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Optimization of Sodium Bicarbonate Production Using Response Surface Methodology (RSM)

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Abstract

The main objective of this study was to evaluate the use of batch bubble column to produce high particle size (>300 micron) of sodium bicarbonate product to improve filtration and drying operations in the production process. Lab scale batch bubble column of 80 mm diameter and 0.5 m height was used to study the process for sodium bicarbonate production using 20% sodium carbonate solution as a starting solution. Three operating variables were considered, CO_2 gas content (20-100 %), temperature (30-70 ºC) and time (0.5-2.5 h). The bicarbonate yield and crystals size were considered to be the objective variables of the process. Response surface methodology (RSM) was used with central composite design (CCD) of experiments. Empirical polynomial multivariable equations were obtained. The reaction time was found to be the most effective operating condition on the yield of sodium bicarbonate, and temperature was found to be the most effective operating condition on crystal size of sodium bicarbonate. The optimum conditions achieved 400 microns particle size at temperature 70 ºC and time 2.5 h. Kinetics study of the process showed that zero order reaction with both sodium carbonate and CO_2 concentrations was approximately fitted the experimental data, useful for shortcut process design purposes.

Keywords: Sodium bicarbonate production, batch bubble column, RSM, optimization.
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1.Introduction

Sodium bicarbonate (baking soda) has many applications; animal feeds, paper industry, plastic foaming, water treatment, leather treatment, flue gas treatment, detergent and cleaning products, drilling mud to improve fluidity, fire extinguisher powder, human food products and domestic uses, and pharmaceutical applications.

Sodium bicarbonate ($NaHCO_3$) appears as an intermediate product in soda ash (sodium carbonate) production, Solvay process. However it is produced from purified sodium carbonate rather than from purifying the intermediate, because of several reasons: the difficulty in drying the intermediate bicarbonate; the presence of a small amount of ammonia lead to be unfit for many uses; and containing many impurities in addition to ammonia [1].

The production process of purified sodium bicarbonate is by the dispersion of a CO_2 gas in a solution of purified soda ash (Na_2CO_3) with the following reaction equations [2];

$$CO_2\,(g) \longleftrightarrow CO_2\,(l) \quad (1)$$
$$CO_2\,(l) + OH^- \longleftrightarrow HCO_3^- \quad (2)$$
$$HCO_3^- + OH^- \longleftrightarrow CO_3^{-2} \quad (3)$$
$$Na^+ + HCO_3^- \longleftrightarrow NaHCO_3 \quad (4)$$

With the following overall reaction;

$$Na_2CO_3 + CO_2 + H_2O \longleftrightarrow 2NaHCO_3 \quad (5)$$

A super-saturation solution of $NaHCO_3$ in the liquid is formed and precipitation of solid $NaHCO_3$ occurs. The equilibrium between $NaHCO_3$, Na_2CO_3 and CO_2 depends on temperature, concentrations of carbonate and bicarbonate, and CO_2 partial pressure over the solution. The process of production of the bicarbonate has a large number of complex physical and chemical phenomena; gas-liquid mass transfer, reaction, solid crystallization in two-component (sodium carbonate and sodium bicarbonate) solution in equilibrium, and three phase gas-liquid-solid hydrodynamics. Sodium bicarbonate production yield and crystal size distribution (CSD) were the most important dependent variables of the process. Previous works studied the effect of operating variables on the reaction and crystallization kinetics. The recommended reactor types for the production of sodium bicarbonate were bubble column [4, 5, 6, 7 & 8] and mechanical stirred tank [9, 10]. Bubble column is the commonly used unit

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operations equipment for sodium bicarbonate production.

Broul et al [11] proposed an equation, Equation 6, of the solubility of $NaHCO_3$ in the presence of Na_2CO_3 at super-saturation, which compared with pure sodium bicarbonate solubility data given by Miller [12] as shown in Figure 1.

$$logx^{*} = 6.71535 - \frac{843.0681}{T} - 2.24336\ logT \quad (6)$$

Where;

x* : Mole fraction of sodium bicarbonate at super-saturation.

T : Liquid temperature (K).

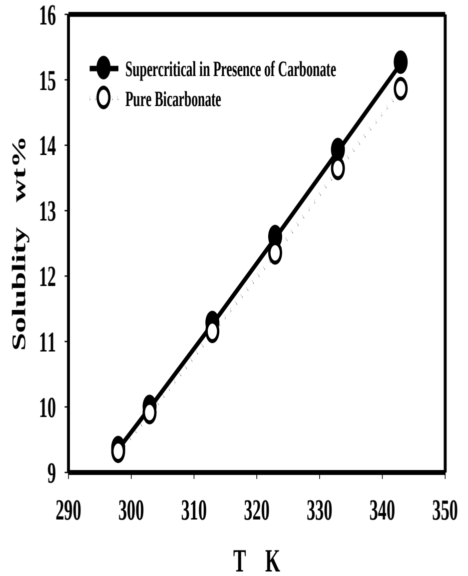

Figure 1: Comparison of solubility of pure bicarbonate [12] with super-saturation in presence of carbonate [11]

All previous works investigated continuous process mode. Little work on batch bubble column reactor has been found in the literature to produce sodium bicarbonate.

The objectives of the present study are to evaluate the use of batch bubble column to produce high particle size (>300 micron) of sodium bicarbonate product to improve filtration and drying operations in the production process, to design and to perform experiments for the effect of the operating conditions (temperature, time, and CO_2 gas content) on the bicarbonate yield & particle size using response surface methodology (RSM), to obtain the optimum conditions of the process, and to study the kinetics of the reaction.

2. Experimental Work

Commercial light soda ash 99.5 purity, supplied by ŞişECAM Company Turkey, was used. Distilled water, from Koprulu Trade Company Kirkuk-Iraq, was used to prepare saturated solution of sodium carbonate. Carbon dioxide (CO_2) cylinder (99.9 %) supplied by Mustafa Otrakici bureau, Kirkuk-Iraq.

Figure 2 shows the methodology diagram for the production of sodium bicarbonate (NaHCO3) process, includes four stages; bubble column process, filtration, drying, and sieve analysis for crystal size distribution (CSD). Lab-scale batch bubble column of inner diameter D=80 mm and height H=500 mm of about 2 liters volume was used. Column temperature was controlled digitally, placed in water bath. Oil free air compressor was used to supply the air to the system, using gas flow meter to regulate the air flow rate. CO_2 cylinder with pressure regulator and flow meter were used to supply the CO_2 to the system. Tube distributor of single nozzle of 6 mm diameter at a depth 50 mm from the bottom of column was used to disperse the gas mixture (CO_2 gas and air). Figure 3 shows the experimental set-up.

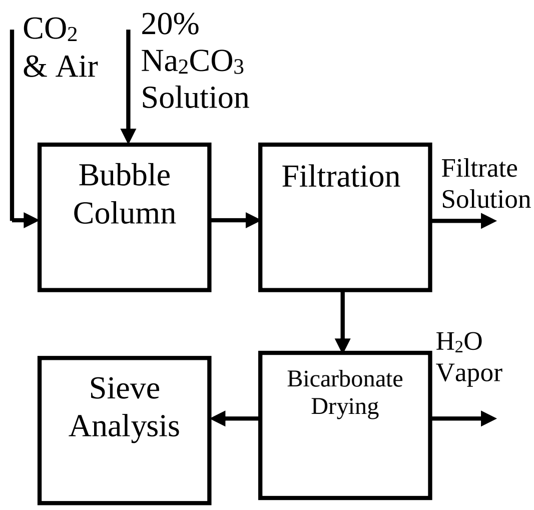

Figure 2: The methodology diagram

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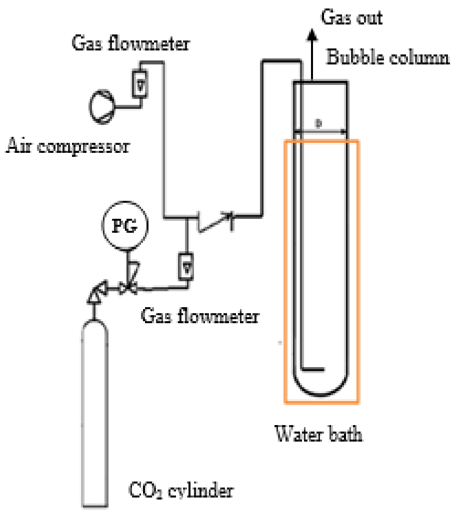

Figure 3: Lab-Scale batch of bubble column experimental Set-up

Three operating variables were considered in the present work; CO_2 gas content (y_{CO2}=20-100 %), temperature (T=30-70 ºC), and time (t=0.5-2.5 h). Constant gas flow rate, of 10 l/min with a superficial gas velocity of 0.03 m/s, was selected to give homogeneous flow regime in the bubble column. A solution of Na_2CO_3 of 20% concentration was used as starting solution.

Gas hold-up was calculated experimentally as following:

$$\varepsilon_g = \frac{\Delta L}{L} \qquad (7)$$

Where, ΔL is the height of solution difference before and after gas mixture flow. The value of ε_g of about (12-13%) was noticed for the constant gas flowrate used.

Running the experiment at a specified temperature and CO_2 gas content until $NaHCO_3$ crystals began formed; set it as t_1 the time before crystallization. The run was continued for a specified reaction time. The total time was; t_2= t_1+ reaction time.

A Buchner funnel vacuum filtration was used to filter the cake of $NaHCO_3$ crystals produced. Drying the $NaHCO_3$ cake was performed in an oven at 65 ºC for 8 hours. The yield of the bicarbonate solid product was calculated from simple mass balance of the overall reaction Equation 5, by the following equation;

$$Y_s = \frac{m_{Bicarb}}{2m_{Carb}} \frac{M_{Carb}}{M_{Bicarb}} \qquad (8)$$

The crystal size was measured using sieves analysis apparatus at different size, and the volume average particle size diameter (d_p) was calculated by;

$$d_p = \sum d_{p_i} z_i \qquad (9)$$

Where d_{p_i} is the particle size in sieve i and z_i is the weight fraction of particle size in sieve i.

3. Experiments Design

In order to study the effect of operating conditions for sodium bicarbonate production and to investigate the interaction between the process variables, Design Expert 6.0.6 software was used, using a central composite design (CCD) of experiments. Three process variables; reaction temperature (T), CO_2 gas content (y_{CO2}), and reaction time (t), were chosen with center values of 50 ºC, 60 %, and 1.5 h respectively, after performing some primary experiments. Coded and actual process variables used in experiments design are presented in Table 1.

Table 1 Coded and actual process variables.

Process variables	Coded and actual variables				
	-2	-1	0	1	2
T ºC	30	40	50	60	70
y_{CO2} %	20	40	60	80	100
t h	0.5	1	1.5	2	2.5

A second-order polynomial response surface model of a central composite design (CCD) required 20 experiments, as shown in Table 2. The center points are usually repeated 6 times to determine the experimental error and the reproducibility of the data[13].

Table 2 Experiments design (CCD), including results.

Exp. No.	Variables						Ys %	dp µm
	T ºC	y_{CO2} %	t h	X_1	X_2	X_3		
1	40	40	1	-1	-1	-1	30.7	238
2	60	40	1	+1	-1	-1	21.8	273
3	40	80	1	-1	+1	-1	42.6	208
4	60	80	1	+1	+1	-1	41.2	282
5	40	40	2	-1	-1	+1	50.7	234
6	60	40	2	+1	-1	+1	42.3	345
7	40	80	2	-1	+1	+1	63.1	237
8	60	80	2	+1	+1	+1	53.7	330
9	30	60	1.5	-2	0	0	50.3	182
10	70	60	1.5	+2	0	0	44.2	304
11	50	20	1.5	0	-2	0	23.9	271
12	50	100	1.5	0	+2	0	59.8	264
13	50	60	0.5	0	0	-2	18.2	289
14	50	60	2.5	0	0	+2	59.8	314
15	50	60	1.5	0	0	0	46.8	271
16	50	60	1.5	0	0	0	45.5	268
17	50	60	1.5	0	0	0	47.8	274
18	50	60	1.5	0	0	0	46.1	266
19	50	60	1.5	0	0	0	46.6	277

4.Results and Discussion

The process of sodium bicarbonate production was analyzed by the application of the response surface methodology (RSM). Design Expert 6.0.6 software was used. Two second-order polynomial models were obtained to predict the

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bicarbonate yield and particle size as a function of three operating variables; reaction temperature (T=30-70 °C), CO_2 mole percentage (y_{CO2}=20-100 %), and time (t=0.5-2.5 h).
The analysis of variances (ANOVA), neglecting the insignificant terms, resulted the two empirical equations; Equation 10 and Equation 11. Figures 4 and 5 show good correlations of the predicted verses actual (experimental) for bicarbonate yield and particle size respectively.

$$Y_s = -23.23 - 0.252\ T + 0.78\ y_{CO2} + 43.46\ t - 3.19 \times 10^{-3}\ y_{CO2}^2 - 7.96\ t^2 \quad (R^2 = 0.9746,\ Std=2.27) \qquad (10)$$

$$d_p = 127.73214 + 7.00804\ T - 184.80357\ t - 0.070893\ T^2 + 30.14286\ t^2 + 2.37500\ T\ t \quad (R^2 = 0.9413,\ Std=10.8) \qquad (11)$$

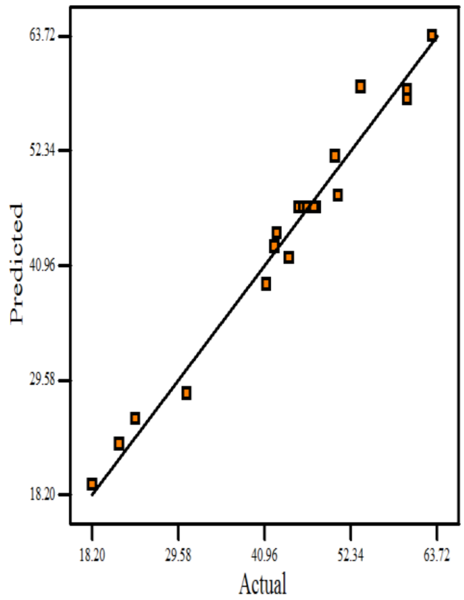

Figure 4: Predicted versus actual NaHCO3 yield (Y_s, %).

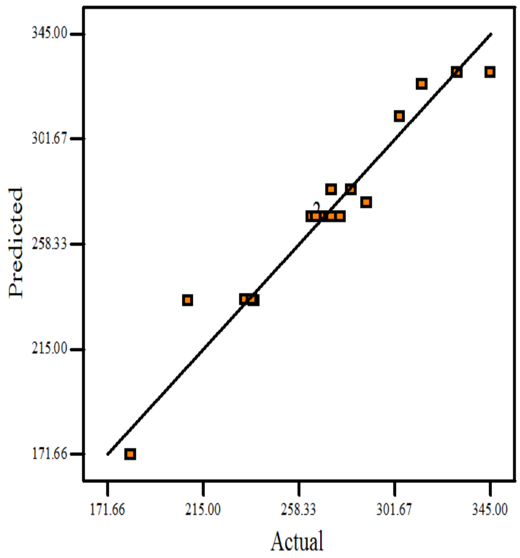

Figure 5: Predicted versus actual crystal size (d_p, μm)

Figure 6 shows the perturbation parameters effect of reaction temperature, CO2 mole fraction, and reaction time on sodium bicarbonate yield. Reference point are center values for the variables; T=50 °C, y_{CO2}=60 %, t= 1.5 h. Reaction time and CO2 mole fraction were the most effective process variable of approximately equal effect.
Figure 7, shows the perturbation parameters effect on sodium bicarbonate crystal size. Reference point for the variables are T=70 °C, and t= 2.5 h. Reaction temperature was the most effective process variable. Crystal size slightly increased with increasing reaction time, with negligible effect of CO_2 gas content.

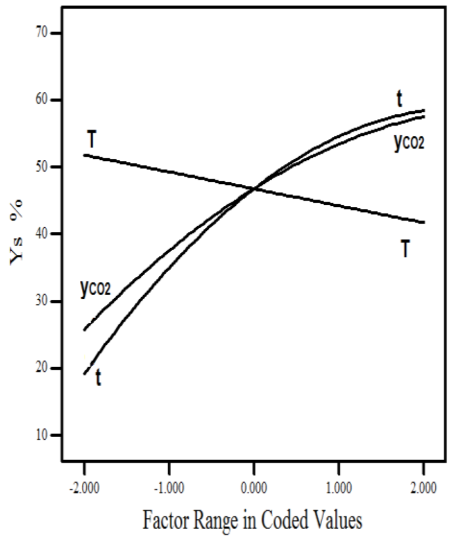

Figure 6: Effect of perturbation parameters on $NaHCO_3$ yield

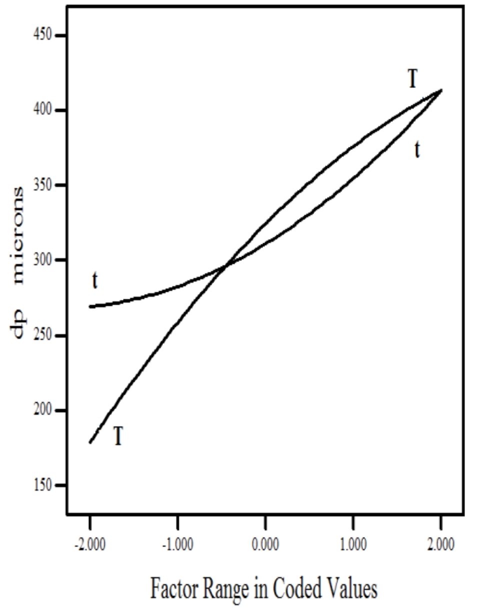

Figure 7: Effect of perturbation parameters on sodium bicarbonate crystal size

The optimum conditions achieved was 400 µm particle size (d_P) of sodium bicarbonate at reaction temperature 70 °C, and time 2.5 h, at any value of CO_2 gas content (particle size was independent on CO_2 gas content), as shown in Figure 8. The range of bicarbonate yield from 32 to 63% was noticed for the optimum conditions of time and temperature at the range studied of CO_2 gas content (y_{CO2}=20-100%).

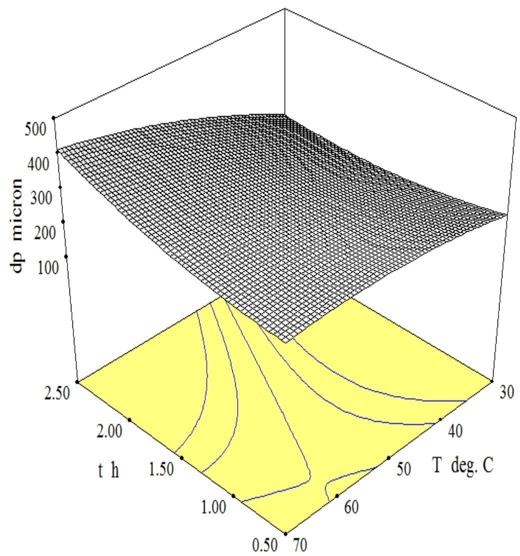

Figure 8: 3D plot for the interaction effect of temperature & time on crystal size

For kinetic study purposes, a correlation of the experimental data of conversion (Y_1) at a time t_1 before sodium bicarbonate precipitation were obtained, as follows;

$Y_1 = 16.99250 + 0.33125\ T$ (R^2=0.9997, Sd.= 0.051) (8)

$t_1 = 3.258+9.5\times10^{-3}\,T-0.057\,y_{CO2}+3.074\times10^{-4}\,y_{CO2}^2$ (R^2=0.9805, Sd.= 0.062) (9)

Where; the total bicarbonate yield or conversion is; $Y_2=Y_1+Y_s$, and the total time is; $t_2= t_1+t$

Figure 9 shows the effect of reaction time on conversion (equals to bicarbonate yield) at optimum operating reaction temperature (T=70 °C) at different values CO_2 gas content.

For approximate process design approach, a zero order reaction with respect to both sodium carbonate and CO_2 concentrations was assumed. The constant of the rate of reaction k_o values obtained from the slopes (slope=k_o/C_o, C_o=1.887 mole/l) of Figures 10 with corresponding correlation coefficients were 0.236 mole/l.h (R^2=8493), 0.472 mole/l.h (R^2=0.9776), and 0.623 mole/l.h (R^2=9794) for CO_2 gas content 20, 60, and 100% respectively.

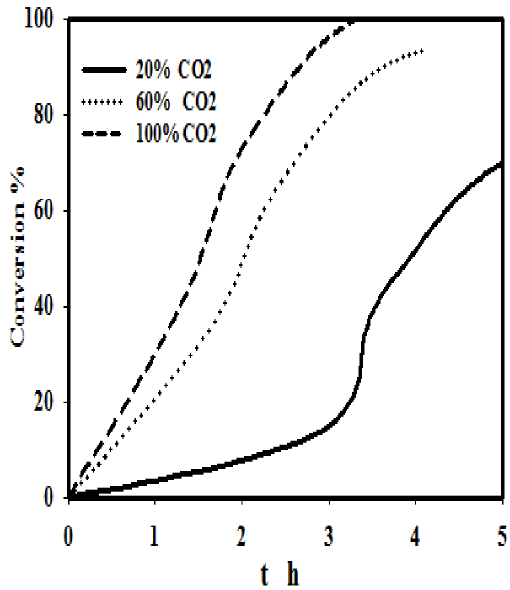

Figure 9: The effect of reaction time on conversion at optimum operating reaction temperature (T=70 °C) and different values of CO_2 mole fraction

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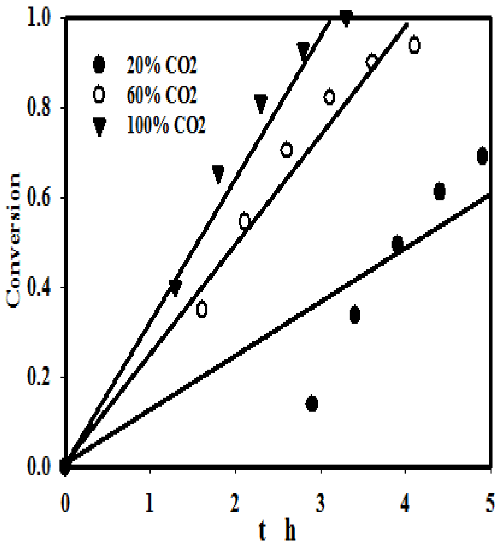

Figure 10: Zero order reaction with respect to both carbonate and CO_2 concentrations

5. Conclusions

Batch bubble column was successfully applied to produce high particle size of sodium bicarbonate (about 400 micron), using response surface methodology (RSM). Second-order polynomial well fitted to the experimental data. Reaction temperature was the most effective variable on bicarbonate particle size. Higher particle size was obtained with higher temperature. Zero order reaction approximation with respect to both sodium carbonate and CO_2 concentrations showed correlation coefficients higher than 0.97, except for low CO_2 gas content (20%) which was 0.8493.

Nomenclatures

C_o	Initial concentration of carbonate, mole/l
D	Diameter of bubble column, mm
d_p	Particle size (volume average), µm
d_{pi}	Sieve size, µm
H	Height of bubble column, mm
k_o	Zero order reaction rate constant, mole/l.h
L	Liquid level without gas flow, mm
L_g	Liquid level with gas flow, mm
M_{Bicarb}	Sodium bicarbonate molecular weight, g/mole
m_{Bicarb}	Solid sodium bicarbonate weight, g
M_{Carb}	Sodium carbonate molecular weight, g/mole
m_{Carb}	Sodium carbonate weight, g
n	Number of independent variables
T	Temperature, °C or K
t	Time of reaction, h
t_1	Time of reaction before precipitation, h
t_2	Total time of reaction, h
X_1	coded variable of reaction temperature, °C
X_2	coded variable of CO_2 gas content %
X_3	coded variable of reaction time
x*	Mole fraction of sodium bicarbonate at super-saturation
Y_1	Yield or conversion before precipitation
Y_S	Yield or conversion for precipitation time
Y_2	Yield or conversion for total reaction time
y_{CO2}	CO_2 gas content %
z_i	Weight fraction of sieve no i

Greek symbols

ε_g	Gas hold-up
ΔL	Liquid level difference with and without gas flow, mm

Abbreviations

ANOA	Analysis of variances
CCD	Central composite design of experiments
CSD	Crystal size distribution
RSM	Response surface methodology
Sd.	Standard deviation

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