# CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

A surfactant (surface-active agent) is a substance that can adsorb on the surfaces or interfaces and change the degree of the surface or interfacial free energies when it presents at low concentration in a system (Rosen, 2012). At the moment, anionic surfactants play a crucial role in surfactant industries. Most anionic surfactants are produced from the sulfonation and sulfation reaction in order to produce sulfonates and sulfates, respectively (Matthew, 2008). Figure 2.1 shows several pathways to synthesize sulfonates and sulfate by using different agents. Sulfonates, which have alkanes as a reactant, can be produced form 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).
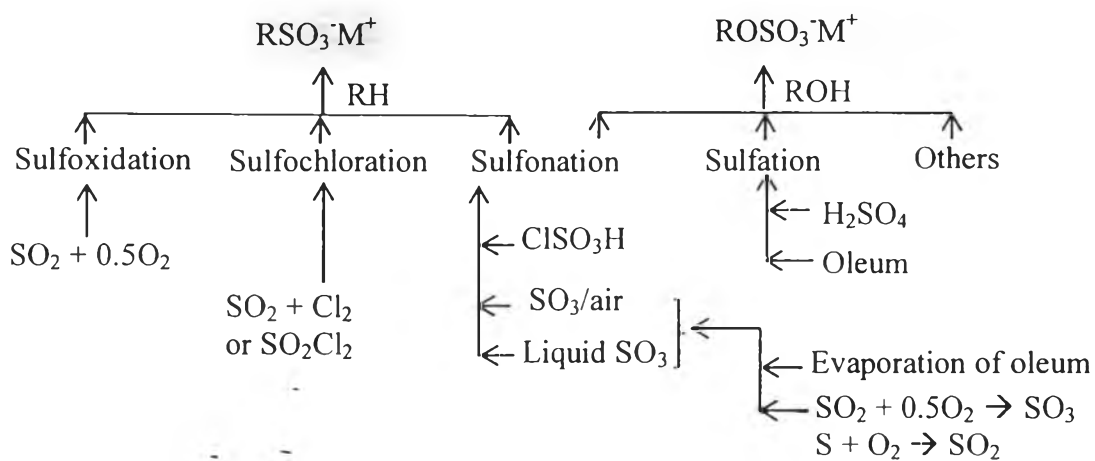
Figure 2.1 Sulfoation and sulfation pathways for manufacturing sulfur-containing anionic surfactant (Norman et al., 2008).

Nowadays, many detergent manufactures 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 sufoxidation are two of the processes to produce MES.

2.1 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.

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

2.1.1.1 Mechanism of α-MES via Sulfonation

The mechanisms of α-MES in the sulfonation reaction were investigated as shown in Figure 2.2 (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 SO₃, but the initially formed sulfonated anhydride.
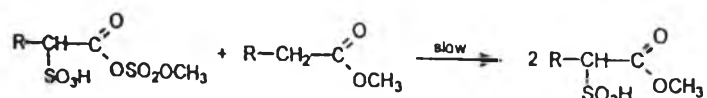
First step:

Intermidates of the first step:
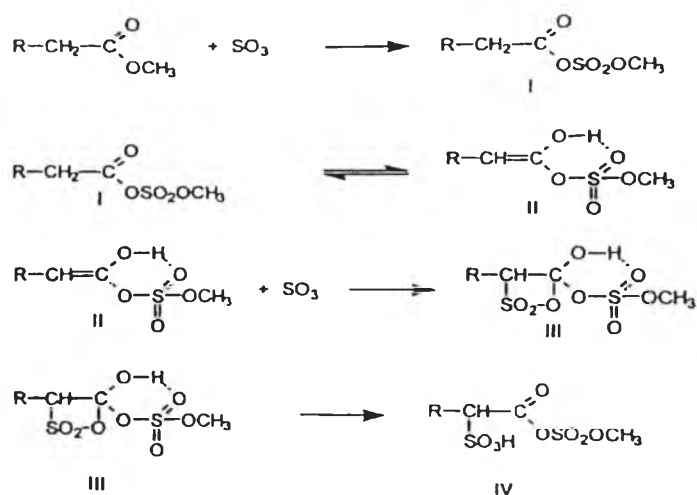
Second step:

Figure 2.2 The two-step mechanism of sulfonation reaction (Holmberg, 2003).

2.1.1.2 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 2.3. 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. 2.1), and then SO_3 formation is promoted as shown in Eq. 2.2 (Martinez *et al.*, 2010).
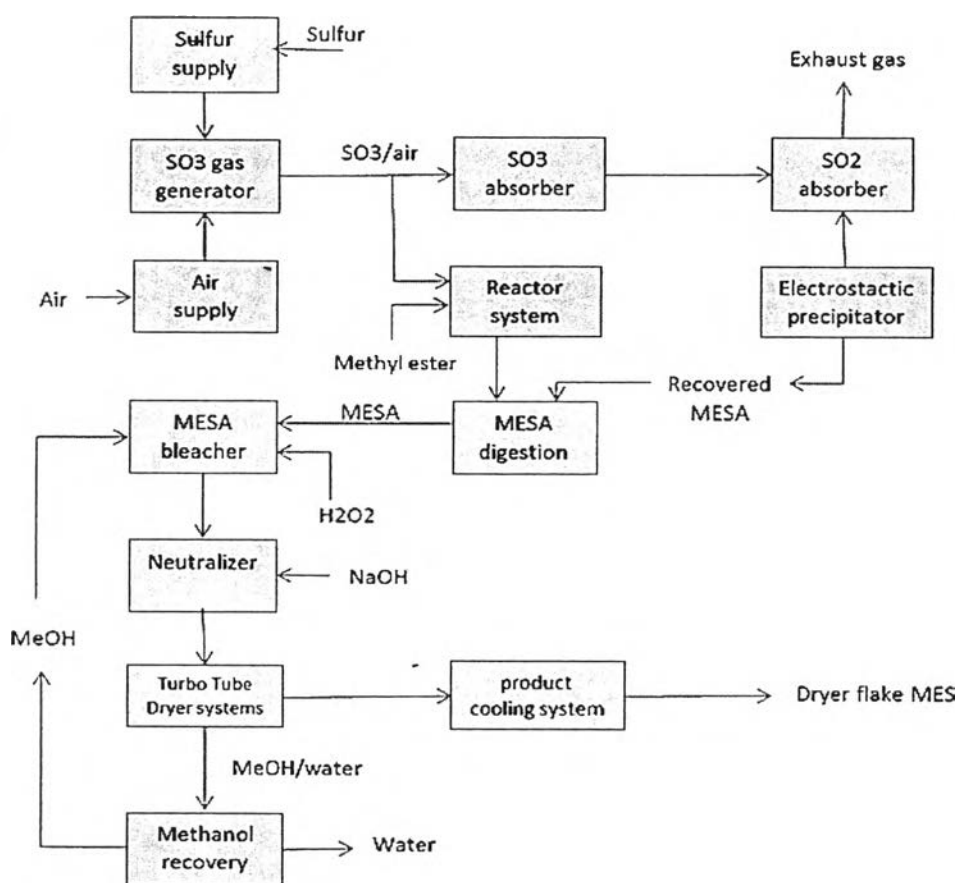
Figure 2.3 The overview of Chemithon sulfonation plant (Norman *et al.*, 2008).

$$S_{(l)} + O_{2(g)} \quad \rightarrow \quad SO_{2(g)} \qquad \text{Eq. 2.1}$$

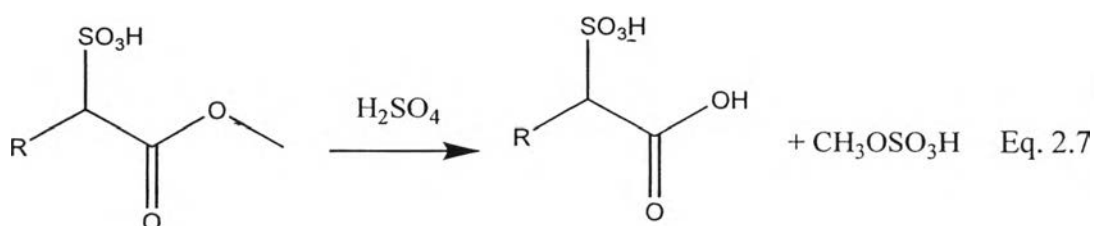$$2SO_{2(g)} + 0.5O_{2(g)} \quad \rightarrow \quad 2SO_{3(g)} \qquad \text{Eq. 2.2}$$
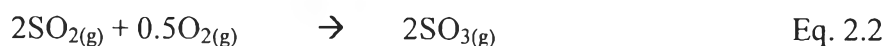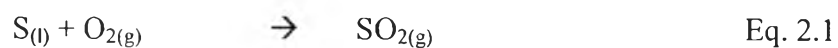
In the sulfonation process, 7 % (volume) of inlet SO_3 at 42 °C and ME feedstock (40 to 52 °C) are fed into a reactor. The mass flow of these

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. 2.3). When they are neutralized, they will be converted to sulfonated soap or disalt (Eq. 2.4). 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.

Eq. 2.3

Eq. 2.4
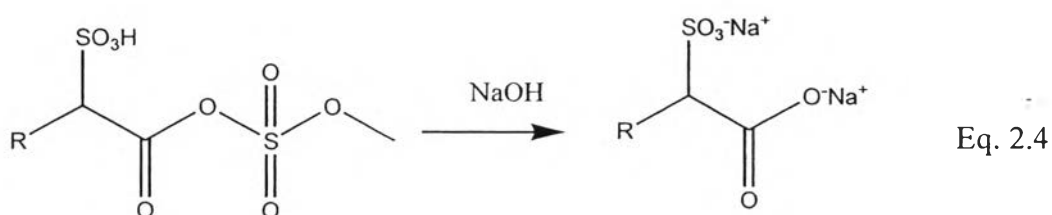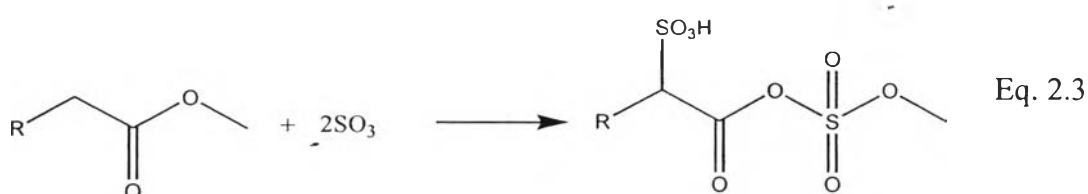
Nevertheless, disalt formation can be controlled by adding methanol. The excess methanol provides the limitation of occurring disalt and also the reduction of viscosity resulting in the improvement of mixing and heat transfer through the bleaching process. In addition, the gas phase reaction between SO_3 and

methanol produces methyl sulfonic acid (Eq. 2.5) preventing the hydrolysis of MES. The hydrolysis is caused by sulfuric acid, derived from the reaction between SO_3 and water (Eq. 2.6), and then sulfuric acid can continuously turn into α-sulfonated acids in Eq 2.7 (Martinez *et al.*, 2010).

$$CH_3OH + SO_3 \rightarrow CH_3OSO_3H \qquad \text{Eq. 2.5}$$

$$H_2O + SO_3 \rightarrow H_2SO_4 \qquad \text{Eq. 2.6}$$

Eq. 2.7

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. 2.8 a 2.9). 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.

$$CH_3OSO_3H + NaOH \rightarrow CH_3OSO_3Na \qquad \text{Eq. 2.8}$$

Eq. 2.9
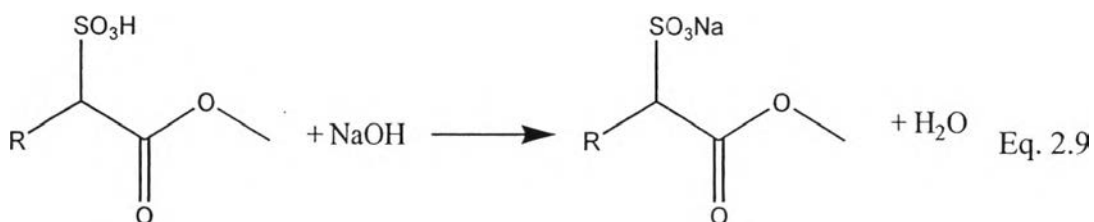
2.1.1.3 α-MES Properties

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). Futhermore, 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 (Commision of the European Commutinities, 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).

2.1.2 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)

2.1.2.1 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.

$$RH + SO_2 + 0.5O_2 \xrightarrow{h\nu} RSO_3H \qquad \text{Eq. 2.10}$$

According to Eq. 2.10 (Denisov *et al.*, 2005), the sulfoxidation is normally performed by the ratio of gaseous reactions $SO_2:O_2 = 2:1$ 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.

2.1.2.2 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.

Formation of radical
$$SO_2 \rightarrow {}^*SO_2 \qquad \text{Eq. 2.11}$$
$$^*SO_2 + RH \rightarrow R^\cdot + HSO_2^\cdot \qquad \text{Eq. 2.12}$$

Reaction chains
$$R^\cdot + SO_2 \rightarrow RSO_2^\cdot \qquad \text{Eq. 2.13}$$
$$RSO_2^\cdot + O_2 \rightarrow RSO_2\text{-O-O}^\cdot \qquad \text{Eq. 2.14}$$
$$RSO_2\text{-O-O}^\cdot + RH \rightarrow RSO_2\text{-O-OH} + R^\cdot \qquad \text{Eq. 2.15}$$

Chain branching reactions
$$RSO_2\text{-O-OH} \rightarrow RSO_2\text{-O}^\cdot + OH^\cdot \qquad \text{Eq. 2.16}$$
$$RSO_2\text{-O}^\cdot + RH \rightarrow RSO_3H + R^\cdot \qquad \text{Eq. 2.17}$$
$$OH^\cdot + RH \rightarrow R^\cdot + H_2O \qquad \text{Eq. 2.18}$$

Secondary reactions
$$
\begin{cases}
RSO_2\text{-}O\text{-}OH + SO_2 + H_2O \rightarrow RSO_3H + H_2SO_4 & \text{Eq. 2.19} \\
RSO_3H + SO_2 + 0.5O_2 \rightarrow HO_3SRSO_3H & \text{Eq. 2.20}
\end{cases}
$$
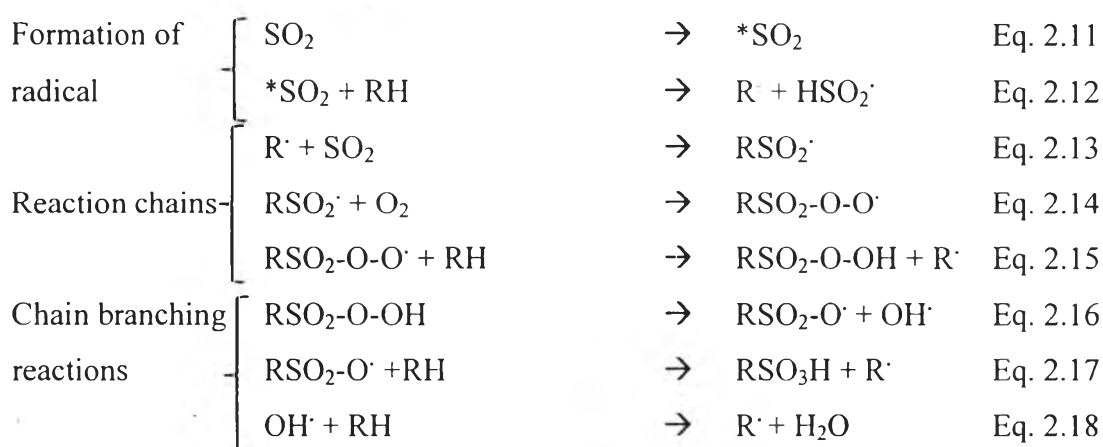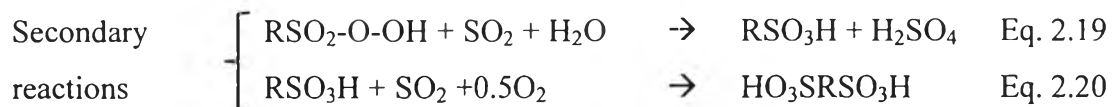
Ramakrishnan (2006) explain how sulfoxidation occur in .Eq. 2.11 to Eq. 2.20. To form radicals, SO_2 is excited by UV light to be in the triplet state (*SO_2), which then abstracts hydrogen from hydrocarbon to produce an alkyl radical (Eqs. 2.11, 2.12). Subsequent chain reactions with SO_2 and O_2 create an alkylpersulfonyl radical (Eqs. 2.13, 2.14), which produces another starter radical and a persulfonic acid (Eq. 2.15). Then, an alkylpersulfonyl radical continuously fragments and abstracts hydrogen (Eqs. 2.16, 2.17) to generate the alkanesulfonic acid. In addition, Eq. 2.18 shows the presence of water formed by the reaction of RH and OH radical. According to Eq. 2.19, the alkanesulfonic acid can also be occurred by the reaction of persulfonic acid, water and SO_2. Besides main products (mono-sulfonic acid), polysulfunic acid in Eq. 2.20 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. 2.19. About the irradiated reaction, the persulfonic acid colludes with RSO_2^- 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:

$$
RSO_2^- + X \rightarrow RSO_2X \qquad \text{Eq. 2.21}
$$

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. 2.11), 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 RSO_2^- 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.
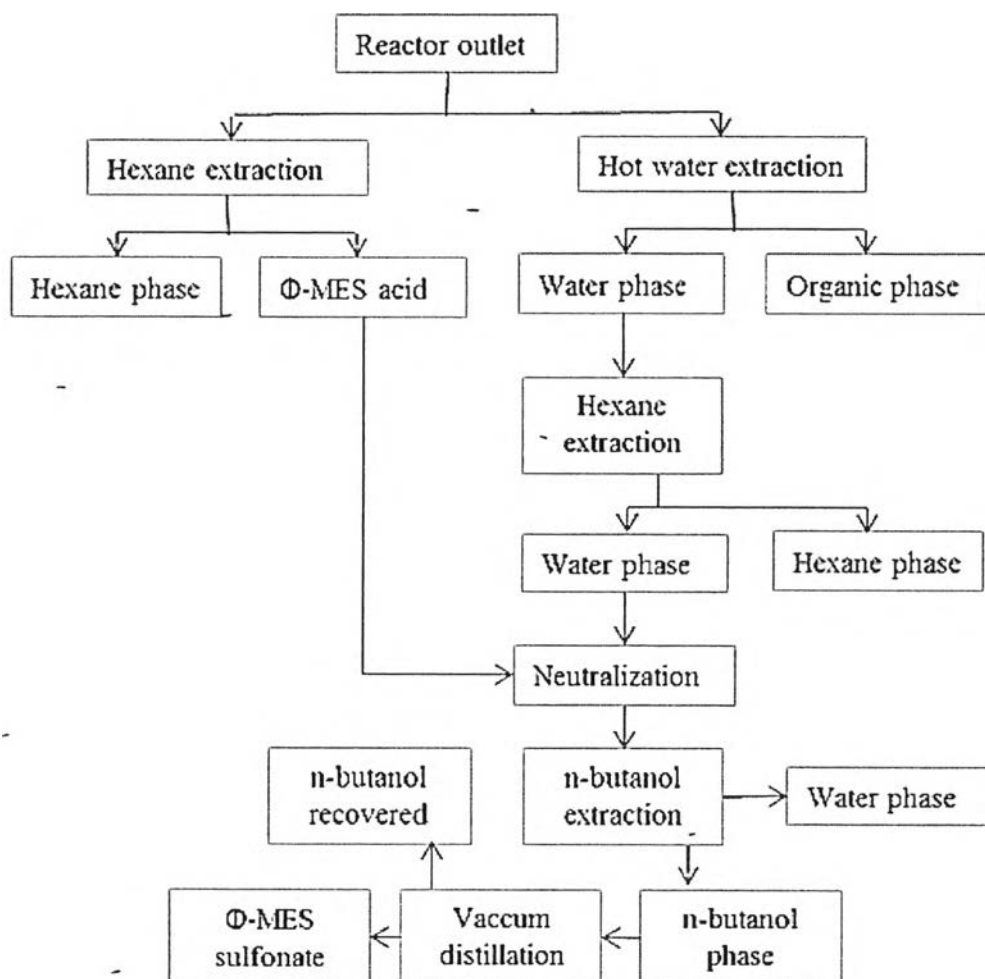
2.1.2.3 MES Synthesis via Sulfoxidation

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 2.4. 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 $C(O)-OCH_3$ 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.

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                        ┌─────────────────┐
                        │  Reactor outlet │
                        └─────────────────┘
              ┌──────────────┴──────────────────┐
              ▼                                  ▼
     ┌──────────────────┐              ┌──────────────────────┐
     │ Hexane extraction│              │  Hot water extraction│
     └──────────────────┘              └──────────────────────┘
        ┌───────┴────────┐               ┌──────────┴──────────┐
        ▼                ▼               ▼                     ▼
 ┌────────────┐  ┌────────────┐   ┌────────────┐      ┌──────────────┐
 │Hexane phase│  │ Φ-MES acid │   │ Water phase│      │Organic phase │
 └────────────┘  └────────────┘   └────────────┘      └──────────────┘
                      │                  ▼
                      │           ┌────────────┐
                      │           │  Hexane    │
                      │           │ extraction │
                      │           └────────────┘
                      │             ┌────┴───────────┐
                      │             ▼                ▼
                      │      ┌────────────┐   ┌────────────┐
                      │      │ Water phase│   │Hexane phase│
                      │      └────────────┘   └────────────┘
                      │             ▼
                      │      ┌───────────────┐
                      └─────►│ Neutralization│
                             └───────────────┘
                                    ▼
 ┌────────────┐              ┌────────────┐        ┌────────────┐
 │  n-butanol │              │  n-butanol ├───────►│ Water phase│
 │  recovered │              │  extraction│        └────────────┘
 └────────────┘              └────────────┘
         ▲                          ▼
 ┌────────────┐  ┌────────────┐   ┌────────────┐
 │  Φ-MES     │◄─│  Vaccum    │◄──│  n-butanol │
 │  sulfonate │  │distillation│   │   phase    │
 └────────────┘  └────────────┘   └────────────┘
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Figure 2.4 The separation and extraction of Φ-MES (Cohen *et al.*, 2001).

2.2.1.4 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.

2.2 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. 2.22, 2.23).

$$RH + O_3 \quad \rightarrow \quad R^{\cdot} + HO_3^{\cdot} \qquad \text{Eq. 2.22}$$

$$RH + O_3 \quad \rightarrow \quad R^{\cdot} + HO^{\cdot} + O_2 \qquad \text{Eq. 2.23}$$

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.