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Central composite design application in oil agglomeration of talc

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Abstract: Talc has many applications in various branches of industry. This material is an inert one with a naturally hydrophobic surface. Talc agglomeration is within the wide interest of pharmaceutical industry. Oil agglomeration experiments of talc were carried out to find out and assess the significance of experimental factors. Central composite design (CCD) was used to estimate the importance and interrelation of the agglomeration process parameters. Four experimental factors have been evaluated, i.e. concentration of cationic surfactant and oil, agitation intensity as well as time of the process. The median size of agglomerates ($D50$) and the polydispersity span (PDI) were used as the process responses. Logarithmic transformations of the responses provide better description of the model, than untransformed responses, with the reduced cubic model for $D50$ and quadratic model for PDI. This was supported by the Box-Cox plots. It was shown that there were many statistically important factors, including the concentration of cationic surfactant and stirring rate for $D50$, concentration of oil and stirring rate for PDI, as well as various interactions, up to third order for $D50$. Optimal conditions for minimum values of reagent amounts as well as mixing time and intensity for the maximum size of agglomerates but of rather narrow size distribution were found.

Keywords*: talc, oil agglomeration, optimization, central composite design, design of experiment*

Introduction

Talc is a magnesium silicate mineral which usually occurs in either foliated, granular or fibrous forms. It is commonly used as a filler and a coating agent in paints, lubricants, plastics, cosmetics, pharmaceuticals and ceramics manufacture. It is also applied as a nucleating agent in plastic foaming processes (Wong and Park, 2012). This substance is an inert one with a naturally hydrophobic surface (Bremmell and Addai-Mensah, 2005). The pharmaceutical industry is one of the branch, where agglomeration of talc is an interesting issue (Jadhav et al., 2011).

Oil agglomeration is a size enlargement method that facilitates separation operations of solid processing (filtration, flotation, sedimentation) (Ennis, 1996). The

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main advantages making this method interesting for industrial applications (e.g. pharmaceutics, pigments, and pesticides) are: high selectivity, possibility of fine particles aggregation (below 5 μm) and simple equipment (Pietsch, 1991; House and Veal, 1992; Huang and Berg, 2003). Oil agglomeration mostly depends on surface properties of particles and oil/water interface (Drzymala, 2007; Bastrzyk et al., 2011; Bastrzyk et al., 2012). In this process, an addition of an immiscible liquid (binder) to a solid aqueous suspension causes adhesion of hydrophobic particles by capillary interfacial forces (Rossetti and Simons, 2003; Negreiros et al., 2015). In the suspension, between these hydrophobic particles liquid bridges are formed, which are responsible for the mechanical strength and stability of agglomerates obtained, whereas, the hydrophilic particles remain un-agglomerated (Sonmez and Cebeci, 2003). Literature data show that the several other factors affected the course of oil agglomeration, which include the oil amount and type, particle size, agitation rate and time, pH, and surfactant concentration (Sadowski, 1995; Aktas, 2002; Sonmez and Cebeci, 2003; Duzyol and Ozkan, 2010; Bastrzyk et al., 2011; Bastrzyk et al., 2012; Duzyol and Ozkan, 2014; Duzyol, 2015).

Success of oil agglomeration depends on selection of suitable operating parameters (Balakin et al., 2015). Therefore, it is very important to determine the operating parameters at which the responses reach their optimum.

The best known method for determining the important operating parameters for agglomeration is to carry out experiments by changing one parameter and keeping the others at a constant level. However, this one-variable-at-a-time technique does not include interactive effects of parameters, and does not depict the exact effects of various parameters on the process (Chary and Dastidar, 2013; Aslan and Unal, 2011; Aslan, 2013). In order to avoid this, optimization studies using design of experiments are of great importance.

Currently, numerous experimental designs are used. The most important first-order designs are: 2^n factorial, where n is the number of control variables (Montgomery, 2001), and the Plackett-Burman design (Plackett and Burman, 1946). The most important second-order models are: central composite (CCD) (Box and Wilson, 1951) and Box-Behnken three-level design (Box and Behnken, 1960). In the literature, a number of useful design or techniques can be found to optimize the parameters for oil agglomeration. It can be listed as the Taguchi method (Chary and Dastidar, 2010; Kumar et al., 2015), response surface methodology (RSM) (Cebeci and Sonmez, 2006; Aslan and Unal, 2009; Aslan and Unal, 2011) and grey relational analysis (GRA) (Aslan, 2013).

Central composite design (CCD) is an experimental design affiliated to response the surface methodology (Liu et al., 2011). This method provides graphs rendering and including the expanded center points (Oney and Tanriverdi, 2012). Results obtained from the experiments in the light of the experimental design are defined as a function of factors. Several polynomial models are used to create the model equation. These polynomials show how the response of the system parameter values obtained

effect at the same time (Oney and Tanriverdi, 2012). CCD is ideal for sequential experimentation and allows a reasonable amount of information for testing lack of fit, while not involving an unusually large number of design points (Demirel and Kayan, 2012). The central composite design has found an application for optimization of chemical processes such as textile dye degradation (Demirel and Kayan, 2012), removal of dyes (Azami et al., 2012; Azami et al., 2013), flocculation and coagulation of wastewater (Fendri et al., 2013) and extraction of protein from wastewater (Ramyadevi et al., 2012). However, until now, there is no information reported on optimization of oil agglomeration of solid particles using CCD.

In this study, the importance of process parameters in oil agglomeration of talc was evaluated using the central composite design. The surface active agent and bridging oil concentrations together with the agitation intensity and process time were evaluated experimental factors. The median size of agglomerates (D_{50}) and the particle size distribution span (PDI) were the process responses.

Materials and methods

A talc powder was purchased from LG Olsztyn (Poland) and originated from IMI Fabi LLC (USA). This mineral sample was used as obtained and was of a pharmaceutical grade and, according to supplier information, conformed to the requirements of Pharmacopea. The average particle diameter of talc, determined using Mastersizer 2000 (Malvern), a laser diffraction instrument, was 9.5 μm. The BET surface area of the powder determined by FlowSorb 2300 II instrument (Micromeritics) was 4.8 $m^2 g^{-1}$.

Oil agglomeration tests were carried out in a glass vessel (250 cm^3 with an inner diameter of 60 mm). A sample of 5 grams of talc together with 100 cm^3 of distilled water was intensively stirred by using the IKA EUROSTAR power control-visc 6000 overhead mechanical stirrer equipped with a 3-bladed propeller. The products of agglomeration were separated and dried, and then subjected to the image analysis. The procedure was as follows. Photographs were taken using the AxioImager M1m microscope (Zeiss), operating in the transmitted light mode, and 8 bit grayscale pictures were collected. Using ImagePro Plus ver. 6.0 software (Media Cybernetics), histogram-based segmentation with 3×3 mesh was applied, resulting in white-on-black image, which was analysed automatically in respect to the mean diameter, counting bright objects. Because, in some cases, particles were bridged, an automatic watershed split was applied. Measurement data were transferred to MS-Excel, and the median size and PDI were calculated.

Oil agglomeration of talc proceeds irregularly without surfactant addition because of the properties of talc surface. The cationic surfactant dodecylammonium hydrochloride (DDAHCl) (POCh) was applied as a wetting agent and an emulsifier, while kerosene (Sigma-Aldrich) was used as a bridging oil (Kelebek et al., 2008; Bastrzyk et al., 2011; Polowczyk et al., 2014).

Central composite design (CCD) was used to estimate the importance of the agglomeration process parameters. The median size of agglomerates (D_{50}) and particle size span (PDI) were the process responses. Data were analyzed using a demo version of Stat-Ease 10.0.5 software (Design Expert).

Results and discussion

Response surface methodology (RSM) is a set of statistical methods for empirical model building (Box and Draper, 1987;; Montgomery, 2001; Khuri and Mukhopadhyay, 2010). Using design of experiment (DoE) techniques, output variables (responses) can be optimized in respect to input variables. An experiment consists of several runs, with varying input variables, in order to identify and quantify changes in output responses. Usually, such relationship can be approximated by low level polynomial:

$$y = f(x)\beta + \epsilon \tag{1}$$

where y is a response of interest, $x = (x_1, x_2, \dots, x_n)$ is the set of input variables, n is the number of variables, $f(x)$ is a vector function consisting of powers and cross-products of powers of $x_1, x_2, \dots, x_n$, up to a certain degree (usually 1 or 2), β is a vector of unknown constant coefficients, called parameters, and ϵ is a random experimental error. The surface represented by $f(x)\beta$ is called a response surface.

There are two most important models used in RSM, that is first and second degree. The former one is represented by equation (Khuri and Mukhopadhyay, 2010):

$$y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \epsilon \tag{2}$$

where β_i are the linear coefficients and β_0 is an intercept. Second order model is described by the following equation:

$$y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{1 \le i < j \le n} \beta_{ij} x_i x_j + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \epsilon \tag{3}$$

where β_{ij} are called cross-product coefficients, and β_{ii} are quadratic coefficients. Sometimes $\sum_{i=1}^{n} \beta_{ii} x_i^2$ term is omitted from the model, which is then called 2-factor interaction (2FI). When complete equation (3) is employed, the model is called either full quadratic or simply quadratic. Sometimes, third level (cubic) equation is also used. Such cubic model is usually too complicated, and there is a potential risk of aliasing, i.e. when estimate of effect also includes the influence of either one or more other effects, usually high-order interactions. Aliasing does not need to confound whole model, because such higher order interaction is often non-existent or insignificant (Antony, 2003).

Frequently used in the industrial applications as well as in scientific research, central composite design (CCD) was selected in this study. Generally, CCD can be

described as 2^n factorial design with additional central and axial points, allowing calculating parameters of a second-order model. It involves 2^n factorial points, $2n$ axial points and one central point. Usually axial and/or central points are replicated. Axial points are placed at the distance α from the design center, thus CCD uses five levels of parameters: $+\alpha, +1, 0, -1, -\alpha$. The value of α is usually chosen to make design either orthogonal or rotatable (Draper, 2008). The experimental design is orthogonal if the effects of any factor sum to zero across the effects of the other factors. The design is rotatable if the variance of the predicted response at any point x depends only on the distance of x from the center point. Rotatability is achieved when:

$$\alpha = \sqrt[4]{2^n}\,. \tag{4}$$

The design studied in the current contribution consisted of four experimental factors, that is DDAHCl-to-talc mass ratio (A), kerosene-to-talc mass ratio (B), stirring time (C) and stirring rate (D). For 4 factors, in order to achieve rotatability, according to equation (4), the value of α should be equal to 2. Unfortunately, this resulted in negative values of parameters A and C at $-\alpha$ level, thus we set $\alpha = \sqrt{2}$. We decided to skip parameter coding and the actual values were used instead. The values of parameters are given in Table 1, and the summary of the design in Table 2.

Table 1. Experimental factors

			Level				
Parameter	Unit	Label	–α	–1	0	+1	+α
DDAHCl-to-talc	mg g^{-1}	A	1.31	1.60	2.30	3.00	3.28
Kerosene-to-talc	g g^{-1}	B	0.38	0.48	0.72	0.96	1.06
Time	min	C	3.44	8	19	30	34.6
Stir rate	rpm	D	620	1200	2600	4000	4580

Table 2. Parameters of experimental design

Parameter	Value
Design type	Central composite
Process order	2FI/Quadratic/Cubic
Number of variables	4
Number of responses	2
Star distance (α)	$\sqrt{2}$
Replicates of factorial points	1
Replicates of star points	2
Center points	2
Total number of runs	34

Table 3. Results of experimental runs

Run	DDAHCl [mg g^{-1}]	Kerosene [g g^{-1}]	Time [min]	Stir rate[rpm]	$D50$ [mm]	PDI
1	1.31	0.72	19.00	2600	0.079	3.14
2	1.31	0.72	19.00	2600	0.168	1.96
3	1.60	0.48	8.00	1200	0.052	2.82
4	1.60	0.48	30.00	1200	0.316	1.34
5	1.60	0.48	8.00	4000	0.093	1.4
6	1.60	0.48	30.00	4000	0.131	0.81
7	1.60	0.96	8.00	1200	0.135	4.47
8	1.60	0.96	30.00	1200	0.263	5.58
9	1.60	0.96	8.00	4000	0.135	3.39
10	1.60	0.96	30.00	4000	0.039	15.42
11	2.30	0.38	19.00	2600	0.171	0.59
12	2.30	0.38	19.00	2600	0.111	0.67
13	2.30	0.72	3.44	2600	0.191	3.04
14	2.30	0.72	3.44	2600	0.24	3.05
15	2.30	0.72	34.60	2600	0.399	1.41
16	2.30	0.72	34.60	2600	0.372	1.84
17	2.30	0.72	19.00	620	0.091	3.58
18	2.30	0.72	19.00	620	0.061	6.85
19	2.30	0.72	19.00	4580	0.159	1.03
20	2.30	0.72	19.00	4580	0.168	1.62
21	2.30	0.72	19.00	2600	0.657	1.22
22	2.30	0.72	19.00	2600	0.62	3.96
23	2.30	1.06	19.00	2600	0.097	4.64
24	2.30	1.06	19.00	2600	0.143	2.89
25	3.00	0.48	8.00	1200	0.144	6.8
26	3.00	0.48	30.00	1200	0.361	2.37
27	3.00	0.48	8.00	4000	0.199	0.58
28	3.00	0.48	30.00	4000	0.404	1.34
29	3.00	0.96	8.00	1200	0.292	5.74
30	3.00	0.96	30.00	1200	0.129	4.31
31	3.00	0.96	8.00	4000	0.193	1.24
32	3.00	0.96	30.00	4000	0.03	9.72
33	3.28	0.72	19.00	2600	0.605	3.77
34	3.28	0.72	19.00	2600	0.574	2.88

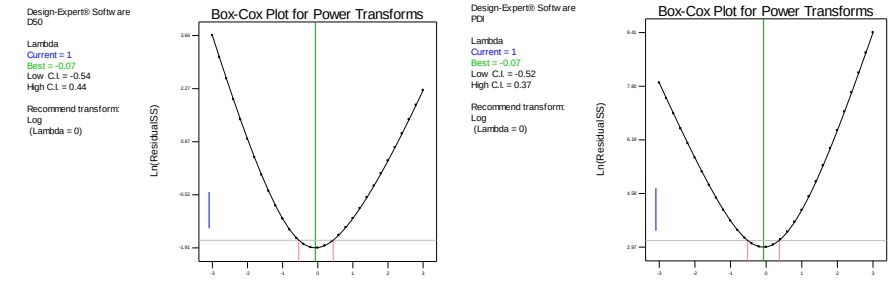
Two responses were analyzed: median particle size ($D50$) and particle size width DPI defined as (Merkus, 2009):

$$\text{PDI} = \frac{D90 - D10}{D50} \tag{5}$$

where *D*10 and *D*90 are first and last deciles (Sheskin, 2004) of particle size distribution, respectively. This parameter, sometimes called span, is commonly accepted as a measure of width of particle size distribution (Merkus, 2009). In practice, in agglomeration processes a relatively uniform and narrow agglomerates size distribution is requested for the granular product (Pietsch, 1991; 2005).

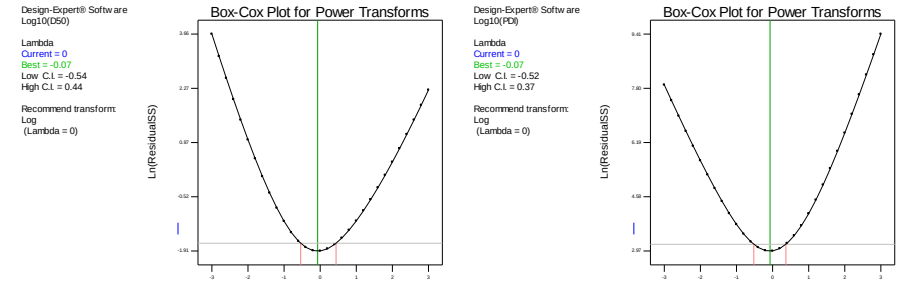
All runs were randomized in order to avoid systematic errors. The results are shown in Table 3.

One can observe that the ratio of maximal to minimal response is, in both cases, greater than 20. This suggests that some transformation should be applied. Base 10 logarithm was selected as the transformation function. This selection was supported by the Box-Cox transformation (Box and Cox, 1964).



a) b)

Fig. 1. The Box-Cox plots of original data a) for *D*50 and b) for PDI



a) b)

Fig. 2. The Box-Cox plots of transformed data a) for *D*50 and b) for PDI

The Box-Cox plots obtained before and after logarithmic transformation by the Design Expert software are shown in Figs. 1 and 2 for *D*50 and PDI, respectively a) and b). Current lambda values were 1 for the original data (Fig. 1) and this value was beyond the confidence intervals (C.I.). However, best value lambda was -0.07 showing the need of logarithmic transformation for the both parameters. After transformation (Fig. 2), the lambda obtained was 0 and this value was very near to -

0.07 and between the confidence intervals showing the efficiency of logarithmic transformation.

All calculations were performed at significance threshold equal to 0.05, and then re-analyzed at the threshold lowered to 0.01. Significance level of the effect of different parameters on two responses was estimated by the Fisher test (*F*-test) (Box, 1953) and corresponding *p*-values. The comparison of models is shown in Tables 4 and 5.

Table 4. Comparison of process orders for log*D*50 response

Parameter	Process order		
	2-Factor interactions vs. linear	Quadratic vs. 2-factor interactions	Cubic vs. quadratic
F value	2.36	5.38	8.27
p-value	0.0639	0.0045	0.0014
		Model summary	
R^2	0.4829	0.7576	0.9713
Adjusted R^2	0.2581	0.5789	0.9052
Predicted R^2	–0.0309	0.2063	0.7675
Adeq. Precision	6.686	8.256	15.046
Aliased terms	None	None	AC^2, AD^2, B^2C, B^2D, BC^2, BD^2, C^2D, CD^2, B^3, C^3, D^3

Table 5. Comparison of process orders for logPDI response

Parameter	Process order		
	2-Factor interactions vs. linear	Quadratic vs. 2-factor interactions	Cubic vs. quadratic
F value	5.04	2.11	0.2746
p-value	0.0020	0.1191	0.2746
		Model summary	
R^2	0.7870	0.8526	0.9368
Adjusted R^2	0.6945	0.7440	0.7914
Predicted R^2	0.4696	0.7914	0.4396
Adeq. precision	11.879	10.728	10.439
Aliased terms	None	None	AC^2, AD^2, B^2C, B^2D, BC^2, BD^2, C^2D, CD^2, B^3, C^3, D^3

In the case of log(*D*50) response (Table 4), one can see that the cubic model gives much better fit than the quadratic one, in terms of determination coefficient (R^2), as well as adjusted and predicted values of R^2. Unfortunately, eleven third order interactions were aliased, as shown in Table 4. However, we decided to compare both models mentioned above. The *F* values for the quadratic and cubic models are equal to 4.24 (Table 6) and 14.70 (Table 7), respectively, indicating that both models are statistically significant.

Table 6. ANOVA table for log(*D*50) – quadratic model

Source	Sum of squares	Degrees of freedom	Mean square	F value	*p*-value Prob > F[a]
Model	2.8647	14	0.2046	4.2411	0.0021
A-DDAHCl	0.4779	1	0.4779	9.9052	0.0053
B-Kerosene	0.0943	1	0.0943	1.9543	0.1782
C-Time	0.0374	1	0.0374	0.7761	0.3893
D-Stir rate	0.0159	1	0.0159	0.3295	0.5727
AB	0.0981	1	0.0981	2.0328	0.1702
AC	0.0811	1	0.0811	1.6817	0.2102
AD	0.0070	1	0.0070	0.1453	0.7073
BC	0.5822	1	0.5822	12.0664	0.0025
BD	0.1810	1	0.1810	3.7508	0.0678
CD	0.2523	1	0.2523	5.2286	0.0339
A^2	0.0065	1	0.0065	0.1354	0.7169
B^2	0.4617	1	0.4617	9.5689	0.0060
C^2	0.0000	1	0.0000	0.0000	0.9982
D^2	0.6400	1	0.6400	13.2640	0.0017
Residual	0.9167	19	0.0482		
Lack of Fit	0.8099	10	0.0810	6.8223	0.0040
Pure Error	0.1068	9	0.0119		
Corr. Total	3.7814	33			

[a] Statistically significant terms for significance threshold 0.05 are underlined.

The chance that *F* values were so high due to the noise which was equal to 0.21 and 0.01%, respectively. *P*-values less than 0.0500 indicate that the model terms are significant. In the case of quadratic model (Table 6) A, BC, CD, B^2, D^2 were significant model terms. Values greater than 0.1000 indicate that the model terms are not significant. At more rigorous significance threshold equal to 0.01, CD term became insignificant. The lack of fit *F* value of 6.82 implied that the lack of fit was significant, which was unfavorable. The model fitting was expected. There was only 0.40% chance that a lack of fit *F*-value this large could occur due to noise. An adequate precision parameter value was 8.256 (Table 4). This indicated an adequate signal, because for a good signal-to-noise ratio it should be greater than 4. The predicted R^2 of 0.2063 was much lower than adjusted R^2 (0.5789). This might indicate a large block effect or a possible problem with model and/or data. Therefore, we decided to analyze the aliased cubic model, with manually removed confounded terms.

Statistically significant terms at significance threshold 0.05 were identified to be, starting from to least significant, according to the *p*-value, D^2, B^2, BC, A^2D, CD, A^3, A, AB^2, BD, A^2, C^2, D, AB, AC, and C. At significance threshold 0.01, several terms

become insignificant, namely C, AB, AC (Table 7). As mentioned above, this model was statistically significant. All control parameters values were remarkably better than in the case of quadratic model. The predicted R^2 of 0.7675 agreed reasonably with the adjusted R^2 of 0.9052 (Table 4). Adequate precision of 15.046 indicated a good signal-to-noise ratio. The lack of fit *F* value of 0.15 implied that the lack of fit was not significant relative to the pure error.

Table 7. ANOVA table for log(*D*50) – cubic model

Source[b]	Sum of squares	Degrees of freedom	Mean square	*F* value	*p*-value Prob > *F*[b]
Model	3.6728	23	0.1597	14.7038	0.0001
A-DDAHCl	0.2484	1	0.2484	22.8710	0.0007
B-Kerosene	0.0046	1	0.0046	0.4271	0.5282
C-Time	0.0660	1	0.0660	6.0776	0.0334
D-Stir rate	0.1164	1	0.1164	10.7175	0.0084
AB	0.0981	1	0.0981	9.0309	0.0132
AC	0.0811	1	0.0811	7.4710	0.0211
AD	0.0070	1	0.0070	0.6455	0.4404
BC	0.5822	1	0.5822	53.6062	0.0000
BD	0.1810	1	0.1810	16.6633	0.0022
CD	0.2523	1	0.2523	23.2284	0.0007
A^2	0.1760	1	0.1760	16.2070	0.0024
B^2	0.6531	1	0.6531	60.1361	0.0000
C^2	0.1605	1	0.1605	14.7787	0.0032
D^2	0.7746	1	0.7746	71.3258	0.0000
ABC	0.0296	1	0.0296	2.7223	0.1300
ABD	0.0058	1	0.0058	0.5308	0.4830
ACD	0.0527	1	0.0527	4.8554	0.0521
BCD	0.0193	1	0.0193	1.7792	0.2118
A^2B	0.0180	1	0.0180	1.6545	0.2273
A^2C	0.0313	1	0.0313	2.8838	0.1203
A^2D	0.2571	1	0.2571	23.6703	0.0007
AB^2	0.2477	1	0.2477	22.8100	0.0008
A^3	0.2504	1	0.2504	23.0563	0.0007
Residual	0.1086	10	0.0109		
Lack of Fit	0.0018	1	0.0018	0.1487	0.7088
Pure Error	0.1068	9	0.0119		
Corr. Total	3.7814	33			

[a] Aliased terms are removed from model.

[b] Statistically significant terms for significance threshold 0.05 are underlined.

Therefore, based on this observation, the median size of talc agglomerates is affected mainly by the concentration of cationic surfactant DDAHCl as well as intensity and, to a lesser extent, mixing time. The agglomerate size is controlled by the balance between agglomerate interaction influenced by capillary forces and the destructive forces determined by the shearing regime. The former are correlated with the water and oil interfacial tension which is affected by the presence of surfactant. Therefore, a quantity of surfactant added to the system is of importance for spherical agglomeration since also affects the attachment of oil droplets to the mineral particle surface and spreading on it (Laskowski and Yu, 2000). The presence of surfactant can lower the strength of oil bridges, even to the point that agglomerates can be torn apart by shear forces (Cebeci and Sönmez, 2004; Ozkan et al., 2005). Also, emulsification by mixing of oil in the presence of surfactant lowers the amount of bridging liquid necessary for agglomeration of mineral particles, due to the decrease of oil droplets size (Laskowski and Yu, 2000). Therefore, depending on the mixing intensity and bridging oil amount, the density and volume of the agglomerates can change. At constant amount of oil added to predetermined amount of the suspension of particles in water and subjected to mixing with constant intensity, the oil agglomeration process takes place in four stages. In the first short stage, pendular oil floccules are formed. In the second stage, so-called zero growth, a complete transition of emulsion droplets into agglomerates is observed. As a consequence, third stage of a rapid growth of aggregates is achieved. The last stage reflects final forming of agglomerates (equilibrium period), which, at appropriately intensive mixing, can become either spherical or form the sphere-like structure. Small decrease in the diameter of agglomerates can be observed due to compression and forcing out water from the structure of aggregates (Drzymala, 2007).

The equation in terms of actual factors can be employed to predict the response for given levels of each factor. The log$D$50 response can be expressed by the polynomial model. In the case of the cubic model, using coded factors, is as follows:

$$\log(D50) = -1825 + 1761A + 0.058C - 2.92 \times 10^{-4}D - 1098AB + 0.059AC + 0.0057BC + 4.77 \times 10^{-4}BD - 1.36 \times 10^{-5}CD - 634A^2 - 1764B^2 - 0.00143C^2 - 1.94 \times 10^{-7}D^2 - 0.00032A^2D + 764.4AB^2 + 92.18A^3. \quad (6)$$

The applied software provides various graphs to help interpreting the model selected. The best practice, when looking at model graphs, is to focus on the terms with significant effects. A graph of the observed (actual) response values versus the predicted ones helps to detect observations that are not well predicted by the selected model. The data points should be divided evenly by the diagonal line in both original or transformed scale.

The plot of predicted and observed values is shown in Fig. 3. On can see that proposed model predicts reasonably well the experimental results of agglomerates diameter.

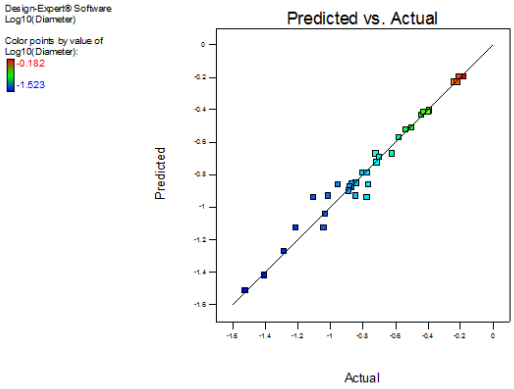


Fig. 3. Predicted vs. observed values of log*D*50 for cubic model, R^2 = 0.7675

The 3D surface plot is a projection of the contour plot giving shape in addition to the colour and contour. Typical model graphs are shown in Figs. 4a and 4b. In Figures 4a and 4b, the influence of the mixed interactions of significant terms DB and DC, i.e. stirring rate with oil-to-talc mass ratio and stirring rate with stirring time, on diameter of talc agglomerates were shown. From this 3D plots maximum value of *D*50 can be identified with increasing mixing intensity and both kerosene amount and process duration.

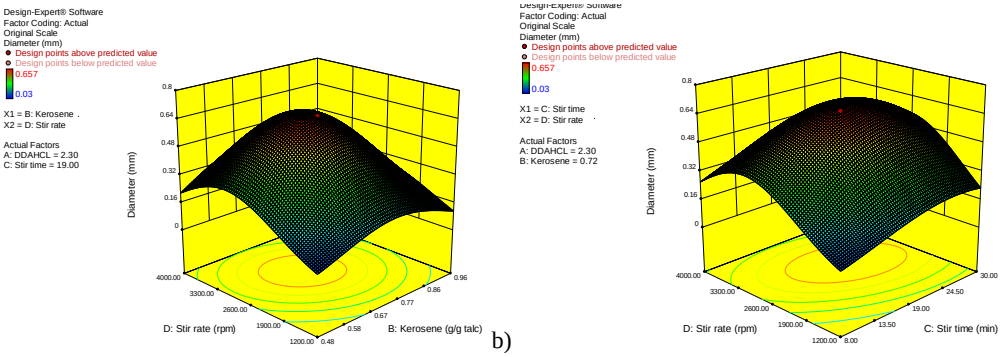


Fig. 4. Exemplary 3D surface plots for *D*50 response. (a) Variable B and D, constant A = 2.30 mg g^{-1} and C = 19 min. (b) Variable C and D, constant A = 2.30 mg g^{-1} and B = 0.72 g g^{-1}.

In the case of log(PDI), the analysis was easier (Table 5). The quadratic model was statistically significant (Table 8), *F* value of 7.85; there is only 0.01% probability that such high value is due to the noise, with reasonable model, adjusted and predicted values of R^2 equal to 0.8526, 0.7440 and 0.7914, respectively (Table 5). In the case of cubic model, the values are comparable, while in the case of predicted R^2 some decrease is even observed (0.4396). Thus, we decided to analyze data using the quadratic model only. Diagnostic parameters of the quadratic model are also sensible

(Table 8). The lack of fit *F*-value of 1.24 implies the lack of fit is not significant relative to the pure error. There is 37.84% chance that a lack of fit *F*-value this large could occur due to the noise. Signal-to-noise of 10.687 (Table 5) is much higher than 4, thus the signal is adequate. B, D, BC, BD, CD, A^2 were identified as significant model terms at threshold level of 0.05, while at threshold level of 0.01 BD and A^2 became insignificant.

Table 8. ANOVA table for log(PDI) response - quadratic model

Source	Sum of squares	Degrees of freedom	Mean square	*F* value	*p*-value Prob > *F*[a]
Model	3.3952	14	0.2425	7.8496	0.0000
A-DDAHCl	0.0014	1	0.0014	0.0456	0.8331
B-Kerosene	1.5124	1	1.5124	48.9516	0.0000
C-Time	0.0003	1	0.0003	0.0096	0.9230
D-Stir rate	0.5049	1	0.5049	16.3436	0.0007
AB	0.0765	1	0.0765	2.4772	0.1320
AC	0.0145	1	0.0145	0.4706	0.5010
AD	0.1274	1	0.1274	4.1231	0.0565
BC	0.2967	1	0.2967	9.6043	0.0059
BD	0.2136	1	0.2136	6.9125	0.0165
CD	0.3866	1	0.3866	12.5143	0.0022
A^2	0.1425	1	0.1425	4.6112	0.0449
B^2	0.0236	1	0.0236	0.7632	0.3932
C^2	0.0262	1	0.0262	0.8483	0.3686
D^2	0.0751	1	0.0751	2.4307	0.1355
Residual	0.5870	19	0.0309		
Lack of Fit	0.3401	10	0.0340	1.2396	0.3784
Pure Error	0.2469	9	0.0274		
Corr. Total	3.9822	33			

[a] Statistically significant terms for significance threshold 0.05 are underlined.

It follows from above that amount of kerosene and stirring rate influence to the greatest degree a span of the agglomerates size distribution of talc. The agglomeration process may be considered as a collision between hydrophobic particle and hydrophobic oil droplet. These collisions lead to adhesion as a result of the formation of pendular oil bridges (Kawashima and Capes, 1974). Physical forms of agglomerates are dependent on solid-oil-water interface properties, and, to a great extent, on amount of oil and the hydrodynamics of the process, i.e. intensity and mixing time. There can be identified three states of agglomerates: pendular, funicular, and capillary (Drzymala, 2007). In the pendular state, oil bridges are formed between particles, bringing them into aggregates in the predominant aqueous phase. Increasing the

amount of oil, as well as intensive mixing, can result in the increased agglomerate density. Consequently, the oil phase starts to dominate and water bridges are formed in the aggregates (funicular state). In the capillary state, the particles are bound together with oil only and there are no bridges. Further oil addition to the system causes formation of a separate oil phase containing the particles (Drzymala, 2007).

The polynomial model describing dependence of log(PDI) is:

$$\log(PDI) = 1.64 + 1.11B - 5.0 \times 10^{-4}D + 0.052BC + 3.0 \times 10^{-4}BD + 1.01 \times 10^{-5}CD + 0.201A^2. \quad (7)$$

The plot of predicted and observed values is shown in Fig. 5. It can be seen that proposed model predicts quite well the experimental results of the agglomerates PDI.

Typical 3D model graphs for size distribution span PDI are shown in Figs. 6a and 6b. Based on the results shown in these figures, in the mixed interactions of stirring time and stirring rate with increasing the kerosene-to-talc mass ratio an increase in the PDI values are achieved.

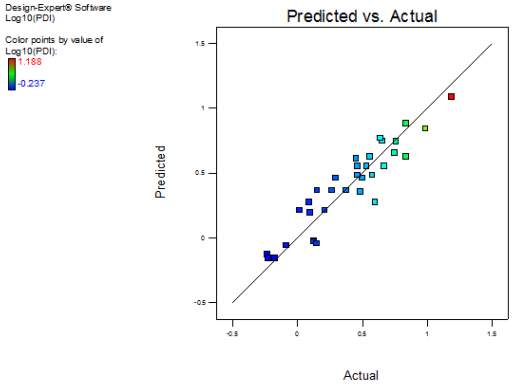


Fig. 5. Predicted vs. observed values of log(PDI) for quadratic model, R^2 = 0.7914

After determining the logarithmic transformation with reduced cubic model for *D*50 and quadratic model for PDI, an optimization study was carried out using the software. To find optimal conditions of oil agglomeration of talc, the minimum input values of the experimental factors were sought in order to achieve minimum values of PDI, i.e. to obtained more narrow agglomerates size distribution. In case of the second response parameter, median diameter of agglomerates, the maximum value of *D*50 was the goal. Such an approach meets requirements for low cost processing and the size of powder agglomerates (Pietsch, 2005). In general, relatively narrow size distribution is requested. Thus, the oversized and undersized material is not acceptable. Desirable results of size enlargement may be, for example, free flowing, dust-free granular products with more or less strict requirements on the limits of size distribution (Pietsch, 1991). It is worth mentioning that factors and responses values

were investigated in the range of lower and upper limits of input values only and all goals to be equally important. With such criteria, numerous results were found with desirability ranging between 0.90-0.95. The selected factors values were: 1.61 mg of DDAHCl and 0.48 cm^3 of kerosene per gram of talc and the process operating parameters set as 1200 rpm for 8 minutes of mixing. The predicted median agglomerates diameter and size distribution span were 0.66 mm and 4.4, respectively.

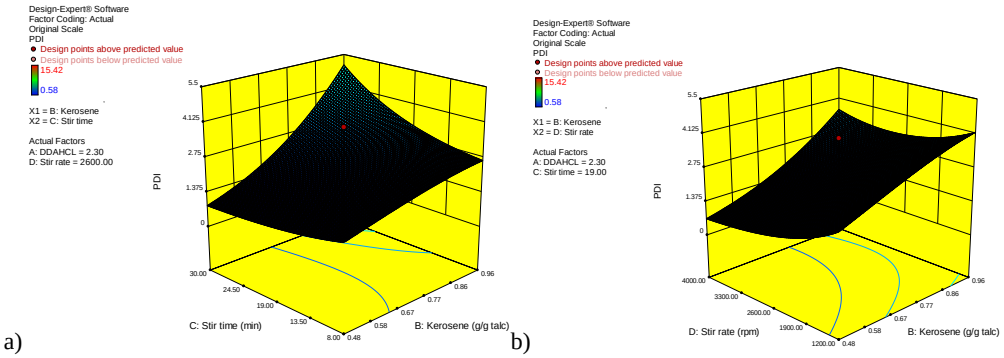


Fig. 6. Exemplary 3D surface plots for PDI response. (a) Variable B and C, constant A = 2.30 mg g^{-1} and D = 2600 rpm. (b) Variable B and D, constant A = 2.30 mg g^{-1} and C = 19 min

Conclusions

In this paper, the experimental parameters for oil agglomeration of talc were designed using a CCD method.

Four variables of the model investigated were: amount of surfactant (DDAHCl) (A), amount of kerosene (B), stirring time (C) and the stirring rate (D). The mathematical model equations were derived for both median size of agglomerates (*D*50) and polydispersity span (PDI) using the specialized package (Stat-Ease 9.0.4 Demo Version).

Logarithmic transformations of the responses provided better description of the model, than untransformed responses. This was supported by the Box-Cox plots.

In the case of *D*50, it was difficult to select the correct model – quadratic one gave much worse results than the cubic one, but the latter contained aliased terms. After removal of confounded parameters from the model, the reduced cubic model predicted the responses correctly. In this case, significant terms were: A, C, D, AB, AC, BC, BD, CD, A^2, B^2, C^2, D^2, A^2D, AB^2, and A^3. Considering main effects, the significance order, calculated by means of *F*-test was: amount of DDAHCl > stirring rate > stirring time. When significance threshold decreased from 0.05 to 0.01, C, AB, AC became insignificant.

In the case of PDI, the quadratic model provided satisfactory description of the experimental data. B, D, BC, BD, CD, A^2 were significant terms, with kerosene

amount being more significant main effect than the stirring rate. When significance threshold decreased from 0.05 to 0.01, CD interaction term became insignificant.

To conclude, it was shown that there were many statistically important factors, including concentration of cationic surfactant and stirring rate and time for *D*50, concentration of kerosene and stirring rate for PDI, as well as various interactions, up to third order for *D*50, even at significance threshold level equal to 0.01.

Response surfaces can be drawn using the cubic model in the case of *D*50 response, and quadratic one in the case of PDI.

Optimal conditions of oil agglomeration of talc were targeted as the minimum values of reagents amounts as well as mixing intensity and process time to obtained the maximum size of agglomerates of a narrow size distribution. It was found that 1.61 mg of DDAHCl and 0.48 cm^3 of kerosene per gram of talc were optimal reagent dosage and the process operating parameters set as 1200 rpm and 8 minutes of mixing intensity and time. The predicted *D*50 and PDI were 0.66 mm and 4.4, respectively.

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