Detergency Stability and Particle Characterization of Phosphate-Free Spray Dried Detergent Powders Incorporated with Palm C16 Methyl Ester Sulfonate (C16MES)

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Abstract: Phosphate-free spray dried detergent powders (SDDP) comprising binary anionic surfactants of palm C16 methyl ester sulfonate (C16MES) and linear alkyl benzene sulfonic acid (LABSA) were produced using a 5 kg/h-capacity co-current pilot spray dryer (CSD). Six phosphate-free detergent (PFD) formulations comprising C16MES/LABSA in various ratios under pH 7 – 8 were studied. Three PFD formulations having C16MES/LABSA in respective ratios of 0:100 (control), 20:80 and 40:60 ratios were selected for further evaluation based on their optimum detergent slurry concentrations. The resulting SDDP from these formulations were analysed for its detergency stability (over nine months of storage period) and particle characteristics. C16MES/LABSA of 40:60 ratio was selected as the ideal PFD formulation since its resulting SDDP has consistent detergency stability (variation of 2.3% in detergency/active over nine months storage period), excellent bulk density (0.37 kg/L), fine particle size at 50% cumulative volume percentage (D_{50} of 60.48 μm), high coefficient of particle size uniformity (D_{60}/D_{10} of 3.86) and large spread of equivalent particle diameters. In terms of surface morphology, the SDDP of the ideal formulation were found to have regular hollow particles with smooth spherical surfaces. Although SDDP of the ideal formulation have excellent characteristics, but in terms of flowability, these powders were classified as slightly less free flowing (Hausner ratio of 1.27 and Carr's index of 21.3).

Key words: palm C16 methyl ester sulfonate, phosphate-free spray dried detergent powders, detergency stability, particle characterization, surface morphology

1 INTRODUCTION

During the twentieth century, petrochemical based linear alkyl benzene sulfonate (LABS) was the dominant surfactant in detergent formulations. In the past decade, green and eco-friendly became two big buzzwords in the marketing of detergents¹⁾ and this development creates a challenge to the detergent industry to find ways in increasing the green oleochemical based surfactants in the detergent formulations²⁾. One of the green oleochemical based

surfactant that draws enormous commercial interest among the detergent manufacturers in recent years is methyl ester sulfonate (MES)³⁻⁵⁾. MES, an oleo-based anionic surfactant, is produced via sulfonation process of methyl esters that derived from natural oil such as palm oil, coconut oil and soybean oil. The research history, chemistry, properties, performance, process economics, technology and application of MES were well documented in the literature⁶⁻²¹⁾.

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Over the last decade, there has been immense interest in China and Southeast Asia to convert saturated palm C16 methyl esters (C16ME), a by-product from biodiesel plant, into MES (C16MES)²²⁾. Besides the biodiesel plant, C16ME also can be produced from oleochemical plants through fatty acid esterification process using methanol²³⁾. The C16MES derived from C16ME has the edge over LABS in the aspects of green, performance, production cost and sustainability. Large corporations in Asia such as Lion Eco Chemicals Sdn. Bhd. (Malaysia), KL-Kepong Oleomas Sdn. Bhd. (Malaysia) and Guangzhou Keylink Chemical Co. Ltd. (China) have recently started their manufacturing operations to produce MES using palm based methyl esters^{2-5, 24)}. It is forecasted that up to 540,000 metric tonnes per annum of MES will be produced worldwide by the end of 2013, which is equivalent to 10% of global LABS capacity²⁵⁾. However, the primary challenge for use of C16MES still lies in the ability to formulate it in the low density detergent powder (LDDP) formulation without affecting the cleaning performance²⁶⁾. LDDP, of density between 0.25 and 0.45 kg/L, is produced via spray drying process and it is still highly preferred by consumers in developing countries due to its low cost options and high volume over weight ratio.

Unlike LABS, detergent formulations containing single MES could not be employed directly into the spray drying process for the production of LDDP without sacrificing its detergency properties. Alkalinity of detergent slurry (pH above 10) and spray drying temperature exceeding 300°C were reported as unfavourable for MES⁶⁾.

Other than detergency, particle characteristics such as particle size, size distribution and surface morphology are also useful parameters in the development of detergent powders. These parameters, which often overlooked by the detergent formulators, are essential particularly for studying the dissolution rate (solubility)²⁷⁾, volume over mass ratio and flowability properties.

This paper emphasizes the study on detergency stability and particle characteristics of phosphate-free spray dried detergent powders (SDDP) comprising binary anionic sur-

factants of C16MES and acidic linear alkyl benzene sulfonic acid (LABSA). The effects of phosphate-free detergent (PFD) formulations having different C16MES/LABSA ratios on detergency stability and particle characteristics of the resulting SDDP are reported in this paper.

2 EXPERIMENTAL

2.1 Ingredients for pilot scale PFD formulations

C16MES powder (87.4% active content) of acceptable color and low disalt content was obtained from KL-Kepong Oleomas Sdn. Bhd., Selangor, Malaysia. This company operates their MES plant using technology developed by Desmet Ballestra. As MES is sensitive to alkaline conditions, acidic LABSA (96.0% active content) with the average molecular weight of 318 and homolog distribution: <C₁₀ (0.4%), C₁₀ (12.3%), C₁₁ (39.3%), C₁₂ (28.2%), C₁₃ (19.5%) and C₁₄ (0.4%), was used instead of LABS. LABSA and other detergent ingredients such as carboxymethyl cellulose (CMC), sodium aluminosilicate (zeolite 4A), citric acid monohydrate, sodium sulphate anhydrous and sodium metasilicate pentahydrate were purchased from commercial suppliers. Sodium tripolyphosphate (STPP), a widely used builder in detergent powder formulation, was excluded in the pilot scale PFD formulations due to its adverse effect on the aquatic environment^{28, 29)}. Other than STPP, the post mix ingredients were also omitted in the pilot scale formulations.

2.2 Pilot scale PFD formulations and production of SDDP

Six PFD formulations, as tabulated in Table 1, were used to produce detergent slurries and its resulting SDDP in a custom built co-current pilot spray dryer (CSD). The CSD was fabricated by AcmeFil Engineering Systems Pvt. Ltd., India (AcmeFil). The schematic diagram of the CSD is shown in Fig. 1. Prior to spray drying process, detergent ingredients such as C16MES, LABSA, CMC, zeolite 4A, citric acid monohydrate, sodium sulphate anhydrous,

Table 1 Pilot scale PFD formulations used for detergent slurry preparation.

Formulation (C16MES/LABSA ratio)	0:100	20:80	40:60	60:40	80:20	100:0
Materials (gram)	(control)					
C16MES	0	85	170	255	340	425
LABSA	425	340	255	170	85	0
CMC	25	25	25	25	25	25
Zeolite 4A	200	200	200	200	200	200
Sodium sulphate anhydrous	1600	1600	1600	1600	1600	1600
Sodium metasilicate pentahydrate	250	250	250	250	250	250
Deionised water		added to attain flowable viscosity				
Citric acid monohydrate		added to attain pH 7 – 8				

Fig. 1 Schematic diagram of pilot spray drying system (PSD).

sodium metasilicate pentahydrate and deionised water were mixed in the feed tanks to form homogeneous detergent slurry. As MES is sensitive to alkalinity, the detergent slurry, which normally prepared under alkaline condition, was neutralized with citric acid monohydrate to attain pH of 7 – 8. This neutralization process is necessary to minimize the hydrolysis of C16MES. Incorporation of C16MES at higher ratios tends to increase the viscosity of the detergent slurry and thus affect the flowability. In order to achieve the flowable viscosity, the high viscous formulations were diluted with deionised water. The dilution process reduces the slurry concentration and would increase the production cost as more energy is required to dry the diluted slurry. Moreover, it also would greatly affect the particle size distribution and surface morphology of the resulting SDDP.

The optimum slurry concentration recommended by AcmeFil for CSD was between 25 and 30%. The detergent slurry concentrations obtained for different PFD formulations of C16MES/LABSA in 0:100, 20:80, 40:60, 60:40, 80:20 and 100:0 ratios were 26%, 29%, 26%, 22%, 16% and 13% respectively. Based on the comparison with the recommended optimum slurry concentration, only two PFD formulations (C16MES/LABSA of 20:80 and 40:60 ratios) were found to have the optimum slurry concentrations within the range required for CSD. These formulations were selected and studied further against control formulation of C16MES/LABSA in 0:100 ratio. The detergent slurries of these selected PFD formulations were then pumped at a controlled rate of 4 kg hr^{-1} to the top of the drying chamber and the atomization was effected by means of compressed air using two fluid nozzle systems.

As small scale spray dryer has its limitations in providing the desired density and hollow-structured detergent particles, the drying chamber was designed at 5.68 m height and 1.42 m diameter in order to provide longer residence time and also to produce particles with hollow structures. The air inlet temperature as provided by the electrical heater was at $250 - 300^\circ\text{C}$. The atomized droplets upon co-current contact with the hot air evaporate the water while the air outlet temperature from the drying chamber was at $90 - 100^\circ\text{C}$. The final SDDP, which obtained at 45°C , were then collected at the bottom of the drying chamber.

2.3 Evaluation on detergency stability and particle characteristics

The SDDP of control and C16MES/LABSA in 20:80 and 40:60 ratios were evaluated for its detergency stability and particle characteristics. Based on the overall evaluation, an ideal formulation was selected. An additional test on tapped density was carried out on the resulting SDDP of the ideal formulation in order to determine its flowability properties using Hausner ratio and Carr's index.

2.3.1 Sample preparation

SDDP samples from control and C16MES/LABSA of respective 20:80 and 40:60 ratios were conditioned at room temperature of $28 - 30^\circ\text{C}$ prior to particle characterization.

2.3.2 Determination of detergency stability

Detergency stability of the SDDP was determined based on variations in terms of detergency/active values upon production and after nine months of storage time. The detergency and active of the SDDP were characterized using ASTM D3050-92 (Standard Guide for Measuring Soil Removal from Artificially Soiled Fabrics) and ASTM

D4251-89 (Standard Test Method for Active Matter in Anionic Surfactants by Potentiometric Titration) test methods respectively.

Detergency. The washing procedure was carried out in Terg-O-Tometer using AS9 test fabrics, which soiled with groundnut oil and pigment. These test fabrics were obtained from Testfabrics, USA. Prior to washing, the reflectance of the test fabrics was measured using Minolta spectrophotometer CM 3600d at 460 nm. A predetermined amount of SDDP samples was used to wash the test fabrics at temperature of 30°C and water hardness of 50 ppm CaCO₃. The washing process was carried out for 10 min. The reflectance was re-measured upon completion of wash, rinse and drying procedures. The change in the reflectance, which signifies the detergency of the SDDP, was calculated using Equation (1):

$$\text{Percentage change in reflectance (Detergency)} = (A - B) / (C_0 - B) \times 100 \quad (1)$$

where A and B denote reflectance after and before wash respectively while C₀ is the reflectance of the original unsoiled test fabric.

Active. The active or the purity of the surfactant present in the SDDP was determined using a two-phase titration technique via Metrohm 809 Titrando.

2.3.3 Determination of bulk density and particle size distribution

Bulk density. The known mass of the SDDP sample was passively filled into a graduated glass cylinder. The untapped volume was measured. Bulk density is determined by dividing the mass of the sample over its untapped volume.

Particle size distribution. Laser particle size analyzer (Model CILAS 1190 Dry; CILAS, France) with operating vacuum pressure of 1000 hPa was used to determine the particle size distribution (PSD) of the SDDP samples. Based on the PSD, the particle diameters at cumulative volume percentage of 10% (D₁₀), 50% (D₅₀), 60% (D₆₀) and 90% (D₉₀) were used to study the particle characteristics of the SDDP.

2.3.4 Surface morphology analysis

The surface morphology of the SDDP samples was observed using EVO LS 10, Carl Zeiss variable pressure scanning electron microscope. Scanning electron microscopy (SEM) was operated under vacuum at 15 kV and the images were taken using 450 times magnification.

2.3.5 Tapped density and flowability properties of ideal PFD formulation

Tapped density. The SDDP sample of the ideal PFD formulation, which contained in the glass cylinder, was tapped 30 times and its final volume was measured. Tapped density is determined by dividing the mass of the sample

over its tapped volume.

Flowability. Hausner ratio (HR) and Carr's index (CI) are generally used as important descriptors of powder flowability. HR of more than 1.25 indicates good flowability, between 1.25 and 1.5 indicates improvement can be made using glidant whereas above 1.25 indicates poor flowability³⁰. As for CI, 5 – 15% indicates excellent flowability, 12 – 16% as good, 18 – 21% as fair and <23% indicates poor flowability³¹. HR and CI as shown in respective Equation (2) and (3) were calculated for the ideal PFD formulation.

$$\text{HR} = \text{Tapped density} / \text{Bulk density} \quad (2)$$

$$\text{CI}(\%) = [(\text{Tapped density} - \text{Bulk density}) / \text{Tapped density}] \times 100 \quad (3)$$

3 RESULTS AND DISCUSSION

3.1 Effect on detergency stability

The detergency/active values of SDDP for three C16MES/LABSA ratios upon initial production and after nine months of storage time are plotted in Fig. 2. It can be clearly seen from Fig. 3 that the incorporation of C16MES in the PFD formulations has significantly improved the detergency/active values. The detergency/active values for SDDP of C16MES/LABSA in 20:80 and 40:60 ratios were increased about 45% and 40% respectively in comparison to the control. In terms of detergency/active values for each ratio upon initial production and after nine months of storage time, the SDDP of C16MES/LABSA in 0:100, 20:80 and 40:60 ratios were varied by 5.1%, 8.4% and 2.3% respectively. Therefore, it can be concluded that SDDP from formulation C16MES/LABSA of 40:60 ratio has the highest

Fig. 2 Effect of C16MES/LABSA ratios on detergency/active upon initial production and after nine months of storage period.

Fig. 3 Effect of different C16MES/LABSA ratios on bulk density.

stability in maintaining the detergency over nine months of storage time. At this ratio, C16MES and LABSA appeared to have a synergistic effect in stabilizing the overall detergency of the SDDP.

3.2 Effect on bulk density, PSD and particle characteristics

The effects of the SDDP resulted from three formulations having different C16MES/LABSA ratios on bulk density (D_b), particle size distribution (PSD), coefficient of particle size uniformity (P_u) and spread of equivalent particle diameter (S_{ed}) are shown in Figs. 3, 4, 5 and 6 respectively. The respective D_b obtained for control and C16MES/LABSA of 20:80 and 40:60 ratios were 0.27, 0.22 and 0.37 kg/L (Fig. 3). The plotted graph in Fig. 3 showed a positive correlation between D_b and the C16MES/LABSA formulations using a 2nd order polynomial regression.

As seen in Fig. 4, the PSD of control and C16MES/LABSA in 20:80 and 60:40 ratios were positively skewed and in order to define their characteristics, three particle diameters ($D_{10}/D_{50}/D_{90}$) on the x-axis were measured. The $D_{10}/D_{50}/D_{90}$ obtained for SDDP of control and C16MES/LABSA in 20:80 and 60:40 ratios are tabulated in Table 2. The D_{10} and D_{50} were found to be inversely proportional to the increase of C16MES content in the PFD formulation except for D_{90} .

The P_u of the SDDP was calculated by dividing the D_{90} over D_{10} . The SDDP resulted from C16MES/LABSA of 40:60 ratio has the highest D_{90}/D_{10} value of 3.86 while the control and 20:80 ratios have values of 2.38 and 2.97 respectively (Fig. 5). The P_u of the SDDP was found to increase proportionally with the increase of C16MES content in the PFD formulations. Higher the P_u , the higher will be the dissolution rate of detergent powders in water. It was evident that as C16MES content increases, the D_b and P_u also increases whereas the D_{10} and D_{50} , on the contrary decreases.

In order to determine the S_{ed} , a separate graph (Fig. 6) was plotted using cumulative volume percentage as the x-axis and log particle size as the y-axis. The SDDP of

Fig. 4 Effect of different C16MES/LABSA ratios on particle size distribution.

Fig. 5 Effect of different C16MES/LABSA ratios on particle size uniformity.

Fig. 6 Effect of different C16MES/LABSA ratios on spread of particle diameters.

C16MES/LABSA of 40:60 ratio was found to have the largest S_{ed} (widest PSD) while the other two formulations have narrow PSD.

3.3 Effect on particle morphology

Further analysis using SEM was carried out to observe the particle morphology of the SDDP. The SEM micrographs in **Fig. 7** display the surface morphology of the SDDP particles for all three formulations. As seen in **Fig. 7a**, the control particles were observed to have unorganized and irregular surfaces. Meanwhile, hollow and fractured spherical particles with rough surfaces were obtained for SDDP resulted from formulation C16MES/LABSA of 20:80 ratio (**Fig. 7b**). In contrast, the SDDP of C16MES/LABSA in 40:60 ratio exhibits more regular and organized hollow spherical particles with smooth surfaces as compared to the other two formulations (**Fig. 7c**). The SEM analysis has indicated that the surface morphology of the SDDP particles can be significantly improved by increasing the C16MES content in the PFD formulation.

3.4 Selection of ideal pilot scale PFD formulation

Based on the overall evaluation, C16MES/LABSA of 40:60 ratio was selected as the ideal PFD formulation. The selection was made based on the detergency stability and particle characteristics of its resulting SDDP. The SDDP of the ideal formulation have the highest D_b (37% greater

Fig. 7 Effect of different C16MES/LABSA ratios on surface morphology of SDDP.

Table 2 Particle diameters for different C16MES/LABSA ratios at 10%, 50% and 90% cumulative volume distribution.

Formulation (C16MES/LABSA ratio)	0:100 (control)	20:80	40:60
Particle diameters (μm)			
D_{10}	46.43	24.33	18.96
D_{50}	97.97	64.14	60.48
D_{90}	210.00	104.73	192.28

than the control), lowest D_{50} (38% lower than the control), highest P_u (62% higher than the control) and largest S_{ed} . It also has more regular hollow spherical particles with smooth surfaces than the other two formulations. Generally, detergent powders containing hollow spherical particles exhibit good flowability as compared to those with irregular particles. Besides, the hollow structure also has the ability to increase the dissolution rate of the detergent powder³²⁾.

3.5 Flowability of SDDP resulting from ideal pilot scale PFD formulation

In order to evaluate the flowability characteristics of the SDDP of the ideal formulation, the tapped density (D_t) was determined. The D_t of the SDDP resulting from ideal formulation was 0.47 kg/L and based on this value, HR and CI were calculated. The HR and CI for SDDP of the ideal formulation were 1.27 and 21.3% respectively. The calculated values were slightly higher than the values required for free-flowing characteristic. Since the SDDP of the ideal formulation has a HR of below 1.4, it can be regarded as non cohesive. However, due to hygroscopic nature of C16MES, the cohesiveness of the SDDP tends to increase upon exposure to high humidity. Hygroscopic materials are known to have strong inter-particle interactions in the form of liquid bridge that would give a major impact on flowability³³⁾. In order to achieve the free flowing characteristic, the HR and CI of the SDDP produced from the ideal formulation have to be reduced with the use of glidant.

CONCLUSIONS

The applicability of using C16MES in the spray drying of LDDP depends mainly on its synergism with LABSA in the PFD formulations. In this paper, the findings revealed that PFD formulations with appropriate ratio of C16MES/LABSA and of controlled pH 7 – 8 have significant effect in yielding better detergency stability and particle characteristics. These research results could be beneficial in determining the success of using C16MES in the spray drying process of LDDP.

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