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, CO2 gas content (20-100 %), temperature (30-70 °C) 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 °C and time 2.5 h. Kinetics study of the process showed that zero order reaction with both sodium carbonate and CO2 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 (NaHCO3) 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 CO2 gas in a solution of purified soda ash (Na2CO3) with the following reaction equations [2]:

\[
\text{CO}_2 (g) \leftrightarrow \text{CO}_2 (l) \quad (1) \\
\text{CO}_2 (l) + \text{OH} \leftrightarrow \text{HCO}_3^- \quad (2) \\
\text{HCO}_3^- + \text{OH} \leftrightarrow \text{CO}_3^{2-} \quad (3) \\
\text{Na}^+ + \text{HCO}_3^- \leftrightarrow \text{NaHCO}_3 \quad (4)
\]

With the following overall reaction;

\[
\text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow 2\text{NaHCO}_3 \quad (5)
\]

A super-saturation solution of NaHCO3 in the liquid is formed and precipitation of solid NaHCO3 occurs. The equilibrium between NaHCO3, Na2CO3 and CO2 depends on temperature, concentrations of carbonate and bicarbonate, and CO2 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
Broul et al. [11] proposed an equation, Equation 6, of the solubility of NaHCO₃ in the presence of Na₂CO₃ at super-saturation, which compared with pure sodium bicarbonate solubility data given by Miller [12] as shown in Figure 1.

\[
\log x^* = 6.71535 - \frac{843.0681}{T} - 2.24336 \log T
\]  

(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 CO₂ 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 (CO₂) 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. CO₂ cylinder with pressure regulator and flow meter were used to supply the CO₂ 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 (CO₂ gas and air). Figure 3 shows the experimental set-up.

**Figure 2:** The methodology diagram
Figure 3: Lab-Scale batch of bubble column experimental Set-up

Three operating variables were considered in the present work; CO₂ gas content (y_{CO₂}=20-100 %), temperature (T=30-70 °C), 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 Na₂CO₃ of 20% concentration was used as starting solution.

Gas hold-up was calculated experimentally as following:

\[ \varepsilon_g = \frac{\Delta L}{L} \] (7)

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

Running the experiment at a specified temperature and CO₂ gas content until NaHCO₃ 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; \( t_2 = t_1 + \text{reaction time} \).

A Buchner funnel vacuum filtration was used to filter the cake of NaHCO₃ crystals produced. Drying the NaHCO₃ cake was performed in an oven at 65 °C 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;

\[ Y_s = \frac{m_{bicarb}}{2m_{Carb}} \] (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:

\[ d_p = \sum d_p z_i \] (9)

Where \( d_{pi} \) 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), CO₂ gas content (y_{CO₂}), and reaction time (t), were chosen with center values of 50 °C, 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.

### 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
bicarbonate yield and particle size as a function of three operating variables; reaction temperature \((T=30-70\, ^\circ C)\), \(CO_2\) mole percentage \((y_{CO_2}=20-100\% )\), 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.

\[
Y_s = -23.23 -0.252\, T + 0.78\, y_{CO_2} + 43.46\, t - 3.19 \times 10^{-2}\, y_{CO_2}^2 - 7.96\, t^2 \\
(R^2 = 0.9746, Std=2.27) \quad (10)
\]

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

Figure 4 shows the predicted versus actual \(NaHCO_3\) yield \((Y_s, \%)\).

Figure 5 shows the predicted versus actual crystal size \((d_p, \mu m)\).

Figure 6 shows the perturbation parameters effect of reaction temperature, \(CO_2\) mole fraction, and reaction time on sodium bicarbonate yield. Reference point are center values for the variables; \(T=50\, ^\circ C, y_{CO_2}=60\, \%, t=1.5\, h\). Reaction time and \(CO_2\) 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 \(T=70\, ^\circ C\), 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.
The optimum conditions achieved were 400 μm particle size (dp) of sodium bicarbonate at reaction temperature 70 °C, and time 2.5 h, at any value of CO₂ gas content (particle size was independent on CO₂ 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 CO₂ gas content (y_{CO2}=20-100%).

For kinetic study purposes, a correlation of the experimental data of conversion (Y₁) at a time t₁ before sodium bicarbonate precipitation were obtained, as follows:

\[ Y₁ = 16.99250 + 0.33125 \times T \]

(R²=0.9997, Sd.= 0.051) \hspace{1cm} (8)

Where; the total bicarbonate yield or conversion is; \( Y₂ = Y₁ + Y_s \), and the total time is; \( t₂ = t₁ + t \)

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 CO₂ gas content.

For approximate process design approach, a zero order reaction with respect to both sodium carbonate and CO₂ 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 (R²=8493), 0.472 mole/l.h (R²=0.9776), and 0.623 mole/l.h (R²=9794) for CO₂ gas content 20, 60, and 100% respectively.
Figure 10: Zero order reaction with respect to both carbonate and CO₂ 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 CO₂ concentrations showed correlation coefficients higher than 0.97, except for low CO₂ gas content (20%) which was 0.8493.

Greek symbols
\( \varepsilon_g \) Gas hold-up
\( \Delta L \) Liquid level difference with and without gas flow, mm

Abbreviations
ANOVA Analysis of variances
CCD Central composite design of experiments
CSD Crystal size distribution
RSM Response surface methodology
SD Standard deviation

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Nomenclatures

- \( C_0 \) 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 CO₂ gas content %
- \( X_3 \) coded variable of reaction time
- \( x^\# \) Mole fraction of sodium bicarbonate at supersaturation
- \( Y_1 \) Yield or conversion before precipitation
- \( Y_2 \) Yield or conversion for total reaction time
- \( Y_{CO₂} \) CO₂ gas content %
- \( z_i \) Weight fraction of sieve no i
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