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Optimization of detergent formulation from different types of plant-based surfactants using Response Surface Methodology

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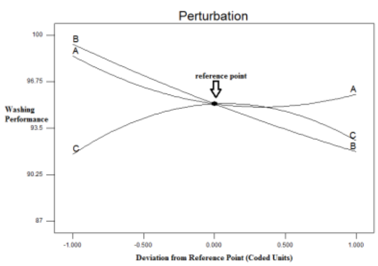
GRAPHICAL ABSTRACT



ABSTRACT

The aim of this study was to formulate and optimize the mixing ratio of three different types of plant-based surfactants for liquid detergent. The surfactants used were sodium laureth sulphate (SLES), coconut fatty acid diethanolamide (CDE) and cocamidopropyl betaine (betaine). The physical responses of the detergent formulations were tested based on the following properties: pH, foaming ability, viscosity and washing performance. A statistical analysis method that is Response Surface Methodology was used to generate the formulation compositions. Seventeen combination components were selected according to the criterion. Contour graphics and perturbation graphs were obtained to assess the changed in the response surface in order to understand the effect of the mixture composition to the physical properties studied. The method proved to be efficient to determine the mixing ratio of the three surfactants that gives optimum foaming ability, viscosity and washing performance. The optimum formulation composition was 2.00 % wt of CDE, 8.31 % wt of SLES and 1.00 % wt of betaine that gives 7.16 cm^3 volume of foam, with the viscosity 3.39 mm^2 s^{-1} and washing performance up to 98%. Comparison study with existing detergent products in the market showing a comparable washing performance despite there is no additives such as builders has been added to the formulations studied.

Keywords: *plant-based surfactant, detergent formulation, Response Surface Methodology*

1. INTRODUCTION

Detergents are used widely as cleaning agents for household and industrial applications such as functional processing aids and cosmetic cleaners. Detergents functions in removing soils from fabrics, dishes and even human bodies. Thus, it is very important to ensure the mildness of detergents in all household goods category since detergent will give direct contact with human body [1]. One of the main ingredients needed in detergents are surfactants. Surfactants are surface-active substances and often known as the heart of a washing product or cleaner. Surfactants are applied widely in science and industry ranging from the used in detergent, paints, cosmetics, pharmaceuticals and foods [2]. In detergent formulations, either single surfactant or mixing multiple surfactants are used. Mixing of surfactants will exhibit better detergency performance compared to detergent with only single surfactant. Mixing of more than one anionic, cationic, nonionic or amphoteric surfactants are generally used in a formulation. Different compositions of combined surfactants will give improved power of detergency [3].

Nowadays, most detergents manufacturers used synthetic-based surfactants. Synthetic-based surfactants have poor biodegradability, high toxicity and classified as a human carcinogen. Due to this problem, a new alternative of using several types of plant-based surfactants for detergent formulation are studied. From the literatures, the plant-based surfactants will give the same washing performance as synthetic-based surfactants but with better biodegradability and less toxicity. However, there is no proper documentation on the optimization of the plant-based detergent formulations. Therefore, in this study, the detergent formulations which contain several types of plant-based surfactants (sodium laureth sulphates (SLES), coconut fatty acid diethanolamide (CDE) and cocamidopropyl betaine (betaine)) will be prepared and optimized using Response Surface Methodology software. The optimized formulations will be compared with commercialized detergent products in the market in terms of their physical properties and washing performance. The finding of this study is significant as a driving force to change the synthetic-based detergents to the more environmentally friendly ingredients.

2. EXPERIMENTAL

2.1. Chemicals

Chemicals (analytical grade) used are sodium laureth sulphates (SLES), coconut fatty acid diethanolamide (CDE), cocamidopropyl betaine (betaine) and cooking oil.

2.2. Detergency evaluation: pH test

pH test is one of the detergency evaluation parameters in detergent formulations. pH metre needs to be calibrated before pH reading is taken. Three readings were taken to obtain the average pH value for each prepared formulation.

2.3. Foaming ability test

The foaming ability is measured based on the height of the foam formed in a beaker. A ratio of 1:10 of detergent and distilled water is used. 1 mL of detergents will be mixed with 10 mL of distilled water in a beaker. The initial height of the solution is recorded and the solution are stirred using mechanical stirrer for 15 minutes to produce the foam. After 15 minutes, the height of the solution and foam is recorded once again and the foam can be determined by calculating the difference between final and initial height. The volume of the foam was calculated by using eqn. 1 where r is the radius of the beaker and h is the height of foam in centimeters [5].

$$Foam\ volume = \pi r^2 h \tag{1}$$

2.4. Viscosity test

The viscosity measurement was carried out using Cole-Palmer Rotational Viscometer with R1, R2, R3 and R4 spindle. A volume of 250 mL of the formulated detergent is poured in a beaker. The viscometer speed was set at 100 rpm. The process was allowed for about 30 minutes. The viscosity is recorded based on increasing temperature from 30 - 60 °C.

2.5. Washing performance test

The removal of oil before and after washing is determined. A white cloth of approximately 2.5 cmx2.5 cm is obtained. The weight of the cloth (W_1) was determined and recorded using analytical balance. The white cloth will then immersed in cooking oil for a few seconds. The cloth was leave for a few minutes before the weight is determined to avoid excess oils included in the weight (W_2). The cloth was then placed in a beaker that contains the formulated detergent of ratio 1:10 of detergent and water and stirred using a mechanical stirrer for 30 minutes. After washing, the cloth was dried in the oven and the final weight (W_3) of the cloth is measured. The washing performance was calculated using eqn. 2.

$$Washing\ performance = \frac{(W_2 - W_1) - (W_3 - W_1)}{(W_2 - W_1)}\ x\ 100\% \tag{2}$$

2.6. Response Surface Methodology (RSM)

A response surface methodological approach was employed to determine the optimize ratio for the mixing of three surfactants (SLES, CDE and betaine). Optimization has been widely used in chemistry as a means of discovering conditions at which to apply a procedure that produces the best possible response [6].The optimum ratio determined for this study were proposed according to conditions outlined as in Table 1.

Table 1 Coded and actual levels of variables for the Box-Behnken design

Variable	Levels		
	-1	0	+1
A: CDE	2	5	8
B: SLES	3	6	9
C: Betaine	1	3	5

3. RESULTS AND DISCUSSION

A total of 17 experiments were tested and the responses considered are pH, foaming ability, viscosity and washing performance. The results for the experiments are as tabulated in Table 2. From the literature, the optimum pH range is from 9 – 10.5 [4] and the pH for all 17 experiments are in that range. For foaming ability, the highest volume of foam formation is 6.28 cm^3 due to high amount of SLES and CDE used. As for viscosity, CDE amount plays an important role for high viscosity value, thus the highest viscosity value of 872.97 $mm^2\ s^{-1}$ that used 8 %wt CDE. Lastly, all 17 experiments showed washing performance of more than 87%. The highest washing performance is 98.17% that uses 5 %wt of CDE, 3%wt of SLES and 5 %wt of betaine.

Table 2 Results of physical responses and washing performance for 17 experiments

Experiment	pH	Volume of Foam (cm^3)	Viscosity ($mm^2 s^{-1}$)	Washing Performance (%)
1	10.17	4.65	22.75	90.68
2	10.36	4.15	31.14	94.47
3	9.49	5.91	3.02	97.15
4	10.16	4.15	15.35	94.68
5	9.81	5.03	24.34	96.12
6	10.20	3.77	47.65	87.91
7	9.78	4.65	25.54	97.57
8	9.72	4.65	38.34	97.45
9	10.12	6.66	167.78	88.98
10	9.52	5.91	0.25	93.85
11	9.49	5.91	96.98	98.17
12	10.28	6.28	872.97	97.45
13	10.73	5.03	799.68	96.68
14	9.39	5.03	3.47	97.62
15	9.41	4.15	6.39	97.86
16	9.70	5.03	33.74	97.10
17	10.41	5.40	7.23	89.72

3.1. Model Fitting and Analysis of Variance (ANOVA) for All Variables

The study selected a Box-Behnken design model that consists of three factor which are A: CDE, B: SLES and C: betaine. Box-Behnken design (BBD) are a class of rotatable or nearly rotatable second-order designs based on three-level incomplete factorial designs [7]. The p-value and F-value obtained through the study are as shown in Table 3.

Table 3 p-value and F-value for each factor and response variables

Response/Variable	Volume of foam (cm^3)		Viscosity ($mm^2 s^{-1}$)		Washing Performance (%)	
	p-value	F-value	p-value	F-value	p-value	F-value
A:CDE	0.87	0.032	<0.0001	2776.46	0.39*	0.94*
B:SLES	0.29	1.51	0.016	16.02	0.05*	7.46*
C:Betaine	0.89	0.032	0.0044	33.72	0.75*	0.12*
Model	0.041	6.64	<0.0001	1157.69	0.31*	1.78*

*Model is not significant

The model F-value of 6.64 and 1157.69 implies that the model for foaming ability and viscosity is significant. There is only a 4.09% chance for foaming ability and 0.01% chance for viscosity that a “Model F-value” this large could occur due to noise. However, the model F-value for washing performance is 1.78 implies that the model is not significant with 30.55% chance that a “Model F-value” this large could occur due to noise. The p-value of the model that is less than 0.05 indicates that the model term are significant. The p-value for foaming ability and viscosity (0.041 and <0.0001) are less than 0.05 indicates that the model term are significant while p-value of washing performance is 0.31 which implies that the model term is not significant. However, response B:SLES with p-value of 0.05 and F-value of 7.46 appears to be significant since a large F-value and smaller p-value gives more significant corresponding coefficient.

The significant model terms for foaming ability are BC, A^2 and A^2B and for viscosity, A, B, C, AB, AC, A^2, C^2, A^2B, A^2C and AB^2 but all coefficients are included to minimize any possible errors [8]. For the washing performance, there is no significant model terms. A good fit model should attain a R^2 of at least 0.80 [9]. The coefficient of determination, R^2= 0.9522 for foaming ability, R^2= 0.9997 for viscosity and R^2= 0.8421 for washing performance illustrate that the model can explain approximately 95% of variability for foaming ability, 99% for viscosity and 84% for washing performance, hence, the generated models are adequate to represent the true relationship between the response and the significant variables. The polynomial was regressed for foaming ability, viscosity and washing performance and shown in Eqn. 3, Eqn. 4 and Eqn. 5 in terms of coded factors.

$$Foaming\ Ability = +4.70 -0.033A -0.22B +0.032C +0.19AB +0.41AC -0.85BC +0.70A^2 -0.37B^2 +0.48C^2 +0.85A^2B +0.38A^2C +0.47AB^2 \quad (3)$$

$$Viscosity = +26.90 +241.05A -18.31B +26.56C +212.59AB -157.28AC -6.35BC +198.56A^2 +1.63B^2 +17.22C^2 +229.44A^2B -185.23A^2C -18.88AB^2 \quad (4)$$

$$Washing\ Performance = +95.21 -1.33A -3.75B +0.47C +0.030AB -1.10AC -1.38BC +2.01A^2 +0.41B^2 -3.05C^2 +3.66A^2B -3.22A^2C +1.22AB^2 \quad (5)$$

The positive sign in front of term meant synergistic effect while the negative sign illustrates antagonistic effect, indicating the influence of independent variables on the foaming ability, viscosity and washing performance. Fitting of the data to various models (linear, two factorial, quadratic and cubic) and their following ANOVA illustrated that the foaming ability were most suitably described with a quadratic polynomial model, and both viscosity and washing performance were most suitably described with linear polynomial model.

3.2. Effect of SLES and betaine on Foaming Ability

Figure 1 (a) illustrates the contour plot for the interactive effects of SLES and betaine on the foaming ability and Figure 1 (b) shows the perturbation plot of foaming ability for each factor, A (CDE), B (SLES) and C (betaine).

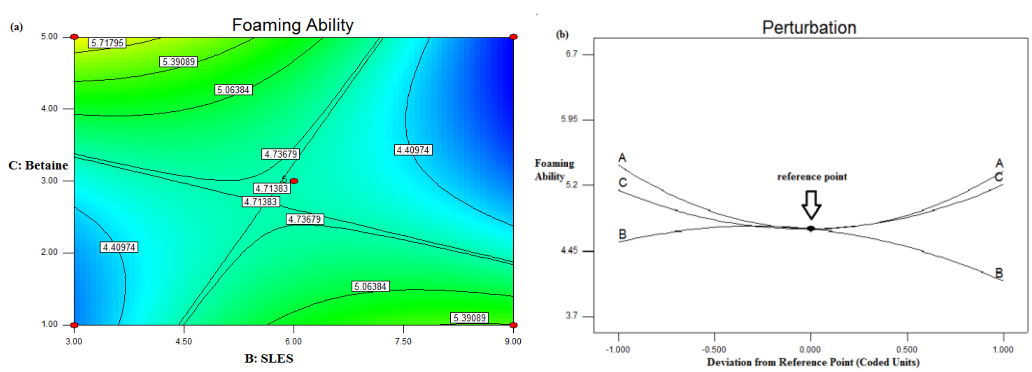


Figure 1 (a) Contour plot showing the effect of mutual interactions between SLES (B) and betaine (C) in foam formation and (b) Perturbation plot of foaming ability for each factor

According to the F-value (Table 3), the effect of SLES (B) is more significant than betaine (C) for foaming ability. From eqn. 3, it can be observed that BC have antagonistic effect where SLES (B) and betaine (C) is inversely proportional to each other. When the amount of SLES increased and the amount of betaine decreased or vice versa, a good foaming ability can be observed. From figure 1(a), it can be seen that high amount of B and low amount of C gives highest foaming ability of 5.39 cm^3 and low amount of SLES and high amount of betaine also gives high foaming ability of 5.72 cm^3. Figure 1(b) shows how the response changes as each factor moves from the chosen reference point, with all other factors held constant at the reference value. From figure 1(b), a maximum foaming ability can be achieved by using high amount of A and C and a little amount of B. It can be conclude that B and C have inversely proportional relationship to each other.

3.3 Effect of CDE and SLES on Viscosity

Figure 2 (a) illustrates the contour plot for the interactive effects of CDE and SLES on the viscosity and Figure 2 (b) shows the perturbation plot of viscosity for each factor.

The effect of CDE (A) is more significant than SLES (B) for viscosity. From eqn. 4, it can be observed that AB have synergistic effect where CDE (A) and SLES (B) is directly proportional to each other. In order to obtain a high value of viscosity, a high amount of CDE and SLES is needed. It can be observed from figure 2(a) that high amount of SLES and CDE gives high viscosity value of 710.78 $mm^2\ s^{-1}$. According to figure 2(b), when the reference point moved to +1, it can be observed that high value of CDE (A) contributes to high value of viscosity.

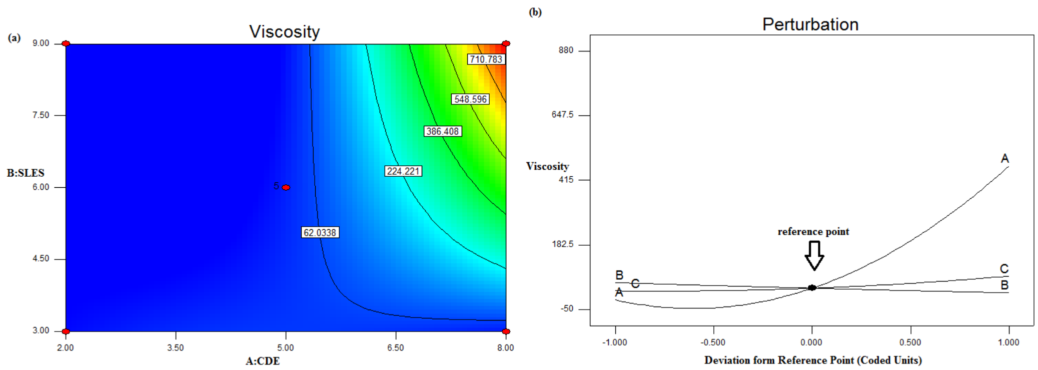


Figure 2 (a) Contour plot showing the effect of mutual interactions between CDE (A) and SLES (B) for viscosity and (b) Perturbation plot of viscosity for each factor

3.4. Effect of CDE and Betaine on Viscosity

Figure 3 illustrates the contour plot for the interactive effects of CDE and betaine on the viscosity. The effect of CDE (A) is more significant than betaine (C) for viscosity. From eqn. 4, it shows that AC have antagonistic effect where CDE (A) is inversely proportional to betaine (C). From figure 3, it can be observed that high amount of CDE (A) of approximately 7.5%wt and a low amount of betaine (C) of approximately 1%wt gives maximum viscosity value of 652.10 mm^2/s. Figure 2(b) of the perturbation plot explain clearly the effect of both CDE (A) and betaine (C) to viscosity. At reference value of +1, a high amount of CDE (A) and very low amount of betaine (C) gives high viscosity value.

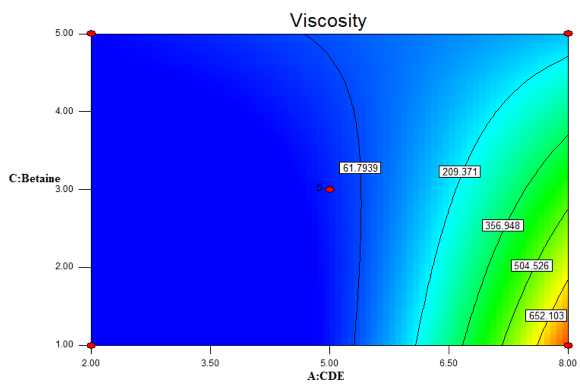


Figure 3 Contour plot showing the effect of mutual interactions between CDE (A) and betaine (C) for viscosity

3.5. Perturbation Graph for Washing Performance

Figure 4 shows the perturbation plot for all factors of washing performance variable. Figure 4 shows that, at reference value of -1 meaning a minimum value of each factor, a high washing performance can be achieved by using high amount of CDE (A) and SLES (B). At +1 reference value, a low amount of SLES (B) and betaine (C) gives approximately 92% of washing performance while high amount of CDE (A) gives approximately 95% of washing performance. However, according to table 3, the p-value and F-value for washing performance is found to be not significant due to the fact that the patterns for washing performance are not stable where by it cannot be determined the exact factors that contribute to poor or excellent washing performance.

3.6. Method Validation Results

The software proposed several experimental ratios in order to find the optimum amount for each surfactants used. The aim is to obtain a ratio that can maximize the foaming ability and also the washing performance of the detergent. The top three predicted ratios are selected and the ratios are as tabulated in Table 4 below. The proposed optimum ratios are tested based on its pH, foaming ability, viscosity and washing performance and compared with the existing market products as shown in Table 5.

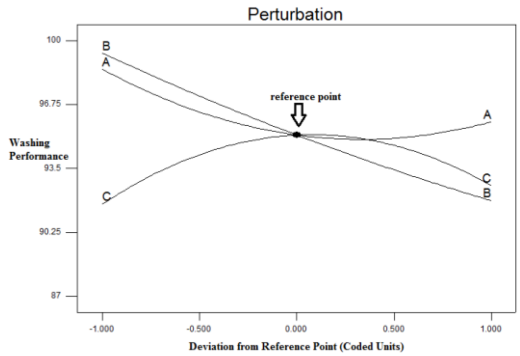


Figure 4 Perturbation plot for washing performance

Table 4 Predicted optimum ratios as proposed by RSM software

Formula	Desirability	RSM Ratio		
		A:CDE	B:SLES	C:Betaine
1	0.929	2.00	8.31	1.00
2	0.928	2.00	8.25	1.02
3	0.899	8.00	9.00	3.00

3.7. Comparison of Optimum Detergent Compositions with Commercial Detergent Products

The optimize formulations obtained are compared with commercial detergent. Three commercial detergents are selected randomly and labelled as brand X, brand Y and brand Z. The commercial detergents are tested for its pH, foaming ability, viscosity and washing performance and compared with the optimum ratio obtained. The results are as recorded in Table 5.

Table 5 Comparison of Optimized Formulation with Commercial Detergent Products

Variables	Formula Validation from RSM			Commercial Detergent Products		
	Formula 1	Formula 2	Formula 3	Brand X	Brand Y	Brand Z
pH	9.58	9.59	9.71	8.86	8.13	8.40
Foaming Ability (cm^3)	7.16	6.66	7.54	3.39	4.15	2.89
Viscosity ($mm^2 s^{-1}$)	3.39	3.07	875.96	44.71	217.83	172.64
Washing Performance (%)	97.53	97.52	95.86	97.64	97.54	97.02

From table 4, the pH for each brand is approximately 8 whereas as mentioned before, the ideal pH is in the range of 9 – 10.5 [4]. The volume of foam formation for all brands are also not as high as compared to the formulated detergent done in this study. However, the viscosity of the commercial detergent are also higher compared to the Formula 1 and Formula 2. The washing performance for both commercial detergents and formulated ratios are almost the same of approximately 97% in cleaning the cooking oil. Noted that, the commercial detergent products contains additives that will enhanced the washing performance of the products while the optimum detergent formulations studies do not contain any additives. It is expected that the washing performance for the detergent formulations obtained from this study can be further improved with the addition of additives such as builder.

4. CONCLUSION

The present study outlines the response methodological technique by box-behnken design to optimize the detergent formulation from three plant-based surfactants which are sodium laureth sulfate (SLES), coconut fatty acid diethanolamide (CDE) and cocamidopropyl betaine (betaine). It was demonstrated that the technique could be applied successfully to predict the optimal ratios for mixing of three surfactants. It was found that the optimal ratio of CDE:SLES:betaine which is 2.00:8.31:1.00 were capable of showing maximum foaming ability of 7.16 cm^3 and approximately the same washing performance of 97.53% as commercial detergents (97.64% for brand X, 97.54% for brand Y and 97.02% for brand Z). The fact that all three surfactants used in this study are plant-based surfactants, its biodegradability is better than synthetic surfactants.

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