Performance of Green Surfactants in the Formulation of Heavy-Duty Laundry Liquid Detergents (HDLD) with Special Emphasis on Palm Based Alpha Methyl Ester Sulfonates (α-MES)

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Abstract: Liquid detergent has an increasing demand in North America, Western Europe, and Southeast Asia countries owing to its convenience to use and efficiency to clean. Alpha methyl ester sulfonates (α-MES), an anionic surfactant derived from palm oil based methyl ester, was reported to have lower manufacturing cost, good detergency with less dosage, excellent biodegradability, higher tolerance to hard water, and lower eco-toxicity as compared to linear alkylbenzene sulfonates (LABS). LABS was known as the workhorse of the detergent industry in the 20th century. Although palm-based α-MES was successfully used as the sole surfactant in powder detergent, there are still some unsettled technical issues related to phase stability and viscosity when using this anionic surfactant in heavy-duty laundry liquid detergent formulations. This paper will review not only the market overview of detergents, the application and performance of green surfactants in laundry detergents but also will highlight the technical issues related to the application of palm-based α-MES in laundry liquid detergent and some of the possible methods to overcome the formulation adversities.

Key words: green surfactants, heavy-duty laundry liquid detergents, palm-based alpha methyl ester sulfonates

1 Introduction

Laundry detergent, used for cleaning of fabrics, has many different formats including powder, liquid, bar, tablet, and sachet to suit consumers’ preferences. Powder detergent was favoured in Asia countries including China, India, and Japan, owing to its low cost per wash load and high volume over weight ratio⁵. Liquid detergent is very popular in North America and Western Europe as it is effective in pre-treating and removing stains, ready for immediate use, have no solubility issues, do not require prewashing, and hence is time and energy saving⁶–⁸. Detergent in bar form was preferred by Indians prior to switching their preferences into powder detergent as they deemed the rubbing action is important to effectively clean the fabrics⁹. On the other hand, detergent in tablet and sachet form was highly preferred in United Kingdom and European Union as it is convenient to use and does not require measurement of amount needed for each wash load⁹. Heavy-duty laundry detergent, commonly available in powder and liquid form, is capable of removing deposition of heavy soil from textiles through washing process¹⁰. Heavy-duty laundry detergent generally has higher concentration as compared to light-duty laundry detergent, therefore it is commonly used in washing machines¹. Table 1 and Table 2 show the typical formulations for unbuilt and built heavy-duty laundry liquid detergent (HDLD)¹¹.

2 Market Overview of Detergents

The major companies in detergent market include Procter & Gamble, Unilever, Henkel, Lion Corporation, Kao

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Accepted April 7, 2021 (received for review March 2, 2021)
Journal of Oleo Science ISSN 1345-8957 print / ISSN 1347-3352 online
http://www.jstage.jst.go.jp/browse/jos/ http://mc.manuscriptcentral.com/jjocs
Corporation, Church & Dwight, Johnson and Son, Colgate-Palmolive, and Amway Corporation.  

2.1 Global

In year 2016, the demand for laundry detergent market had reached USD 133.3 billion globally and it was anticipated for a compound annual growth rate (CAGR) of about 4.9% from year 2017 to 2025, and to exceed a total revenue of USD 205.2 billion by year 2025. Among all products, powder detergent had the biggest market share, accounting for more than 31% of the total revenue in year 2016. Among all applications, household application occupied the largest share with an expected demand of over USD 118 billion by year 2025, growing at a CAGR of 4.9%.

Figure 1 shows the global market share of laundry detergent by region in year 2016.

Table 1  Typical Formulation for Unbuilt HDLD.

<table>
<thead>
<tr>
<th>Components</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonionic surfactant</td>
<td>20-40</td>
</tr>
<tr>
<td>Anionic surfactant</td>
<td>10-30</td>
</tr>
<tr>
<td>Triethanolamine</td>
<td>0-8</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0-7</td>
</tr>
<tr>
<td>Fluorescent whitening agent</td>
<td>0.2-0.4</td>
</tr>
<tr>
<td>Perfume</td>
<td>0.05-0.1</td>
</tr>
<tr>
<td>Dye</td>
<td>q.s.</td>
</tr>
<tr>
<td>Water</td>
<td>to 100</td>
</tr>
</tbody>
</table>

Table 2  Typical Formulation for Built HDLD.

<table>
<thead>
<tr>
<th>Components</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonionic surfactant and/or anionic surfactant</td>
<td>5-15</td>
</tr>
<tr>
<td>Builder</td>
<td>20-30</td>
</tr>
<tr>
<td>Sodium silicate</td>
<td>2-5</td>
</tr>
<tr>
<td>Polymeric stabilizers</td>
<td>0-2</td>
</tr>
<tr>
<td>Sodium xylene sulfonate</td>
<td>0-5</td>
</tr>
<tr>
<td>Emulsifying agents</td>
<td>0-2</td>
</tr>
<tr>
<td>Sodium carboxymethylcellulose</td>
<td>0-2</td>
</tr>
<tr>
<td>Fluorescent whitening agent</td>
<td>0.2-0.4</td>
</tr>
<tr>
<td>Perfume</td>
<td>0.05-0.1</td>
</tr>
<tr>
<td>Dye</td>
<td>q.s.</td>
</tr>
<tr>
<td>Water</td>
<td>to 100</td>
</tr>
</tbody>
</table>

Fig. 1  Global market share of laundry detergent by region in year 2016.

including China, India, and Brazil as the consumers in these countries would prefer economical products. There is also a large percentage of population based in rural areas that would prefer powder detergent than other products.

Liquid detergent is likely to have a higher growth rate as compared to powder detergent due to large-scale adoption in North America and Western Europe countries. Liquid detergent is more convenient and comfortable to use as compared to powder detergent. The market growth of liquid detergent in Asia Pacific, North America, and Europe are expected to be 5.9%, 4.6%, and 4.5% respectively during year 2019 to 2025.

Detergent in tablet form is likely to observe slow growth and decreasing trend in market share by year 2025. This is because tablet detergent is less popular as compared to rising demand of liquid products in developed economies and great penetration of powder products in developing countries.

2.2 Asia Pacific

The laundry detergent market in Asia Pacific had achieved USD 34.5 billion in year 2019, which had significant contribution in the growth of the global laundry detergent market. China, being the major market in Asia Pacific, accounted for about 70% of the contribution. In coming few years, India is expected to grow more rapidly as compared to China. Hence, China and India are the market leaders that have major effect on Asia Pacific laundry detergent market with their rising demand.

Detergent in tablet form is leading in Asia Pacific region with expected robust growth of liquid products in coming years due to its convenience and ease to use. The driving forces of Asia Pacific laundry detergent market include rapid urbanization and changing lifestyles of people, growing in both middle-class population and their disposable incomes, growing public awareness on health and hygiene, and growth of tourism and hospitality industries.
3.2 Oleo-based fatty alcohol ethoxylates (FAE)

Oleo-based fatty alcohol ethoxylates (FAE) are non-ionic surfactant produced from the reaction of fatty alcohol and ethylene oxide with the presence of alkaline catalysts\(^1\). FAE are commonly used as foaming agent in personal care, wetting agent in detergent, and surfactant in household and industrial products\(^2\). Figure 3 shows the chemical structure of FAE.

3.3 Oleo-based fatty alcohol ether sulfates (FAES)

Oleo-based fatty alcohol ether sulfates (FAES) are produced with addition of ethylene oxide to fatty alcohol, followed by sulphation of fatty alcohol ethoxylates, then neutralized using different alkaline\(^3\). FAES are highly water soluble, less sensitive to hard water, more stable in alkaline environment, have good rheological behaviour, good foaming ability, and better skin compatibility\(^4,5\). They have wide application in heavy-duty and light-duty detergents, personal care products, and industrial cleaners\(^6\). Owing to their low skin irritation property, FAES are suitable to be used in formulation of baby products\(^7\). Figure 4 shows the chemical structure of FAES.

3.4 Oleo-based methyl ester ethoxylates (MEE)

Oleo-based methyl ester ethoxylates (MEE) are non-ionic surfactant produced from the reaction of methyl ester and ethylene oxide under calcium or magnesium based catalysts\(^8\). The properties of MEE are similar with FAE except for having lower foaming power and being less skin irritating\(^9\). MEE are common alternative detergent product to FAE owing to their lower cost\(^10\). However, the poor hydrolytic stability of MEE in alkaline environment and lack of gel phase limit their application in some powder and liquid detergent formulations\(^11\). The lack of gel phase was due to terminal methoxy group in MEE that reduces their hydrogen bonding and subsequently reduces their solubility in water and their tendency to form aqueous gels\(^12\). Despite that, MEE may be useful in reducing the gelling of aqueous solution in formulation of liquid products\(^13\). Figure 5 shows the chemical structure of MEE.
3.5 Oleo-based methyl ester sulfonates (MES)

Oleo-based alpha methyl ester sulfonates (α-MES) are anionic surfactant mainly derived from palm oil based methyl ester. The manufacturing process of α-MES is relatively simple and requires lower manufacturing cost as compared to LABS, the workhorse of detergent industry which are derived from petrochemicals. Due to the inexpensive feedstock of α-MES, the cost of a α-MES plant would be only around one fifth of that required to produce LABS on an equal capacity basis. α-MES have several advantages as compared to LABS which include greater detergency with less dosage, greater biodegradability, higher tolerance to hard water, lower toxicity to environment, better skin compatibility, and good return on investment owing to the low manufacturing cost.

Figure 6 shows the chemical structure of α-MES.

3.6 Sophorolipids

Sophorolipids are one of the nonionic glycolipid surfactants, produced by non-pathogenic yeast such as Candida bogoriensis, Candida bombicola, and Candida apicola. Sophorolipids can be widely applied in various industries such as cosmetics, food, cleaning, and petroleum industry. For instance, Ecover Belgium, MG Intobio Co. Ltd, and Synthexyme LLC have included sophorolipids as surfactant in some of their formulation in producing variety of products. In Table 3, the Krafft points of some surfactants were listed. It can be observed that although the Krafft point of α-MES is higher than LABS, their Krafft point is still lower than FAS. Hence, α-MES surfactants are less soluble than LABS but are more soluble than FAS.

4 MES and Its Performance in Liquid Detergent Formulation

The performance of surfactants in liquid detergent formulation can be determined by looking at the following properties which include solubility, viscosity, phase stability, tolerance in hard water, detergency, wettability, foaming ability, biodegradability, and eco-toxicity. Emphasis will be given on the performance of α-MES as compared to LABS, the workhorse of detergent industry.

4.1 Solubility

The solubility of surfactants depends on their individual Krafft point. Krafft point is the temperature where the solubility of an ionic surfactant is equal to its critical micelle concentration (CMC). At temperature below Krafft point, surfactants will form precipitates instead of micelle, which result in less effective performance of surfactants in cleaning. The Krafft points of α-MES surfactants are in the range of 10.1°C to 24.8°C depending on their carbon chain length while it is 65°C for their di-salt. Therefore, with higher Krafft point and presence of large amount of di-salt, significant amount of precipitates will form and reduce the solubility of surfactant, result in poorer quality of α-MES.

In Table 3, the Krafft points of some surfactants were listed. It can be observed that although the Krafft point of α-MES is higher than LABS, their Krafft point is still lower as compared to FAS. Hence, α-MES surfactants are less soluble than LABS but are more soluble than FAS.

4.2 Viscosity

Viscosity, defined as the resistance against deformation for a fluid, varies between different fluid. Viscosity is used to measure the thickness of a fluid to make sure it is not too thick to pour nor too thin to appear watery. Viscosity can be measured using rheometer. Detergent within a certain range of viscosity has more pourable flow without the need to modify the detergent formulation. It was re-

Table 3 Krafft points of some surfactants.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Krafft Point (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LABS (C₁₀/C₁₆)</td>
<td>8/13</td>
<td>Dobson et al.</td>
</tr>
<tr>
<td>α-MES (C₁₀/C₁₆)</td>
<td>10.1/24.8</td>
<td>Yavrukova et al.</td>
</tr>
<tr>
<td>FAS (C₁₂/C₁₆)</td>
<td>26/36/56</td>
<td>Zelmer</td>
</tr>
</tbody>
</table>

- MES and Its Performance in Liquid Detergent Formulation

- 4.1 Solubility

- 4.2 Viscosity
ported that viscosity build-up issue is very common when it comes to incorporation of α-MES surfactant in formulation of liquid detergent.

4.3 Phase stability

Liquid detergent has to be fluid, homogeneous and phase-stable across storage conditions. Phase stability is an essential criterion in liquid detergent formulation and therefore phase separation that will result in shorter shelf life must be prevented. In addition, it will also result in poor quality of liquid detergent and negative impact in consumers’ acceptance. Phase stability test can be evaluated by placing 300 mL of liquid detergent in a 500 mL plastic jar with sealed cap for at least 48 hours at 5°C, 25°C, and 40°C respectively under atmospheric pressure. If the liquid detergent did not split into layers or split into layers with major layer consists of at least 95% of the composition by weight, then it is considered as phase stable. It was reported that phase stability is one of the commonly associated issues with the formulation of α-MES in liquid detergent. Generally, hydrotropes are often added to the liquid detergent composition to prevent phase separation. Surfactants that preferred for use in liquid detergent formulation are those with low CMC and cloud points. The cloud point of a detergent is the temperature at which a detergent solution passes from an isotropic micellar system into a two-phase system. The cloud points of some surfactants including α-MES are shown in Table 4.

4.4 Tolerance in hard water

Tolerance of surfactants in hard water is evaluated by their ability to tolerate the water hardness ions, which are calcium and magnesium ions, commonly present in hard water. The water hardness ions might cause precipitation of surfactants and hence affect their performance. Surfactants that have higher tolerance and are less sensitive to these water hardness ions generally have better detergency than the other. Michael Shea stated that α-MES have higher detergency and higher tolerance in hard water as compared to LABS. Figure 7 shows the detergency of α-MES and LABS on different types of soil in different water hardness in terms of cumulative soil removal index. The types of soil were listed in Table 5 together with the fabric used. It can be easily observed that the detergency

| Table 4 | Cloud point of some surfactants. |
|-----------------|-----------------|-----------------|
| Surfactant   | Cloud Point (°C) | Reference         |
| LABS         | – 3 – 11         | Cohen et al.45    |
| α-MES        | 20 – 26          | Cohen et al.45    |
| MEE          | 53 – 62          | Kolane et al.29   |
| FAE          | 78.5             | Kolane et al.29   |

| Table 5 | Types of soil and fabric used to measure the detergency of α-MES and LABS. |
|-----------------|-----------------|-----------------|
| Swatches   | Soil             | Fabric          |
| JB-01       | Mineral oil, carbon black | Cotton          |
| JB-02       | Egg yolk         | Cotton          |
| JB-03       | Sebum, pigment   | Cotton          |
| W20D        | Sebum, pigment   | Polyester/Cotton |
| W20PF       | Vegetable oil, pigment | Polyester/Cotton |

Fig. 7 Detergency of α-MES and LABS on different types of soil in different water hardness.
of α-MES is always better than LABS regardless of the types of soil and the water hardness. Hence, it was proven that α-MES have higher tolerance in hard water than LABS.

4.5 Detergency

Detergency of surfactants is defined as their capability to remove soil from fabric during cleaning process. The detergency test for detergent with different formulations can be evaluated by the washing of artificially soiled swatches either through standard top loading washing machine or Terg-O-Tometer. The reflectance of original unsoiled swatches and the reflectance of swatches before and after washing were measured using Minolta spectrophotometer. The values were then used to calculate the detergency of different detergent formulations using Equation 1.

\[
\text{Detergency} = \left( \frac{\text{AW} - \text{BW}}{\text{OC} - \text{BW}} \right) \times 100
\]

where AW is the reflectance of swatches after washing, BW is the reflectance of swatches before washing, and OC is the reflectance of original swatches before soiling. Researches shown that α-MES have better detergency than LABS and require less concentration of surfactant to achieve comparable detergency. The detergency of α-MES and LABS in terms of cumulative soil removal index can also be observed in Fig. 7. By looking at the value of cumulative soil removal index, it was proven that no matter at which level of water hardness, the detergency of α-MES is always better than LABS regardless of the types of soil.

4.6 Wettability

Wettability is the degree of wetting to measure the ability of a liquid to spread on a solid surface or on another immiscible liquid. Wettning test can be conducted by dropping a 2 cm × 2 cm unsoiled cotton swatch, conditioned at relative humidity of 20% for 24 h, using a pair of tweezers, into the prepared 100 mL round container consists of 0.1% detergent solution and record the time taken for complete immersion of solution. The time taken for the unsoiled cotton swatch to have complete immersion in α-MES and LABS detergent solution at different water hardness is shown in Table 6. It can be observed that α-MES takes longer time to completely immerse into the unsoiled cotton swatch than LABS, which means the wettability of α-MES is weaker than LABS.

### Table 6

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Water Hardness (ppm)</th>
<th>Time Taken (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LABS</td>
<td>150</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>300</td>
</tr>
<tr>
<td>α-MES</td>
<td>150</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>300</td>
</tr>
</tbody>
</table>

4.7 Foamability

Foamability, which include foam producing power, foam stability, and foam durability, is commonly used to characterize stable foam. Foamability is a measure of foam volume immediately after the generation of foam, while foam stability is a measure of the lifetime of the foam. The foamability test can be conducted by filling 200 mL of 0.1% detergent solution into a 500 mL measuring cylinder and perform constant rate stirring for 30 times using a glass rod with perforated base to generate foam. The initial volume of foam generated was recorded as the foamability of detergent solution. After 5 minutes, the final volume of foam was recorded and the rate of decay is the foam stability. Table 7 shows the initial foam height at t = 0 min and the foam height at t = 5 min of α-MES and LABS, measured in mm. It can be observed that the foamability of α-MES is weaker but comparable with the foamability of LABS.

### Table 7

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Foam Height (mm) (t = 0 min)</th>
<th>Foam Height (mm) (t = 5 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LABS</td>
<td>190</td>
<td>135</td>
</tr>
<tr>
<td>α-MES</td>
<td>170</td>
<td>115</td>
</tr>
</tbody>
</table>

4.8 Biodegradability

Biodegradation is a process where microorganisms undergo series of enzymatic reaction to break down the organic substances into less complex chemicals include carbon dioxide, water, and biomass. To measure the biodegradability of detergent solution, Closed Bottle Test was carried out following the Organisation for Economic Co-operation and Development (OECD) Guidelines. In this test, the dissolved oxygen (DO) content of two bottles contained certain amount of active sludge, one with and one without detergent solution, was measured. The biodegradation profile was then developed by using the measured DO content over a 28-days period at 22-25°C. To qualify as readily biodegradable, 60% biodegradation should be reached within 28 days under aerobic conditions.
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4.9 Eco-toxicity

Eco-toxicity, also can be referred as aquatic toxicity, is a measurement of toxicity of detergent solution when discharged into aquatic environment\(^{(41, 48)}\). Eco-toxicity of detergent solution can be determined using Fish Acute Toxicity Test, which is also under OECD Guidelines\(^{(48)}\). The test was conducted in two stages, the first stage is the range-finding test and the second stage is the definitive test\(^{(48)}\). In the first stage, the fish were exposed to varying concentration of detergent in logarithmic series for a period of 24 h\(^{(48)}\). The concentration where there is no mortality and where there is 100% mortality was recorded and was utilized in the second stage where the fish were exposed to varying concentration of detergent in geometric series and the mortalities were recorded respectively at period of 24, 48, 72, and 96 h\(^{(48)}\). The concentration of detergent that killed 50% of the fish, labelled as LC\(_{50}\), was determined and the eco-toxicity was rated based on a rating scheme from the U.S. Fish and Wildlife Services\(^{(48)}\). Table 9 shows the LC\(_{50}\) of LABS and \(\alpha\)-MES on Tilapia nilotica\(^{(46)}\). It was proven that \(\alpha\)-MES have lower eco-toxicity as the LC\(_{50}\) for \(\alpha\)-MES is higher than LAS, which means it requires higher concentration of \(\alpha\)-MES to kill 50% of the fish.

<table>
<thead>
<tr>
<th>Surfactants</th>
<th>Percentage of degradation (Duration)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LABS (C(<em>{10})/C(</em>{13}))</td>
<td>70 % (13 days)</td>
<td>Ishak \textit{et al.} (^{(50)})</td>
</tr>
<tr>
<td>FAS</td>
<td>100 % (1 day)</td>
<td>Swisher(^{(45)})</td>
</tr>
<tr>
<td>FAES</td>
<td>95-98 % (5 days)</td>
<td>Steber \textit{et al.} (^{(52)})</td>
</tr>
<tr>
<td>FAE (Linear)</td>
<td>&gt; 80 % (28 days)</td>
<td>Kravetz \textit{et al.} (^{(44)})</td>
</tr>
<tr>
<td>FAE ( Branched)</td>
<td>40 % (28 days)</td>
<td>Kravetz \textit{et al.} (^{(54)})</td>
</tr>
<tr>
<td>(\alpha)-MES (C(<em>{12}/C</em>{14}/C_{16}))</td>
<td>&gt; 90 % (8 days/14 days/26 days)</td>
<td>Ishak \textit{et al.} (^{(50)})</td>
</tr>
</tbody>
</table>

Table 8 readily biodegradability of some surfactants under aerobic conditions.

<table>
<thead>
<tr>
<th>Surfactants</th>
<th>LC(_{50}) (mg/L), 96 h</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAS (C(<em>{10})/C(</em>{13}))</td>
<td>11.4</td>
<td></td>
</tr>
<tr>
<td>MES (C(<em>{12}/C</em>{14}/C_{16}))</td>
<td>22.6/12.6/56.6</td>
<td></td>
</tr>
</tbody>
</table>

Table 9 LC\(_{50}\) of LABS and \(\alpha\)-MES on Tilapia nilotica\(^{(45)}\).

5 Application of Palm Oil Based \(\alpha\)-MES in Formulation of Liquid Detergent

The application of palm oil based \(\alpha\)-MES in formulation of powder detergent has been successfully developed by a number of researchers. Besides that, palm oil based \(\alpha\)-MES has also been used in the formulation of liquid products such as household cleaning product, personal care, laundry, and industrial cleaning product.

In year 2007, a patent was published by World Intellectual Property Organization on the process for manufacturing liquid detergent containing \(\alpha\)-MES\(^{(50)}\). The first step is to form a liquid detergent partial composition in the first vessel which has a pH of 5 to 9\(^{(56)}\). The second step is to adjust the pH to make sure it is in the range of 7 to 9\(^{(56)}\). Then, about 0.5% to 15% of \(\alpha\)-MES is added with mixing to form liquid detergent at temperature of about 20°C to 60°C\(^{(56)}\). The detailed ingredients used in the liquid detergent formulation can be found in the patent.

In year 2010, a US patent regarding laundry detergent containing \(\alpha\)-MES was published\(^{(57)}\). Successful formulation of liquid laundry detergent with great cleaning performance and stability was developed using \(\alpha\)-MES with higher level of di-salt, and the color of \(\alpha\)-MES can be reduced by carrying out a more rigorous bleaching step\(^{(57)}\). The liquid laundry detergent shall consists of about 6% to 35% of surfactant, where the ratio of C\(_{16}\) \(\alpha\)-MES to total surfactant is preferably less than 0.2\(^{(58)}\). The detailed formulation can be found in the patent.

In year 2014, R & D Department from Lion Eco Chemicals Sdn Bhd presented MES Technical Presentation for Liquid Detergent. It shows that MIZULAN, which is one of the \(\alpha\)-MES surfactants, has superior detergency as compared to LABS and FAS\(^{(58)}\). The detergency of \(\alpha\)-MES on sebum is excellent compared to AES and LABS under different concentration of surfactant, different water hardness, and different temperature\(^{(50)}\). \(\alpha\)-MES have good enzyme compatibility, anti-soil deposition property, and biodegradability\(^{(58)}\).

In year 2017, Maurad \textit{et al.} \(^{(43)}\) had successfully formulated five palm-based liquid detergents (PBLDs) with clear appearance, single phase, and pourable viscosities using C\(_{16}/18\) \(\alpha\)-MES as surfactant. There are a few important points to take note, where the heat sensitive ingredients including optical brightener, enzyme, preservative, and fragrance should be added in the cooling stage, and the pH of the de-
tergent solution should be maintained below 10 to prevent increase of hydrolysis rate that would affect the stability of liquid detergent. Study has shown that the PBLDs possess excellent detergency in removal of oil based stains and protein based stains, similar foamability and foam stability, and greater wettability and biodegradability as compared to the commercial liquid detergent.

In year 2018, Tai et al. had formulated a dishwashing liquid detergent with α-MES surfactant. It was shown that the α-MES solution was stable and did not hydrolyse obviously at pH range of 4 to 9, while at pH larger than 10, the hydrolysis occurs. α-MES and LABS both have good foam stability, however the foamability of α-MES is slightly weaker than LABS, hence it is suitable in application of detergent formulation that requires low foam. Study shown that α-MES have better calcium soap dispersing power, greater tolerance in hard water, and better detergency as compared to LABS. The prepared dishwashing detergent using α-MES in this research had been proven to exhibit good stability with no phenomenon of flocculation or stratification observed after storing for 6 months.

In year 2019, Djohan et al. had synthesized α-MES surfactant from purified waste cooking oil and combined with ZnO nanoparticles to produce nanofluid detergent. The stability and detergent performance of the nanofluid detergent with constant ZnO concentration of 0.1% and varying α-MES concentration of 10%, 12.5% and 15% were discussed. The stability test was conducted 24 h after synthesis of nanofluid detergent, which shows that nanofluid detergent that contains 15% α-MES concentration has the highest stability. On the other hand, the detergency test was also carried out, with and without UV lamp that helps to activate the nanoparticles to degrade methylene blue. It was shown that the nanofluid detergent with 15% α-MES concentration has the best performance, with and without the presence of UV lamp, among all. With the presence of UV lamp, the performance for all nanofluid detergents had improved.

In year 2019, Permadani and Slamet had also synthesized α-MES surfactant from purified waste cooking oil and combined with carboxymethyl cellulose and TiO2 nanoparticles to form nanofluid detergent. The detergent stability and performance were tested with constant concentration of TiO2 nanoparticles at 0.1% and varying concentration of α-MES surfactant as well as carboxymethyl cellulose. The results show that nanofluid detergent is stable with the concentration of α-MES above 1.1 wt%. The detergent performance increases with increase concentration of α-MES surfactant. With the presence of mercury lamp that activates TiO2 nanoparticles for stain degradation, the performance of nanofluid detergent achieves further improvement. It was shown that with the addition of 4% carboxymethyl cellulose, the stability of the nanofluid detergent can be improved while maintaining the optimum detergent performance.

6 Technical Issues Associated with Palm Oil Based α-MES in Heavy Duty Laundry Liquid Detergent (HDLD) Formulation and Possible Methods to Overcome the Technical Issues with Enhanced Formulation

α-MES was not extensively used in the formulation of HDLD due to some of the technical issues regarding phase stability and viscosity build-up of liquid detergent upon prolonged storage. The technical issues and possible methods to overcome with enhanced formulation are discussed in this section.

6.1 Phase stability

It was reported in some of the researches that phase stability issue of liquid detergent formulated with α-MES surfactant may occur at lower temperature, at higher pH and upon prolonged storage. This is one of the challenges when formulating liquid detergent with α-MES surfactant. Through years of researches, some possible methods to overcome the phase stability issue with enhanced formulation have been proposed.

One of the methods is to incorporate appropriate hydro trope to the formulation that may display synergism with palm based α-MES and is expected to produce a phase stable HDLD formulation with acceptable viscosity. However, these hydrotropes might be expensive and require great quantity in some formulations. Hence, the cost effectiveness of the formulation shall also be taken into consideration besides studying the synergistic effect between α-MES and hydro trope as well as the resulting performance of liquid detergent.

Another US patent had suggested the addition of inorganic salts, for example formaldehyde-cross-linked hydrolyzed polyacrylonitrile into the liquid detergent formulation to improve the phase stability.

Morigaki et al. had published a patent on methods to formulate a phase stable liquid detergent with α-MES. The liquid detergent should contain α-MES, an alkylbenzene sulfonate, a polyoxyethylene alkyl ether sulfate, and an alkanolamine. Following the mass ratio mentioned in the patent, the improved phase stability of liquid detergent under low temperature of about −20°C to room temperature was proven.

Lion Eco Chemical Sdn. Bhd. had also proposed another enhanced formulation using 15% α-MES-Na, 5% alkanolamine, preferably monoethanolamine, and control the pH to 7.5 using sulphuric acid to produce clear and free flowing liquid detergent without phase separation. It was shown that the solubilisation temperature had decreased from 34°C to 22°C.
Regarding the phase stability issue due to higher pH, Maurad et al.\(^\text{43}\) and Tai et al.\(^\text{40}\) had reported that hydrolysis occurred at pH above 10 and it is stable at pH range of 4 to 9. On the other hand, some ingredients that were sensitive to the order of addition into the formulation will also contribute to the phase stability issue of formulation. Hence, Maurad et al.\(^\text{43}\) suggested to add ingredients that were sensitive to heat in the cooling stage and to control the pH of the formulation below 10.

### 6.2 Viscosity
Viscosity build-up issue was reported in some studies when it comes to formulation of liquid detergent with α-MES surfactants especially when high concentration of α-MES is used. Viscosity is a significant factor to be considered when developing liquid detergent formulation because high viscosity will cause issue in stability and flow of liquid while low viscosity will lead to mechanical loss of detergent during washing process using machine\(^\text{48}\). There are some proposed methods to modify the viscosity of liquid detergent formulation.

Viscosity modifier is commonly used in formulation of liquid detergent to modify the viscosity of a composition to achieve desired viscosity. Branched non-ionic surfactant and water-soluble metal salt were some of the viscosity modifier used in the industry\(^\text{49}\). Another patent from World Intellectual Property Organization mentioned that an active blend of alkyl polyglucosides and alcohol ethoxylates can also act as viscosity-reducing agent\(^\text{50}\).

### 7 Conclusion
With increasing consumer awareness on the environmental issues caused by LABS, the workhorse in detergent industry, demand in development of green surfactants aroused. α-MES, an anionic surfactant derived from palm oil based methyl ester, is one of the promising and potential candidates to substitute LABS. This is owing to its lower manufacturing cost, greater detergency with less dosage, greater biodegradability, higher tolerance to hard water, and lower eco-toxicity as compared to LABS. α-MES had been successfully incorporated in heavy-duty laundry powder detergent formulations as a sole surfactant for years. There are also some successful incorporation of α-MES in some of the liquid detergent formulations in recent years. Although there were some technical issues associated with the phase stability and viscosity build-up issues when incorporating α-MES in liquid detergent formulations, many researches had worked on the methods to overcome these technical issues to make it possible. To address the phase stability issue, hydrotrope, inorganic salts, and enhanced formulations are introduced and are proven effective. To address the viscosity build-up issue, viscosity modifiers are introduced to the formulation as well. Hence, there is huge potential for α-MES to replace LABS in near future.

### Acknowledgment
This work was funded by Xiamen University Malaysia Research Fund (Grant no. XMUMRF/2019-C3/ENG/0012).

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