

TABLE OF CONTENTS

	Contents	Page
	ACKNOWLEDGEMENTS	
	ABSTRACT	
	LIST OF PUBLICATIONS	
	LIST OF TABLES	vi
	LIST OF FIGURES	viii
	INTRODUCTION	xii
	Part 1: <u>LITERATURE REVIEW</u>	
CHAPTER 1	THE STOCHASTIC METHODS IN CRYSTALLIZATION	
1.1	Introduction	1
1.2	The Monte Carlo method	2
1.2.1	<i>Application of MC method in Chemical Engineering</i>	6
1.2.2	<i>Application of MC method in Crystallization</i>	25
1.2.2.1	Modelling of growth rate dispersion of citric acid monohydrate in continuous crystallizer	25
1.2.2.2	Mathematical modelling and MC simulation of CSD in continuous urea crystallizer	26
1.2.2.3	Simulation of CSD in a continuous sodium chloride crystallizer under diffusion controlled conditions	31
1.2.2.4	Growth rate dispersion in a continuous sucrose crystallizer and its effect on CSD	35
1.2.2.5	Mixing in continuous FC crystallizer	40
1.2.2.6	MC simulation of transient CSD in a continuous crystallizer	43
1.2.2.7	Effect of dispersions on CSD in continuous MSMR crystallizer	49
1.2.2.8	MC simulation of the CSD in a continuous sucrose crystallizer	56
1.2.2.9	Analysis of transient CSD in a continuous sodium chloride crystallizer	58

1.2.2.10	MC simulation of transient CSD in a continuous crystallizer under stochastic dispersion effects	64
1.2.2.11	A stratified MC simulation of CSD in a continuous crystallizer for size-dependent growth	68
1.2.2.12	ASL model for prediction of CSD in a continuous crystallizer	73
1.3	The Markov chain method	77
1.3.1	<i>Application of Markov chain method in Chemical Engineering</i>	80
1.3.2	<i>Recent development of Markov chain method in Crystallization</i>	85
1.3.2.1	Effect of size-dependent growth rate on fluctuations of transient CSD in a batch crystallizer	86
1.3.2.2	Modelling fluctuations in the growth rate of a single crystal	99
1.4	Present contribution	112
Part 2: <u>TRANSIENT CRYSTAL SIZE DISTRIBUTION</u>		
CHAPTER 2	MONTE CARLO SIMULATION OF TRANSIENT CRYSTAL SIZE DISTRIBUTION IN A CONTINUOUS CRYSTALLIZER USING THE ASL MODEL	115
2.1	Introduction	115
2.2	The simulation scheme	118
2.3	Results and discussion	120
2.4	Conclusions	121
CHAPTER 3	TRANSIENT CRYSTAL SIZE DISTRIBUTION IN DTB AND FC CRYSTALLIZERS	128
3.1	Introduction	128
3.2	Residence time for an imperfectly mixed DTB crystallizer	131
3.3	Residence time for an imperfectly mixed FC crystallizer	133
3.4	The simulation scheme	134
3.5	Results and discussion	135
3.6	Conclusions	138
CHAPTER 4	MONTE CARLO SIMULATION OF TRANSIENT CRYSTAL SIZE DISTRIBUTION IN AN IMPERFECTLY MIXED CONTINUOUS	145

	CRYSTALLIZER UNDER STOCHASTIC DISPERSION EFFECTS	
4.1	Introduction	145
4.2	The simulation scheme	146
4.3	Results and discussion	147
4.3.1	<i>DTB Crystallizer results</i>	148
4.3.2	<i>FC Crystallizer results</i>	149
4.4	Conclusions	151
	Part 3: <u>ATTRITION PROCESS</u>	
CHAPTER 5	MONTE CARLO SIMULATION OF THE CRYSTAL SIZE DISTRIBUTION WITH ATTRITION EFFECTS IN A MIXED SUSPENSION CRYSTALLIZER	160
5.1	Introduction	160
5.2	Random Breakage model	162
5.3	Monte Carlo Technique	164
5.4	Results and Discussions	165
5.5	Conclusions	167
CHAPTER 6	EFFECT OF LOW STIRRING RATE AND DURATION ON THE ATTRITION PHENOMENA IN A MECHANICALLY STIRRED CRYSTALLIZER	173
6.1	Introduction	173
6.2	Experimental Procedures	174
6.3	Results	175
6.4	Mathematical modelling	176
6.5	Discussion	179
6.6	Conclusions	181
CHAPTER 7	THE EFFECT OF VOLUME SHAPE FACTOR ON THE CRYSTAL SIZE DISTRIBUTION OF FRAGMENTS DUE TO ATTRITION	188
7.1	Introduction	188
7.2	Physical attrition model	190
7.3	The simulation scheme	196
7.4	Results and discussion	198
7.5	Conclusions	201
APPENDIX I		
I.1	Outline of Simulation Algorithm for Steady State CSD	208
I.2	Outline of Simulation Algorithm for Transient CSD	209

I.3	The Detailed Procedure of Generating Random Samples of Growth Rate and Shape Factor from the Normal Density Function	210
I.4	Derivation of Eqs. (1.92), (1.93) and (1.94)	212
I.5	Multinomial Distribution	215
I.6	Derivation of Eqs. (1.129) and (1.130)	217
APPENDIX II		
II.1	Sample Program and Results for Transient CSD for the Size-Dependent Growth by Employing the ASL Model	219
APPENDIX III		
III.1	Outline of Simulation Algorithm for Transient CSD in DTB and FC Crystallizers	233
III.2	Sample Program and Results for Transient CSD in DTB Crystallizer	234
III.3	Sample Program for Transient CSD in FC Crystallizer	261
APPENDIX IV		
IV.1	Outline of Simulation Algorithm for Transient CSD in DTB and FC Crystallizers under Stochastic Dispersion Effects	265
IV.2	Sample Program for Transient CSD in DTB Crystallizer under Stochastic Dispersion Effects	266
IV.3	Sample Program and Results for Transient CSD in FC Crystallizer under Stochastic Dispersion Effects	270
APPENDIX V		
V.1	A Summary of the Derivation of the Random Breakage Model	281
V.2	Outline of Simulation Algorithm for Steady State CSD with Random Breakage Model	284
V.3	Sample Program and Results for Steady State CSD with Random Breakage Model	285
APPENDIX VI		
VI.1	Experimental Procedure	292
VI.2	Sample Program and Results for Simulation of the Experimental Results Generated from the Coulter Counter -LS Particle Size Analyzer	293
APPENDIX VII		
VII.1	Outline of Simulation Algorithm for CSD of	300

VII.2	Fragments due to Attrition	
	Sample Program and Results for CSD of Fragments due to Attrition	301
	OVERALL CONCLUSIONS AND RECOMMENDATIONS	311
	NOMENCLATURE	314
	FLOW CHART NOTATION	327
	REFERENCES	331

LIST OF TABLES

Table	Description	Page
1.1	Parameters used in the transient CSD simulation	46
1.2	Parameters used in the transient CSD simulation under "no dispersion" conditions	47
1.3	Number distribution of crystals at dispersion	47
1.4	Number distribution of crystals at "no dispersion"	47
1.5	Dispersion range of parameters	55
1.6	List of parameters	61
1.7	Number distribution of crystals (<i>Case I</i>)	61
1.8	Number distribution of crystals (<i>Case II</i>)	61
1.9	Number distribution of crystals for transient analysis	66
1.10	Parameters used in the ASL model simulation	74
2.1	Number distribution of crystal for Experiment No.1	123
2.2	Summary of MC simulation (transient state) for each experiment	123
3.1	Cumulative mass fraction in urea crytallizer (DTB type)	140
3.2	Cumulative mass fraction in urea crytallizer (FC type)	141
4.1	Parameters used in the simulation	147
4.2	Number distribution of crystals at selected time intervals for N equals to one, three, five and seven	152
4.3	Differential mass distribution of crystals at selected time intervals for PFR equals to 0%, 10%, 20% and 30%	153
5.1	Parameter values at $\dot{w} = 0$ for 3 different scenarios	163

6.1	Cumulative size distribution (volume %) at three different stirring rates	182
7.1	Vicker Hardness H_v , average shear modulus μ_{VRH} , and the critical work to form cracks W_c , for magnesium sulphate heptahydrate (MS) and potash alum (PA)	202
7.2	The fragments size distribution for magnesium sulphate heptahydrate (MS) with $\alpha = 0.5236$, $\alpha = \alpha_n$ and $\alpha = 1$ at $W_p = 1E-4$ J	202
7.3	The fragments size distribution for potash alum (PA) with $\alpha = 0.5236$, $\alpha = \alpha_n$ and $\alpha = 1$ at $W_p = 1E-4$ J	203

LIST OF FIGURES

Figure	Description	Page
1.1	Transient cumulative mass distribution in % at dispersion	48
1.2	Transient cumulative mass distribution in % at "no dispersion"	48
1.3	Cumulative mass distribution (<i>Case I</i>)	62
1.4	Cumulative mass distribution (<i>Case II</i>)	63
1.5	Cumulative mass distribution of transient CSD	67
1.6	Cumulative mass distribution from stratified MC simulation	72
1.7	Cumulative mass distribution for different residence times (Experiment No. 1 and 2)	75
1.8	Cumulative mass distribution for different residence times (Experiment No. 3 and 4)	76
1.9	Transient and finite-state mean CSD's for the case of the size-dependent growth rate: $\lambda_j(t) = 500 \exp(-5t) / j, \text{ min}^{-1}$	95
1.10	Transient and finite-state variances around the mean CSD's given in Figure 1.9	96
1.11	Transient and finite-state mean CSD's for the case of the size-dependent growth rate: $\lambda_j(t) = 10 \exp(-5t) j, \text{ min}^{-1}$	96
1.12	Transient and finite-state variances around the mean CSD's given in Figure 1.11	97
1.13	Comparison of the moments of the present stochastic model with those defined in a deterministic population balance model	97
1.14	Transient and final- state mean CSD's for the case of the size-independent growth rate: $\lambda_j = 200 \exp(-5t), \text{ min}^{-1}$	98

1.15	Transient and finite-state variances around the mean CSD's given in Figure 1.14	98
1.16	Experimentally measured single crystal growth data (GARSIDE and RISTIC, 1983) and the predicted results by the CHOU <i>et al.</i> (1998a) model: ■ $a=4.892 \text{ min}^{-1}$, $k=-0.1907$; • $a=1.679 \text{ min}^{-1}$, $k=-0.07320$	110
1.17	Experimentally measured single crystal growth data (GARSIDE and RISTIC, 1983) and the predicted results by the CHOU <i>et al.</i> (1998a) model: ■ $a=18.81 \text{ min}^{-1}$, $k=-0.7039$; • $a=2.443 \text{ min}^{-1}$, $k=-0.2230$	110
1.18	Experimentally measured single crystal growth data (MATHIS-LILLEY and BERGLUND, 1985) and the predicted results by the CHOU <i>et al.</i> (1998a) model: ■ $a=9416 \text{ min}^{-1}$, $k=-2.460$; • $a=30120 \text{ min}^{-1}$, $k=-3.832$	111
1.19	Experimentally measured single crystal growth data (MATHIS-LILLEY and BERGLUND, 1985) and the predicted results by the CHOU <i>et al.</i> (1998a) model: ■ $a=110.08 \text{ min}^{-1}$, $k=-0.8565$; • $a=7.452 \text{ min}^{-1}$, $k=-0.4980$	111
2.1	Cumulative mass fraction at different residence time for Experiment No. 1	124
2.2	Cumulative mass fraction at different residence time for Experiment No. 2	125
2.3	Cumulative mass fraction at different residence time for Experiment No. 3	126
2.4	Cumulative mass fraction at different residence time for Experiment No. 4	127
3.1	Cascade of perfectly mixed crystallizers	132
3.2	Block diagram for mixing in the FC crystallizer	133
3.3	CSD transition for run no. 113 with $N = 1$	142
3.4	CSD transition for run no. 191 with 0% PFR	143
3.5	CSD transition for run no. 192 with 30% PFR	144

4.1	DTB with 1 stage	154
4.2	DTB with 3 stages	155
4.3	DTB attaining steady state at different stages	156
4.4	FC with 0% PFR of total volume	157
4.5	FC with 10% PFR of total volume	158
4.6	FC attaining steady state at different % PFR	159
5.1	Comparison between Adams-Moulton-Shell (A-M-S) and Runge-Kutta-Nystrom (R-K-N) method in solving the Random Breakage model	168
5.2	Comparison between the deterministic and stochastic results for the theoretical exponential population distribution in MSMR crystallizer	169
5.3	Comparison between the Runge-Kutta-Nystrom (R-K-N) and Monte Carlo (MC) approach in solving the Random Breakage model with $m = 4$, $q = 0.2$	170
5.4	Comparison between the Runge-Kutta-Nystrom (R-K-N) and Monte Carlo (MC) approach in solving the Random Breakage model with $m = 4$, $q = 0.5$	171
5.5	Comparison between the Runge-Kutta-Nystrom (R-K-N) and Monte Carlo (MC) approach in solving the Random Breakage model with $m = 1$, $q = 0.2$	172
6.1	Experimental set-up and fluid flow pattern	183
6.2	Photograph of experimental set-up	183
6.3	Experimental cumulative crystal size distribution at three different time distribution	184
6.4	Experimental cumulative crystal size distribution at three different stirring rates	185
6.5	Photo of NaCl crystals before attrition (magnification 1000x)	186

6.6	Photo of NaCl crystals after attrition (magnification 1000x)	186
6.7	Comparison between experimental and simulated cumulative crystal size distributions at three different stirring rates for 1 hour run	187
7.1	(a) Assumed geometry of the plastically deformed zone; (b) Stress created in the elastic zone	204
7.2	Particle size distribution of fragments for MS at $W_p=1\text{E-}4\text{J}$ with $\alpha = 0.5236$, $\alpha = \alpha_n$ and $\alpha = 1$	205
7.3	Particle size distribution of fragments for PA at $W_p=1\text{E-}4\text{J}$ with $\alpha = 0.5236$, $\alpha = \alpha_n$ and $\alpha = 1$	205
7.4	Particle size distribution of fragments for MS at $W_p=1\text{E-}5\text{J}$ with $\alpha = 0.5236$, $\alpha = \alpha_n$ and $\alpha = 1$	206
7.5	Particle size distribution of fragments for PA at $W_p=1\text{E-}5\text{J}$ with $\alpha = 0.5236$, $\alpha = \alpha_n$ and $\alpha = 1$	206
7.6	Particle size distribution of fragments for MS at $W_p=1\text{E-}6\text{J}$ with $\alpha = 0.5236$, $\alpha = \alpha_n$ and $\alpha = 1$	207
7.7	Particle size distribution of fragments for PA at $W_p=1\text{E-}6\text{J}$ with $\alpha = 0.5236$, $\alpha = \alpha_n$ and $\alpha = 1$	207

INTRODUCTION

Deterministic analysis of attrition process and transient crystal size distribution (CSD) is a difficult task owing to the complexity of the basic population balance equation (PBE). Often, the solution is very difficult except for simple cases. Alternatively, one could employ the stochastic analysis in solving the PBE that could easily account for growth rate dispersion, size-dependent growth, shape factor dispersion, birth size dispersion and change in nucleation rate simultaneously. These considerations introduce non-linearity in the PBE in the conventional deterministic approach and a lack of mathematical tool has been a major impediment in solving these equations.

Two different stochastic methods are commonly employed to predict the behavior of the CSD, namely the Markov process and the Monte Carlo (MC) technique. The basic advantages of the Markov process over the MC simulation are as under:

- (i) CSD's are available on a continuous time scale.
- (ii) It is more efficient with respect to computation time for the simple cases that it can handle.

Unlike the Markov process, the simulation results obtained from the MC simulation are discrete on a time scale. However, due to the following remarkable

features, MC technique has been recognized as a more versatile tool than the Markov process:

- (i) One can account for the influence of shape factor dispersion on CSD.
- (ii) The CSD can be expressed as both number and mass fractions for steady and non-steady state conditions.
- (iii) One can use any statistical density function to represent the dispersion effects.
- (iv) The simultaneous dispersion in growth, shape factor, nucleation rate and birth size can be accounted for in the calculation of steady state and transient CSD's.
- (v) It is a direct simulation technique and is free from any iterative calculations.

The present contribution involves application of MC technique to handle complex problems of transient CSD analysis (Chapter 2, 3, and 4 of Part 2). In addition, the MC is also employed to simulate the CSD of crystals as the result of attrition processes (Chapter 5, 6, and 7 of Part 3). For the former problem, it includes the simulation of transient CSD under size-dependent growth rate and stochastic dispersion effects for an imperfectly mixed crystallizer. While for the latter, it focuses on the effects of attrition on the theoretical CSD, modelling of experimental CSD results in a mechanically agitated crystallizer and finally the effects of volume shape factor dispersion on the CSD of fragments generated from a mechanically stirred crystallizer.

In Chapter 2, the transient CSD is simulated using the MC method under size-dependent growth rate conditions. The classical approach in simulating the CSD in a continuous mixed suspension mixed product removal (MSMPR) crystallizer is based on several hypotheses. A very important assumption is the constant growth rate of the crystals known as McCabe's delta L law. However, there is ample evidence that growth rate is a function of size in some systems. Under the present work, a MC simulation scheme is proposed for transient CSD in a continuous crystallizer to account for size-dependent growth rate. Crystal growth rates are described by ABEGG, STEVENS and LARSON (ASL) model. The proposed model is used to predict the transient CSD from potassium carbonate crystallizer. The agreement between theory and available data confirms the validity of the model.

In Chapter 3, the transient analyses of CSD for an imperfectly mixed draft tube baffled (DTB) and forced circulation (FC) crystallizers are predicted using the MC technique. To account for the non-ideal mixing conditions, the DTB and FC crystallizers are described by the compartmental and mixed models respectively. The simulation results have been compared and agreed with the available experimental data of BENNETT and VAN BUREN (1969) for continuous urea crystallizer. This work has been further extended in Chapter 4 to forecast the transient CSD in a crystallizer for simultaneous dispersion effects in growth rate, shape factor and birth size. It also takes into account the possible variation in nucleation rate in a crystallizer. The earlier work of SEN GUPTA and DUTTA (1991) has been used to validate the results.

In Chapter 5, the effect of attrition on the CSD in a continuous mixed suspension crystallizer was predicted by a Random Breakage model as proposed by RANDOLPH (1969). The CSD was computed by MC technique and compared with the deterministic solution of the PBE proposed by RANDOLPH (1969). The agreement between the two approaches confirms the validity of the MC technique.

Chapter 6 reports the experimental work carried out to determine the CSD resulting from breakage and abrasion occurring in agitated crystal suspensions. The effect of two operating variables, i.e. duration of run (≤ 1 hour) and low stirring rates (≤ 400 rpm) are shown with reference to sodium chloride crystals. The experimental results were used to validate the model proposed by MAZZAROTTA (1992) and BISCANS *et al.* (1996).

The effect of volume shape factor on CSD is usually ignored to simplify the analysis of PBE. In Chapter 7, the CSD of fragments generated from a mechanically stirred crystallizer as the result of attrition mechanism has been reported. The physical model of GAHN and MERSMANN (1997) which relates the attrition resistance of crystalline substances to its mechanical properties has been employed with suitable modification. The simulation of fragment size distribution was performed by MC technique.