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Study on car shampoo formulation using D-optimal statistical design

Duduku Krishnaiah[*], Rosalam Sarbatly, SM Anisuzzaman and Enddy Madais

Abstract

Background: In this investigation car shampoo formulation was studied. The quality of car shampoo is directly linked to the basic material used in the formulation. By varying the ratio of ingredients such as sodium metasilicate (SMS), sodium lauryl ether sulphate (SLES), coco dimethyl betaine (betaine), coconut fatty acid diethanolamide (CDE) and linear alkyl benzene sulphonate (LABS), the final product characteristics were determined. A common problem in pre-formulation is the optimization of the mixture composition which is aimed to obtain a product with the required characteristics.

Results: In this work, various composition surfactants were used to prepare the car shampoo formulations. The D-optimal mixture design was performed to obtain the optimum formulation. Twenty-five combination components were selected according to the D-optimal criterion. Physical properties of the car shampoo such as pH, power of removal and foaming ability were studied. Contour graphics were formed to assess the change in the response surface in order to understand the effect of the mixture composition on car shampoo characteristics.

Conclusion: The statistical study shows that the fitted model was adequate to describe the viscosity response. The optimum composition formulation was SMS 1.48%, SLES 3.52%, betaine 4.0%, CDE 4.5% and LABS 1.5%.

Keywords: Surfactant, Car shampoo formulation, D-optimal mixture design, Foaming

Background

The production of new cars is increasing year by year. The detergent demand for car washing is also increasing in parallel with production of cars. Car shampoo is produced from the combination of surfactant, fragrance, stabiliser and other materials [1]. The good formulation consists at least of five components. Surfactant is the base material of the car shampoo formulation. It is the chemical species that is active and has a preference for a surface or interface which is the boundary between two phases. When the surfactant is used as emulsifier, it decreases the energy differences between the two phases to allow a relative stable mixture of oil and water. Generally, surfactant can be divided into four main groups: anionic, nonionic, cationic and amphoteric based on the chemical group [2-4].

The problem faced in the car shampoo formulation development is to achieve the optimum performance with good appearance and stability. In the formulation

work, statistical experimental design is commonly used to obtain a product with the required characteristics.

The primary goal of designing an experiment statistically is to obtain valid results at minimum of effort, time and resources [5]. There were several experimental design techniques used for formulation work such as factorial design and mixture design. However, it should be noted that factorial design cannot be used to study in such mixtures since the variables are not independent. The sum of all fractions of the components used must be equal to 1 [6-10]. The mixture design represents an efficient approach for solving such optimisation problem. It was found to be an effective tool to select the best liquid detergent formulation [11].

This research was based on the five main surfactants, namely, sodium metasilicate (SMS), sodium lauryl ether sulphate (SLES), coco dimethyl betaine (betaine), coconut fatty acid diethanolamide (CDE) and linear alkyl benzene sulphonate (LABS). These surfactants are widely used in detergent industry as these are biodegradable. The formulations were based on the composition designed by D-optimal mixture method. Physical properties of the car

* Correspondence: krishna@ums.edu.my
Chemical Engineering Programme, School of Engineering and Information Technology, Universiti Malaysia Sabah, Kota Kinabalu, Sabah 88400, Malaysia

shampoo such as pH, foaming ability and power of removal were studied. The responses of these components were analysed and optimised. Contour graphics were formed to assess the change in the response surface in order to understand the effect of the mixture composition on car shampoo characteristics.

Methods

Chemicals

All the chemicals (analaytical grade), sodium metasilicate (SMS), sodium lauryl ether sulphate (SLES), coco dimethyl betaine (betaine), coconut fatty acid diethanolamide (CDE) and linear alkyl benzene sulphonate (LABS) were purchased from Sigma-Aldrich (St. Louis, MO, USA).

Detergency evaluation: pH test

The pH test is the one of the detergency evaluation parameters in car shampoo formulation. The pH metre was calibrated before the pH test was performed. Five readings were taken to get the average pH data for each formulation.

Foaming ability test

The foaming was measured based on the height of the foam in the used container. The mechanical stirrer has been used to produce the foam. The volume of the foam was calculated by using Equation 1.

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

where r is the radius of beaker and H is the height of foam in millimetres.

Viscosity test

The viscosity measurement was carried out using Cole-Palmer Rotational Viscometer (Cole-Palmer, Chicago, IL, USA) with R2 spindle. A volume of 250 ml of car shampoo is poured into a beaker. The viscometer speed was set at 10 rpm. The process was allowed for about 20 min before the reading is taken. The reading was taken after 20 min.

Power of removal test

The power of removal of car shampoo formulation was estimated by using weighed soil before and after washing. The soil used in this research is the motor oil waste (degraded motor oil). The substrate used in the laboratory test is steel plate. One layer of soil (motor oil) was spread in the entire surface of the plate before the test was performed (initial weight). The mechanical stirrer assisted the removal of the oil. After washing, the plate was dried in the oven and the final weight was measured. The formula used in this test is shown in Equation 2 [12,13].

$$W = W_F - W_i, \tag{2}$$

where W is the soil removed, W_F is the final weight, and W_i is the initial weight.

Results and discussion

Relationship between composition and pH

Tables 1 and 2 represent the results of mean, linear, quadratic, special cubic and full cubic models of the data obtained. The computations were performed using Design Expert computer programme (version 6.09, Stat-Ease Inc., Minneapolis, MN, USA). The sequential F-tests in these tables indicate that the contribution of the mean, linear and special cubic model is significant. However, the terms in special cubic and cubic model are aliased and were ignored. Furthermore, the quadratic model is chosen because it has a larger adjusted R value compared to the other models.

The model for D-optimal is based on the following quadratic model in Scheffé equation:

$$E(y) = \sum_{i=1}^{q} \beta_i X_i + \sum \sum_{i<j=2}^{q} \beta_{ij} X_i X_j. \tag{3}$$

Final equation in terms of pseudo components becomes:

$$\begin{aligned}
Y = &-89.52X_1 + 6.52X_2 - 3.74X_3 + 116.75X_4 \\
&+ 32.72X_5 + 176.40X_1X_3 + 169.91X_1X_4 \\
&+ 106.31X_1X_5 + 21.28X_2X_3 - 36.16X_2X_4 \\
&- 25.47X_2X_5 - 20.56X_3X_4 - 18.89X_3X_5 \\
&- 58.39X_4X_5
\end{aligned} \tag{4}$$

Table 1 Sequential model sum of squares

Source	Sum of squares	Degrees of freedom	Mean square	*F*-value	Probability > *F*
Mean	1,841.10	1	1,841.10	-	-
Linear	291.02	4	72.76	34.22	<0.0001
Quadratic	31.84	10	3.18	2.98	0.0499
Special cubic	9.58	5	1.92	8.67	0.0167
Cubic	0.000	0	-	-	-
Residuals	1.11	5	0.22	-	-
Total	2,174.64	25	86.99	-	-

Table 2 ANOVA summary statistics of model fit

Source	Standard deviation	R^2 value	Adjusted R^2 value	Predicted R^2 value	PRESS
Linear	1.46	0.8725	0.8470	0.7996	66.83
Quadratic	1.03	0.9680	0.9231	0.6615	112.91
Special cubic	0.47	0.9967	0.9841	-	-

where X_1 = SMS, X_2 = SLES, X_3 = betaine, X_4 = LABS and X_5 = CDE.

Figures 1 and 2 present a normal probability of the studentized residuals and residual values. Based on this analysis, the probability plot of the studentized residuals was determined for the standard deviation of the actual values from their respective predicted values [5,6]. The second analysis has been plotted with the residuals versus the predicted responses. As shown in the Figures 1 and 2, there is no systematic pattern, and the points must be within a horizontal band centred at zero [5,14]. Departure from this may suggest a violation of the constant variance assumption. The size of the studentized residual should be independent of its predictive value, which means that the spread should be the same across all levels of the predicted values [11]. Figures 1 and 2 also present the normal probability plot of the studentized residual and plot of the studentized residuals versus the prediction of this model. These plots are satisfactory and it is concluded that the quadratic model is suitable to describe the pH by response surface of the car shampoo formulation. Figure 3 presents the three-dimensional response surface plot of pH. These plots are very important in interpreting the results. At this stage the prediction of the model is being used to generate the response surface graphs and the contour plots of the combination of the each component mixture [5]. Based on Figure 3, the
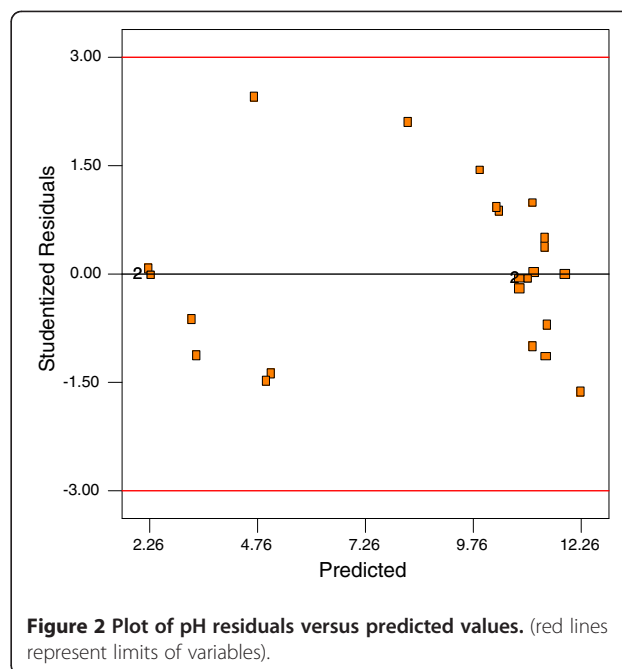

Figure 2 Plot of pH residuals versus predicted values. (red lines represent limits of variables).

composition of A (SMS), D (LABS) and E (CDE) is the main factor to influence the pH value. The LABS and CDE increased the pH of the car shampoo. Meanwhile for the SMS, when this surfactant is increased, the pH decreases in the formulation.

Relationship between composition and foaming ability

Tables 3 and 4 present the results of mean, linear, quadratic, special cubic and full cubic models of the data obtained. The sequential F-tests in Table 3 indicate that the contribution of the mean, linear, and quadratic is significant. In this analysis also the two models, the linear and quadratic, were
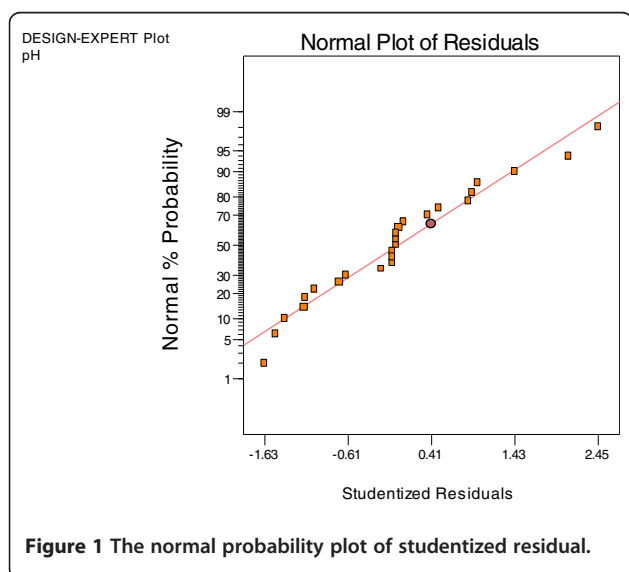

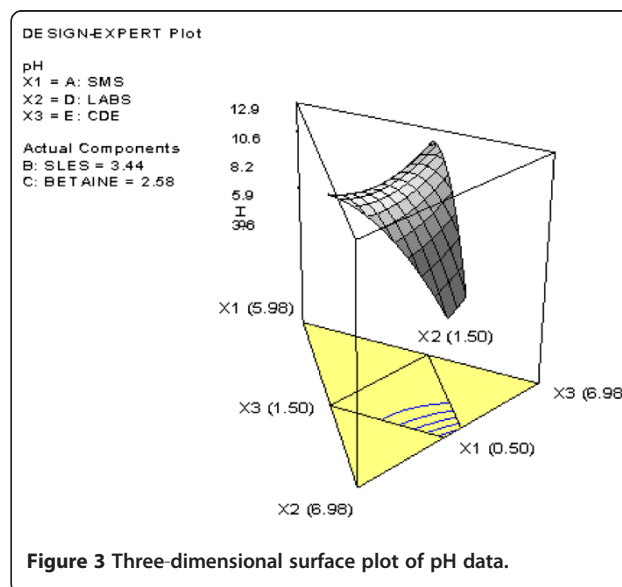**Figure 1 The normal probability plot of studentized residual.**

Figure 3 Three-dimensional surface plot of pH data.

Table 3 Sequential model sum of squares

Source	Sum of squares	Degrees of freedom	Mean square	F-value	Probability > F
Mean	1.79×10^7	1	1.793E + 007	-	-
Linear	5.715×10^5	4	1.429E + 005	4.70	0.0078
Quadratic	4.928×10^5	10	49,275.37	4.27	0.0157
Special cubic	75,656.66	5	15,131.33	1.90	0.2483
Cubic	0.000	0	-	-	-
Residuals	39,730.50	5	7,946.10	-	-
Total	1.911×10^7	25	7.645E + 005	-	-

significant. However, the quadratic model fits well because it has a larger R squared value compared to other models. However, the terms in special cubic and cubic models are aliased and should be ignored. Therefore, the fitted quadratic model has been chosen from D-optimal model (Scheffé equation).

Final equation in terms of pseudo components becomes:

$$\begin{aligned}
Y = &-5,896.65X_1 - 743.75X_2 + 1,775.74X_3 \\
&+ 4,669.52X_4 + 571.94X_5 + 9,335.53X_1X_2 \\
&+ 8,403.48X_1X_4 + 4,059.83X_1X_5 \\
&+ 2,831.20X_2X_3 - 2,987.98X_2X_4 \\
&+ 3,142.32X_2X_5 - 8,401.44X_3X_4 \\
&- 4,230.65X_4X_5
\end{aligned} \quad (5)$$

where X_1, X_2, X_3, X_4, and X_5 refer to SMS, SLES, betaine, LABS and CDE, respectively.

Figures 4 and 5 present the normal probability plot of studentized residual and plot of studentized residuals versus the predicted values of the model. These plots are satisfactory, and the quadratic model is suitable to describe the foaming ability response surface of the car shampoo formulation. Figure 6 presents the three-dimensional response surface plot of foaming ability. Based on the contour plot, the composition of A (SMS), C (betaine) and D (LABS) is the main factor to influence of the foaming ability. The betaine and LABS will influence the foaming ability of the car shampoo formulation. When both surfactant composition is increased, the foaming ability also decreased. However, for the SMS, when this surfactant is increased, the foaming ability also increased in the car shampoo formulation. The optimum foaming ability was found to be 1,038 mm.

Table 4 ANOVA summary statistics of model fit

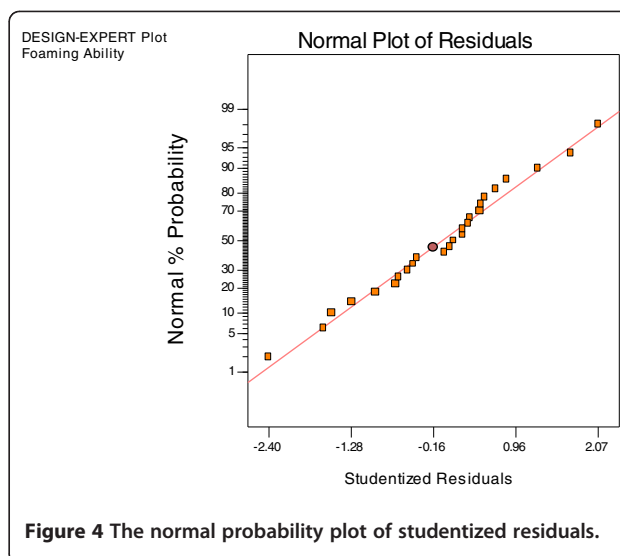| Source	Standard deviation	R^2 value	Adjusted R^2 value	Predicted R^2 value	PRESS
Linear	174.38	0.4845	0.3814	0.1599	9.910×10^5
Quadratic	107.42	0.9022	0.7652	0.0628	1.106×10^6
Special cubic	89.14	0.9663	0.8383	-	-

Figure 4 The normal probability plot of studentized residuals.

Relationship between composition and viscosity

Tables 5 and 6 present the result of mean, linear, quadratic, special cubic and full cubic models of the data obtained. The sequential F-tests in Table 5 indicate that the contribution of the linear model is significant since the adjusted R value is larger and better than the other models. However, terms in special cubic and cubic model are aliased and should be ignored.

Therefore, the fitted linear model based on Scheffé equation is

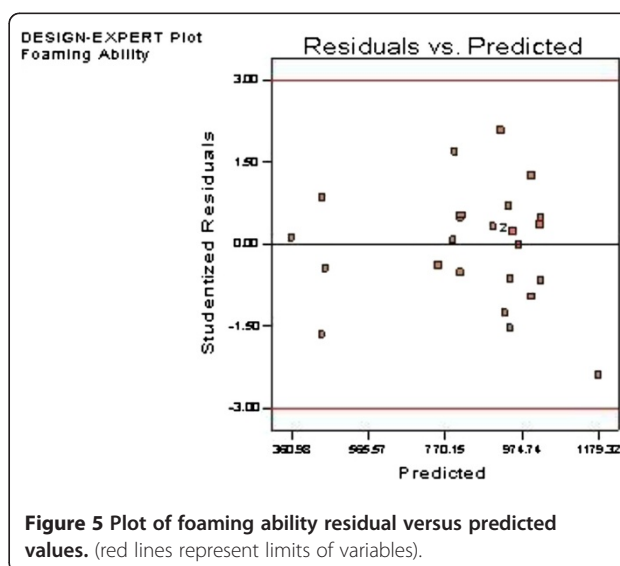$$E(y) = \sum_{i=1}^{q} \beta_i X_i. \quad (6)$$

Figure 5 Plot of foaming ability residual versus predicted values. (red lines represent limits of variables).
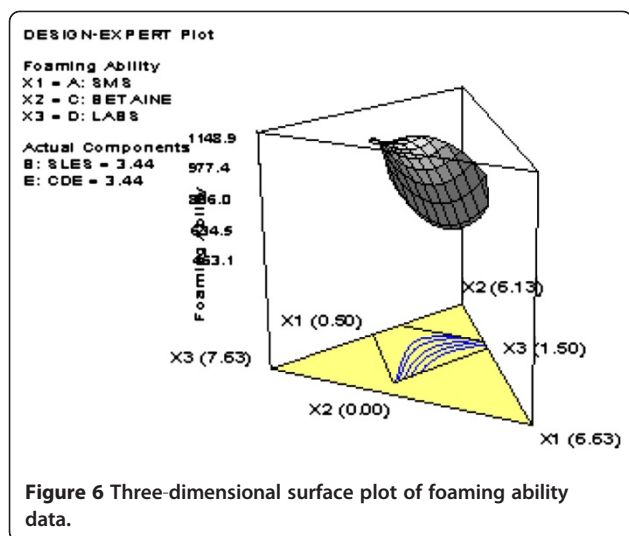
Figure 6 Three-dimensional surface plot of foaming ability data.

The final equation in terms of pseudo components becomes

$$\hat{Y} = 3196.70X_1 - 4176.66X_2 + 3284.97X_3 \\ - 1223.92X_4 + 6028X_5 \quad (7)$$

where X_1, X_2, X_3, X_4, and X_5 are SMS, SLES, betaine, LABS and CDE respectively.

Figures 7 and 8 present a normal probability of the studentized residuals and residual plotted versus predicted responses from the quadratic model. The figures also present the normal probability plot of studentized residual and plot of studentized residuals versus predicted values. These plots are satisfactory, and the linear model is suitable to describe the viscosity of response surface of the car shampoo formulation. Figure 9 presents the three-dimensional response surface plot of viscosity. Based on the plot, the composition of B (SLES), C (betaine) and E (CDE) is the main factor to influence of

Table 5 Sequential model sum of squares

Source	Sum of squares	Degrees of freedom	Mean square	F- value	Probability > F
Mean	3.948×10^7	1	3.948×10^7		
Linear	3.459×10^7	4	8.647×10^6	3.33	0.0303
Quadratic	2.406×10^7	10	2.406×10^6	0.86	0.5889
Special cubic	2.123×10^7	5	4.246×10^6	3.21	0.1129
Cubic	0.000	0	-	+	+
Residuals	6.606×10^6	5	1.321×10^6	-	-
Total	1.260×10^8	25	5.039×10^6	-	-

Table 6 ANOVA Summary statistics of model fit

Source	Standard deviation	R^2 value	Adjusted R^2 value	Predicted R^2 value	PRESS
Linear	1,610.90	0.3999	0.2799	0.0825	7.936×10^7
Quadratic	1,668.50	0.6781	0.2275	−3.6470	4.019×10^8
Special cubic	1,149.46	0.9236	0.6334	-	+
Cubic	-	-	-	-	+

the viscosity. The betaine and CDE will influence the viscosity of the car shampoo formulation. When both surfactant are increased, the viscosity decreases. Meanwhile for the SLES, when the surfactant composition is increased, the viscosity also increased in the car shampoo formulation.

Relationship between composition and the power of removal

Tables 7 and 8 present the results of mean, linear, quadratic, special cubic and full cubic models of the data obtained. The sequential *F*-tests in Table 7 indicate the significant contribution of linear model. In this analysis, the linear model has been suggested because the value of the predicted residual sums of squares (PRESS) is lower compared to the quadratic model. However, terms in special cubic and cubic model are aliased and should be ignored.

The final equation in terms of pseudo components becomes

$$Y = 0.64X_1 + 0.46X_2 + 0.37X_3 + 0.31X_4 + 0.26X_5 \quad (8)$$

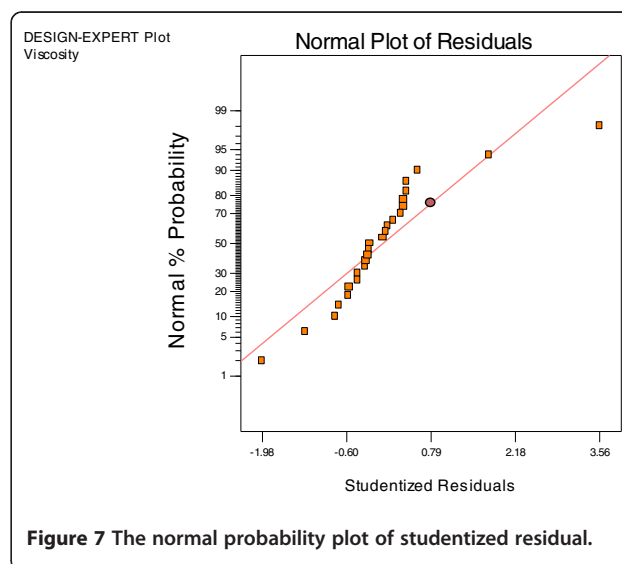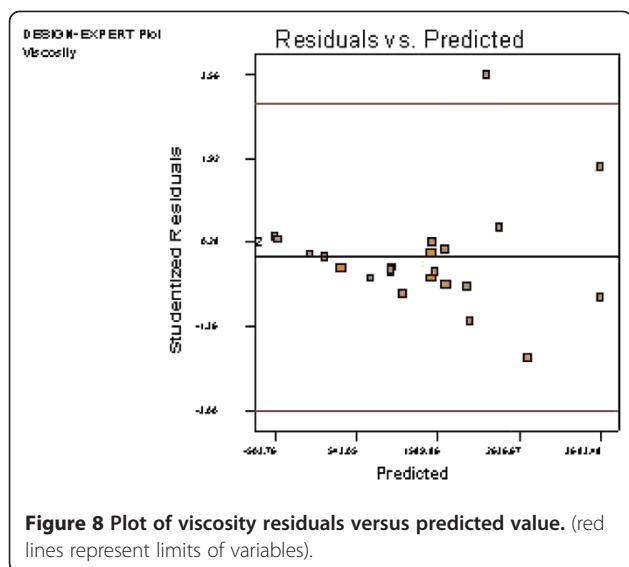where X_1 X_2, X_3, X_4, and X_5 are SMS, SLES, betaine, LABS and CDE respectively.

Figure 7 The normal probability plot of studentized residual.

Figure 8 Plot of viscosity residuals versus predicted value. (red lines represent limits of variables).

Figures 10 and 11 present a normal probability of the studentized residuals and residual plotted versus predicted responses from the quadratic model. The figures also present plot of studentized residuals versus predicted values. These plots are satisfactory, and we concluded that the quadratic model is suitable to describe the power of removal response surface of the car shampoo formulation. Figure 12 presents a three-dimensional response surface in power of removal. The composition of A (SMS), B (SLES) and C (betaine) is the main factor to influence of power of removal. The betaine and SLES influenced the power of removal of the car shampoo formulation. When both compositions of these surfactants increased, the power of removal also increased. However for the SMS, when its surfactant composition is increased, the power of removal decreased.
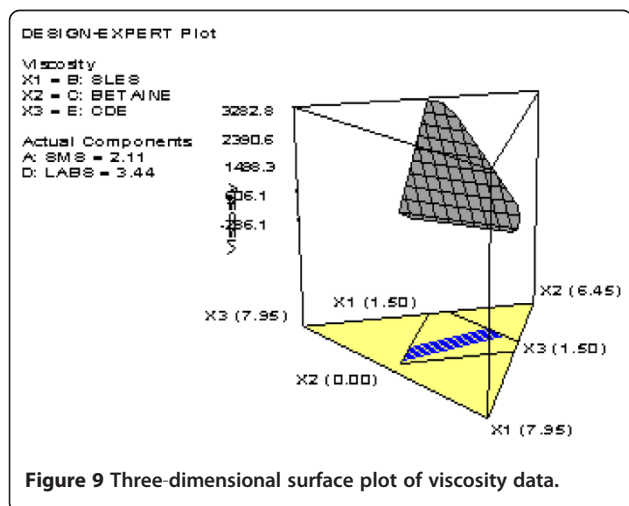

Figure 9 Three-dimensional surface plot of viscosity data.

Table 7 Sequential model sum of squares for power of removal

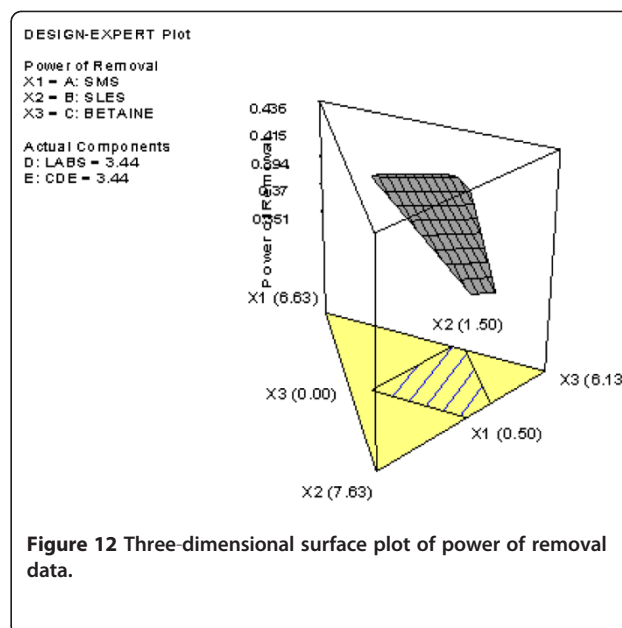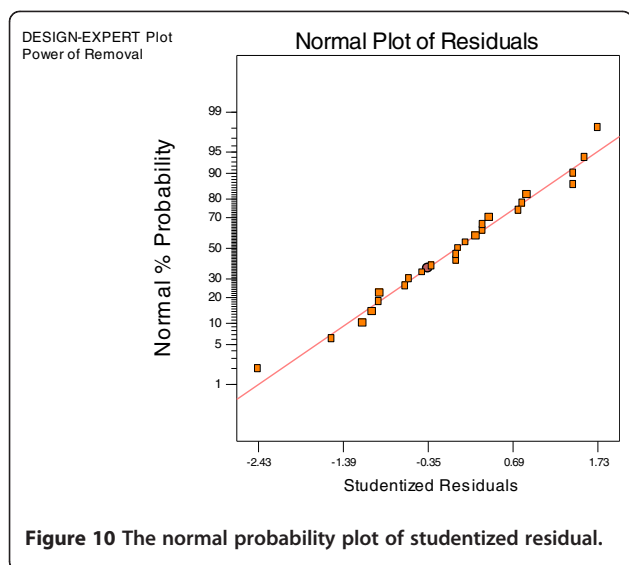| Source	Sum of squares	Degrees of freedom	Mean square	F-value	Probability > F
Mean	3.90	1	3.90	-	-
Linear	0.037	4	9.293×10^{-3}	5.07	0.0055
Quadratic	0.027	10	2.696×10^{-3}	2.78	0.0610
Special cubic	6.839×10^{-3}	5	1.368×10^{-3}	2.40	0.1794
Cubic	0.000	0	-	+	+
Residuals	2.850×10^{-3}	5	5.70×10^{-4}	-	-
Total	3.98	25	0.16	-	-

Optimization of car shampoo formulation

For pH the expected values were in the range of 7 to 12, since at low pH, very acidic condition causes skin irritation [15]. Thus, the viscosity test is very important. Besides, the optimum foaming ability is also needed in the formulation, since the optimum removal of the soil depends on the foaming ability. Nevertheless, heavy foaming can cause overflowing in the machinery and often accompanied by considerable loss of active ingredients. The function of the foaming in each formulation is to assist the surfactant itself especially LABS and SLES to remove the soil in every substrate and in any surface. The optimum power of removal is needed to determine the effectiveness of the formulation formed. The optimization process was conducted by using numerical values as shown in Table 9. The optimization and analyses of all the parameters such as pH, viscosity, power of removal and foaming ability were done using D-optimal method. Table 10 shows the optimal composition of each component to achieve the response desired.

Experimental

The experimental settings were performed by mixture experimental design. The experimental design of five-component system was conducted by using Design Expert (version 6.10, Stat-Ease Inc., Minneapolis, MN, USA). A set of candidate points in the design space were selected using the D-optimal criterion [5,16-19].

Table 8 ANOVA summary statistics of model fit for power of removal

Source	Standard deviation	R^2 value	Adjusted R^2 value	Predicted R^2 value	PRESS
Linear	0.043	0.5035	0.4042	0.1964	0.059
Quadratic	0.031	0.8688	0.6850	−0.8483	0.14
Special cubic	0.024	0.9614	0.8147	-	+
Cubic	-	-	-	-	+

Figure 10 The normal probability plot of studentized residual.

Figure 12 Three-dimensional surface plot of power of removal data.

In this study, there are restrictions on the component proportions X_j that take the form of lower L_j and upper U_j constraint. Constraints in this research are shown in Table 11. In this work, 25 car shampoo formulations were prepared in laboratory scale according to the composition designed by the D-optimal criterion. The ingredients used in car shampoo formulation were water as solvent, colour, fragrance and surfactants such as SMS, SLES, betaine, CDE and LABS. The components, starting with water and followed by SMS, SLES, betaine, CDE and LABS, were added together in a reactor. The mixture was then homogenised by using mechanical stirrer at

Table 9 The criteria used in numerical optimization

Response	Target	Range	
		Low	High
pH	In range	7	12
Viscosity	Maximum	7	7,483
Power of removal	Maximum	0.23	0.48
Foaming ability	Maximum	316	1,097

Figure 11 Plot of foaming ability residuals versus predicted values. (red lines represent limits of variables).
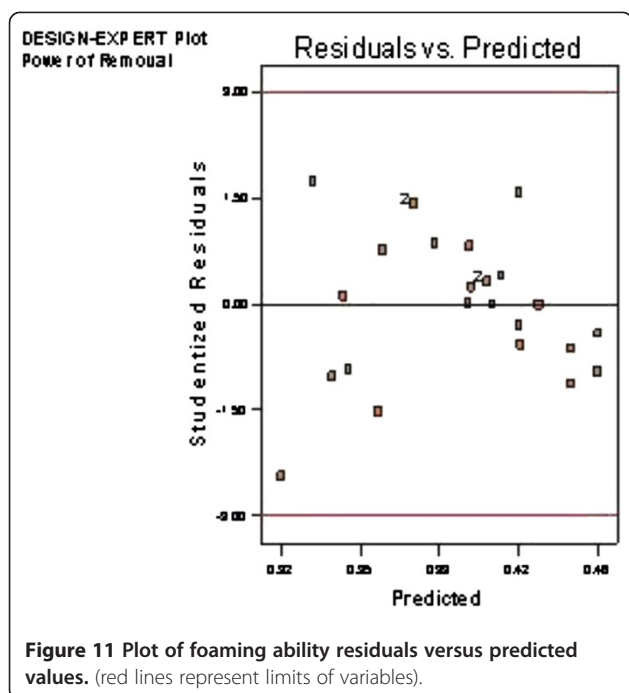
Table 10 The optimised formulation of car shampoo

Component	Percentage
SMS	1.48
SLES	3.52
Betaine	4.00
LABS	1.50
CDE	4.50
Total of mixture (%)	15.00

Table 11 Constraints of the component proportion

Component	Low limit (%)	High limit (%)
SMS, X_1	0.50	3.0
SLES, X_2	1.5	4.5
Betaine, X_3	0.0	4.0
LABS, X_4	1.5	4.5
CDE, X_5	1.5	4.5

280 rpm. The car shampoo produced was stored in a bottle for 24 h at 30°C.

Conclusions

Twenty-five samples were prepared and four responses were tested based on formulation formed. The responses tested in this study were pH test, foaming ability test, viscosity test and power of removal test. The analysis was done by using the D-optimal statistical method. The best model, based on the results of pH test, foaming ability test and power of removal test, was found to be the quadratic model. However, for viscosity test, the linear model has been chosen. The results indicate that the performance and characteristics of the car shampoo can be manipulated by changing the composition of the surfactant used in the formulation. The optimal composition of the car shampoo formulation was obtained based on the each desired response. From the analysis, the optimal formulation consists of 1.48% SMS, 3.52% SLES, 4.00% betaine, 1.50% LABS, and 4.5% CDE, which gives the viscosity of 2481.61 cP, power of removal of 0.44 g and foaming ability at 1,038 mm.

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