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ORIGINAL ARTICLE

Characterization of Phosphate-Free Detergent Powders Incorporated with Palm C16 Methyl Ester Sulfonate (C16MES) and Linear Alkyl Benzene Sulfonic Acid (LABSA)

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Abstract Laboratory and pilot scale investigations were carried out on phosphate-free detergent (PFD) formulations comprising binary anionic surfactants of C16 palm methyl ester sulfonates (C16MES) and linear alkyl benzene sulfonic acid (LABSA) with the aim of maximizing the incorporation of C16MES into low density detergent powders without compromising the detergency and other significant properties. Initial laboratory experiments revealed that the detergent powder resulting from C16MES/LABSA with a 50:50 ratio and pH 7–8 has acceptable detergency stability over 1 week of accelerated ageing test at 50 °C and 85 % relative humidity. Subsequent experiments were carried out in a 5-kg/h-capacity pilot spray dryer using PFD formulations of C16MES/LABSA over the whole range of weight ratios under the same pH of 7–8. The concentration of the detergent slurry and cleaning performance (detergency, foaming ability and wetting power) of the resulting spray dried detergent powder (SDDP) were evaluated. C16MES/LABSA in a 40:60 ratio was selected as the ideal formulation based on its optimum detergent slurry concentration and comparable cleaning performance against the control formulation. Further environmental tests have confirmed that SDDP obtained from the ideal formulation is readily biodegradable (60 % in 13 days) and exhibits low eco-toxicity properties (LC_{50} of 11.3 mg/L).

Keywords Palm C16 methyl ester sulfonate · Linear alkyl benzene sulfonic acid · Phosphate-free detergent formulation · Pilot spray dryer · Detergency stability · Foaming ability · Wetting power · Biodegradability · Eco-toxicity

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Abbreviations

C16ME	Palm oil based saturated C16 carbon chain methyl ester
C16MES	Palm C16 methyl ester sulfonate
CMC	Carboxymethyl cellulose
DO	Dissolved oxygen
Disalt	Disodium carboxy sulfonate
FAES	Fatty alcohol ether sulfate
FAS	Fatty alcohol sulfate
HDDP	High density detergent powders
LC_{50}	Concentration of detergent at which 50 % of the fish died
LABSA	Linear alkyl benzene sulfonic acid
LABS	Linear alkyl benzene sulfonate

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LDDP	Low density detergent powders
MES	Methyl ester sulfonate
MPOB	Malaysian Palm Oil Board
OECD	Organization for Economic Corporation and Development
PFD	Phosphate-free detergent
PSD	Pilot spray dryer
SDPP	Spray dried detergent powders
STPP	Sodium tripolyphosphate
THOD	Theoretical oxygen demand
Zeolite 4A	Sodium aluminosilicate

Introduction

Detergents typically contain surfactants, builders, bleaching agents, enzymes and fillers in various proportions. Among these ingredients, surfactants exert a pivotal role in detergent formulation where its cleaning chemistry has been the driving force in detergent innovation for years [1]. Surfactants can be described as being anionic, cationic, non-ionic, and amphoteric or zwitterionic by the charge on the surface active component [2]. In the production of detergents, anionic surfactants are used in greater volume than others because of their ease of use and low cost [3].

The conventional raw materials for the production of anionic surfactants are primarily derived from two sources, petrochemicals and oleochemicals [4]. During the 20th century, petrochemical based linear alkyl benzene sulfonate (LABS) was the dominant workhorse in the detergent industry [5]. Since the beginning of this millennium, LABS has been under relentless pressure due to a dramatic surge in crude oil prices [6, 7] and heightened public concern over its environmental impact on aquatic ecosystems [8, 9]. This scenario has shifted the attention of the detergent formulators into detergent products that address the cost, environment and sustainability [1].

Since oleochemistry holds the key for a sustainable future, extensive studies on detergent formulation have been carried out. However, the challenge for today's detergent still lies in providing high performance with low cost of production [10]. This development has created an enormous opportunity for oleochemical based palm methyl ester sulfonate (MES) to emerge into the limelight after several decades of research. MES is an anionic surfactant and well known for its superior detergency, water hardness tolerance, rapid biodegradability and low production cost [11]. It has the potential to substitute LABS and other oleochemical-based anionic surfactants such as fatty alcohol sulfate (FAS) and fatty alcohol ether sulfate (FAES) [12].

MES was fundamentally studied in the early 1960s [13, 14] but only known as a class of surfactant in the 1980s [15]. The 2000s was the decade where MES became the main topic of interest in the detergent industry. The interest was driven by the development of palm oil based biodiesel in Southeast Asia, which offers possibilities for more abundant palm oil based saturated C16 carbon chain methyl ester (C16ME) at competitive cost [16–18]. Although C16ME is a by-product of biodiesel production, it is the most suitable methyl ester feed for the production of C16 methyl ester sulfonate (C16MES) [6]. Besides the biodiesel process route, C16ME can also be produced in oleochemical processing plants. In terms of cleaning performance, C16ME has better detergency compared to methyl esters of C14 and C18 carbon chains [19]. C16MES produced from C16ME was found to have great potential as a single surfactant or co-surfactant in the production of detergent powders [20].

In general, MES derived from natural oils have all the advantages to outperform LABS. However, there is still one outstanding technical issue with MES in the manufacturing process of detergent powders. MES has been reported as suitable for non-tower production of high density detergent powders (HDDP) but not for spray tower production of low density detergent powders (LDDP) [21]. The density of HDDP is generally in the range of 0.55–0.75 kg/L while the LDDP is in the range of 0.25–0.45 kg/L [22]. Earlier studies have indicated that MES will undergo partial hydrolysis (decomposition of the ester group) under spray drying conditions and degrades into a less active by-product-disalt [23]. Disalt possesses inferior detergency properties and will result in a deterioration in the detergency performance [24]. The hydrolysis normally occurs when MES is exposed for a long periods at a pH of below 3 or above 10 [25, 26] and also at a high spray drying temperature [27]. Satsuki reported that binary anionic surfactants containing MES and LABS may eliminate the technical disadvantage of MES in the spray drying process [19]. However, extensive studies on detergent formulations using binary anionic surfactant system are necessary to evaluate its suitability for the spray drying process.

The primary aim of this research was to overcome the technical disadvantage of MES in the spray drying process and thus to maximize its use in the common LDDP formulation. An attempt was made to solve this problem by using binary surfactants of C16MES and acidic linear alkyl benzene sulfonic acid (LABSA). This paper highlights the results obtained from both laboratory and pilot scale investigations on phosphate-free detergent (PFD) formulations comprising C16MES and LABSA. In the initial laboratory process, a suitable pH condition that is able to stabilize the detergency of the resulting detergent powders was identified. Based on these laboratory results, a number of pilot scale PFD formulations having different C16MES/LABSA ratios were studied. The pilot scale process was carried out using a pilot spray dryer (PSD) to determine the optimum detergent slurry concentration and cleaning performance (detergency, foaming ability and wetting power) of the resulting spray dried detergent powders (SDDP). Among the studied pilot scale PFD formulations, an ideal PFD formulation was selected and further evaluation on its resulting SDDP was carried out to determine the environmental properties (biodegradability and eco-toxicity).

Experimental

Materials for PFD Formulations

Two anionic surfactants, C16MES (87.4 % active matter) and acidic LABSA (96 % active matter), were used in the selected PFD formulations for both laboratory and pilot scale experiments. C16MES of acceptable color and disalt content was obtained in powder form from KL-Kepong Oleomas Sdn. Bhd., Selangor, Malaysia. This company operates their MES plant using technology developed by Desmet Ballestra. Other materials such as LABSA, sodium hydroxide (32 %), carboxymethyl cellulose (CMC), sodium aluminosilicate (zeolite 4A), citric acid monohydrate, sodium sulfate anhydrous, sodium silicate and sodium metasilicate pentahydrate, which were necessary for the PFD formulations, were purchased from commercial suppliers. Due to the sensitivity of C16MES towards alkaline ingredients, acidic LABSA with the average molecular weight of 318 and homolog distribution: $<C_{10}$ (0.4 %), C_{10} (12.3 %), C_{11} (39.3 %), C_{12} (28.2 %), C_{13} (19.5 %) and C_{14} (0.4 %), was used instead of alkaline sodium LABS. Sodium tripolyphosphate (STPP), a commonly used detergent ingredient to enhance cleaning efficiency, was excluded in the PFD formulations as it has been linked to the process of eutrophication [28, 29]. The PFD formulations were also prepared in the absence of post mix ingredients such as enzyme, optical brightener, colorant, anti-redeposition agent, bleaching agent and perfume.

Laboratory Scale Production of Detergent Powders

Laboratory experimental setup consisted of a 500-mL glass beaker equipped with variable speed control mechanical stirrer, a thermometer and a temperature controlled hot plate. Detergent slurries and its resulting detergent powders were prepared in two steps. The first step involves the preparation of detergent slurry. C16MES was put into a half-filled beaker with deionized water and it was allowed to dissolve completely at 60 ± 5 °C with continuous stirring at 150 rpm. Other basic detergent ingredients such as LABSA, CMC, zeolite 4A, sodium silicate and sodium sulfate anhydrous were then added intermittently to the water, which dissolved with C16MES, in order to form the detergent slurry. Further addition of deionized water to the detergent slurry is necessary to achieve a 60 % slurry concentration. The second step involves the drying of detergent slurry on a hot plate until it completely turns into a fine solid powder.

Table 1 Laboratory scale PFD formulations

Formulation (C16MES/LABS ratio 50:50) materials (gm)	L1 (control)	L2
C16MES	9.5	9.5
LABSA	9.5	9.5
CMC	0.8	0.8
Zeolite 4A	8.9	8.9
Sodium silicate	17.8	17.8
Sodium sulfate anhydrous	64.2	64.2
Deionized water	To achieve 60 %	Slurry concentration
Citric acid monohydrate	–	To pH 7–8
Sodium hydroxide	To pH 10	–

MES was reported to be stable at pH of 5–9 [30] and it also possesses high detergency and low crystallinity when mixed with LABS in 1:1 ratio [19]. In view of these characteristics, detergent slurries of two laboratory-scale PFD formulations (L1 and L2) comprising C16MES/LABSA in 50:50 ratio, which differentiated by its respective pH 10 and 7, were prepared. These formulations are tabulated in Table 1. The pH of L1 and L2 formulations were adjusted accordingly with the respective addition of citric acid monohydrate and sodium hydroxide. The slurries of the laboratory PFD formulations were then dried on a hot pan. The dried detergent powders were subjected to one-week of accelerated ageing test by continuous heating in an oven at 50 °C with 85 % relative humidity. The detergency of the dried detergent powders was measured before and after one-week of accelerated ageing test.

Pilot Scale Production of SDDP

Experiments were carried out using a co-current PSD, a custom built pilot spray drying system by Acmefil Engineering Systems Pvt. Ltd., India for continuous transformation of detergent slurry into a dried fine solid detergent powder. The specifications, technical parameters and operating data of the PSD are shown in Table 2. Based on the laboratory results, six PFD formulations comprising binary surfactants of C16MES/LABSA were selected for the pilot scale study. The C16MES/LABSA with respective

Table 2 Pilot spray dryer specifications, technical parameters and operating data

Pilot spray dryer specification	Value
Height of drying chamber (m)	5.68
Diameter of drying chamber (m)	1.42
Technical parameters and operating data	
Optimum slurry concentration (%)	25–30
Feed rate (kg/h)	20
Evaporate rate (kg/h)	15
Product output rate (kg/h)	5
Air inlet temperature (°C)	250–300
Air outlet temperature (°C)	90–100
Ambient air temperature (°C)	30
Powder temperature (°C)	45
Final moisture (%)	<3

Table 3 Pilot scale PFD formulations

Formulation (C16MES/LABSA ratio) materials (gm)	0:100 (control)	20:80	40:60	60:40	80:20	100:0
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 sulfate anhydrous	1,600	1,600	1,600	1,600	1,600	1,600
Sodium metasilicate pentahydrate	250	250	250	250	250	250
Deionized water	Added to achieve flowable viscosity					
Citric acid monohydrate	Added to attain pH 7–8					

weight ratios of 0:100 (control), 20:80, 40:60, 60:40, 80:20, 100:0 at pH 7–8 were studied and their formulations are shown in Table 3. Figure 1 illustrates the detailed schematic diagram of the PSD for SDDP production process. The production of SDDP involves three main steps.

The first step begins with the incorporation of deionized water into two feed tanks, which were equipped with stirrers and immersion electrical heaters. Deionized water was heated to 60 °C and then followed by the addition of C16MES powder into the feed tanks. C16MES powder was allowed to dissolve completely in the hot deionized water. Other basic detergent ingredients such as LABSA, CMC, zeolite 4A, sodium metasilicate pentahydrate and sodium sulfate anhydrous were then mixed into the C16MES solution. All these ingredients were stirred continuously in the feed tanks for 15 min at 150 rpm to form a homogeneous detergent slurry. High viscosities were observed for some of the PFD formulations during slurry preparation. The concentration of these formulations was optimized by adding enough deionized water in order to achieve flowable viscosity.

In the second step of the process, the detergent slurry was pumped into the spray drying chamber using a plunger pump at a controlled rate where fine spray droplets were distributed through two fluid nozzle systems. The co-current contact between the spray droplets and the hot air (entering from the top of the drying chamber through the air distributor) evaporates the water and allows the dried fine solid detergent powder to drop down to the bottom of the drying chamber. The final step involves the collection of SDDP with the desired moisture content from the bottom of the chamber. The residual moisture of the SDDP was controlled by varying the feed rate. The exhaust air was treated for product recovery using a cyclone separator and wet scrubbing system. The exhaust blower was used to vent out the clean air to the atmosphere through an exhaust chimney. The collected SDDP were cooled to ambient temperature and then analyzed for cleaning performance (detergency, foaming ability and wetting power). Based on the overall evaluation, the ideal formulation that exhibits comparable cleaning performance with the control was selected. Additional environmental tests were performed on the SDDP of the ideal formulation in order to determine its biodegradability and eco-toxicity properties.

Detergent Slurry Analysis—Slurry Concentration and pH

The percentage of slurry concentration was determined by dividing the total mass of materials (excluding water) by the overall mass of materials used for spray drying. The pH test was performed on 0.1 % solution of the detergent slurry. The pH was measured using pH strips.

Detergent Powder Analysis—Detergency, Foaming and Wetting Characteristics

Detergency Detergency performance of detergent powders (produces from both laboratory and pilot scale formulations) was characterized via the tergotometry method as per the Standard Code of China, GB/T 13174-2008 test method (determination of detergency and cycle of washing property for laundry detergents). The detergency test was carried out in one of the leading detergent manufacturers in China, Lonkey Industrial Chemical Co. Ltd. The detergency evaluations were performed on three types of artificially soiled fabrics at 50 ppm in accordance to the typical water hardness in South China and Malaysia. Fabrics used were JB01 (carbon soil), JB02 (protein soil) and JB03 (sebum soil). Reflectance (whiteness) of the fabrics

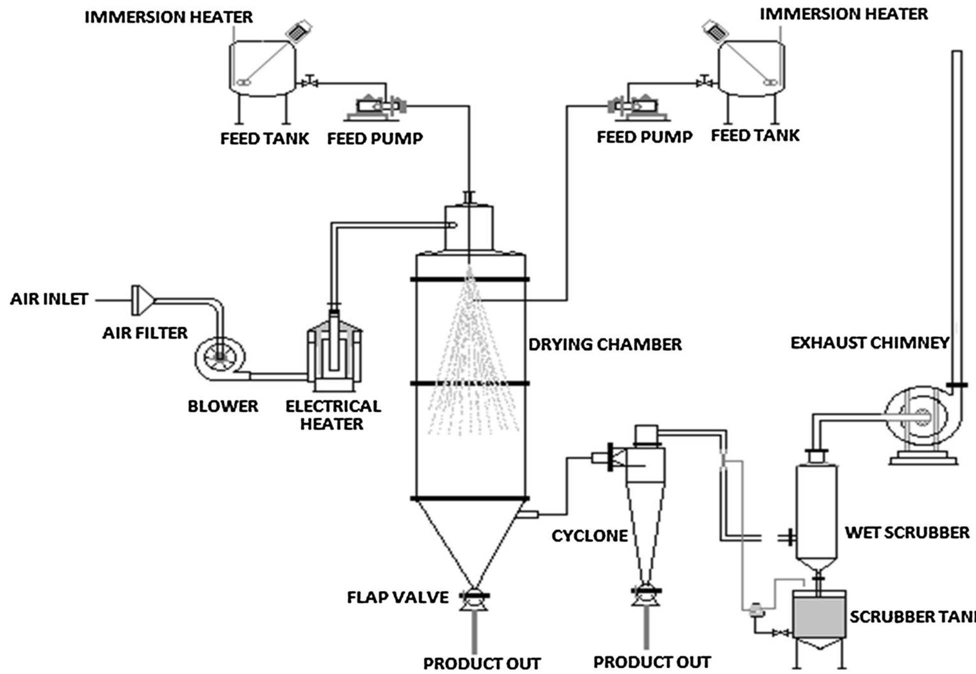

Fig. 1 Schematic diagram of pilot spray dryer (PSD)

was measured prior to washing with a whiteness meter at 457 nm. Four strips of each type of fabric (6 cm × 6 cm dimension) were washed at 30 °C water temperature. A predetermined amount of detergent powder samples from the studied PFD formulations (laboratory and pilot scale) was used to wash the fabrics. The wash load was stirred at 120 rpm for about 20 min. This was followed by measuring the reflectance after washing, rinsing and drying procedures. In this test method, standard detergent powder was used as reference. The detergency performance of the PFD powders was determined according to Eq. (1):

$$\text{Detergency} = \frac{(R_{\text{AW}} - R_{\text{BW}})}{(R_{\text{AW}}{}^{\text{R}} - R_{\text{BW}}{}^{\text{R}})} \quad (1)$$

where R_{AW} and R_{BW} denote respective average reflectance for detergent sample after and before washing while $R_{\text{AW}}{}^{\text{R}}$ and $R_{\text{BW}}{}^{\text{R}}$ denote respective average reflectance for standard detergent powder after and before washing.

Foaming The foaming test was performed in accordance to the Malaysian Palm Oil Board (MPOB) in-house method. A 0.1 % of detergent solution was prepared using SDDP samples obtained from the studied pilot scale PFD formulations. The foaming test was performed by agitating the solution up and down 30 times in a measuring cylinder using a standard plunger. This action generates the foam. Foaming ability was determined by measuring the initial foam height upon agitation and the subsequent foam height after 5 min. The variation in the foam height determines the foaming stability.

Wetting Wetting test was conducted as per in-house test method developed by MPOB. The dried unsoiled cotton, which was cut into 2-cm by 2-cm squares and conditioned at 20 % relative humidity for 24 h, was dropped on the surface of the 0.1 % solution prepared using SDDP samples from the studied pilot scale PFD formulations. The time was recorded from the point the dried unsoiled came into contact with the surface of the solution until it completely immersed.

Environmental Tests—Biodegradability and Eco-Toxicity

Biodegradability and eco-toxicity properties were determined using the respective standard methods: OECD 301D, the closed bottle test and OECD 203, the Fish Acute Toxicity Test in accordance to the Organization for Economic Cooperation and Development (OECD) Guidelines for Testing of Chemicals [31, 32].

A 2-mg/L solution was prepared using an SDDP sample from the ideal pilot scale PFD formulation. The biodegradability test was carried out on the solution in a mineral medium, at 2–5 mg/L concentration. The solution was inoculated with inoculums (a mixed bacterial population) derived from the secondary effluent of a treatment plant treating domestic sewage and kept in completely full, closed bottles in the dark at constant temperature. The test was performed by analysis of dissolved oxygen (DO) at 22–25 °C for a 28-day period. The amount of oxygen taken up by the microbial population during biodegradation process, corrected for uptake by the blank inoculums run in parallel, was expressed as a percentage of the theoretical oxygen demand (THOD). The DO of the SDDP sample (from the ideal formulation) was measured every 4 days in order to construct a biodegradation curve. In general, a substance is considered readily biodegradable if it is ≥60 % biodegraded in 28 days of test period.

In the eco-toxicity test, an SDDP sample from the ideal pilot scale PFD formulation was used as the test substance. *Tilapia nilotica* fishes were exposed to the test substance in two stages. The first stage was the range-finding test in which the fishes were exposed to various concentrations (in logarithmic series) of the test substance for 24 h. The concentration range between no mortality and 100 % mortality was taken and used in the second stage of the test (the definitive test). The fish were then exposed to various concentrations (in geometric series) of the test substance for 96 h. Mortalities were recorded at 24, 48, 72, and 96 h. The geometric mean of the highest concentration causing no mortality and the lowest concentration causing 100 % mortality were calculated and expressed as LC_{50}. LC_{50} is the concentration of detergent at which 50 % of the fish died during the test period. The LC_{50} rating in accordance to the scheme by the U.S. Fish and Wildlife Services was used as reference to rate the eco-toxicity [33] of the ideal formulation.

Results and Discussion

Detergency Stability of Laboratory Scale Detergent Powders

The effect of pH on L1 and L2 formulations was studied via detergency test on three types of fabrics. The L1 formulation was prepared based on the common detergent powder formulation (pH 10). This formulation was used as control in this study. Figure 2 illustrates the corresponding detergency of the L1 and L2 formulations before and after one week of the accelerated ageing test. The accelerated ageing test was developed in-house in order to determine the detergency stability of the dried detergent powders when subjected to prolonged periods of storage. The detergency of the L1 formulation on JB01, JB02 and JB03 fabrics was observed to decrease up to 11.2, 22.8 and 35.8 % respectively after 1 week of the accelerated ageing test. The L2 formulation, which was prepared using C16MES/LABSA in 50:50 ratio (pH 7–8), had a better detergency stability as compared to the L1 formulation. The detergency of the L2 formulation on JB01, JB02 and JB03 fabrics only decreases 2.8, 1.9 and 19.0 % respectively. In summary, it can be concluded that the detergent formulation comprising C16MES/LABSA in a 50:50 ratio and a pH of 7–8 is capable of minimizing the partial hydrolysis (degradation) of C16MES into disalt, thus has a satisfactory effect on the detergency stability of the resulting detergent powders.

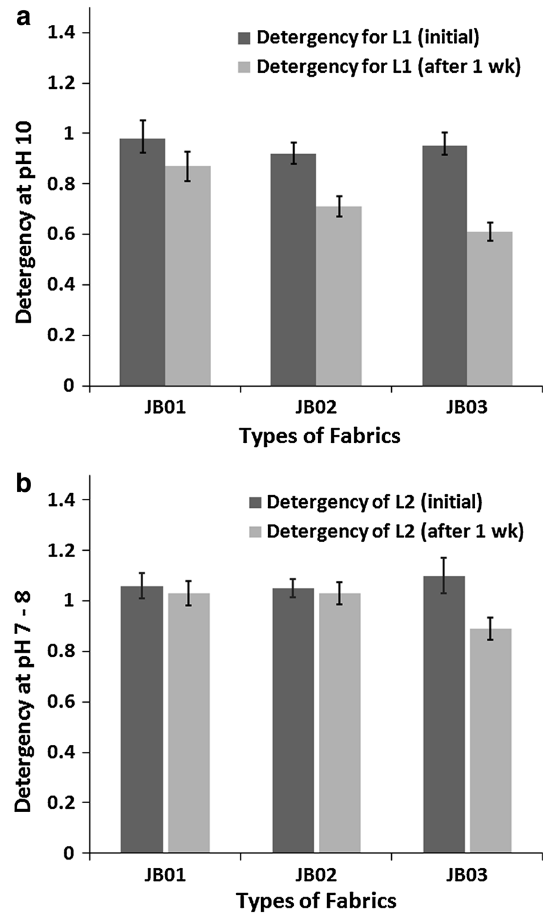

Fig. 2 Detergency of laboratory scale PFD formulations initially and after 1 week of an accelerated ageing test. **a** L1 (pH 10). **b** L2 (pH 7–8)

Concentration of Detergent Slurry

Optimum slurry concentration is an important parameter to maintain proper atomization and to ensure correct droplet formation in the spray drying operation. The optimum concentration of detergent slurry that is recommended for the PSD is 25–30 %. Figure 3 shows the slurry concentrations for PFD formulations having different ratios of C16MES and LABSA. Formulation comprises C16MES/LABSA in 0:100 ratio was used as control. According to the experimental results, the slurry concentrations for C16MES/LABSA with 20:80 and 40:60 ratios were 29 and 26 % respectively. These concentrations were within the recommended optimum slurry concentration for PSD. However, during the preparation of detergent slurries, the PFD formulations with C16MES/LABSA of 60:40, 80:20 and 100:0 ratios were observed to have high viscosities at the recommended slurry concentration. The increase in the viscosity, which was due to the typical behavior of C16MES, would restrict the flow of the slurry from the feed tank to the drying chamber. The slurry with high

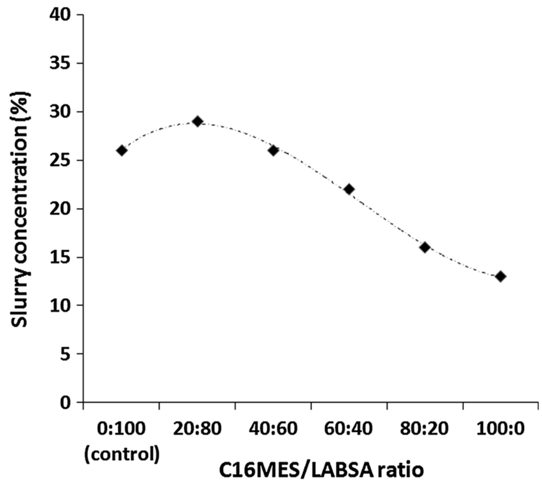

Fig. 3 Detergent slurry concentrations at different C16MES/LABSA ratios

viscosity will impede the spray droplet formation [34] and therefore it has to be diluted with deionized water to obtain the flowable viscosity. It can be seen in Fig. 3 that as the C16MES content in the PFD formulations increases, the viscosity increases and therefore decreases the optimum slurry concentration for formulation with C16MES/LABSA in 60:40, 80:20 and 100:0 ratios.

Cleaning Performance of SDDP

Basically, an effective way to characterize the cleaning performance of detergent powders is by evaluating its detergency, foaming ability and wetting power. Formulation with single LABSA surfactant (C16MES/LABSA in 0:100 ratio) was used as the control in this study.

Detergency Detergency performance is the most critical parameter in determining the cleaning ability of detergent powders to remove stains from fabrics. Figure 4 illustrates the detergency of studied pilot scale PFD formulations containing different ratios of C16MES/LABSA ratios over JB01, JB02 and JB03 soiled fabrics. The detergency tests have shown that the detergency for all the C16MES/LABSA ratios over JB01 was in the range of 0.87–1.00. The results were consistent and comparable to the detergency of the control of 0.94 (Fig. 4a). For detergency over JB02, a declining trend was observed for all the ratios upon increases in C16MES content in the PFD formulations except for 60:40 ratio (Fig. 4b). It can also be seen in Fig. 4c that the detergency on JB03 increased logarithmically with the increased quantity of C16MES in the PFD formulations. This result indicates that the detergency performance of the PFD formulations in removing the sebum soil from the fabric can be enhanced significantly with the increased quantity of C16MES.

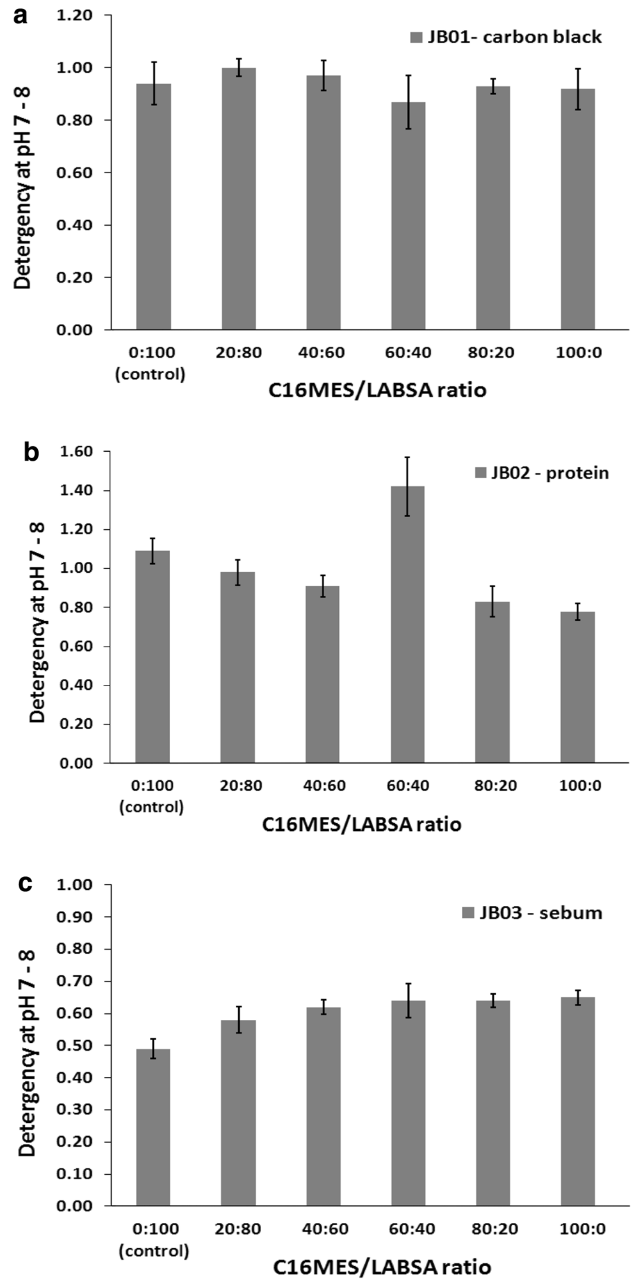

Fig. 4 Detergency of pilot scale PFD formulations over different ratios of C16MES/LABSA. **a** JB01 (carbon black), **b** JB02 (protein), **c** JB03 (sebum)

Foaming ability Foaming ability in the context of a detergent can be defined as its ability to generate a mass of small bubbles or froth on the surface of the detergent solution via agitation. Figure 5 illustrates the foam heights, as measured in mL, for the studied pilot scale PFD formulations containing different ratios of C16MES/LABSA ratios. The variations between the foam heights (initial and after 5 min) for all the ratios were compared against the control. The differences in the initial foam heights were in

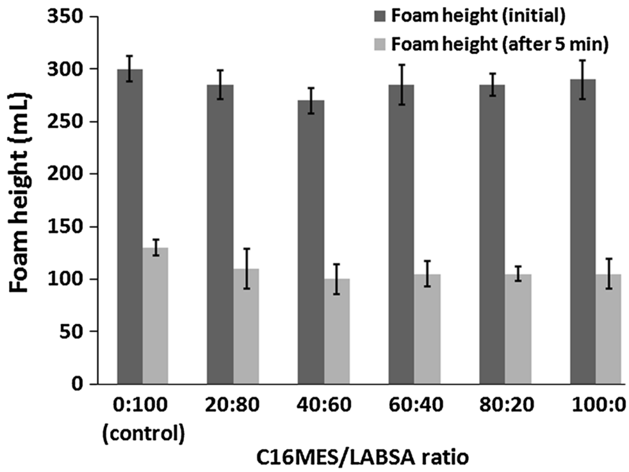

Fig. 5 Foaming ability of pilot scale PFD formulations over different ratios of C16MES/LABSA

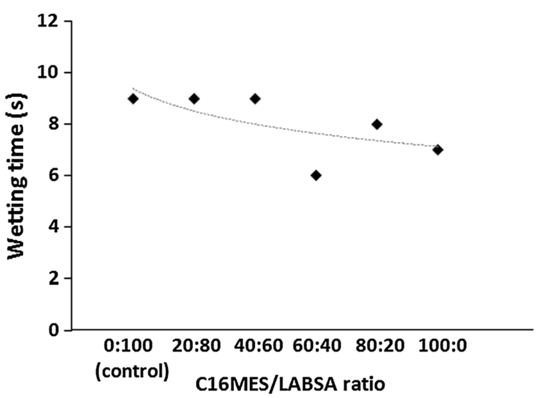

Fig. 6 Wetting power of pilot scale PFD formulations over different ratios of C16MES/LABSA

the range of 270–290 mL while for the control it was 300 mL. The foam heights after 5 min varied from 105 to 110 mL and for the control it was 130 mL. The results show that all the studied PFD formulations have comparable foam heights to the control. A similar trend also was observed in terms of the foam height variations.

Wetting power The duration taken for the fabrics to be completely wet will determine the wetting power of the detergent products used. This characteristic is one of the important factors in the evaluation of washing performance. According to Fig. 6, the wetting power of pilot scale PFD formulations with C16MES/LABSA in 20:80 and 40:60 ratios was 9 s each and found to be similar to the control. However, significant improvement in the wetting power was observed for formulations with C16MES/LABSA in 60:40, 80:20 and 100:0 ratios. This was due to the increased quantity of C16MES used in the PFD formulations. MES, in general, is known to have a superior wetting power over LABS and this could be the reason for the improvement in the wetting power.

Table 4 Characteristics of ideal pilot scale PFD formulation in comparison with the control

Formulation (C16MES/LABSA ratio) characteristics	0:100 (Control)	40:60 (Ideal formulation)
Slurry concentration (%)	26	26
Detergency		
JB01	0.94	0.97
JB02	1.09	0.91
JB03	0.49	0.62
Foaming ability (mL)		
Initial	300	270
After 5 min	130	100
Wetting power (s)	9	9

Identification of the Ideal Pilot Scale PFD Formulation

The ideal pilot scale PFD formulation was selected upon consideration of its optimum slurry concentration and overall cleaning performance (detergency, foaming ability and wetting power) against the control formulation. Based on these findings, formulations with C16MES/LABSA in 20:80 and 40:60 ratios were found to have comparable properties with the control. However, formulation with C16MES/LABSA in a 40:60 ratio was selected as the ideal pilot scale PFD formulation due to its higher C16MES content. Table 4 summarizes the comparison between the characteristics of ideal formulation and the control. Subsequent biodegradability and eco-toxicity tests were performed on SDDP resulted from the ideal formulation in order to evaluate its environmental acceptability.

Environmental Properties of the Ideal Pilot Scale PFD Formulation

Biodegradability Biodegradation is a process whereby the decomposition of organic substances occurs naturally via microbial activity. The biodegradability evaluation is not only an important parameter for assessing environmental risk, but also required by the relevant legislation. Figure 7 shows the biodegradation curve for the ideal pilot scale PFD formulation in comparison to reference substance and toxicity control. Results have shown that the biodegradability pass level of 60 % was achieved in 13 days while the maximum biodegradability level of 95.6 % in 24 days. The toxicity control, however, requires 20 days to reach the 60 % pass level. This study has demonstrated that the resulting SDDP from the ideal formulation is a

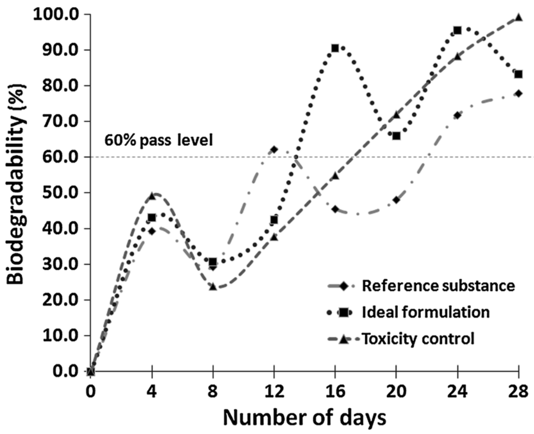

Fig. 7 Biodegradability of ideal pilot scale PFD formulation

Table 5 Fish mortalities after 96 h for SDDP resulted from ideal pilot scale PFD formulation

Concentration (mg/L)	Number of dead fish	Mortality (%)
0.0	0	0
4.0	0	0
8.0	0	0
16.0	10	100
32.0	10	100

readily biodegradable compound. Therefore, it is not likely to cause environment concern due to its high biodegradability.

Eco-toxicity Eco-toxicity test is essential to determine the toxicity level of detergent products when discharged into aquatic environment by the wastewater pathways. The eco-toxicity test was performed on the resulting SDDP from the ideal pilot scale PFD formulation in order to rate its aquatic toxicity. Table 5 indicates the mortalities of fish for ideal formulation after 96 h. Based on these results, the LC_{50} of ideal formulation was calculated as the geometric mean of the highest concentration that kills none/new fish (8.0 mg/L) and the lowest concentration that kills all fish (16.0 mg/L). The calculated LC_{50} for the ideal formulation was 11.3 mg/L and is considered as slightly toxic in accordance to the rating scheme by the U.S. Fish and Wildlife Services. Maurad et al. 2006 [35] found that the LC_{50} for detergent powders incorporated with single MES surfactant was in the range of 5.66–8.0 mg/L (falls under the moderately toxic classification). Although huge quantities of surfactants are being discharged into the waterways, they do not pose a serious impact on the aquatic environment [36, 37].

It was evident from previous studies that the spray drying process conditions that are generally used for manufacturing LDDP were not directly applicable to detergent formulation incorporated with the single MES surfactant. In this study, the overall findings have demonstrated that PFD formulations with an appropriate ratio of binary C16MES/LABSA anionic surfactants and of neutral pH condition can play a significant role in determining the success of using C16MES in the spray drying process. The effective PFD formulation from this study can be used advantageously to produce SDDP without sacrificing its cleaning performance and environmental properties.

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