

Analysis of the Monochloroacetic Acid Crystallization Process by Entropic Modeling

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The process of crystallization has always been regarded as a key operation in the separation and purification of chemical products, particularly in fine chemistry and due to this, new analytical techniques, new control and optimization methods have been developed. The analysis presented for the monochloroacetic acid (MCAA) crystallization system has been derived from the mass and energy balances associated with the entropy balance, taking a solid-equilibrium diagram into account. A methodology that minimizes the entropy production was used to find the optimal operating conditions for the crystallization process, operating under the minimum rate. The theoretical results are in good agreement with the experimental data, indicating that entropy analysis is a simple methodology, easy to apply and one which requires less computational effort.

1. Introduction

Due its importance in the separation and purification of various chemical products, the crystallization process has been the object of several studies with the aim of making it more efficient and profitable. The classical analysis of crystallization processes has been led by models based on mass balances and energy associated with the population balance (Randolph and Larson, 1971). However it has been verified, at least from the theoretical point of view, that the best operating conditions can be obtained when the entropy concept is used in association with such an analysis. Thus, the methodology applied for the analysis of the monochloroacetic acid (MCAA) crystallization process, presented in this paper, also known as entropy generation minimization (EGM), which combines the basic principles of thermodynamics, heat transfer and fluid mechanics (Bejan, 1996), has been used to determine the optimal operating conditions. Despite the concept of entropy concept having been well-established for a long time, it was only in the early 1970s that an entropy generation minimization methodology made a significant emergence, with successful applications in cryogenics, heat transfer operations and the conversion of solar energy (Bejan, 1996).

In recent years, considerable progress has been made related to entropy generation, and EGM can be considered as a powerful tool for the analysis and optimization of reactive or non-reactive systems, as shown in the specific literature (Andresen, 2011). The EGM has been used to establish the optimum operation conditions of chemical reactors, and the results show there are new operating conditions whereby the minimum entropy generation rate can be reached, and this is emphasized. Such results have been presented by Manzi et al. (2009), where the analytical potential of the procedure can be evidenced, highlighting the flexibility and the ease of use when applied to reactive systems.

The purpose of this paper is to establish an analytical approach for the MCAA crystallization process, by means of developing and analyzing the entropy production rate. Using the results from such an analysis, the optimum operating conditions may be found and verification undertaken made on whether the process is operating under the minimum entropy generation condition.

2. The System

2.1 Production of MCAA

MCAA is normally used as an intermediary in the chemical industry, being applied in the synthesis of several products, such as pesticides, organic chemicals and pharmaceuticals. Its main route of manufacture is based on the catalytic chlorination of acetic acid when acetic anhydride is used as a catalyst, as shown by the following equation,



The reaction is carried out in a semi-continuous reactor where the chlorination of acetic acid (AA) is continuously performed until the appropriate degree of conversion is reached. The product obtained from the reaction is a solution of 68 % MCAA, 28 % acetic acid and 4 % by-products, which is sent to a buffer tank and maintained at 310 K.

With a view to achieving separation of MCAA from the mother liquor, the process of crystallization of MCAA is used, since it is considered to have advantage over other methods due to its cost-benefit, besides safety factors, and the facility with which MCAA can be stored and transported. The production route of MCAA is shown in Figure 1.

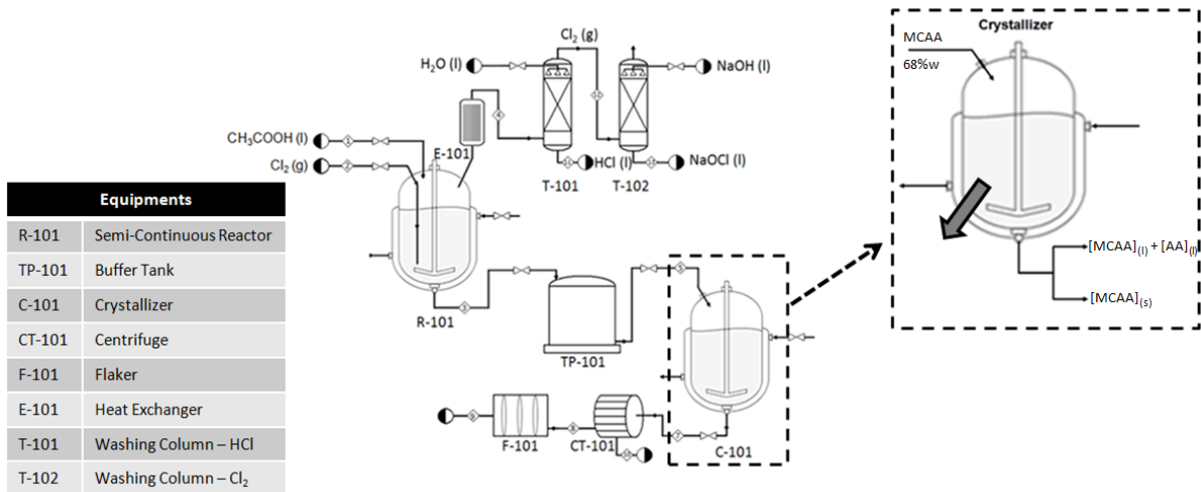


Figure 1 – Diagram of the Monochloroacetic acid production process

The physical and chemical properties and the data used to simulate the system are listed in Table 1.

Table 1: Operating conditions and parameters of the crystallizer applied to production of MCAA

Parameter	Value	Units	Parameter	Value	Units
F^e	10	L s^{-1}	V	100	L
X_{MCAA}^e	0.68		C_p	1.52	$\text{J g}^{-1} \text{K}^{-1}$
T	273.15	K	ΔH_c	-11.25	J g^{-1}
ρ^e	1.58	g L^{-1}	ΔG_c	11.80	J g^{-1}
ρ	1.37	g L^{-1}	PM_{MCAA}	94.50	g mol^{-1}

2.2 Theoretical Formulation

Figure 1 shows that the product of the reaction is continuously fed to the crystallizer resulting in an output stream consisting of the mother liquor and MCAA crystals. The modeling of the crystallization system has been developed based on mass and enthalpy balances, taking a solid-liquid equilibrium diagram (see Section 3 below) into account to determine the concentration of MCAA in the mother liquor as a function of the temperature. It should be emphasized that the equilibrium diagram of the system MCAA-AA has been theoretically obtained and is in very good agreement with the experimental data.

2.2.1 Mass balance

Considering that no reaction occurs in the crystallizer, and having in mind that the feed stream consists solely of MCAA and AA, the mass balances for the components can be established as per the following equations:

$$PM_{MCAA} \left(\frac{dn_{MCAA}}{dt} \right) = F^e \rho^e X_{MCAA}^e - F \rho X_{MCAA} - F^e \rho^e \left[\frac{X_{MCAA}^e - X_{MCAA}}{1 - X_{MCAA}} \right] \quad (2)$$

$$PM_{AA} \left(\frac{dn_{AA}}{dt} \right) = F^e \rho^e X_{AA}^e - F \rho X_{AA} \quad (3)$$

2.2.2 Enthalpy balance

Since the enthalpy (H) balance can be given by,

$$\frac{dH}{dt} = \dot{H}_{T(e)}^e - \dot{H}_T^{s(l)} - \dot{H}_T^{s(MCAA(s))} - \dot{Q} \quad (4)$$

Given that (H) is a function of temperature and the number of moles of each component present in the system and considering the balances established by Eq. (2) and (3), then, based on the concept of a total differential, the following equation can be obtained:

$$\frac{dH}{dt} = \left(\frac{\partial H}{\partial T} \right)_{n_i} \frac{dT}{dt} + \left(\frac{\partial H}{\partial n_{MCAA}} \right)_{T, n_{AA}} \frac{dn_{MCAA}}{dt} + \left(\frac{\partial H}{\partial n_{AA}} \right)_{T, n_{MCAA}} \frac{dn_{AA}}{dt} \quad (5)$$

Substituting Eq. (5) into Eq. (4), results in,

$$\rho V C_p \frac{dT}{dt} = \dot{H}_{T(e)}^e - \dot{H}_T^{s(l)} - \dot{H}_T^{s(MCAA(s))} - \dot{Q} - \left(\frac{\partial H}{\partial n_{MCAA}} \right)_{T, n_{AA}} \frac{dn_{MCAA}}{dt} - \left(\frac{\partial H}{\partial n_{AA}} \right)_{T, n_{MCAA}} \frac{dn_{AA}}{dt} \quad (6)$$

Since $dH/dT = \rho V C_p$ and $\partial H / \partial n_i = \tilde{H}_i$ representing the partial molar enthalpy, and taking into account mass balances for each component given by Eq. (2) and (3), the enthalpy balance can be rewritten as follows:

$$\rho V C_p \frac{dT}{dt} = F^e \rho^e \left\{ \left[\frac{X_{MCAA}^e - X_{MCAA}}{1 - X_{MCAA}} \right] \Delta H_c + C_p (T^e - T) \right\} - \dot{Q} \quad (7)$$

where V , X_{MCAA}^e , X_{MCAA} , T , ρ , C_p , ΔH_c are, respectively, the crystallizer volume, the inlet mass fraction of MCAA, the mass fraction of MCAA in the mother liquor, the crystallizer operating temperature, specific gravity, specific heat and the heat of crystallization.

2.2.2 Entropic modelling

The rate of entropy generation has been developed in order to establish the optimal operation conditions for the crystallization system. Thus, the following entropy balance must be considered:

$$\frac{dS}{dt} = \dot{S}_{T(e)}^e - \dot{S}_T^{s(l)} - \dot{S}_T^{s(MCAA(s))} - \frac{\dot{Q}}{T} + \dot{\sigma} \quad (8)$$

Since entropy is a function of temperature and of the number of moles of the components involved in the crystallization process, and taking into account the concept of a total differential, the following relation, given by Eq. (9), can be obtained.

$$\frac{dS}{dt} = \left(\frac{\partial S}{\partial T} \right)_{n_i} \frac{dT}{dt} + \left(\frac{\partial S}{\partial n_{MCAA}} \right)_{T, n_{AA}} \frac{dn_{MCAA}}{dt} + \left(\frac{\partial S}{\partial n_{AA}} \right)_{T, n_{MCAA}} \frac{dn_{AA}}{dt} \quad (9)$$

Considering the mass and enthalpy balances, Eqs. (9) and (8), as well as the relations given by $dS/dT = \rho VC_p/T$ and $\partial S/\partial n_i = \tilde{S}_i$ where \tilde{S}_i denotes the partial molar entropy, then Eq. (10) is obtained, which describes the entropy generation rate for the MCAA crystallization process.

$$\dot{\sigma} = F^e \rho^e \left[\left(\frac{X_{MCAA}^e - X_{MCAA}}{1 - X_{MCAA}} \right) \left(\frac{\Delta G_c}{T} \right) \right] + C_p \left(\frac{T - T_e}{T} + \ln \left(\frac{T_e}{T} \right) \right) \quad (10)$$

3. Results and Discussion

3.1 Analysis of the crystallization process

By using the thermodynamic criterion of equilibrium applied to a binary system as per Nylyt (1985) it is easy to derive the equation that drives the diagram of equilibrium for the crystallization process of MCAA, as shown below:

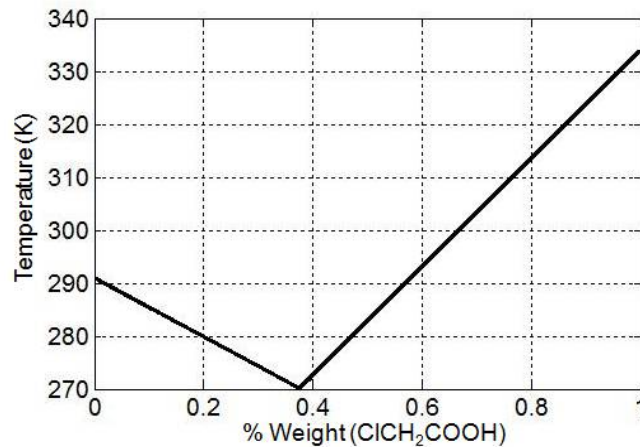


Figure 2: Diagram of solid-liquid equilibrium for the crystallization process of MCAA

By analyzing the diagram of equilibrium, the operating points for the crystallization system can be found, for which, at first glance, the best performance can be obtained. For the case in study, the feed solution containing 68 % MCAA and kept at 310 K is continuously cooled until the concentration of MCAA in the mother liquor reaches approximately 40 % by weight, corresponding to a temperature of around 273 K.

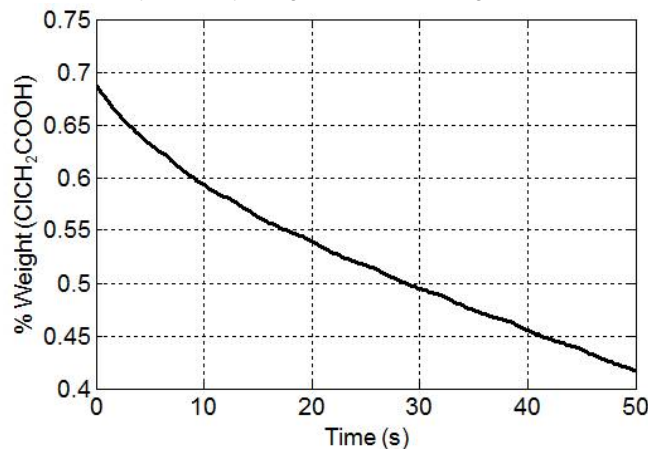


Figure 3: Dynamic behavior of the concentration of MCAA

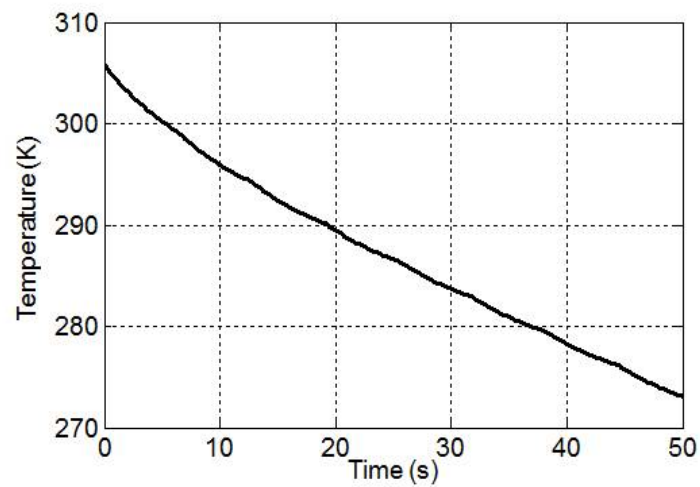


Figure 4: Dynamic cooling of the crystallization system

Figures 3 and 4 shows the dynamic behavior of the MCAA concentration, as well as the temperature of the system, which reaches 273 K, and which is considered as the best condition.

3.2 Entropic Analysis

The analysis of the entropy production rate given by Equation (10) and depicted in Figure 5, considering the range of temperature for practical applications, enables the verification that the point of minimum entropy generation for the process can be established when the operating temperature is equal to the temperature of the eutectic point.

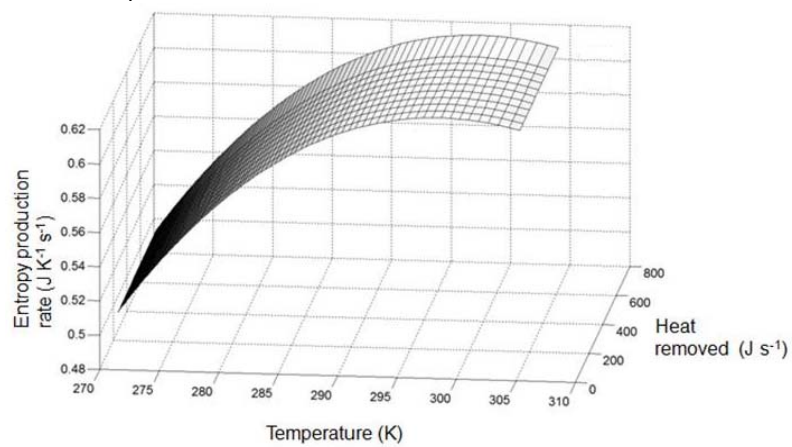


Figure 5: The response surface of the entropy production for different values of heat removed

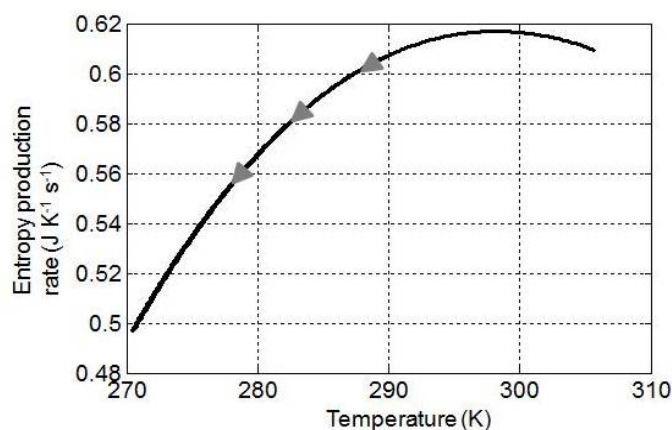


Figure 6: Behavior of the entropy production rate

It can be verified from Figure 6 that the reduction in the entropy generation rate is associated with the reduction of temperature in the crystallizer, it being observed that the entropy generation rate reaches its minimum value when the temperature of the system is approximately 270 K.

In practice, operation at this point is inappropriate due to the possible occurrence of both the MCAA and AA components, in their crystal states. Therefore, it is necessary to set some constraints on the temperature so that the system operates safely. Thus, taking into account the limits imposed by the operational constraints, it can be verified that the optimal operating conditions when the process is under the minimum entropy production are found to be equal to 273 K and 40 % w/w, as shown in Figures 3 and 6. It should be emphasized that the practical operation of an industrial plant follows the operating conditions that are set out in this paper.

4. Conclusion

A model for the entropy generation rate applied to the monochloroacetic acid (MCAA) crystallization process has been developed from the mass, enthalpy and entropy balances in addition to which a solid-liquid equilibrium diagram has been used. The analysis of the model based on minimum entropy was used to establish the optimal process conditions, and was shown to be in very good agreement with the current modus operandi, thereby enabling the conclusion that, in practice, the process operates under the minimum entropy generation conditions. Finally, this methodology is easy to apply and can be done so at low computational cost, and thus shows itself as being a powerful tool for analyzing the process.

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