MATHEMATICAL MODELING & DYNAMICS STUDY OF BATCH CRYSTALLIZER FOR PURIFIED TEREPHTHALIC ACID (PTA) CRYSTALLIZATION PROCESS USING gPROMS

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Abstract

Crystallization is a complex and critical chemical engineering process which is carried out for high purity products in process industry. Purified Terephthalic Acid (PTA) is commodity chemical, it is principal raw material mainly used in Polyester industry. During production process of Purified Terephthalic Acid (PTA), crystallization process is used to separate crystals from water. Crystalline materials generally have a high degree of purity even when obtained from a relatively impure solution. Control of crystal size distribution (CSD) is an end objective in PTA crystallization process. To fulfill CSD, needs the mathematical model based optimization for PTA unit, developed mathematical model is solved in gPROMS (general PROcess Modeling System).In present work, research achievement are batch crystallization modeling, simulation, optimization & parameter estimation. Within the proposed control strategy, a dynamic optimization is performed to obtain optimal cooling temperature profile of batch crystallizer, maximizing the total volume of seeded crystals. Simulation is implemented to track the resulting optimal temperature profile.

***Keywords:** Purified Terephthalic Acid process, Mathematical model, Batch Crystallizer, simulation, gPROMS*

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1. INTRODUCTION

Crystallization is an important process, which is carried out for production of high purity in Terephthalic Acid industry. In the production process, oxidation and purification stages are carried out at high temperature and pressure, creating severe operating conditions. The process for purification can accept crude containing higher levels of impurities and still be able to produce suitable PTA. Efforts to purify PTA through crystallization using organic solvents have failed due to the inability to discover a solvent to economically purify by crystallization and a lack of understanding of the crystal growth mechanism. The effects of the process conditions and new crystallization method must be demonstrated at the pilot scale to stimulate industry investment. The common crystallization objective is to produce large crystals with minimum fines production by minimizing nucleation and optimizing the temperature profile. In batch cooling crystallization, the solution is cooled to super saturation causing crystal formation and its growth.

2. MATHEMATICAL MODEL DEVELOPMENT

2.1 Population Balance Equation

Mathematical representation of the crystallization rate can be achieved through basic mass transfer considerations or by writing a population balance represented by its moment equations. The population balance equation (PBE) is developed based on the following assumption: volume change in the system is negligible, crystal agglomeration or breakage phenomena are neglected and the crystal density and the supersaturation are homogeneous in all part of the crystallizer.

$$\frac{\partial f(L,t)}{\partial t} + G(t)\frac{\partial f(L,t)}{\partial L} = 0 \qquad (1)$$

The nucleation rate, B (t), and the growth rate, G (t) are [2], [4], [5], [7], [13] given by:

$$B(t) = k_b\, e^{-Eb/RT}\left(\frac{C-Cs(t)}{Cs(t)}\right)^{b} \mu_3(t) \qquad (2)$$

$$G(t) = k_g\, e^{-Eb/RT}\left(\frac{C-Cs(t)}{Cs(t)}\right)^{g} \qquad (3)$$

2.2 Model Implementation

In the seeded batch crystallizer of PTA, the saturation concentration of the solute (C_s) is given by

$$Cs = 4.29 \times 10^{-6}\; e^{0.0392\; T} \qquad (4)$$

By applying this moment operator to the population balance equation, a set of moment equation can be developed with the general form.

The values of the model parameters of seeded batch crystallizer are shown in Table 1

Symbol	Unit	Value
b	-	0.4719
k_b	(s µm^3)$^{-1}$	6.5179 x 10^{-12}
E_b /R	K	3.0068 x 10^3
U	kJ (m^2 h K)$^{-1}$	1800
ΔH_c	kJ/Kg	122.7587
M	kg	27.00
K_v	-	1.5
Vj	m^3	0.015
ρj	Kg/m^3	1000
g	-	0.984
kg	µm/s	1.7251
Eg/R	K	1.7637 x 10^3
A	m^2	0.25
Cp	kJ (kg K)$^{-1}$	3.86
ρ_c	Kg/m^3	1.58 x 10 $^{-12}$
T_f	min	30
Fj	m^3/s	0.001
Cp_j	kJ (kg K)$^{-1}$	4.184

Notations:
A is the total heat transfer surface area
b is an exponent relating nucleation rate to supersaturation
C is the solute concentration
C_p is the heat capacity of the solution
C_s is the saturation concentration of the solute
E_b is the nucleation activation energy
E_g is the growth activation energy
f (*L*,*t*) is the population density of crystals size *L* at time *t*
G(*t*) is the growth rate of crystals.
F_j is cooling water flow rate
g is an exponent relating growth rate to the supersaturation

G is crystallization growth rate
k_v is the volumetric shape factor
M is the mass of solvent is the crystallizer
T is the reactor temperature
T_j is the jacket temperature
T_{jsp} is set point of the jacket temperature
U is the overall heat-transfer coefficient
V_j is jacket volume
ρ_c is the density of the crystal
ΔH_c is the heat of crystallization.
µ3 is the third moment of the CSD

2.3 Dynamic Optimization

The aim of dynamic optimization is to maximize the average crystal size (Lw) where to keep the coefficient of variations (CV_w) small. The optimal cooling temperature profiles were obtained by solving the optimal control problem with different optimization problems.

2.4 Simulation of model

gPROMS is strongly typed modeling language for simulation and optimization of physical systems. Simulation models in gPROMS are defined using four different entities; DECLARE MODEL, TASK and PROCESS. The DECLARE entity is used to declare variables types and stream types, which will be used as templates for variables and streams. The model entity is use to describe the physical behavior of primitive elements of the system to be modeled.

Simulation result from gPROMS generated for Average Crystal Size (Lw) with respect to time (s)

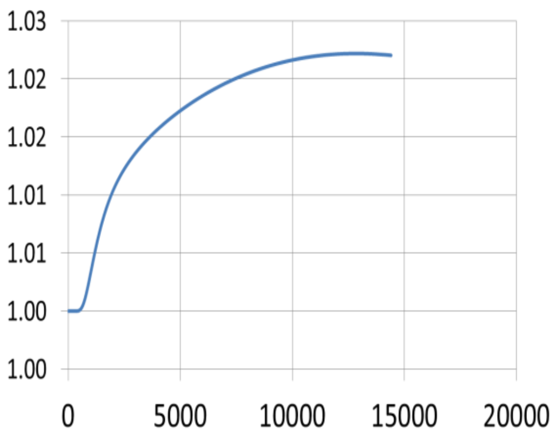

Fig 1: Lw Vs. T

Optimal profile for saturation concentration of solute (Cs) is maintained with time

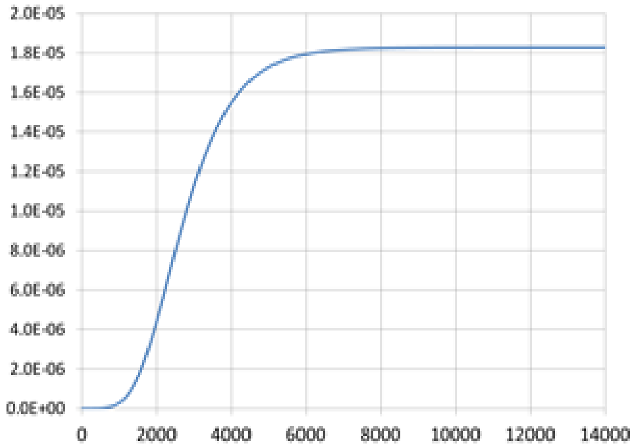

Fig 2 Cs Vs. T

It is noted here that only the optimal cooling temperature profile obtained from selected optimized function in which the μ3 (tf) is minimized, is considered since such a temperature policy provides less fine crystals leading to efficient operation in downstream processes whereas the volume of seeded crystal (μ3) is still satisfy the product quality requirement.

Output of Simulation result shows with different Liquid Volume in the same vessel does not matter to crystal size

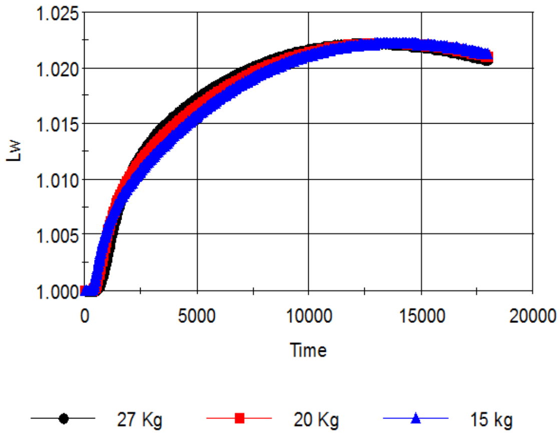

Fig 3: Effect of liquid volume on Lw Vs. T

Output of simulation shows different concentration of solids are maintained with respect to time However smaller liquid volumes help faster growth of crystals.

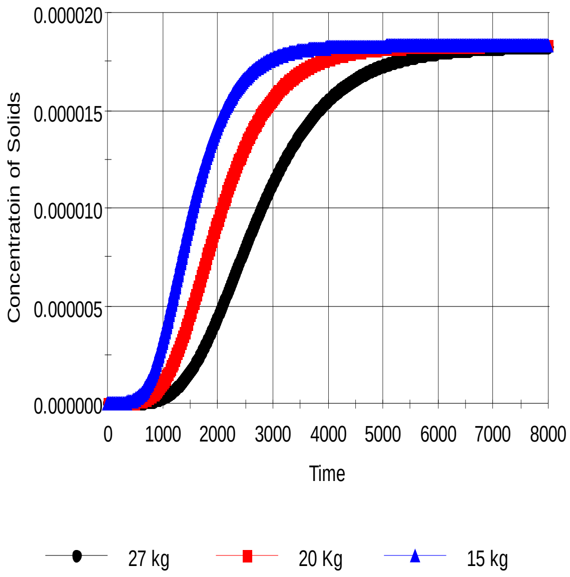

Fig 4: Effect of liquid volume on Cs Vs Time

Output shows Increase in overall heat transfer coefficient (U) causes faster heat transfer leading to faster crystallization as observed.

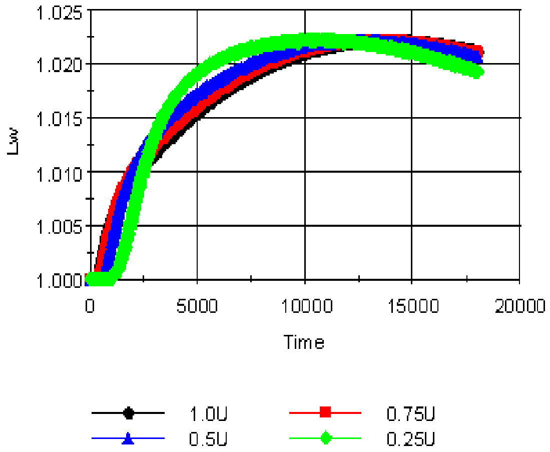

Fig 5: Effect of U on Lw Vs. T

Output of Simulation result shows, Average crystal size decreases with lesser U owing to longer heater transfer time.

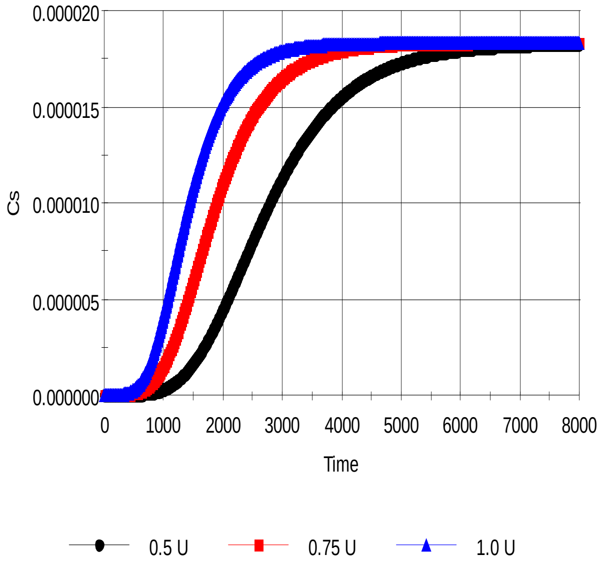

Fig 6: Effect of change of U on Cs Vs. T

Output of simulation for Moment of CSD against time, with change in heat transfer co-efficient

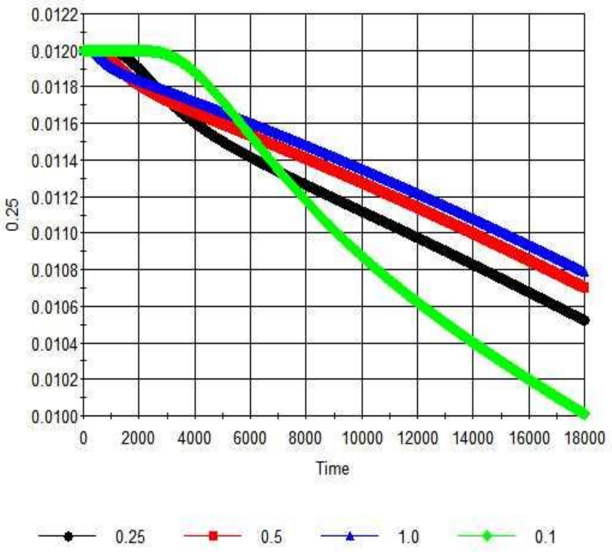

Fig 7: Effect of change of U on μ and Time

Output of simulation for Moment of CSD against time, with change in heat transfer co-efficient

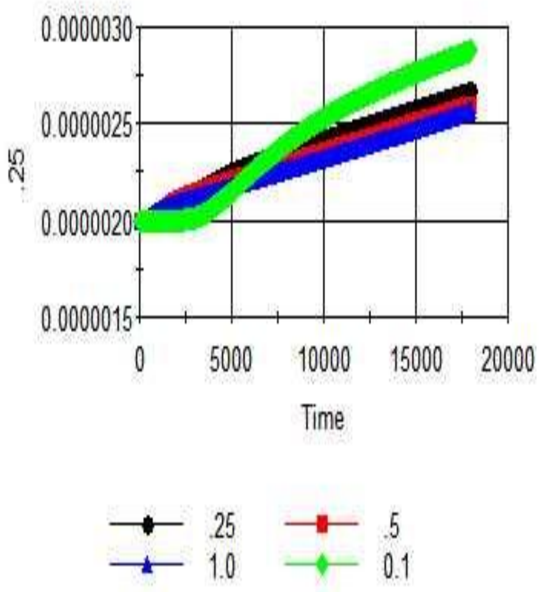

Fig 8: Effect of change of U on Temperature &Time

Output of simulation for Moment of CSD against time, with change in heat transfer co-efficient

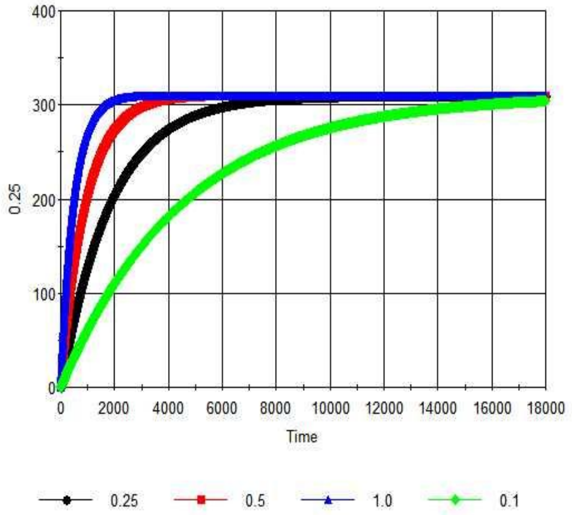

Fig 9: Effect of change of U on Lw and Time

3. PTA BATCH CRYSTALLIZER GPROMS PROGRAM CODE:

Model Crystallizer

```
PARAMETER
#exponent relating nucleation rate to the supersaturation
b AS REAL

kb AS REAL

#the nucleation activation energy
EbbyR AS REAL

#the overall heat-transfer coefficient
U AS REAL

#the heat of crystallization.
dHc AS REAL

#the mass of solvent is the crystallizer
M AS REAL

#the volumetric shape factor
Kv AS REAL

#jacket volume
Vj AS REAL

# the density of jacket fluid
rhoj AS REAL

# an exponent relating growth rate to the supersaturation
g AS REAL

kg AS REAL

# the growth activation energy
EgbyR AS REAL
```

```
# total heat transfer surface area
A AS REAL

# the heat capacity of the solution
Cp AS REAL


# the density of the crystal
rhoc AS REAL

# Tf in min
Tf AS REAL

# cooling water flow rate
Fj AS REAL

#the heat capacity of jacket fluid
Cpj AS REAL

mu0s AS REAL

VARIABLE
# the saturation concentration of the solute (Cs)
Cs AS Concentration

# the solute concentration
C AS Concentration

# Crystalliser Temperature
T AS Temperature

# Jacket Temperature
Tj AS Temperature

# set point of the jacket temperature
Tjsp AS Temperature

# the growth rate of crystals
Gt AS NoType

#the ith moment of the CSD that explains the total volume of crystals
mu0n, mu1n, mu2n, mu3n, mu4n,mu5n AS NoType
mu1s, mu2s, mu3s, mu4s, mu5s AS NoType
mu0, mu1, mu2, mu3,mu4,mu5 AS NoType

# The nucleation rate
Bt AS NoType

# Average crystal size
Lw AS NoType

#CVw coefficient of variations
CVw AS NoType

DISTRIBUTION_DOMAIN

SET
BOUNDARY
```

```
EQUATION
# Model equations
#      Cs = exp(0.0523-0.0027*(T-273)-3e-5*(T-273)^2+8e-9*(T-273)^3);
#    Cs = (0.0523-0.0027*(T)-3e-5*(T)^2+8e-9*(T)^3);
# Eqn proposed by Ramakanth
#    Cs = 7e-8*T^3 - 6e-5*T^2 + 0.017*T -1.716 ;
Cs   = 9.70063529E-11*exp(3.91838338E-02*T) ; # interm of mol/lit data from internet for water solubility

Bt = kb*exp(-EbbyR/T)*(C/Cs-1)^b*mu3;
Gt = kg*exp(-EgbyR/T)*(C/Cs-1)^g;
#    Gt = kg*exp(-EgbyR/T)*(Cs/C-1)^g;
#    Bt = kb*exp(-EbbyR/T)*(Cs/C-1)^b*mu3;
$C =-3*rhoc*kv*Gt*mu2;
$T =(-3*dHc*rhoc*kv*Gt*mu2/Cp)-U*A*(T-Tj)/(M*Cpj);
$Tj = Fj*(Tjsp-Tj)/Vj+U*A*(T-Tj)/(rhoj*Vj*Cpj);

$mu0n =Bt;
$mu1n =Gt*mu0n;
$mu2n =2*Gt*mu1n;
#the third moment of the CSD that explains the total volume of crystals
$mu3n =3*Gt*mu2n;
$mu4n =4*Gt*mu3n;
$mu5n =5*Gt*mu4n;

$mu1s = Gt*mu0s;
$mu2s = 2*Gt*mu1s;
$mu3s = 3*Gt*mu2s;
$mu4s = 4*Gt*mu3s;
$mu5s = 5*Gt*mu4s;

mu0 = mu0s + mu0n;
mu1 = mu1s + mu1n;
mu2 = mu2s + mu2n;
mu3 = mu3s + mu3n;
mu4 = mu4s + mu4n;
mu5 = mu5s + mu5n;

Lw = mu4/mu3;
CVw = 100*sqrt(mu3*mu5/mu4^2-1);

INITIAL
#----------------------------------------------------------------------
# Process Description
#----------------------------------------------------------------------

UNIT # Equipment items
#   AP101 AS Crystalliser
AP101 AS Crystallisation


SET
# Parameter values
#exponent relating nucleation rate to the supersaturation
AP101.b:= 0.4719;

#coeff relating nucleation rate to the supersaturation um/s
AP101.kb:= 6.5179e-12;
```

```
#the nucleation activation energy
AP101.EbbyR:= 3.0068e+3;

#the overall heat-transfer coefficient kJ/m2sK
AP101.U:= 0.5;  #  =1800  kJ/(m2 h K)

#the heat of crystallization.kj/kg
AP101.dHc:= 122.7587;

#the mass of solvent is the crystallizer in kg
AP101.M:= 27.0;

#the volumetric shape factor constant
AP101.Kv:= 1.5;

#jacket volume in m3
AP101.Vj:= 0.015;

# the density of jacket fluid  kg/m3
AP101.rhoj:= 1000;

# an exponent relating growth rate to the supersaturation
AP101.g:= 0.984;

# ancoeff relating growth rate to the supersaturation m/s
AP101.kg:= 1.7251e-6;

# the growth activation energy K
AP101.EgbyR:= 1.7637e3;

# total heat transfer surface area m2
AP101.A:= 0.25;

# the heat capacity of the solution kJ/(kg K)
AP101.Cp:= 3.86;

# the density of the crystal kg/m3 Orig = 1.58e12
AP101.rhoc:= 1.58E3;

# Tf in sec
AP101.Tf:= 30*60;

# cooling water flow rate m3/s
AP101.Fj:= 0.001;

#the heat capacity of jacket fluid kJ/(kg K)
AP101.Cpj:= 4.184;
AP101.mu0s:= 0.0;
# condition

ASSIGN
WITHIN AP101 DO
Tjsp: =310;
END

INITIAL
WITHIN AP101 DO
C =0.012;
Tj = 303.15;
#       T =500;
mu0n =1e-6;
mu1n =1.0e-6;
mu2n  =1.0e-6;
mu3n  =1.0e-6;
mu4n  =1.0e-6;
mu5n  =1.0e-4;
mu2s =1.0e-6;
mu3s=1.0e-6;
mu4s =1.0e-6;
mu5s=1.0e-6;
$mu0n =10e-6;
$mu2s =10e-6;
#       CvW = 0;
END # Within AP101

SOLUTIONPARAMETERS
Reporting Interval :=1 ;

SCHEDULE
CONTINUE FOR 5*3600
```

4. CONCLUSIONS

From the above studies the following conclusions are made

1. Mathematical Modelling is developed for batch crystallizer
2. Developed mathematical model is solved in gPROMS
3. Model is used to predict the concentration and crystallizer temperature profile in this process
4. Optimal temperature profile for best Crystal size distribution (CSD)
5. In seeded batch crystallization process, large average crystal size leading to product quality is desired.

ACKNOWLEDGEMENTS

Author would like to acknowledge the support from my family and the department of Chemical Engineering, Faculty of Chemical Engineering, TKIET Warananagar and Shivaji University, Kolhapur.

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