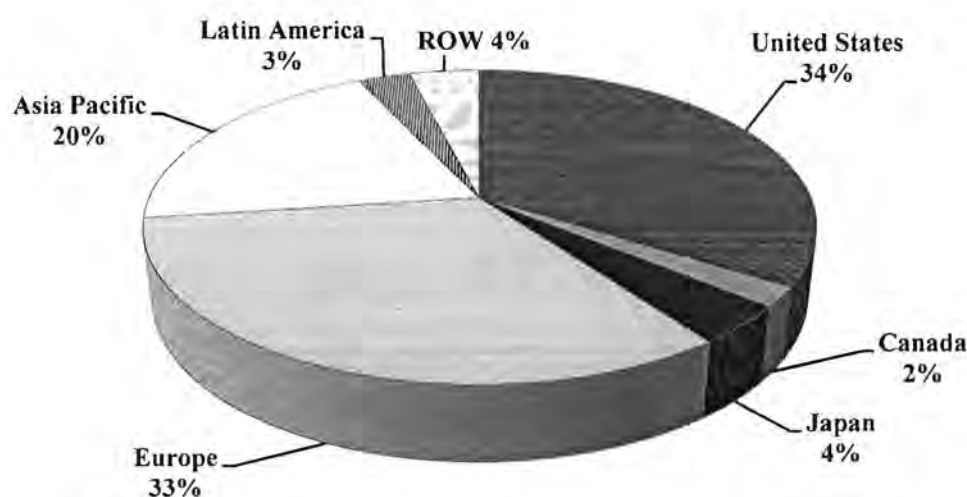


Figure 1.1 Estimated percentage of annual global volume sales of surfactants for 2006 based on a total of 13 million metric tons (Matthew, 2008).

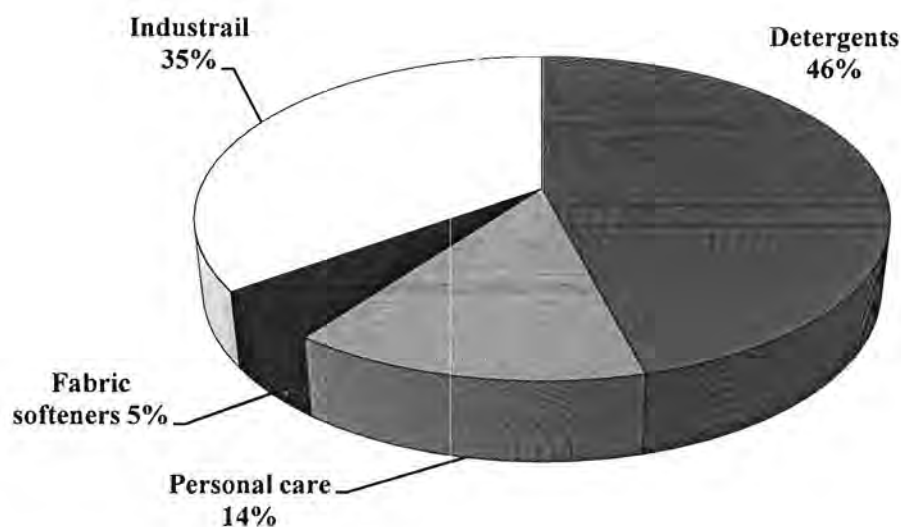


Figure 1.2 Percentage of global surfactant consumption by major application area for 2006 based on total sales of 13 million metric tons (Matthew, 2008).

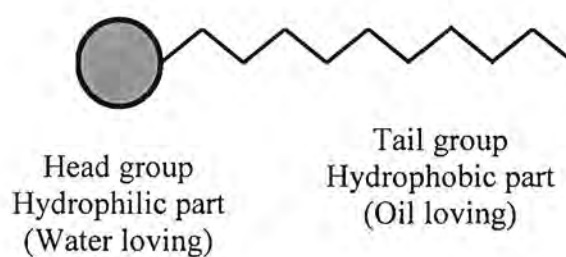


Figure 1.3 Structure of surfactant monomer.

Figure 1.4 shows an equally large number of anionic and nonionic surfactants (□ 40%) in 2006 while the chart shows only 11% and 3% of cationic and amphoteric surfactants, respectively. Nowadays, anionic surfactants play a crucial role in surfactant industry. Most of the anionic surfactants are produced from sulfonation and sulfation reaction to produce “sulfonates and sulfates” surfactants (Matthew, 2008).

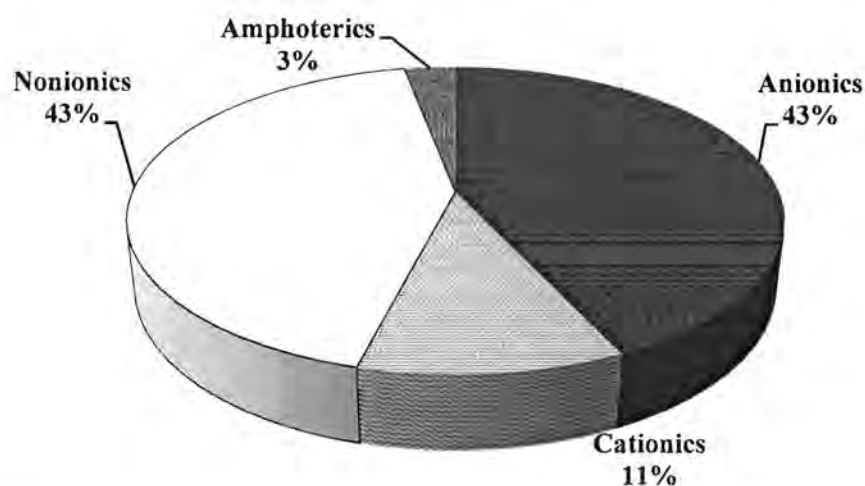


Figure 1.4 Percentage of global surfactant consumption by major application area for 2006 based on total sales of 13 million metric tons (Rosen, 2012).

A number of sulfonates results from a sulfonation reaction that creates carbon-sulfur bonds and utilizes sulfur VI reagent SO_3 . Regarding the sulfation reaction, it can create carbon-oxygen-sulfur bonds and can utilize SO_3 , sulfuric acid and cholorsulfonic acid to form alcohol sulfates. Sulfation reaction must be handled under milder conditions than sulfonation reaction during formation and neutralization. Figure 1.5 and 1.6 show anionic surfactants based on SO_3 and SO_2 , respectively.

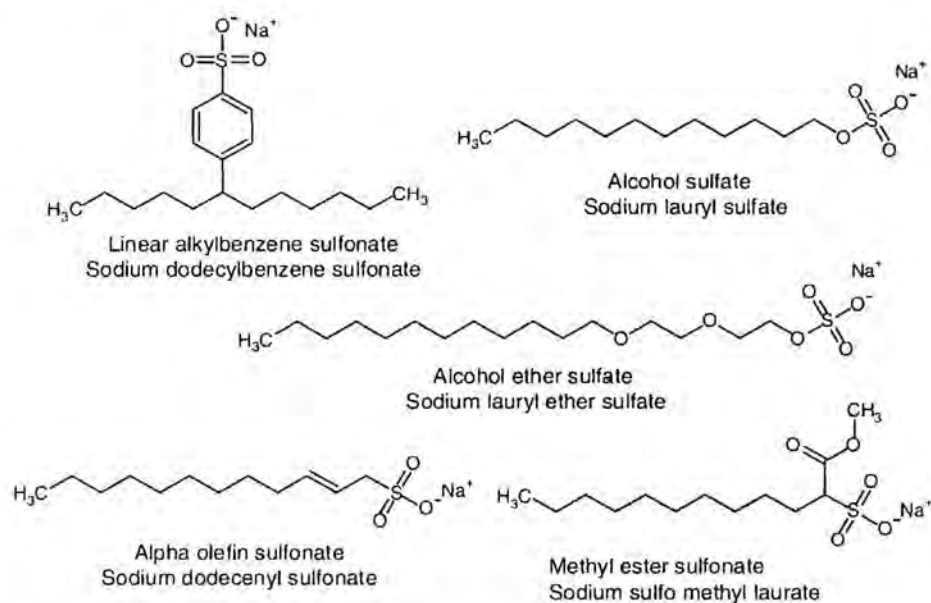


Figure 1.5 Anionic surfactants based on SO_3 with non-IUPAC generic and industry-specific nomenclature (Matthew, 2008).

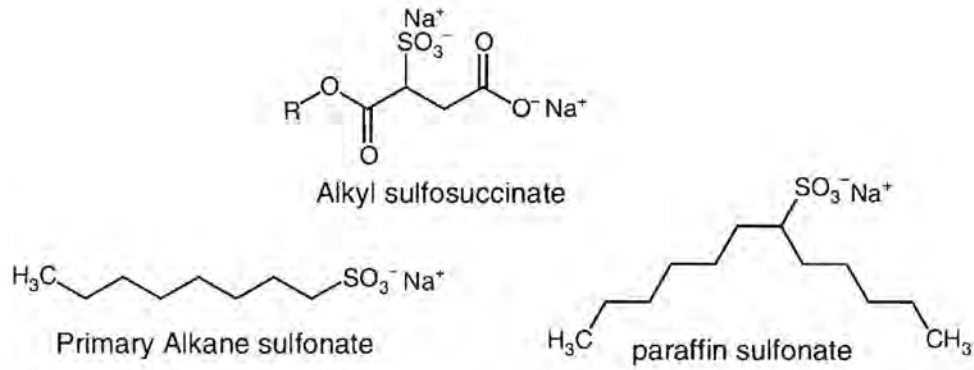


Figure 1.6 Anionic surfactants based on SO₂ with non-IUPAC generic and industry-specific nomenclature (Matthew, 2008)

Figure 1.7 shows several pathways to synthesize sulfonates and sulfate by using different agents. Sulfonates, which have alkanes as a reactant, can be produced from sulfonation, sulfochloration and sulfoxidation while sulfates, which have an alcohol group as a reactant, can be generated by sulfonation, sulfation and others (Norman *et al.*, 2008).

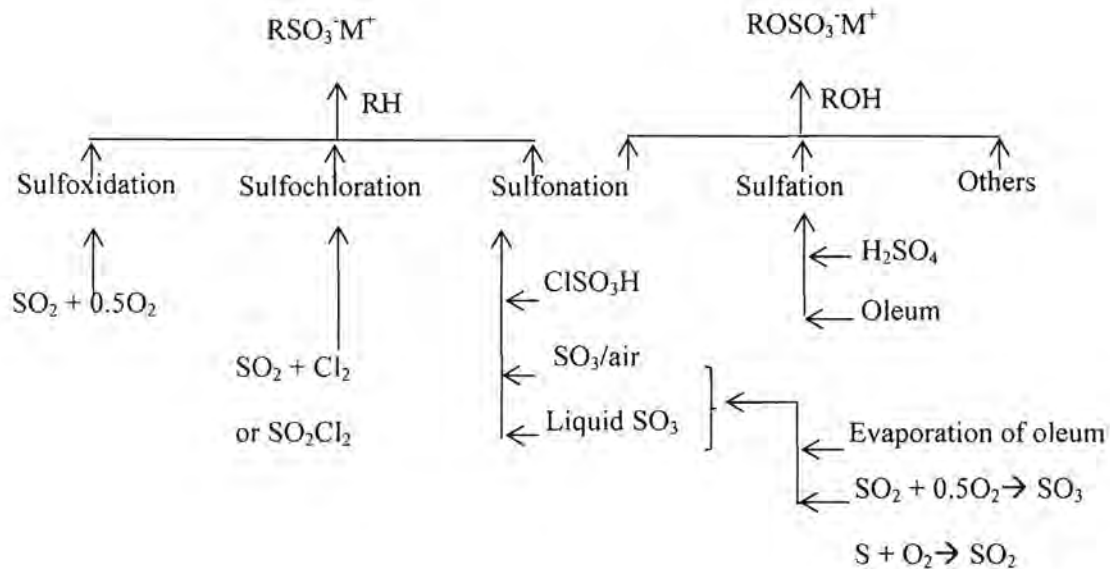


Figure 1.7 Sulfoation and sulfation pathways for manufacturing sulfur-containing anionic surfactant (Norman *et al.*, 2008).

Nowadays, many detergent manufacturers attempt to find ways to produce natural-based detergent. Methyl ester sulfonate (MES) is an interesting detergent since it can be produced from palm oil and coconut and shows excellent cleaning properties. Sulfonation and sulfoxidation are two of the processes to produce MES.

1.5.2 Methyl Ester Sulfonate

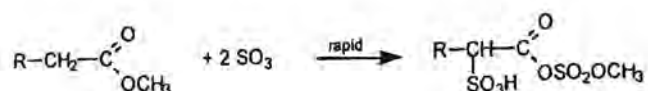
Methyl ester sulfonate (MES) is one of the most popular and interesting due to several reasons. First, the price of linear alkyl benzene (LAB) derived from petroleum oil is depended on the price of oil. At present, the price of oil tends to increase continuously, which directly affects the price of linear alkyl benzene sulfonate (LAS). Since the price of palm is cheaper than that of petroleum-based material like paraffin and benzene, palm-based MES can be an interesting alternative to other commercial surfactants. Furthermore, even though the national price of methyl ester (ME) have a tendency to increase, the final price of α -MES was lower than the current price of LAS derived from LAB (Martinez *et al.*, 2010). Second, the used of worldwide toxic chemicals is severely concerned. LAS causes a major problem of water contaminations which have an impact on animals, plants and humans. Chemical measures are currently regulated, which forces manufacturing companies to meet the requirement of the environment law and consumer needs by searching for innovative products. MES based on a renewable oleo-based raw material provides an environment friendly because of the high biodegradation of MES lower quantity of carbon dioxide release in its entire life cycle than LAS (Ghazali *et al.*, 2004). Besides its excellent biodegradability, this oleo-based surfactant also has good calcium hardness tolerance and good detergent properties.

1.5.2.1 Alpha Methyl Ester Sulfonate (α -MES) via Sulfonation

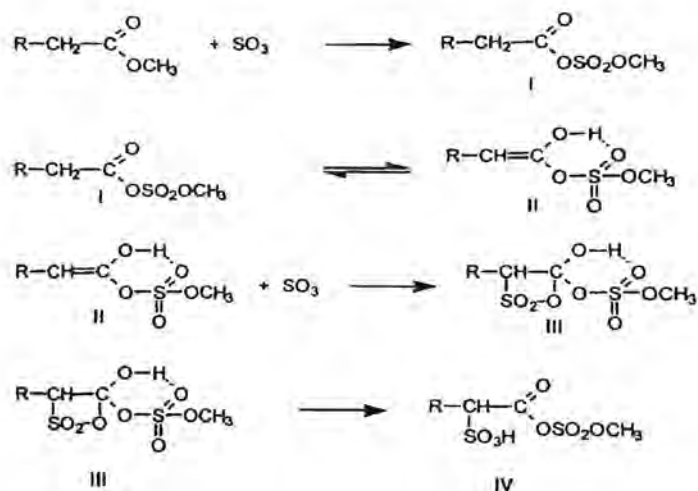
Mechanism of α -MES via Sulfonation

The mechanisms of α -MES in the sulfonation reaction were investigated as shown in Figure 1.8 (Holmberg, 2003). In the first step, SO_3 is added into fatty acid methyl ester. A SO_3 molecule is inserted into the ester binding to form mixed anhydride of sulfuric acid (I), and then the anhydride continuously form its cyclic enol (II), and it reach equilibrium very fast. A second molecule of SO_3 attacks the double bonding of cyclic enol to form intermediate III before it turns into intermediate IV through a fast electrophilic addition. In the second step, the α -sulfonated anhydride is slowly arranged into the ester sulfonate, while one molecule of SO_3 is released to react with a new molecule of fatty acid ester. Additionally, it is believed that the real sulfonation agent of the acid ester is not SO_3 , but the initially formed sulfonated anhydride.

First step:



Intermidates of the first step:



Second step:

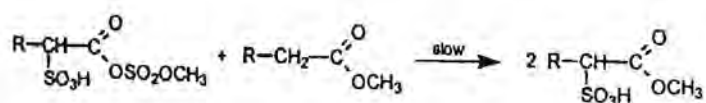


Figure 1.8 The two-step mechanism of sulfonation reaction (Holmberg, 2003).

α -MES Production

There are a number of companies, for example, Lion Coporation (Lion), Stepan Company (Stepan), and Chemithon Corporation (Chemithon) having patent technologies for manufacturing MES based on acid bleaching. The advantages of acid bleaching over neutral bleaching are lower color products, lower a total residence time and less risk in storing. Hence, most commercial MES processes have incorporated with acid bleaching (Norman *et al.*, 2008).

The commercial-scale plant of Chemithon α -MES production is shown in Figure 1.9. In an air supply unit, air needs to be removed because moisture can cause acid formation leading to corrosion. For a SO_3 generator, sulfur is burned with oxygen to generate SO_2 (Eq. 1.1), and then SO_3 formation is promoted as shown in Eq. 1.2 (Martinez *et al.*, 2010).

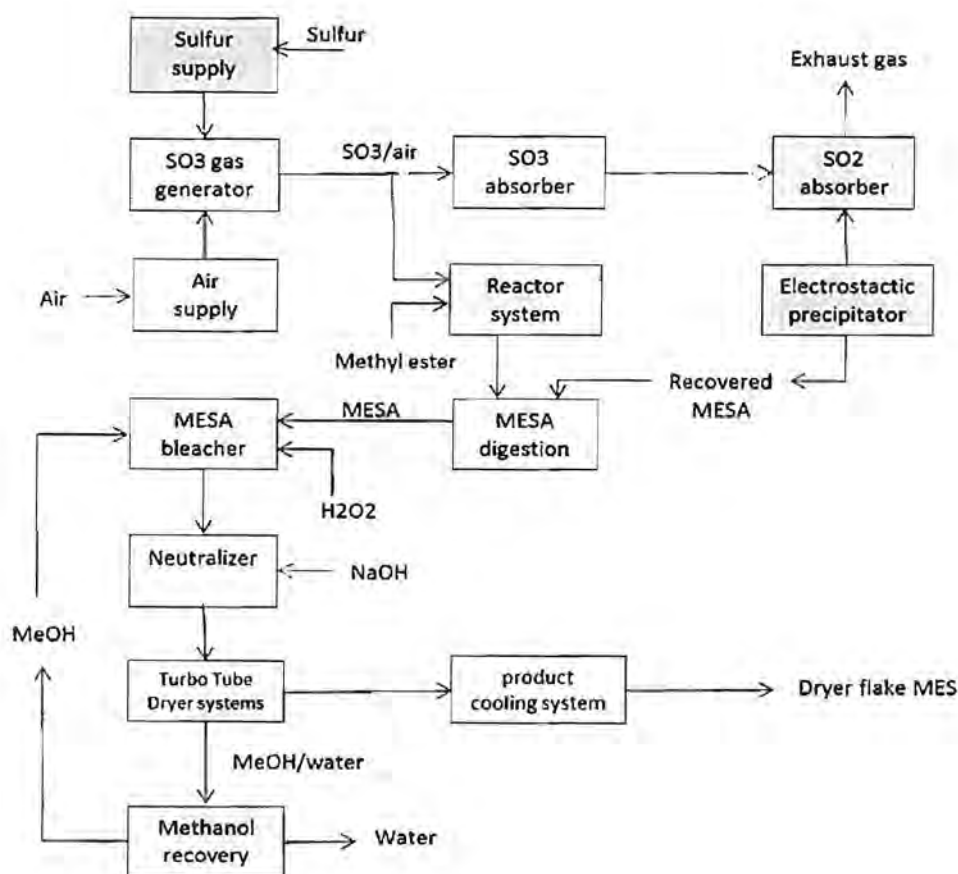
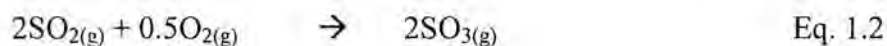
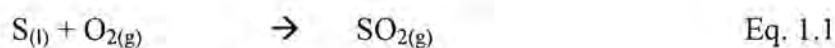
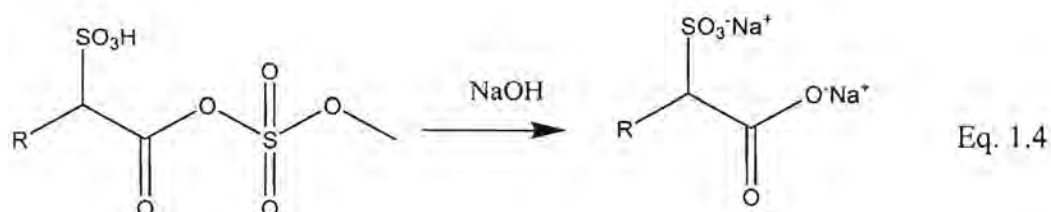
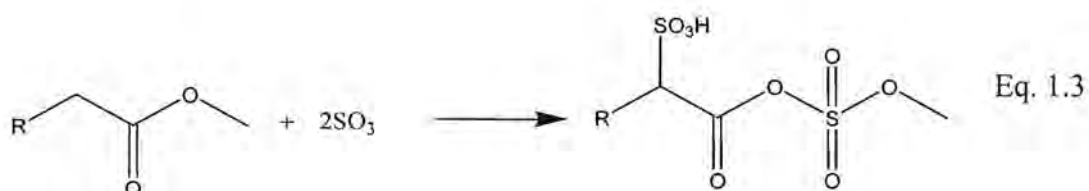


Figure 1.9 The overview of Chemithionsulfonation plant (Norman *et al.*, 2008).

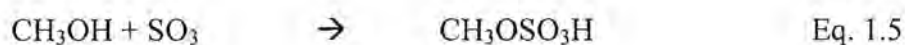


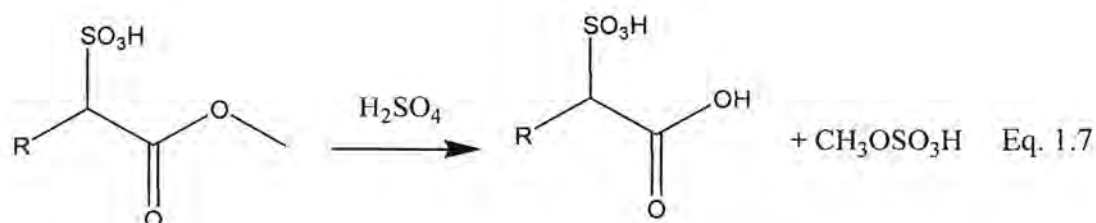
In the sulfonation process, 7 % (volume) of inlet SO_3 at 42 °C and ME feedstock (40 to 52 °C) are fed into a reactor. The mass flow of these reactants is controlled by maintaining a fixed molar ratio of SO_3 to ME ranging from 1.15 to 1.25. After reactants pass into the falling-film reactor, methyl ester sulfonate acid (MESA) is transferred to an acid digester system. In the MESA bleacher unit, methanol (30-35 wt%, digested MESA basis) and H_2O_2 (50 wt%) are mixed with the MESA. The acid bleaching step, which is an exothermic reaction, requires about 1-1.5 hours to proceed this step. The disalt formation is formed by

the reaction between one mole of ME and two moles of SO_3 at high temperature. Formation of disalt is one of the biggest problems in α -MES production (Martinez *et al.*, 2010). Disalt is occurred when too much SO_3 is present during the sulfonation providing the excess intermediates (Eq. 1.3). When they are neutralized, they will be converted to sulfonated soap or disalt (Eq. 1.4). In general, disalt has lower surface activity as compared to α -MES, causing poor detergent properties. If disalt is formed too much, the products will not only lower detergency but also the poor biodegradability. Ghazali (2002) studied the effect of disalt on the biodegradability of α -MES. They varied the disalt content of α -MES by controlling the re-esterification step. It was clearly seen that the presence of disalt reduced biodegradability because of its low surface activity and its poor solubility in water.

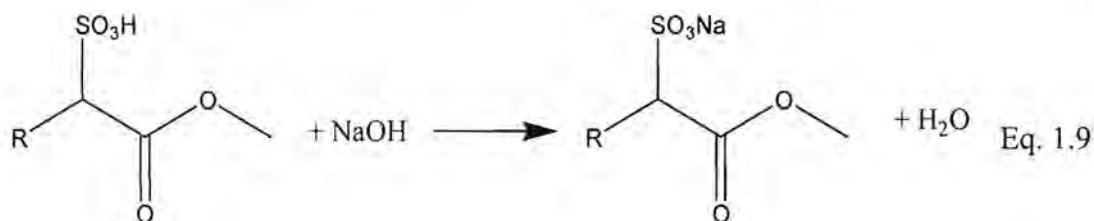


Nevertheless, disalt formation can be controlled by adding methanol. The excess methanol provides the limitation of occurring disalt and also the reduction of viscosity resulting in the improvement of mixing and heat transfer through the bleaching process. In addition, the gas phase reaction between SO_3 and methanol produces methyl sulfonic acid (Eq. 1.5) preventing the hydrolysis of MES. The hydrolysis is caused by sulfuric acid, derived from the reaction between SO_3 and water (Eq. 1.6), and then sulfuric acid can continuously turn into α -sulfonated acids in Eq. 1.7 (Martinez *et al.*, 2010).





Bleached MESA is forwarded to the neutralizer where 50 % NaOH is added so as to neutralize both acidic substances and acidic MES in the stream (Eqs. 1.8, 1.9). After neutralization, MES paste is continuously sent to a dryer to remove the excess amount of water and methanol at 145 °C under vacuum conditions of 120-200 torr.



α -MES Properties

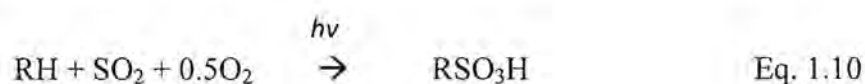
Many researchers have studied about α -MES properties, such as water hardness, foaming ability, lime soap dispersion power and biodegradability. α -MES has good properties in hard water and provides a good property of lime soap dispersion power; therefore, ester sulfonates can be combined with soaps to help lime soap dispersion (Matthew, 2008). Furthermore, the effect of combinations of α -MES with other surfactants was also studied, such as MES/POESE (Lim *et al.*, 2002), a long-chain alcohol in α -MES (Lim, 2004) and MES/TAB (Wong *et al.*, 2011). Besides, the biodegradability and toxicity of detergent surfactants, especially LAS, are concerned (Commission of the European Communities, 2004). LAS is poorly biodegradable under anaerobic conditions. Even if it can be rapidly degraded under aerobic conditions, the toxic benzene derivatives still remain in the environment (Ghazali *et al.*, 2004).

1.5.2.2 MES via Sulfoxidation

Although α -MES is now manufactured in commercial scale, there is a limitation in water solubility. Since α -MES is synthesized through an electrophilic substitution, the sulfonate group is presented only at α position of the alkyl chain which does not reduce the hydrophobicity of the carbon chain (Cohen *et al.*, 2008). In addition, 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. This reason makes α -MES dissolve poorly in water. To overcome this drawback, Cohen *et al.* (1998) suggested the use of UV light with SO_2 and O_2 to synthesize Φ -MES via a radical mechanism. (" Φ " symbol represented the random of sulfonate group in alkyl chain)

Photochemical Sulfoxidation

Photochemical sulfoxidation or photosulfoxidation 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. Platz *et al.* (1943) were the first German group to discover photosulfoxidation under UV light and the Hoechst company successfully developed the production of alkanesulfonates in the late 1940s.



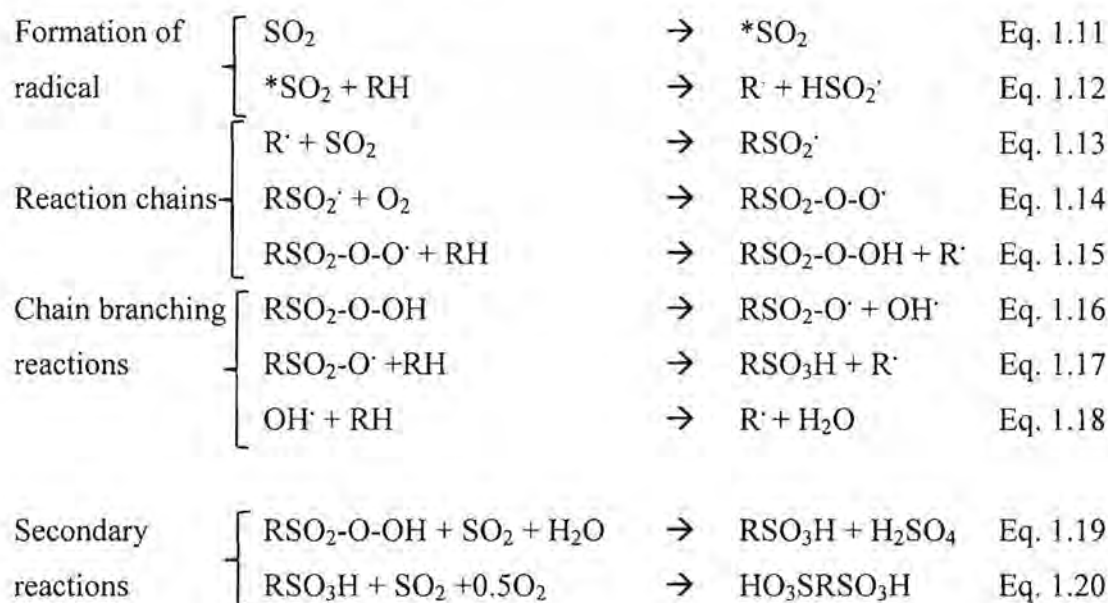
According to Eq. 1.10 (Denisov *et al.*, 2005), the sulfoxidation is normally performed by the ratio of gaseous reactions $\text{SO}_2:\text{O}_2 = 2:1$ at an atmospheric pressure. Regarding the temperature of sulfoxidation, it relies on the source of initiation. For example, UV light, γ -radiation and ozone occur at room temperature, but peroxide and organic peroxides are initiated at elevated temperatures (320-360 K). The primary products of alkane sulfoxidation are alkylsulfonic acids, sulfuric acid and alkylpolysulfonic acids.

Moreover, some researchers applied catalysts into sulfoxidation. The aliphatic sulfonic acids from saturated aliphatic hydrocarbon were prepared by using SO_2 , O_2 and the

catalyst, such as Pb^{IV} in the form of lead tetraacetate (Bradley, 1950). By using this catalyst without UV light, the photochemical reaction can generate MES as well.

Mechanism of Sulfoxidation

The mechanism of alkane sulfoxidation is clarified by Gref's studies (Gref, 1952). UV sulfoxidation occurs via free radicals, which SO_2 absorbs light and initiates the reaction.



Ramakrishnan (2006) explain how sulfoxidation occur in .Eq. 1.11 to Eq. 1.20. To form radicals, SO_2 is excited by UV light to be in the triplet state ($*\text{SO}_2$), which then abstracts hydrogen from hydrocarbon to produce an alkyl radical (Eqs. 1.11, 1.12). Subsequent chain reactions with SO_2 and O_2 create an alkylpersulfonyl radical (Eqs. 1.13, 1.14), which produces another starter radical and a persulfonic acid (Eq. 1.15). Then, an alkylpersulfonyl radical continuously fragments and abstracts hydrogen (Eqs. 1.16, 1.17) to generate the alkanesulfonic acid. In addition, Eq. 1.18 shows the presence of water formed by the reaction of RH and OH radical. According to Eq. 1.19, the alkanesulfonic acid can also be occurred by the reaction of persulfonic acid, water and SO_2 . Besides main products (mono-sulfonic acid), polysulfonic acid in Eq. 1.20 can be occurred as well.

Cohen *et al.* (2010) concluded about the hydrocarbon reaction mechanism of sulfoxidation in the anhydrous media. There are two pathways that a sulfonic acid can be generated; dark and irradiated reactions in the batch photochemical reactor. The dark reaction or thermal decomposition is explained in Eq. 1.19. About the irradiated reaction, the

persulfonic acid colludes with $\text{RSO}_2\cdot$ so as to produce the sulfonic acid. They summarized that continuous irradiation from UV light is needed because recycled radicals are consumed by impurities (X) according to the following reaction:



Additionally, Nagayama *et al.* (1972) improved the method of paraffin sulfoxidation for the continuous system. Since the responsibility of UV light is to excite SO_2 to SO_2^* (Eq. 1.11), they introduced UV light only in the early stage and turned off UV light in other steps. Instead of using both O_2 and SO_2 at the beginning, oxygen is fed after $\text{RSO}_2\cdot$ is formed. This is due to oxygen can deactivate SO_2^* species, which can suppress next reaction steps to continue. This method produced more amount of sulfonic acid as compared to conventional method.

MES Synthesis via Sulfoxidation

Cohen *et al.* (1998) studied about the synthesis of Φ -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 Φ -MES. After 6 hours, reactor outlet was characterized by IR and GC to confirm the present of Φ -MES.

In 2001, Cohen studied the separation and extraction of Φ -MES as shown in Figure 1.10. There were two ways to extract unreacted methyl ester. The first method was a liquid-liquid extraction by using hexane, which is heated to reflux for 6 to 8 hours. For the other method, hot water at 60 to 80 °C was mixed with the reactor outlet in a separatory funnel. Reactor outlet was immediately separated into two phases; an organic phase and water phase. The organic phase (or the upper layer) contained nonreacted methyl ester and a small amount of fatty acid, while the water phase (or the lower layer) contained sulfonic acid, some fatty acids and sulfuric acids. After that, water phase was neutralized by sodium hydroxide (30 %w/w). For purification procedure, n-butanol was used in the liquid-liquid extractor and needed heating to reflux about 8 hours so as to separate water out. n-butanol phase which contained n-butanol and Φ -MES was distilled under vacuum by a rotary evaporator. Purified Φ -MES sodium salt was titrated with Hymine, which gave more than 75 % active ingredient.

Conversion and selectivity at different chain lengths and reaction times were evaluated (Cohen *et al.*, 2006). For Φ -MES C16, the result showed that when the reaction time increased from 0.5 to 6 hours, conversion increased up to 40 %w/w, while the ratios of mono- and disulfonates decreased to 2.3. Regarding the effect of the chain length on conversion and selectivity, carbon numbers were varied from C12 to C18. Conversion increased from 24.8 % for C12 to 50.2 % for C18. This was suggested by a radical mechanism in the sulfoxidation reaction. The farther away the CH_2 group from $\text{C}(\text{O})\text{-OCH}_3$ was, the easier the radical formed. However, the primary (ω), the carboxylic and α carbon did not react, meaning that C18 had 15 secondary active carbons to form radicals as compared to the C16 methyl ester that had only 13 sites (Cohen *et al.*, 2010). Thus, the probability of reaction with SO_2/O_2 would be higher for the longer number of homologs.

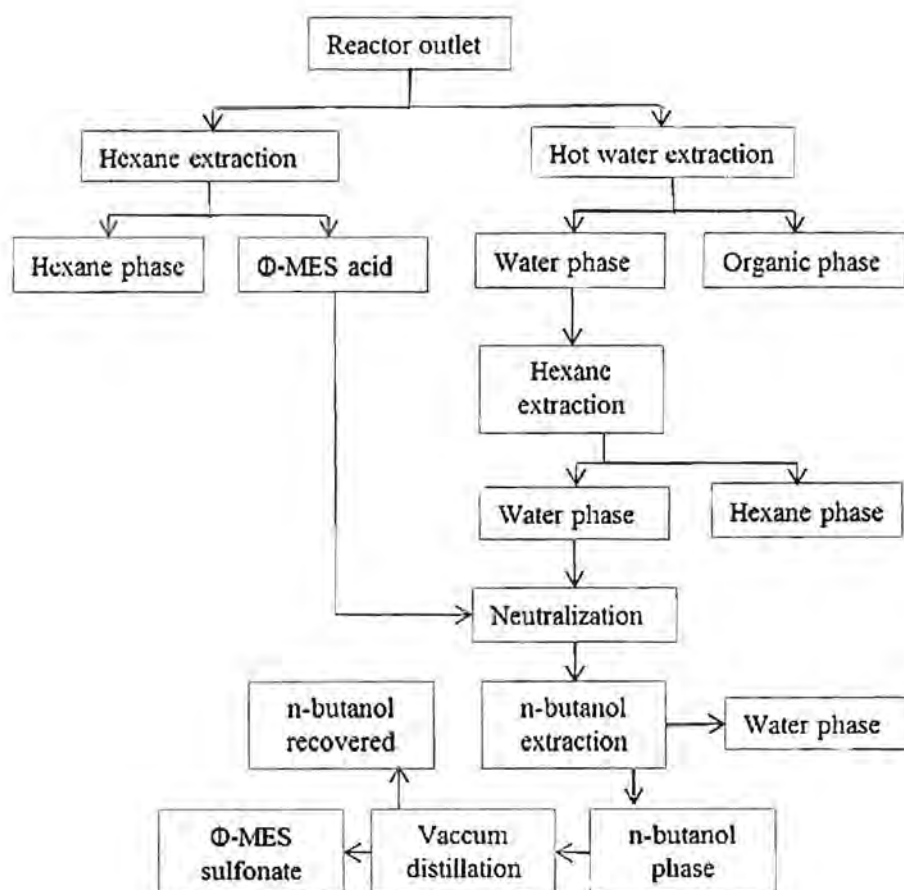


Figure 1.10 The separation and extraction of Φ -MES (Cohen *et al.*, 2001).

MES Properties from Sulfoxidation

Cohen *et al.* (1998) studied the effect of carbon chain length of Φ -MES on physicochemical and surface properties. It was revealed that CMC of Φ -MES was more efficient and effective than α -MES. Viscosity of Φ -MES was varied from 10 to 200 cps, while LAS was about 9500 cps at 30 % active ingredient. Therefore, Φ -MES is a low viscous liquid compared to LAS. Regarding stability to water hardness and foaming power, C16 could highly tolerant to calcium hardness and had the highest foam height at 300 ppm Ca^+ .

Cohen *et al.* (2008) also studied the performance of Φ -MES C16 compared to LAS, secondary alkane sulfonates (SAS) and α -MES. The water solubility (turbidity point) of SAS was higher than LAS, Φ -MES and α -MES, respectively. This was because SAS and LAS had a higher number of soluble isomer and Φ -MES had synergic interactions between homologues and isomers. On the contrary, products of α -MES were not water soluble because a CO_2Me group at α position did not reduce the hydrophobicity of the carbon chain. In other words, the ester group of Φ -MES hindered the sulfonate groups and decreased its interaction with water. They also found that Φ -MES was more stable to water hardness than LAS and SAS. In addition, Φ -MES showed the good properties of foaming power, wetting power and dishwashing performance, especially at a higher water hardness. Moreover, the irritation of human skin was tested by observing the formation of a complex between the protein presence in the skin and the surfactant. They found that Φ -MES had lower Zein number because the presence of the ester linkage of Φ -MES had weaker hydrophobicity to bind with the protein.

In summary, in addition to excellent biodegradation, Φ -MES provides several good detergent properties, such as good water solubility which is easy to include in liquid formulations (Cohen *et al.*, 2001), very low viscosity of aqueous solutions which is easy to handle and pump, very good wetting power, excellent water hardness stability which allows them to be formulated in hard water regions, and excellent skin compatibility which good for hand dishwashing formulations and body care products.

1.5.3 Ozone with Hydrocarbon

Though Φ -MES can be synthesized by using UV light and SO_2/O_2 , Φ -MES production is hard to scale up to commercial scale because of the need of expensive equipment costs and a large amount of energy. Therefore, this study attempts to find another initiator to combine with UV light. Ozone is a well-known initiator which can initiate sulfoxidation (Ramakrishnan, 2006). Ozone shows the property of highly oxidize power and the ability to react with organic compounds rapidly under mild conditions.

Galimova *et al.* (1973) studied the kinetics and products of oxidation of cyclohexane in the presence of ozonied oxygen in CCl_4 solution at 22 °C. Cyclohexane could be transformed simultaneously into cyclohexanol, cyclohexanone, adipic acid, H_2O_2 and organic peroxide. They introduced the limiting step of the process which was cleavage of C-H bond in the reaction of RH with ozone (Eq. 1.22, 1.23).



In general, the combination of UV light and ozone is more powerful for the decomposition of organic compounds than ozone alone. Gurol *et al.* (1987) studied the effect of ozone and ozone + UV light on the oxidation of phenolic compounds by varying pH value. It was revealed that the rates of ozone decomposition increased with increasing pH due to hydroxyl radical became the predominant oxidizing species. When ozonation combined with UV radiation for specific pH, the results showed that the summation of the removals by ozone and by UV was equal to the removals by ozone + UV light. Moreover, the overall removal of total organic carbon (TOC) increased in the following order: ozone + UV light > ozone > UV light.

In conclusion, even though α -MES is well-known anionic surfactants for decades, there are some disadvantages, such as having disalt formation in products and having low water solubility property. In this study, the sulfoxidation reaction of methyl ester to MES was conducted in the presence of different initiator systems focusing on UV, ozone, and UV/ozone. The effects of using different initiators and reactants were studied. Reaction time on different initiator systems was investigated as well.

CHAPTER II

EXPERIMENTAL

2.1 Materials

1. Methyl ester (white grade), Thai Oleochemicals Co., Ltd., Thailand
2. Alpha methyl ester sulfonate C16 and C18, Lion Corporation, Japan
3. n-Hexane (AR grade)
4. n-Butanol (AR grade)
5. propan-2-ol (HPLC grade)
6. Acetonitrile (HPLC grade)
7. Methanol (HPLC grade)
8. Methanol (AR grade)
9. Water (HPLC grade)
10. Deionized water
11. Sodium hydroxide
12. Oxygen
13. Nitrogen
14. Sulfur dioxide

2.2 Equipment

1. Photochemical reactor with 16 lamps (UVC, 35 watt, 253.7 nm)
2. Thermo Nicolet, Nexus 670, Fourier Transform Infrared Spectrometer (FT-IR)
3. Agilent[®] 7890, Gas Chromatography-Mass Spectrometry, Time of Flight (GC-TOF)
4. Shimadzu Scientific Instrument, High performance liquid chromatography with UV detector (HPLC-UV)
5. BrukerDaltonics, Micromass Q-TOF Mass Spectrometer (ESI-MS)
6. BuchiRotavapor[®]R-III, Rotary Evaporator
7. Ozone generator
8. Liquid Extractor (solvents lighter than water)
9. Separatory funnel

2.3 Methodology

2.3.1 Analysis of Methyl Ester and Alpha Methyl Ester Sulfonate

The main functional groups and compositions of methyl ester and commercial α -MES were identified by using a Fourier transform infrared spectrometer (FT-IR), a gas chromatography-mass spectrometer (GC-MS), and Electrospray Ionization Mass Spectrometer (ESI-MS).

2.3.2 MES Synthesis

To synthesize Φ -MES, 200 mL of methyl ester (density $\approx 0.86 \text{ g/cm}^3$) was added into a photochemical reactor as shown in Figure 2.1, which consisted of 16 lamps at the wavelength of 253.7 nm. All experiments were performed in a batch reactor at 40 °C in anhydrous medium. After that, SO_2 and O_2 were flowed into a reactor continuously for certain time. 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. Procedure flow diagrams of synthesis, separation, and purification steps are shown in Figure 2.2

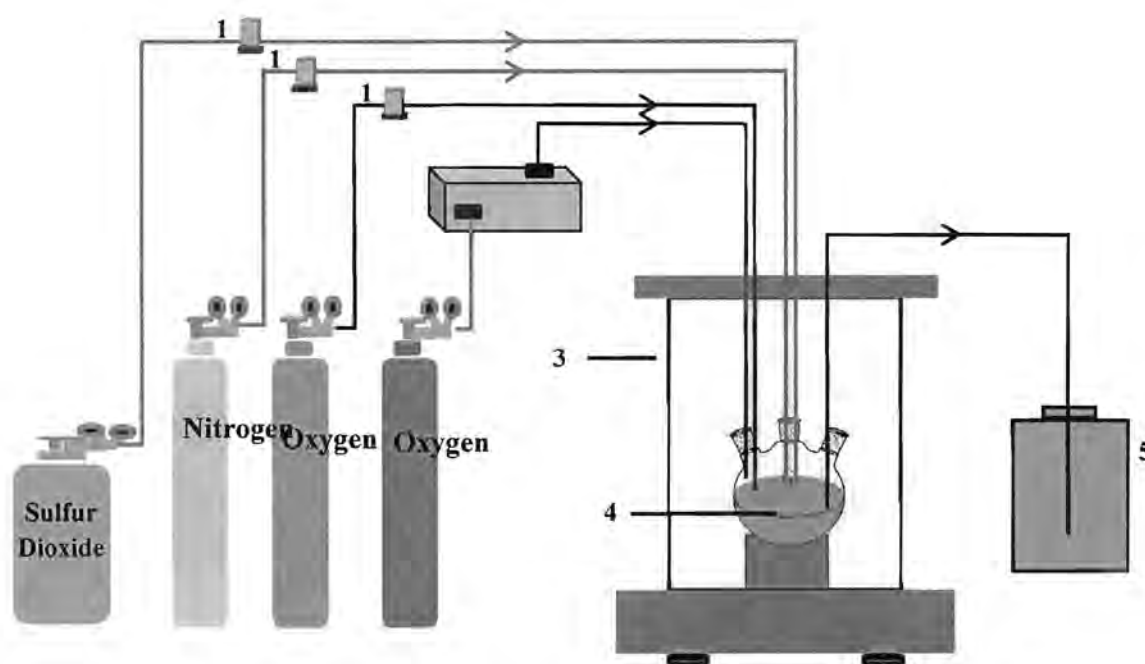


Figure 2.1 Schematic of experimental set-up: 1 = Flow meter, 2 = Ozone generator, 3 = 16 UVC lamps (253.7 nm), 4 = Reactor 5 = Water container.

2.3.3 Separation Technique

In this step, undesired products were separated from reactor outlet by liquid extraction techniques. Reactor outlet was mixed with hot water in a separatory funnel. Water (150 ml) was heated to 70 °C before shaking with product outlet. Mixture solution was left over night in the oven set 60 °C. There were two phases in the funnel: an upper layer (or organic phase) and a lower layer (or aqueous phase). After the water phase was separated out, 150 ml of hot water was mixed again with the organic phase and left in the oven. All aqueous phase was then blended with 300 ml of methanol.

For the organic phase which contained 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 a small amount of water in methyl ester and the left unreacted methyl ester was weighed to calculate conversion.

For water-methanol solution, it contained methyl ester sulfonic acid, sulfuric acids, and a 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) as shown in Figure 2.3. 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 a rotary evaporator. Methanol was evaporated out by slightly reducing pressure from 280 to 160 mbar at 50°C for 2 h.

2.3.4 Purification Technique

To acquire the MES product, n-butanol was used as a solvent to extract desirable products from the water phase. In this step, 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. Finally, the acid solution was neutralized with a 30 %w/w sodium hydroxide solution until pH was equal to 7.

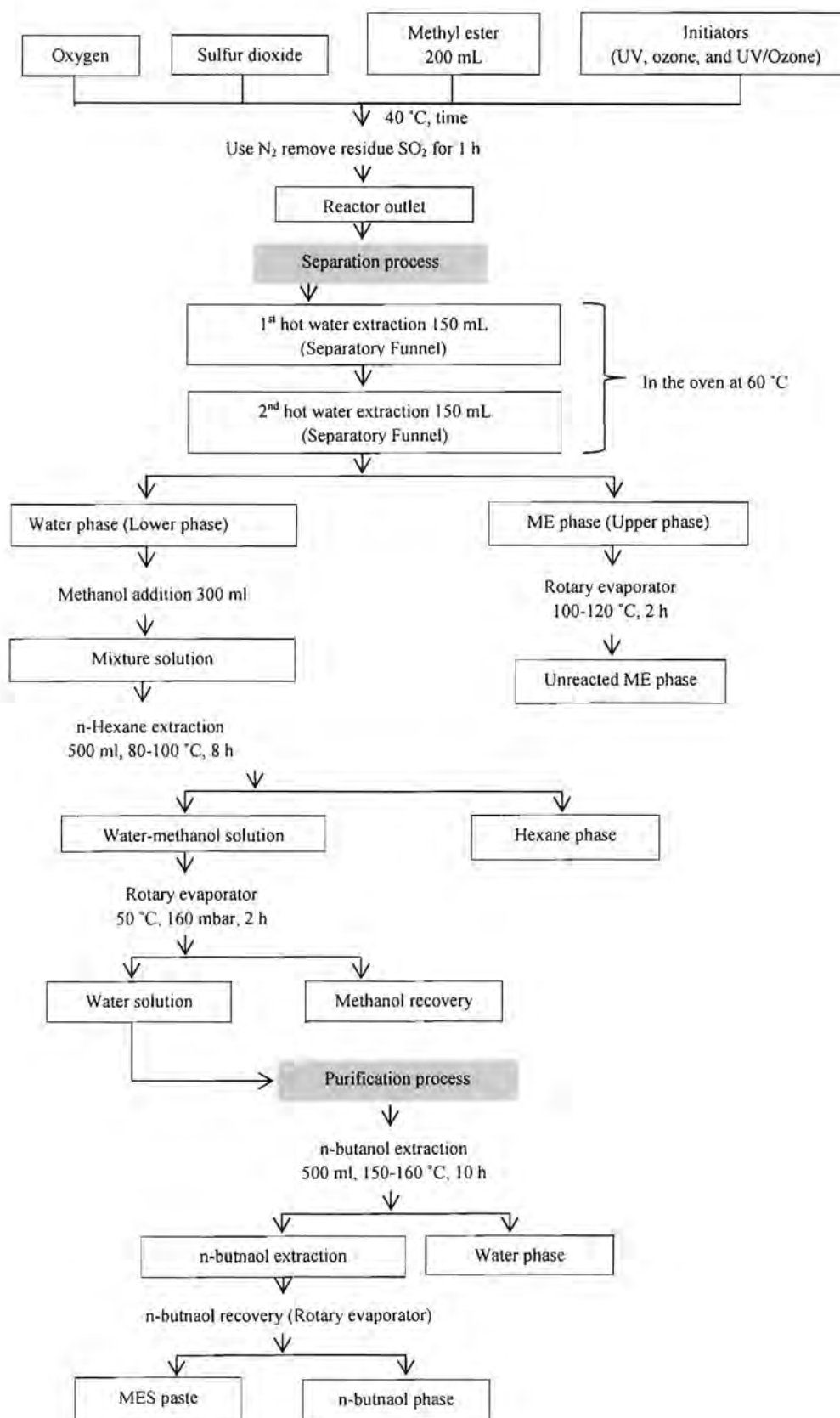


Figure 2.2 Synthesis, separation, and purification procedure flow diagrams.

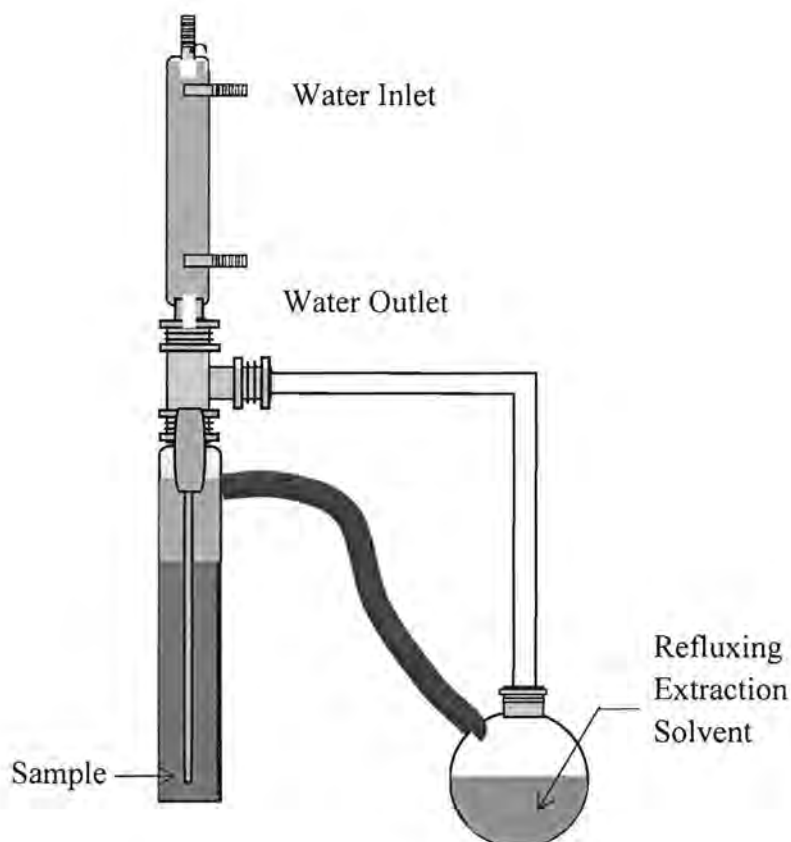


Figure 2.3 Schematic of liquid-liquid extractor for solvents lighter than water.

2.3.5 Product Analysis

2.3.5.1 *Conversion Calculation*

Conversion calculation was based on mass balance of methyl ester, which are the amount of starting methyl ester (200 ml) minus the recovered unreacted methyl ester and divided by the starting amount of methyl ester.

2.3.5.2 *Fourier Transform Infrared Spectroscopy (FT-IR)*

Fourier Transform Infrared Spectroscopy (FT-IR) was performed to confirm the presence of sulfonic acid 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 $4,000\text{--}650\text{ cm}^{-1}$. A ZnSe disc was used as a background material of a liquid sample.

2.3.5.3 *Gas Chromatography-Mass Spectrometry (GC-MS)*

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 and unreacted methyl ester. Samples were injected to the GC-MS after dilution with

carbon disulfide (CS₂) at a ratio of 1:100. 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, final temperature of 280 °C, held for 10 minutes, and split ratio at 1:20.

2.3.5.4 High Performance Liquid Chromatography (HPLC-UV)

In order to calculate a ratio between mono- and disulfonates, aqueous solutions were analyzed by using a high performance liquid chromatography (HPLC). HPLC consisted of a pump (LC-20AD, Shimadzu Scientific Instrument), a column oven (CTO-10AS VP, Shimadzu Scientific Instrument), and a UV detector (SPD-20A, Shimadzu Scientific Instrument). A HPLC column was Inertsil[®]ODS-3 (Octadecyl column; length = 250 mm; diameter = 4.6 mm; particle sizes = 5µm). Propan-2-ol and methanol at the ratio of 20:80 was used as a mobile phase to perform the chromatography separation at the wavelength of 220 nm and at temperature of 30 °C.

2.3.5.5 Electrospray Ionization Mass Spectrometry (ESI-MS)

Samples were analyzed by direct infusion ESI at the flow rate of 180 µL/h. ESI-MS fingerprints were obtained in the negative ion modes in a Q-TOF mass spectrometer (microOTOP II, BrukerDaltonics). Typical ESI-MS conditions were set as follows: 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 1000. Sodium formate, which was prepared by 40 µL of formic acid, 10 mL of isopropyl alcohol, and 10 mL of sodium hydroxide (1 M), was used as a standard. All samples were diluted to 10 µL/1 mL of acetonitrile.

CHAPTER III

RESULTS AND DISCUSSION

In this chapter, the methyl ester and alpha methyl ester sulfonate characterization results are discussed in Section 3.1. The influences of the different reactant and initiator systems, and reaction time of the suitable system are analyzed and discussed in Sections 3.2 and 3.3, respectively. The reaction was performed in a photochemical reactor consisting of 16 lamps (253.7 nm) at 40 °C under atmospheric pressure.

3.1 Characterization of Palm Oil Methyl Ester and Alpha Methyl Ester Sulfonates C16 and 18

This section discusses about the characterization of methyl ester (ME) and alpha methyl ester sulfonate C16 and 18 (α -MES C16 and C18) by using several characterization techniques. Functional groups of samples were analyzed by Fourier Transform Infrared Spectroscopy (FT-IR). The carbon distribution of methyl ester was determined by Gas Chromatography-Mass spectrometry (GC-MS). The ions of m/z in negative mode of α -MES were analyzed by Electrospray Ionization Mass Spectrometry (ESI-MS).

3.1.1 Characterization of Palm Oil Methyl Ester

The Infrared spectrum of palm oil methyl ester was investigated. IR spectrum is plotted in Figure 3.1. The IR spectrum shows the typical frequencies of linear alkane and carbonyl groups. As the palm oil methyl ester is mainly monoalkyl ester, the high intensity of -C-O and -C=O band of ester appears at 1,170 and 1,742 cm^{-1} , respectively. Moreover, -CH₂- symmetric and asymmetric stretching frequencies of linear alkane show two peak ranging from 2,852 to 2,929 cm^{-1} , while -CH₂- bending frequency appears at 1,460 cm^{-1} (Imahara *et al.*, 2008).

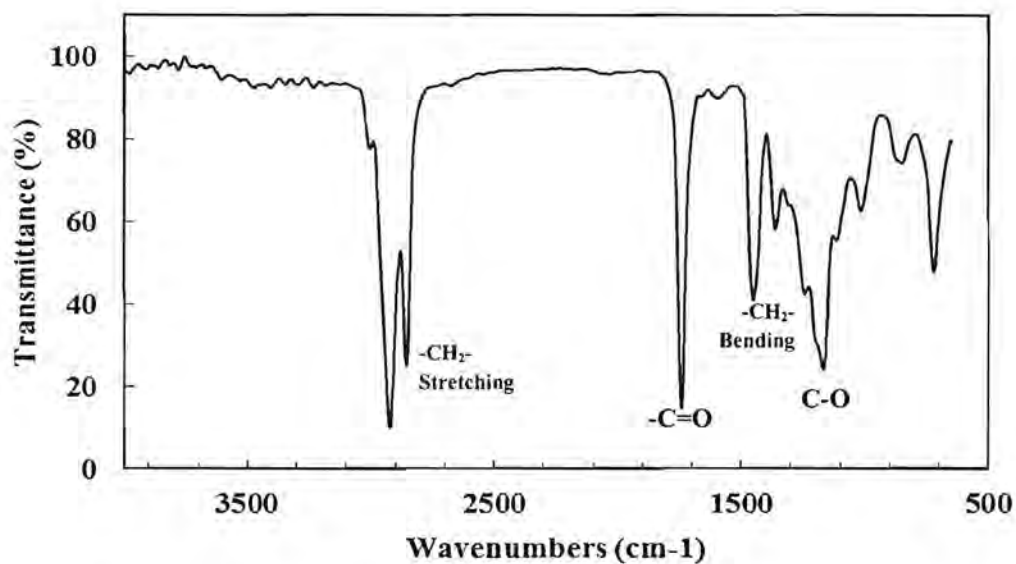


Figure 3.1 Infrared spectrum of palm oil methyl ester (ME).

Gas chromatographic-mass spectrometry (GC-MS) was used to find the carbon distribution of palm oil methyl ester as shown in Figure 3.2. The distribution and composition of each component are concluded in Table 3.1. Methyl ester used in this experiment consists of 36.0 % C16 and 64.0 % C18.

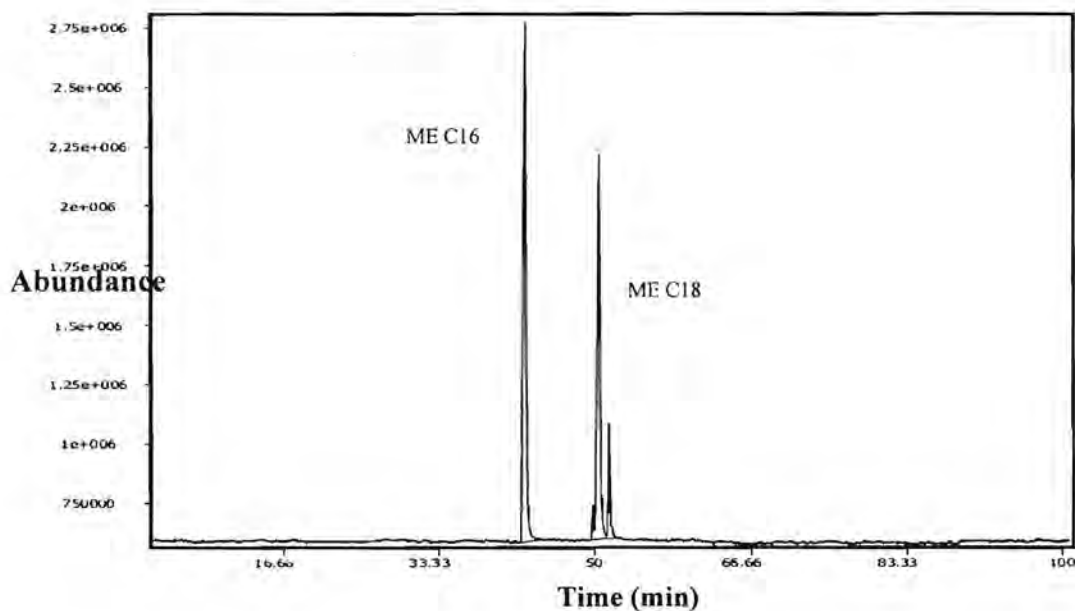
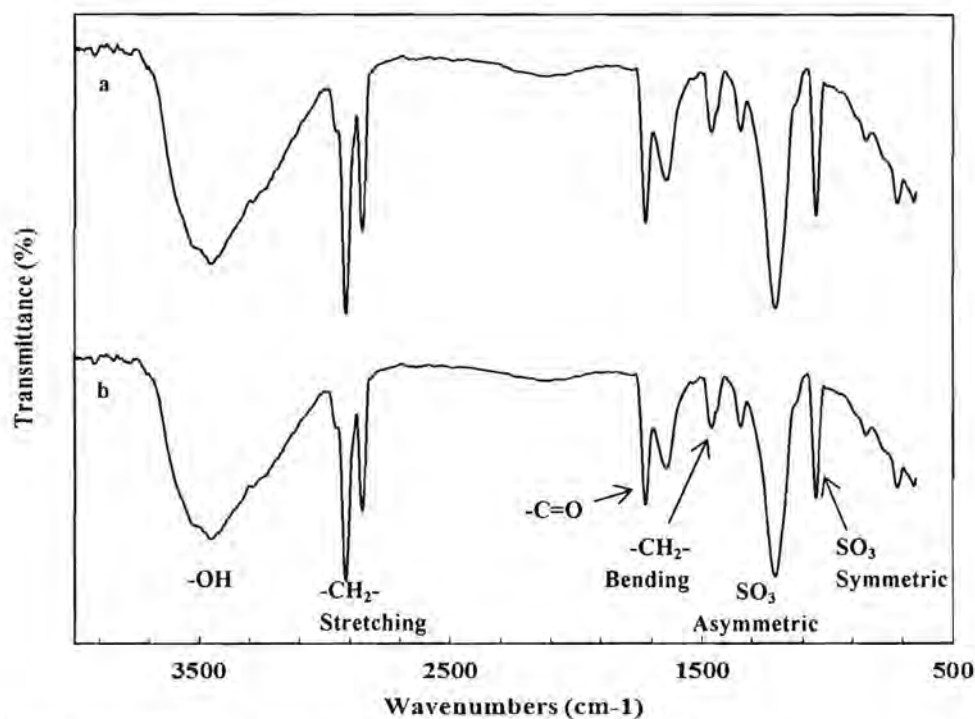


Figure 3.2 Total ion chromatogram (TIC) of palm oil methyl ester.

Table 3.1 Fatty acid composition in palm oil methyl ester

Fatty acid	Formula	Molecular weight	Area (%mol)	
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

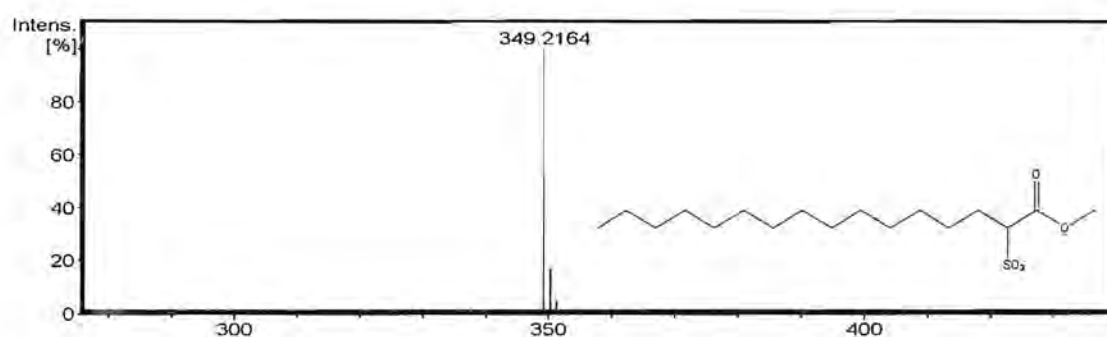
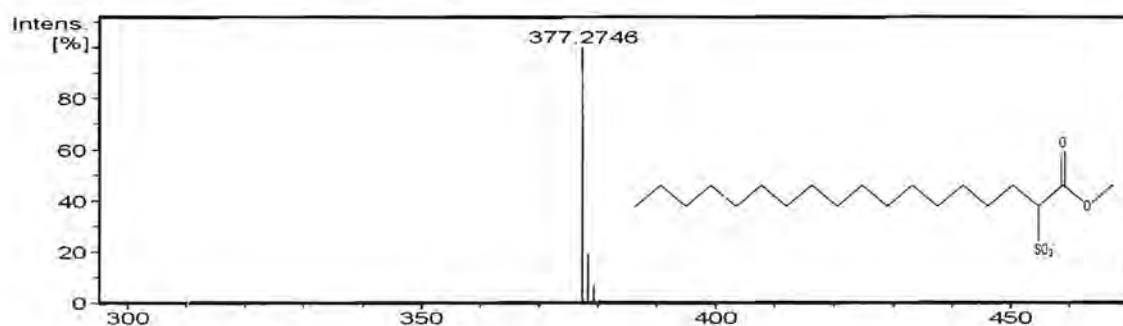
3.1.2 Characterization of Alpha Methyl Ester Sulfonates C16 and 18

**Figure 3.3** Infrared spectra of (a) α -MES C16 and (b) α -MES C18.

The IR spectra of α -MES C16 and 18 are shown in Figure 3.3 and concluded in Table 4.2. The broad IR peak of hydroxyl group results from water presenting at $3,429\text{ cm}^{-1}$. Strong peaks around $2,850\text{--}2,930\text{ cm}^{-1}$ corresponds to CH_2 - symmetric and asymmetric stretching frequency. The bands at $1,046$ and $1,210\text{ cm}^{-1}$ indicate the presence of sulfonate symmetric and asymmetric stretching frequency, respectively (Cohen *et al.*, 1998, Elraies *et al.*, 2010). The ESI-MS fingerprints of α -MES C16 and 18 observed in the negative mode fingerprints are shown in Figure 3.4 and 3.5, respectively. For the fingerprints of α -MES C16, the ion of m/z 349 is obviously appeared, whereas α -MES C18 shows the ions of m/z 377 which is the most intense in the sample.

Table 3.2 The main IR peaks and the corresponding functional groups of α -MES C16 and 18

Peak (cm^{-1})	Functional groups
3,429	OH stretching frequency
1,725	-C=O stretching frequency of ester
2,850-2,930	CH ₂ - symmetric and asymmetric stretching frequency
1,467	CH ₂ - bending frequency
1,210	SO ₃ asymmetric stretching frequency
1,046	SO ₃ symmetric stretching frequency in R-SO ₃

**Figure 3.4** ESI-MS fingerprints of α -MES C16.**Figure 3.5** ESI-MS fingerprints of α -MES C18.

3.2 Effect of Different Reactants and Initiators

This section discusses about the investigation of the presence of different reactants and initiators in order to convert methyl ester to methyl ester sulfonate. There are four systems as follows: UV/O₂, O₃/O₂, UV/O₃/O₂, and UV/O₃. In this case, flow rate of SO₂ and O₂ were fixed at 100 ml/min, whereas O₃ was at 0.5 l/min (Table 3.3). The reaction was performed at 40 °C under atmospheric pressure for 4 h.

Table 3.3 Experimental design for studying the effect of different reactants and initiators

System	Experimental Set				Reaction time (h)	Abbreviation
	Initiator		Reactant			
	UV	O ₃ (l/min)	SO ₂ (ml/min)	O ₂ (ml/min)		
1	YES	0	100	100	4	UV/O ₂
2	NO	0.5	100	100	4	O ₃ /O ₂
3	YES	0.5	100	100	4	UV/O ₃ /O ₂
4	YES	0.5	100	0	4	UV/O ₃

3.2.1 Conversion Calculation

After an upper layer in a separatory funnel was transferred to a rotary evaporator, the small amount of water was separated out, and then unreacted methyl ester was weighed to calculate conversion. Conversion percentages are reported in Table 4.4. The first and second systems were studied so as to investigate the effect of different initiators. UV light and O₃ are individually used as an initiator for the first and second systems, respectively. The conversion of these two systems is 7.5 %w/w and 6.9 %w/w, which are not significantly different. However, when UV light and O₃ are used together in the third system, conversion increases up to approximately 13.5 %w/w, which is improved by 6.0 %w/w and 6.6 %w/w for the first and second systems, respectively. In addition, the effect of the presence of O₂ was studied in the third and fourth systems. It can be noticed that when O₂ is not fed into the system, conversion dramatically drops from 13.5 %w/w to 3.6 %w/w. This can be concluded that oxygen plays an important role in generating sulfonate groups. According to Eq. 2.14, O₂ collides with RSO₂[·] in order to form RSO₂OO[·], which further react and become RSO₃Has a desired product (Ramakrishnan, 2006). Therefore, O₂ is one of the main factors for synthesizing MES.

Table 3.4 Conversion of each system

Systems	Conversion (%w/w)
1 UV/O ₂	7.5
2 O ₃ /O ₂	6.9
3 UV/O ₃ /O ₂	13.5
4 UV/O ₃	3.6

3.2.2 Characterization of Products

3.2.2.1 Fourier Transform Infrared Spectroscopy

When reaction was done, product outlets were mixed with hot water in order to separate desired products into a water phase and left only unreacted methyl ester in an upper phase. Unreacted methyl ester of all systems was investigated by FT-IR in order to compare with palm oil methyl ester.

From Figure 3.6, the spectra of unreacted methyl ester from four systems (b - e) show mostly the same functional groups as palm oil methyl ester. However, it can be clearly seen that there are two separated peaks at $\approx 1,700 - 1,725 \text{ cm}^{-1}$ in unreacted methyl ester. The first peak at $\approx 1,725 \text{ cm}^{-1}$ refers to a carbonyl group of ester, whereas the other at $\approx 1,710 \text{ cm}^{-1}$ represents a carbonyl of saturated carboxylic acids (Amornsit *et al.*, 1991). In addition, the low and broad band around $2,500 - 3,500 \text{ cm}^{-1}$, which overlap with the C-H region, represents O-H single bond stretching band of carboxylic acid (Soderberg, 2014). The cause of carboxylic acid may be due to methyl ester groups are hydrolyzed by water to become carboxylic groups. Nevertheless, 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. 3.1 (Prateepchaikul *et al.*, 2007). As a result, unreacted methyl ester can be reused.



Regarding the aqueous phase, after separation and purification steps, liquid samples were neutralized with 30 %w/w NaOH and were tested by FT-IR. Figure 3.7 shows the IR spectra of α -MES C18 compared to those of synthesized MES from four systems. It is found that all synthesized MES samples show the same frequencies as α -MES C18, which are $3,456 \text{ cm}^{-1}$ (OH stretching), $2,859\text{-}2,928 \text{ cm}^{-1}$ ($-\text{CH}_2-$ symmetric and asymmetric stretching), $1,742 \text{ cm}^{-1}$ ($-\text{C}=\text{O}$ stretching of ester), $1,457 \text{ cm}^{-1}$ ($-\text{CH}_2-$ bending), $1,200 \text{ cm}^{-1}$ (SO_3 asymmetric stretching), and $1,040 \text{ cm}^{-1}$ (SO_3 symmetric stretching in R-SO_3). This can be used to confirm that MES products are successfully sulfonated via the sulfoxidation reaction.

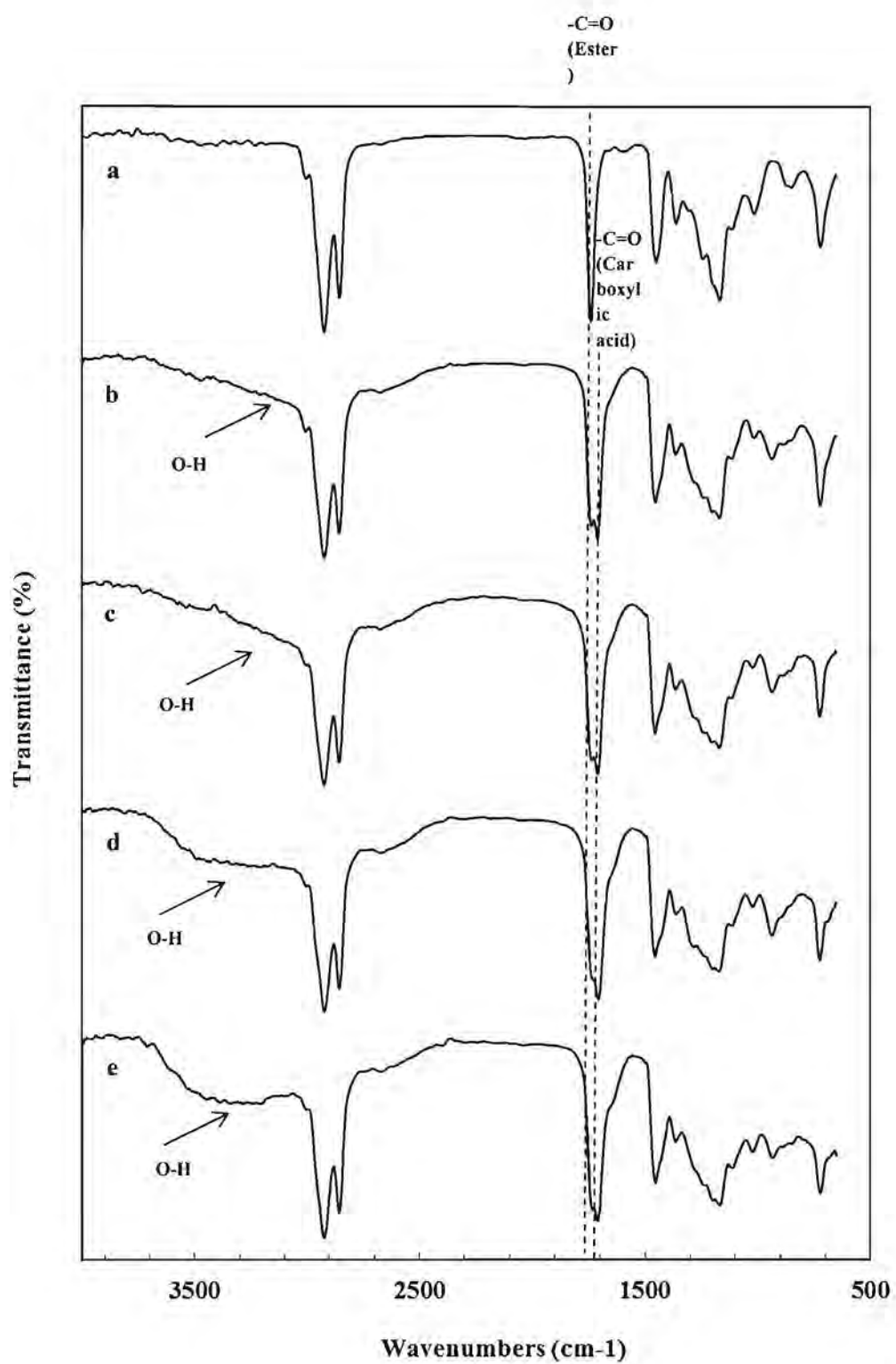


Figure 3.6 Infrared spectra of a) ME compared to unreacted ME from different systems b) UV/O₂ c) O₃/O₂ d) UV/O₃/O₂ e) UV/O₃.

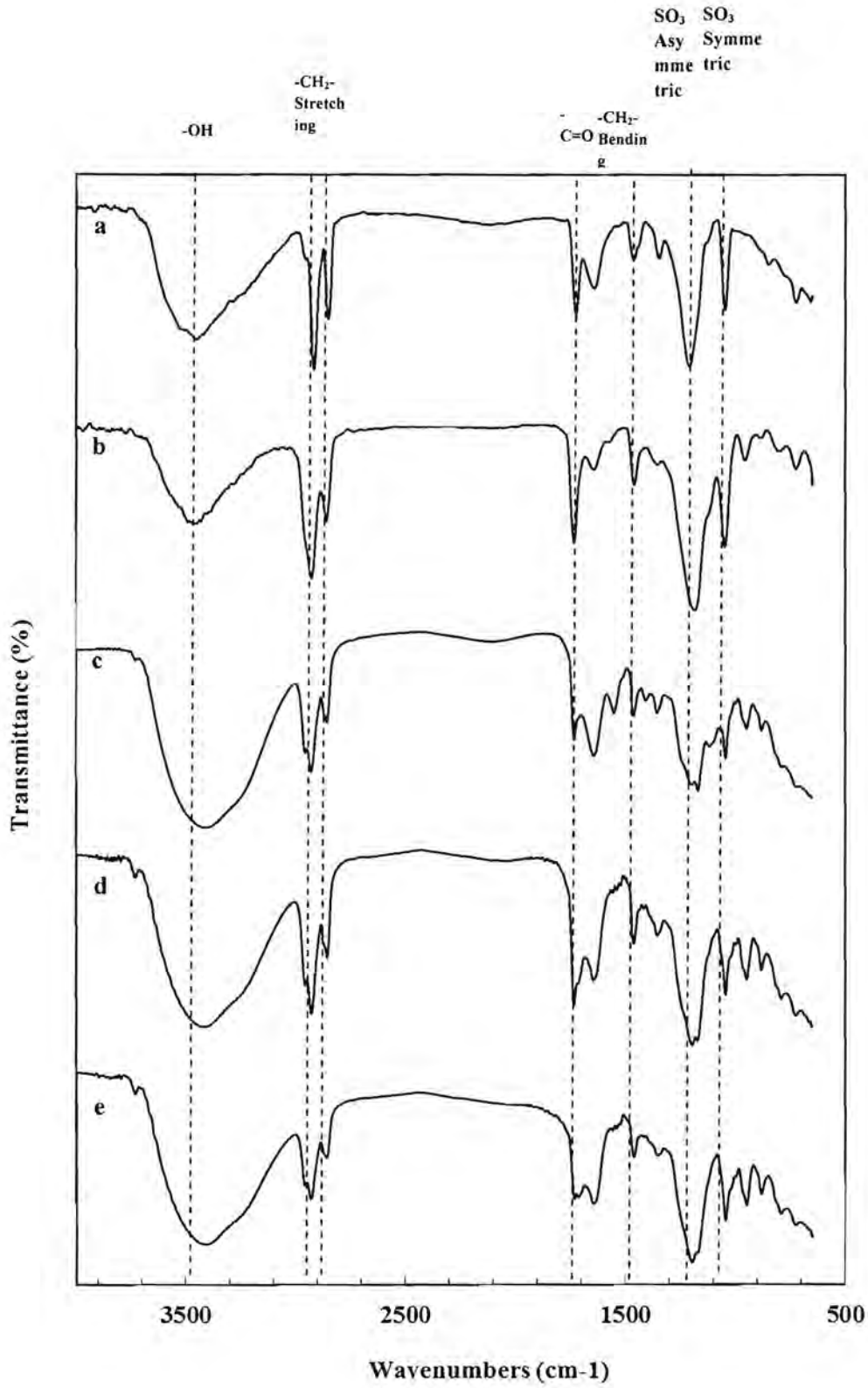


Figure 3.7 Infrared spectrum of a) alpha MES C18 compared to neutralized MES from different systems b) UV/O₂ c) O₃/O₂ d) UV/O₃/O₂ e) UV/O₃.

3.2.2.2 Gas Chromatography-Mass Spectrometry

GC-MS was used to carry out the relative sulfonatability of different homologs (C16 and C18). As mention before, starting methyl ester consists of C16 and C18. When methyl ester was sulfoxidized, the composition of unreacted methyl ester was changed as shown in Table 3.5. The results show that a small amount of C12 and C14 methyl ester is occurred after the reaction is finished. The cause of a small amount of shorter carbon chains may come from two reasons. The first reason is due to ozonolysis at double bonds of methyl ester (Soriano Jr *et al.*, 2003). The second reason is photolysis, which is a chemical process that molecule are broken down into smaller units through the absorption of light. In this case, UV carries enough energy to break carbon-carbon bonds since UVC at wavelength of 253.7 nm contains about 4.9 eV (Havinga, 1991), which is higher than the energy of a carbon-carbon bond (3.6 eV) (Luo, 2002). As a consequence, UV can decompose this single carbon-carbon bond to become shorter carbon chain. In addition, it can be seen that the relative content of C18 starting ME is less than that of C18 unreacted ME in all systems (1 - 4). On the other hand, the relative content of C16 unreacted ME for all systems increases compared to that of C16 starting ME. It means that the sulfonatability of the C18 ME is higher than that of C16 ME. This is because C18 ME have a longer carbon chain which provides more probability for gaseous reactants (SO_2 , O_2 , and O_3) to collide with carbon chain (Cohen *et al.*, 2006).

Table 3.5 Sulfonatability of methyl ester and unreacted methyl ester

Carbon Chain Length of Methyl ester	Starting Methyl Ester (% mol)	Unreacted Methyl ester of each System (% mol)			
		1) UV/O ₂	2) O ₃ /O ₂	3) UV/O ₃ /O ₂	4) UV/O ₃
C12	0.0	0.5	1.1	1.2	3.3
C14	0.0	4.6	7.0	8.0	11.8
C16	36.0	46.8	45.1	43.0	48.7
C18	64.0	48.1	46.8	47.8	36.1

3.2.2.3 Electro spray Ionization Mass Spectrometry

MES products were analyzed by direct infusion negative ion mode electro spray ionization mass spectrometry (ESI-MS). All fingerprints (Figure 3.9 (a – d)) display ions of m/z 361, 379, 393, 443, 459, 473, and 491 with various intensities. The ions of m/z 361, 379, and 393 represent monosulfonates of C18, whereas 443, 459, 473, and 491 refer to disulfonates of C18. According to the sufoxidation mechanism in Eq 2.11-2.10, there are many intermediates happening during the reaction, such as RSO_2^\cdot , RSO_3^\cdot , and RSO_4^\cdot . It can be noted that the three large peaks at 361, 379, and 393 mass units correspond to monosulfonates in the forms of RSO_2H , RSO_3H , and RSO_4H , respectively. Furthermore, the four peaks having the masses 443, 459, 473, and 491 represent disulfonates. The first peak at 443 refers to C18 having $-\text{SO}_2\text{H}$ and $-\text{SO}_3\text{H}$. The second peak at 459 refers to C18 having two groups of $-\text{SO}_3\text{H}$. The third peak at 473 refers to C18 having $-\text{SO}_3\text{H}$ and $-\text{SO}_4\text{H}$. Finally, the mass at 491 refers to C18 having two groups of $-\text{SO}_4\text{H}$. Figure 3.8 shows the possible structure of mono- and disulfonates presenting in MES products. The height of peaks does not reflect the abundance of the different sulfonated species. Therefore, the ESI results only indicate that there are both mono- and disulfonates in MES products.

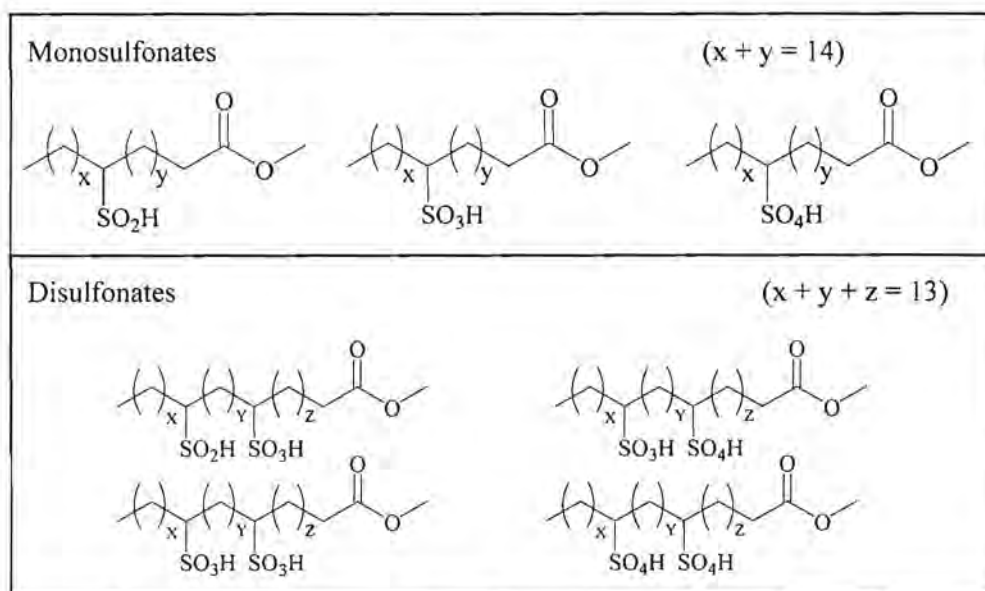


Figure 3.8 The possible structure of mono- and disulfonates in MES products.

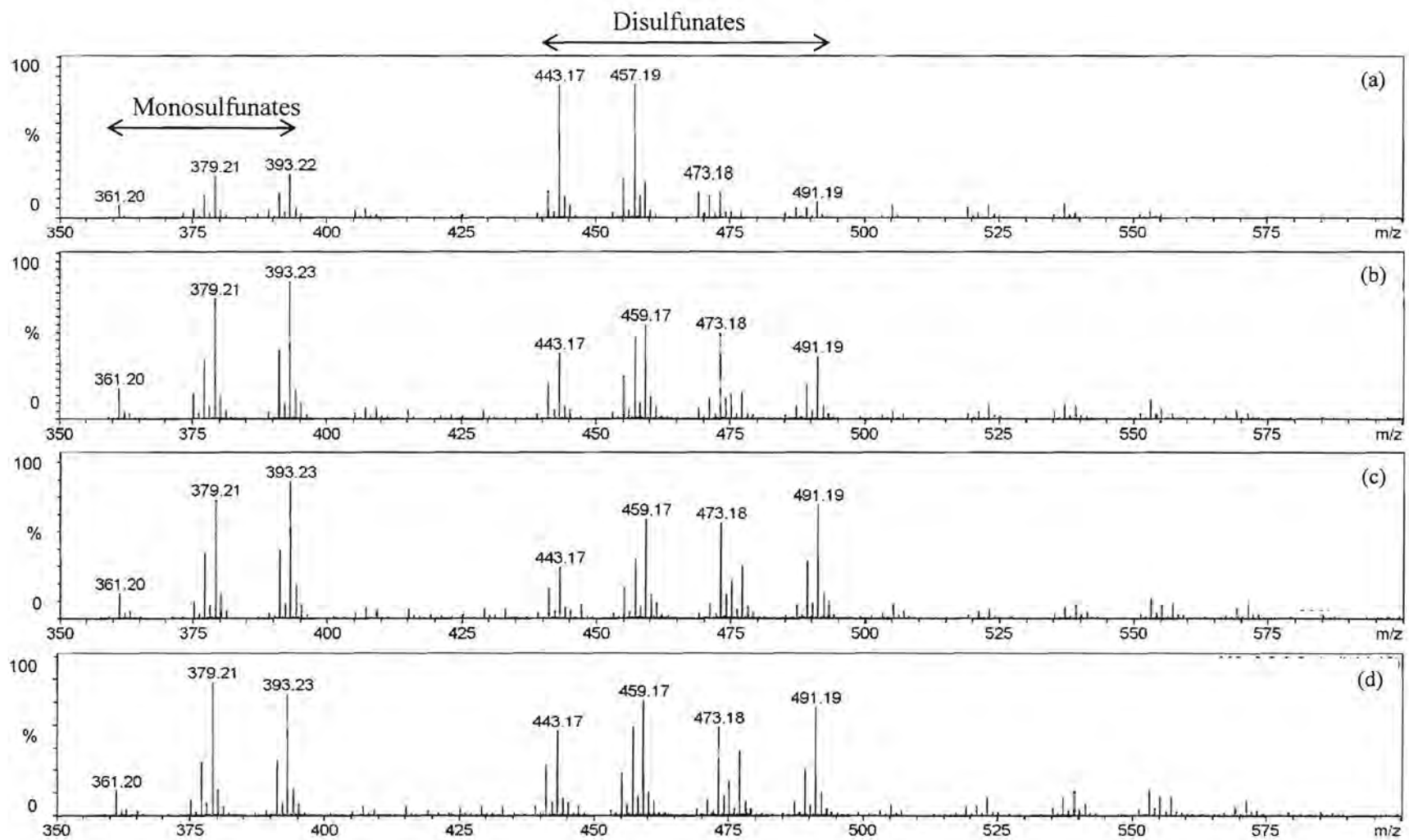


Figure 3.9 ESI-MS fingerprints in the negative ion mode of a) UV/O₂ b) O₃/O₂ c) UV/O₃/O₂ d) UV/O₃.

3.3 Effect of Reaction Time

This section discusses about the influence of increasing reactant reaction time. According to section 4.2, when both UV and O₃ were used as an initiator, it provides the highest conversion compared to using individual UV or O₃. Thus, the UV/O₃/O₂ system was used to study the effect of reaction time. Reaction time was 1, 2, 4, and 6 h. The flow rates of SO₂ and O₂ were fixed at 100 ml/min, whereas that of O₃ was at 0.5 l/min. The reaction was performed at 40 °C for 4 h. The experiment design and conditions for studying the effect of reaction is shown in Table 4.6.

Table 3.6 Experimental design for studying the effect of reaction time

System	Experimental Set				Reaction time (h)	Abbreviation
	Initiator		Reactant			
	UV	O ₃ (l/min)	SO ₂ (ml/min)	O ₂ (ml/min)		
5	YES	0.5	100	100	1	1UV/O ₃ /O ₂
6	YES	0.5	100	100	2	2UV/O ₃ /O ₂
7	YES	0.5	100	100	4	4UV/O ₃ /O ₂
8	YES	0.5	100	100	6	6UV/O ₃ /O ₂

3.3.1 Conversion Calculation

Conversion percentages and the total products are calculated and reported in Table 4.7. As expected, conversion and the weight of total products increase with reaction time. Conversion is approximately 4.7, 10.2, 13.5, and 14.7 %wt for 1, 2, 4, and 6 h, respectively. In addition, the total MES products for 1, 2, 4, and 6 h are about 5.9, 13.0, 17.5, and 20.8 g, respectively, when using 172 g (200 ml) of methyl ester in each batch.

Table 3.7 Conversion and weight of total products at 1, 2, 4, and 6 h

System	Reaction Time(h)	Conversion (%w/w)	Total products (g)
1UV/O ₃ /O ₂	1	4.7	5.9
2UV/O ₃ /O ₂	2	10.2	13.0
4UV/O ₃ /O ₂	4	13.5	17.5
6UV/O ₃ /O ₂	6	14.7	20.8

3.3.2 Selectivity Calculation

For selectivity calculation, HPLC-UV was used to calculate peak areas of mono- and disulfonates. In this study, selectivity is the ratio of monosulfonates to disulfonates. Figure 3.10 shows chromatogram of α -MES C18, which presents one intense peak at 5.4 min. HPLC chromatograms of the UV/O₃/O₂ system at different reaction time are shown in Figure 3.10 - 3.14. ESI-MS fingerprints (Figure 3.15 and 3.16) are used to identify that the first peak at \square 4.7 min represents disulfonates and the second peak at \square 5.7 - 6.1 min refers to monosulfonates. It is found that the percent composition of monosulfonates increases, while percent composition of disulfonates increases. In other words, the ratios of monosulfonates to disulfonates slightly decline with the increase of reaction time as reported in Table 3.8 and plotted in Figure 3.17. The selectivity of each system is roughly 11.7, 10.9, 7.9, and 5.3 for 1, 2, 4, and 6 h, respectively.

Table 3.8 Percent composition of sulfonates and selectivity at 1, 2, 4, and 6 h

System	Reaction Time (h)	% Di sulfonates	% Mono sulfonates	Selectivity
1UV/O ₃ /O ₂	1	7.9	92.1	11.7
2UV/O ₃ /O ₂	2	8.4	91.6	10.9
4UV/O ₃ /O ₂	4	11.3	88.7	7.9
6UV/O ₃ /O ₂	6	16.0	84.0	5.3

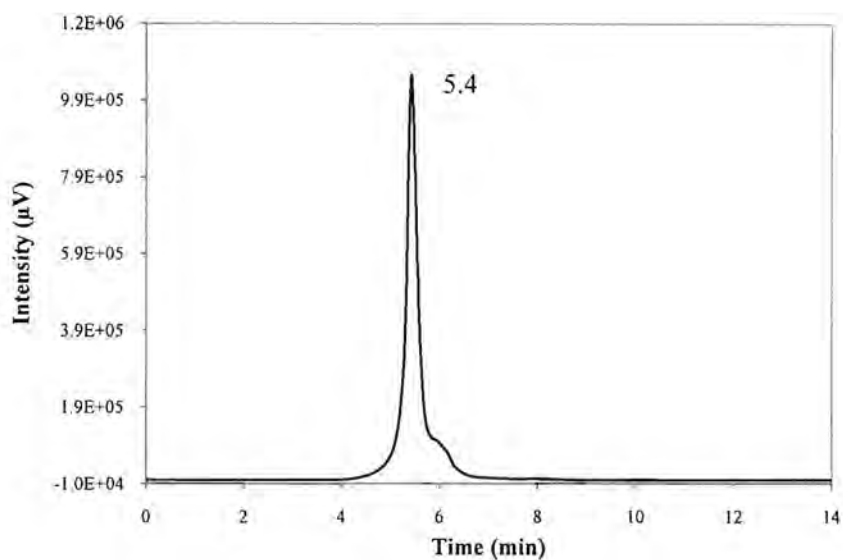


Figure 3.10 Liquid Chromatogram of α -MES C18 solution.

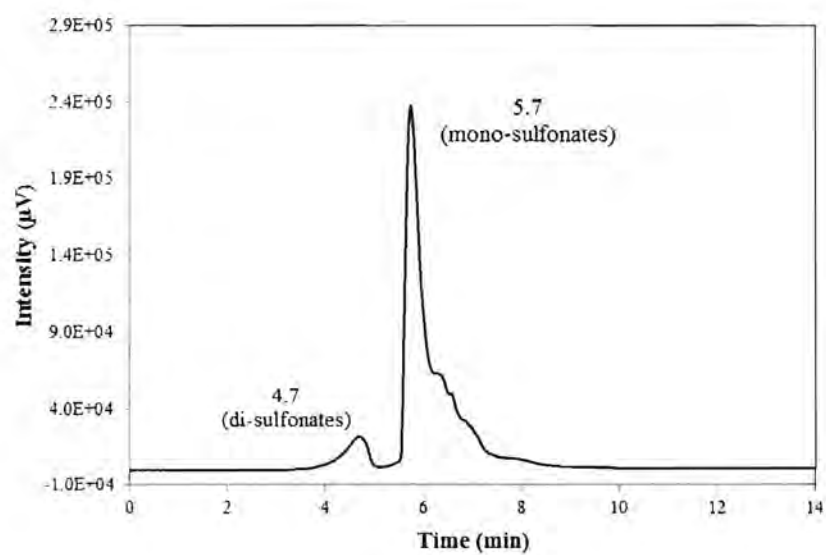


Figure 3.11 Liquid Chromatogram of MES solution of 1UV/O₃/O₂ at 30 °C.

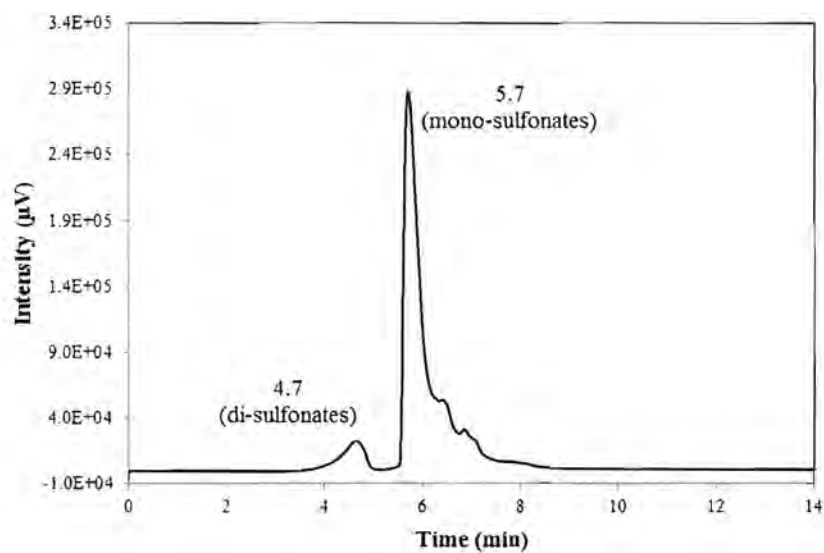


Figure 3.12 Liquid Chromatogram of MES solution of 2UV/O₃/O₂ at 30 °C.

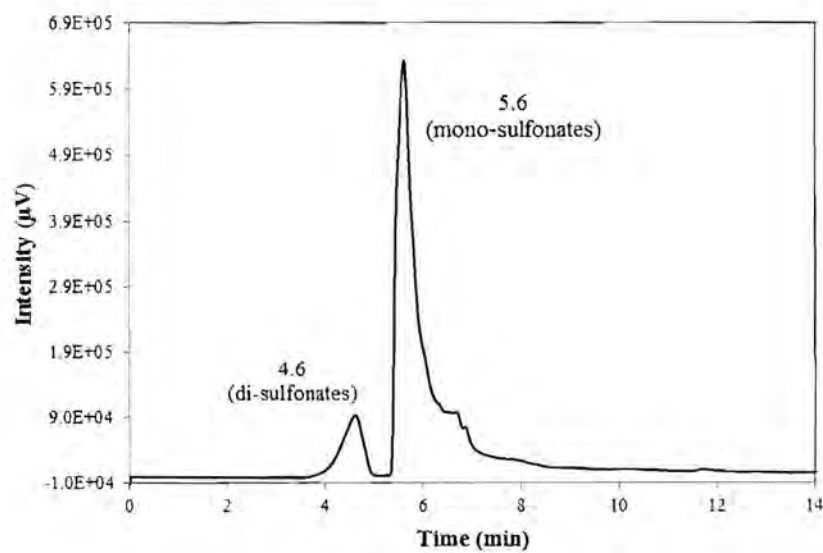


Figure 3.13 Liquid Chromatogram of MES solution of 4UV/O₃/O₂ at 30 °C.

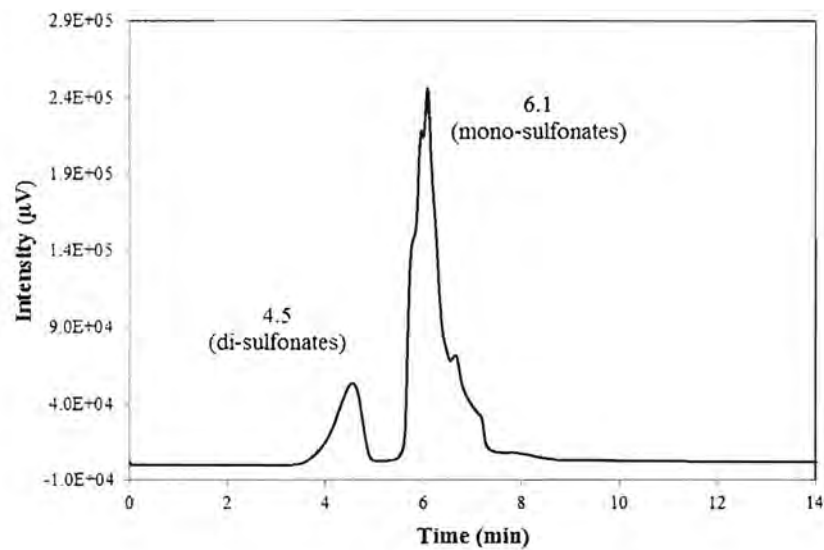


Figure 3.14 Liquid Chromatogram of MES solution of 6UV/O₃/O₂ at 30 °C.

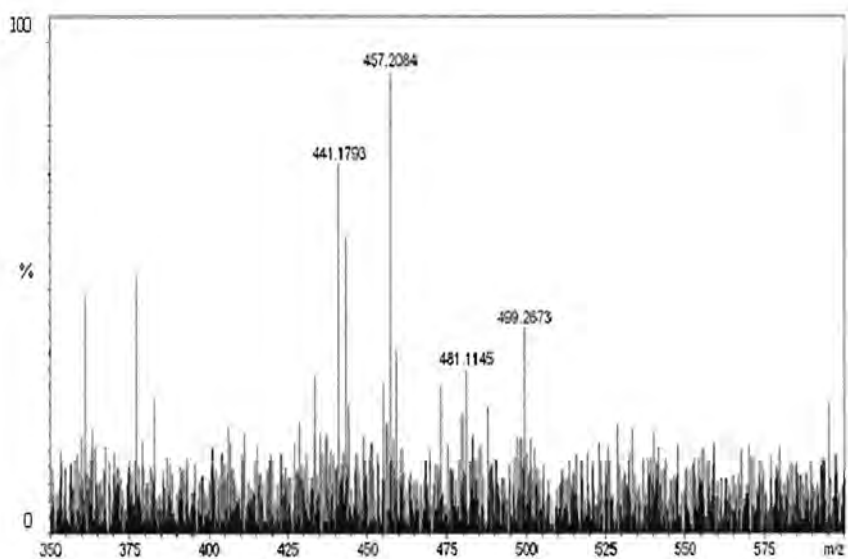


Figure 3.15 ESI-MS fingerprints of 4UV/O₃/O₂ at □ 4.7 min.

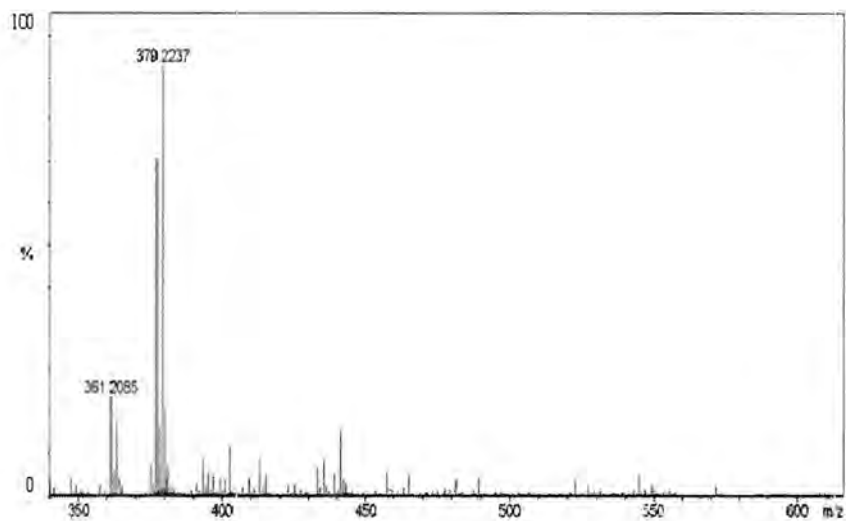


Figure 3.16 ESI-MS fingerprints of 4UV/O₃/O₂ at □ 5.7 min.

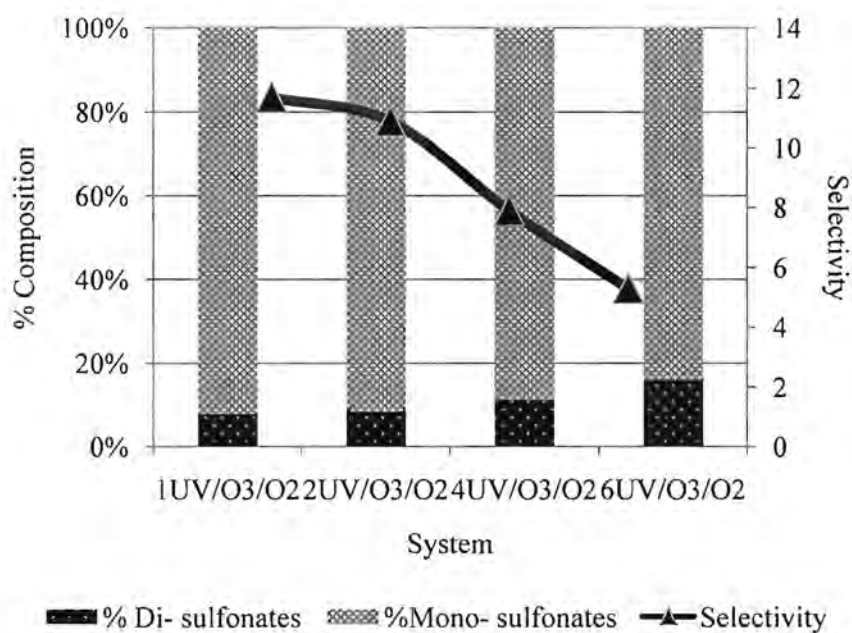


Figure 3.17 Percent composition of mono- and disulfonates and selectivity at different reaction time.

CHAPTER IV

CONCLUSIONS

MES was successfully synthesized by using UV and O₃ as an initiator, and O₂ and SO₂ as a reactant. The reaction was carried out at 40 °C in a photochemical reactor under atmospheric pressure. After the synthesis step, product outlet was separated and purified by using liquid-liquid extraction techniques, such as a separatory funnel and a liquid-liquid extractor for solvents lighter than water. In this work, we have investigated two effects on synthesizing MES.

For the first effect, the influence of different reactants and initiators was studied. FT-IR confirmed the presence of sulfonate groups and ESI-MS showed that there were both mono- and disulfonates of C18 in MES solution. Conversion was calculated based on mass balance of methyl ester. Conversion was increased as follows: UV/O₃/O₂ > UV/O₂ > O₃/O₂ > UV/O₃. The highest conversion was □ 13.5 %w/w when the combination of UV, O₃, and O₂ was used as an initiator and a reactant. In addition, it was also found that O₂ is one of the important reactant, which is required for the MES synthesis.

For the second part, the UV/O₃/O₂ system was chosen to study the effect of reaction time. When reaction time increased, conversion also increased and it was up to 14.7 %w/w for 6 h. Moreover, ratio of mono- to disulfonates decreased with reaction time.

CHAPTER V

REFERENCES

- Amornsit, M. and Petsom, A. (1991). Principles and Techniques of Instrumental Analysis. Bangkok: Rongpim Chonpim.
- Aparicio, J., MacArthur, B. W., Sheats, W. B., and Brooks, B. J. (2012). MES – Myths, Mysteries and Perspectives on Properties and Use. ICSD Shanghai, China.
- Bradley, H. W. (1950). U.S. Patent and Trademark Office. Washington, DC. 2,507,08.
- Cohen, L., Roberts, D. W., and Pratesi, C. (2010). Φ -Sulfo Fatty Methyl Ester Sulfonates (Φ -MES): A Novel Anionic Surfactant. CHEMICAL ENGINEERING, 21.
- Cohen, L., Soto, F., and Luna, M. S. (2001). Separation and extraction of Φ -methyl ester sulfoxylates: New features. Journal of Surfactants and Detergents, 4(1), 73-74.
- Cohen, L., Soto, F., and Luna, M. S. (2001). Sulfoxylated methyl esters as potential components of liquid formulations. Journal of Surfactants and Detergents, 4(2), 147-150.
- Cohen, L., Soto, F., Melgarejo, A., and Roberts, D. (2008). Performance of α -Sulfo Fatty Methyl Ester Sulfonate Versus Linear Alkylbenzene Sulfonate, Secondary Alkane Sulfonate and Φ -Sulfo Fatty Methyl Ester Sulfonate. Journal of Surfactants and Detergents, 11(3), 181-186.
- Cohen, L., Soto, F., Pratesi, C., and Faccetti, L. (2006). Sulfoxidation of fatty acid methyl esters: Conversion and selectivity. Journal of Surfactants and Detergents, 9(1), 47-50.
- Cohen, L., and Trujillo, F. (1998). Synthesis, characterization, and surface properties of sulfoxylated methyl esters. Journal of Surfactants and Detergents, 1(3), 335-341.

- Commission of the European Communities (2004). Report from the commission to the European Parliament and the Council Pursuant to Article 16 of Regulation (EC)No 648/2004 of the European Parliament and of the Council of 31 March 2004 on detergents, concerning anaerobic biodegradation.
- Denisov, E. T., and Afanas'ev, I. B. (2005). Oxidation of Polymers. Oxidation and Antioxidants in Organic Chemistry and Biology, CRC Press: 1-454.
- Elraies, K. A., Tan, I. M., Awang, M. and Saaid, I. (2010). The Synthesis and Performance of Sodium Methyl Ester Sulfonate for Enhanced Oil Recovery. Petroleum Science and Technology, 28(17), 1799-1806.
- Imahara, H., Minami, E., Hari, S. and Saka, S. (2008). Thermal stability of biodiesel in supercritical methanol. Fuel, 87(1), 1-6.
- Galimova, L. G., Komissarov, V. D., and Denisov, E. T. (1973). Kinetics and products of oxidation of cyclohexane by ozonized oxygen. Bulletin of the Academy of Sciences of the USSR, Division of chemical science, 22(2), 295-298.
- Ghazali, R. (2002). The effect of disalt on the biodegradability of methyl ester sulphonates (MES). Journal of Oil Palm, 14(1), 45-50.
- Ghazali, R., and Ahmad, S. (2004). Biodegradability and ecotoxicity of palm stearin-based methyl ester sulphonates. Journal of Oil Palm Research, 16(1), 39-44a.
- Gref, R. (1952). The mechanism of sulfoxidation. Justus Liebigs Ann. Chem., 578, 50-82.
- Guroi, M. D., and Vatisas, R. (1987). Oxidation of phenolic compounds by ozone and ozone + u.v. radiation: A comparative study. Water Research, 21(8), 895-900.
- Havinga, E. (1991). Photochemistry with UV light. leopoldshohe germany, DELTA UV GmbH: 1-28.
- Holmberg, K. (2003). Novel surfactants preparation, applications, and biodegradability. New York: Surfactant science series.

- Lim, W. (2004). Phase diagram of α -sulfonate methyl esters derived from palm stearin/alcohol/water systems. Journal of Surfactants and Detergents, 7(3), 263-270.
- Lim, W., and Ahmad, S. (2002). Dishwashing performance of mixed palm stearin sulfonated methyl esters and polyoxyethylene sorbitan esters. Journal of Surfactants and Detergents, 5(1), 33-38.
- Luo, Y. (2002). Tabulated BDEs of C-C bonds. Handbook of Bond Dissociation Energies in Organic Compounds, CRC Press.
- Martinez, D., Orozco, G., Rincon, S., and Gil, I. (2010). Simulation and pre-feasibility analysis of the production process of α -methyl ester sulfonates (α -MES). Bioresource Technology, 101(22), 8762-8771.
- Matthew, L. (2008). Handbook of Detergents, Part F: Surfactant Production. CRC Press.
- Nagayama, M., and Kawana, T. (1972). SULFOXIDATION OF PARAFFIN. U.S. Patent and Trademark Office. Washington, DC. 3,658,671.
- Norman, F., Brian, M., Sheats, W. B., Michael, S., and Sanjay, T. (2008). Handbook of Detergents, Part F: Production of Methyl Ester Sulfonates. CRC Press.
- Platz, C., and Schimmelschmidt, K. (1943). Sulfonic acids, German Patent 735096.
- Prateepchaikul, G., Allen, M. L., Leevijit, T. and Thaveesinsopha, K. (2007). Methyl ester production from high free fatty acid mixed crude palm oil. Songklanakarinn J. Sci. Technol, 29(6), 1551-1561.
- Ramakrishnan, A. (2006). Visible light induced catalytic sulfoxidation of alkanes. (Doctoral dissertation).
- Rosen, M. J. (2012). Surfactants and interfacial phenomena. New York: Wiley Inter-science.
- Soderberg, T. "Section 4.2: Infrared spectroscopy." ChemWiki 31 March 2014. <http://chemwiki.ucdavis.edu/Organic_Chemistry/Organic_Chemistry_With_a_Biological_Emphasis/Chapter_4%3A_Structure_Determination_I/Section_4.2%3A_Infrared_spectroscopy>

- Soriano Jr, N. U., Migo, V. P. and Matsumura, M. (2003). Functional group analysis during ozonation of sunflower oil methyl esters by FT-IR and NMR. Chemistry and Physics of Lipids, 126(2), 133-140.
- Wong, S. P., Lim, W. H., Cheng, S. F., and Chuah, C. H. (2011). Biological properties of sodium alkyl methyl ester sulfonate/alkyltrimethylammonium bromide surfactant mixtures. Colloids and Surfaces B: Biointerfaces, 89(0), 48-52.

APPENDICES

Appendix A Total Ion Chromatography of Methyl Ester and Unreacted Methyl Ester

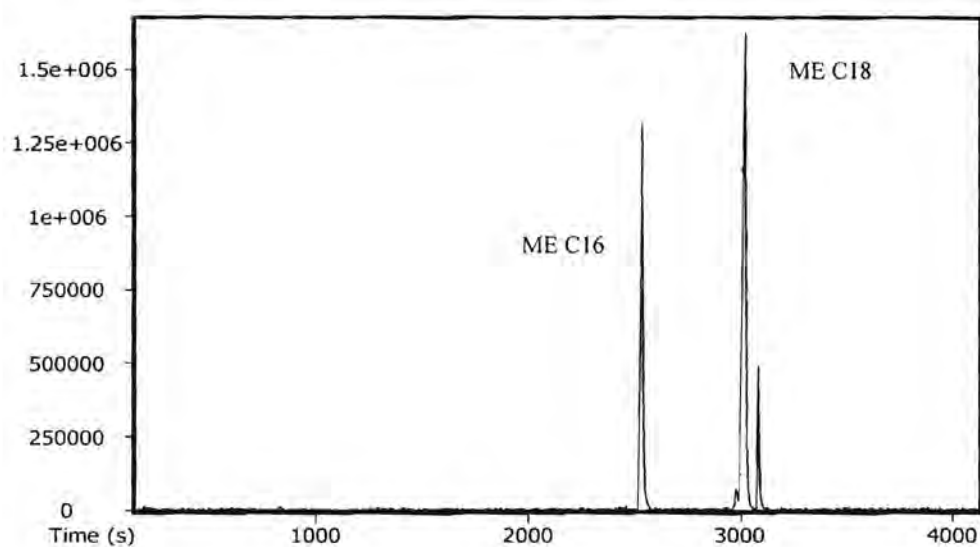
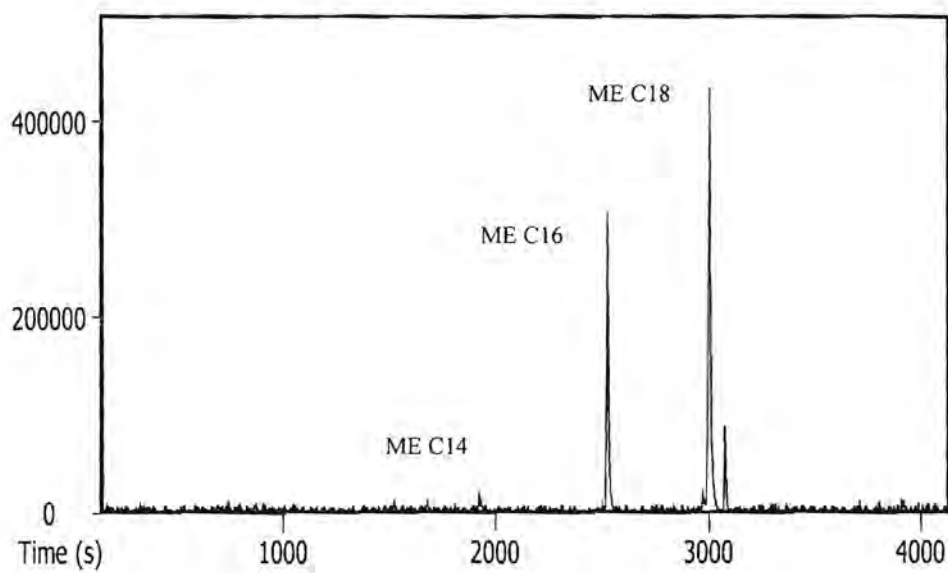


Figure A1 Total ion chromatography of methyl ester.

Figure A2 Total ion chromatography of unmethyl ester from the UV/O₂ system.

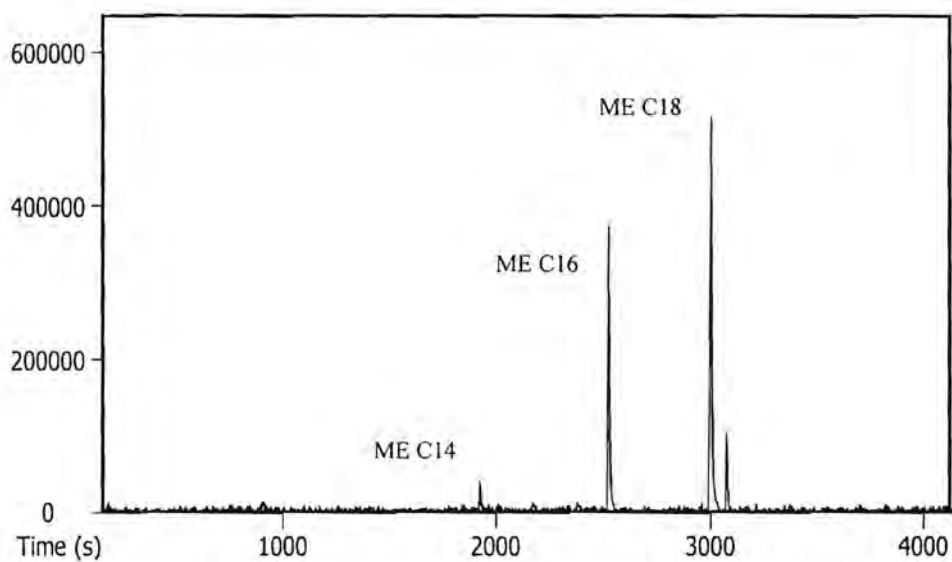


Figure A3 Total ion chromatography of unmethyl ester from the O₃/O₂ system.

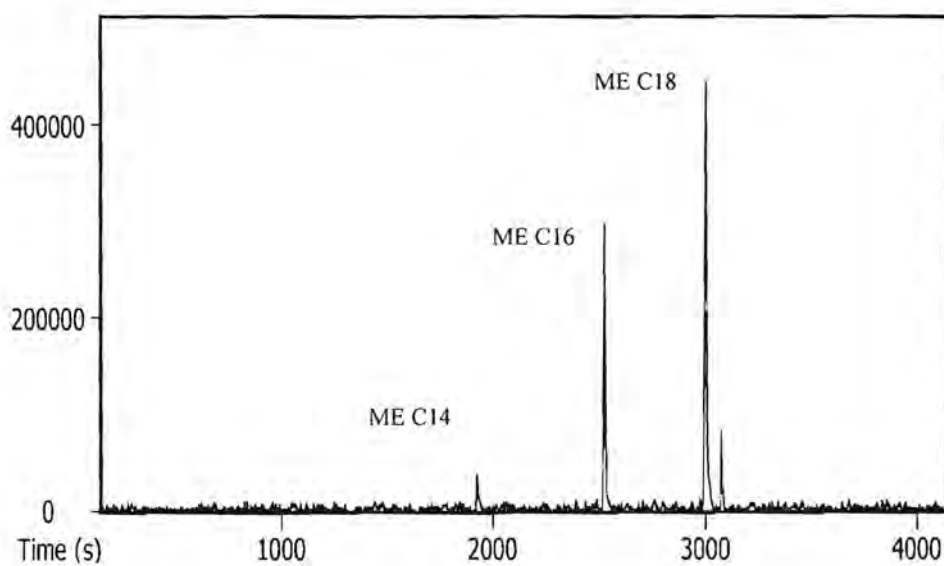


Figure A4 Total ion chromatography of unmethyl ester from the UV/O₃/O₂ system.

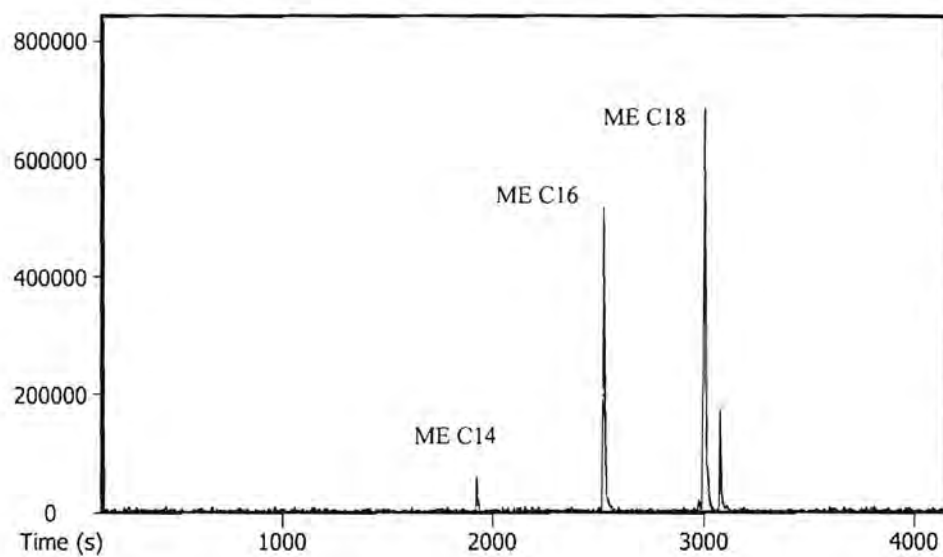


Figure A5 Total ion chromatography of unmethyl ester from the UV/O₃ system.

Table A1 Methyl ester and unreacted methyl ester compositions from GC-MS analysis

Component	White ME		unME UV/O ₂		unME O ₃ /O ₂		unME UV/O ₃ /O ₂		unME UV/O ₃	
	Time (min)	Composition (wt%)	Time (min)	Composition (wt%)	Time (min)	Composition (wt%)	Time (min)	Composition (wt%)	Time (min)	Composition (wt%)
C12:0	1295	0.00	1297	0.51	1297	1.08	1297	1.22	1296	1.28
C14:0	1922	0.00	1922	4.57	1922	6.98	1922	7.97	1922	0.38
C16:0	2552	36.01	2525	46.81	2525	45.13	2524	43.00	2527	50.78
C18:2	3034	0.51	2973	0.80	2973	0.56	2974	0.62	2974	0.19
C18:1	3095	45.34	3003	43.98	3003	33.45	3002	34.98	3006	38.88
C18:0	3096	18.14	3075	3.33	3075	12.80	3075	12.22	3076	8.49

Appendix B Experimental Condition and Conversion Calculation

Table B1 Experimental conditions and conversion calculation of the effect of different reactants and initiators

System	Time (h)	SO ₂ (ml/min)	Total volume SO ₂ (ml)	O ₂ (ml/min)	Total volume O ₂ (ml)	O ₃ (l/min)	Total volume O ₃ (l)	Starting ME (g)	Reactor Outlet (g)	Unreacted ME (g)	Conversion (%wt/wt)	
1	UV/O ₂	4	100	24000	100	24000	0	0	172.17	182.26	159.34	7.45
2	O ₃ /O ₂	4	100	24000	100	24000	0.5	120	172.22	183.99	160.34	6.90
3	UV/O ₃ /O ₂	4	100	24000	100	24000	0.5	120	172.87	183.05	149.50	13.52
4	UV/O ₃	4	100	24000	0	0	0.5	120	172.75	182.89	166.51	3.61

Table B2 Experimental conditions and conversion calculation of the effect of reaction time

System	Time (h)	SO ₂ (ml/min)	Total volume SO ₂ (ml)	O ₂ (ml/min)	Total volume O ₂ (ml)	O ₃ (l/min)	Total volume O ₃ (l)	Starting ME (g)	Reactor Outlet (g)	Unreacted ME (g)	Conversion (%w/w)	Total product (g)	
5	1UV/O ₃ /O ₂	1	100	6000	100	6000	0.5	30	172.63	177.30	164.51	4.70	5.91
6	2UV/O ₃ /O ₂	2	100	12000	100	12000	0.5	60	172.32	180.10	154.71	10.22	12.99
7	3UV/O ₃ /O ₂	4	100	24000	100	24000	0.5	120	172.87	183.05	149.50	13.52	17.45
8	4UV/O ₃ /O ₂	6	100	36000	100	36000	0.5	180	172.37	186.18	146.98	14.73	20.8

Appendix C Liquid Chromatography Analysis

Table C1 Liquid chromatography analysis of effect of reaction time

System	Reaction Time (h)	Di-sulfonates			Mono-sulfonates			% Composition		Ratio Mono/Di
		Time (min)	Area	Height	Time (min)	Area	Height	% Di-sulfonate	% MONO-sulfonate	
α -MES C18	-	-	-	-	5.42	22747592	1052709	-	-	-
5	1	4.69	695038	20487	5.74	8128127	235925	7.88	92.12	11.69
6	2	4.65	745103	22074	5.70	8086646	285762	8.44	91.56	10.85
7	4	4.61	2829715	92969	5.60	22264419	630573	11.28	88.72	7.87
8	6	4.55	1931967	51341	6.08	10179423	242454	15.95	84.05	5.27

SYNTHESIS OF METHYL ESTER SULFONATE SURFACTANT FROM METHYL ESTER

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Keywords: Methyl Ester Sulfonate; MES; Sulfoxidation; Ozone; UVlight

ABSTRACT

Methyl ester sulfonate (MES) is a potential anionic surfactant derived from palm oil methyl ester. MES shows excellent cleaning and surface properties. Although alpha methyl ester sulfonate (α -MES) is commercially available, it still has some drawbacks, such as disalt formation and low water solubility. Since ozone possesses high oxidizing power, it can react with organic compounds rapidly under mild conditions. In this work, MES was synthesized by the sulfoxidation reaction via a UV/ozone initiator. The reaction was carried out in a photochemical reactor (253.7nm) at 40 °C. The starting methyl ester was comprised of 36.0 % C16 and 64.0 % C18. The reactant flow rates (SO₂ and O₂) were fixed at 100 ml/min, whereas the ozone flow rate was 0.5 l/min. The product outlet was continuously sent to separation processes. Subsequently, MES was confirmed by FT-IR and ESI-MS. The conversion was around 4.7, 10.2, 13.5, and 14.7 wt% at 1, 2, 4, and 6 h, respectively.

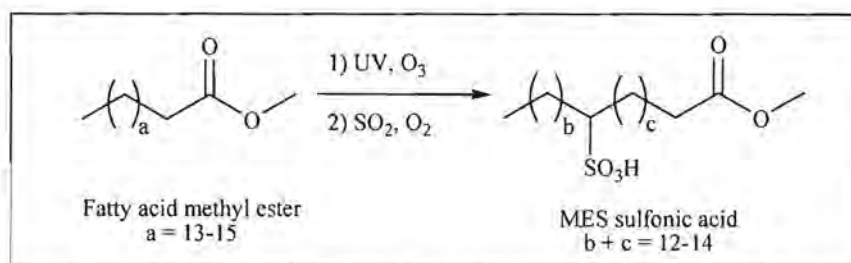
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INTRODUCTION

Nowadays, a number of widely-used surfactants are synthesized from petroleum and natural gas. However, some difficult problems for surfactant industries today are a lack of raw materials and an environmental issue, forcing surfactant producers to change some traditional products, to meet environmental requirements, and to give the required performance of synthesized surfactants at the same time.

There has recently been an increased focus by global detergent producers in formulating MES-based products because methyl ester sulfonate (MES) derived from palm and coconut offers an environment friendly and has good detergent properties(Satsuki *et al.*, 1992). Many companies, such as Lion Coporation, Stepan Company, and Chemithon Corporation, have produced alpha methyl ester sulfonate (α -MES) conducted in a film-falling reactor (Ortega, 2012) via the sulfonation reaction of methyl ester and sulfur trioxide (SO₃). Even though α -MES production has already been produced in commercial scale, there are some limitations, which are disalt formation(Martinez *et al.*, 2010) and low water solubility at room temperature (Aparicio *et al.*, 2012). To overcome these disadvantages, Cohen *et al.* (1998) proposed the use of sulfur dioxide/oxygen (SO₂/O₂) and ultraviolet (UV) irradiation via sulfoxidation reaction, providing a random of sulfonated group in alkyl chain (Φ -MES). In addition, Cohen *et al.* (2001) improved separation and extraction methods to purify MES products.

In this work, the study was focused on using ozone to help generate free radicals which is cheaper than using only UV light. Ozone (O₃) is one of the most interest chemicals because it is an effective oxidizing agent(Galimova *et al.*, 1973). The purpose of this work was to synthesize MES via the sulfoxidation reaction by using UV/ozone as an initiator, and SO₂ and O₂ as a reactant gas, as shown in Scheme 1. The effect of reaction time is also evaluated.



Scheme 1 Sulfoxidation reaction of fatty acid methyl ester.

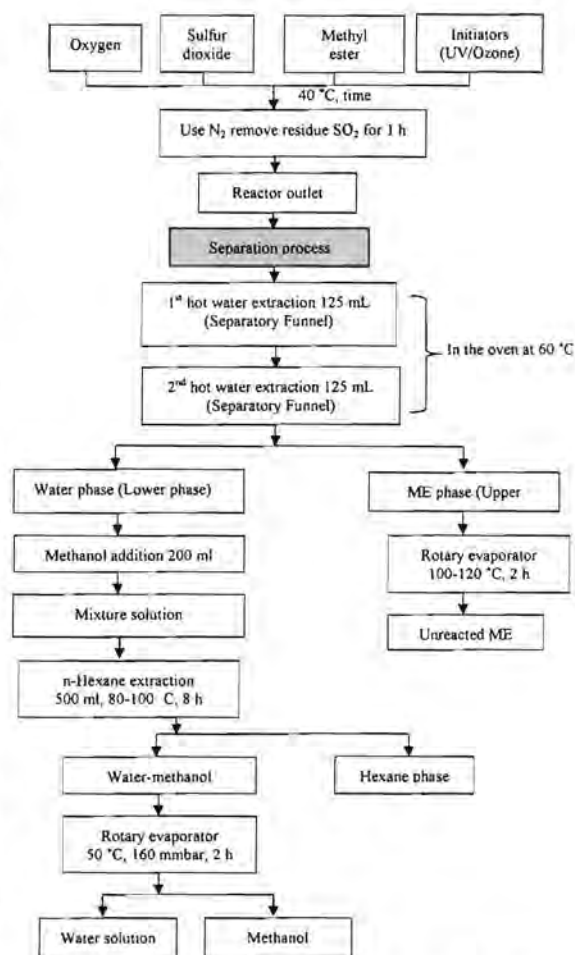
EXPERIMENTAL

A. Materials

Methyl ester (density $\approx 0.86 \text{ g/cm}^3$) was obtained from Thai Oleochemicals Co., Ltd., Thailand. Gas reactants were oxygen, nitrogen, sulfur dioxide. For a separation step, all chemicals including methanol (99.9%), n-Hexane (99.0%) and n-butanol (99.4%) were analytical reagent (AR) grade. Sodium hydroxide (NaOH) was used to neutralize MES products. Water was deionized.

B. Synthesis and Separation Methods

Scheme 2 shows overall procedures of synthesis and separation steps. Methyl ester (200 mL) was added into a photochemical reactor, which consisted of 16 UVC lamps (253.7 nm). All experiments were performed in a batch reactor at 40 °C in anhydrous medium. SO_2 , O_2 (100 ml/min) and O_3 (0.5 l/min) were continuously flowed into methyl ester which was in the round-bottom flask for certain time. After reaction was done, N_2 was used to purge into the reactor for an hour so as to remove residual SO_2 . For a separation step, 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. The solution mixture was left over night in the oven set 60 °C. Then, the phase separation happened: an upper layer (organic phase) and a lower layer (aqueous phase). After 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 contains unreacted methyl ester, a small amount of fatty acid and water, it was transferred to a rotary



Scheme 2 Overall procedures of synthesis and separation steps.

evaporator (80 to 100 °C for 2 h) to remove a small amount of water in methyl ester and then the unreacted methyl ester was weighed to calculate conversion. For water-methanol solution, it contained methyl ester sulfonic acid, sulfuric acids and a 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 a rotary evaporator. Methanol was evaporated out by slightly reducing pressure from 280 to 160 mbar at 50 °C for 2 h. Finally, the acid solution was neutralized with a 30% sodium hydroxide solution until pH was equal to 7.

C. Measurements

- 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. 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, final temperature of 280°C, held for 10 minutes.
- A Fourier transform infrared (FTIR) 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.
- 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 (microTOF II, BrukerDaltonics). Typical ESI-MS conditions were set as follows: 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.
- Conversion calculation was based on mass balance of methyl ester.

RESULTS AND DISCUSSION

A. Methyl Ester Compositions

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

Table 1 Fatty acid compositions 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

B. Characterizations

FT-IR analyses were done to investigate the functional groups found in MES products. Figure 1 shows the IR spectra of (a) α -MES C18 and (b) synthesized MES. Summary of characteristic bands were concluded in Table 2. The main functional groups are $1,725\text{ cm}^{-1}$, C=O stretching frequency of ester; $1,046\text{ cm}^{-1}$, sulfonate symmetric stretching frequency in R-SO_3 ; and $1,210\text{ cm}^{-1}$, asymmetric stretching frequency (Cohen *et al.*, 1998). It was found that the α -MES C18 spectrum is similar to that of synthesized MES. Therefore, it could be used to confirm that MES products were successfully sulfonated via the sulfoxidation reaction.

MES products were analyzed by direct infusion negative ion mode of electrospray ionization mass spectrometry (ESI-MS). Figure 2 shows fingerprints of synthesized MES, 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 correspond to RSO_2H , RSO_3H , and RSO_4H of mono-sulfonate C18, respectively. Additionally, there are four peaks of di-sulfonates C18, such as the masses at 443 ($-\text{SO}_3\text{H}$ and $-\text{SO}_4\text{H}$), 459 (two groups of $-\text{SO}_2\text{H}$), 473 ($-\text{SO}_3\text{H}$ and $-\text{SO}_4\text{H}$), and 491 (two groups of $-\text{SO}_4\text{H}$). The ESI-MS result indicates that there are both mono- and di-sulfonates of C18 in MES compounds.

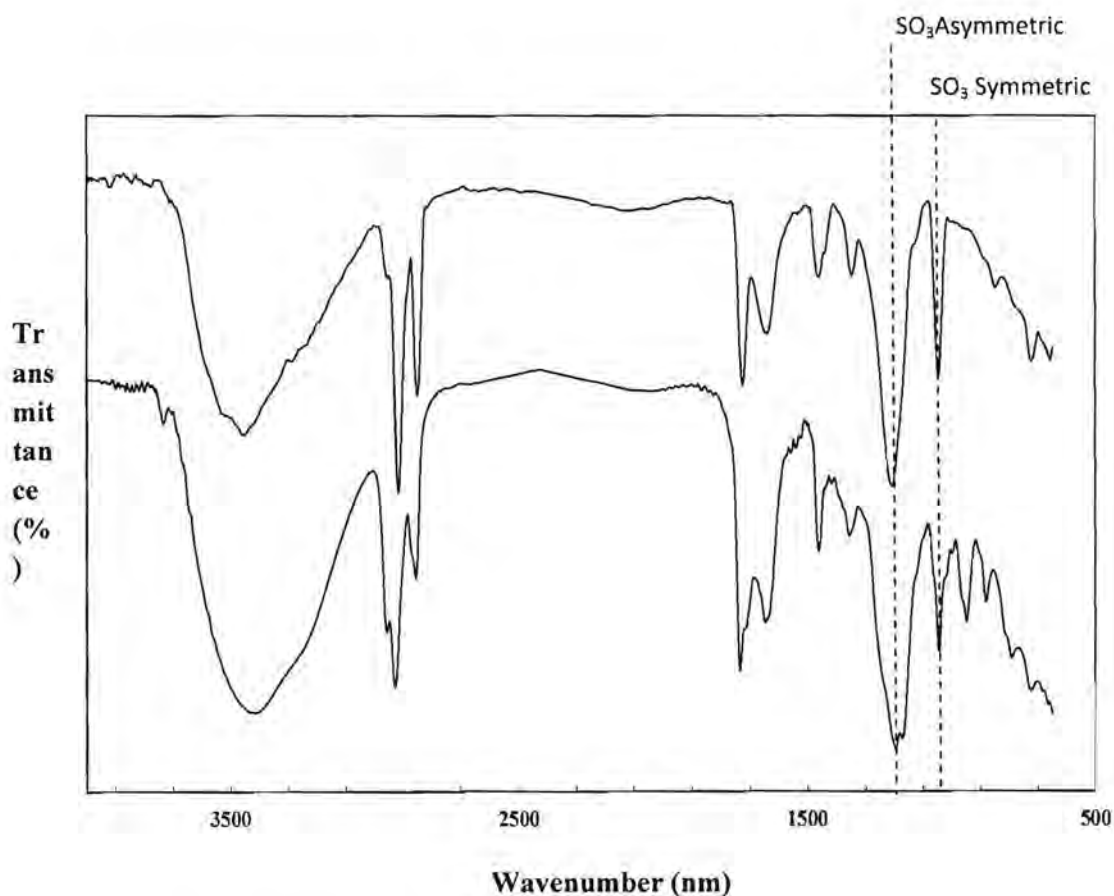


Figure 1 Infrared spectra of (a) α -MES C18 and (b) synthesized MES.

Table 2 The main IR peaks and the corresponding functional groups of α -MES C18 and synthesized MES

Peak (cm^{-1})	Functional groups
3,429	OH stretching frequency
1,725	-C=O stretching frequency of ester
2,850-2,930	CH ₂ - symmetric and asymmetric stretching frequency
1,467	CH ₂ - bending frequency
1,210	SO ₃ asymmetric stretching frequency
1,046	SO ₃ symmetric stretching frequency in R-SO ₃

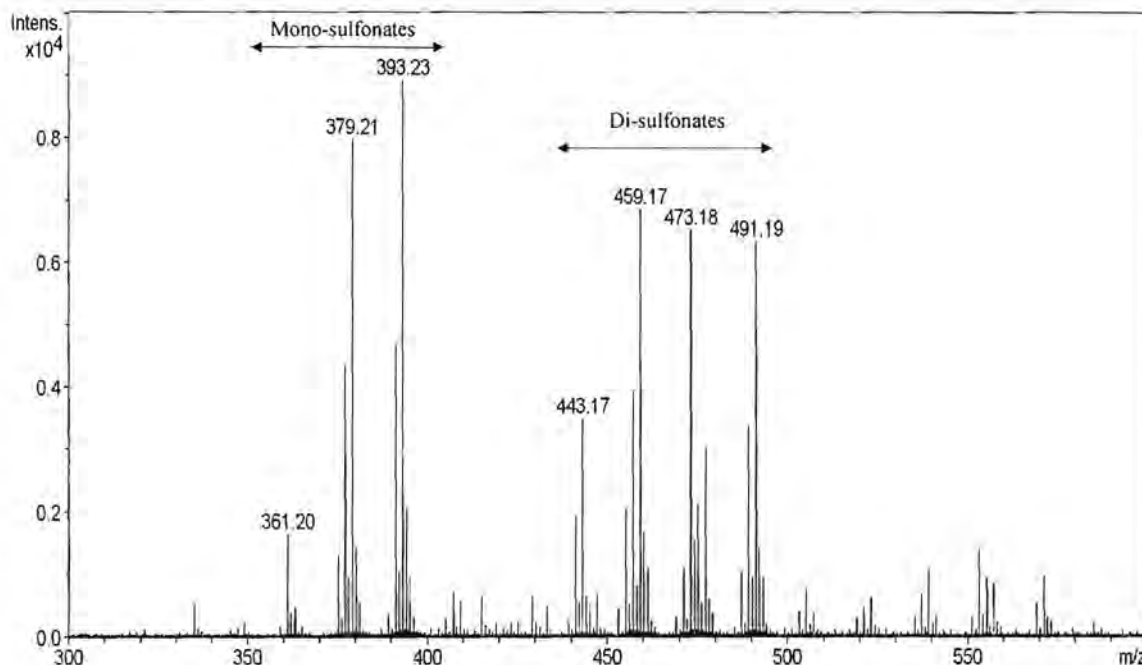


Figure 2 ESI-MS fingerprints of synthesized MES

C. The Effect of Reaction Time

Conversion percentages and total products are calculated and reported in Table 3. As expected, conversion and the weight of total products increase with reaction time. Conversion is approximately 4.7, 10.2, 13.5, and 14.7 %wt for 1, 2, 4, and 6 h, respectively. In addition, the total MES products for 1, 2, 4, and 6 h are about 5.9, 13.0, 17.5, and 20.8 g, respectively, when using 172 g (200 ml) of methyl ester in each batch.

Table 3 Conversion and total products

Reaction Time (h)	Conversion (%w/w)	Total products (g)
1	4.7	5.9
2	10.2	13.0
4	13.5	17.5
6	14.7	20.8

CONCLUSIONS

MES can be successfully synthesized by using UV/Ozone as an initiator, and SO₂ and O₂ as a reactant. The conversion percentage of UV/ozone is up to 14.7 %wt for 6 h, which total products are approximately 22.6 g. The FT-IR results confirm that there are sulfonate groups in the MES structure. Furthermore, the ESI-MS result indicates that not only mono-sulfonates are generated but also di-sulfonates of C18 are present.

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REFERENCES

- Aparicio, J., MacArthur, B. W., Sheats, W. B. and Brooks, B. J. (2012).** MES – Myths, Mysteries and Perspectives on Properties and Use. ICSD Shanghai, China.
- Cohen, L., Soto, F. and Luna, M. S. (2001).** Separation and extraction of Φ -methyl ester sulfoxylates: New features. *Journal of Surfactants and Detergents*, **4(1)**, 73-74.
- Cohen, L. and Trujillo, F. (1998).** Synthesis, characterization, and surface properties of sulfoxylated methyl esters. *Journal of Surfactants and Detergents*, **1(3)**, 335-341.
- Galimova, L. G., Komissarov, V. D. and Denisov, E. T. (1973).** Kinetics and products of oxidation of cyclohexane by ozonized oxygen. *Bulletin of the Academy of Sciences of the USSR, Division of chemical science*, **22(2)**, 295-298.
- Martinez, D., Orozco, G., Rincon, S. and Gil, I. (2010).** Simulation and pre-feasibility analysis of the production process of α -methyl ester sulfonates (α -MES). *Bioresource Technology*, **101(22)**, 8762-8771.
- Ortega, J. A. T. (2012).** Sulfonation/sulfation processing technology for anionic surfactant manufacture, (www.intechopen.com).
- Satsuki, T., Umehara, K. and Yoneyama, Y. (1992).** Performance and physicochemical properties of α -sulfo fatty acid methyl esters. *Journal of the American Oil Chemists Society*, **69(7)**, 672-677.

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ผลงานวิจัย

PATENTS

8. D. E. Resasco, B. Kitiyanan, W. E. Alvarez, and L. Balzano "Method and apparatus for producing carbon nanotubes", Mexican Patent Number: 237966 (2007).
7. D. E. Resasco, B. Kitiyanan, J. H. Harwell, and W. E. Alvarez "Method of producing single-walled carbon nanotubes", US Patent 7,094,386 (2006).
6. D. E. Resasco, B. Kitiyanan, J. H. Harwell, and W. E. Alvarez "Carbon nanotube product comprising singled carbon nanotubes", US Patent 6,994,907 (2006).
5. D. E. Resasco, B. Kitiyanan, J. H. Harwell, and W. E. Alvarez "Metallic catalytic particle for producing single-walled carbon nanotubes", US Patent 6,962,892 (2005).
4. D. E. Resasco, B. Kitiyanan, W. E. Alvarez, and L. Balzano "Method and apparatus for producing carbon nanotubes", US Patent 6,955,800 (2005).
3. D. E. Resasco, B. Kitiyanan, W. E. Alvarez, and L. Balzano "Process and apparatus for producing single-walled carbon nanotubes", US Patent 6,919,064 (2005).
2. D. E. Resasco, B. Kitiyanan, W. E. Alvarez, and L. Balzano "Method and apparatus for producing carbon nanotubes", US Patent 6,413,487 (2002).
1. D. E. Resasco, B. Kitiyanan, J. H. Harwell, and W. E. Alvarez "Method of producing carbon nanotubes", US Patent 6,333,016 (2001).

PUBLICATIONS

- 31 A. Siangsai, Y. Suttisawat, P. Sridechprasat, P. Rangsunvigit, B. Kitiyanan, S. Kulprathipanja "Effect of Ti Compounds on Hydrogen Desorption/Absorption of $\text{LiNH}_2/\text{LiAlH}_2/\text{MgH}_2$ " Journal of Chemical Engineering of Japan, 2010, 43, 95-98.
- 30 Y. Suttisawat, P. Rangsunvigit, B. Kitiyanan, M. Williams, P. Ndungu, M.V. Lototskyy, A. Nechaev, V. Linkov, S. Kulprathipanja "Investigation of hydrogen storage capacity of multi-walled carbon nanotubes deposited with Pd or V" International Journal of Hydrogen Energy, 2009, 34, 6669-6675.
- 29 S. Sawetaporn, K. Bunyakiat, B. Kitiyanan "CO₂ gasification of Thai coal chars: Kinetics and reactivity" Korean Journal of Chemical Engineering, 2009, 26, 1009-1015.
28. S. Kungsanant, B. Kitiyanan, T. Rirksomboon, S. Osuwan, J.F. Scamehorn "Recovery of Nonionic Surfactant from VOC-contaminated coacervate phase solutions by co-current vacuum stripping: Effect of surfactant concentration, temperature, and solute type" Separation and Purification Technology, 2009, 66, 510-516.

27. S. Thaicharoensutcharittham, V. Meeyoo, B. Kitiyanan, P. Rangsunvigit, T. Rirksomboon "Catalytic combustion of methane over NiO/Ce_{0.75}Zr_{0.25}O₂catalyst" *Catalysis Communications*, 2009, 10, 673-677.
26. P. Chungchamroenkit; S. Chavadej; J. F. Scamehorn; U. Yanatatsaneejit; B. Kitiyanan. "Separation of carbon black from silica by froth flotation part 1: Effect of operational parameters" *Separation Science and Technology*, 2009, 44, 203-226.
25. K. Nomura, J. Liu and B. Kitiyanan, "Nonbridged half-titanocenes as effective catalysts for synthesis of new polyolefins by olefin copolymerization", *Current Topics in Catalysis*, 2009, 7, 1-20.
24. S. Kungsanant, B. Kitiyanan, T. Rirksomboon, S. Osuwan, J.F. Scamehorn "Toluene removal from nonionic surfactant coacervate phase solutions by vacuum stripping" *Separation and Purification Technology*, 2008, 63, 370-378.
23. K. Nomura, B. Kitiyanan "Recent progress in precise synthesis of polyolefins containing polar functionalities by transition metal catalysis" *Current Organic Synthesis*, 2008, 5, 217-2266.
22. A. Bampenrat, V. Meeyoo, B. Kitiyanan, P. Rangsunvigit, T. Rirksomboon "Catalytic Oxidation of Naphthalene over CeO₂-ZrO₂Mixed Oxide Catalysts" *Catalysis Communications*, 2008,6, 2349-2352.
21. P. Chungchamroenkit, S. Chavadej, U. Yanatatsaneejit, B. Kitiyanan "Residue catalyst support removal and purification of carbon nanotubes by NaOH leaching and froth flotation" *Separation and Purification Technology*, 2008, 60, 206-214.
20. B. Kitiyanan and K. Nomura "Synthesis of Half-Titanocenes Containing Aryloxy Ligands Attached to the ROMP Polymer Chain End: Unique Catalyst Precursors for Ethylene (Co)polymerization" *Organometallic*, 2007, 26, 3461-3465.
19. C. Jindarom, V. Meeyoo, B. Kitiyanan, T. Rirksomboon, P. Rangsunvigit "Surface characterization and dye adsorptive capacities of char obtained from pyrolysis/gasification of sewage sludge" *Chemical Engineering Journal*, 2007, 33, 239-246.
18. Y. Suttisawat, P. Rangsunvigit, B. Kitiyanan, N. Muangsin and S. Kulprathipanja "Catalytic effect of Zr and Hf on hydrogen desorption/absorption of NaAlH₄ and LiAlH₄" *International Journal of Hydrogen Energy*, 2007, 32, 1277-1285.
17. K. Nomura, J. Liu, S. Padmanabhan and B. Kitiyanan "Nonbridged half-metalocenes containing anionic ancillary donor ligands: New promising candidates as catalysts for precise olefin polymerization" *Journal of Molecular Catalysis A: Chemical*, 2007, 267, 1-29.
16. Y. Suttisawat, V. Jannatisin, P. Rangsunvigit, B. Kitiyanan, N. Muangsin and S. Kulprathipanja, "Understanding the effect of TiO₂, VCl₃, and HfCl₄ on hydrogen desorption/absorption of NaAlH₄" *Journal of Power Sources*, 2007, 163, 997-1002.

15. P. Chungchamroenkit, B. Kitiyanan, J.E. Herrera, S. Chavadej, D.E. Resasco, "Growth of single-walled carbon nanotubes by disproportionation of CO over Co-Re/SiO₂ catalysts" *Diffusion and Defect Data Pt.B: Solid State Phenomena*, 2007, 121-123, 337-341.
14. P. Thipkhunthod, V. Meeyoo, P. Rangsunvigit, B. Kitiyanan, K. Siemanond, T. Rirksomboon, "Pyrolytic characteristics of sewage sludge" *Chemosphere*, 2006, 64, 955-962.
13. B. Kitiyanan, and K. Nomura, "Effect of catalyst loading in olefin polymerization catalyzed by supported half-titanocenes on polystyrene through phenoxy linkage" *Studies in Surface Science and Catalysis*, 2006, 161, 213-218.
12. J. Jitputti, B. Kitiyanan, P. Rangsunvigit, K. Bunyakiat, L. Attanatho, and P. Jenvanitpanjakul, "Transesterification of crude palm kernel oil and crude coconut oil by different solid catalysts", *Chemical Engineering Journal*, 2006, 116, 61-66.
11. M. Termtanun, P. Rangsunvigit, B. Kitiyanan, S. Kulprathipanja, W. Tanthapanichakoon, "Effect of metal type and loading on hydrogen storage on NaAlH₄", *Science and Technology of Advanced Materials*, 2005, 6, 348-351.
10. P. Thipkhunthod, V. Meeyoo, P. Rangsunvigit, B. Kitiyanan, K. Siemanond, and T. Rirksomboon "Predicting the heating value of sewage sludges in Thailand from proximate and ultimate analyses", *Fuel*, 2005, 84, 849-857.
9. C. Sun, H. Miyazawa, Y. Kondo, N. Yoshino, K. Abe, M. Sagisaka, B. Kitiyanan, T. Ohkubo, H. Sakai, and M. Abe, "Solution properties of sulfate-type fluoro-hybrid anionic surfactants with a benzene ring in their molecules" *Journal of Oleo Science*, 2004, 53(8), 371-376.
8. J.H. O'Haver, R. D. Walks, B. Kitiyanan, J.H. Harwell and D. A. Sabatini, "Packed column and hollow fiber air stripping of a contaminant-surfactant stream" *Journal of Environmental Engineering*, 2004, 130(1), 4-11.
7. P. Punnaruttanakun, V. Meeyoo, C. Kalambaheti, P. Rangsunvigit, T. Rirksomboon, and B. Kitiyanan, "Pyrolysis of API separator sludge", *J. Anal. Appl. Pyrolysis*, 2003, 68-69, 547-560.
6. M. Sagisaka, S. Yoda, Y. Takebayashi, K. Otake, B. Kitiyanan, Y. Kondo, N. Yoshino, K. Takebayashi, H. Sakai, and M. Abe, "Preparation of a W/scCO₂ microemulsion using fluorinated surfactants", *Langmuir*, 2003, 19, 220-225.
5. D. E. Resasco, W. E. Alvarez, F. Pompeo, L. Balzano, J. E. Herrera, B. Kitiyanan and A. Borgna, "A scalable process for production of single-walled carbon nanotubes (SWNTs) by catalytic disproportionation of CO on a solid catalyst", *Journal of Nanoparticle Research*, 2002, 4, 131-136.
4. W. E. Alvarez, B. Kitiyanan, A. Borgna and D. E. Resasco, "Synergism of Co and Mo in the catalytic production of single-wall carbon nanotubes by decomposition of CO", *CARBON*, 2001, 39, 547-558.
3. B. Kitiyanan, W. E. Alvarez, J. H. Harwell and D. E. Resasco, "Controlled production of single-wall carbon nanotubes by catalytic decomposition of CO

- on bimetallic Co-Mo catalysts", *Chemical Physics Letters*, 2000, 317, 497-503.
2. B. Kitiyanan, J. H. O'Haver, J. H. Harwell and D. A. Sabatini, "The use of liquid-liquid extraction in hollow fiber membrane for the removal of organic contaminants from aqueous surfactant streams" in "Surfactant-Based Separations Science and Technology" J. F. Scamehorn and J. H. Harwell eds. ACS Symposium Series 740, page 76, 1999.
 1. B. Kitiyanan, J.H. O'Haver, J.H. Harwell and S. Osuwan, "Adsolubilization of styrene and isoprene into cetyltrimethylammonium bromide admicelle on precipitated silica", *Langmuir*, 1996, 12, 2162-2168.

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2. T. Vitidsant, C. Saeung, “Preparation of activated carbon from Petrochemical waste by chemical and physical activations” proceeding of Naresuan University, 2009.
3. K. Siemanond, Y Charoeyamai, B. Boonsanit, and C. Saeung, “Laboratory Safety and Systematic Handling of Chemical Reagents and Waste in the Petroleum and Petrochemical College”, Asahi 2013
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2. Tulathammakit, H.; and Kitiyanan, B. (2014, August 23-27) Synthesis of Methyl Ester Sulfonate Surfactant from Palm Oil Methyl Ester by Using UV or Ozone as an Initiator. Proceedings of the 17th Conference Process Integration, Modelling and Optimisation for Energy Saving and Pollution Reduction (PRES 2014), Prague, Czech Republic.