

## **CHAPTER I**

### **INTRODUCTION**

#### **1.1 Background**

Crystallization from a solution plays an important role in the industrial field, as many materials are required in crystalline form. Examples of crystallization applications include the production of sugar, salt, glass, and instant coffee powder without residue (McCabe & Smith, 2000). Crystallization is a separation process in which a solute crystallizes from its multicomponent solution. When carried out properly, it produces crystals with a high degree of purity. Therefore, crystallization is one of the most practical methods to obtain pure chemicals of a quality that meets market requirements. In the crystallization of a solution, the solute will crystallize, forming a two-phase mixture called magma: the liquid phase known as the mother liquor, and the solid crystalline phase.

#### **1.2 Problem Statement**

In this experiment, crystallization operations were carried out using the UOP 14 MKII Crystallization Unit in a batch system. The responses observed from this experiment were the effects of heating, cooling temperature, and the addition of potassium chloride mass on the mass of crystals produced, as well as the crystal size distribution (CSD) of the potassium chloride obtained.

#### **1.3 Practicum Objectives**

1. To be able to explain the types of crystallizers.
2. To be able to explain the operational parameters in crystallization, namely the degree of supersaturation of the solution, heating temperature, cooling temperature, nucleation, crystal growth rate, and CSD product.
3. To be able to operate the UOP 14 MKII Crystallization Unit with solution cooling.
4. To be able to collect experimental data accurately, process it, and present it in the form of graphs showing the effect of heating temperature, cooling temperature, and the addition of potassium chloride mass on the mass of crystals produced, as well as the relationship between average particle diameter and the number of crystals produced (CSD).



#### 1.4 Practicum Benefits

1. Students are able to explain the types of crystallizers.
2. Students are able to explain the operational parameters in crystallization.
3. Students are able to operate the UOP 14 MKII Crystallization Unit.
4. Students are able to collect experimental data accurately.



## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Definition

Crystallization plays a very important role in the chemical industry, considering that approximately 70% of chemical products are produced in the form of solids/crystals. Crystallization is the process of separating a solute from its solution in the form of solid crystals. The advantages of producing products in solid form include lower transportation costs, greater resistance of solids to damage due to decomposition, and ease of packaging and storage. The objective of the crystallization process is to produce crystal products with the desired quality. Crystal quality can be determined by three parameters: crystal size distribution (CSD), crystal purity, and crystal habit/shape.

Crystallization is based on the principle of solubility, namely that a solid compound tends to dissolve faster in a hot liquid than in a cold one. If a solution of the compound is saturated in a hot state until it reaches a supersaturated condition and then cooled, the solubility of the dissolved compound will decrease, and it will begin to precipitate in the form of pure crystals due to crystal growth of the solute (Puguh et al., 2003).

Crystallization can occur from three different phases: the formation of crystalline solid particles from a vapor phase, from a solute in a solution, or from a molten phase. Crystallization can be carried out by cooling, solvent evaporation, or the addition of certain solvents. The purpose of crystallization from a solution is to separate a solvent from a multicomponent solution to obtain a product in a purer crystal form. Crystallization is often chosen as a purification method because it is more economical.

#### 2.2 Stages of Crystallization Operation

Crystallization operations can be divided into several stages as follows:

1. Preparation of a supersaturated solution

When a solution reaches a certain degree of supersaturation, crystalline solids will begin to form in the solution. Therefore, the degree of supersaturation is the most important factor in controlling the crystallization process. Several methods to achieve a supersaturated solution are as follows:

- a. Cooling the solution



The solubility of a solid in a liquid is a function of temperature. Thus, when a solution intended for crystallization is cooled, supersaturation occurs, where the solute concentration in the solution exceeds the concentration of a saturated solution at that temperature.

b. Solvent evaporation

The solvent from a multicomponent solution is evaporated so that the concentration of the solute increases until supersaturation is reached. This method is used for substances with a relatively flat solubility curve.

c. Adiabatic evaporation

When a hot solution is introduced into a vacuum chamber, spontaneous evaporation occurs because the total pressure becomes lower than the vapor pressure of the solvent at that temperature. The evaporation, accompanied by a decrease in temperature, will bring the solution to a supersaturated condition.

d. Chemical reaction

When a chemical reaction is carried out in the liquid phase, the concentration of the solute (reaction product) gradually increases until it reaches a supersaturated condition.

e. Addition of another substance

The addition of another substance can reduce the solubility of the compound to be crystallized. For example, when glycerol is added to an NaOH solution, the solubility of NaOH decreases, leading to supersaturation.

2. Crystal nucleus formation

The systematic formation of crystal nuclei can be seen in the following image.

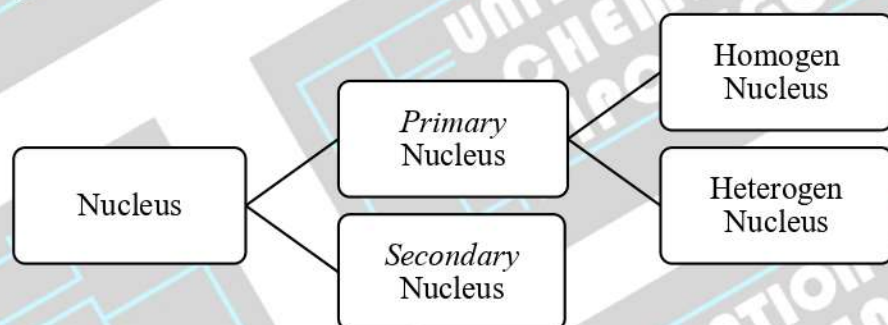


Figure 2.1 Crystal Nucleation

a. Primary Nucleus



The process of primary crystal nucleation occurs when the solution reaches a sufficiently high level of saturation (supersaturation). Primary nucleation can take place through the following two mechanisms:

- Homogeneous Nucleation

This type of nucleation occurs spontaneously in a highly saturated solution without the presence of foreign particles as triggers. The crystal nucleus forms from the aggregation of solute molecules themselves.

- Heterogeneous Nucleation

In heterogeneous nucleation, the formation of crystal nuclei also occurs under saturated conditions. However, the process is accelerated by the presence of foreign particles such as dust or other solid surfaces that serve as initial sites for crystal nucleus formation.

b. Secondary Nucleus (Contact Nucleation)

Crystal nuclei formation can also result from contact, such as collisions between parent crystals, collisions between parent crystals and the impeller stirrer, collisions with the crystallizer wall, or friction between the parent crystal surface and the solution. The number of crystal nuclei formed can be expressed by the equation:

$$N = (a)(L)^b (\Delta C)^c (P)^d \quad (2.1)$$

Where:

N = number of nuclei formed (count/hour)

L = size of the parent crystal (mm)

$\Delta C$  = degree of supersaturation of the solution (mol/L) or ( $^{\circ}\Delta C$ )

P = stirring power (HP)

a,b,c,d = constants

Based on Equation (2.1), the following conclusions can be drawn:

- If L increases significantly, the number of crystals formed will also increase. Larger crystals lead to more collisions, and fragments from these crystals result in more nuclei formation.
- If  $\Delta C$  increases significantly, the number of crystals formed will also increase. A higher degree of supersaturation increases the likelihood of new nuclei formation.



- If  $P$  increases significantly, the frictional forces between particles or collision forces will also be greater, increasing the number of nuclei formed due to the breaking of larger particles.

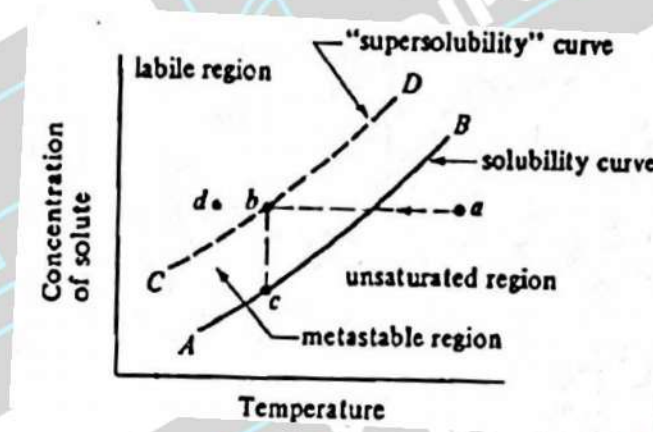


Figure 2.2 Miers' Theory

Miers' theory states that a supersaturated solution can be obtained by cooling a solution that was initially unsaturated (point  $a$ ). After passing the saturation curve A–B, the solution enters the supersaturated condition, referred to in the diagram as the metastable region. When the level of supersaturation reaches a certain threshold, crystallization begins with the formation of primary crystal nuclei (point  $b$ ). These initial points of crystal nucleus formation are referred to by Miers as the supersolubility curve.

The crystal nuclei then grow through the attachment of solute molecules onto their surfaces, causing the solute concentration in the solution to decrease (from point  $b$  to point  $c$ ). Furthermore, Miers identifies the region of very high supersaturation, where primary nuclei form spontaneously, as the labile region.

In industrial practice, primary nucleation is generally avoided because it produces crystals of very small size. Instead, secondary nucleation is preferred—this is achieved by adding seed crystals into the solution under conditions of low supersaturation or near-saturation. These seeds act as initial growth sites for crystal development, triggering the formation of secondary crystals. In continuous systems, seeding is performed only once at the start of operation (*start-up*), while in batch systems, seeding must be carried out at the beginning of each batch process.

### 3. Crystal Growth

In general, for crystals larger than 100 microns, the growth rate is independent of size and can be expressed as:



$$r = a(\Delta C)^b \quad (2.2)$$

Where:

$R$  = crystal growth rate (mm/hour)

$\Delta C$  = degree of saturation (mol/L)

$a, b$  = constants

The degree of saturation ( $\Delta C$ ) is the most important factor in crystal growth. In highly saturated solutions, the concentration difference between the crystal surface and the bulk solution is greater, which increases the crystal growth rate.

**Theory of Solute Diffusion from Solution to Crystal Surface**  
The crystallization process is essentially the reverse of the dissolution process. A crystal in solution forms a boundary layer at its surface. The solute concentration in this boundary layer is equal to its saturation concentration because it is always in a solid-liquid equilibrium state.

- If the solution is supersaturated ( $\Delta C^+$ ), solute molecules will diffuse from the solution to the crystal surface (arrow from left to right) and attach, forming part of the crystal structure.
- If the solution is unsaturated ( $\Delta C^-$ ), crystal molecules at the surface will dissolve into the solution (arrow from right to left).

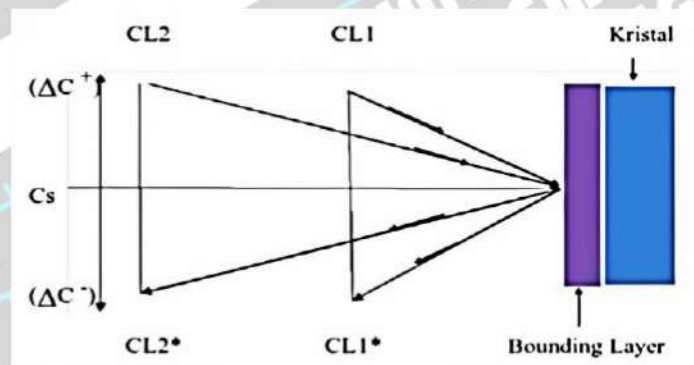


Figure 2.3 Diffusion of Solute from Solution to the Crystal Surface

Description:

$C_s$  = saturation concentration (fully saturated)

$(\Delta C^+)$  = supersaturation concentration (above saturation)

$(\Delta C^-)$  = undersaturation concentration (below saturation)

$CL1, CL1^*$  = indicate the influence of stirring in the solution, resulting in a shorter diffusion distance

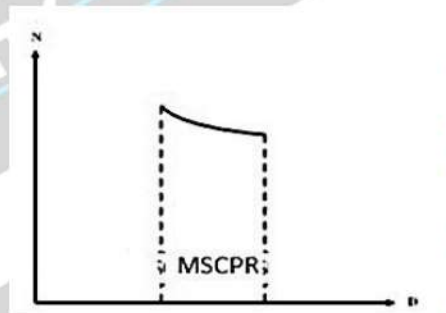
$CL2, CL2^*$  = indicate the absence of stirring in the solution, resulting in a longer diffusion distance



### 2.3 CSD Graph and Types of Crystallizers

The uniformity of product size from a crystallizer is expressed as CSD (Crystal Size Distribution) and is highly dependent on the type of crystallizer used. There are two types of crystallizers: MSCPR (Mixed Suspension Classified Product Removal) and MSMPR (Mixed Suspension Mixed Product Removal). The MSCPR crystallizer can produce products with relatively more uniform sizes compared to the MSMPR type because it has a classification mechanism.

#### 1. Uniform product size – MSCPR crystallizer

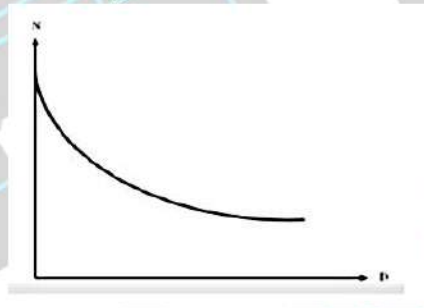


Description:

$N$  = number of crystals

$D$  = diameter

#### 2. Non-uniform product size – MSMPR crystallizer



Description:

$N$  = number of crystals

$D$  = diameter

Figure 2.4 CSD Graph

For the MSMPR type, the crystals obtained have non-uniform sizes, with diameters ranging from microscopic to large sizes.

Types of Crystallizers:

#### 1. Oslo Surface Cooled Crystallizer

This crystallizer uses a cooling system in which the feed ( $G$ ) is cooled in a cooler ( $H$ ) to create a supersaturated solution. The supersaturated solution is then brought into contact with the crystal suspension in the suspension chamber ( $E$ ). At the top of the suspension chamber, part of the mother liquor ( $D$ ) is removed to reduce the number of secondary crystal nuclei that form excessively. The slurry product is discharged from the bottom.



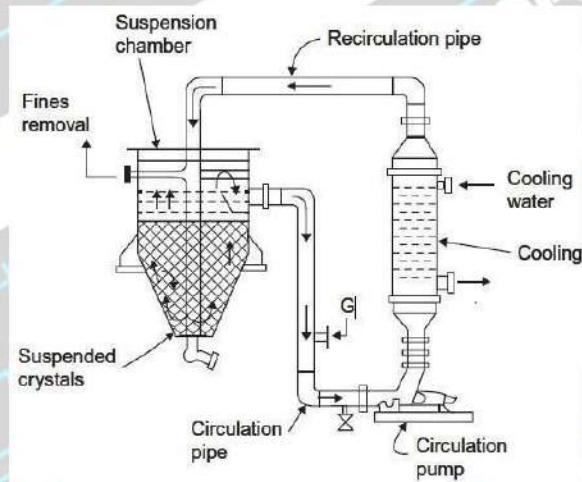


Figure 2.5 Oslo Surface Cooled Crystallizer

## 2. Oslo Evaporative Crystallizer

This type of crystallizer uses the solvent evaporation method to obtain a supersaturated solution. The solution leaving the evaporation chamber, in a supersaturated condition close to the metastable region, will not form primary nuclei. Contact between the supersaturated solution and the crystal bed in section E promotes crystal growth while also generating secondary nuclei. The feed solution is introduced through point G and is heated in the heat exchanger (HE) before entering the solvent evaporation chamber at point A. By creating a vacuum pressure in the evaporation chamber, part of the solvent evaporates, accompanied by a temperature drop, bringing the solution to the supersaturation level required for crystal growth. In this type of crystallizer, the liquid circulation system functions to reheat the solution while simultaneously redissolving part of the secondary nuclei. This prevents the product size from continuously decreasing over time.

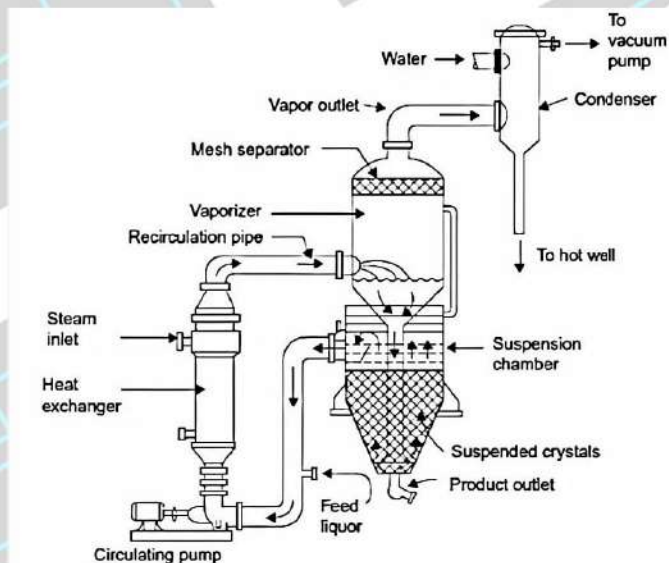


Figure 2.6 Oslo Evaporative Crystallizer



### 3. Draft Tube Baffle – DTB Crystallizer

This crystallizer is an MSCPR type because it is equipped with baffles and a propeller that function to regulate the circulation of the crystal magma, while outside the crystallizer body a pump is added for the circulation system and classification of product size. To achieve supersaturation conditions, a solvent evaporation system with vacuum pressure is used.

The lower part of this crystallizer is equipped with an elutriation leg which functions to classify crystals so that crystal products with a certain relatively uniform size are obtained. The classification of crystal size here is based on gravitational force as follows:

If heterogeneous-sized crystals have formed inside the crystallizer, these crystals are classified by flowing part of the solution from the bottom to the top in the elutriation leg chamber using a circulation pump. With this liquid flow, large-sized crystals will be able to resist the upward flow force so they can still sink down due to gravity and exit as product. Thus, a product with a homogeneous size is obtained. Therefore, to obtain crystals of a certain size, it can be adjusted by regulating the upward flow in the elutriation leg. If the liquid has a high velocity, large-sized crystals will be obtained, and vice versa. Small crystals that cannot resist the upward force will be carried back up to the crystallization chamber to be grown until they reach a certain size which, due to their own weight, can resist the upward force in the elutriation leg.

This crystallizer is also equipped with a liquid and crystal nuclei circulation system out of the crystallizer to reduce the number of crystal nuclei in the crystallizer. Excess crystal nuclei will dissolve again when passing through the HE due to heating. This reduction of crystal nuclei is intended so that the number of nuclei decreases because if left for too long, they will increase, resulting in finer crystal products. This is because crystal nuclei require solute for further growth, while the amount of solute entering in the feed remains constant, so the nuclei do not get enough solute to grow into larger crystals.



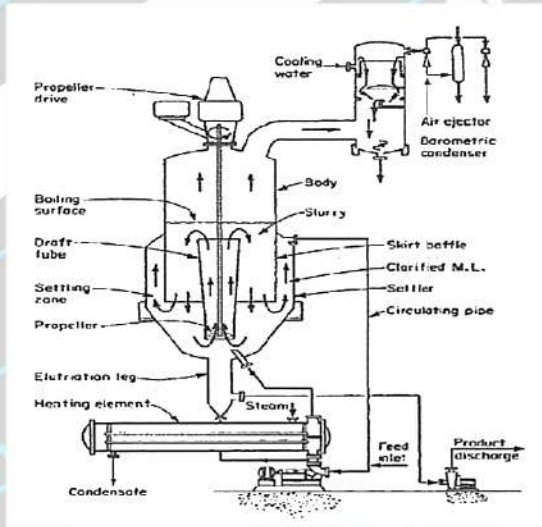


Figure 2.7 Draft Tube Baffle Crystallizer

## 2.4 Potassium Chloride Characteristics

### 1. Physical and Chemical Properties

Form	: Powder, solid
Color	: White
Odor	: Odorless
Melting point	: 773°C
Boiling point	: 1,413°C at 1.013 hPa
Density	: 3.13 g/cm <sup>3</sup> at approximately 20°C
Flammability	: Non-flammable
Solubility in water	: 347 g/l at 20°C

### 2. Hazard Identification

Not a hazardous substance or mixture according to Regulation (EC) No.1272/2008.

### 3. First Aid Measures

- If inhaled  
Breathe fresh air. If breathing stops, provide artificial respiration either mouth-to-mouth or mechanically. Provide an oxygen mask if possible. Seek medical attention immediately.
- In case of skin contact  
Rinse with plenty of water.
- After eye contact  
Rinse with plenty of water. Seek immediate medical attention from an eye specialist. Remove contact lenses.
- If swallowed



Give water to drink (a maximum of two glasses). Immediately seek medical advice. Only in special cases, if medical assistance is not available within one hour, induce vomiting (only if the victim is conscious).

(SmartLab, 2019)

## 2.5 Potassium Chloride Crystal Formation Process Using the Cooling Method

KCl crystals can be formed using the cooling method, which involves lowering the temperature so that the solute separates from its saturated solution in the form of crystals. The formation of KCl crystals occurs in two stages. The first stage is the formation of nuclei particles. The KCl solution is cooled to become a supersaturated solution at a temperature that crosses the solubility line or enters the metastable zone. In this condition, crystals will form spontaneously. The driving force for the nucleation and crystal growth process is supersaturation. In general, the nucleation rate and crystal growth rate increase with a higher degree of saturation. When the temperature is lowered further, the crystals will reach the metastable limit where the growth of KCl crystal size occurs. It can be concluded that process parameters such as cooling rate and agitation intensity will affect the saturation, nucleation, and growth rate of KCl crystals (Kardum et al., 2005).

## 2.6 Potassium Chloride Crystal Size Distribution

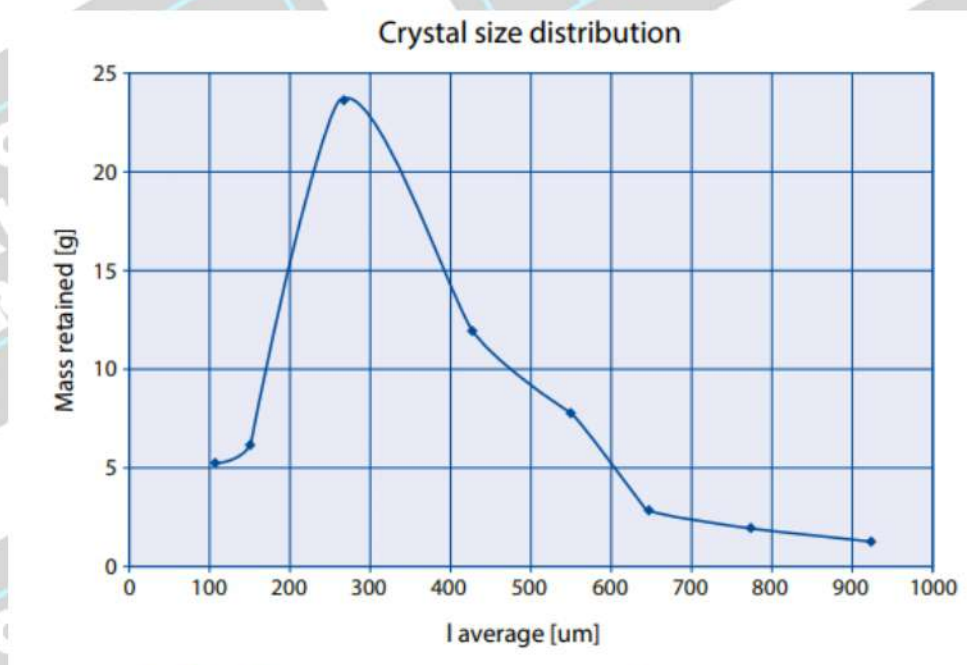


Figure 2.8 Potassium chloride crystal size distribution



The larger the diameter, the fewer crystals are produced.

$$\text{Number of crystals formed}(N) = \frac{\text{Weight of crystals formed}}{\frac{4}{3} \times \pi \times r^3 \times \rho} \quad (2.3)$$

Where:

$$r = \frac{D}{2} \quad (2.4)$$

Another equation to calculate the number of crystals produced:

$$dN = \frac{dM}{\alpha \rho C L^3} \quad (2.5)$$

From the three equations above, it can be seen that the value of  $dN/dD$  is inversely proportional to  $r$  ( $D/2D/2$ ). Therefore, the larger the average diameter, the fewer crystals are produced. A smaller diameter results in finer particle sizes. In addition, the crystal product formation process begins with the formation of small crystal nuclei, followed by the growth of the crystal structure into larger ones, so that more crystals are formed for smaller crystal sizes. The formation of secondary crystal nuclei is caused by collisions (contact) between parent crystals, between parent crystals and the impeller stirrer, collisions with the crystallizer wall, or friction between the parent crystal surface and the solution, resulting in a greater number of crystals for smaller sizes (Surya and Intifada, 2008). The movement of expanding grain boundaries causes the surface diameter of the grains to increase over the growth period. This condition leads to competition among grains to enlarge their surface diameter, which in turn sacrifices the growth of neighboring grains. This phenomenon is caused by the formation of precursor clusters before reaching the surface of the film or substrate (Saragih et al., 2004).



## **CHAPTER III METHODOLOGY**

### **3.1 Experimental Design**

#### **3.1.1 Practicum Framework**

The crystallization practicum begins with dissolving KCl with a solution volume according to the variables. Next, connect the crystallizer to a PC or laptop. Then install the ArmSoft software on the PC or laptop to control and monitor the operating conditions of the crystallization process in progress. This is followed by circulating hot water from the heater into the crystallizer vessel and setting the heating temperature according to the variables. The process continues with feeding the KCl solution into the crystallizer reactor for heating. After the heating process is complete, the KCl solution is cooled by adjusting the cooling temperature and flow rate according to the variables. The next step is to collect the solution and the crystals produced through the drain plug, then separate the solution from the crystals. Once the crystal product is obtained, it is dried using a vacuum pump.

#### **3.1.2 Variable Determination**

1. Constant Variables :
2. Independent Variables :
3. Dependent Variables :

### **3.2 Materials and Equipment Used**

#### **3.2.1 Materials**

1. Technical grade potassium chloride solid
2. Distilled water

#### **3.2.2 Equipment**

1. Crystallizer unit
2. Thermometer
3. Filter paper
4. Hot plate
5. Stirrer
6. 1000 ml beaker glass
7. Crystal container
8. Vacuum pump
9. Sieving tool



### 3.3 Equipment Setup Diagram

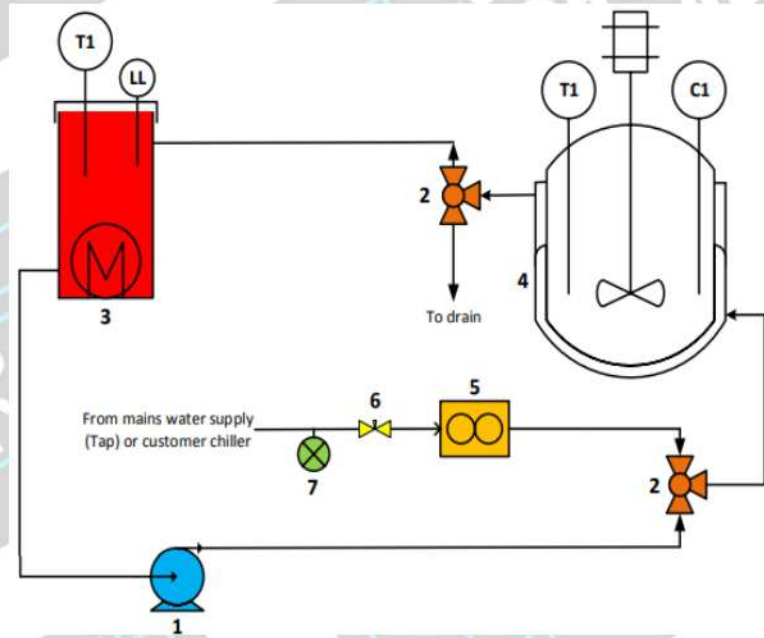


Figure 3.1 UOP14-MKII Crystallizer Setup

Description:

1. Hot water pump
2. Solenoid valves
3. Hot water vessel with heating element
4. Crystallisation vessel
5. Flowrate
6. Needle valve
7. Pressure regulator

### 3.4 Practicum Procedure

#### A. KCl Dissolution Stage

1. Prepare the tools and materials to be used.
2. Weigh the KCl solid according to the variables.
3. Add distilled water and KCl solid into a beaker glass according to the given concentration variables.
4. Set the heating temperature for dissolving KCl according to its solubility in water and maintain the heating temperature constant.
5. Ensure all crystal solids are dissolved, then pour the solution into the crystallizer reactor.

#### B. Setting Operating Conditions via ArmSoft

1. Connect the crystallizer unit to a PC/laptop by installing the ArmSoft application on the PC/laptop.



2. After installation, click ArmSoft and select *batch operation mode*.
3. Activate ArmSoft by installing the driver on the laptop/PC.
4. Ensure that ArmSoft runs properly on the PC/laptop and that the software is connected to the crystallizer unit.

#### C. Crystallization Process

In general, the crystallization process is carried out by performing heating and cooling through the following steps:

1. Pour distilled water into the heater until it passes the low liquid level sensor.
2. Click *heating mode* on the software, ensure the green light appears on the liquid level (LL) menu, and ensure the temperature data can be read on the software.
3. Click the *control* tab to set the PID Controller to *automatic* on the heater and ensure the temperature set point (T2) is 60°C.
4. When T2 approaches the temperature set point of 60°C, set the heating temperature (T1) according to the variable.
5. Pour the previously dissolved KCl solution into the crystallizer reactor.
6. Adjust the stirring power according to the variable.
7. When the set point of T1 is reached, stop the heating process and leave the solution in the crystallizer reactor for 10 minutes.
8. Start the cooling system by switching the operating condition to *cooling mode*.
9. Open the water valve to allow cooling water to flow.
10. Open and turn the pressure regulator to set the maximum cooling water flow rate, then adjust the flow rate using the needle valve according to the variable.
11. Set the temperature set point for the cooling process according to the variable and monitor the cooling temperature achieved at T1.
12. After the cooling temperature is reached, close the water valve and reduce the cooling water flow rate using the needle valve to 0 L/min.
13. Leave the solution in the crystallizer reactor for 15 minutes to stabilize the system while observing the initial formation of crystal nuclei.
14. Deactivate the *heating mode* via the control tab to stop heating.
15. After 15 minutes, open the drain plug to remove the solution and crystals from the crystallizer reactor.



16. Separate the solution from the obtained crystals and place the crystals in a dish for drying.
17. Dry the crystals using a vacuum pump.

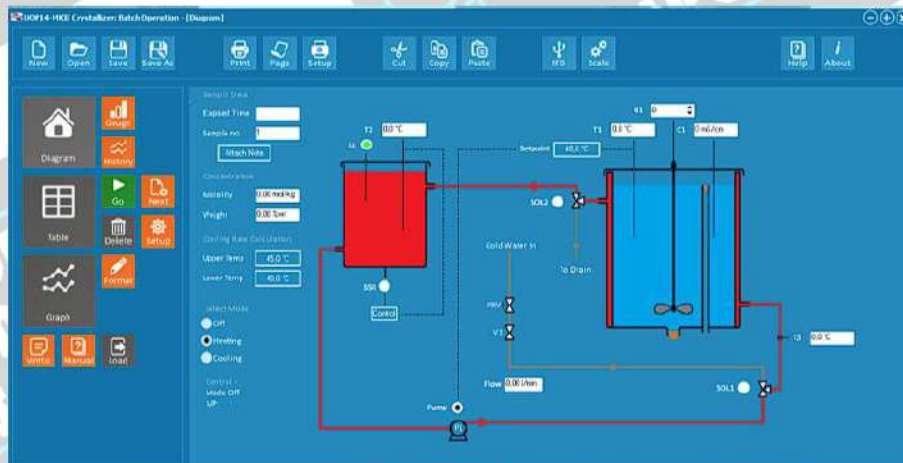


Figure 3.2 Heating mode on UOP14-MKII

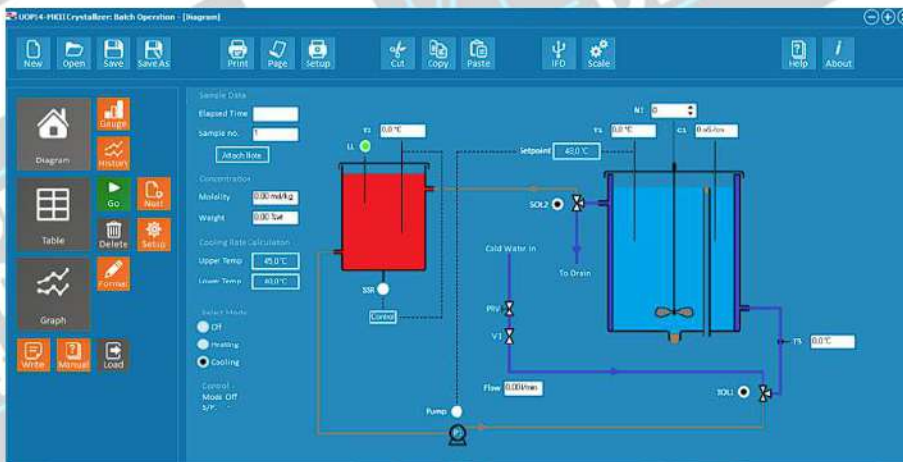


Figure 3.3 Cooling mode on UOP14-MKII

#### D. Determining Crystal Size Distribution

1. Air-dry the crystals for one day.
2. Weigh the results from each variable.
3. Perform sieving analysis by arranging the screens according to mesh size, place the weighed crystals on the arranged screens, and shake them at a constant particle mass.



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