



## METHYL ESTER SULFONATE PRODUCTS

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### ABSTRACT

Sulfonation studies conducted on a variety of methyl ester feedstocks, derived from coconut, palm kernel, palm stearin, tallow and soya are described. These feedstocks are of general interest because they are derived from renewable oils and as a class methyl ester sulfonates have superior detergent and environmental properties. The studies were performed at the pilot plant scale in continuous processing equipment specifically designed for making methyl ester sulfonates. The feedstock, intermediates and resulting product characteristics and compositions are discussed. Important process conditions are also discussed starting from the initial sulfonation to the final concentrated or ultra-concentrated product.

### RÉSUMÉ

Les études de sulfonation réalisées sur des stocks d'alimentation à base d'éther méthylique dérivés des noix de coco, des noix de palmier, de stéarine de palmier, de suif et de soja sont décrites. Ces stocks d'alimentation présentent un intérêt général étant donné qu'ils sont dérivés d'huiles renouvelables et dans cette catégorie, les sulfonates à base d'éther méthylique ont des propriétés détergentes supérieures et sont favorables à l'environnement. Les études ont eu lieu à l'usine pilote à l'aide d'un équipement de traitement continu spécialement conçu pour la fabrication d'éther méthylique. Les

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caractéristiques du stock d'alimentation, les produits intermédiaires et les produits qui en résultent ainsi que leur composition font l'objet de la discussion. Les conditions importantes du processus font aussi partie de la discussion, à partir de la sulfonation initiale jusqu'au produit final, lequel est concentré ou super-concentré.

## ZUSAMMENFASSUNG

Beschrieben werden Untersuchungen der Sulfurierung von verschiedenen Methylester-Futterprodukten, erzeugt aus Kokosnuss, Palmkern, Palmstearin, Talg und Soja. Diese Futterstoffe sind allgemein von Interesse, da sie aus erneuerbaren Ölen erzeugt werden, und Methylester-Sulfonate insgesamt haben vorteilhafte waschaktive und umweltfreundliche Merkmale. Die Untersuchungen wurden im Rahmen eines Pilotwerkes an dauerbetriebenen Fertigungsanlagen speziell zur Erzeugung von Methylester-Sulfonaten durchgeführt. Die Merkmale und Zusammensetzung der Futterstoffe, Zwischen- und Endprodukte werden diskutiert. Wichtige Verarbeitungsbedingungen werden ebenfalls beschrieben, von der ersten Sulfurierung bis hin zum endgültigen, konzentrierten oder ultrakonzentrierten Produkt.

## INTRODUCTION

Much of the recent work in the area of methyl ester sulfonates (MES) has focused on highly hydrogenated and refined methyl ester feedstock.<sup>1</sup> As the market for MES matures, developing a product database for a wide variety of feedstocks is of interest, especially when one considers the manufacturing costs associated with improving feedstock quality. Less refined feedstocks from natural and renewable sources are particularly interesting. With this in mind two of the feedstocks discussed have iodine values greater than 1.0 as well as interesting carbon-chain distributions. This study was performed with process equipment using a series of dominant bath and plug flow operations. Sulfonation was accomplished in an annular falling film reactor (FFR) with a dominant bath recycle loop followed by plug flow digestion at elevated temperature. The color of the dark sulfonic acid is then reduced in a continuous hydrogen peroxide acid bleaching system where the components are admixed in a loop and further bleached in a plug flow vessel.

The light colored bleached methyl ester sulfonic acid is neutralized to a controlled pH and sent to a stripper or dryer as required. MES concentrated pastes may be dried to form flakes or needles (>90% active), which are easy to store and transport and are readily processed to a powder by milling or grinding. The powdered MES has excellent properties for agglomeration in detergent granules and tablets. The process technology to make concentrated and ultra-concentrated forms of the product has been commercialized and is becoming more widely applied as economic and environmental factors are understood.<sup>2</sup> Availability of raw materials for conversion to MES is increasing, particularly palm oil which is growing at a rate of almost 3% per year. Demand for palm oil is expected to exceed soya as number one shortly after 2005.<sup>3</sup>

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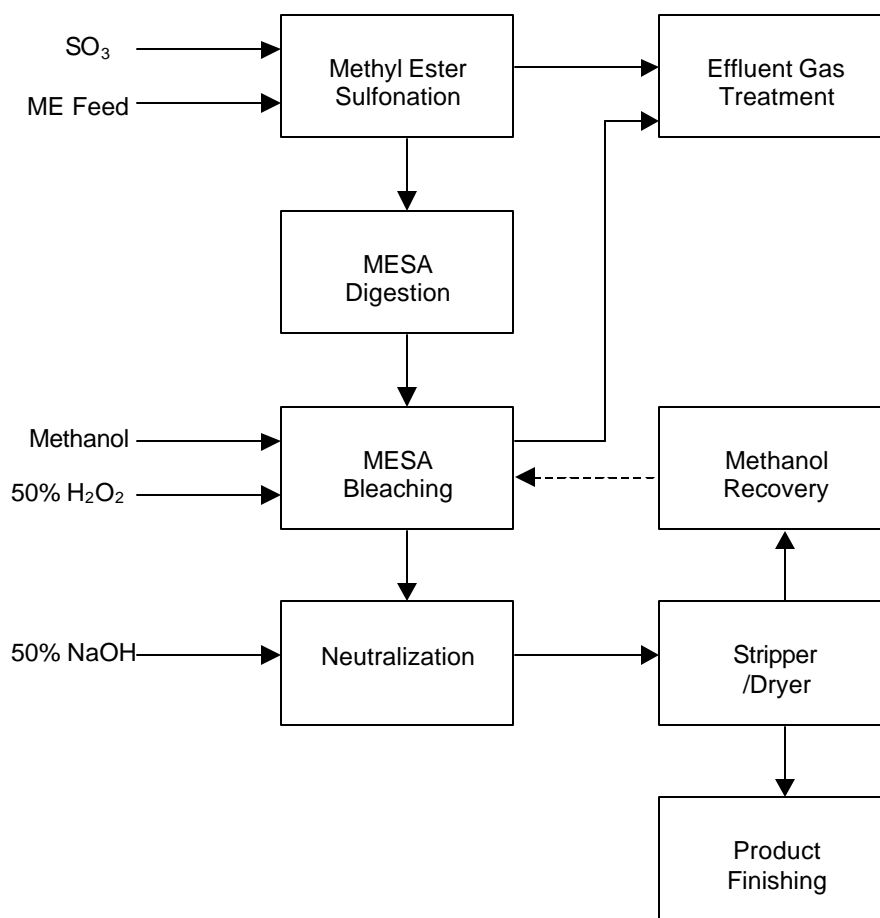
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## PROCESS

The preferred continuous process for manufacturing concentrated and ultra-concentrated MES is illustrated in Figure 1 and described in detail elsewhere.<sup>4,5,6</sup> Sulfur trioxide ( $\text{SO}_3$ ) diluted with air is typically supplied from a sulfur-burning unit coupled to a sulfur dioxide ( $\text{SO}_2$ ) to  $\text{SO}_3$  converter. The sulfonation is done in an annular FFR with a sulfonic acid recycle system that reduces the effluent gas particulate load by utilizing a high-efficiency cyclone. The reactor is continuously cooled with a large flow of tempered water through external jacketing. The sulfonation is carried out at process temperatures higher than are typical when making

other anionic surfactants. The methyl ester sulfonic acid (MESA) is discharged from the loop and passes through a plug-flow digester where the MESA temperature is maintained at  $85^\circ\text{C}$  for 0.7 hours.

**Figure 1: Continuous Process for the Manufacture of (Ultra-)Concentrated MES**



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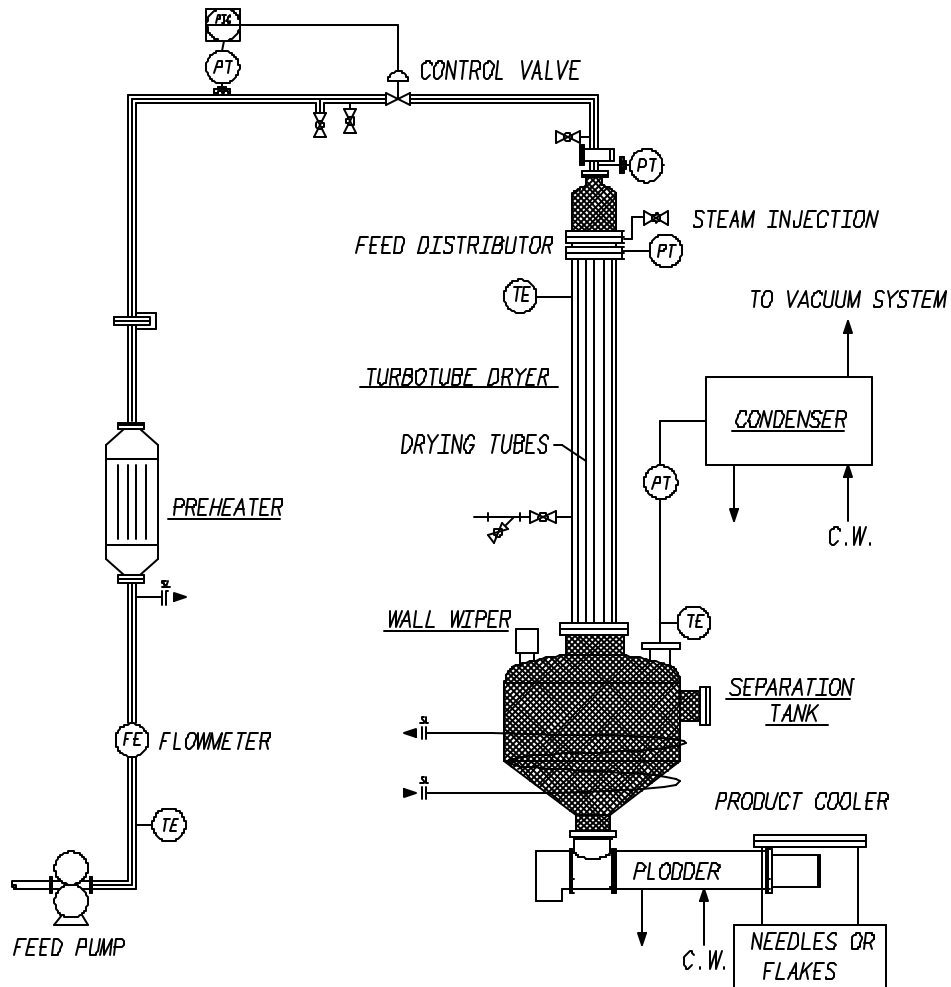
The aging process in the digester completes the sulfonation reaction but causes a four-fold increase in the color of the MESA. The digested MESA, methanol and dilute hydrogen peroxide are combined in a loop and the reaction mixture is passed through a methanol refluxing vessel where the bleaching of the MESA is completed (1-1.5 hours). The process temperature (95-100°C) in the bleaching vessel is controlled by heat transfer surfaces submerged in the reactants. The process pressure is independently controlled (<100 kPag). The non-condensable vapors discharged from the bleaching vessel are processed in an effluent gas treatment system. The bleached MESA is continuously neutralized with 50% sodium hydroxide to a pH of 5.5 to 7.5 at a temperature of 55°C. Any residual peroxide can be decomposed by the addition of a molar equivalent of sodium sulfite.<sup>7</sup> The neutral paste is transferred to a concentrating and / or methanol removal system. MES based on a methyl ester below a molecular weight of 245 is stripped rather than dried to remove the methanol making the concentrated product. Higher molecular weight MES is dried, removing both methanol and water, making the ultra-concentrated solid product forms. The recovered methanol is distilled and recycled back to the bleaching process. The stripper / dryer consists

of a supply system, a preheater, a proprietary dryer, a separation vessel, a product discharge device (typically a plodder), a vacuum system and an overhead condenser, Figure 2.<sup>8,9</sup> The MES product is powdered or diluted as appropriate for application in liquid, bar, granular, and tablet detergent products.

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Figure 2: Dryer for Ultra-Concentrated MES



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## METHYL ESTER

The coconut, palm stearin and tallow based methyl ester (ME) feedstocks used in this study are typical of commercially available material. The distillation cuts are narrow, mostly incorporating just two carbon numbers, Table 1. The iodine value (IV) for these three feedstocks is 0.3 or less. The IV of methyl esters is used as a measure to predict intermediate digested acid color and final bleached product color<sup>10</sup> but other components besides unsaturation have a significant influence.<sup>11</sup> The palm stearin methyl ester feedstock used in this study is a typical sulfonation feedstock for use in laundry detergent formulations.<sup>12</sup> For this palm stearin ME the C16 to C18 ratio is 2:1. MES with this carbon –chain distribution has a minimum Krafft point (17°C) and thus maximum solubility as compared to any other combination of C16 and C18.<sup>13</sup> This is a useful feature for formulating low temperature laundry detergents. For the tallow methyl ester feedstock used in this study the C16 to C18 ratio is 1:2. The Krafft point of the resulting sulfonate would be closer to 27°C. The coconut methyl ester feedstock used in this study has a C12 to C14 ratio of 2.5:1. The palm kernel methyl ester feedstock used in this study, Table 1, has an IV of 1.4 indicating about a 90% reduction in unsaturation by hydrogenation since the palm kernel oil is up to 19% oleic.<sup>14</sup> This particular feedstock has the complete carbon-chain distribution of the palm kernel oil. The C10 and lower methyl esters are usually stripped from the feedstock,<sup>15</sup> as the sulfonates of the corresponding methyl esters should not have good detergent properties. The unrefined nature of this feedstock would be reflected in its cost so it was of interest. The soya methyl ester feedstock used in this study, Table 1, has an IV of 1.1 indicating about a 99% reduction in unsaturation since soybean oil is about 30% oleic, 50% linoleic and 7% linolenic.<sup>16</sup> As expected the composition of this feedstock is almost 90% C18. This feedstock requires a relatively large amount of hydrogenation to reduce the IV to a sulfonatable level, but it represents a renewable source of predominately C18 methyl ester so it was of interest.

**Table 1: Methyl Ester Feedstocks and Quality Comparison**

|                                  | Coconut<br>C12-C14 | Palm<br>Kernel<br>C8-C18 | Palm<br>Stearin<br>C16-C18 | Tallow<br>C16-18 | Soya<br>C18 |
|----------------------------------|--------------------|--------------------------|----------------------------|------------------|-------------|
| Molecular weight                 | 222                | 227                      | 279                        | 287              | 295         |
| Iodine value (cg iodine/g ME)    | 0.1                | 1.4                      | 0.3                        | 0.1              | 1.1         |
| Carboxylic acid (wt%)            | 0.1                | 0.2                      | N/a                        | 0.1              | 1.0         |
| Acid value (mg KOH/g ME)         | 0.2                | 0.5                      | 0.4                        | 3.8              | 0.4         |
| Saponification no. (mg KOH/g ME) | 252                | 240                      | N/a                        | N/a              | N/a         |
| Freeze point (°C)                | 0                  | 18                       | 26                         | 31               | 33          |
| Moisture (wt%)                   | 0.03               | 0.03                     | 0.02                       | 0.04             | 0.01        |
| Carbon-chain length (wt%)        |                    |                          |                            |                  |             |
| <C10                             | 0.0                | 5.2                      | 0.0                        | 0.0              | 0.0         |
| C10                              | 0.0                | 4.4                      | 0.0                        | 0.0              | 0.0         |
| C12                              | 71.5               | 51.0                     | 0.2                        | 0.0              | 0.0         |
| C14                              | 28.0               | 15.1                     | 1.5                        | 3.1              | 0.0         |
| C16                              | 0.6                | 7.2                      | 65.4                       | 31.6             | 10.4        |
| C17                              | 0.0                | 0.0                      | 0.0                        | 1.2              | 0.0         |
| C18                              | 0.0                | 17.2                     | 32.2                       | 63.6             | 89.6        |
| >C18                             | 0.0                | 0.0                      | 0.7                        | 1.8              | 0.0         |

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## PRODUCT COMPOSITION

The product composition for the five methyl ester sulfonate examples are presented in Table 2. The MES products were analyzed principally based on the methods described by Battaglini.<sup>17</sup> Analysis of the sodium methyl sulfate content using the prescribed method yielded incorrect results for the lower molecular weight examples of MES in this study. The phenol red titration does not quantitatively determine the di-salt content. For the coconut and palm kernel based MES examples the results in Table 2 for the di-salt are presented as determined and the results for the sodium methyl sulfate are calculated by difference from 100 percent. The residual methanol content in the MES product was determined using a headspace sampling - gas chromatography technique utilizing internal standard and standard additions. The water content was determined by Karl Fischer potentiometric autotitration. The Klett color was determined using a Klett colorimeter with a #42 filter and a 40 mm path length at 5% active concentration. Note that in Table 2 the pure component - sodium methyl ester sulfonate - is designated as  $\alpha$ -Mes, as opposed to the composite MES.

**Table 2: Methyl Ester Sulfo nates**

| Wt%                                                         | Coconut<br>C12-C14 | Palm<br>Kernel<br>C8-C18 | Palm<br>Stearin<br>C16-C18 | Tallow<br>C16-18 | Soya<br>C18 |
|-------------------------------------------------------------|--------------------|--------------------------|----------------------------|------------------|-------------|
| Sodium methyl ester sulfonate ( $\alpha$ -Mes)              | 71.5               | 69.4                     | 83.0                       | 77.5             | 75.7        |
| Disodium carboxy sulfonate (di -salt)                       | 2.1                | 1.8                      | 3.5                        | 5.2              | 6.3         |
| Methanol (CH <sub>3</sub> OH)                               | 0.48               | 0.60                     | 0.07                       | 0.00             | 0.03        |
| Hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> )          | 0.10               | 0.04                     | 0.13                       | 0.15             | 0.05        |
| Water (H <sub>2</sub> O)                                    | 14.0               | 15.2                     | 2.3                        | 2.9              | 1.4         |
| Petroleum ether extractables (PEX)                          | 2.6                | 2.7                      | 2.4                        | 4.8              | 7.2         |
| Sodium carboxylate (RCOONa)                                 | 0.2                | 0.2                      | 0.3                        | 0.3              | 0.5         |
| Sodium sulfate (Na <sub>2</sub> SO <sub>4</sub> )           | 1.2                | 1.8                      | 1.5                        | 2.3              | 2.4         |
| Sodium methyl sulfate (CH <sub>3</sub> OSO <sub>3</sub> Na) | 8.0                | 8.4                      | 7.2                        | 7.7              | 2.5         |
| 10% pH                                                      | 5.0                | 5.3                      | 5.3                        | 5.4              | 5.8         |
| Klett color, 5% active ( $\alpha$ -Mes + di -salt)          | 30                 | 310                      | 45                         | 180              | 410         |

The coconut and palm kernel products were once-through steam stripped to a low level of methanol in pilot plant equipment. Typical desired level of residual methanol is 0.5 wt% or less. The steam to MES ratio is the primary factor in controlling the final methanol concentration in the stripped MES. Stripping MES versus drying leaves most of the water in the product, which results in a paste unless cooled to crystallization temperature. Drying low molecular weight (C12-14) MES produces a viscous paste that is difficult to crystallize and is not easily flaked or needled in the pure form. Typically, C12-14 MES is used in light duty liquid detergent products.<sup>18</sup> The stripped product of the coconut MES made in this study is of sufficiently low moisture for most formulation needs and can be diluted to a clear, low viscosity solution if necessary. Coconut MES bleaches effectively at a relatively low

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hydrogen peroxide addition rate to very low color (30 Klett). This is comparable to sulfonates of good quality linear alkyl benzene. It has been observed that MES of equal Klett reading to

LAS looks significantly lighter to the naked eye. The palm kernel MES was also stripped rather than dried, based on its low average molecular weight and carbon-chain distribution. This particular palm kernel ME has a high IV (1.4) and the resultant stripped MES has a Klett color of 310, Table 2. In other respects such as the PEX and di-salt content the product quality is equivalent to the coconut-based product. Unrefined palm kernel based MES may be of interest for formulating into detergent products in situations where feedstock costs are paramount. The palm stearin MES example shown in Table 2 has low color, low di-salt, and low PEX and with these parameters it can be readily formulated into both light and heavy-duty products, dry and liquid. In spite of the IV of 0.3 this feedstock produced very light colored MES. As a comparison the tallow based ME with an IV of 0.1 produced much darker MES (180 Klett). Previous work has noted that as the molecular weight of the ME increases so does the difficulty in bleaching.<sup>19</sup>

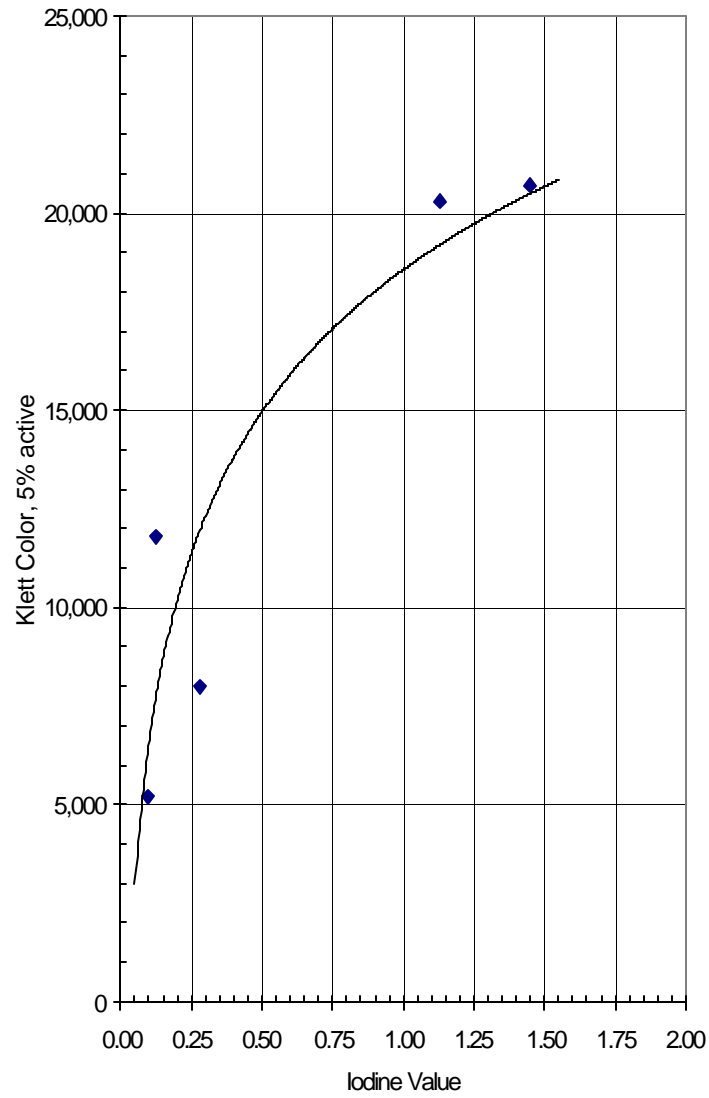
Several factors influence digested MESA color, including minor constituents in the ME,<sup>20</sup> SO<sub>3</sub> to ME mole ratio, post-sulfonation MESA digestion time and digestion temperature, degree of unsaturation measured as IV in the ME, and ME molecular weight.<sup>21</sup> The color of digested MESA is somewhat correlated with the IV of the starting ME, Figure 3. The color of the digested MESA is determined by sample dilution in 2-propanol to an appropriate concentration for an on-scale meter reading on the Klett colorimeter. The log fit of the data suggests that additional starting unsaturation does not linearly increase the color of the acid. The same effect is seen in reverse with bleaching, as the unsaturation is reduced, the color decreases more slowly as the bleaching progresses.

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**Figure 3: Effect of Iodine Value on Digested MESA Color**

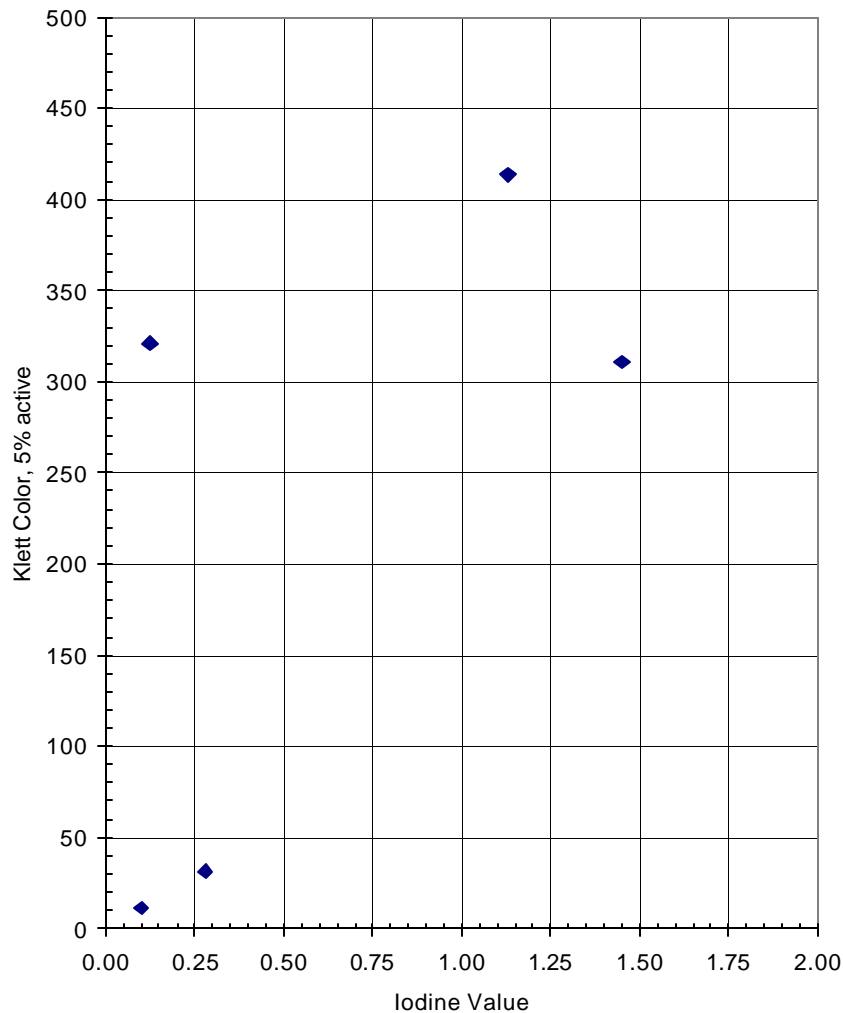


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The same factors that impact digested MESA color also effect the color of the final product. Additional factors affecting the product color are the level of bleaching agent (hydrogen peroxide preferred) addition, the level of methanol addition, the bleaching temperature and time, the neutralization temperature, and the dryer process temperatures. All of these process factors are well controlled in the technology available today. Figure 4 is a plot of the IV of the starting ME versus final product color for the five MES examples. The data shown in Figure 4 (MES product) shows more variability compared to the data shown in Figure 3 (digested MESA), this is due to the additional factors affecting the color of the MES product. Still the overall trend suggests that higher IV is deleterious to final product color.

**Figure 4: Effect of Iodine Value on Stripped / Dried MES Color**



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## PROCESS CONDITIONS

Sulfonation of methyl ester feedstocks in the pilot plant is performed in a tubular falling film reactor at a rate of about 0.1 kg-mole per hour. The reactor inlet  $\text{SO}_3$  gas concentration is 7 mole %. The reactor inlet gas temperature is about  $42^\circ\text{C}$ . The ME feedstock is supplied to the reactor at a temperature ranging from  $40^\circ\text{C}$  to  $56^\circ\text{C}$ , Table 3, well above the freeze point of the particular ME feedstock, Table 1. The reactants are mass flow controlled to maintain a fixed mole ratio of  $\text{SO}_3$  to ME (MR). For the five feedstocks the MR ranged from 1.2 to 1.3. The choice of MR is dependent on the expected selectivity of the particular ME to side-reactions and byproduct formation. These include oxidation of the alkyl chain by  $\text{SO}_3$ , sulfonation of some of the resulting olefin sites,<sup>22</sup> formation of methyl sulfuric acid, and hydrolysis of the ester to form di-salt. The reactor jacket temperature is maintained at  $50^\circ\text{C}$  to  $60^\circ\text{C}$  depending on the feedstock molecular weight. The MESA is transferred to the acid digester system where it rapidly reaches the desired digestion temperature of  $85^\circ\text{C}$ . After the MESA is digested the methanol (31 to 40 wt%, digested MESA basis) and hydrogen peroxide (1 to 4%, digested MESA basis) are ratio added with the MESA into a loop controlled at  $75^\circ\text{C}$ . A significant amount of exothermic reaction occurs in the loop. From the loop the bleach mix is transferred into a methanol refluxing bleaching digester where the temperature is held at 95 to  $100^\circ\text{C}$ . The acid bleaching step requires 1 to 1.5 hours. More bleaching time is better in terms of degree of color reduction as long as not all of the available peroxide is consumed. The excess methanol effectively limits the production of di-salt, and significantly reduces the viscosity of the mixture, which improves mixing and heat transfer through the bleaching process. Bleached MESA is forwarded to the neutralizer where a controlled proportion of 50% sodium hydroxide is admixed with the bleached MESA and a large recycle stream of neutralized paste at about  $55^\circ\text{C}$ . Neutralized MES paste continuously discharges to the stripper / dryer pilot plant, where the excess water and methanol are removed. The dryer pilot plant functions as a distinct processing system, and processes concentrated pastes at rates of about 60 kg/hr. For the stripping process the MES inlet temperature is about  $100^\circ\text{C}$  and the separation vessel operates under vacuum conditions at 200 Torr or greater. For the drying process the MES inlet temperature is about  $145^\circ\text{C}$  and operates under vacuum conditions at 120 to 200 Torr. No significant increase in di-salt occurs at the elevated process temperatures of the dryer, and the product color is stable.

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**Table 3: Operating Parameters**

|                                      | Coconut<br>C12-C14 | Palm<br>Kernel<br>C8-C18 | Palm<br>Stearin<br>C16-C18 | Tallow<br>C16-18 | Soya<br>C18 |
|--------------------------------------|--------------------|--------------------------|----------------------------|------------------|-------------|
| Methyl ester into reactor (°C)       | 42                 | 40                       | 40                         | 56               | 51          |
| Methyl ester into reactor (kg/hr)    | 18.9               | 19.3                     | 23.4                       | 29.5             | 26.1        |
| Sulfur trioxide into reactor (kg/hr) | 8.5                | 8.5                      | 8.5                        | 10.7             | 9.0         |
| MESA loop (°C)                       | 67                 | 62                       | 68                         | 67               | 73          |
| MESA digestion (°C)                  | 85                 | 82                       | 83                         | 87               | 84          |
| MESA digestion (hours)               | 0.6                | 0.8                      | 0.7                        | 0.7              | 0.7         |
| Methanol (kg/hr)                     | 8.5                | 8.5                      | 9.9                        | 12.3             | 10.8        |
| 50% hydrogen peroxide (kg/hr)        | 1.2                | 1.9                      | 1.9                        | 1.8              | 2.5         |
| Bleacher loop (°C)                   | 75                 | 75                       | 75                         | 75               | 75          |
| Bleacher digester (°C)               | 95                 | 95                       | 95                         | 97               | 95          |
| Bleacher digester (kPag)             | 90                 | 90                       | 90                         | 60               | 35          |
| Bleacher digestion (hours)           | 1.6                | 1.5                      | 1.3                        | 1.4              | 1.2         |
| 50% sodium hydroxide (kg/hr)         | 8.6                | 8.5                      | 8.6                        | 10.8             | 9.1         |
| Neutralization (°C)                  | 52                 | 49                       | 55                         | 63               | 55          |
| Stripper/Dryer inlet (°C)            | 103                | 96                       | 144                        | 146              | 140         |
| Stripper/Dryer (Torr)                | 200                | 280                      | 150                        | 190              | 130         |
| Stripper/Dryer outlet (°C)           | 74                 | 70                       | 105                        | 117              | 120         |

## CONCLUSION

Production of high quality MES requires more sophisticated equipment than linear alkylbenzene sulfonate or fatty alcohol sulfate but it has strong appeal because ME is an inexpensive, natural and renewable feedstock. Methyl ester sulfonates provide superior surfactant properties at low cost, and therefore a strong economic incentive to substitute MES for traditional surfactants in many applications. Production capacity of MES will increase in the next few years. More formulation work can be expected utilizing different types of ME feedstock based on the concentrated and ultra-concentrated forms of MES. There will be many new competitive products introduced into the marketplace.

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