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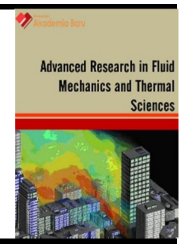

Optimization of Moisturizing Clay Soap Containing Pitaya (*Hylocereus polyrhizus*) Seed Extract Using D-Optimal Mixture Experimental Design

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ABSTRACT

Pitaya seed oil, extracted from red pitaya seeds, was utilized as a major antioxidant source in soap formulation for skin application. Bentonite (grey clay powder) with various beneficial properties also was incorporated in the formulation to enhance the positive effect toward skin's structure. The influence of the main compositions of soap formulation containing different fatty acid and oils (cocoa butter, virgin coconut oil, olive oil, palm oil) on the hardness of the soap that undergoes saponification process was investigated by employing D-optimal mixture experimental design. Analysis of variance (ANOVA) was carried out and the polynomial regression for prepared soap hardness in terms of the six design factors was developed by utilizing the experimental data. Results revealed that the best soap formulation included 9.027% A, 29.098% B, 19.588% C, 9.223% D, 23.860% E and 9.204% F. The results showed that the hardness of the soap was greatly affected by the different in the level of fatty acid and oils in the formulation. Depending on the appropriate level of those six variables, the production of moisturizing clay soap containing pitaya seed extract with the most desirable properties which is much better than those of commercial ones is possible.

Keywords:
Pitaya, mixture design, saponification, clay

1. Introduction

In the recent times, the consumers had become more aware on what they are using and what they are consuming. The polemics related to chemical-personal care products which may cause dermatological problem like irritation, itching and burning of skin had create one situation where the consumers aggressively urged on utilize of natural ingredients in the product. The consumer is

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internet savvy, searching the medical archives for ingredients that will make her or his skin do better than just looking better [1]. For the consumers, “natural products” superficially would seem to be synonymous with “safe” products.

To meet the demand, the revolution in the cosmetic technology had brought one accepted point of view in the development of cosmeceutical industry where the products produced are natural plant-based. Acted as a bridge between the pharmaceutical and personal care products, cosmeceutical is believed to create one phenomena in which the cosmetic product will just not only functioning to beautify and give protection to the skin, but can also deliver the nutrient needed by the skin and possesed healing properties [2,3]. Hence, the aesthetic value of skin can be improved by topical application of cosmeceutical product as it is typically claimed to improve texture, skin tone and radiance, while reducing wrinkle [4].

Pigment lightener, moisturizer, sunscreen, facial soap and other formulations have been altered to increase the results on the outer layer of skin which called epidermis by the addition of active ingredients [2]. The features of active agents are efficacy, safety, formulation stability, novelty and patent protection, metabolism within skin and inexpensive manufacture [3]. These advance benefits caused the cosmeceutical to form the fastest growing segment in dermatology.

The fruits of red pitaya, Hylocereus polyrhizus had gained so much interest recently due to its low economic value, potential health benefits, attractive color and unique shape [5,6]. Pitaya fruits are reported to contain high fiber, protein, minerals, probiotic properties, high phenolic content and high antioxidant level [7]. The red-deep purple pigment of pitaya fruits can be used to replace the application of synthetic dyes, especially in the food products [6]. The essential fatty acid (EFA) found in the oil are linoleic acid (49.6%), oleic acid (21.6%) and palmitic acid (17.9%) [8]. Linoleic acid form the largest contribution to promote the human health as it may relieve flaky or rough skin, treat acne, soften and moisturize skin and many more. Recent study also stated that EFAs also able to nourish skin, hair and nails [9].

Bentonite, or more familiar with the name of grey clay powder had been used in the early days for medicinal purposes Due to its active principle, clay powder is used in oral applications as osmotic oral, antidiarrhoeaics, laxatives and gastrointestinal protectors [10]. Besides that, these ‘golden’ minerals also able to combat lipodystrophies, acne and cellulite [11]. The fundamental principle of clay powder that had been used in pharmaceutical are due to their high specific area and sorptive capacity, chemical inertness, rheological properties and low or zero toxicity for the patient [11]. Clay powder can also be manipulated in topical application as dermatological protector. An active principle of clay powder causes it to be able to give opacity, cover blemishes and eliminate shine from the skin.

In this present study, red pitaya extracts is used as an emollient since it can function to keep the desired smooth, soft and moist skin. It gives protection against dryness and irritation by forming an oily layer that traps water on top of epidermis. While, active ingredients is rich in nutrients level that increase human health. It may act as the main source of antioxidant that provides the benefits that need by the body. The aesthetic value of the moisturizing clay soap containing pitaya seed extract is exhibited by an addition of inactive ingredients like colorant and fragrance. Inactive ingredients help to deliver the benefits of active ingredients. In order to get the desired characteristics and functional stability, multivariate statistical technique like D-optimal mixture design is used. The design is used commonly and widely in the product formulation, such as in the food, pharmaceutical and cosmeceutical industries. The design was reported to be able to reduce the number of experimental runs needed to evaluate multiple variables and it also able to recognize interactions statistically, which is able to overcome the shortcomings of the traditional formulation method.

2. Materials and Method

2.1. Materials

Samples of olive oil were purchased from Coreysa, Spain. Samples of palm oil were purchased from Yee Lee Corporation, Berhad, Malaysia. Samples of castor oil and virgin coconut oil were purchase from Euro Chemo–Pharma Sdn Bhd, Malaysia. Cocoa butter and bentonite (clay) was obtained from Making Cosmetics Inc., USA. Sodium hydroxide (NaOH) was obtained from R&M Chemical (Essex, UK). Water was deionised by a Purelab Flex (Elga, Albania) filtration system. All other chemicals were in analytical and cosmetic grades.

2.2 Pre-Treatment of Pitaya Seed

Red pitaya fruits, Hylocereus polyrhizus, were collected from local farm which is located in Sepang, Selangor. The fruits were peeled and the seeds were separated from the pulp manually under running water. The seeds were cleaned by using tap water a few times to discard all the pulp leftover and mucilage. The seeds then were fully dried for about 6 hours at 40℃ and kept in the container for further processes.

2.3 Extraction of Pitaya Seed Extract

Dried pitaya seeds were grinded and sieved into fine sized (0.85mm particle sized) in order to increase the surface area for an extraction of oil to take placed. The ground seed were extracted with solvents having different extraction's behavior. Specifically, the seed were extracted using different type of solvent that show varies in polarity. Polar solvent such as ethanol extracted polar fraction of oil out from the seeds. Meanwhile, for non-polar solvent, hexane extracted non-polar oil out from the seeds. As the extraction was completed, the solvents were discarded from the oil using rotary evaporator.

2.4 Saponification of Moisturizing Clay Soap containing Pitaya Seed Extract

Soap samples were prepared according to ingredients formulated from the design matrix. The clay soap was formulated using a mixture of oils, fatty acids and pitaya seeds extract as natural antioxidants, with additional ingredients by saponification process. The method described by Borhan et al., 2014, was modified and used for the soap preparation [12].Sodium hydroxide (NaOH) pellet were weighed and dissolved in water. NaOH solution was allowed to cool in the temperature between 27℃ until 38℃ since the process to dissolve the pellets released heat (exothermic reaction). Saponification process was continued by heating the oil up to ≥71℃ and ≤82℃ with constant stirring. After the temperature of oil was achieved, NaOH solution was added slowly into the oil while stirring. The mixture was heated with uniform stirring until pudding like consistency was formed. The stirring and heating process were stopped. The mixture was transferred into the beaker for further saponification. After that, an active ingredient which was pitaya seed oil was added into the mixture. The ratio of pitaya seed used was 1:3. About 0.125 g of ethanolic extract and 0.375 g of hexanic extract were pipetted and transferred into the mixture. Five grams of colorant (estimated to be 10 drops) and 5g of fragrance (estimated to be 6 drops) were added into the mixture. Lastly, the mixture was placed in the mold and allowed to cure in the room temperature for about 3 weeks.

2.5 D-optimal Mixture Experimental Design

The effect of the fatty acid (A), mixture of oil (B-D), distilled water (E) and caustic soda (F) on the hardness (Yi) of the soap formulation was determined by employing six-factor D-optimal design mixture. Table 1 listed the coded levels of the variables used in the formulation. About 31 runs of design matrix was generated using Design Expert® 7.0.0 software (Stat. ease Inc., Minneapolis, USA), as shown in Table 2. Each of the design was analysed one by one, based on the interaction of each composition of variables towards the response (Yi). The effect of undetermined variability on the actual response was minimized by running the composition of soap formulation according to the D-optimal design in a randomized order.

Table 1
Coded levels of the variable used in the formulation

	Causal factor variables[1,2]	Coded level of variables (%)	
		Low	High
A	Cocoa butter	24.00	28.00
B	Virgin coconut oil	15.00	20.00
C	Olive oil	6.00	10.00
D	Palm oil	15.00	20.00
E	Distilled water	6.00	10.00
F	Caustic soda	2.00	7.00

1) The mixture was composed of cocoa butter (A), virgin coconut oil (B), olive oil (C), palm oil (D), distilled water (E), and caustic soda (F).
2) Fixed portion of clay, pitaya seed oil and ingredient that kept constant was incorporated in the formulation, so that the total gross amount of soap was $\pm$51 g.
3) A + B + C+ D + E + F + constant ingredients = $\pm$50%

2.6 Determination of the Hardness of the Moisturizing Clay Soap Containing Pitaya Seed Extract

TA HDplus texture analyser (Stable Micro System Ltd., Surrey, UK) with a load's cell of 500 N was used to measure the hardness of clay-pitaya seed oil soap. The hardness was measured using needle geometry. A stainless P/2:2 diameter needle cylinder of probe was used to carry out the analysis. Hardness was reported as the maximum penetrating force (N) required for the needle to penetrate through a sample (70.5 mm × 40 mm, depth 10 mm) at 25°C, over a distance of 8 mm at a constant speed of 10 mm/s.

2.7 Statistical Analysis

D-optimal mixture design is conducted to determine the effects of the ingredient compositions on the hardness of the soap (Y*i*). A few statistical parameters were used in the evaluation such as coefficient of variation (C.V), regression (*P* value), regression (*F* value), lack of fit, adjusted multiple correlation coefficients (adjusted R^2) and multiple correlation coefficient (R^2). The best-fitting mathematical method is selected. The design was expressed by the polynomial regression equation to generate the model as shown below:

$$Yi = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 - \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{44} x_4^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{14} x_1 x_4 + \beta_{23} x_2 x_3 + \beta_{24} x_2 x_4 + \beta_{34} x_3 x_4 \quad (1)$$

Where Y*i* is the predicted response, β_0, β_i and β_{ii} are the linear, quadratic and interaction coefficients, respectively. The suitable polynomial equations for the design, such as linear, quadratic or special cubic models, were chosen according to the fittest model.

The mixture design space and three-dimensional (3D) contour plots of the fitted polynomial regression were generated to show the interaction of the response variables and factor variables. An optimum condition was obtained by conducting graphical and numerical optimisations. Response optimiser is used to predict values for the desirable response [13].

Table 2
31-run of formulation of moisturizing clay soap containing pitaya seed extract using D-optimal mixture design

Exp no.	A	B	C	D	E	F
1	10.000	29.998	15.006	9.998	25.000	9.999
2	9.999	29.999	20.000	7.647	22.357	9.999
3	10.000	27.919	18.475	8.606	25.000	9.999
4	9.844	29.787	19.836	5.682	25.000	9.851
5	9.999	27.644	20.000	8.893	23.467	9.998
6	9.080	29.239	19.957	7.512	24.213	10.000
7	9.999	30.000	18.319	9.999	23.698	7.984
8	10.000	29.998	15.006	9.998	25.000	9.999
9	9.998	29.998	20.000	9.998	20.007	9.998
10	7.189	27.814	19.999	10.000	24.999	9.999
11	8.847	27.879	19.500	10.000	24.716	9.058
12	9.998	25.007	19.998	9.999	25.000	9.998
13	9.998	29.998	20.000	9.998	20.007	9.998
14	8.268	29.967	19.986	9.994	25.000	6.786
15	9.902	29.006	18.878	9.141	23.883	9.190
16	6.540	29.997	19.999	8.466	25.000	9.998
17	6.520	30.000	18.484	9.999	24.999	9.998
18	10.000	27.842	20.000	8.552	24.998	8.608
19	10.000	27.602	18.717	10.000	23.683	9.998
20	7.098	29.999	20.000	9.999	22.905	9.999
21	7.814	29.267	20.000	9.247	24.356	9.317
22	9.198	30.000	19.999	8.829	23.310	8.665
23	9.998	29.999	17.565	9.109	23.328	10.000
24	9.999	28.357	20.000	9.999	23.311	8.334
25	9.999	28.558	18.259	9.999	25.000	8.185
26	7.098	29.999	20.000	9.999	22.905	9.999
27	8.275	30.000	18.546	9.999	23.901	9.280
28	9.396	29.994	18.256	8.409	25.000	8.945
29	6.508	29.994	19.998	9.999	25.000	8.501
30	8.268	29.967	19.985	9.994	25.000	6.786
31	9.998	25.007	19.998	9.999	25.000	9.998

2.8 Verification of the Model

The models were validated using several random formulations that had been prepared. The experimental values were compared with the predicted value obtained from the final response regression equations to verity the model. The optimum values predicted by the model were also verified by performing the recommended optimum composition [14].

3. Result and Discussion

3.1 Screening of Variables

The main characteristic of a mixture design is every single component cannot be changed independently of one another as the total components used must be added up to 100%. The statement above stated that the mixture factors are expressed as the fraction of the total amount and their experimental ranges lie between 0 to 100%. Upper- and lower- bound restrictions on the component proportion were determined based on the data of the construction and analysis of mixture designs. The standard range of hardness of soap formulation was about 500 N – 600 N.

3.2 Fitting the Response Surface Model

The aim of the optimization of bar soap formulations is generally to determine the levels of the variable from which a robust product with high quality characteristics may be produced. Each of the design was analysed one by one, based on the interaction of each composition of variables towards the response (Yi). The effect of undetermined variability on the actual response was minimized by running the composition of soap formulation according to the D-optimal design in a randomized order. The experimental data of all model formulation obtained for the response (Yi) based on the D-optimal mixture design matrix were listed in Table 3 as following. The hardness of soap was represented by the variation in penetration force (N).

The responses were applied in order to fit the suitable model (linear or quadratic) after the formulation had been analysed. The model was tested for goodness of fit correlation of determination (R^2) and analysis of variance (ANOVA) was applied to verify the adequacy of the regression model in terms of a lack-of-fit test. The best fitted model for the six independent variables also was determined by utilizing the analysis of variance (ANOVA). This test implies that the residual response sum of squares is separated into the components model error and pure error, and their significances were obtained by an F-test as shown in Table 5. Table 4 show the analysed statistical parameter values, including estimated regression coefficients, standard deviation, PRESS, R^2, adjusted R^2, regression (*P-value*), regression (*F-value*) were related to the consequences of the independent variables. A response was investigated regarding to outliers and it was found that all points were placed in a normal distribution. Table 4 shows that the “Predicted R-Squared” of 0.9255 is in reasonable agreement with the “Adjusted R-Squared” of 0.9992. “Adequate Precision” measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 157.863 indicates an adequate signal. This model can be used to navigate the design space. That value had showed that more than 90% of the variation of the hardness could be described by mixture models, which are a desirable physical characteristic of the moisturizing clay soap containing pitaya seed oil. Other than that, the lack of fit had no indication of significance ($P < 0.05$) for the final reduced models. It indicated that the models were the fittest models towards the response.

Table 3
31-runs of design matrix and experimental values of the response (Y_i) of moisturizing clay soap containing pitaya seed extract (%)

Experiment	A	B	C	D	E	F	Y
1	10.00	30.00	15.01	10.00	25.00	10.00	595.61
2	10.00	30.00	20.00	7.65	22.36	10.00	1172.87
3	10.00	27.92	18.48	8.61	25.00	10.00	867.87
4	9.84	29.79	19.84	5.68	25.00	9.85	872.50
5	10.00	27.64	20.00	8.89	23.47	10.00	732.98
6	9.08	29.24	19.96	7.51	24.21	10.00	775.71
7	10.00	30.00	18.32	10.00	23.70	7.98	291.71
8	10.00	30.00	15.01	10.00	25.00	10.00	597.44
9	10.00	30.00	20.00	10.00	20.01	10.00	744.62
10	7.19	27.81	20.00	10.00	25.00	10.00	1285.72
11	8.85	27.88	19.50	10.00	24.72	9.06	751.41
12	10.00	25.01	20.00	10.00	25.00	10.00	1057.68
13	10.00	30.00	20.00	10.00	20.01	10.00	741.88
14	8.27	29.97	19.99	9.99	25.00	6.79	150.98
15	9.90	29.01	18.88	9.14	23.88	9.19	574.60
16	6.54	30.00	20.00	8.47	25.00	10.00	605.77
17	6.52	30.00	18.48	10.00	25.00	10.00	946.63
18	10.00	27.84	20.00	8.55	25.00	8.61	374.00
19	10.00	27.60	18.72	10.00	23.68	10.00	644.00
20	7.10	30.00	20.00	10.00	22.91	10.00	686.49
21	7.81	29.27	20.00	9.25	24.36	9.32	479.27
22	9.20	30.00	20.00	8.83	23.31	8.67	234.85
23	10.00	30.00	17.57	9.11	23.33	10.00	809.88
24	10.00	28.36	20.00	10.00	23.31	8.33	226.93
25	10.00	28.56	18.26	10.00	25.00	8.19	207.06
26	7.10	30.00	20.00	10.00	22.91	10.00	674.50
27	8.28	30.00	18.55	10.00	23.90	9.28	0.00
28	9.40	29.99	18.26	8.41	25.00	8.95	549.97
29	6.51	29.99	20.00	10.00	25.00	8.50	185.11
30	8.27	29.97	19.99	9.99	25.00	6.79	152.33
31	10.00	25.01	20.00	10.00	25.00	10.00	1076.72

Table 4
Regression coefficients of the final reduced models

Regression Coefficient	Value
Standard deviation	8.57
PRESS	1.85E+05
R2	0.9998
Adjusted *R2*	0.9992
Predicted *R2*	0.9255
Adequate Precision	157.863

The model F-value of 1877.40 implies the model is significant. There is only a 0.01% chance that a "Model F-value" this large could occur due to noise. Value of "Prob > F" less than 0.0500 indicate the model terms are significant. Values greater than 0.1000 indicate the model terms are not significant. The "lack of Fit F-value" of 2.10 implies the Lack of Fit is not significant relative to the pure error. There is a 21.84% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good.

Table 5
Analysis of variance (ANOVA) of the fitted linear/quadratic equation for hardness of moisturizing clay soap containing pitaya seed extract

Source	Mean Square	F-value	P-value
Model	1.38E+05	1877.4	<0.0001
Linear Mixture	3.58E+05	4873.81	<0.0001
AB	57393.93	782.09	<0.0001
AC	19737.99	268.96	<0.0001
AD	1.49E+05	2031.04	<0.0001
AE	1.29E+05	1755.2	<0.0001
AF	3405.33	46.4	0.0001
BD	1204.69	16.42	0.0037
BE	89919.86	1225.31	<0.0001
BF	6742.12	91.87	<0.0001
CD	3743.86	51.02	<0.0001
CE	3473	47.34	0.0001
CF	20210.01	275.39	<0.0001
DE	28283.42	385.41	<0.0001
EF	29537.24	402.49	<0.0001
Residual	73.39		
Lack of fit	109.2	2.1	0.2184
Pure error	52.9		

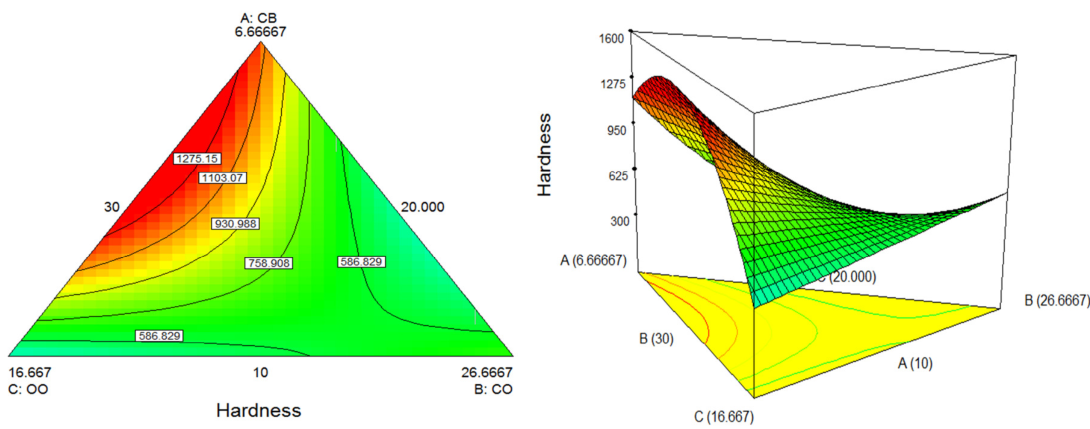
3.3 3-Dimension (3D) Response Surface Analysis

The response contour plots had illustrated the model equations. It also shows the relationship and effects of variables on the hardness of moisturizing clay soap containing pitaya seed extract. Each variable that being utilized in the response surface was represented at the corner of an equilateral triangle where the composition of the components were different from one another. The contour plots exhibited the minimum percentage of the component by the regression at the corresponding corner while the maximum percentage of the component was locate at the middle of the opposite side of the triangle. Three types of variables (components) were placed at each corners of the triangle while the other three variables (components) were fixed at their average compositions. The contour plots also show the equal mixture of the variables at the centroid (the center of the triangle). Generally, the most suitable model to the mixture design was the quadratic model.

The relationship between cocoa butter, olive oil and virgin coconut oil and palm oil had contributed to the hardness of soap. Cocoa butter has the major fatty acid like oleic acid, followed by stearic acid and palmitic acid. It helps to harden the soap and it also caused the soap to be rich in moisturizing effect toward skin. Greater amount of force is needed to penetrate the soap when the percentage of olive oil increased [12]. Basically, olive oil can be categorized as two different types of oils such as soft oil and hard oil [15]. As the soft oil being applied in the soap formulation, it produces good lathering ability and improved solubility of soap in cold water [16]. Olive oil is one of the oils that possessed higher level of unsaturated fatty acid. Usually, soap made from high percentage of this kind of oil produced softer soap, but the only exception to this rule is olive oil. Softer condition of soap only occurred at early stage of curing, but it turned to really hard form as the curing process had completed [16].

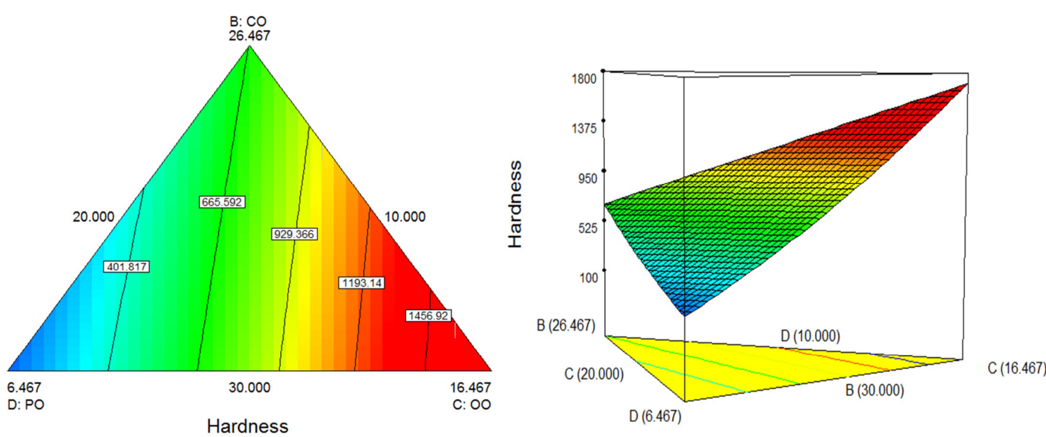
Meanwhile, the Figures also illustrated that as the percentage of virgin coconut oil increased, the hardness of the soap was increased. The hardness of the soap was indicated by the increased in the force needed to penetrate the soap at certain distance. Virgin coconut oil was composed of dominant fatty acid like lauric acid, which is the saturated fatty acid. According to the theory, soap that being made from high percentage of saturated fatty acid produced hard soap [17]. However, virgin coconut oil just not only played an important role towards the hardness of the soap, but it also able to deliver therapeutic values to the skin such as antioxidant, antibacterial and antiviral activities [18]. The increased in the percentage of palm oil in the mixture had caused the soap to be harder since the palm oil is rich in palmitic acid, the saturated fatty acid. Aside from that, palm oil also delivers the beneficial effect towards as it able to decrease UV-ray penetration which can cause aging [19].

Figures 1 and 2 show the relationship between the cocoa butter, virgin coconut oil and olive oil. The influence of the reaction between all these oils in the mixture had increased the hardness of soap. Virgin coconut oil was the main oil that had contributed to the hardness, while the cocoa butter and olive oil gave equal hardness to the soap. Next, the relationship between the cocoa butter, virgin coconut oil and palm oil had been illustrated in Figures 3 and 4. As cocoa butter reacted with virgin coconut oil, equal contribution to hardness of soap had been observed. The Figures also shows that palm oil form the major influenced on the hardness of soap.



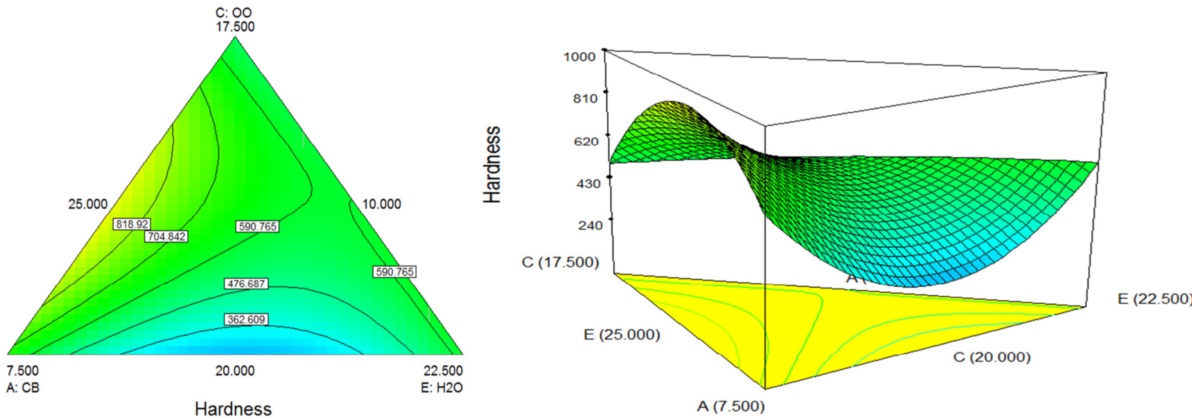
X_1 (A) : Cocoa Butter ; X_2 (B) : Coconut oil; X_3 : Olive oil (C) Actual components: Palm oil (D) : 9.167 ; water (E) : 25.000 ; NaOH (F) : 9.167

Fig. 1. Contour plot (two-dimensional) (1a) and three-dimensional (1b) surface showing the interaction effect between three (Y*i*). Variables: Cocoa butter (A), virgin coconut oil (B), olive oil (C) towards the response hardness**.**



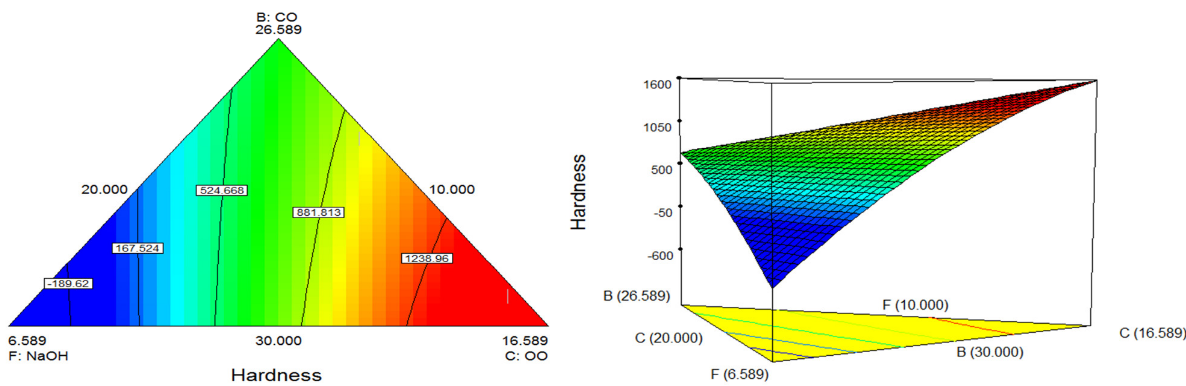
X_1 (B) : VCO ; X_2 (D) : Palm oil; X_3 : Olive oil (C) Actual components: cocoa butter (A) : 9.093 ; water (E) : 24.723 ; NaOH (F) : 9.717

Fig. 2. Contour plot (two-dimensional) (2a) and three-dimensional surface (2b) showing the interaction effect between three variables: Virgin coconut oil (B), olive oil (C), palm oil (D). towards the response hardness



X_1 (C) : Olive oil ; X_2 (A) : Cocoa butter; X_3 : water (E) Actual components: VCO (B) : 26.167 ; (D) : 9.167 ; NaOH (F) : 9.167

Fig. 3. Contour plot (two-dimensional) (3a) and three-dimensional surface (3b) showing the interaction effect between three variables (Y*i*). Variables : Cocoa butter (A), olive oil (C), water (E) towards the response hardness



X1 (B) : VCO ; X2 (F) : NaOH; X3 : Olive oil (C) Actual components: cocoa butter (A) : 9.093 ; water (E) : 24.723 ; Palm oil (D) : 9.595

Fig. 4. Contour plot (two-dimensional) (4a) and three-dimensional surface (4b) showing the interaction effect between three variables: Virgin coconut oil (B), olive oil (C), caustic soda (F) towards the response hardness

Figure 3 and 4 show the relationship between the mixture of oil with water or NaOH. Basically, the composition of water and NaOH also had influence the hardness of soap. High percentage of water in the mixture caused the pudding like structure to experience difficulty to pass tracing stage. Hence, complete saponification cannot be achieved. Meanwhile, high percentage of NaOH caused the soap to undergo supercracking effect as the soap was too hard or brittle [20]. Appropriate proportion of water and NaOH must be applied in the experiment to ensure the soap can undergoes complete saponification process.

The contribution of each of the six components and the effects of the different proportions of the variables was supported by the final equation of the model that describing the penetration force of the soap which can be written as:

$$Y_i = 3318.46A + 1068.84B + 595.81C + 1220.45D + 744.36E - 1999.20F - 4257.49AB + 5472.33AC - 9712.97AD - 6397.25AE + 1235.14AF - 290.56BD - 1999.50BE + 1235.67BF - 779.35CD + 449.89CE + 2295.76CF + 812.62DE + 3320.28EF \quad (2)$$

where; Y*i* = Response, A = Cocoa butter, B = Virgin coconut oil, C = Olive oil, D = Palm oil, E = Distilled water, F = Caustic soda (NaOH)

The positive term in the regression equation indicates an effect that favors optimization, owing to synergistic effects, whereas a negative term represents antagonistic effects between the factors and the response [21].

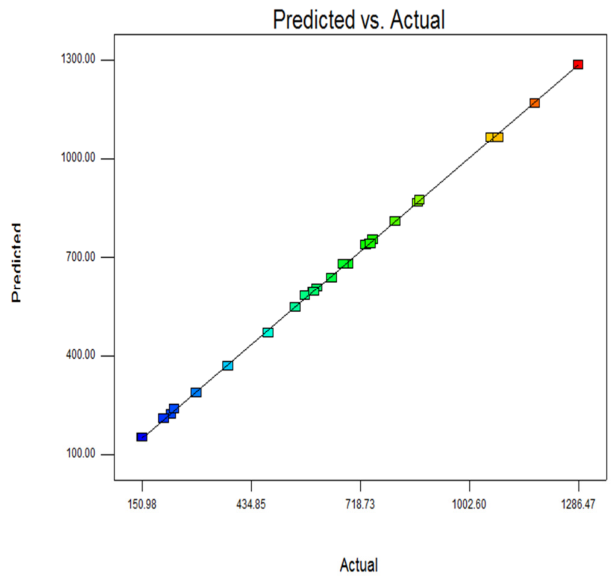


Fig. 5. Scatter plot of the observed values versus the predicted values

The commercial soaps had been screened to determine the hardness of the soap. The results revealed that commercial soaps exhibited hardness in the range of 1000 N -2000 N [12]. It proved that the soaps are harder bars since it may only use sodium palmate and sodium palm kernelate.as the major ingredients. Past studies had stated that the soap with higher percentage of palm- and palm-kernel-based oils possess higher tendency to crack as it getting harder [17, 22]. Other than that, palm-based oils soap has higher possibility to cause soap erosion rate and dry the skin [23]. Hence, the composition of the oils and fatty acid were adjusted so that the optimum hardness of the soap will be in the range of 500 N - 600 N.

3.4 Validation for Verification

To verify the adequacy of the surface response equation, the predicted and actual values of the responses were compared as shown Table 6. Based on the design, the optimized formulation of moisturizing clay soap containing pitaya seed extract has a hardness value of 585.47 N. There was no significant ($P > 0.05$) difference was detected. Hence, the results as shown in Table 6 were found to be on good agreement with the predicted values. In addition to that, Figure 5 shows the good prediction of the actual hardness with the predicted hardness with lowest root standard error value (RSE) calculated by the following equation:

$$RSE = (\text{Predicted value} - \text{Experimental value})/(\text{Predicted value}) \times 100 \quad (3)$$

Table 6
Predicted and observed for the optimized formulation

Response (Y*i*)	Predicted	Observed	RSE (%)
Y*i* : hardness (N)	544.76	546.34	0.290

4. Conclusions

The present study had shown that the D-optimal mixture experimental design is the beneficial and effective method to carry out an optimization study of the hardness of moisturizing clay soap containing pitaya seed extract. The design was implemented by combining 6 different independent variables: cocoa butter, virgin coconut oil, olive oil, palm oil, water and caustic soda. The relationship and composition of the variables was determined by measuring the hardness of the soap. A quadratic mathematical model was suggested for the response which is hardness (Yi). The analysis of variance corroborates the accuracy of the model, using a high F value (1877.40) and a very low P value (<0.0001), a non significant lack of fit, and a coefficient of determination of R^2 = 0.9998. As a summary, an optimization of moisturizing clay soap containing pitaya seed extract with desired hardness can be successfully studied by performing the D-optimal mixture experimental design that makes used multiresponse optimisation utilizing a polynomial equation. The guideline on improving specific desirable characteristics can be obtained through this research since D-optimal design was capable to study a lot of variables at one time. In addition, the research finding also exposed a guideline on the influence of ingredients toward the physical properties of cosmeceutical products.

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