Continuous Membrane-assisted Airlift Crystallization

Design, control and integration

Master Thesis

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Werin Mohangoo

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TU Delft Delft University of Technology

Challenge the future

Continuous Membrane-assisted Airlift Crystallization

Design, control and integration

By

Werin Mohangoo

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Supervisors:	Dr. ir. H.J.M. Kramer
	F. Anisi, MSc.
Thesis committee:	Prof.dr.ir. A.I. Stankiewicz
	Dr.ir. A.J.J. Straathof

TU Delft Delft University of Technology

Abstract

In previous research, batch experiments with an airlift crystallizer on ammonium sulphate, adipic acid and L-ascorbic acid have shown significant reduction of secondary nucleation compared to conventional stirred crystallizers. Furthermore, the crystal size distribution (CSD) achieved by the airlift crystallizer is almost 60% narrower than the CSD achieved by a conventional stirred tank. Optimal process conditions were found for cooling batch experiments on L-ascorbic acid.

One of the disadvantages of cooling crystallization is the tendency for scaling on the cooling surfaces. An alternative method to create the supersaturation in crystallization processes is the removal of the solvent from the solution, which is mostly achieved by evaporation, which is however an energy intensive method. Application of membrane separation, either by reverse osmosis or membrane distillation, to assist crystallization is a novel, sustainable, concept. In previous research, a study on Sweeping Gas Membrane Distillation (SGMD) has shown better control on the level and rate of supersaturation generation. Optimal process conditions were found for experiments on L-ascorbic acid.

To disentangle crystallization phenomena, such as primary and secondary nucleation, growth, dissolution, attrition and agglomeration, and to investigate these phenomena independently for further optimization and improvement of crystal properties, such as purity, shape of crystals, polymorphic form and CSD, a new experimental setup, called Membrane-assisted Crystallization (MaC), is designed, constructed and automated in this research. The experimental setup is designed and constructed in a modular way to perform experiments with standalone units, both in batch and continuous operation, as well as in combined modes in which the crystallizer is connected to a membrane unit. Therefore, it is possible to perform batch and continuous operated cooling and membrane-assisted crystallization experiments, in both the airlift crystallizer, as well as in stirred tank crystallizer. Process conditions, such as temperatures and flow rates, are automated in this research. The MaC setup consists of an airlift crystallizer, a stirred tank crystallizer, membrane module, feed vessel, buffer vessel, make-up vessel, and instruments for online monitoring and controlling.

For the online monitoring and control of the experimental setup, a Distributed Control Station (DCS) of Yokogawa Europe B.V. is connected to the MaC setup. The monitoring and control system with the Yokogawa system has been designed, tested and calibrated in this research. The use of the DCS system allows the monitoring and centralised storage of all the relevant process variables, and the implementation of all basic control loops of the different process configurations.

In addition, test experiments have been designed and performed with the different parts of the MaC setup, with water, melamine and L-ascorbic acid for troubleshooting and optimization.
Lastly, experiments with L-ascorbic acid were designed and performed to reproduce the results of previous batch experiments. With the optimal process conditions found in previous research, continuous experiments and membrane-assisted experiments have been designed and performed. The results of these experiments were analysed and compared to each other.

Batch experiments with an airlift crystallizer on L-ascorbic acid, showed similar results to the previous research. Effect of secondary nucleation is clearly minimized with an airlift crystallizer, compared to conventional stirred crystallizers. Continuous cooling crystallization experiments with L-ascorbic acid resulted in an absence of secondary nucleation, compared to cooling batch experiments. Continuous membrane-assisted crystallization experiments have shown a narrower CSD compared to the cooling batch and the continuous cooling operations. In conclusion, the new MaC setup is a promising new type of crystallizer with many possibilities to optimize the final crystal quality. Important crystallization phenomena such as nucleation and, generation and maintenance of supersaturation can be optimized and controlled with the Continuous Membrane-assisted Airlift Crystallizer.

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1 Introduction

1.1 Background information

In pharmaceutical industries, crystallization is a widely used process for the formation of crystals. These crystals (pharmaceutical ingredients) of small organic molecules form more than 90% of all active pharmaceutical ingredients (APIs) [1].

Crystallization is a separation process of forming solids from a liquid mixture. This is a very complicated separation process and difficult to control, because the quality of the final crystals is determined by a large number of properties, such as purity, shape of the crystals, polymorphic form and crystal size distribution (CSD). In addition, the product quality is the result of a number of kinetic phenomena that take place in an industrial crystalliser, such as primary and secondary nucleation, growth, dissolution, attrition and agglomeration, which have all a different dependency on process conditions. Numerous research studies have been conducted into the optimization of crystallization processes of traditional well-mixed crystallizers. However, it is difficult to optimize each physical phenomenon of a crystallization process, because of interdependency of the different physical phenomena [2]. Optimizing some process conditions on the one hand can lead to large batch-to-batch variations in industry, which increases the consumption of energy on the other hand [3]. As an alternative, an alternative crystallizer design has been proposed in which the different crystallization phenomena are separated in different process units [2]. This approach allows for the optimization of the different crystallization phenomena independently, yielding a higher product quality, a higher efficiency and improved flexibility to produce different product grades.

For a crystallization process a supersaturated solution is required. In industries, the supersaturation is generated mainly by either cooling a solution or increasing the concentration of the solute by removing the solvent [3]. The formation of new crystalline particles, also referred as nucleation, is divided into primary nucleation, formation of new particles in the absence of crystals, and secondary nucleation, formation of new particles in the presence of crystals [4]. An often used process to produce crystals is a seeded batch crystallization, in which seed crystals are added to a supersaturated solution and allowing them to grow until the desired size. The growth of the seed crystals is mainly determined by the residence time, proper mixing and the concentration profile of the supersaturated solution, if proper mixing can be achieved and nucleation can be avoided. Nucleation is often undesired, as nucleation broaden the CSD [5]. The ideal case for this process is when all the final crystals have the same physical properties (purity, size, shape). This can be achieved when there is no secondary nucleation, no attrition, good mixing and optimal process conditions [6]. Producing crystals with the same properties will reduce filtration time and equipment, with large energy saving in the overall process. Especially for pharmaceutical compounds, it is important to produce crystals with constant properties [7].

In seeded cooling batch crystallization processes, several phenomena such as nucleation, growth and agglomeration are involved [2, 8], which are interdependent. Growth is often the only desired phenomenon in a crystallization process. Growth is dependent on the level of supersaturation and the mixing intensity (mass transfer). As mentioned earlier, the different kinetic phenomena have all a different dependency on the process conditions. Therefore, isolating and optimizing growth, without influencing nucleation, is difficult in conventional cooling batch crystallizers. Due to a built-in flexibility for control of temperature, supersaturation, nucleation and crystal growth in continuous crystallizers, continuous operations are attractive to isolate crystal growth, compared to batch crystallizers (Mullin, 2001). In a continuous membrane-assisted process, the different crystallization phenomena can be disentangled in different process units, and can be optimized independently.

The results of research study conducted by Lakerveld et al. [5] [9], with a crystallizer design, the airlift crystallizer, at the Technical University of Delft (TU Delft) have shown that it is possible to suppress secondary nucleation at a higher supersaturation compared to a stirred crystallizer. There is no impeller present in the airlift crystallizer, which means that attrition and breakage of the crystals are minimized in the airlift crystallizer compared to conventional crystallizers (stirred). As such, instead of a stirrer, air bubbles are used in the airlift crystallizer to perform the mixing. A 10 L bubble column was designed and constructed to study the product quality of ammonium sulphate crystals. Experiments performed by J. van Royen [10] showed minimization of secondary nucleation, although, it was observed that air bubbles were entrained in the downcomer and lowered the circulation velocity. Independent of the seed properties and cooling curve, no ammonium sulphate crystals larger than a median size (X_{50}) of 260 µm were achieved. A gas disengagement zone was designed and constructed on the top of the 10 L airlift crystallizer in the work of Soare et al. [6]. The total volume of the airlift crystallizer became 18 L and experimental studies were performed on ammonium sulphate solution. In conclusion, entrainment of gas bubbles in the downcomer were minimized, which allows high circulation velocity and crystal size up to 600 µm were achieved. The suppression of secondary nucleation was experimentally demonstrated in the work of Soare et al. [6] by using the airlift crystallizer. Several experiments on L-ascorbic acid were performed in the research done by Lakerveld et al. [5] [9] by generating a supersaturated solution through cooling. The objective of this research was to compare final L-ascorbic acid crystals achieved by the airlift crystallizer versus a conventional stirred crystallizer. A cooling batch operation was used to perform these experiments. Experimental studies on L-ascorbic acid, performed by J. van Krochten [9], have shown improved CSD achieved by the airlift crystallizer. Optimal process conditions (temperature profile, airflow rate, seed load) were found in the aforementioned research. In conclusion, at an intermediate level of supersaturation, the airlift crystallizer shows significant reduced secondary nucleation compared to a conventional stirred crystallizer. The crystal size distribution (CSD) achieved by the airlift crystallizer is almost 60% narrower than the CSD achieved by a conventional stirred vessel tank. At a higher supersaturation (higher crystal growth rate), however, it is also possible to decrease the batch time, but then the secondary nucleation becomes considerable. The secondary nucleation problem may then be improved by process control, for example by integrating a novel technology e.g. membrane distillation.

The most used method to remove solvent to increase the concentration of the solute is evaporation. Drawbacks of evaporative crystallization are high energy consumption and a lack in flexibility for design and operation [11]. One of the novel technologies to generate supersaturation is using membrane distillation (MD). In a MD process, the solvent is removed from the solution due to the vapour pressure difference across a porous hydrophobic membrane. The concentration of the solute increases by removing the solvent from the solution. Compared to evaporative crystallization,

solvent removal by membrane separation is claimed to be more energy efficient and allows for more flexibility in the design. Therefore, numerous research studies have been conducted into the use of membrane modules for increasing the concentration of a solution. Experimental and theoretical study of a Membrane-assisted Crystallization using Reverse Osmosis, performed by Lakerveld [11], at TU Delft, has shown promising results in the feasibility of such an equipment, and in reduction of energy consumption. A shell and tube type RO membrane module (MIC-RO 240) was used in combination with a stirred vessel crystallizer to study the energy savings potential, compared to evaporative crystallizers. Two types of membrane modules were studied by S. Goddrie [12] at TU Delft, the MIC-RO 240 and the Membrana Liquicel Extraflow module. The category of membrane distillation that was studied here, is called Direct Contact Membrane Distillation (DCMD). Experiments with the aforementioned modules were performed to study the membrane flux of a L-ascorbic acid solution. In conclusion, while the MIC-RO 240 module was not able to remove the solvent from the L-ascorbic acid solution (due to high osmotic pressure of this compound), the Membrana Liquicel module has shown potentially promising results. It was advised to further investigate the Membrana Liquicel module by using sweeping gas due to temperature and concentration polarization in case of DCMD. Sweeping Gas Membrane Distillation (SGMD) was studied in previous research, conducted by K. Mathew Thomas [13] at TU Delft. The Membrana Liquicel module was integrated with a stirred vessel crystallizer to study the rate of supersaturation and quality of L-ascorbic acid crystals. Crystal size up to 1000 µm were achieved by experiments. The research conducted by K. Mathew Thomas has shown promising results for generation and maintenance of supersaturation by the use of the Liquicel membrane module. Optimal process conditions (flow rates, temperature) were achieved in this research. Changing the airflow rate or temperature, increases or decreases the membrane flux, which has direct influence on the level and rate of the generation of supersaturation. Therefore, membrane modules allow for more flexibility in the crystallization design, compared to evaporation crystallizers.

Combining the airlift crystallizer with a membrane module has therefore the potential to become a moderate system which has the ability to suppress secondary nucleation, to control over the generation of supersaturation and reduce energy consumption.

1.2 Aim of this thesis

While airlift crystallizer has the potential to suppress secondary nucleation, and membrane distillation (MD) improves the level and rate of supersaturation, the combination of these two units into one setup is a novel concept to increase the quality of the crystals and to reduce energy consumption. High flexibility of the process can be achieved and properties such as size and shape of the crystals, polymorphic form and CSD can be improved by changing circulation velocities in the crystallizer, and changing the airflow rate of the membrane module.

In this project, the integration of a membrane unit with the airlift crystallizer is designed, constructed and tested for an experimental setup (mini-pilot plant), entitled the “Membrane-assisted Crystallizer” (MaC). An alternative crystallizer, the airlift crystallizer, and a membrane unit have been designed and built together in a new experimental setup. The challenge comes at the time when connecting these units and optimizing the process conditions so as to allow for a flexible operation of the MaC unit. Before the new experimental setup can be used for experiments, the setup has to be made functional, automated and validated. For online monitoring and control, a Distributed Control Station (DCS) of Yokogawa Europe B.V. is connected to the MaC setup. Operation with the control unit is designed, integrated and calibrated in this research. Therefore, instruments connected to the MaC unit can be controlled from the computer, and experimental data can be recorded and saved for analysis.

A simplified flowsheet of the new MaC setup is shown in Figure 1.1. The membrane module removes the solvent from the solution in the buffer vessel to increase the concentration in the solution. The concentrated solution is transported to the airlift crystallizer, which is then supersaturated for the temperature of the airlift crystallizer.

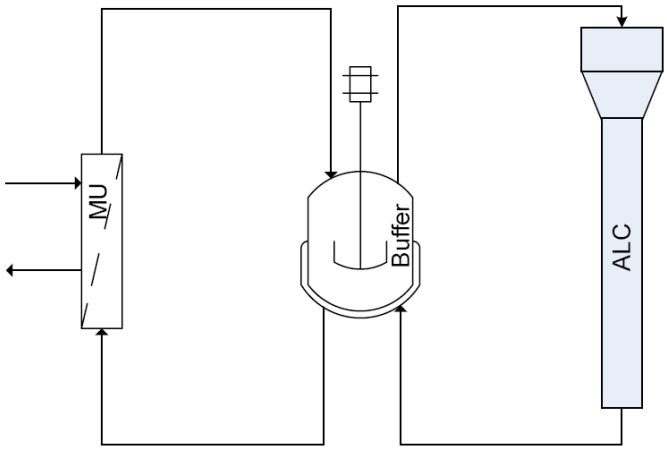


Figure 1.1: Simplified flowsheet of the integrated process

This project will focus on designing, controlling and integrating the membrane unit with the airlift crystallizer and on performing experiments to investigate the feasibility of the crystallization process in such a system. The objective of this project is to launch and validate the new setup, as well as to design and perform experiments with the combined system. Tasks of this thesis include:

- Completing the design phase of the new MaC setup;
- Designing the control system;
- Design of experiments;
- Performing experiments;
- Comparing experimental (batch) results with previous experiments;
- Performing continuous experiments to check the feasibility;
- Troubleshooting and optimization.

1.3 Report structure

The remainder of this document is as follows: Chapter 2 provides a brief introduction to the theory of crystallization processes related to the new MaC setup. This includes the theory of the airlift crystallizer, membrane unit and properties of the solution that are used for validating the setup (melamine and L-ascorbic acid) and performing experiments (L-ascorbic acid). Chapter 3 provides the design of the new experimental setup, the process flowsheet, process description and a description of all equipment used in the new setup. The design and validation of the control system used in the new setup are described in Chapter 4. After the new setup is constructed at an external location and moved to the new laboratory of the Process & Energy department, test operations were performed with water, melamine and L-ascorbic acid to locate and solve errors. The procedure and results of these test experiments are described in Chapter 5. After testing the functionality of the new setup, experiments with L-ascorbic acid were designed and performed. The design of experiments is described in Chapter 6. The results of these experiments are described in Chapter 7. Chapter 8 provides the overall conclusions and recommendations of this project.

2 Theory

This chapter describes the important phenomena in crystallization techniques, theory of the airlift crystallizer, theory of the membrane unit and properties of the experimental compounds: melamine and L-ascorbic acid.

2.1 Crystallization

One of the oldest separation techniques in chemical industries are crystallization processes. The advantage of crystallization is producing high purity product in one processing step at relatively mild process conditions [4]. Especially in pharmaceutical industries, crystals of small organic molecules form more than 90% of all active pharmaceutical ingredients (APIs) [1]. Where the global pharmaceutical industries reported revenue of US$ 390.2 billion in 2001, in 2013 the revenue increased to almost US$ 1.0 trillion [static.com, revenue of worldwide pharmaceutical market]. Figure 2.1 clearly indicates the ever-increasing economic value and societal benefits of crystallization processes in pharmaceutical industries on a global level.

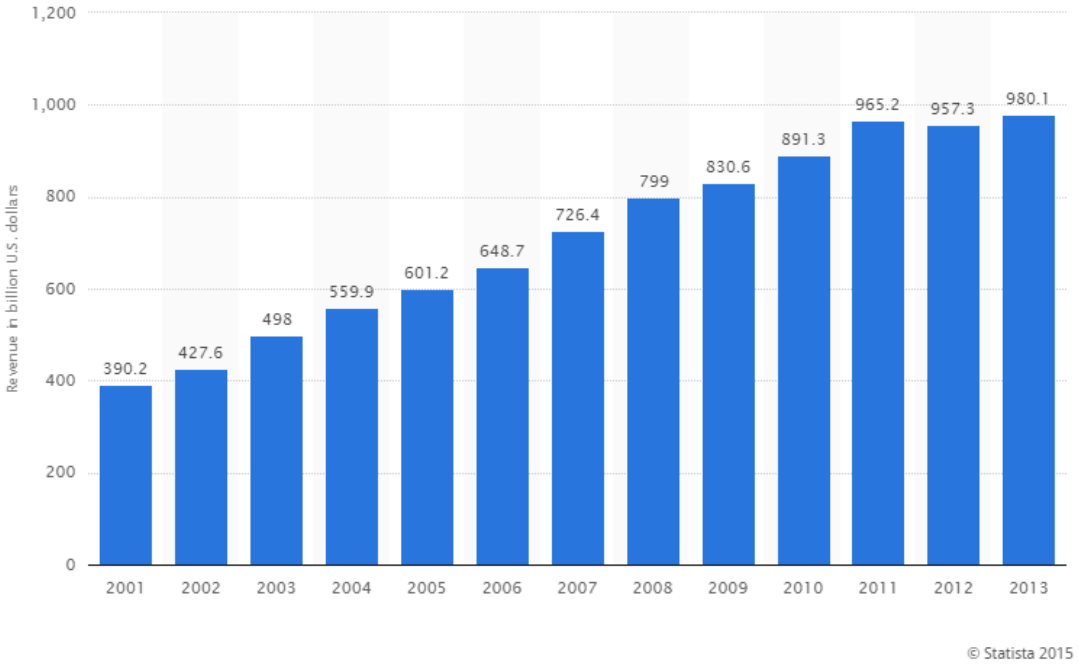


Figure 2.1: Revenue of worldwide pharmaceutical market from 2001 to 2013

Other business sectors in where crystallization is the core technology are: agrochemicals, catalyst, dyes, electronics, food, health products, nano-materials, nuclear fuel and personal products [14].

As a unit separation, crystallization is a separation process in which mass is transferred from a liquid solution to a pure solid crystal [15]. This technique is used to purify solid compounds. Crystals appear in various sizes, shapes and forms which affect both the performance during processing and the quality in application. Many fundamental steps such as nucleation, crystal growth, mixing, heat exchange and generation of supersaturation, occur simultaneously and are related to each other. This poses many difficulties to the design and operation of crystallization processes. In Figure 2.2, adapted from the work of Agba et al. [16], the relation between common crystallization parameters, transformations and attributes are shown.

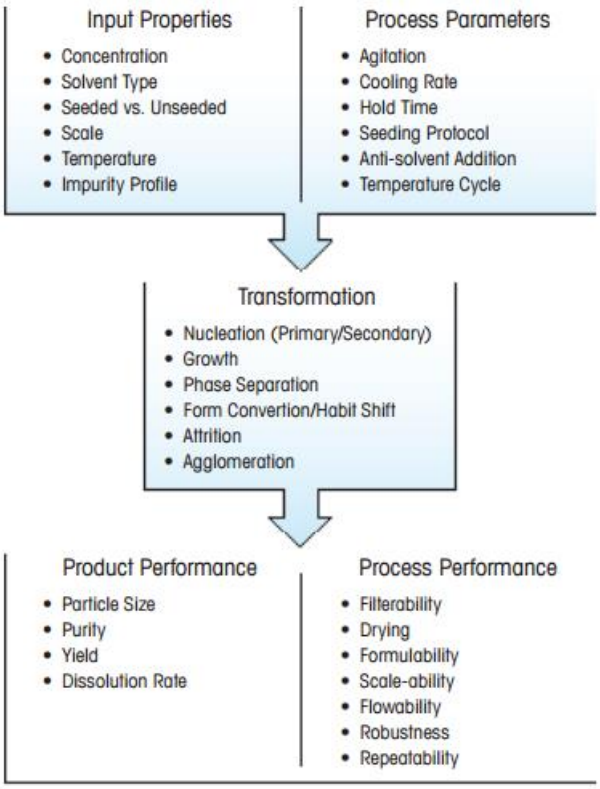


Figure 2.2: Relation between common crystallization parameters, transformations and attributes [16]

2.1.1 Solubility and supersaturation

The equilibrium concentration of the solute in the solvent at given process conditions (pressure, temperature) is called the solubility. A general solubility diagram is shown in Figure 2.3.

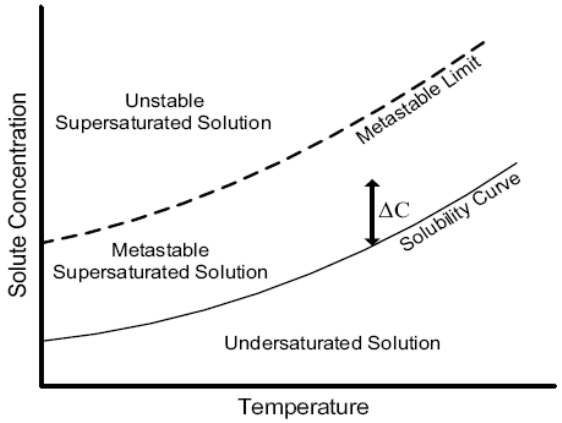


Figure 2.3: Solubility diagram (general) [4]

In Figure 2.3 it can be seen that, if the solution operates in the region below the solubility curve, the solution is undersaturated. Adding more solute to the solution will be dissolved (unless the solubility curve is reached) and a crystallization process is not feasible.
Beyond the solubility curve and below the metastable limit, the solution is in the metastable zone and is supersaturated. The metastable zone width (MSWZ) is defined as the temperature difference between the saturation temperature and the temperature at which spontaneously crystals are formed when a constant cooling rate is applied. This region accommodates the growth of crystals in the absence of nucleation of the solution.
If the concentration of the solute in the solution increases beyond the metastable limit, the supersaturated solution becomes unstable and the solution nucleates spontaneously.

The driving force for crystallization is concentration excess (supersaturation) of the solution (liquid mixture) above the saturation level. The degree of supersaturation can be approximated by the difference between the solute concentration and the solubility of the compound. The degree of supersaturation is calculated by the difference in chemical potential of the solute in the liquid and in the solid phase at temperature T [8]:

$$\Delta\mu = \mu_L(T) - \mu_S(T) \qquad (2\text{-}1)$$

For practical reasons, the supersaturation in cooling crystallization can be translated via the solubility curve into a concentration difference [8]:

$$\Delta C = C - C^* \qquad (2\text{-}2)$$

Where
C is the actual solute concentration
C^* is the solubility concentration at a given temperature.

There are mainly four ways to generate supersaturation [3]:

1. Cooling of the solution, where supersaturation is generated by a reduction in the solubility at lower temperatures;
2. Evaporation of solvent. Solvent evaporation increases the concentration of the solute in the solution and becomes supersaturated;

3. By a chemical reaction. For example, reactive crystallization or precipitation, in which a very large supersaturation is created by adding two streams containing separate reactants that form a product with a very low solubility;
4. Addition of an anti-solvent composition. In this process an additional component is added which influences the solubility.

As mentioned earlier, nucleation is required to produce the crystalline phase, while growth is needed to produce crystals of the desired size. Nucleation can be divided into primary and secondary nucleation. Primary nucleation is a strong non-linear function of the supersaturation, while secondary nucleation is a strong function of the turbulence (for example, collisions of the larger crystals with the hardware of the crystallizer), and only a weak function of the supersaturation. Growth is dependent on the concentration profile of the supersaturated solution and the mixing intensity (mass transfer). Among the different phenomena in batch crystallization, crystal growth is often the only desirable one, whereas nucleation (primary and secondary) and agglomeration are influencing both the process and product control [2]. For example, in seeded batch crystallization process, the rate of supersaturation has direct influence on secondary nucleation [5]. Damaged and broken crystals by attrition and collision grow with a different rate, depending on the concentration profile of the supersaturation. This results in a broad CSD of the final product. Therefore, a balance between the generation of supersaturation and consumption of this supersaturation by the desired crystals is important.

The important issues in this research are suppression of secondary nucleation and dominance of growth (control with airlift crystallizer) and, generation and maintenance of supersaturation (membrane module). Experiments performed by J. van Krochten (on airlift crystallizer) [9] and K. Mathew Thomas (on membrane module) [13] have individually shown promising results.

In this research experiments are performed on cooling crystallization (batch and continuous mode) and an alternative method for creating a difference in chemical potential (membrane technology) to study the control of the process. Secondary nucleation is undesired, and the aim is to study the relation between process control and width of the CSD.

2.1.2 Nucleation

As mentioned earlier, the formation of new crystalline particles is called nucleation and is divided into primary nucleation, in the absence of crystals, and secondary nucleation, in the presence of crystals. Primary nucleation is the formation of spontaneous new crystals from a clear liquid or solution [7]. Primary nucleation can be subdivided into homogenous and heterogeneous nucleation [7], where in heterogeneous nucleation the nuclei are formed on the surface of heterogeneous particles or surfaces, while homogeneous nucleation are formed in the clear solution. As mentioned earlier, primary nucleation is highly non-linear with respect to supersaturation. This means that slightly larger supersaturations lead to large increases in the nucleation rate.

Secondary nucleation is the formation of new crystals due to external forces acting upon (existing) parent crystals in the supersaturated solution. In seeded batch cooling stirred crystallizers, secondary nucleation often occurs by collisions of crystals to each other and collisions of crystals with the hardware of the crystallizer (vessel wall, impellers) [6].

2.1.3 Seeding

One of the operations to produce final product (crystals) in batch operated crystallization processes is to add seed crystals to the supersaturated solution and allowing them to grow until the desired

size. Seed crystals are smaller crystals with the same shape as final product, which are achieved by sieving. Sieving is a critical step in seeded crystallization processes. By sieving, a certain optimal crystal size is selected for the seed crystals which is added to a supersaturated solution in the crystallizer and is expected to grow. At the end of an experiment, grown crystals are compared with seed crystals for analysis. In this way, sieved crystals can be distinguished from other crystals that might have been formed from any nuclei. Seed growth is mainly based on the residence time, proper mixing and the concentration profile of the supersaturated solution during the batch. In batch operated industrial processes, seeding has become one of the most critical steps in optimizing crystallization behaviour, process efficiency, and product quality [8]. The seed load, time of applying the seeds into the process, and their sizes are important variables on the way to optimize crystallization processes. For example, a low seed load will grow to larger crystals with a broader CSD, compared to a higher seed load with the same amount of supersaturation, as discussed in the work of Soare et al. [6].

2.1.4 Crystal growth

The growth rate determines the shape of the crystal [8] and, together with the growth mechanism, also the crystal surface structure. Rapid growth has a negative effect on the crystal structure. Crystals will only grow if the solution is supersaturated. Crystals in an undersaturated solution dissolve. Crystal growth mechanism can roughly divided into two steps [8]: diffusion of growth units towards the crystal-solution surface and, integration of these growth units into the crystal surface.

2.1.5 Agglomeration and breakage

Agglomeration is attachment of crystals to each other. This can be caused by the transportation and collision of particles, and the attachment of these particles followed by either cementation or disruption [8]. This is a kinetic process that depends on collisions [8]. Solution is incorporated between crystals during agglomeration, resulting in larger crystal sizes, which are less pure and have unequal shape. The agglomeration could take place during the filtration at the end of the experiment, during the measurement, or during the experiment itself [6]. In a stirred tank crystallizer, breakage of crystals may occur due to attrition between the impeller and the crystals. Breakage of crystal is also possible due to attrition between crystals. Both, agglomeration and breakage, affect the CSD of the final product. Therefore, to optimize final crystal quality, agglomeration and breakage of crystals are unwanted phenomena in industrial crystallizers.

2.1.6 Mixing

Sufficient mixing is an important aspect in crystallization processes to keep the crystals in suspension, stimulate growth, and to prevent local temperature differences. The instrument (impeller, pump, etc.) that is designed and constructed for a crystallizer is therefore important, as shear forces acting on crystal surface can activate secondary nucleation.

In an airlift crystallizer, gas bubbles are added into the riser of the crystallizer, to perform mixing. Due to the gas bubbles, the density of the suspension in the riser is lower than the density in the downcomer (assuming no entrainment of gas bubbles in the downcomer). The difference in density between the riser and the downcomer results in a circulation of the liquid.

2.1.7 Crystallization balances

By employing the total mass and component balance over the crystallizer, the total amount of produced crystals can be estimated for a certain crystallizer. Enthalpy of the feed, product and vapour (in evaporative crystallizer) is needed to calculate the production rate in crystallization

processes. Information on the CSD, and thereby the quality of final product, is calculated with the population balances.

This research is a continuation of previous experimental work done by J. van Krochten [9] on the airlift crystallizer and K Mathew Thomas [13] on Sweeping Gas Membrane Distillation. Optimal process conditions are achieved by J. van Krochten [9] and K. Mathew Thomas [13] which are now used to design and perform experiments with the integrated process. No modelling is involved in this research, and therefore, detailed information on crystallization balances and equations for modelling can be found in [8].

The total mass balance of the airlift crystallizer in combination with a membrane unit is:

$$\frac{dM_{total}}{dt} = \emptyset_{V,feed} \cdot \left(\varepsilon_{feed} \cdot \rho_{feed,liquid} + \left(1 - \varepsilon_{feed}\right) \cdot \rho_{crystal}\right) - \emptyset_{V,prod.} \cdot \left(\varepsilon \cdot \rho_{liquid} + (1 - \varepsilon) \cdot \rho_{crystal}\right) - \emptyset_{V,vap;MU} \cdot \rho_{vap;MU} \quad (2\text{-}3)$$

Where:
φ is the volume flow [m^3/h]
ε is the liquid fraction of the slurry [-]
ρ is the density [kg/m^3]
feed is the feed to the crystallizer, *prod.* is the product from the crystallizer, and *vap;MU* is the amount of water removed by the membrane module.

The component balance for each component is given by the following equation:

$$\frac{dM_i}{dt} = \emptyset_{V,feed} \cdot \left(\varepsilon_{feed} \cdot \rho_{feed,liquid} \cdot \omega_{feed,liquid,i} + \left(1 - \varepsilon_{feed}\right) \cdot \rho_{crystal} \cdot \omega_{feed,crystal,i}\right) - \emptyset_{V,prod.} \cdot \left(\varepsilon \cdot \rho_{liquid} \cdot \omega_{liquid,i} + (1 - \varepsilon) \cdot \rho_{crystal} \cdot \omega_{crystal,i}\right) \quad (2\text{-}4)$$

With
i = 1 (main component that has to be crystallized)
N_{comp} (impurities in the suspension)
ω is the concentration of the solute [-]

The mass of a component is calculated by the volume, density and liquid fraction:

$$M_i = V\left(\varepsilon \cdot \rho_{liquid} \cdot \omega_{liquid,i} + (1 - \varepsilon) \cdot \rho_{crystal}\omega_{crystal,i}\right) \quad (2\text{-}5)$$

According to the work of Kramer et al. [8] it is more convenient to combine the solvent mass balance together with the component balance, which results in:

$$\frac{dV\varepsilon\rho_{liquid}\omega_{liquid,sovent}}{dt} = \emptyset_{V,feed}\left(\varepsilon_{feed} \cdot \rho_{feed,liquid} \cdot \omega_{feed,solvent}\right) - \emptyset_{V,prod}\left(\varepsilon \cdot \rho_{liquid} \cdot \omega_{liquid,solvent}\right) - \emptyset_{V,vap;MU} \cdot \rho_{vap,MU} \quad (2\text{-}6)$$

The sum of the mass fractions in solid and liquid phase must equal one:

$$\omega_{liquid,solvent} + \sum_i \omega_{liquid,i} = 1 \quad (2\text{-}7)$$

$$\sum_i \omega_{crystal,i} = 1 \quad (2\text{-}8)$$

Furthermore, the enthalpy balance with the production rate P can be calculated with [8]:

$$\frac{dH}{dt} = \emptyset_{H,feed} - \emptyset_{H,prod} - \emptyset_{H,vap,MU} + Q_{heat} + P \cdot \Delta H_{cryst.} \quad (2\text{-}9)$$

Feed, product and vapour (membrane unit) enthalpies can be calculated with:

$$\emptyset_{H,feed} = \emptyset_{V,feed}\left(\varepsilon_{feed} \cdot \rho_{feed,liquid} \cdot C_{p,liquid} + \left(1 - \varepsilon_{feed}\right) \cdot \rho_{crystal} C_{p,crystal}\right) \cdot T_{feed} \quad (2\text{-}10)$$

$$\emptyset_{H,prod} = \emptyset_{V,prod}\left(\varepsilon \cdot \rho_{liquid} \cdot C_{p,liquid} + (1 - \varepsilon) \cdot \rho_{crystal} C_{p,crystal}\right) \cdot T \quad (2\text{-}11)$$

$$\emptyset_{H,vap,MU} = \emptyset_{V,vap,MU}\left(\rho_{vap,MU} \cdot C_{p,vap,MU} \cdot T + \rho_{vap,MU} \cdot \Delta H_{evap;MU}\right) \quad (2\text{-}12)$$

For a chosen volume fraction, the production rate can be calculated with:

$$P = \emptyset_{V,prod} \cdot (1 - \varepsilon) \cdot \rho_{crystal} = \emptyset_{V,prod} \cdot M_T \quad (2\text{-}13)$$

The residence time that is needed to grow sufficient large crystals is calculated with:

$$\tau = \frac{L_{mean}}{4G_{mean}} \quad (2\text{-}14)$$

Where:
L_{mean} is the size of the crystal which must be chosen dependant on its solubility diagram and growth rate G_{mean}. This value can be estimated from a correlation given in the work of Mersmann et al. [17] and Kind et al. [18], or must be determined by laboratory experiments.

The product flow rate can now be calculated with:

$$\emptyset_{V,prod} = \frac{V}{\tau} \quad (2\text{-}15)$$

Where V is the suspension volume in the crystallizer [m^3].

2.2 Airlift crystallizer

The airlift crystallizer is a bubble column with a gas disengagement zone on the top [6]. On the bottom of the crystallizer a sparger is mounted for the entrance of gas to the riser. Instead of a stirrer, gas is used for the circulation and mixing of the suspension inside the crystallizer. Entrance of gas in the riser will decrease the density of the suspension in the riser, while the density of the suspension in the downcomer is higher (assuming no gas entrainment in the downcomer). The riser is the inner tube of the crystallizer in which gas is added via a sparger. The downcomer is the space between the riser and the outer tube of the crystallizer. The design of the airlift crystallizer started with the research of Lakerveld et al. [19] in 2008, and was further optimized in the research of Soare et al. [6] in 2012, and Lakerveld et al [5] in 2014. For the existing airlift crystallizer, optimal process conditions are achieved by experimental research performed by J. van Krochten [9] in 2014. Some of these optimal process conditions are, metastable zone width of L-ascorbic acid, seeding and final temperature in batch operation, seed load and optimal flow rate of gas.

2.2.1 Gas hold-up

As mentioned earlier, mixing is an important phenomenon in crystallization processes. A uniform temperature across the crystallizer and type of mixer influences the final product quality. In the airlift crystallizer, the mixing is performed by the difference in the gas hold up between the riser and the downcomer. The driving force of circulation is the density difference between the riser and the downcomer. As mentioned earlier, the gas injected into the riser will lower the total density in the riser, while the density in the downcomer is higher, which results in a circulation. In bubble columns [6], three flow regimes can be recognised, see Figure 2.4.

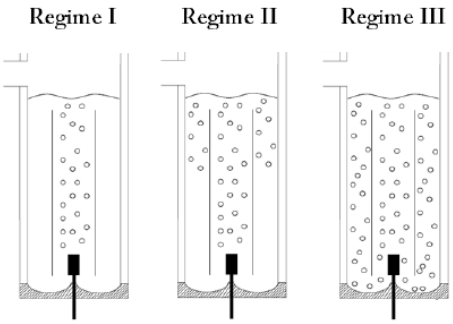


Figure 2.4: Bubble regimes in bubble columns [10]

In regime I, all the air injected into the riser escapes from the top, which is the ideal situation for circulation. In regime II, a small amount of air is entrained in the downcomer, and in regime III there is entrainment of gas bubbles in the downcomer. Implementation of a gas disengagement zone at the top of the bubble column, have shown improved circulation and operation in region I and II [6].

The airlift crystallizer has three pressure transmitters connected, one measures the pressure difference between the top and bottom in the riser, the second one measures the pressure difference between the top and bottom in the downcomer, and the third one measures the pressure difference between the riser and the ambient pressure. In the previous design, the pressure transmitter connected to the riser was placed at the top part, and the transmitter connected to the downcomer was placed at the lower part of the crystallizer, see Figure 2.5.

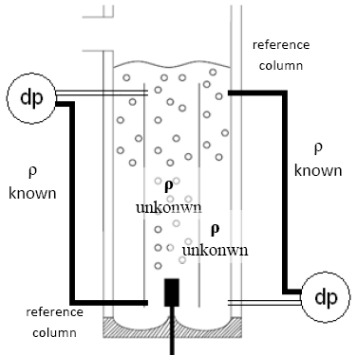


Figure 2.5: Riser and downcomer measurement system [10]

The pressure difference between the top and bottom in the riser and downcomer (gas holdup) is expressed by:

$$\Delta p = p_{ref} - p \tag{2-16}$$

$$p_{ref} = \rho_{ref}(T_{ref}, c_{ref}) \cdot g \cdot h_{ref} \tag{2-17}$$

$$p = \rho(T, C) \cdot g \cdot h \quad (2\text{-}18)$$

Where:
$\rho_{ref}(T_{ref}, c_{ref})$ is the density of the mother liquid in the reference column [kg/m^3]
$\rho(T, c)$ is the density of the contents in the riser/downcomer [kg/m^3]
h is the height of the reference column [m]

Combining the above-mentioned equations gives an expression for the average density in the riser/downcomer:

$$\rho = \frac{p_{ref} - \Delta p}{g \cdot h} \quad (2\text{-}19)$$

The average density can also be calculated with the densities and volume fractions of liquid, gas and solids:

$$\rho = \rho_L \cdot \varepsilon_L + \rho_S \cdot \alpha_S + \rho_G \cdot \alpha_G \quad (2\text{-}20)$$

$$\varepsilon_L = 1 - \alpha_S - \alpha_G \quad (2\text{-}21)$$

The gas holdup can be calculated with:

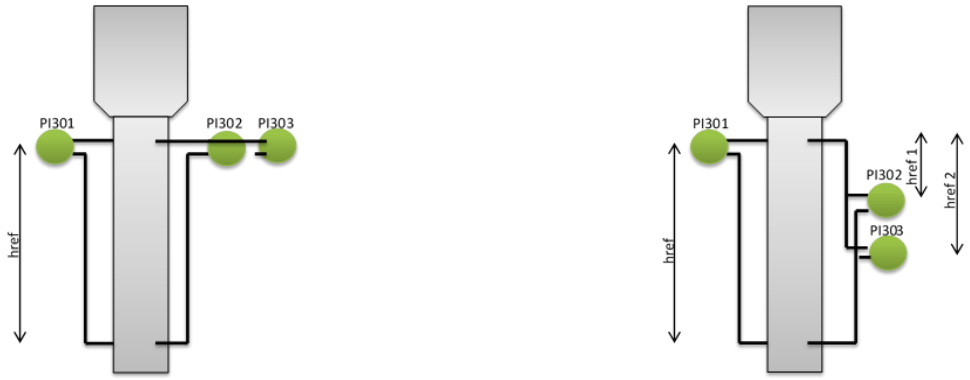
$$\alpha_G = \frac{\rho - \rho_L}{\rho_G - \rho_L} + \alpha_S \cdot \frac{\rho_L - \rho_S}{\rho_G - \rho_L} \quad (2\text{-}22)$$

For a 2-phase system (liquid-solid) the solid holdup in the downcomer can be calculated with a simplified equation:

$$\alpha_D = \frac{\rho - \rho_L}{\rho_S - \rho_L} = \frac{dp - \rho_L \cdot g \cdot h_{ref}}{g \cdot h_{ref} \cdot (\rho_S - \rho_L)} \quad (2\text{-}23)$$

The above-mentioned equations are applied in the control system to measure the solid holdup in the downcomer during experiments. The downcomer is assumed to be gas free, due to the gas disengagement zone at the top of the crystallizer. The solid holdup can be calculated by measuring the pressure difference (equation (2-23)). Due to sufficient mixing in an airlift crystallizer, the solid holdup in the riser is assumed to be similar to the solid holdup in the downcomer. The gas holdup in the riser can then be calculated with equation (2-22).

The pressure transmitters shown in Figure 2.6 are connected with two tubes, one horizontal to the crystallizer, which is measuring the pressure according to the level in the crystallizer. The other tube is connected to the reference column, which measures the pressure in this column and in the crystallizer. The difference in pressures of these two tubes is the value shown on the monitor of the transmitter. In the current situation (new MaC setup), the pressure transmitters connected to the riser are replaced from their previous position, which changes the height of the reference column. Therefore, the gas holdup is re-evaluated to verify the above-mentioned equations for the gas holdup. The new locations of the pressure transmitters are shown in Figure 2.6.



(a) (b)

Figure 2.6: Location of the pressure transmitters: (a) previous setup, (b) current setup

The pressure transmitters that are changed from their position are PI302 (connected to the riser) and PI303, measuring the pressure difference between the riser and the ambience. PI303 is only connected to measure the level in the airlift crystallizer. Therefore, only PI302 is validated.

In the following calculations, p1 is the gauge pressure measured at the top, and p2 the gauge pressure measured at the bottom of the crystallizer. For the **previous** setup, the pressure difference in the riser is expressed by:

$$p1 = \rho_{slurry} \cdot g \cdot h \tag{2-24}$$

$$p2 = \rho_{slurry} \cdot g \cdot h + \rho_{slurry} \cdot g \cdot h_{ref} - \rho_{liq.} \cdot g \cdot h_{ref} \tag{2-25}$$

$$p1 - p2 = g \cdot h_{ref} \cdot (\rho_{liq.} - \rho_{slurry}) \tag{2-26}$$

Where h is the height difference between the level in the crystallizer and the level of the pressure transmitter, ρ_{slurry} is the average density and $\rho_{liq.}$ is the density of the solution in the reference column.

For the **current** situation, the differential pressure is expressed by:

$$p1 = \rho_{slurry} \cdot g \cdot h + \rho_{liq.} \cdot g \cdot h_{ref1} \tag{2-27}$$

$$p2 = \rho_{slurry} \cdot g \cdot h + \rho_{slurry} \cdot g \cdot h_{ref} - \rho_{liq.} \cdot g \cdot (h_{ref} - h_{ref1}) \tag{2-28}$$

$$p1 - p2 = g \cdot h \cdot (\rho_{liq.} - \rho_{slurry}) \tag{2-29}$$

The differential pressure of the current configuration is the same as the previous configuration, therefore the equations for the gas holdup are valid.

2.2.2 Liquid circulation velocity

With the equations of the gas holdup, the liquid circulation velocity can be calculated. With the liquid circulation velocity the following three processes in the airlift crystallizer can be estimated:

- Solid entrainment: the liquid circulation velocity should be greater than the settling velocity of crystals;
- Bubble regime: as mentioned before, three bubble regimes are available, see Figure 2.4;

- Liquid mixing: 95% homogeneity is achieved within seven circulations [20].

A simple force balance holds up for an airlift system, where gravity force is equal to friction force:

$$\Delta p_g = \Delta p_f \tag{2-30}$$

The driving force of motion is calculated with:

$$\Delta p_g = \rho_D \cdot g \cdot H_e - \rho_r \cdot g \cdot H_e \tag{2-31}$$

Where H_e is the effective height.

Combination of equation (2-20) and (2-22) with (2-31) gives:

$$\frac{\Delta \rho_g}{g \cdot H_e} = \rho_D - \rho_R = (\alpha_{GR} - \alpha_{GD}) \cdot \rho_L - (\alpha_{SR} - \alpha_{SD}) \cdot (\rho_S - \rho_L) \tag{2-32}$$

The frictional force is calculated with:

$$\Delta p_f = \frac{1}{2} \cdot K_f \cdot \rho_L \cdot v_L^2 \tag{2-33}$$

Where K_f is a friction coefficient, depending on the circulation velocity v_L.

The combination of equation (2-32) and (2-33) gives the simplest form of the liquid circulation velocity:

$$v_L^2 = \frac{2g \cdot H_e}{K_f} \left[(\varepsilon_{GR} - \varepsilon_{GD}) - (\varepsilon_{SR} - \varepsilon_{SD}) \left(\frac{\rho_s}{\rho_L} - 1 \right) \right] \tag{2-34}$$

Assuming maximum solids are entrained in the downcomer, the difference in solids-holdup between riser and downcomer is calculated with [20]:

$$\varepsilon_{SR} - \varepsilon_{SD} = 2\varepsilon_S \cdot \frac{v_{sp}}{v_L} \tag{2-35}$$

Where v_{sp} is the particle swarm velocity.

2.2.3 Calculation of friction number K_f

The friction coefficient in equation (2-34) is calculated by each individual contribution to the friction coefficient. The important contributors are:

- Flow reversal at bottom and top of the airlift crystallizer;

$$K_{f,bottom+top} = 2.5 \cdot \left(\frac{1}{m} + \xi \frac{m}{(1-m)^2} \right) \tag{2-36}$$

$$m = \frac{A_R}{A} \tag{2-37}$$

Where:
m is the draught tube cross-sectional area fraction [-]

A_R is the cross-sectional area of the riser [m^2]
A is the total cross-sectional area [m^2]

- Friction of the wall. For the riser and the downcomer, this can be calculated with:

$$K_{f,Riser+Downcomer} = \sqrt{2}\frac{H_e}{D}\frac{f}{m^2} + \frac{\sqrt{2}}{\sqrt{2}-1}\frac{H_e}{D}\frac{f}{(1-m)^2} \quad (2\text{-}38)$$

Where D is the column diameter [m]

- Restrictions of the flow.

Flow restriction caused by e.g. sparger, glass window, can be calculated with:

$$K_f = 2.5\left(\frac{1}{m} + \xi\frac{m}{(1-m)^2}\right) + 1.6\left(\frac{0.007}{m^2} + \frac{0.017}{(1-m)^2}\right)\frac{H_e}{D} \quad (2\text{-}39)$$

These expressions depends only on geometry and not on the scale.

2.2.4 Particle swarm velocity

The particle swarm velocity in the riser, for a three-phase system, can be calculated with:

$$v'_{sp} = \frac{R_e \cdot \eta}{2 \cdot r_p \cdot \rho_L} \quad (2\text{-}40)$$

$$v_{sp} = v'_{sp} \cdot \varepsilon_L^p \quad (2\text{-}41)$$

With:
$p = 4.26 - 0.73 \log(Re)$ $\quad 0.1 < R_e < 500$
$p = 2.29$ $\quad R_e > 500$
η is the viscosity and r_p the radius of a single particle

The Reynolds number can be calculated with:

$$c_w R_e^2 = \frac{84}{6}\frac{\rho_L(\rho_S - \rho_L)g \cdot r_p^3}{\eta^2} \quad (2\text{-}42)$$

$$\log(R_e) = \frac{log(c_w \cdot R_e^2 - 1.365)}{1.318} \quad (2\text{-}43)$$

2.2.5 Evaporation rate of water

Gas (air or nitrogen) is added to the airlift crystallizer for mixing. This gas can cause solvent evaporation, due to forced circulation of the solution in the crystallizer. The large amount of evaporation can fasten the rate of supersaturation, which may have a negative effect on crystal growth. Therefore, the amount of evaporated water can be calculated by multiplying the humidity ratio with the mass flow rate of air. The humidity ratio is given by:

$$x(T) = \frac{M_{water}}{M_{air}} \cdot \frac{P_{vap.,water}(T)}{P_{tot.} - T_{vap.,water}(T)} \quad (2\text{-}44)$$

And the estimated evaporated water is expressed by:

$$\dot{m}_{evap.,water} = x(T) \cdot \dot{m}_{air} \quad (2\text{-}45)$$

Where:
$x(T)$ is the humidity ratio [kg_{water}/kg_{air}]
M_{water} is the molar mass of water [g/mol]
M_{air} is the molar mass of air [g/mol]
$P_{vap.,water(T)}$ is the partial pressure of water at temperature T [bar]
$P_{tot.}$ is the total pressure [bar]
m_{air} is the massflow rate of air [kg/s]

2.3 Membrane distillation

Membrane distillation (MD) is an innovative concept in crystallization processes [21]. Removing solvent from a solution will increase the concentration of the solute and thereby generate supersaturation. The solvent is removed due to a vapour pressure difference across the hydrophobic membrane. Only vapour molecules are transported from the feed side of the membrane to the permeate side. According to the work of Drioli et al. [21] and Zhao et al. [22], MD processes are carried out in four configurations: direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), vacuum membrane distillation (VMD) and sweeping gas membrane distillation (SGMD). A schematic illustration of MD across a porous membrane is shown in Figure 2.7.

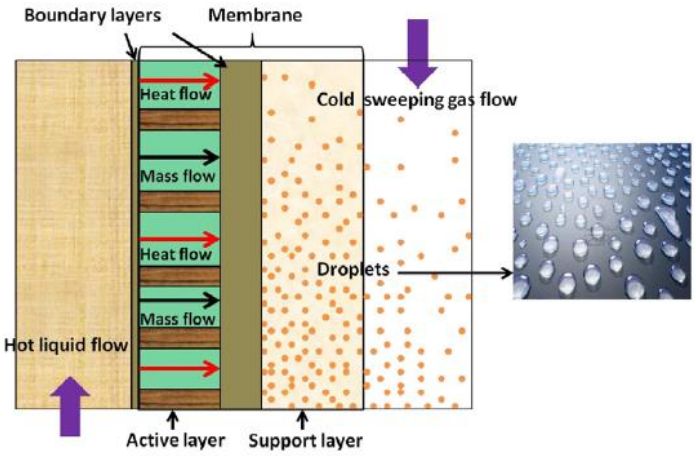


Figure 2.7: Schematic illustration of an MD across a porous membrane [22]

The similarities of these four configurations are that the feed side is in direct contact with the membrane layer. The differences lie in the method by which water vapour is recovered on the permeate side. In DCMD, the vapour condenses inside the membrane, in AGMD, an air gap is introduced to condense the vapour, in VMD, vacuum is maintained to remove the vapour and in SGMD, an inert gas is used to sweep the vapour.

Important phenomena in membrane modules are membrane characteristics, and the mass and heat transfer. The amount of solvent that can be removed by the use of a membrane module is dependent on the membrane flux. The driving force for the membrane flux is the vapour pressure difference

induced by temperature. Integrating a membrane module in a crystallization setup is a promising concept, although they have their limitations [23]. Reduction in the driving force across the membrane can be experienced due to a thermal gradient in the fluid layers. This phenomenon is called temperature polarization. Concentration differences along the membrane can be experienced due to a concentration gradient over the fluid layers. This phenomenon is called concentration polarization. Increasing the airflow rate increases the pressure drop across the membrane. For this phenomenon an equation is developed and validated with experimental results conducted by K. Mathew Thomas [11]. The relation between the airflow rate and pressure drop can be seen in Figure 2.8.

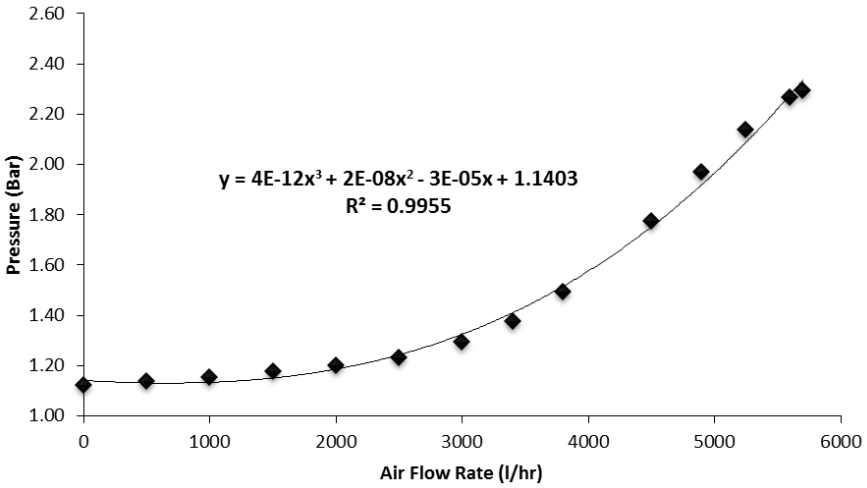


Figure 2.8: Relation between airflow rate and pressure drop [13]

L-ascorbic acid experiments with two membrane modules, MIC-RO 240 from PCI Membranes and the Membrana Liquicel extra flow, were performed by S. Goddrie [12] in 2013. In conclusion, the MIC-RO 240 module is not suited for membrane-assisted crystallization of L-ascorbic acid due to high osmotic pressure of this compound, while with the Membrana Liquicel extra flow module a reasonable flux was achieved. Further research on the Membrana Liquicel extra flow module performed by K. Mathew Thomas [13], has revealed detailed knowledge on this module. This module in combination with a crystallizer is a potential novel concept to control process conditions and increase product quality. Detailed information on mass and heat balances on the membrane module can be found in the report of K. Mathew Thomas [13].

For the Membrane-assisted Crystallization (MaC) process, the following equations are important:

The mass balance for each component can be calculated with:

$$\frac{dM_i}{dt} = \sum \dot{m}_{in,i} - \sum \dot{m}_{out,i} \tag{2-46}$$

The concentration balance is calculated with:

$$\frac{dM\omega_i}{dt} = \sum \dot{m}_{in,i} \cdot \omega_{in,i} - \sum \dot{m}_{out,i} \cdot \omega_{out,i} \tag{2-47}$$

Where *i* denotes the component.
To maintain the total mass inside the system (airlift crystallizer with membrane unit) a total system mass balance is used, which can be calculated with:

$$\dot{m}_{feed} = N \cdot A + \dot{m}_{product} \quad (2\text{-}48)$$

Where:
N is the membrane flux [kg/m^{2}s]
A is the surface area of the membrane [m^2]

During experiments the average membrane flux is calculated according to the volume of solvent that is removed, divided by the total surface area of the membrane and the time required for the experiment:

$$N = \frac{V_{removed,solvent}}{A_{membr.} \cdot t_{experiment}} \quad (2\text{-}49)$$

2.3.1 Properties of experimental compounds

In this research, melamine is used as a trial-and-error compound, and L-ascorbic acid for experimental research.

2.3.2 Properties of melamine

As mentioned earlier, the driving force for crystal growth is supersaturation. Therefore, the solubility curve is important to design a crystallization operation.
Melamine is an organic base with the chemical formula $C_3H_6N_6$. Especially in paints and plastics, melamine is a common used material. The solubility of melamine in water is adapted from the work of Chapman et al. [24]. According to this report, melamine is relatively not very soluble in water. It was found (experimentally validated) that the solubility curve should obey the Clausius-Clapeyron equation, which is given by:

$$\log(solubility) = -1642 \times \frac{1}{T} + 5.101 \quad (2\text{-}50)$$

The solubility curve of melamine in water is shown in Figure 2.9.

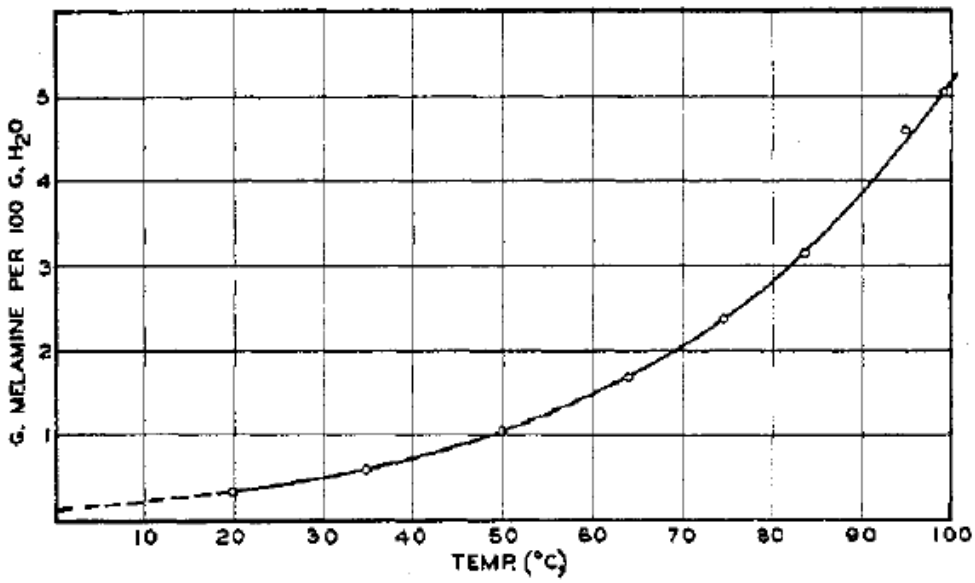


Figure 2.9: Solubility curve of melamine [24]

Other scientific data on melamine crystallization is hard to find. Therefore, the above-mentioned diagram is used for the trial-and-error experiments.

2.3.3 Properties of L-ascorbic acid

L-ascorbic acid ($C_6H_8O_6$), also known as vitamin C, is a commonly used nutrient in pharmaceuticals, foods, and cosmetic applications. Exposure of L-ascorbic acid solution to the open air will destabilize the solution and oxidize very fast (within 24 hours). More information on oxidation of L-ascorbic acid is described in section 5.2 of this report.

The solubility curve for L-ascorbic acid in water is adapted from the research of F. Goddrie [12]. The curve is shown in Figure 2.10. The measured solubility curve is used in this research, during the experiments.

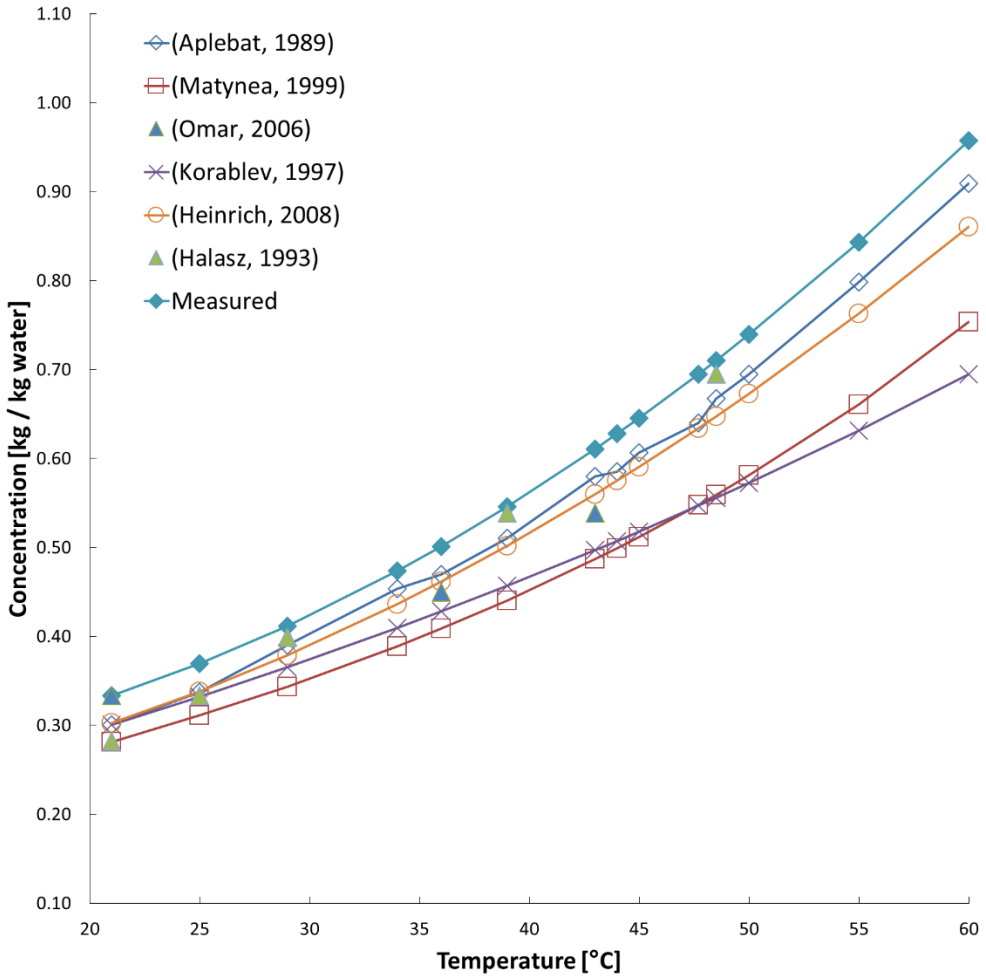


Figure 2.10: Solubility curve of L-ascorbic acid

Detailed information on the metastable zone width of L-ascorbic acid in an airlift crystallizer is obtained from the research of Lakerveld et al. [5].

For the concentration measurements during experiments, a calibration curve between concentration and density is used. This curve is developed and validated by K. Mathew Thomas [13]. The calibration is validated at a temperature of 35 ^{o}C, which is shown in Figure 2.11.

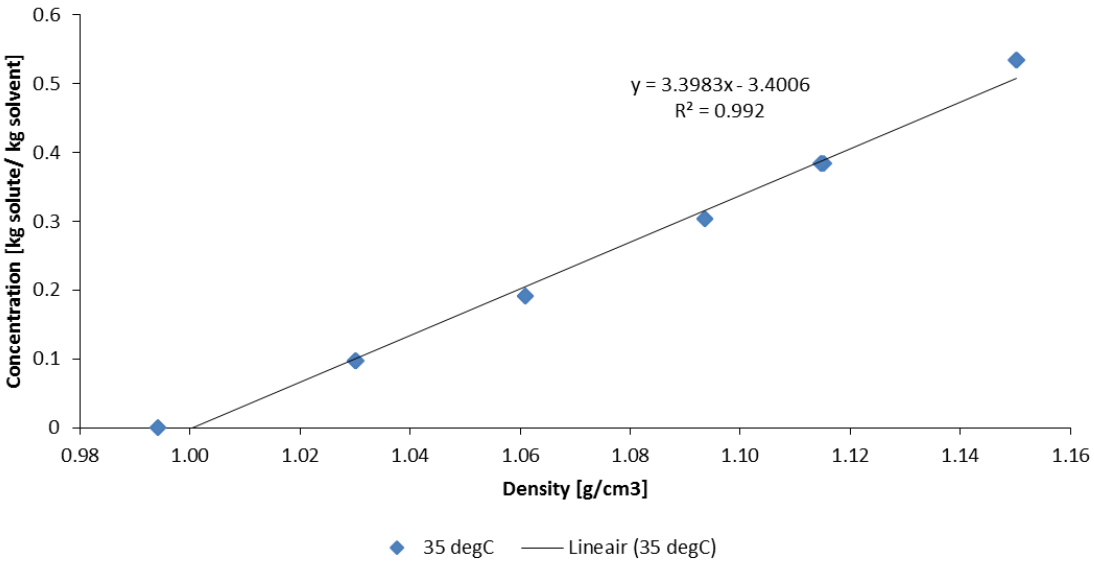


Figure 2.11: Concentration – density curve L-ascorbic acid at 35 ^{o}C

It can be seen that, at a temperature of 35 ^{o}C, the relation between concentration and density is almost linear.

3

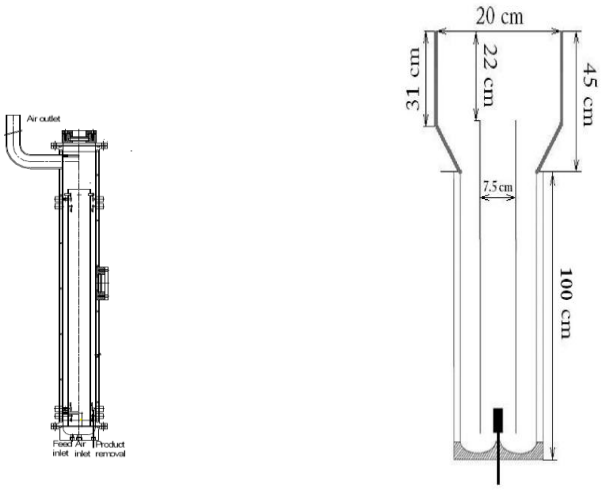
Experimental setup

3.1 Design of the MaC

The key phenomenon of a crystallization process is crystal growth. Sufficient mixing and minimization of shear forces acting on particles are important aspects to enhance the key phenomenon. To improve the quality of final crystals and enhance the flexibility of the crystallization process, a new experimental setup is designed, constructed, validated and used, entitled the Membrane-assisted Crystallizer (MaC).

3.1.1 History of the design

The aforementioned MaC is a combination and extension of two existing units: a standalone airlift crystallizer and a standalone membrane unit. The design of the airlift crystallizer at TU Delft started years ago (2008) with the research done by Lakerveld et al. [19], using a bubble column. The bubble column is commonly used in the biotechnology, where air is used for mixing instead of a stirrer, to prevent damage to microorganisms. Therefore, using this concept in a crystallizer may prevent the damage to crystals during the operation. The main goal in the research of Lakerveld et al. [19] was to investigate if secondary nucleation can be minimized when no stirrer is used. The total volume of the crystallizer used in the work of Lakerveld et al. [19] was10 L, see Figure 3.1. Further research conducted by Soare et al. [6] showed improved results of the hydrodynamics inside the bubble column with the implementation of a gas disengagement zone at the top of the column (airlift crystallizer). With the extension of the gas disengagement zone, the total volume of the airlift crystallizer increased to 18 L. In prior work of Lakerveld et al. [5] the 18 L airlift crystallizer was implemented with several extensions, e.g. image probe for in-situ crystal shape and size, novel sparger was designed and used to improve the hydrodynamics inside the crystallizer, and pressure transmitters where used for the quantification of velocities. This crystallizer is now used in the design of the MaC setup.



(a) (b)

Figure 3.1: (a) 10 L airlift, (b) 18 L airlift with gas disengagement zone

Integration of membrane modules with crystallizers at TU Delft started in 2010, conducted by Lakerveld et. al. [11], and resulting in promising results. These experiments were performed for ammonium sulphate and adipic acid solutions. A 5L jacketed crystallizer with a stirrer was used as reference.

In 2013 S. Goddrie [12] has studied two types of membrane modules: reverse osmosis (MIC-RO 240) and Membrana Liquicel Extraflow. As described in section 1.1, the MIC-RO 240 module is not able to remove the solvent from L-ascorbic solution due to high temperature polarization. The use of sweeping gas was recommended for further investigations on the Membrana Liquicel Extraflow module. The research of SGMD with L-ascorbic acid solution was conducted by K. Mathew Thomas [13] in 2014. Promising results were achieved to control the rate of supersaturation for L-ascorbic acid solution. However, the membrane module has its limitations, due to temperature and concentration polarization. This membrane module (Liquicel) is now used in the design of the MaC setup.

As described in section 1.1, both technologies (airlift crystallizer and membrane module) individually improves the crystallization process. The challenge now is to combine the airlift crystallizer with the membrane unit to further improve L-ascorbic acid crystal quality and generate controlled supersaturation with low energy consumption.

3.1.2 Process flow sheet

To design an optimal process of the combination of the airlift crystallizer with a membrane unit, a task-based decomposition strategy is adapted from Bermingham et al. [25]. This procedure decomposes the design problem of a solution crystallization process into four design levels. According to the report of Bermingham et al. [25], these design levels are:

- Level I: Design of the crystalline product;
- Level II: Physical/Chemical design of the crystallization task;
- Level III: Flowsheet design of the crystallization process;
- Level IV: Design of a crystallization stage.

The above-mentioned design levels are basically used for the design of a new crystallizer. As mentioned earlier, the design of the airlift crystallizer started in 2008. The hierarchy mentioned above was used to design the airlift crystallizer [2] at that time. To disentangle the crystallization phenomenon, an external separated operation unit is designed, called the membrane unit, with the above-mentioned hierarchy as a guideline, to generate and provide the airlift crystallizer with concentrated solution (supersaturated solution).

This thesis is a continuation of previous investigations with L-ascorbic acid as solute and water as solvent where the basic product performance criteria, such as solubility curves, metastable zone width, and operation conditions for certain processes are already known. As such, the design levels are only partially used for optimization and extension of the different detailed variables in the existing airlift crystallizer.

The following aspects have been taken into account for the process variables and design:

- **Operation mode:** batch or continuous
  The experimental setup should be able to run batch and continuous processes. For the batch operation, the solution can be made inside the crystallizer, proceeding with the crystallization process. Therefore, no additional feed or product vessel is needed. However, a combination with a membrane unit requires minimum one extra vessel for the generation of supersaturation, see Figure 1.1. This extra vessel is also needed for the safety of the membrane unit to keep the solution under the saturation point while circulating over the membrane. An undersaturated solution is required to prevent the formation of crystals on the membrane wall.
  Operation in continuous mode requires a continuous flow of the feed and product stream. One extra vessel is needed to accumulate the product flow and to provide the fresh feed solution (closed system).
  As result, two vessels are added to the MaC setup, to provide the crystallizer with concentrated solution. From now on, the vessel connected to the membrane unit is called the Buffer vessel and the Feed vessel is used for the feed flow.
- **Flexibility:** standalone or in combination
  For increasing the operating window of the experimental setup, the setup is designed and constructed in a modular way to perform experiments with standalone units, both in batch and continuous operation, as well as in combined modes in which the crystallizer is connected to a membrane unit. Therefore, it is possible to perform batch and continuous operated cooling and membrane-assisted crystallization experiments, in both the airlift crystallizer as well as in stirred tank crystallizer.
- **Sustainability**: feed, product and recycle stream;
  The aim of an experimental setup on mini-pilot scale is to investigate different phenomena related to product quality, which can be (finally) implemented in industries for better and purer products. Experimental compounds can be very expensive and might be needed in huge amounts for investigations. In the design of the MaC, an additional vessel is added, called the make-up vessel. In the make-up vessel the solution can be saved after an experiment and used for a couple of experiments. It must be noted that saving of the solution depends on the properties of the compound. The properties of the solution should be measured and replenished after every experiment. The saving of L-ascorbic acid is described in chapter 5. The objective on this level is to increase efficiency and to reduce energy (filtration). A membrane module is often operated at lower temperatures compared to evaporative crystallization [11] and has therefore promising results in reduction of energy.

- **Generation of supersaturation**
  As mentioned earlier, supersatured solution can be generated either by cooling the solution or removing the solvent from the solution. For removing solvent from the solution, a membrane unit is added to the experimental setup. Depending on the design of the crystallization process, cooling crystallization or membrane-assisted crystallization experiments can be performed.
- **Material and heat exchanging rates**
  To maintain process temperatures, a high heat exchanging rate is required between the heat exchanger and the solution. The setup should allow fast and slow heating and cooling of the solution. Therefore, the airlift crystallizer, buffer vessel and make-up vessel are made of stainless steel with a jacket. In this jacket the heating or cooling medium is transported to maintain the temperature of the solution inside the vessel. Because the feed vessel is only needed for controlling the level in continuous processes, this is made of glass.
- **Equipment dimensions**
  The existing airlift crystallizer is a 18 L jacketed vessel and the buffer vessel is a 30 L jacketed vessel. As the make-up vessel is used for preparing the solution and saving the total required solution, the volume of the make-up vessel is 70 L. The feed vessel is only needed for controlling the level during continuous processes. This is a 10 L glass vessel. Information about the dimensions of the equipment are indicated in Appendix B.
- **Pressure and temperature range**
  The setup should be able to withstand the required operating pressure and temperature, depending on the design of the crystallization process. Crystallization of L-ascorbic acid is performed at ambient pressure and temperatures between 20 – 50 ^{o}C. Therefore, the setup should be able to fulfil these requirements.
- **Type of heat exchangers, pumps, valves and tubes**
  Heat exchangers are necessary for the temperature control during an experiment. As mentioned earlier, the heat exchanger should be able to control and persist the temperature of the solution in the vessels. The heat exchanger used in the design, are thermostatic baths of Lauda which are connected to the jacket of the vessels.
  Pumps are needed to transport solution from one to another vessel. At start-up and shutdown high flow rates are required, while during experiments low flow rates, dependant on the residence time of an experiment. Therefore, peristaltic pumps with a capacity between 6.6 ml/min and 880 ml/min is aimed to fulfil the operating requirements. For the membrane unit a plunger pump (model 5CP6221 of Cat pumps) is used, as higher flow rates are required for an optimal flux.
  Valves are needed to open or close one or more streams in the different streamlines. The locations of the valves are chosen in such a way that it is possible to handle quickly in case of calamity.
  The tubing is chosen in such a way that no phase changes take place inside the tubing, there is low resistance, there is possibility for high and low flow rates and easy to extend. Therefore, tubing of stainless steel is used with tracing. Tracing is an electric wire around the tubing to control the temperature.
- **Location of equipment**
  In continuous processes a continuous feed and product flow is required. Location and distance between equipment becomes an important aspect to reduce heat losses during the continuous flow. The longer the distance, the bigger the losses. In case of calamity the vessels should be accessible. Therefore, a space of minimum 0.5 m is kept between the vessels.

- **Availability and controllability of subsystems**
  As mentioned earlier, tubes, valves and locations of equipment are used in such a way to make operation, availability and controllability in a human friendly way.
- **Rinsing**
  An important aspect in crystallization processes is cleaning the equipment. Left over chemical compounds may cause blockages of tubes, valves, flow meters and other equipment, and may affect the properties of next experiments. Therefore, possibilities of rinsing is implemented on the experimental setup.
- **Computer control of the system**
  The analyses of experimental results requires good operating conditions. To collect reliable data during experiments, a distributed control system (DCS) is connected to the experimental setup. This control unit also allows for controlling several parameters automated, such as flows and temperatures.
- **Feed and product location**
  One of the important aspects of the crystallizer is the location of feed and product. In order to perform sufficient mixing and prevent entrapment of gas bubbles during filling, the feed pipeline is connected at the bottom of the crystallizer. During the crystallization process the grown crystals will settle on the bottom of the crystallizer, which is based on the circulation velocity. As such, the product is removed from the bottom as well. Before the entrance of the make-up vessel, an extra valve is adapted for samples during experiments.

Taking all the aforementioned variables into account, the process flowsheet of the new experimental setup has been built. The process flowsheet of the MaC is shown in Figure 3.2 and Appendix A.

The new experimental setup has been moved to the new building of the Process & Energy department, called the Frans Nieuwstadt hall after it was built at an external location.

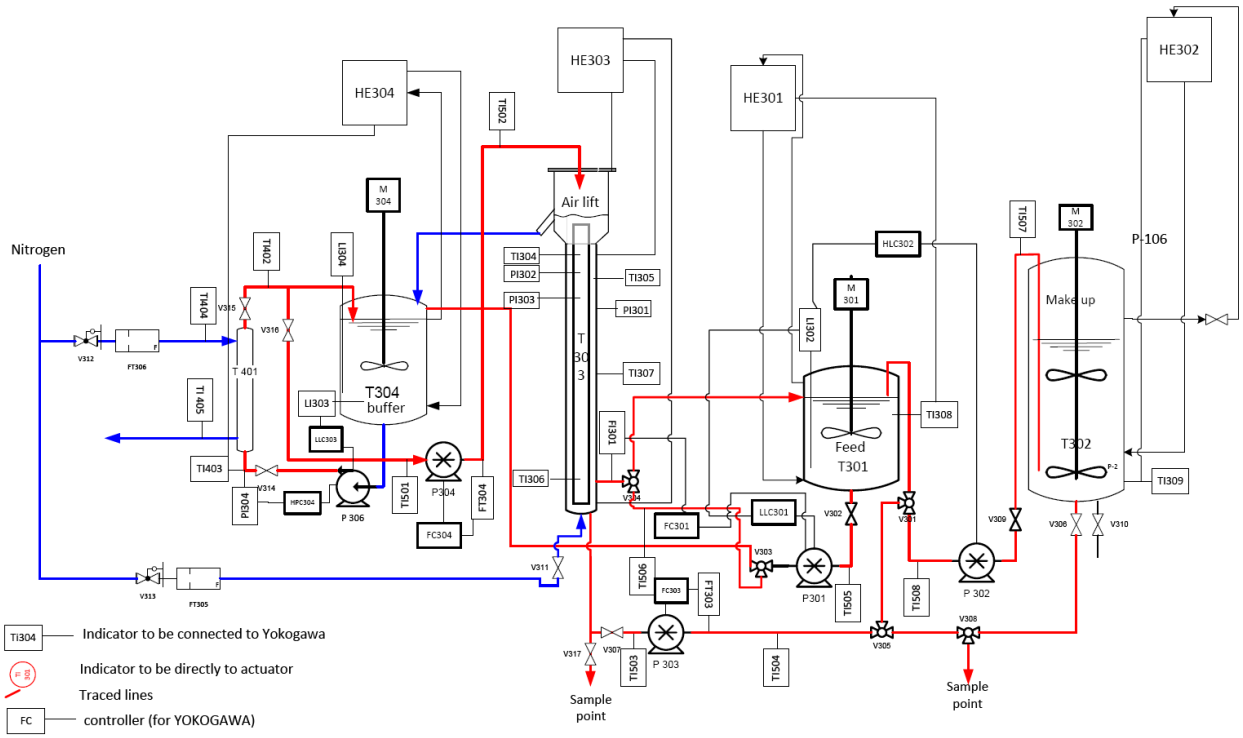


Figure 3.2: PFD of the MaC setup

3.2 Description of the process

As shown in Figure 3.2, a multifunctional and flexible setup is designed for crystallization experiments.

In general, the crystallization process starts with making a (saturated) solution, followed by the crystallization process with final crystals as a product. The solution is made in the make-up vessel (T302). This is transported to the feed vessel (T301) through a peristaltic pump (P302). Using a 3 way valve (V303), connected to the pipeline (PL302), the solution is transported either to the airlift crystallizer (T303) or the buffer vessel (T304). To measure and control the flow rate of the feed stream, a flow meter (FC301) is connected to the feed pipeline (PL302). The solution in the buffer vessel (T304) is transported to the membrane module (T401) through a plunger pump (P306) for the generation of supersaturation. Air is used as a sweeping gas for this process. The supersaturated solution is transported with a peristaltic pump (P304) to the airlift crystallizer (T303). A flow meter (FC304) is measuring and controlling the aforementioned peristaltic pump (P304). The product flow of the airlift crystallizer is connected to the inlet of the make-up vessel (T302). A peristaltic pump (P303) is used to transport the product of the airlift (T303) to the make-up vessel (T302). The mass of the product flow is measured with a mass flow meter (FC303). The temperature in the make-up vessel, feed vessel, airlift crystallizer and buffer vessel are measured and controlled with thermostatic baths. The mixing inside the airlift crystallizer is controlled by adding air or nitrogen through the sparger at the bottom. The mixing in the other vessels is performed with stirrers. Note that temperature and flow control is automated.

A detailed operating procedure with the setup is shown in Appendix C. As cleaning is also an important aspect after an experiment, a procedure of cleaning is made which is shown in Appendix D.
A complete list of the experimental setup is shown in Appendix B.

The setup is able to run the following processes:

- Cooling batch crystallization
- Continuous cooling crystallization
- Membrane-assisted Crystallization (MaC) batch
- Continuous Membrane-assisted Crystallization (MaCC)
- Membrane Distillation (MD)

3.2.1 Cooling batch crystallization

The cooling batch crystallization process is performed with the airlift crystallizer (T303) as a standalone unit. The saturated solution can be prepared either in the airlift crystallizer (T303) or in the make-up vessel (T302) and shifted to the crystallizer. After a saturated condition of the solution is reached, a cooling profile and residence time is applied to the crystallizer, depending on the design of the experiment. The cooling profile and residence time are set by the control system.

3.2.2 Continuous cooling crystallization

The continuous cooling crystallization process is performed with the feed vessel (T301), airlift crystallizer (T303) and make-up vessel (T302). The saturated solution is prepared in the make-up vessel (T302). After the solution is saturated, this is shifted to the feed vessel (T301) and the airlift crystallizer (T303). Depending on the residence time, a product flow rate and feed flow rate are calculated. A continuous flow is maintained between T301, T302 and T303. The crystallizer is

operated at a lower temperature, compared to the feed temperature, based on the design of the experiment.

3.2.3 Membrane-assisted Crystallization (MaC) batch

The MaC batch operation is performed with the buffer vessel (T304), membrane module (T401) and the airlift crystallizer (T303). First the crystallizer and buffer vessel is filled with a saturated solution. The membrane module removes the solvent from the solution in the buffer vessel to increase the concentration in the solution. The concentrated solution is transported to the airlift crystallizer, which is then supersaturated for the temperature of the airlift crystallizer.

3.2.4 Continuous Membrane-assisted Crystallization (MaCC)

The MaCC operation is performed with all the vessels: make-up vessel (T302), feed vessel (T301), airlift crystallizer (T303) and buffer vessel (T304). Compared to the continuous cooling crystallization, the membrane unit (T401) is used for the generation of supersaturation instead of cooling the solution. In this way the process can be operated at a constant temperature.

3.2.5 Membrane distillation

The membrane section can be used as a separate unit to perform experiments on membrane distillation. The membrane module can be operated with a 2L crystallizer in a batch experiment.

3.3 Components of the MaC

The MaC is built up with the following main equipment:

- Airlift Crystallizer (T303);
- Membrane module (T401);
- Make-up vessel (T302);
- Feed vessel (T301);
- Buffer vessel (T304);
- Thermostatic baths (HE301, HE302, HE303 and HE304);
- Pumps (P301, P302, P303, P304 and P306);
- Flow meters (FT301, FT303 and FT304);
- Tubes and valves.

3.3.1 Airlift Crystallizer

The airlift crystallizer (T303) is an 18 L stainless steel tube in a tube system with a gas disengagement zone at the top. The airlift crystallizer (ALC) consists of two concentric stainless steel tubes of 1.0 m in height. The flow in the inner tube is called the riser and the flow between the inner and outer tube is called the downcomer. The outer cylinder has a jacket which is connected to a 10 L thermostatic bath (HE303) to control the temperature of the fluid inside the ALC. On the bottom of the ALC, a sparger is mounted which is connected to the air and nitrogen supply. Instead of a stirrer, air or nitrogen is used for the mixing in the crystallizer, which is added through the sparger in the riser of the ALC. As mentioned earlier, mixing is possible due to the density difference between the fluid in the riser and the fluid in the downcomer. To measure the density difference between the riser and the downcomer, three pressure transmitters of Siemens (Sitrans DSIII) are mounted on the ALC. One pressure transmitter (PI302) measures the pressure difference between the top and bottom of the ALC in the riser. The second one (PI301) measures the pressure difference between the top and bottom of the ALC in the downcomer. And the third transmitter (PI303) measures the pressure difference between the riser and the ambient pressure. PI303 is used to calculate the level in the ALC. To prevent air bubbles in the downcomer, a gas disengagement part is mounted on the top of the ALC. The gas disengagement part is 45 cm in height and has a larger diameter than the ALC. In research studies conducted by Soare et al. [6] experiments have shown that this design has the optimum geometry for preventing air bubbles in the downcomer. Furthermore, there are four temperature sensors (PT100) connected to the ALC, two at the bottom and two at the top, in the riser and the downcomer respectively. These pt100s are used to monitor and control the temperature of the solution in the ALC. Beneath the gas disengagement zone, an in-situ Particle Video Microscope (PVM) of Mettler Toledo (MTS) is mounted for live images of crystal growth during experiments. At the opposite side of the PVM, there is a glass window in the middle of the crystallizer. The construction of the ALC can be seen in Figure 3.3.

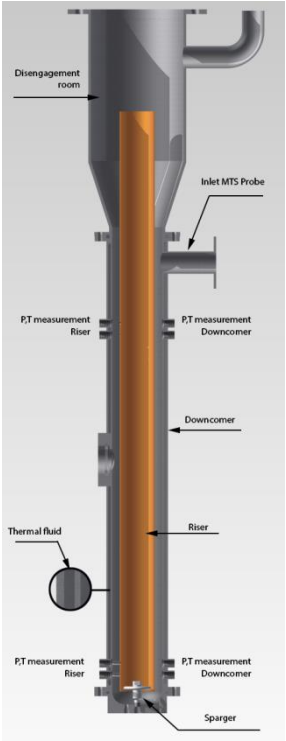


Figure 3.3: The Airlift crystallizer

3.3.2 Membrane unit

As described in chapter 2, membrane processes are carried out in four configurations: direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), vacuum membrane distillation (VMD) and sweeping gas membrane distillation (SGMD). Depending on the compound and research, the mode can be switched in the membrane unit.

The membrane module (T401) in this research is a Liqui-cel®Extraflow 2.5x8 module supplied by Membrana. The type of the membrane is an X50 fibre made of polypropylene. The capacity of the 2.5x8 Extraflow lies between the 0.1 and 0.7 m^3/hr.
The component is a microporous hollow fibre membrane, which is knitted into an array and wrapped around a centre tube inside of the housing. The hollow fibre has a shell side (outside) and a lumen side (inside). During operation the (liquid) solution flows over the shell side, while the sweep gas (air) is applied to the lumen side. Because the membrane is hydrophobic it allows direct contact between gas and liquid phase without dispersion. Due to a pressure difference between the shell side and the lumen side, solvent molecules are removed from the solution and carried by the sweeping gas. In the Extra-flow variant there is a baffle in the middle of the unit, which directs liquid radially across the array. The principle of the membrane unit can be seen in Figure 3.4.

At the inlets and outlets of T401, pt100 temperature sensors are connected to measure the solution and air temperatures. These temperature sensors are connected to the Yokogawa control system.

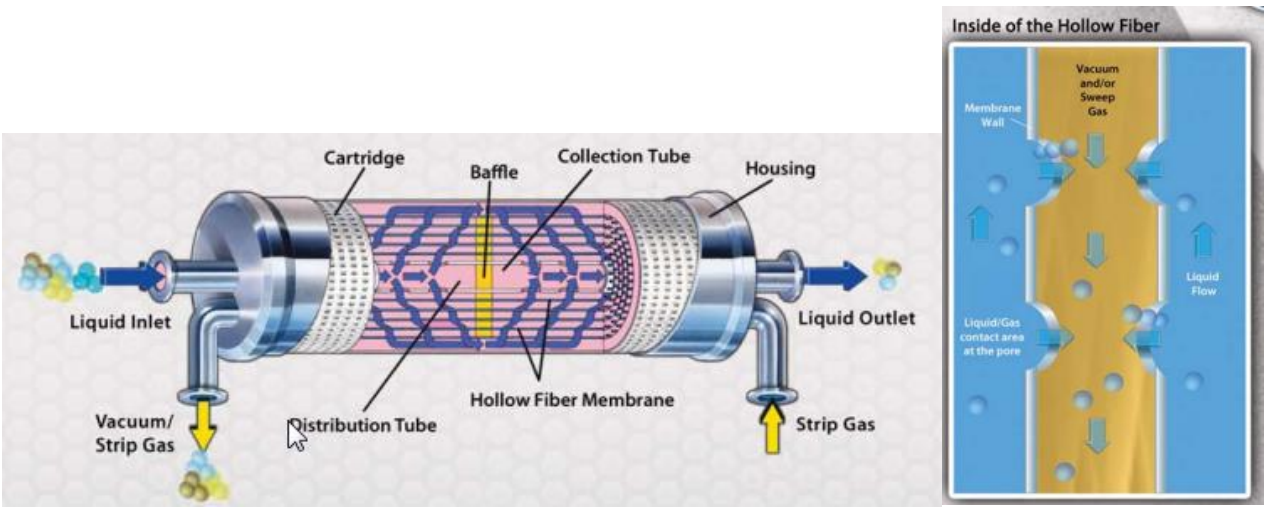


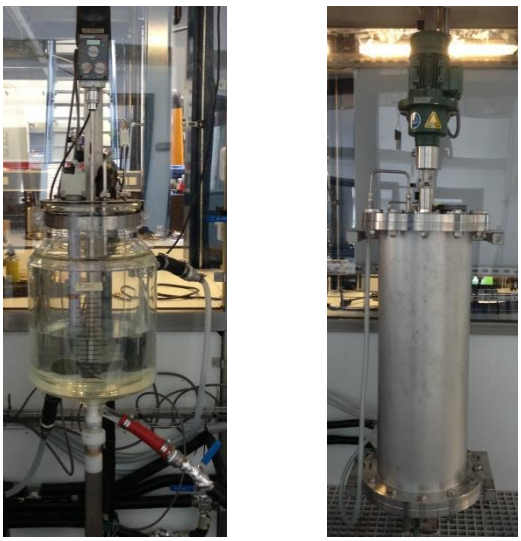
Figure 3.4: Membrane unit (source: [26])

3.3.3 Make-up vessel

The make-up vessel (T302) is a 70 L stainless steel vessel with 1.0 m in height and has a diameter of 0.3 m. The make-up vessel has a jacket which is connected to a 10 litre thermostatic bath. T302 is used for preparing the solution for an experiment and for storing the solution after an experiment. As mentioned earlier, storage of solution is mainly based on the properties of the chemical compound used to experiment. The solution in the make-up vessel (T302) is mixed with a stainless steel stirrer with 2 impellers. This stirrer is connected to a Mi5P1 frequency controlled mixer of Lightnin, (M302) which is connected to a Hitachi frequency controller in the electrical cabinet. The frequency controller is controlled from the Yokogawa control system. The temperature of the solution in the make-up vessel (T302) is monitored with a pt100 (TI309) temperature sensor and controlled with the 10 L thermostatic bath (HE302), which are both connected to the Yokogawa control system. An image of the make-up vessel is shown in Figure 3.5.

3.3.4 Feed vessel

The feed vessel (T301) is a 10 L glass jacketed vessel with 0.45 m in height and has a diameter of 0.3 m. The jacket of the feed vessel (T301) is connected to a 4 litre thermostatic bath (HE301) for temperature control. An external pt100 (TI308) is connected to the Yokogawa control system for monitoring and controlling the temperature of the solution inside the vessel. The solution is mixed with a RZR 2021 mixer of Heidolph (M301). The level in the feed vessel is measured with a 12” eTape liquid level sensor (LI302) with Teflon jacket which is connected to the control system. An image of the feed vessel is shown in Figure 3.5.



(a) (b)

Figure 3.5: (a) Feed vessel and (b) make-up vessel

3.3.5 Buffer vessel

The buffer vessel (T304) is a 30 L stainless steel jacketed vessel with 0.4 m in height and has a diameter of 0.3 m. The jacket of the vessel is connected to a 4 L thermostatic bath (HE304). A pt 100 (TI403) is used to control the temperature inside the buffer vessel. HE304 and TI403 are both connected to the Yokogawa control system for monitor and control. The level in the vessel is measured with an ultrasound level sensor (LI304). The solution in the buffer vessel is mixed with a RZR 2051 mixer of Heidolph.

Figure 3.6: Buffer vessel with membrane unit

3.3.6 Thermostatic bath

As mentioned earlier, the airlift crystallizer (T303), make-up vessel (T302), feed vessel (T301) and buffer vessel (T304) are each connected to an individual thermostatic bath for controlling the temperature of the medium inside these vessels. The thermostatic bath (HE303) used for the airlift crystallizer (T303) and HE302 used for the make-up vessel (T302) are a 10 L R1040 model of

Lauda, and for the feed vessel (T301) and buffer vessel (T304) a 4 L T4010 model of Lauda (HE301 and HE304 respectively). The thermostatic baths are controlled from the Yokogawa control system.

3.3.7 Pumps and flow meters

In the new setup four peristaltic pumps and one plunger pump (P306) are used to maintain the flow rates during experiments. Three of the peristaltic pumps, P301, P303 and P304, are of type 323U and one, P302, of type 525U of Watson Marlow. The flow rate is dependent on the diameter of the tubing. Marprene tubes with internal diameter of 4.8 mm are used for the 323U pumps. For the 525U pump Marprene tubing with an internal diameter of 8.0 mm is used.
The plunger pump (P306), model 5CP6221 of Cat Pumps, is connected to a Hitachi frequency controller, which is controlled from the Yokogawa control unit.

The feed line from feed vessel (T301) and buffer vessel (T304) to the airlift crystallizer (T303) are implemented with Magnetic flow meters, type FMG82, of Omega. These flow meters can measure flow rates between 114 ml/min and 11,365 ml/min. The product line of the setup is implemented with an M15 type Coriflow mass flow meter (FT303) of Bronkhorst, which measures mass flows between 0.6 kg/h and 30.0 kg/h.

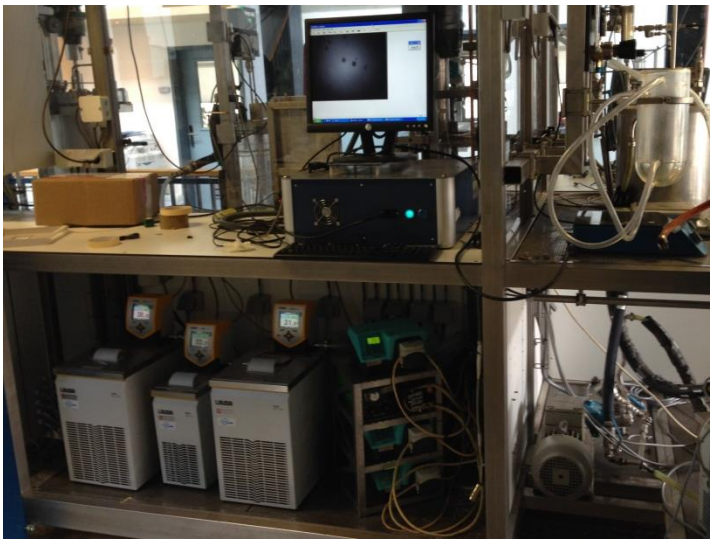


Figure 3.7: Thermostatic baths and pumps

3.3.8 Tubes and valves

Stainless steel tubes with an internal diameter of 8 mm and outer diameter of 10 mm are used for optimal flow rates. For the part of the buffer vessel and membrane unit, stainless steel tubes with an internal diameter of 10 mm and outer diameter of 14 mm are used. As mentioned earlier, Marprene tubes are used for the peristaltic pumps. To choose the correct flow direction, 2-way and 3-way valves are connected to the different pipelines, see Figure 3.2 and Appendix A.

4

Process monitoring and control system

4.1 Process control hierarchy

In process industries, process control has become an essential part of the total industrial plant. Therefore, process engineers need to master this subject in order to be able to design and operate modern plants. Implementing control units on industrial plants, maintains a process at the desired operating conditions, safety and efficiency, while satisfying environmental and product quality requirements. Manually controlled systems (without a control unit) cause many disturbances, which may affect the process variables. For example, a heat exchanger which is controlled manually, will show a bath temperature on the monitor, while the actual temperature of the solution in a vessel is different. With an automated control unit, the temperature of the heat exchanger will adjust to the temperature in the vessel, which is more reliable. Process control units are basically used for two purposes:

- **Measurements** of process variables such as pressures, temperatures, flow rates, etc.
- **Controlling** process variables. Feedback control systems compare measured values with desired values, and then adjust the manipulated variable according to the differences in measured and set point values.

The design of a control system is mainly based on the typical process and the desired inputs and outputs. The hierarchy incorporated to develop the control activities of the MaC setup is adapted from Process Dynamics and Control book [27]. This hierarchy is divided into five levels:

1. Level 1: Measurement and actuation. Measurement devices and actuation equipment are used to measure process variables and reproduce the calculated control values.
2. Level 2: Safety and Environmental/Equipment protection. The importance of this level is to design a control system in such a way, that this ensures a safe operation (safety of equipment and the environment).
3. Level 3a: Regulatory control. This level is achieved by applying standard feedback and feedforward control techniques.

   Level 3b: Multivariable and constraint control. This level is applied when several process variables have significant interactions and operating a process close to the limiting constraint is an important objective, for example not crossing a high limit level.
4. Level 4: Real-time optimization. During a process, the optimal operating conditions may change continuously. Therefore, real-time optimization (RTO) calculations are made based on a steady-state model of the plant and economic data such as costs and product values. Models are developed to minimize operating costs or maximize operating profit.

5. Level 5: Planning and scheduling. The industrial plant consists of several processes which are related to each other. Based on equipment constraints, storage capacity and operation of other plants, the production of all products and intermediates must be planned and coordinated.

In the aforementioned hierarchy the levels 1 – 3a are required for all manufacturing plants, while the levels 3b – 5 are optional. Incorporation of these last levels depends on economic considerations and company priorities. Based on these five levels, the important aspects employed in the design of the MaC control system are summarized in Table 4.1.

Table 4.1: Important aspects of the MaC setup

Level 1	• Temperature sensors on airlift crystallizer to measure the temperature of the solution inside the airlift crystallizer; • Pressure transmitters on airlift crystallizer to measure the pressure difference between the riser and the downcomer to validate mixing; • Temperature sensors on the membrane unit to measure the temperature of the solution and sweeping gas; • Feed and make-up vessel temperature sensors to measure the temperature of the solution inside the vessels; • Tracing temperature sensors to measure the temperature of the solution inside the pipelines; • Feed and product flow measurements; • Level measurement in the feed and buffer vessel; • Bath temperature measurements of the thermostatic baths.
Level 2	• Low level controller in the buffer vessel for the safety of the plunger pump; • Emergency switch on every corner of the setup in case of calamity; • The limits of the temperature of (Marprene) tubes. The maximum operating temperature of these tubes is 70 ^{o}C; • Limits of the temperature in the membrane module.
Level 3a	• Control of the tracing temperatures; • Temperature control in the make-up vessel, feed vessel and buffer vessel; • Temperature control in the crystallizers (airlift and stirred tank); • Flow control in feed and product lines; • Stirrer control of the make-up vessel; • Plunger pump control of the membrane unit; • Thermostatic bath control; • Level control in the buffer vessel.
Level 3b	• This level requires an advanced model based control strategy, which is out of the scope of this project.
Level 4	• This level requires real time and off-line optimizations, which are out of the scope of this project.
Level 5	• Fixed direction of feed flow and product flow in continuous mode. This can be monitored by applying flow meters; • Operating temperatures in the different vessels according to the crystallization process; • Coordination of operation. For example: heating up the vessel before filling, filling the airlift crystallizer before filling the feed vessel, adding air or nitrogen to the crystallizer before filling, etc.

4.2 Process control systems

Process control systems are classified into analog and digital control systems. The basic loop of an analog and digital control system is shown in Figure 4.1.

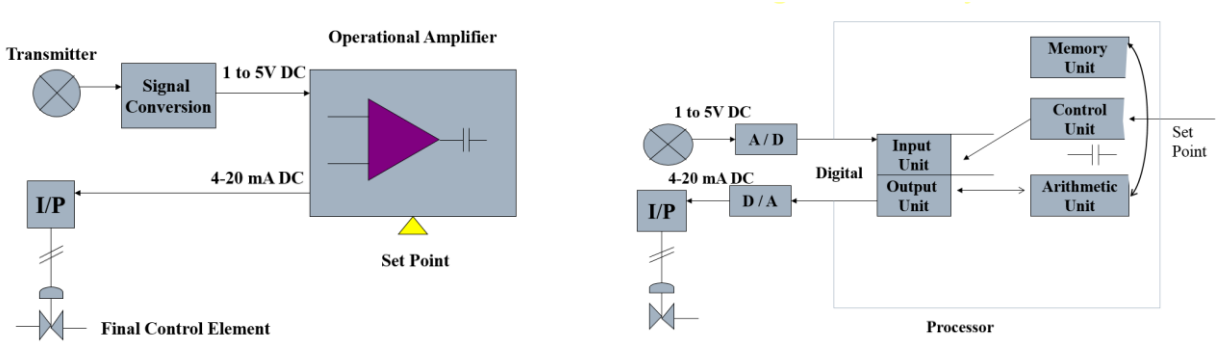


Figure 4.1: (a) analog control system, (b) digital control system (source: Yokogawa manual)

Digital control systems are further classified into centralized control systems (CCS) and distributed control systems (DCS). The key concept behind the CCS is centralized controlling and centralized monitoring. Therefore, in a CCS all the signals from the field (inputs), and manually applied set points are monitored and processed in a central processing unit (CPU). After the output values are calculated in the same CPU, these values are sent to the output ports in the field. The main drawback of a CCS is that the entire plant gets affected if the CPU fails.
On the other hand, a DCS has a distributed control and centralized monitoring. Input and output signals are processed in the distributed control part, while monitoring is processed at an external unit. Basic components of a DCS are:

- Field control station (FCS), used to control the process. All the function blocks created by its software, reside in the memory of the FCS. Field instruments, such as temperature sensors, pressure sensors, flow meters, are wired to the FCS;
- Operator station (OPS), used to monitor the process and to operate various units connected in the field;
- Communication bus, used to communicate between the FCS and the OPS.

Compared to the CCS, the DCS has various advantages. The control function of a DCS is distributed among multiple CPU's (FCS). Therefore, the failure of one FCS does not affect the entire plant. The control drawings of the DCS are created with a built-in software, which is able to memorize and reload designed processes. Maintenance and troubleshooting are easier due to less field wiring and several available formats of information regarding the process. The control unit used in the MaC setup is a DCS type. Further information on the used DCS is described in section 4.4.

4.3 Feedback controllers

As mentioned earlier, controlling of process variables has become an essential part in process plants. Feedback controllers are one of the most applied control blocks in the design of a control system. All the controllers applied in the design of the MaC are feedback controllers.

The objective in a feedback control is to reduce the error signal to zero. The error signal is calculated with the following equation:

$$e(t) = y_{sp}(t) - y_m(t) \quad (4\text{-}1)$$

where:
$e(t)$ = error signal
$y_{sp}(t)$ = set point
$y_m(t)$ = measured value of the controlled variable (or equivalent signal from the sensor/transmitter)

Predominant types of feedback controllers are proportional-integral-derivative (PID) control and on-off control. A simple diagram of a feedback controller is shown in Figure 4.2.

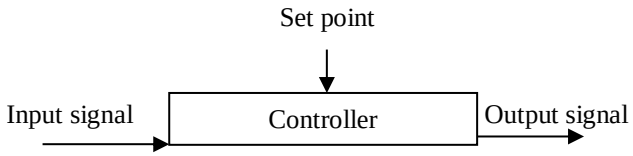


Figure 4.2: Simple diagram of a feedback controller

Three basic feedback control modes are: proportional control, integral control and derivative control:

4.3.1 Proportional control

In the proportional control mode, the desired deviation between set point and controlled variable can be set accurately by adjusting the controller gain. The sign of the controller gain can be chosen to make the controller output increase or decrease as the error signal increases or decreases respectively. For proportional controlling, the controller output is proportional to the error signal:

$$p(t) = \bar{p} + K_c(t) \quad (4\text{-}2)$$

Where
$p(t)$ = controller output
$\bar{p}$ = bias (steady-state) value
K_c = controller gain (usually dimensionless)

The transfer function of the proportional control is given by:

$$\frac{P\prime(s)}{E(s)} = K_c \quad (4\text{-}3)$$

Where $P'(s)$ and $E(s)$ are the Laplace transformations of the output and error respectively.

4.3.2 Integral control

The key concept behind the integral control is elimination of the offset. Due to the integration function the output of the control changes until it attains the value required to make the steady-state error zero. The controller output is calculated with:

$$p(t) = \bar{p} + \frac{1}{\tau_I}\int_0^t e(t^*)dt^* \quad (4\text{-}4)$$

In an integral control system, the control action takes place until the error signal has persisted for some time. However, integral control systems are seldom used, since it can cause the present value to overshoot the set point value. The more common applied controller is an integral controller in conjunction with a proportional controller. This combination is called the proportional-integral (PI) controller. The output of a PI controller is shown in the following equation:

$$p(t) = \bar{p} + K_c\left(e(t) + \frac{1}{\tau_I}\int_0^t e(t^*)dt^*\right) \quad (4\text{-}5)$$

The corresponding transfer function of the PI controller is given by:

$$\frac{P\prime(s)}{E(s)} = K_c\left(1 + \frac{1}{\tau_I s}\right) = K_c\left(\frac{\tau_I s+1}{\tau_I s}\right) \quad (4\text{-}6)$$

4.3.3 Derivative control

The derivative controller first considers the rate of change of the error signal, followed by anticipating the future behaviour of the output value. The output of the derivative controller is calculated with:

$$p(t) = \bar{p} + \tau_D\frac{de(t)}{dt} \quad (4\text{-}7)$$

Where τ_D = the derivative time.

The derivative control is always used in conjunction with proportional (P) or proportional-integral (PI) control. The corresponding transfer function of the derivative control is:

$$\frac{P\prime(s)}{E(s)} = K_c(1 + \tau_D s) \quad (4\text{-}8)$$

4.3.4 Proportional-Integral-Derivative Control (PID)

The combination of the aforementioned proportional, integral and derivative control mode is called proportional-integral-derivative (PID) control. According to (Desborough and Miller, 2001), PID controllers form 97% of the control systems in process industries. PID controllers can be applied in many variations. The controller block that is applied in the design of the MaC, is a built-in PID controller designed by Yokogawa control systems. The PID controller can be operated in manual, automatic or cascade mode.

4.4 MaC control system

For monitoring and controlling the MaC variables, the Yokogawa Centum CS3000 R3 control unit is applied. The distributed control unit (DCS) of the CS3000 consists of a Field Control Station (FCS) and a Human Interface Station (HIS) integrated with an Engineering station (ENG). The FCS is connected directly (analog or digital) to the different measuring and controlling instruments of the crystallization setup. The HIS is a standalone computer running on Windows XP service pack 2, integrated with the ENG station (software). The software is licensed to TU Delft with CRYSCODE

as project name. The overview of the control system is shown in Figure 4.3. The communication bus between the HIS and FCS is called V-Net. Maximum 32 stations can be connected to the V-Net of the CS3000 model.

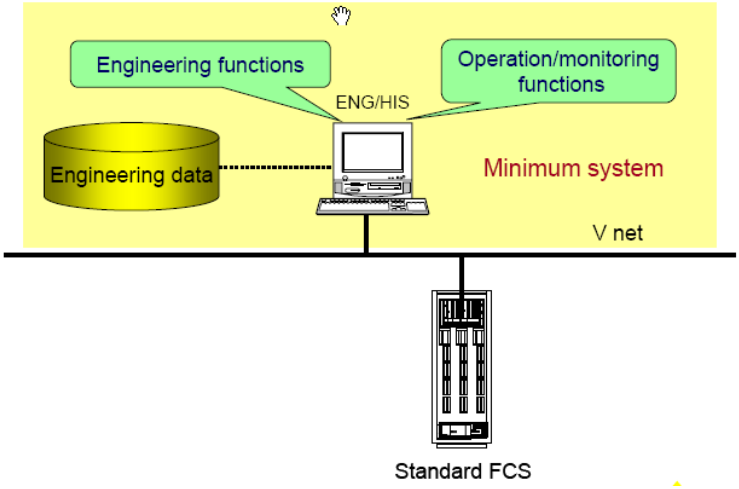


Figure 4.3: Overview of Yokogawa control system

The design of the control system for the MaC setup is therefore developed in the software program of Yokogawa. The procedure to develop the control system is by applying the following steps:

1. Defining the input and output terminals (analog or digital);
2. Creating the control drawings for monitoring and controlling;
3. Creating the graphical interface for operation;
4. Identifying the trending data for saving experiment results.

4.4.1 Defining inputs and outputs

The Yokogawa DCS has 8 modules on which the different instruments of the setup are connected. These are:

- Three Resistance Temperature Detector (RTD) modules for resistance thermometers (pt100). The pt100s are temperature sensors mounted on the different vessels and tubes. The type of the module is AAR145-S and has 16 input channels. These modules are operating on the 4-20 mA current;
- One digital module, type ADV859-P, with 16 input and 16 output channels, operating on the 4-20 mA current. This module is mainly applied for the level controllers and control of the tracing;
- One analog module, type AAI141-S, with 16 input channels, operating on the 4-20 mA current. This module is mainly applied for the monitoring of flow and level sensors;
- Three analog modules, type AAI841-S, with 8 input and 8 output channels, operating on the 4-20 mA current. These modules are applied for controlling pumps, stirrers and thermostatic baths.

All the instruments on the crystallization setup are defined by a tag name. These tag names are incorporated in the design of the control system. The input and output signals in the Yokogawa software are recognized by their tag names. A complete list of the applied channels and tag names is shown in Appendix B.

In the Yokogawa software, named System View, the input and output signals of the FCS are defined in folder "NODE1" under FSC0101, where all the aforementioned modules are visible. As mentioned earlier, each input and output terminal is defined with the correct tag name in the correct module, as shown in the list in Appendix B. These tag names are now used in the second step, creating the control drawings.

4.4.2 Control drawings

The control drawing is a unit in which the function blocks, the minimum components of the basic control function, are grouped for the control system. Control drawings are created in the folder "Function block" of the System View. An example of a control drawing is shown in Figure 4.4.

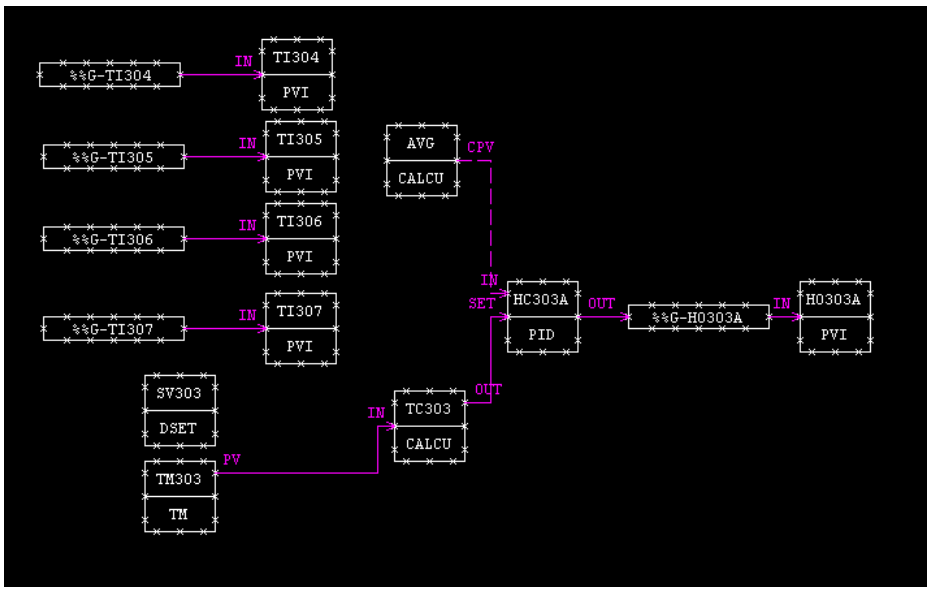


Figure 4.4: Control drawing to maintain the temperature inside the crystallizer

The PID block is used to control an equipment connected on the setup. Tag names with "%%-G" are inputs and outputs connected directly to the setup. Low and high limit values, as well as engineering units and alarms can be defined in these blocks. Calculation blocks are used to define equations.

The drawing shown in Figure 4.4 is used to set a cooling profile during a cooling batch crystallization process and to maintain a constant temperature inside the airlift crystallizer. The temperature sensors (TI304-TI307) mounted on the airlift crystallizer (T303) are used as input signals from a (input) terminal on the FCS for monitoring. The hardware connection of the temperature sensor to the FCS is defined in a process input-output block (PIO) (for example, %%G-TI304). The RTD module of the control system is converting the measured resistance directly into a temperature, which is defined by the PVI block (for example, TI304). A calculation block (AVG) is used to calculate the average temperature inside the crystallizer. The average temperature (AVG) is used as an input signal to the PID controller HC303A. Therefore, AVG is the process value of HC303A. HC303A is a PID controller which calculates the difference between the process value and the set point value, and sent the calculated value to the thermostatic bath, which is defined as %%G-HO303A, via an output card on the FCS. The set point value of the PID controller (HC303A)

can be set manually or is calculated from the equations of the cooling profile, which are defined in the calculation block TC303. The cooling profile is only required when performing cooling batch experiments. A timer block (TM303) is required when using a cooling profile. The timer can be applied either in seconds or minutes, up to a value of 1,000,000. During continuous cooling and continuous membrane-assisted experiments, no cooling profile is required. Therefore, the PID controller is operated manually or automatically. As mentioned earlier, the PID controller is calculating the difference between the process value and the set point value, which is called the manipulated value, and uses this as an output signal back to the (output) terminal of the FCS. This terminal, HO303A, is connected to the thermostatic bath of the airlift crystallizer. In this way, temperature sensors connected to the airlift crystallizer are used to control the thermostatic bath.

For each instrument an individual control drawing is created to develop a reproducible and user friendly control system. Some of the important drawings are given in Appendix B. In the Yokogawa CS3000, 200 drawings can be specified.

Airlift temperature

The monitoring and controlling of the temperature in the airlift crystallizer is described through the aforementioned example. The control drawing of the temperature control of the airlift crystallizer can be seen in Figure 4.4 The resistance thermometers (pt100) connected on the airlift crystallizer are operating on the 4 – 20 mA current. The 4 mA is related to the low limit temperature, which is set to 0 ^{o}C and the 20 mA is related to the high limit temperature, which is set to 100 ^{o}C. To adjust the temperature of the solution to the temperature of water in the jacket, a 10 L thermostatic bath (HE303) is connected. This thermostatic bath is operating on the 4-20 mA current which is related to the low and high limit of 0 ^{o}C and 100 ^{o}C respectively.

Membrane unit temperatures

The resistance thermometers (pt100) connected to the inlets and outlets of the membrane unit (T401) are used for monitoring the inlet and outlet temperatures of the solution and sweeping gas. A process value indicator (PVI) block is used in the software to define the temperature sensors of the membrane unit. The temperature sensors connected to the setup are wired to the RTD module of the FCS. The resistance measured by this card is converted directly to temperatures. The low limit of the temperature is set to 0 ^{o}C and the high limit is set to 100 ^{o}C.

Airlift pressures

On the crystallization setup three pressure transmitters of Siemens (Sitrans DSIII) are used to measure the pressure differences in the crystallizer. The functions of these transmitters are mentioned in paragraph 3.3. PVI blocks are used for monitoring the pressure differences. The pressure transmitters assembled on the airlift crystallizer are wired to the digital input of the FCS, which converts the measured value directly into a pressure difference. During experiments, the measured pressure difference is used to determine the liquid circulation velocity in the airlift crystallizer. The pressure differences in the riser and downcomer are operated between 0 and 125 mbar. The pressure difference between the riser and the ambient pressure is operated between 0 and 75 mbar. This pressure transmitter is used to determine the level in the airlift crystallizer during the

experiments. The lower and higher limit values of the pressure transmitters are also used in the design of the control system, which are related to the 4 – 20 mA current.

Tracing control
Tracing is used to prevent crystallization in the pipelines due to the lower temperature of the environment. The temperature of the pipelines is measured with pt100 sensors. PVI blocks are used to define these input signals. As the tracing is only a wire which can be turned on or off, and exceeds temperatures beyond 100 ^{o}C, it is important to limit these temperatures for the safety of plastic tubes. Temperatures far below or above the required temperatures can cause unwanted density and concentration changes in the pipelines. Therefore, a calculation block is used to limit the temperatures for tracing. The temperatures measured by the pt100s on the pipelines are used as inputs for the (digital) output of the tracing. The control of the tracing is operating on the 4 – 20 mA current. Low and high limits are applied as 0 ^{o}C and 100 ^{o}C respectively.

Stirrer control make-up vessel
The stirrer (M302) of the make-up vessel (T302) is a SPX Lightnin model Mi5P1 of Axflow B.V. operating by a Hitachi frequency controller, integrated in the electronics cabinet. A set point controller block (DSET) is applied to control the stirrer. The low and high limit is set to 0 and 1500 rpm respectively. These limits relate to 0 to 50 Hz on the frequency controller. According to the electrician, it is mandatory to operate the stirrer at a minimum speed of 250 rpm (20% of the frequency). This is for the electronically safety of the controller.

Stirrers of the feed vessel and buffer vessel are not connected to the FCS and must be operated manually.

Flow and pump control
There are 2 Omega flow meters (model FMG82) assembled on the setup. One is connected to the feed line to the airlift crystallizer and the other one is connected to the supersaturated line from the membrane unit to the crystallizer. The Omega flow meters are operated on the 4-20 mA current. According to the specifications of the manufacturer the 4 and 20 mA are related to a flow rate of 0.114 l/min and 11.365 l/min respectively. The values of the flow meters are applied as inputs to control the peristaltic pumps (Model 323U). For the control of these pumps PID control blocks are used. It must be noted that the flow rate of the pumps depends on the diameter of the tubing. Currently, Marprene tubes with an internal diameter of 4.8 mm are installed. The lower and higher limit values according to the description provided by the manufacturer are 0.096 ml/min and 0.880 ml/min respectively.

As mentioned earlier, the mass flow meter is an M15 type Coriflow designed by Bronkhorst Nederland BV and is applied to monitor the mass flow of the product (in continuous operation). Therefore, a PVI block is applied for monitoring. According to the description provided by the manufacturer the analog connection is operating between 0.6 kg/h (4 mA) – 30.0 kg/h (20 mA).

The peristaltic pump between the make-up and feed vessel is not connected to the FCS. This pump has to be controlled manually.

Level sensors
The following level sensors are applied in the design of the MaC:

- Feed vessel: in the feed vessel an eTape is applied for measuring the level. The total length of the eTape is 30 cm, where 0 mA is related to 0 cm and 20 mA to 30 cm. A PVI block is applied to monitor the level in the feed vessel.
- Buffer vessel: in the buffer vessel an ultrasound level sensor is applied to measure the level in the vessel. The low limit of 4 mA is related to -9 mm and the high limit of 20 mA is related to 294 mm.

Thermostatic bath monitor and control

The make-up vessel (T302), feed vessel (T301), airlift crystallizer (T303) and buffer vessel (T304) are each connected to individual thermostatic baths. According to the description provided by the manufacturer, two input and two output signals can be connected to the FCS. There is an option given on the monitor of the device to select the desired inputs and outputs. Contrary to the inputs and outputs of the FCS, the inputs and outputs on the device (thermostatic baths) are inputs to and outputs from the device. Currently, only one input and one output are used. The internal bath temperature of the thermostatic bath is applied as an input to the FCS and set point values are applied as output from FCS to thermostatic bath. Both the input and output are set to the 4-20 mA current on the device. The lower limit corresponds to 0 ^{o}C and the higher limit to 100 ^{o}C respectively. The control drawing of the airlift crystallizer is shown in Figure 4.4. A brief description of the different blocks is given in the **Airlift temperatures** section.

To control the thermostatic bath of the make-up vessel (T302) and feed vessel (T301), the temperature sensor assembled in the vessels is employed to define the PID block.
The same principle is applied to control the thermostatic bath (HE304) of the buffer vessel (T304). Instead of a temperature sensor inside the vessel, the temperature sensor (T403) before the entrance of the membrane unit is used to control the bath.

The control of the thermostatic bath (HE303) connected to the airlift crystallizer (T303) depends on the crystallization process. For continuous processes one (constant) temperature is required. A PID control block is used in manual or automatic mode to maintain the constant temperature. During the cooling crystallization process, a cooling profile is required. The cooling profile is divided into a linear profile and a third-order profile. Therefore, the PID controller block is extended with a calculation block and a timer. The timer can be set to operate in seconds or minutes. Seconds are used to set the timer. To set a cooling profile, it is mandatory to run the PID block in cascade mode.

Plunger pump control

The plunger pump (P306) is used for the flow to the membrane unit (T401) and is connected to a frequency controller to increase or decrease the pump speed. At the lower side of the buffer vessel (T304) an on-off level switch (LI303) is assembled. This switch is sending a signal to the control system. If the level in the vessel is lower than the switch, the process value is one (PV = 1), and if the level is higher than the switch, the PV = 0. This input is applied for the safety of the plunger pump (P306). A calculation block is used in combination with a set point block, to control the pump and automatically switch off the pump if the level in the vessel is lower than the switch.

Table 4.2: Summary of the limits

Instrument	Analog or digital current [mA]	Value	Engineering units
Airlift temperatures	RTD card	0 – 100	[°C]
Membrane unit temperatures	4 – 20	0 – 100	[°C]
Pressure difference in airlift	4 – 20	0 – 75/0 – 125	[mbar]
Tracing temperatures	4 – 20	0 – 100	[°C]
Thermostatic baths	4 – 20	0 – 100	[°C]
Vessel temperatures	4 – 20	0 – 100	[°C]
Volume flow meters	4 – 20	0.114 – 11.365	[l/min]
Mass flow meter	4 – 20	0.6 – 30.0	[kg/h]
Level feed vessel	4 – 20	0 – 30	[cm]
Level buffer vessel	4 – 20	-9 – 294	[mm]
Peristaltic pumps	4 – 20	0.096 – 0.880	[l/min]
Stirrer make-up vessel	Frequency controller (0-50 Hz)	0 – 1500	[rpm]
Plunger pump	Frequency controller (0-50 Hz)	0 – 1410	[rpm]

A detailed description of Table 4.2 is given in Appendix B.

4.4.3 Graphical interphase

After defining the input and output signals of all the relevant function blocks, the graphical interphase is created. The graphical interphase is created in the folder “windows” under HIS032 of the System View. This interphase is a drawing with the main menus of the process equipment to monitor and control. In the graphical interphase the defined input values, set point values and output values are shown when defined. These are known by their tag names used in the function blocks. Various possibilities are available to create a graphical interphase, for example call windows, process variables, set point variables, trend data, tuning, etc. An important aspect to develop a user friendly and reproducible interphase is to draw a clear overview and make a difference between monitoring and controlling values. In Figure 4.5 the main window of the crystallization process is shown.

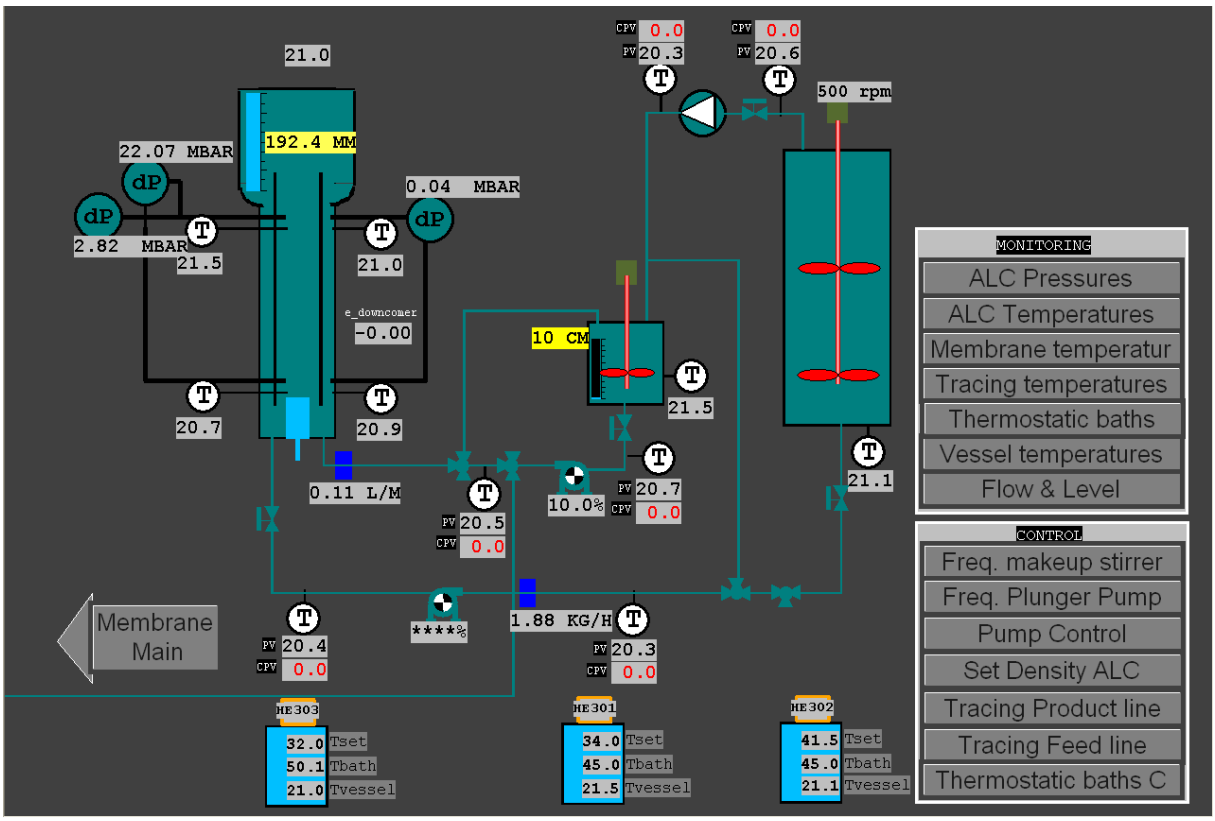


Figure 4.5: Graphical interphase of main menu airlift

4.4.4 Trending and saving results

One of the important parts of a control unit is saving all important input and output data for analysis. The data of the CS3000 are defined in the folder "Configuration" under HIS0132. Recorded data are processed in the so called trend acquisition data. The sampling period of the trending data can be set to 1 sec, 10 sec, 1 min, 2 min, 5 min or 10 min. Depending on the sampling period, the software is recording and saving the data to its related time. Currently the trending period is set to 10 sec. Using a period of 10 sec, the software is saving data up to 8 hours.

In each group 8 process variables can be defined for trending. It is important to define the tag names used in the function block for the correct saving of data. In case of saving process values, the tag name is extended with .SV. Currently, eleven groups are used to record and save data from the control unit. These are: airlift temperatures, membrane unit temperatures, tracing temperatures, peristaltic pump flow rates, flow and levels, airlift pressure differences, vessel temperatures, temperatures of thermostatic baths connected to make-up vessel, feed vessel, airlift crystallizer and buffer vessel.

For the extraction of data from the Yokogawa database, an MS-DOS batch file is made and saved under "My Documents". The name of this file is storedataAirlift.bat. To extract data, the user has to double click on this batch file. The saved data can then be found under C:\CS3000\his\save\TREND. Note that every double click on the batch file overwrites previous saved data. Therefore, it is important to copy and save the data to another location. It must be noted that the Yokogawa software is only recording the data according to its trending period. All data before this trending period is not saved. For example, if the trending time is set to 10 sec, data are recorded for 8 hours. If an experiment exceeds 8 hours, it is important to save data, with the batch file, before 8 hours after the start of an experiment, and so on.

5

Testing, troubleshooting and optimization

After the construction of the MaC setup and the integration of the control unit, test experiments were designed and performed to troubleshoot and eventually solve detected errors. The approach and results of these test experiments are described in this chapter.

5.1 Test procedure and troubleshooting

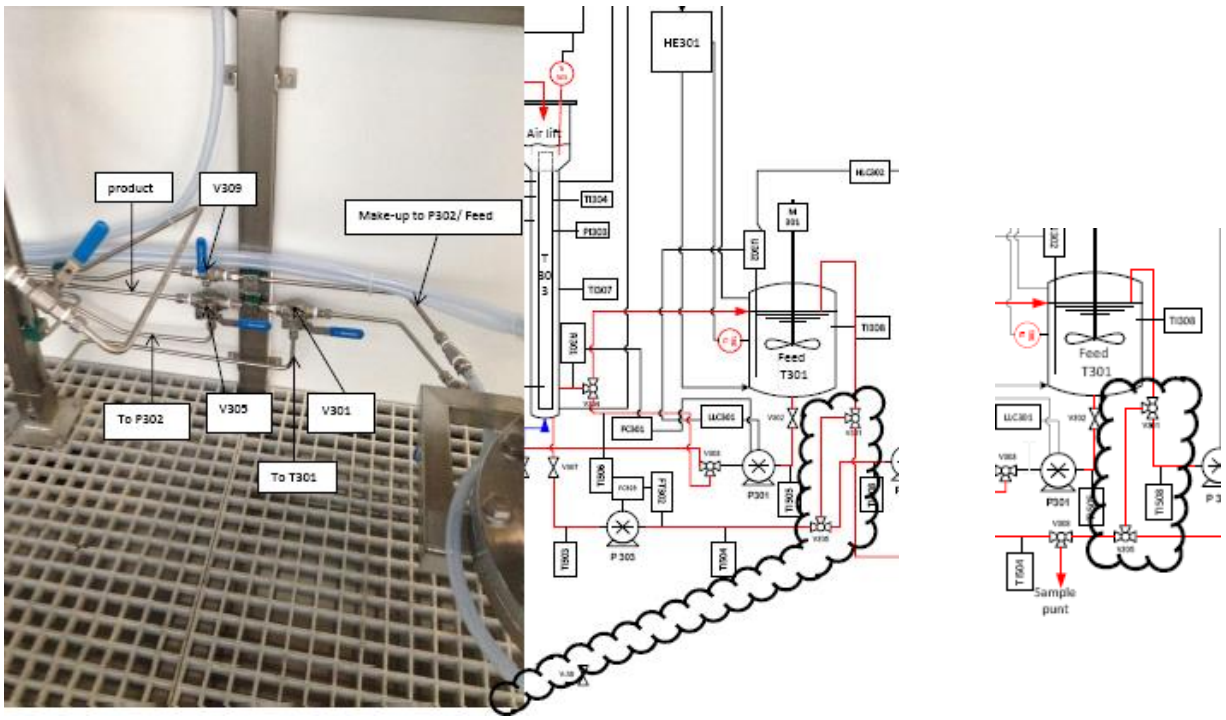
The main goal here is to detect failure of equipment, and to calibrate and validate the operation of the MaC setup. The following procedure has been applied to the testing of the setup, including the equipment:

1. Inspection of the setup, to detect hardware errors;
2. Inventory of the primary needing to perform test experiments;
3. Testing of all the instruments individually and in combination;
4. Testing of the control unit;
5. Perform test experiments.

5.1.1 Setup inspection

Inspection of the setup had been started during its construction. The new experimental setup is assembled by MB Mechanisatie in Maasland. During the construction, a few meetings were organized at site for inspection and discussion. After the construction of the new setup was finished, this was moved to the new laboratory of the Process & Energy department. At the new laboratory, a special team from the P&E workshop integrated the control unit on the setup.

Every part of the setup was inspected according to the process flowsheet (PFD) of the MaC. The inspection of the setup resulted in three errors. First, the 3-way valve (V305) in the product line (PL304) was connected to the wrong tubes. According to the PFD, the product flow (PL304) from the airlift crystallizer (T303) is connected via a 3-way valve (V305) directly to the make-up vessel (T302). From this 3-way valve (V305) there is a connection back to the feed vessel (T301) via another 3-way valve (V301). This connection is used during rinsing. Instead of connecting the product flow directly to the make-up vessel, this was connected back to the feed vessel. In Figure 5.1 the difference between the designed and constructed connection is shown.



(a) (b)

Figure 5.1: (a) wrong construction, (b) according to PFD

The second error during the inspection was the connection of the flow meter (FC301) between the feed vessel and the airlift crystallizer. The flow meter was assembled upside down and could not send any signal to the control unit.

A third error during the inspection was the connection of pressure transmitter PI302 which measures the pressure difference in the riser of the airlift crystallizer. The “plus” and “minus” sign of the transmitter was changed. In this way, the pressure transmitter gives a negative value. As the control system is not able to process a negative value (low limit is zero), wrong data will be saved during experiments.

After the inspection, the above-mentioned errors were fixed, partially by MB Mechanisatie and partially by myself.

5.1.2 Inventory of needed supplements

Before performing test experiments, it is important to inventory the primary needing to perform the experiment. The test experiments are performed first with the airlift crystallizer section, second with the membrane unit section and third airlift crystallizer in combination with the membrane unit. In this way, standalone operations, as well as operations in combinations are performed to have a first feasibility test. Prior to these unit operations, all the equipment on the setup were first tested individually with water. The needed supplements for these operations are listed in table 5.1.

Table 5.1: List of primary needing per equipment

Operation	Needed
Airlift crystallizer (with make-up and feed vessel)	• Water (vessels) • Electricity (220 V/50 Hz) for pumps (P301, P302, P303), thermostatic baths (HE301, HE302, HE303) and stirrer feed vessel • Electricity for the frequency controller of the stirrer on the make-up vessel • Air/N2 for mixing the medium in the crystallizer
Membrane unit	• Water (buffer vessel) • Electricity for the plunger pump P306 (frequency controlled) and stirrer of the buffer vessel • Air as sweeping gas
MaC	• Above-mentioned points + electricity for pump P304 (membrane to airlift)
Control unit	• Signal between instruments and FCS

5.1.3 Equipment test

As shown in Table 5.1, the equipment test is mainly divided into three sections: airlift crystallizer section, membrane unit section and airlift in combination with membrane unit.

Airlift crystallizer section

The airlift crystallizer section consists of a make-up vessel (T302), feed vessel (T301) and airlift crystallizer (T303), where water is circulated continuously through these vessels to detect errors.

(a) (b)

Figure 5.2: (a) Airlift crystallizer section, (b) membrane unit section

The procedure starts with filling the make-up vessel (T302) with enough water, after the thermostatic bath (HE302) is switched on and the vessel is preheated. The main focus here is to detect leakages of the vessels and the signal between the pt100 (TI309) connected to the vessel and the FCS. Another important point to observe is, if there is enough water in the thermostatic bath

(beyond the heater), and if the flow from the thermostatic bath to the vessel is circulating from the bottom to the top. This is important to prevent air in the jacket when this is filled for the first time.

The second step of the test is to shift the water from the make-up vessel (T302) to the feed vessel (T301). Prior to the shifting of water, all the valves on the pipeline (PL301) between the make-up vessel (T302) and feed vessel (T301) have to be switched to the correct direction. The thermostatic bath (HE301) connected to the feed vessel (T301) is turned on to heat up the vessel, followed by transferring the water from the make-up vessel (T302) to the feed vessel (T301) by starting the peristaltic pump P302. All the valves, tubes and connections between the make-up vessel and feed vessel are observed on leakages.

The third step is to transfer the water from the feed vessel (T301) to the airlift crystallizer (T303). The thermostatic bath (HE303) connected to the airlift crystallizer (T303) is switched on to heat up the crystallizer. Pressurized air of 2 bar and a flow rate of 200 l/h is added to the airlift crystallizer (T303) for the circulation of the water. All the valves on the pipeline (PL302) between the feed vessel (T301) and the airlift crystallizer (T303) are switched to the correct direction. Shifting of the water starts by starting the peristaltic pump P301. All the valves, tubes and connections are observed on leakages. Together with the physical observation, the communication between the instruments and the FCS is noticed. If no errors are detected, the procedure is continued by opening all the valves in the product line (PL304). By starting the peristaltic pump P303, there is a continuous flow between the make-up vessel, feed vessel and the airlift crystallizer. According to the PFD, there is a sample point (V308) integrated with PL304, and a circulation line (PL302) of the feed vessel is designed. The flow in these tubes is then tested by switching the valves to the correct position.

The last step is to stop the experiment and drain the vessels. Draining is performed by transferring all the water back to the make-up vessel (T302) and drain from the bottom of the vessel (V310). Good coordination is required to drain the vessels. First, pump P302 is stopped to empty the feed vessel. Second, pump P301 is stopped to empty the airlift crystallizer and last, pump P303 is stopped. The make-up vessel can now be drained from the bottom and all the thermostatic baths can be switched off.

Membrane unit section

The membrane unit section consists of a buffer vessel (T304), membrane module (T401) and the plunger pump (P306). Testing this section on errors starts with switching on the thermostatic bath (HE304) connected to the buffer vessel (T304) and observe on leakages, followed by filling the buffer vessel with water. The second step is to open the valves on the pipelines (PL401 and PL402) between the buffer vessel and the membrane module. Third step is to switch on the plunger pump P306, which is operating on a frequency controller. This pump should never be switched on when there is no medium in the buffer vessel. That is why the buffer vessel is constructed with a low limit switch (LI303). Air is added to the membrane module as sweeping gas. All the tubes, valves and connections are observed on errors and leakages. The connected ultrasound level sensor (LI304), low level switch (LI303) and pt100s are observed in communication with the FCS.

The last step is to stop the experiment and drain the buffer vessel. It is important to first stop the plunger pump P306 and close the valves (V314 and V315) of the membrane module (T401), to keep the membrane module wet. Once the membrane module is operated with liquid, it should always be kept filled with water to prevent drying of the membrane. An open-close valve is connected to the plunger pump to drain the buffer vessel.

In combination
To complete testing of the total setup, the airlift crystallizer section is combined with the membrane unit section. The steps one to three from the airlift crystallizer section are followed to start the testing. From this point, the buffer vessel can be filled either through the overflow (PL303) or by the feed vessel (T301). Both of them have to be noticed on errors. After the buffer vessel (T304) is filled and the valves (V314 and V315) between the buffer vessel (T304) and membrane module (T401) are opened, the plunger pump is switched on. The testing is continued by switching on the peristaltic pump P304 between the membrane module and the airlift crystallizer. In this way, there is a continuous flow between the make-up vessel (T302), feed vessel (T301), airlift crystallizer (T303), buffer vessel (T304), membrane module (T401) and back to the make-up vessel (T302) through the airlift crystallizer (T303). All the parts of the setup is observed on errors. After the test, the vessels are drained, according to the aforementioned methods. A detailed flowsheet on performing experiments and cleaning can be found in Appendix C and D respectively.

After an experiment, left over solution may stay or stick to the wall of the vessels and tubes. These left over may clog tubes and valves, and may affect next experiments. Therefore, to prevent blockage of tubes and valves, and prevent side reactions in next experiments, it is important to carefully rinse the vessels and tubes. It is recommended to use warm water (> 50 ^{o}C and < 70 ^{o}C) for the rinsing, and the pumps should operate at maximum flow rates. Another recommendation is to leave a small amount of water in the vessels and tubes after an experiment, and remove this before starting with a new experiment.

Calamities
In case of calamity during experiments, for example a broken Marprene tube, first stop the related pumps, then close the valves of the related vessels.
Pressing the emergency stop, connected to every corner of the skid, will shut down the total power supply, except the power supply to the Yokogawa control system. In such a case, it is recommended to consult the electrician of the workshop.

5.1.4 Control unit

After the instruments of the new setup are wired with the FCS and the design of the control unit is downloaded to the HIS, all the instruments can be monitored and controlled via the computer. During the test experiments, all these instruments are observed by its functioning and if possible, calibrated with external instruments. The first experiences with these instruments have shown that it is important to connect the wires to the correct terminals. For example, the first connected pt100s showed no signal to the FCS. After the “plus” and the “minus” sign of the wires were changed by an electrician, the signal between all the pt100s and the FCS was optimal. These errors were also detected for the flow meters, pumps and frequency controllers.

Flow meters and pumps
The control unit only processes current signals between 4 – 20 mA. Due to an unknown problem, the 323U peristaltic pumps are not operating with the current signals. The 0 – 10 V signal of the pump is converted to a current signal by applying resistance wires. According to the description given by the manufacturer, the operating condition of the peristaltic pumps lies between 6.6 – 880.0 ml/min, when using a tube with an internal diameter of 4.8 mm. To validate these limits, the pumps are manually and analogue tested with water at room temperature. The results of the test experiments with the pumps are shown in Table 5.2 and Figure 5.3.

Table 5.2: Flow rates of the 323U pump, Marprene tube 4.8 mm

Pump speed [rpm]	Pump speed [%]	Manufacturer Flow rate [ml/min]	Manual Flow rate [ml/min]	Analogue Flow rate [ml/min]
3	0.0	6.6		52.4
11	2.0	24.2	24.7	194.8
23	5.0	50.6	51.2	218.2
35	8.1	77.0	78.4	241.0
43	10.1	94.6	98.4	257.5
82	19.9	180.4	188.7	331.5
162	40.1	356.4	392.2	495.9
202	50.1	444.4	483.9	588.2
241	59.9	530.2	600.0	666.7
321	80.1	706.2	810.8	789.5
400	100.0	880.0	1090.9	967.7

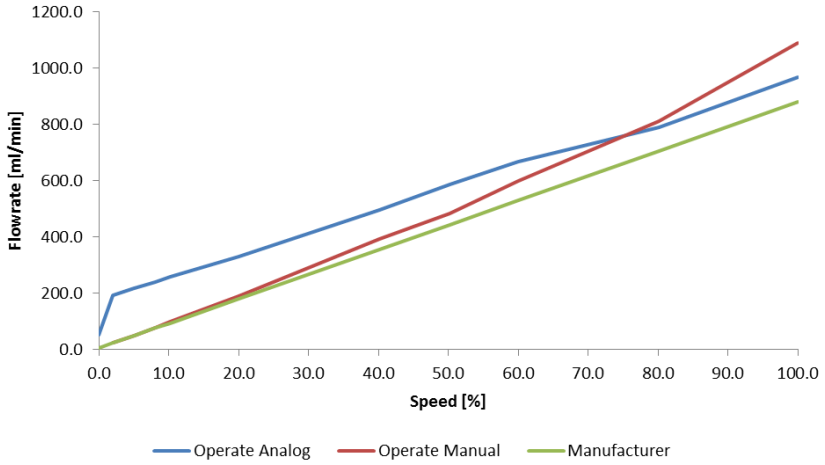


Figure 5.3: Flow rates of the 323U pump, Marprene tube 4.8 mm

As shown in Figure 5.3, there is a difference between the values given by the manufacturer, operating manually values and operating analogue values. According to the manufacturer, the measured values are better than the given values. The difference between the manufacturer values and manual operating values exist because of differences in distances. A height difference between the sucking section and the blowing section may build a hydrostatic pressure. The difference between the analogue results and manually measured results is generated by the inaccuracy of the resistance. When the high limit of the pump (P301) is set to 880 ml/min in the control system, and the pump is operating at maximum speed, it can be seen that the value of the flow rate measured by the flow meter (FT301), is higher than 880 ml/min. Instead of using the values given by the manufacturer, the measured values (analogue) are applied to the control unit.

Temperature sensors

Another minor problem is the inaccuracy of the pt100s. Differences between 0.5 and 1.5 ^{o}C are experienced in the airlift crystallizer during the experiments. Unfortunately this error cannot be minimized, as the resistance of the pt100 depends on various aspects, for example distance between pt100 and the FCS, type of the wires, etc.

Level sensors

The limits of the ultrasound level sensor (LI304), connected to the buffer vessel (T304), are set between -9 mm and 294 mm. These are the optimal values for the sensor. The sensor is responding fast and has good accuracy. Although, the 12” eTape level sensor (LI302) connected on the feed

vessel (T301) is less precise and responds slow. The eTape gives only a respond beyond the 2 cm level.

Other measuring and controlling equipment are not calibrated with external instruments.

Tuning of PID controllers

In the new setup, PID controllers are applied for flow meters and temperature control (thermostatic baths). The design of the PID controller is described in chapter 4. According to Process Dynamics and Control book [27] Section 11.5.1, a trial-and-error procedure is available for online controller tuning:

- Step 1. After the process has reached steady state, eliminate the integral and derivative control action by setting the derivative time to zero and integral time to the largest possible value.
- Step 2. Set the gain K_c equal to a small value (e.g., 0.5) and place the controller in the automatic mode.
- Step 3. Introduce a small, momentary set point change so that the controlled variable moves away from the set point. Gradually increase K_c in small increments until continuous cycling refers to a sustained oscillation with constant amplitude. The numerical value of Kc that produces continuous cycling is called the ultimate gain, K_{cu}. The period of the corresponding sustained oscillation is referred to as the ultimate period, P_u.
- Step 4. Calculate the PID controller settings using the Ziegler-Nichols (Z-N) tuning relations. These relations are shown in table 11.4 of [27] Section 11.5.1.
- Step 5. Evaluate the Z-N controller settings by introducing a small set point change and observing the closed-loop response. Fine-tune the settings, if necessary.

The tuning of the controller is tested for the thermostatic baths, as well as for the flow meters and peristaltic pumps. The PID controller has three modes: automatic, manual and cascade. Manual mode is very useful during plant start-up, shutdown, or emergency situation. Tuning parameters are only active when the controller is operated in automatic or cascade mode.

For the tuning of the thermostatic bath, first the vessel is filled with a medium (water or solution). The pt100 inside the vessel measures the actual temperature, which is called the process value (PV). Flow meters are tested during transferring water from one to another vessel. In automatic or cascade mode, the PID controller calculates the difference between the PV and the set point value (SV). If SV is greater than PV, then the manipulated value (MV), which is the output of the PID, has to increase, and vice versa. In case of a thermostatic bath, the MV value is an input for the thermostatic bath. In case of a flow meter, the MV value is an input for the pump. Tuning parameters determines how fast or slow the increase or decrease of the MV is. The default values of the Yokogawa PID controller are: P = 140, I = 20 and D = 0. If default values are used in the automatic or cascade mode, the MV will increase very fast to the maximum, or decrease very fast to the minimum (and will end up in an error of the unit). This abrupt change (fast oscillation) is an unwanted situation in processes. After changing the P and I values to maximum and minimum, the optimal condition was found at P = 500 and I = 400 sec., when the SV is close to the PV. If the difference between the SV and PV is large, the I value can be lowered first to 50 sec. When the PV reaches the SV, the I value must then again be increased to 400. A more user friendly operation is to operate the PID in manual mode during start-up and shutdown, and when the PV is close to the SV, switch to the automatic mode.

5.2 Design of test crystallization experiments

After the testing and troubleshooting the MaC equipment and control unit, test experiments were designed and performed with melamine and L-ascorbic acid. As melamine is relatively cheaper compared to L-ascorbic acid, melamine was used only as a test compound to check the behaviour of the crystallization setup. From Figure 2.9 and Figure 2.10 can be seen that less melamine is needed compared to L-ascorbic acid to form a saturated solution. For example, to prepare a saturated solution at 50 ^{o}C, 1 g melamine per 100 g water is needed (Figure 2.9), while for L-ascorbic acid almost 60 g is needed, per 100 g of water. As mentioned earlier, the objective of this research is to study the crystallization behaviour of L-ascorbic acid. The properties of melamine, as well as for L-ascorbic acid are given in chapter 2. A summary of the test experiments is shown in Table 5.3. The orders of these experiments are built up with the results that were achieved after every experiment.

Table 5.3: Summary of the test experiments

Exp. ID #	Time [h]	Ms [g]	Seed [µm]	Tsat [^{o}C]	Ts [^{o}C]	Tf [^{o}C]	Cooling profile
1. MEL-B-Cool-20150506	1.5	-	-	50	-	40	LIN
2. MEL-B-Cool-20150508	2.0	11.6	150	50	48	40	LIN
3. ASC-B-Cool-20150521	2.0	-	-	40	-	31	LIN
4. ASC-B-Cool-20150522	4.0	11.6	200	40	31.6	31	LIN
5. ASC-C-Cool-20150604	4.0	-	-	40	-	31	LIN

Where:

- Experiment ID : Compound (melamine or L-ascorbic acid) – Batch or Continuous – Cooling or membrane module – date of the experiment
- Time: total time of the experiment inside the crystallizer, excluding preparation and filtering
- M_s: Seed load in grams
- $T_{sat.}$: Saturated temperature of the solution
- T_s: Temperature at seeding point
- T_f: Final temperature
- Cooling profile: Linear or 3rd order

5.2.1 Melamine experiments

Data on melamine crystallization processes, e.g. concentration change, influence of impurities on nucleation, metastable zone width, are hard to find. Therefore, theoretical and experimental data on the crystallization of melamine found in the work of Chapman et al. [24] and some confidential reports provided by DSM are used for the test experiments. The crystallization experiments performed by DSM were operated at high temperatures (70 – 90 ^{o}C) and impure melamine (ureidomelamine, melem) was used.
The aim of the test experiments with melamine is to test the behaviour of the airlift crystallizer by first, generating a supersaturated solution until the formation of crystals can be observed (primary nucleation) and second, observe the growth of the formed crystals. Therefore, the test experiments on melamine were performed in batch operation.

Preparation
Technical pure grade melamine provided by DSM, The Netherlands, is used for the crystallization experiments. The solubility curve of melamine is shown in Figure 2.9. Since melamine is not very soluble when pure, particularly at lower temperatures, change of the solubility obeys the Clausius-Clapeyron equation, which for melamine is written as:

$$\log(solubility) = -1642 \times \frac{1}{T} + 5.101$$

This above-mentioned equation is used to prepare a saturated solution. As the maximum operating temperature of the Marprene tubing of the MaC setup is 70 ^{o}C, it is recommended to operate at lower temperatures (40 – 60 ^{o}C). As the metastable zone width of melamine is unknown, it was chosen to prepare a saturated solution at 50 ^{o}C, and cool this down to 40 ^{o}C to observe the formation of crystals by primary nucleation. The PVM camera of Mettler Toledo, assembled on the crystallizer, is used to observe the formation of crystals. During the experiments, the density of the solution was measured with an Anton Paar DMA 5000 measurement equipment. However, no reference material of density and concentration was available, the density measurement was only used to analyse the increasing and decreasing trend.

Procedure of the experiments
Batch experiments were designed to observe the formation of crystals by primary nucleation and the growth of these formed crystals. 18 L of normal water was mixed with 185 g melamine for a saturated solution at 50 ^{o}C. According to the solubility curve of melamine, it is assumed that the solution is saturated at this ratio. The airlift crystallizer was operated as a standalone unit. The solution of the first experiment (#1. MEL-B-Cool-20150506) was prepared in the airlift crystallizer (T303). For the second experiment (#2. MEL-B-Cool-20150508), this was prepared in the make-up vessel (T302) and shifted to the crystallizer (T303) by bypassing the feed vessel (T301). The design of this experiment was as follows:

- Measuring the crystal size distribution (CSD) of the pure melamine provided by DSM by using a laser diffraction instrument (Microtrac S3500);
- Preheating the vessel by operating the thermostatic bath at 55 ^{o}C (the thermostatic bath was controlled manually, as this was not connected to the control unit yet);
- Filling the vessel with 18 L water and heating up the water;
- Adding the solute until the solution is saturated;
- Setting a linear cooling profile, measuring the density and tracing of crystals by the use of the PVM camera.

For the second experiment, # 2. MEL-B-Cool-20150508, seed crystals were prepared by using a shaker machine (Retch AS200 Basic) with 212 µm sieves. During the sieving, it was observed that the melamine was agglomerating very fast which makes it difficult to sieve. The reason for agglomeration is unknown and is not investigated further. Therefore, unsieved melamine was used as seed crystals.

5.2.2 L-ascorbic acid experiments

After the behaviour of the crystallizer was tested with melamine, test experiments with L-ascorbic acid were designed and performed. For this compound enough data, such as solubility curve, metastable zone width, the relation between density and concentration, is available from previous experiments with L-ascorbic acid performed by J. van Krochten [9] and K. Mathew Thomas [13]. It is known that L-ascorbic acid solution is oxidizing very fast when it is exposed to open air. To minimize the rate of oxidation, nitrogen is used as a blanket in all the vessels. The technical pure grade L-ascorbic acid is provided by DSM, The Netherlands. Test experiments on L-ascorbic acid were performed for both, batch and continuous operations. The aim of the batch test experiment is to test the behaviour of L-ascorbic acid in the new setup and environment (new building of the P&E department), since the properties of air, nitrogen and water may be different, and to reproduce the

results achieved by J. van Krochten [9]. Since the airlift crystallizer is operating for the first time in continuous mode, one test experiment is performed in continuous operation.

Preparation
For the measurement of the concentration, a density-concentration curve, developed at 35 ^{o}C, is used. This curve is designed and calibrated by K. Mathew Thomas [13] during previous experiments. Therefore, only the density (Anton Paar DMA 500) is measured during all the L-ascorbic acid experiments in this document. In case seed crystals are used, seeds from the 212 µm sieves are collected and measured before an experiment. Operating conditions were used from the reports of J. van Krochten and K. Mathew Thomas [9, 13] to reproduce the same results.

Procedure of the experiment
Batch (#3 and #4) and continuous (#5) experiments were designed and performed. A saturated solution of L-ascorbic acid in water was prepared at 40 ^{o}C, with a concentration of 0.482 g solute/g solvent, in the make-up vessel (T302) and shifted to the crystallizer (T303). Linear cooling profiles were applied for the cooling of the solution from 40 ^{o}C to 31 ^{o}C based on the data from the reports of J. van Krochten and K. Mathew Thomas [9, 13]. Seed crystals are applied at a temperature of 31.6 ^{o}C if used, according to the data found in the reports of J. van Korchten and K. Mathew Thomas [9, 13].
The procedure of the batch operation was as follow:

- Measuring the CSD of the pure L-ascorbic acid, and seeds if used;
- Heating up the make-up vessel (T302) by operating the thermostatic bath (HE302) at 42 oC;
- Switching on the nitrogen to the make-up vessel;
- Fill the make-up vessel with 20 L water and heat up the water (batch experiments);
- Adding 9.64 kg of L-ascorbic acid gradually to the solvent and waiting until the solute is dissolved (batch experiments);
- Preheating the feed vessel (T301) and airlift crystallizer (T303);
- Adding nitrogen to the crystallizer and start filling the crystallizer via the feed vessel;
- Setting a linear cooling profile, measuring density and observing crystal growth by the use of the PVM camera;
- In case of seeds, adding seeds.

The continuous operation was performed without seed crystals and the solution in the crystallizer was cooled from 40 ^{o}C to 31 ^{o}C to detect the formation of crystals by primary nucleation. The same procedure was followed as for the batch operation. 14.46 kg of L-ascorbic acid was added to 30 L water to make a saturated solution with a concentration of 0.482 g solute/g solvent at 40 ^{o}C. In the continuous operation, there is a continuous flow in the following order: make-up vessel (T302) to feed vessel (T301), feed vessel (T301) to airlift crystallizer (T303) and from airlift crystallizer (T303) back to the make-up vessel (T302). A pump speed of 100 rpm (230 ml/min) was chosen for the feed flow, as well as for the product flow.

5.3 Results of the test experiments

#1. MEL-B-Cool-20150506
The first experiment with melamine was carried out for 1.5 hour. The cooling profile of the experiment was linear. First, the solution was cooled down from 55 ^{o}C to 50 ^{o}C in 60 minutes to make this saturated. According to the solubility curve, the solution is assumed to be saturated at 50 ^{o}C (concentration of 1 g melamine/ 100 g water). After the solution was saturated, this was

cooled from 50 °C to 40 °C in 120 min to generate a supersaturation and observe for crystals formed by primary nucleation. Pressurized air of 2 bar and an air flow rate of 200 l/h was added to the airlift. After 90 min. the mixing of the solution in the airlift crystallizer had to be stopped, and the experiment was aborted, because a large amount of crystals were settled on the sparger. Although, no clear crystals were visible during the experiment. Due to the blockage of the sparger, the mixing was stopped. The following solutions have been recommended for next experiments: preparing the solution in the make-up vessel (T302), and by using a higher airflow rate (400 l/h instead of 200 l/h).

#2. MEL-B-Cool-20150508

Accordingly the solution of the second experiment was prepared in the make-up vessel T302) and transported to the airlift crystallizer (T303). Pressurized air of 2 bar and an airflow rate of 400 l/h was added to the crystallizer. The solubility information such as where the metastable zone exactly lies cannot be found in literature. As also no clear crystals were visible in experiment #1, seed crystals were added to test the behaviour of the crystallizer. The CSD of the seed crystals are shown in Figure 5.4. As mentioned earlier, it was observed that melamine has a high agglomerating behaviour which makes it difficult to sieve.

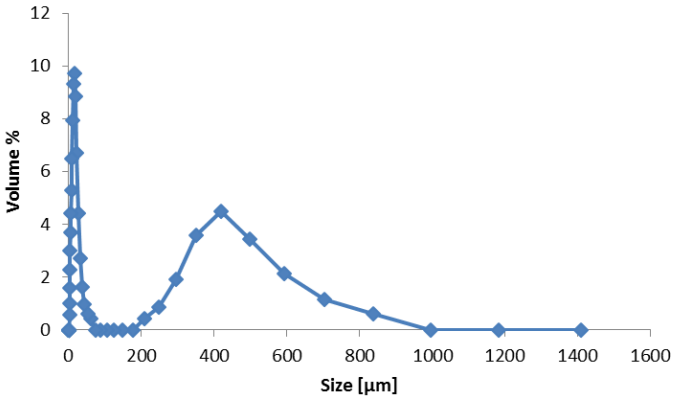


Figure 5.4: CSD of the pure melamine

As shown in Figure 5.4, the CSD of the seed crystals consist of very small crystals (15.5 µm) and a quantity of large crystals (418 µm) in between. The variation between the crystal size is caused by agglomeration. The solution in the crystallizer was set to 50 °C (saturated according to Figure 2.9). At the same temperature of 50 °C, 11.6 g seed crystals, with size variation as shown in Figure 5.4, were added into the solution. Experiment #1 was started from a clear solution and ended up with a blocked sparger within 90 minutes. This indicates that melamine has possibly a fast growth and agglomeration problem. This was already observed during sieving. Therefore, experiment #2 was designed to cool down to 46 °C (instead of 40 °C) in 120 minutes (slower cooling). In such a way, the supersaturation generated for the growth of the seed crystals is expected to be controllable. As mentioned earlier, the metastable zone width cannot be found in literature whereby it is difficult to design a controllable rate of supersaturation for melamine.

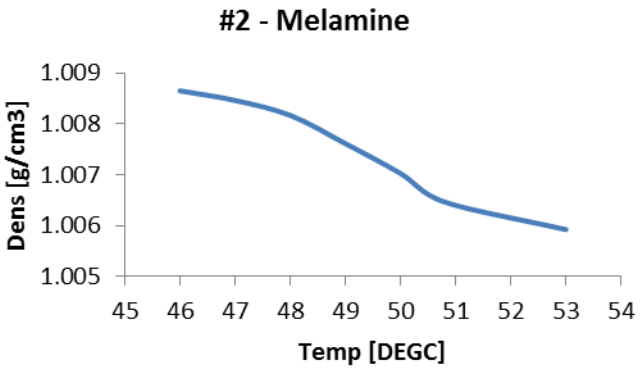
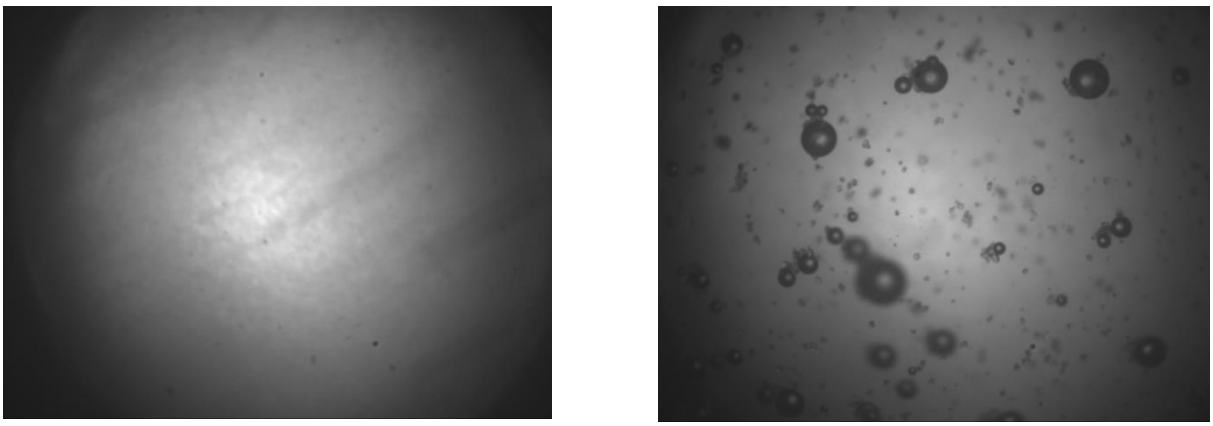


Figure 5.5: Density measurement of experiment #2

In Figure 5.5 the density measurement during the experiment is shown. It can be seen that the density slightly increases during the cooling. Only one sample was taken at each time point for the measurement of the density. Adding seed crystals in a supersaturated solution should (start) consume the supersaturation and the density should decrease. In Figure 5.5 it can be seen that there is no decrease of density from 50 ^{o}C to 46 ^{o}C, possibly due to fast cooling. On the PVM camera, no clear crystals were detected. Possible reasons for this are: no optimal focal settings and point of the lens in the crystallizer, small crystals which cannot be detected by the camera and/or agglomeration behaviour of melamine, which causes the facets of the crystals not to be clear enough to be detected by the camera. As few data are available for experiments on melamine, and no clear crystals were detected during the experiments, it is difficult to conclude on crystal growth and shape. The advice after the experiments on melamine was to abort these experiments with melamine and continue with L-ascorbic acid, as L-ascorbic acid is the main compound for this research.

#3. ASC-B-Cool-20150521

Saturated solution at 40 ^{o}C was prepared for the experiment. A linear cooling profile was set from 40 ^{o}C to 31 ^{o}C in 120 min to generate supersaturation and observe the formation of crystals by primary nucleation. Pressurized nitrogen of 2 bar and a flow rate of 200 l/h was used. The measured density during the experiment was unstable, probably due to the set point temperature of the measurement device. The temperature on the device was set to 20 ^{o}C, while the relation between density and concentration is calibrated at 35 ^{o}C [13]. Possible small crystals were detected by the PVM, which is shown in Figure 5.6.



(a) (b)

Figure 5.6: Crystals of experiment #3: (a) at 40 ^{o}C, (b) after 2 h at 31 ^{o}C

It was advised to optimize the focal point of the PVM camera and perform the next experiment with seed crystals. The lens of the PVM camera was placed close to the wall of the downcomer to make sure that the crystals in the downcomer will pass through the gap of the probe. The settings of the focus was changed online during the next experiment (#4) to collect reliable images.

#4. ASC-B-Cool-20150522

The saturated solution of experiment #3 was kept in the airlift overnight and used for experiment #4. Before starting the experiment, the density was measured. Seed crystals from the 212 µm sieve were collected for the experiment. The solution in the crystallizer was cooled linearly from 40 ^{o}C to 31.6 ^{o}C in 30 min. According to the recipe provided by J. van Krochten [9], 11.6 g seeds were added to the solution at the (seed point) temperature of 31.6 ^{o}C. Prior to the addition of the seeds in the crystallizer, the seeds were first mixed in 100 ml saturated solution for healing. The experiment was continued with a linear cooling profile from 31.6 ^{o}C to 31 ^{o}C in 240 min. During the experiment, the density was measured to analyse the behaviour of concentration, which is shown in Figure 5.7.

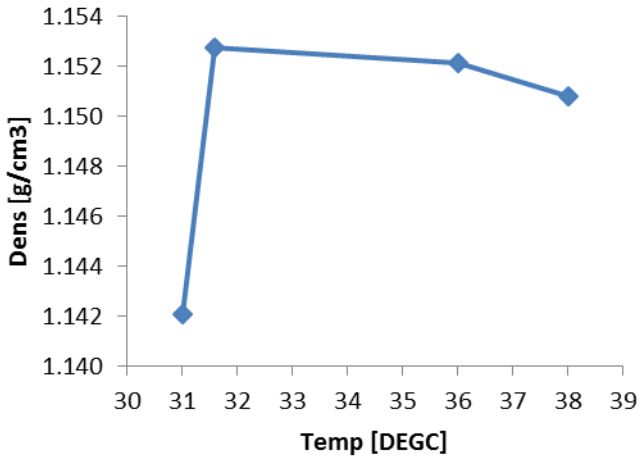
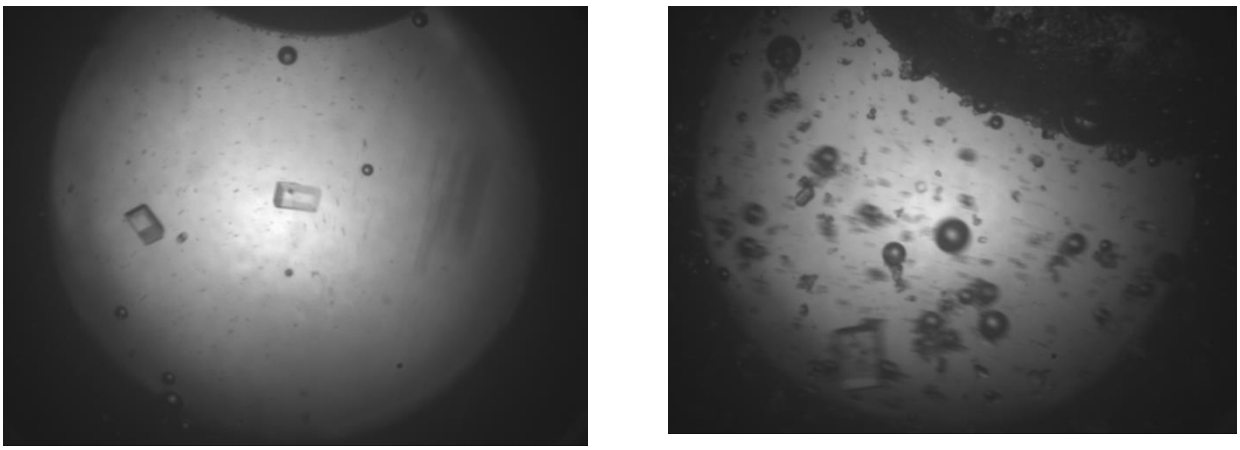


Figure 5.7: Density measurement of experiment #4

In Figure 5.7 it can be seen that the density is slightly increasing while cooling the solution to the seed point (31.6 ^{o}C). From the seed point to final batch, the density is decreased, possibly due to consumption of the supersaturated solution by seed crystals. Only one sample for density measurement was taken at each time point and therefore, no reliable conclusions can be made based on this data. As illustrated in Figure 5.8, the images taken from the PVM camera show promising results.



(a) (b)

Figure 5.8: Crystals of experiment #3: (a) at 40 ^{o}C, (b) after 2 h at 31 ^{o}C

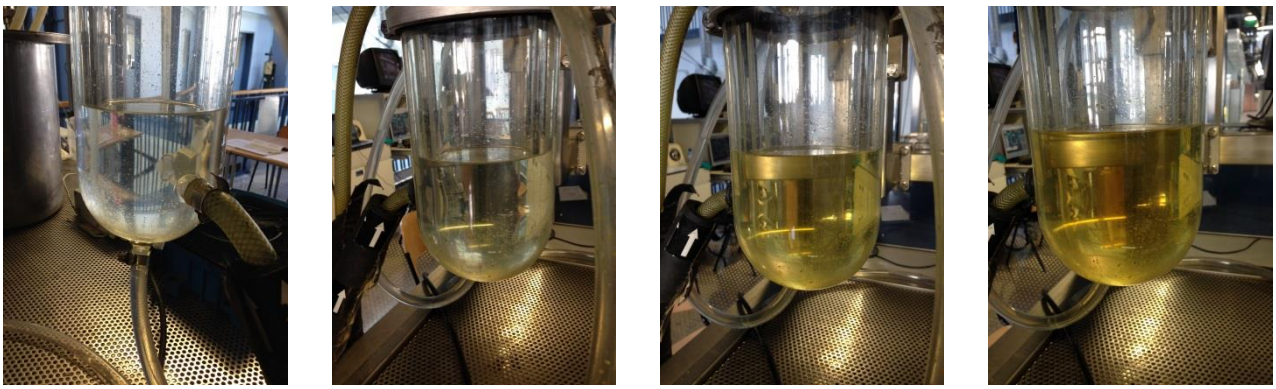
It can be seen that at the end of the experiment, numerous small crystals are formed and some grown crystals are achieved. The small crystals are formed by possibly secondary nucleation due to the fast cooling from 40 ^{o}C to 31.6 ^{o}C and a linear cooling profile.

After the experiment, the crystals were dissolved before draining the crystallizer.

A major problem experienced after the experiment was clogging of the Marprene tubes and the flow meter, see Figure 5.9.

Figure 5.9: Blockage of the flow meter

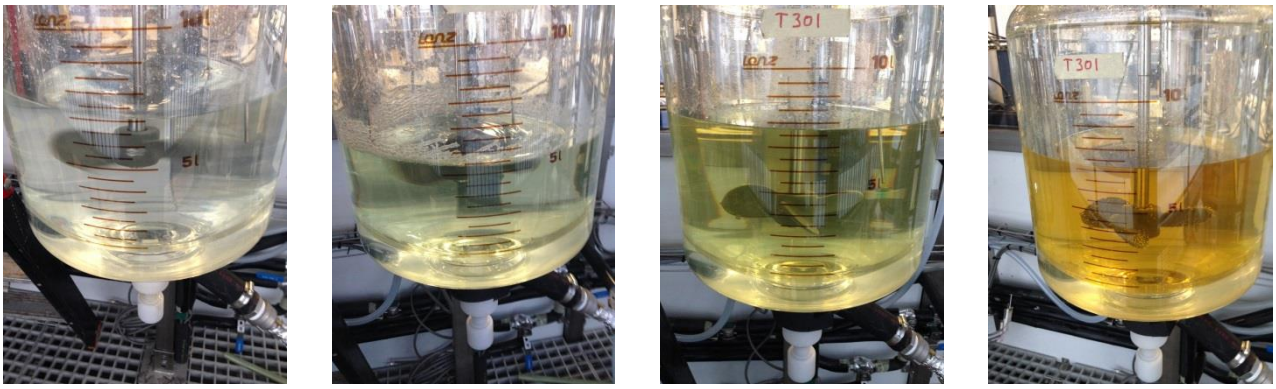
Due to the blockage, it was advised to run a test experiment in continuous mode to check the feasibility, which is described in experiment #5.
Another problem experienced during the experiments, is oxidation of the solution. After some time the solution becomes yellow to orange, see Figure 5.10. Note that no nitrogen blanket was used in the experiments #1 to #4.



Day of solution | After 1 day | After 2 days | After 3 days

Figure 5.10: Oxidation of L-ascorbic acid solution

A small amount of L-ascorbic acid solution was made with distilled water and kept under a blanket of nitrogen to test the oxidation rate, see Figure 5.11. From the comparison of Figure 5.10 and Figure 5.11 has shown that there are slight differences between distilled water with a nitrogen blanket and distilled water without the blanket. It has been experienced that the rate of oxidation depends on the operating temperature and the surface area. The greater the surface area and the higher the temperature, the faster the oxidation. It was advised to equip all the vessels with a blanket of nitrogen.



Day of solution | After 1 day | After 2 days | After 3 days

Figure 5.11: Oxidation of L-ascorbic acid solution in Feed vessel at 40 ^{o}C

#5. ASC-C-Cool-20150604

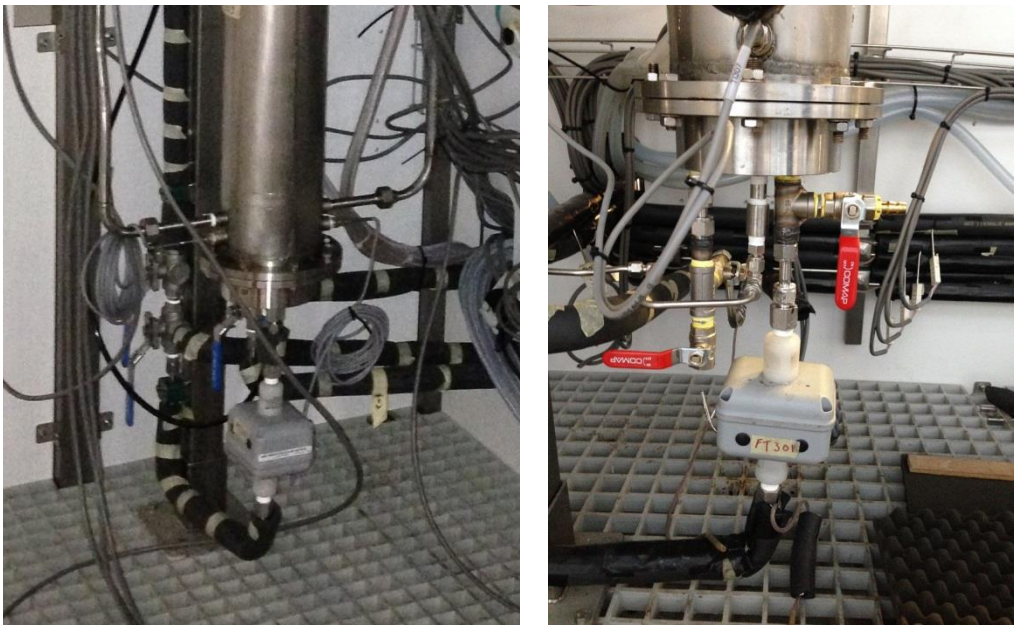
A saturated solution at 40 ^{o}C was pepared in the make-up vessel (T302), including a blanket of nitrogen. The solution was transported to the feed vessel (T301)and from the feed vessel (T301) to the airlift crystallizer (T303), after the vessels were preheated and nitrogen was added. No seed crystals were used in this experiment. A linear cooling profile was applied to the airlift crystallizer from 40 ^{o}C to 31 ^{o}C in 240 min to observe the formation of crystals by primary nucleation. After the temperature of 31 ^{o}C was reached, the temperature was kept constant at 31 ^{o}C for 60 min. to observe crystals. No clear crystals were visible during the experiment. Small black dotted shapes were observed, probably due to primary nucleation or impurities in the L-ascorbic acid packages. The measured density profile was unstable and a lot of oscillation was experienced through the data from the mass flow meter (FT304). The continuous operation resulted in no blockage of tubes and other instruments. For the measurement of the density it was decided to increase the set point value on the meter from 20 ^{o}C to 35 ^{o}C and measure all the L-ascorbic acid samples at this temperature. Changing of the temperature is automatically adapted in the density meter. This decision was made

because the relation between concentration and density, Figure 2.11, is only developed and validated at 35 ^{o}C.

5.4 Optimizations

The test experiments resulted in three optimizations. First, all the vessels were provided with a nitrogen line, to create a blanket of nitrogen during experiments.

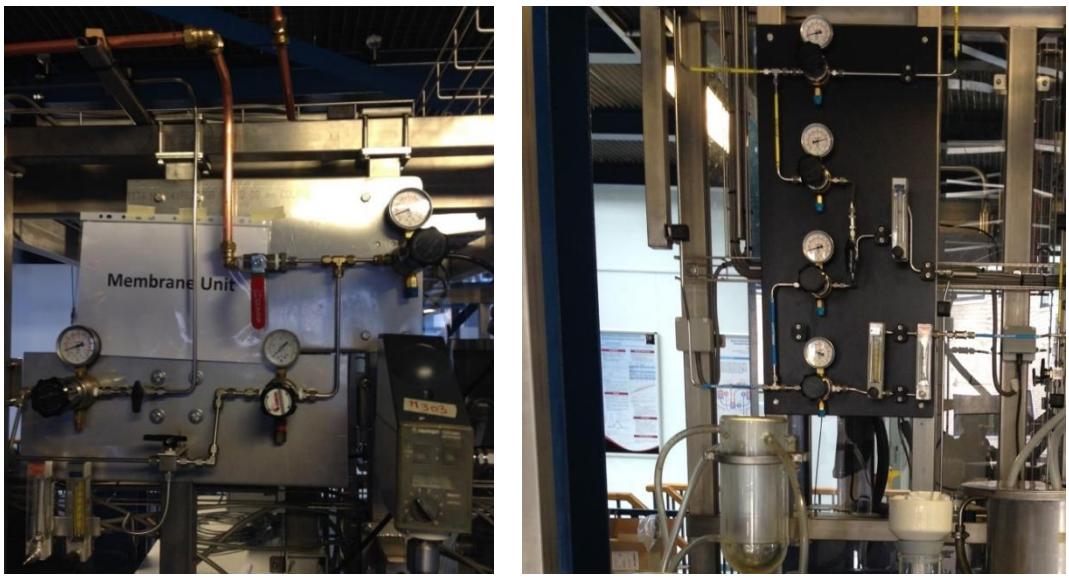
Second, the tubing of the feed and product at the bottom of the airlift crystallizer was implemented with extra valves. The valve (V318) on the feed line is implemented for rinsing, and the valve (V317) in the product line is implemented in order to take samples for CSD measurements.



(a) (b)

Figure 5.12: Valves on the bottom of airlift crystallizer, (a) before, (b) after

A third important optimization is the choice between air and nitrogen to the airlift crystallizer, nitrogen to all the vessels and air as a sweeping gas to the membrane module, see Figure 5.13. This panel was reconfigured.



(a) (b)

Figure 5.13: Air and nitrogen supply, (a) before, (b) after

In chapter 6, the design of the experiments performed with L-ascorbic acid are described. Batch experiments are performed to reproduce the results of previous experiments [9]. Furthermore, continuous operation including and excluding the membrane module is performed. Results and analysis of these experiments are given in chapter 7.

6

Setup and experiments

Trial-and-error experiments have been designed and performed to check the feasibility of the new experimental setup, which is described in chapter 5. After trial-and-error experiments, experiments with the airlift crystallizer and membrane module are designed and performed with the use of L-ascorbic acid.

6.1 Setup

The description of the MaC setup is given in chapter 3. This setup consists of a feed vessel (T301), make-up vessel (T301), airlift crystallizer (T303), buffer vessel (T304) and the Membrana Liquicel module (T401). As mentioned earlier, temperature sensors, pressure sensors, flow meters, level meters and pumps are connected to the setup for online monitoring and controlling by the Yokogawa control unit. A simplified PFD of the total setup is shown in Figure 6.1. A full PFD with a detailed explanation is given in Appendix A.

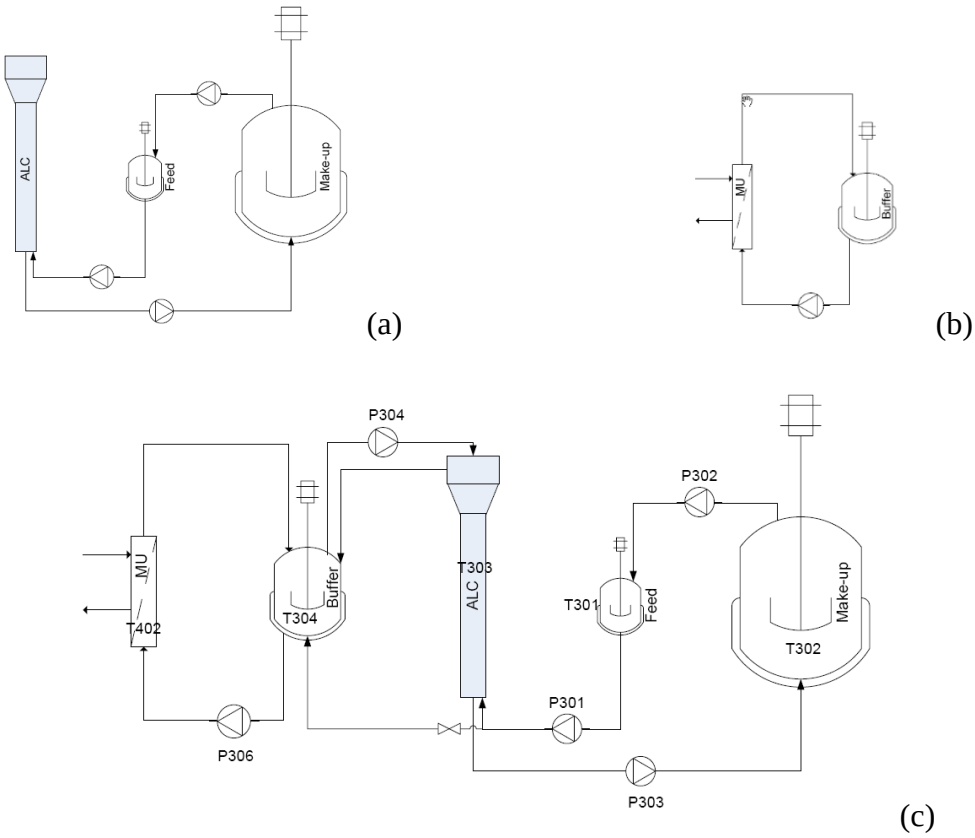


Figure 6.1: Simplified flowsheet of the setup: (a) ALC section, (b) MU section and (c) MaC setup

6.2 L-ascorbic acid experiments

An overview of the experiments on L-ascorbic acid is shown in Table 6.1. Since the new experimental setup is transported to the new laboratory of the P&E department of TU Delft, air and nitrogen properties may be different, compared to the previous building. The objective of experiments, # 6 and #7, is to validate the type of cooling profile and the effect of a low circulation velocity (low pressure and flow rate). Experiment #7 is a repetition of experiment #6, with a longer cooling profile. Both the experiments, #6 and #7, are cooling batch experiments.
Experiment #8 is a cooling batch experiment designed to reproduce the results of the experiments performed by J. van Krochten [9]. For this experiment, the theoretical product mass is calculated with Equation (2-2), to validate the seed load, and the CSD for batch experiment. The results from experiment #8 are compared with #6 and #7 to analyse the type of cooling profile and the effect of circulation velocity inside the airlift crystallizer.
Experiment #9 is the first continuous cooling crystallization operation. The purpose of this experiment is to check the feasibility of a continuous operation. An important parameter is the density difference between the riser and the downcomer, which is measured by the pressure transmitters, during the continuous operation.. The liquid circulation velocity is estimated with data from the measurements. These data are used in equations (2-22) and (2-34). The data on liquid circulation velocity is required, to analyse if crystals until a certain size stays in the suspension.
The objective of experiment #10 (continuous cooling crystallization) is to reproduce the results achieved by experiment #9 and, to check the effect on product quality and CSD, when increasing the seed load and operating at higher temperatures.
The last two experiments, #11 and #12, are continuous operations in combination with the membrane module. Higher and lower operating temperatures are applied to experiment #11 and #12 respectively, to study the influence of the membrane module on final crystal products. Another difference between experiment #11 and #12 is the method of feeding the buffer vessel. In experiment #11, the buffer vessel is fed directly from the feed vessel and the airlift crystallizer directly from the buffer vessel, while in experiment #12 the buffer vessel is only fed by an overflow from the airlift.

Table 6.1: Overview of the experiments

Exp. ID #	Experimental time [h]	Ms [g]	Seed size [µm]	Tsat [^{o}C]	Ts [^{o}C]	Tf [^{o}C]	Cooling profile [-]
6. ASC-B-Cool-20150625	3.0	11.6	200	40	31.6	31	LIN
7. ASC-B-Cool-20150526	4.0	11.6	200	40	31.6	31	LIN
8. ASC-B-Cool-20150702	3.5	11.6	200	40	31.6	31	3rd
9. ASC-C-Cool-20150715	2.5	1x 11.6	200	35	30	30	-
10. ASC-C-Cool-20150716	5.0	3x 11.6	200	40	35	35	-
11. ASC-C-MU-20150721	4.0	3x 11.6	200	40	38	38	-
12. ASC-C-MU-20150723	2.0	2x 11.6	200	34	32	32	-

Where:

- Experiment ID : Compound (melamine or L-ascorbic acid) – Batch or Continuous – Cooling or membrane module – date of the experiment
- Time: total time of the experiment inside the crystallizer, excluding preparation and filtering
- M_s: Seed load in grams
- Seed: size of the seed crystals
- $T_{sat.}$: Saturated temperature of the solution
- T_s: Temperature at seeding point

- T_f: Final temperature
- Cooling profile: LIN: cooling with linear cooling profile, 3rd: cooling with 3rd order cooling profile.

6.3 Experimental procedure

The experimental procedure is divided into three categories: first, a procedure for cooling batch operation is given, second a procedure for continuous cooling operation and third, a procedure for a continuous membrane-assisted airlift crystallization.

6.3.1 Cooling batch operation

Preparation of the solution

The procedure for the cooling batch operation starts with preparing a saturated solution in the make-up vessel (T302). First, the total volume of the needed solution, and accordingly the saturated concentration are calculated. The make-up vessel is filled with distilled water and an excess of L-ascorbic acid solute (provided by DSM) to make sure that the solution is completely saturated. Prior to the preparation of the solution, the distilled water is stripped of oxygen by adding nitrogen to the vessel and stir this for four hours. The temperature inside the vessel is measured with a pt100 sensor (TI309), and controlled with a 10 L thermostatic bath (HE302) of Lauda. The solution is prepared one day before the experiment, to make sure that the solution is saturated and homogenous, and oxygen is stripped from the solution to prevent (very fast) oxidation. During the preparation of the solution, the stirrer M302 is set to 1000 rpm, for fast mixing. During the night, the stirrer was operated at a lower speed (400 rpm). A total volume of minimum 18 L is prepared to completely fill the airlift crystallizer.

Start of experiment

The experiment starts with the preheating of the feed vessel (T301) and airlift crystallizer (T303) by setting the temperature of the thermostatic bath HE301 and HE303 on 41 ^{o}C (the solution is saturated at 40 ^{o}C). The thermostatic bath is set 1 degree higher because of the difference between bath temperature and solution temperature. The manual mode of the PID controller is used for the setting of the temperature. Nitrogen is added to the feed vessel, to prevent oxidation of L-ascorbic acid. Nitrogen is added to T303 with a (low) flow rate of 100 l/h only for the mixing. During experiment #6 and #7, the flow rate is increased to 150 l/h and during experiment #8 to 400 l/h. In experiment #8, nitrogen with a pressure of 7 bar is used, while in experiment #6 and #7, a pressure of 2 bar was used during the whole experiment. The tracing of the pipelines PL301 and PL302 are set to 38 ^{o}C with a ΔT of 1 ^{o}C for on-off, which is controlled from the control unit. The solution is transported from the make-up vessel (T302) to the feed vessel (T301) by starting the peristaltic pump P302. From the feed vessel (T301), the solution is transported to the airlift crystallizer (T303) by starting the peristaltic pump P301. In this stage, these pumps are operated manually for fast operation. Prior to the filling of the airlift crystallizer, the valves V307 and V717 in the product line are closed. After the crystallizer is filled, a time of 30 min is given to the solution to stabilize the temperature at starting point. Meanwhile, the make-up vessel (T302) and feed vessel (T301) is filled with hot water and rinsed, including the tubes.

Setting a cooling profile

The operating conditions of the cooling process is adapted from previous experimental results [9], [13],[5]. The temperature profile of the cooling batch crystallization is divided into two segments: a linear cooling profile, followed by a third order cooling profile to the final temperature. The cooling profile is shown in Figure 6.2. In experiment #6 and #7, linear cooling profiles are applied to investigate the influence on product quality.

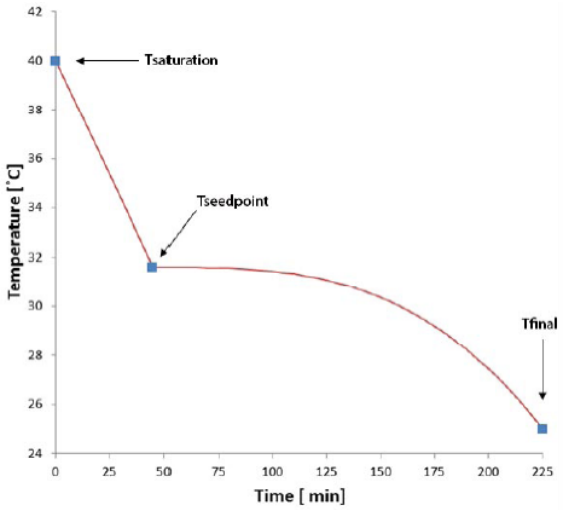


Figure 6.2: Cooling profile during batch experiments

The cooling profile is set on the control unit, after the average temperature in the airlift has reached equilibrium. To start the cooling profile, first the temperatures and times are defined, then the PID controller is set to operate in cascade mode, after which the timer button is pressed to start. The third order cooling profile is given by:

$$T(t) = T_s - (T_s - T_f) \cdot \left(\frac{t}{t_f}\right)^3 \qquad (6\text{-}1)$$

Where:
T_s is the seeding temperature [^{o}C]
T_f is the final temperature of the crystallization process [^{o}C]
t is the time of the timer [s]
t_f is the time and the end of the batch [s]

The next steps are preparing seeds, sampling, measuring CSD and saving data. These steps are similar for all the crystallization experiments, and therefore, described in section 6.4 to 6.7.

6.3.2 Continuous cooling operation

Preparation of the solution
Similar steps are followed as for batch operation to prepare the solution. The difference in a batch operation lies in the total volume of needed solution and the advantage that no additional (excess) solute should be added for a saturated solution.

Start of experiment
The continuous operation starts with adding nitrogen to the feed vessel (T301) and preheating the vessel. The thermostatic bath HE301 and HE303 connected to the feed vessel (T301) and crystallizer (T303) respectively, are switched on. For experiment #9 the feed temperature is set to 36 ^{o}C and in experiment #10 the feed temperature is set to 41 ^{o}C. For experiment #9 the airlift temperature is 30 ^{o}C and for experiment #10 35 ^{o}C During start-up (and shutdown) the PID controller is set to manual mode, because no solution is in the vessel for an automatic control. Nitrogen of 2 bar and a flow rate of 200 l/h is added to the airlift crystallizer at start point. During experiments, the pressure is increased to 7 bar and a flow rate of 400 l/h is used. Tracing TI503 to TI508 on the pipelines PL301, PL302 and PL304 are switched on according to the temperatures in

the vessels minus 2 ^{o}C. A ΔT of 1 ^{o}C is used for automatic on-off of the tracing. The valves V309, V301 on pipeline PL301, V302, V303 and V304 on pipelinePL302 and V305, V306 and V307 on PL304 are opened to the correct directions. Pump P302 is switched on to start filling the feed vessel. If there is enough solution in the feed vessel, stirrer M301 is switched on, and pump P301 is switched on to start filling the airlift crystallizer. A residence time of three hours was set for the continuous operations. Therefore, a product flow rate of 100 ml/min (43 rpm) was set, and a feed flow rate of 115 ml/min (50 rpm). The pumps were operated manually. After the vessels are filled, the PID controllers for controlling the thermostatic baths are set to automatic mode. Before the solution is transported to the other vessels, the product line is checked for clogging. During the preparation of the solution in the make-up vessel, undissolved solute may settle in the tubing and block this. Clogging is checked by disconnecting the Marprene tube from the stainless steel tube, and observe on a reverse flow from the make-up vessel.

Filling airlift crystallizer and resetting the differential pressure transmitters to zero
Filling the airlift crystallizer requires a special procedure. First, the air or nitrogen flow to the airlift is closed. The equalizer valve of the pressure transmitter connected to the downcomer (PI301) and riser (PI302) is opened, followed by filling the crystallizer. This is performed to make sure that there are no air bubbles stuck in the tubes. When the level in the crystallizer is beyond the opening of the transmitters, the equalizer valve is closed. At the pressure transmitter, three buttons are available for settings. Mode M7 is chosen to set the differential pressure to zero. After the differential pressure is set to zero, nitrogen or air is added to the airlift crystallizer.

6.3.3 Continuous membrane-assisted airlift crystallization

Preparation of the solution
Similar steps are followed as for the continuous operation to prepare the solution. The total needed volume is calculated prior to the preparation.

Start of experiment
Similar steps are followed as for the continuous operation. According to the process flow sheet, the buffer vessel (T304) can be either filled from the feed vessel or from the overflow of the airlift crystallizer. In experiment #11 the buffer vessel is fed directly from the feed vessel, and in experiment #12 from the overflow. During filling, the thermostatic bath HE304 is controlled manually, and during experiments the mode is switched to automatic. The temperature of the solution in the buffer vessel is set to 50 ^{o}C to prevent crystallization on the membrane. This data is adapted from the experimental research performed by K. Mathew Thomas [13]. The airflow rate of sweeping gas through the membrane is adapted from [13]. An optimal airflow rate of 3000 l/h is used in experiments #11 and #12. After the level in the buffer vessel is beyond the level switch LI303, valve V314 in PL402 and V315 in PL401 are opened. The plunger pump P306 is started for the flow between the buffer vessel (T304) and the membrane module (T401). A frequency of 20 Hz is used for the flow rate. Peristaltic pump P304 is switched on for the flow from the buffer vessel (T304) to the airlift crystallizer (T303). Because of a pressure drop between the buffer vessel and the airlift crystallizer, a flow rate of 170 ml/min (74 rpm) is set for pump P304. The calculation of the pressure drop is described in chapter 7.

6.4 Preparation of the seeds

Technical pure L-ascorbic acid provided by DSM is sieved by using a shaker machine (Retch AS300). First, the CSD of the solute from the package is measured using the Microtrac S3500 machine. The CSD of the solute is shown in Figure 6.3.

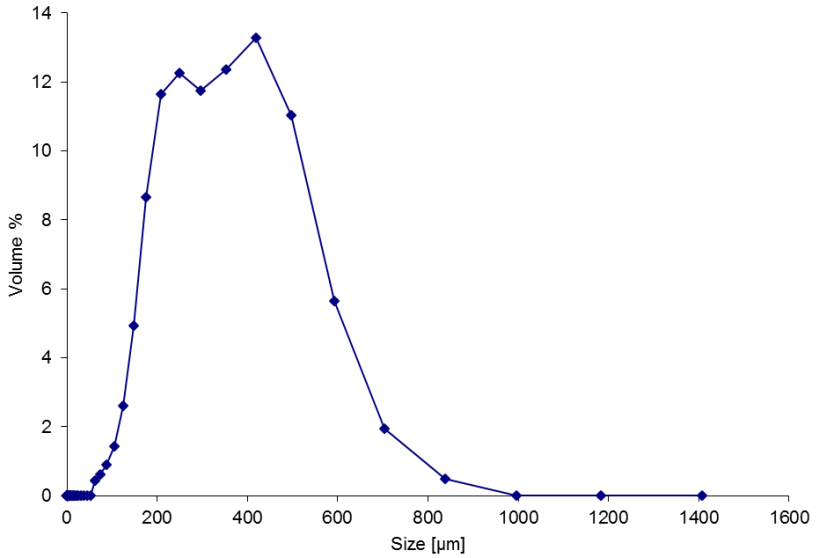


Figure 6.3: CSD of pure L-ascorbic acid solute

According to the available sizes of the solute, it was chosen to collect seed crystals from the 212 µm sieves for all the experiments (#6 to #12). A seed load of 11.6 g is adapted from the research conducted by Lakerveld et al. [5], and used in all the experiments. The theoretical product mass is calculated in chapter 7 to validate the seed load. Before adding the seed crystals to the crystallizer, the seeds were kept in a saturated solution of 100 ml for 5 minutes. A heating plate (IKA, RTC basic) was used to keep the suspension on temperature and the magnetic stirrer, with a rotational speed of 500 rpm was chosen for mixing. This preparation is required to heal the (broken) seed crystals, caused by grinding.

6.5 Sampling

For the measurement of the concentration before and during the experiments, samples for density measurement were taken from the bottom of the crystallizer, and the feed and buffer vessel. Three samples of 3 ml each were taken with a syringe every 30 minutes (for the crystallizer) and measured by an Anton Paar DMA 5000 density measurement instrument. The concentration is calculated with the correlation between the density and the concentration, shown in Figure 2.11.

At the end of an experiment, samples for the CSD were taken from the bottom of the airlift crystallizer. The samples were filtered on a 60 µm filter paper using a vacuum pump (KNF Laboport Neuberger). To prevent agglomeration, the samples were washed with saturated solution and distilled water. After filtering and washing, the samples were placed in an oven for 10 to 15 min. at a temperature of 50 ^{o}C.

6.6 CSD measurements and online observation

After drying the samples, the crystals were observed on agglomeration. In case of agglomeration, the crystals were separated carefully with a spoon. The CSD of the final samples was measured by the Microtrac S3500 laser diffraction instrument.

During the experiments an in-situ PVM camera (PIA 524) of Mettler Toledo connected to the crystallizer was used to observe crystal growth and gas bubbles in the downcomer. Some of the samples were observed with a Nikon Optihut 200 microscope.

6.7 Saving data

As described in chapter 4, all the data of the instruments connected to the control unit are recorded for 8 hours. After an experiment, the recorded data is saved by double clicking on the created batch file in My Documents on the control computer. The saved data are used for further analyses.

7

Results and discussion

7.1 Cooling batch crystallization

Table 6.1summarizes the operating conditions for the cooling batch experiments, #6, #7 and #8.

Evaporation of water

The evaporation rate of water at different temperatures and airflow rates are calculated using equation (2-43) and (2-44). To determine the water loss by evaporation, the value of humidity ratio and vapour pressure are used from the Handbook of Chemistry [28]. The calculated water loss due to evaporation is shown in Figure 7.1. At an air flow rate of 400 l/h and a temperature of 40 °C the water loss has an amount of 23 g/h, due to evaporation. Loss of water by evaporation is neglected in all the experiments.

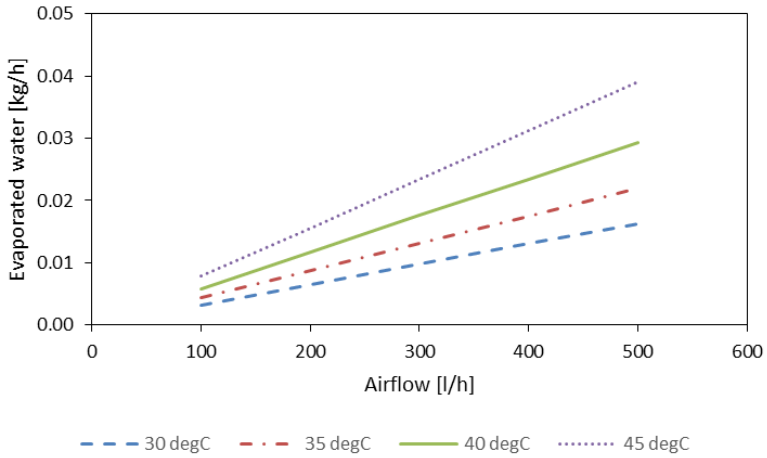


Figure 7.1: Solvent loss due to evaporation

Theoretical product mass and seed load validation

The yield of the cooling batch experiment is calculated with equation (2-2). A saturated solution of 40° C is used at the beginning of the batch experiments. Assuming saturation at the final temperature of 31 ^{o}C, the theoretical product mass is 1.12 kg. Compared to the theoretical product mass calculated by J. van Krochten [9], the difference in yield is negligible. A seed load of 11.6 g [5] is used in all the cooling batch experiments.

Density measurements

In the cooling batch crystallization, supersaturation is achieved by cooling the saturated solution, as shown in Figure 2.3. The measured densities of experiments #7 and #8 are shown in Figure 7.2. As explained in section 6.5, three samples were taken at each time point. The average values, as well as the standard deviations (error bars), which are the variations in measurements, are plotted in Figure

7.2. In addition, plots of densities at saturated conditions are given at different temperatures of the cooling profile, which are based on the results achieved by K. Mathew Thomas [13] and J. van Krochten [9]. The density of a saturated solution at the start point (40 ^{o}C) is 1.1379 g/cm^3, and the density of a saturated solution at the end point (31 ^{o}C) is 1.1185 g/cm^3.

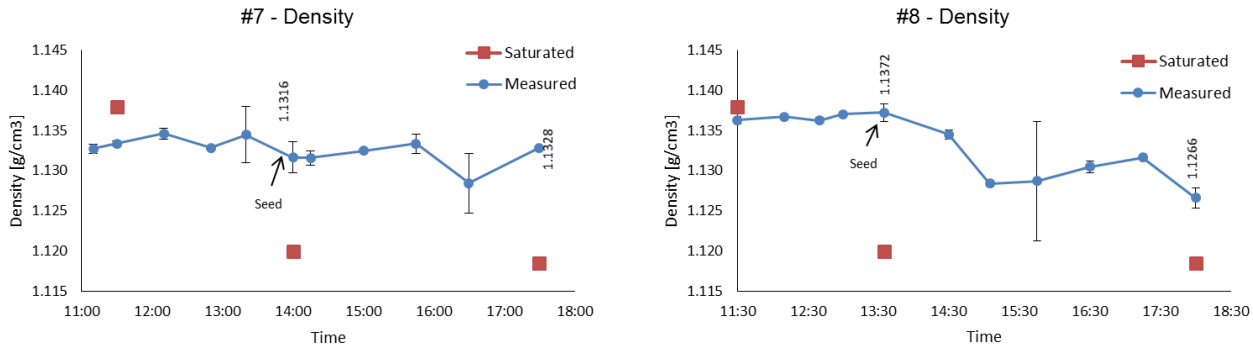


Figure 7.2: Density measurements of experiments #7 and #8

At the beginning of experiment #7 can be observed that the measured density is lower than the density at the saturated condition, which indicates that in this point the solution was slightly undersaturated. The seed points of the experiments are indicated with an arrow in Figure 7.2. In both experiments, #7 and #8, before and after the seed point a fluctuation is observed in the density measurement. Some of the measured points show larger variations as shown by the error bars. Although the fluctuations in density measurements, there is a constant behaviour shown before the seed points in both the experiments (#7 and #8). This indicates the generation of supersaturation, compared to the saturated condition. However, after the seed point, density measurement of experiment #7 still shows a constant behaviour, while measurement of experiment #8 shows decreasing values, which indicates consumption of supersaturation by seed crystals. Lower consumption of supersaturation by the seed crystals in experiment #7 is possibly caused by the linear cooling profile from seed point to the final batch, and a low gas flow rate of the airlift crystallizer.

As mentioned earlier, fluctuations in density measurements are observed with large variations at certain points, see Figure 7.2. Possible reasons for these fluctuations are small air bubbles that are entrapped in the syringe during sampling and/or formation of crystals on the wall of the syringe and the density meter.

The density of experiment #6 was not measured at starting conditions and is therefore not mentioned in this report.

Product quality batch experiments

Experiment #6 and #7 were operated at a lower nitrogen flow rate (150 l/h), and a linear cooling profile was applied from the seed point to the final batch temperature. Experiment #8 was operated at a nitrogen flow rate of 400 l/h and a third-order cooling profile was applied from the seed point to the final batch temperature. The results of the product quality are shown in Table 7.1.

Table 7.1: Results cooling batch experiments

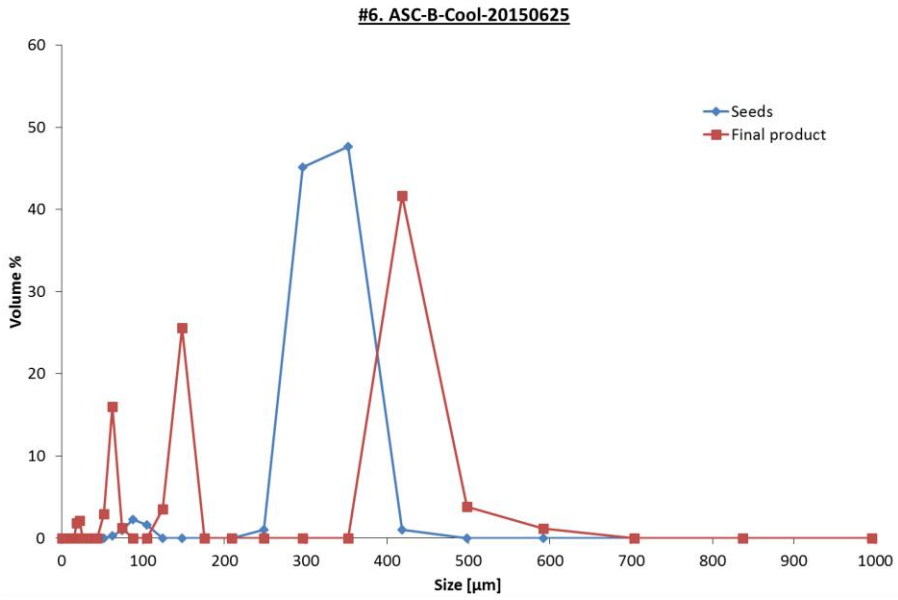
Exp. ID #	N_2 flow rate [l/h]	Experimental time [1)] [h]	Mean size [µm]	Median size [µm]	CV (X_{90}/X_{10}) [-]	$Mass_{theor.}$ [kg]	$Mass_{prod.}$ [kg]
6. ASC-B-Cool-20150625	150	3.0	255.9	144.9	7.6	1.12	0.99
7. ASC-B-Cool-20150526	150	4.0	174.5	115.4	5.7	1.12	0.90
8. ASC-B-Cool-20150702	400	3.5	461.4	440.0	2.8	1.12	1.01

[1)] In cooling batch experiments, the residence time is equal to the experimental time

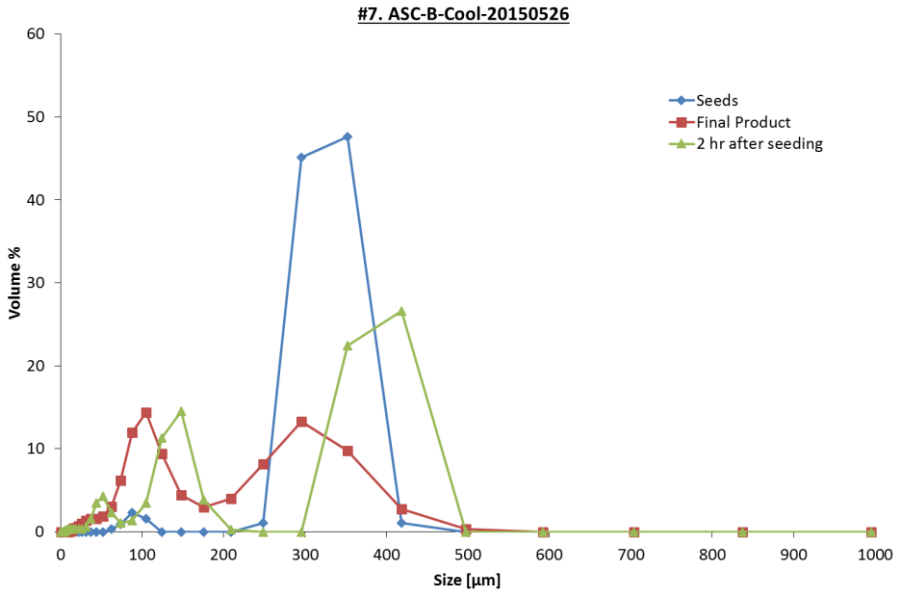
Where:

- Experiment ID : Compound (melamine or L-ascorbic acid) – Batch or Continuous – Cooling or membrane module – date of the experiment.
- Mean size is the average crystal size of the CSD.
- Median size is described with the X_{50} quantile. This means that 50% of the total amount of crystals have a size below the X_{50} size, and 50% of the total amount of crystals have a size larger than the X_{50} size.
- The coefficient of variation (CV) is the ratio of the X_{90} quantile and the X_{10} quantile. This ratio gives information on the width of the CSD. The higher the ratio, the wider the width of the CSD is.
- $Mass_{theor.}$ is the theoretical product mass gained by using equations (2-1) to (2-7) and the solubility curve
- $Mass_{prod.}$ is the product mass gained by using equations (2-1) to (2-7) and the measured densities during experiments.

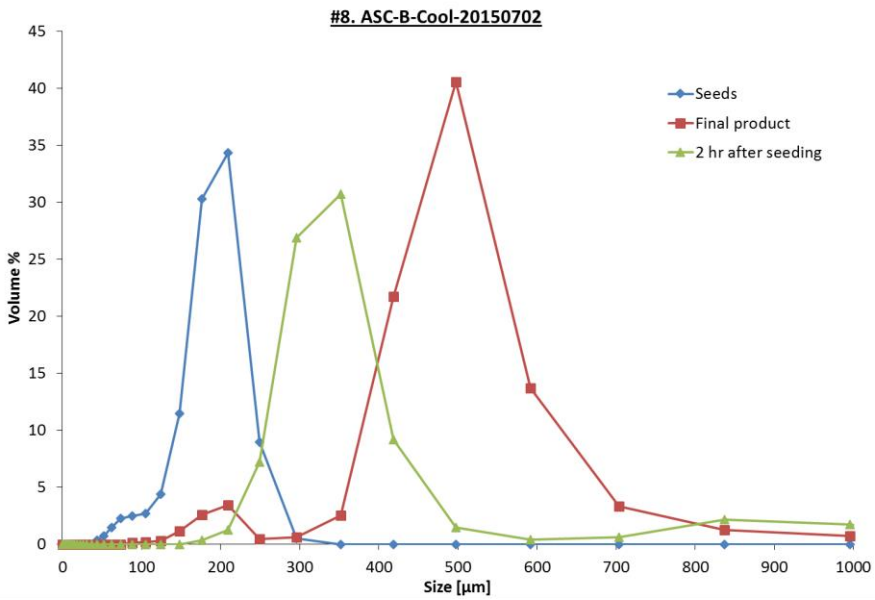
The CSD of the experiments #6, #7 and #8 are shown in Figure 7.3. Images taken from the PVM camera are shown in Figure 7.4 for experiment #7 and #8. During experiment #6, problems with the PVM were experienced. Therefore, these results are not mentioned in this report.



(a)



(b)



(c)

Figure 7.3: CSD cooling batch experiments, (a) #6, (b) #7 and (c) #8

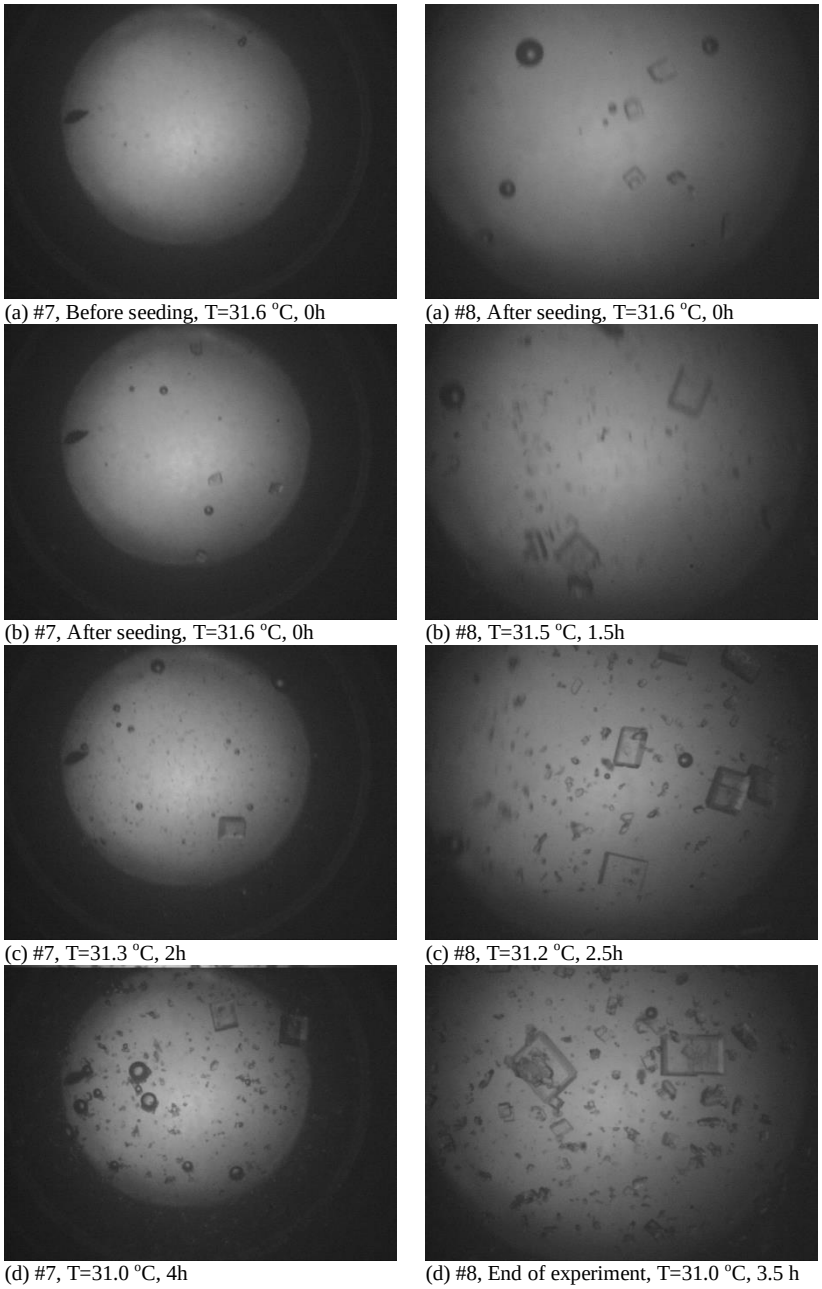


Figure 7.4: Images of experiment #7 and #8 taken from the PVM

As can be seen from Figure 7.4, experiment #7 has a different magnification than experiment #8. The camera was not in optimal position during experiment #7, but at the end of the experiment the probe was realigned for a better view.

For experiment #6 and #7, in accordance with the CSD (Figure 7.3), the images taken from the PVM (Figure 7.4) show a wide variation in crystal size. The CV values of experiment #6 and #7 are higher than the CV of experiment #8, possibly due to the linear cooling profile and the lower gas flow rate.
Using a linear cooling profile, the temperature of the solution in the crystallizer is cooled down faster in the beginning of the batch compared to a third-order profile, see Figure 7.5.

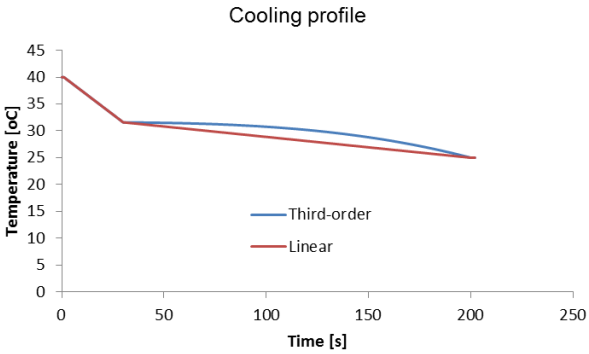


Figure 7.5: Difference between the linear and third-order cooling profile

This faster cooling of the solution may activate nucleation. As can be seen in Figure 7.3 and Figure 7.4, a lot of small crystals were produced from experiment #6 and #7. The measurement of the CSD is in line with the measured density, which is shown in Figure 7.2. As discussed earlier, the density of the solution of experiment #7 shows a constant behaviour after the seed point. Formation of small crystals is a known problem in cooling batch operations, due to the interdependency of kinetic crystallization phenomena. The smallest crystals in experiments #7 and #8 are possibly formed by secondary nucleation. Experiment #6 and #7 show a greater variation in CSD measurement, compared to experiment #8, possibly due to the linear cooling profile and the low gas flow rate.

To keep the crystals in suspension, a certain gas flow rate in the airlift crystallizer is required, as shown in the work of Soare et al. [6]. At higher circulation rates more crystals remain in suspension and more surface area is available for depletion of the supersaturated solution, which result in larger crystals and less nucleation. The influence of the circulation velocity is clearly seen between experiment #7 and #8. A lower gas flow rate and a linear cooling profile were used in experiment #7. This resulted in lower consumption of supersaturation by seed crystals (Figure 7.2), and a lot of small crystals were formed (Figure 7.3, Figure 7.4), compared to experiment #8.

As discussed before, the generation of the supersaturation is more gradual when using a third-order cooling profile and time is given to the seed crystals to consume the supersaturation gradually. Based on the data from the density measurements, as well as from the CSD measurements, it can be concluded that only a small volume fraction of small crystals was observed in experiment #8, which is possibly achieved by secondary nucleation. The CSD found in this research is comparable to the results found by J. van Krochten [9] for the same cooling profile, but in a longer batch time (6 hours), see Figure 7.6. J. van Krochten [9] compared his results to the results found with a conventional stirred crystallizer, and showed that the airlift crystallizer has the potential to suppress secondary nucleation compared to stirred crystallizers. Therefore, the results found in this research are in line with the conclusions from J. van Krochten [9] and Lakerveld et al. [5].

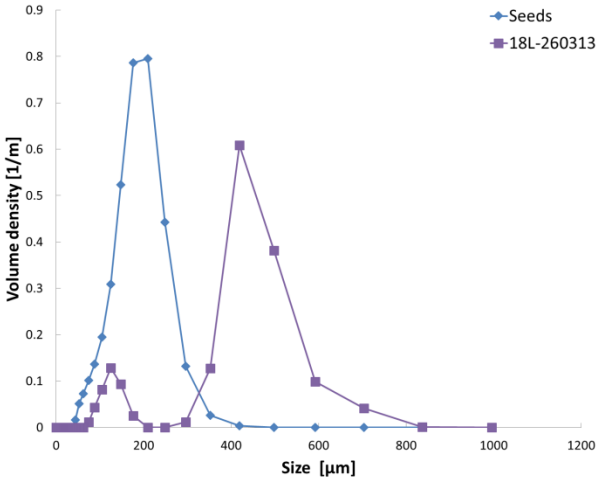


Figure 7.6: CSD of results achieved by J. van Krochten [9]

7.2 Continuous cooling crystallization

Two experiments were performed in continuous cooling operation. Experiment #9 was designed to start with a saturated feed solution at 40 ^{o}C and cool down to the operating temperature of the crystallizer at 35 ^{o}C. Due to an undersaturated solution experienced at the starting point, the choice was made to change the operating conditions and to cool down from 35 ^{o}C to 30 ^{o}C in 2.5 hours. The reason for the short time was the fact that this was the first continuous operation and more time was needed to prepare the experiment. At the end of the experiment, extra solute was added to the solution to prepare a saturated solution at 40 ^{o}C for the next experiment (#10). Experiment #10 had a cooling profile from the saturated condition at 40 ^{o}C to a final temperature at 35 ^{o}C in 5.0 hours, see Table 6.1.

Density measurements

The average values of the density measurements, as well as the variations in measurements, of experiment #9 and #10 are shown in Figure 7.7. In addition, plots of densities at saturated conditions are given at different operating temperatures for the feed solution, as well as for the crystallizer.

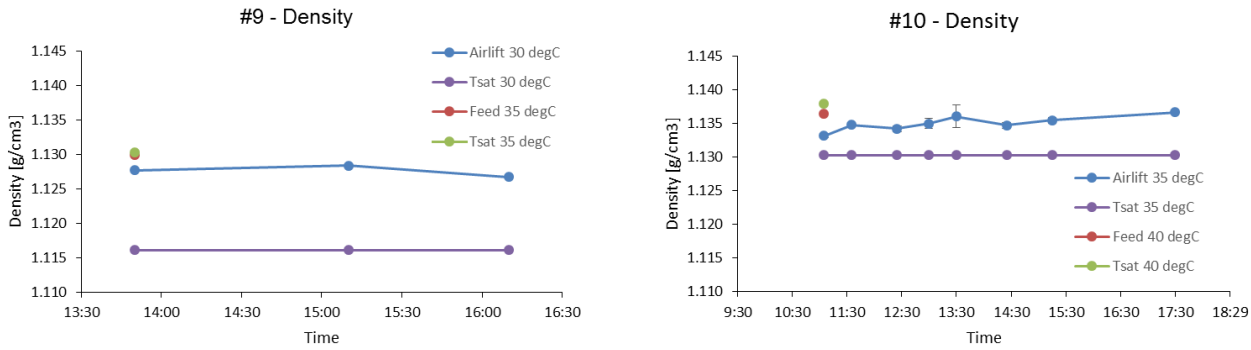


Figure 7.7: Density measurement of experiment #9 and #10

The density of the solution from the feed vessel shows negligible difference compared to the density at the saturated condition in both the experiments, #9 and #10. The density measured in the airlift crystallizer has almost a constant behaviour in experiment #9, while the difference between the density at saturated condition and measured density is increasing in time, in experiment #10.

Increasing density indicates that possibly a low surface area of crystals was available for depletion of the supersaturation. Note that the operation time of experiment #9 is too short to give reliable conclusions on the rate of generation of supersaturation and crystal growth.

Product quality continuous cooling operation

The results of the product quality and CSD measurements of the experiments are shown in Table 7.2 and Figure 7.8 respectively.

Table 7.2: Results continuous cooling experiments

Exp. ID #	Mean size [µm]	Median size [µm]	CV (X_{90}/X_{10}) [-]	N_2 flow rate [l/h]	Residence time [h]	Operation time [h]
9. ASC-C-Cool-20150715	255.9	144.9	7.6	400	3.0	2.5
10. ASC-C-Cool-20150716	174.5	115.4	5.7	400	3.0	5.0

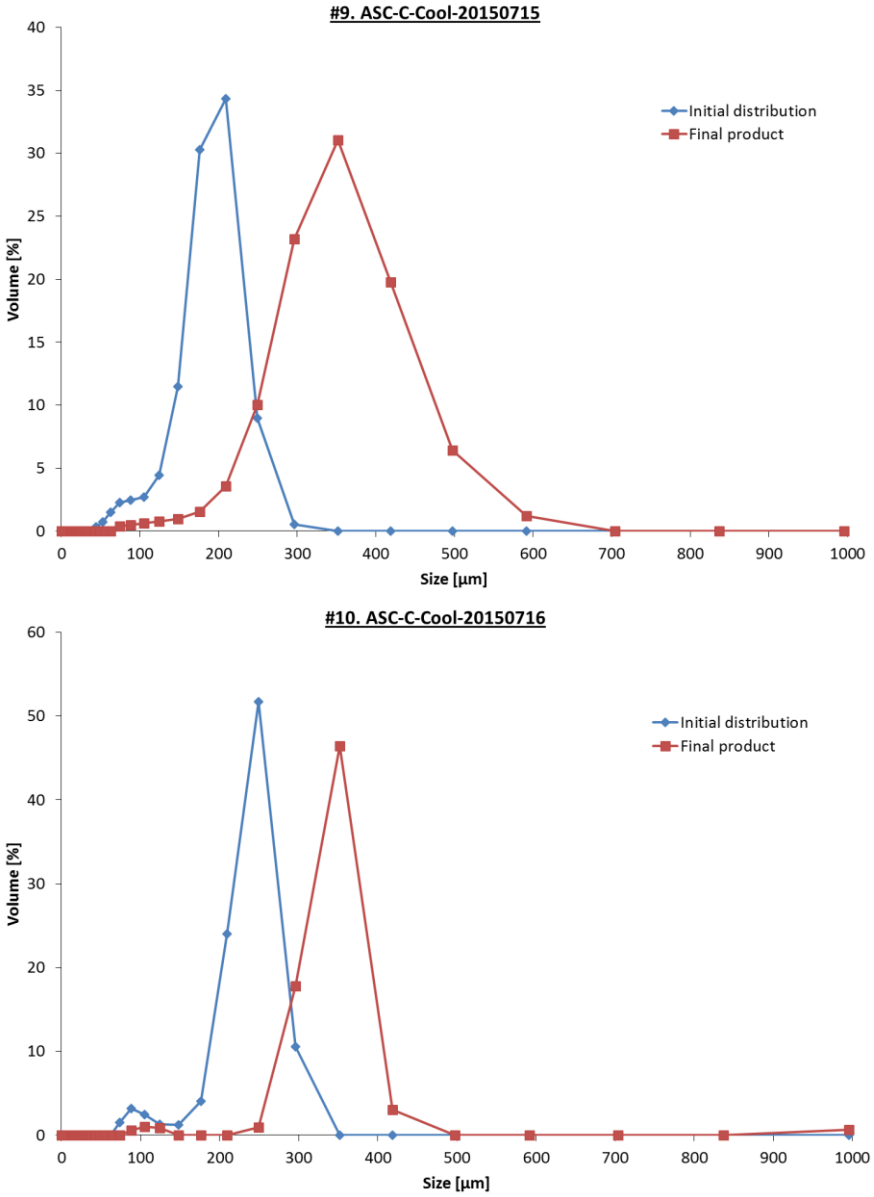
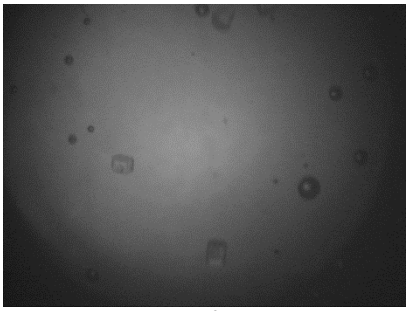
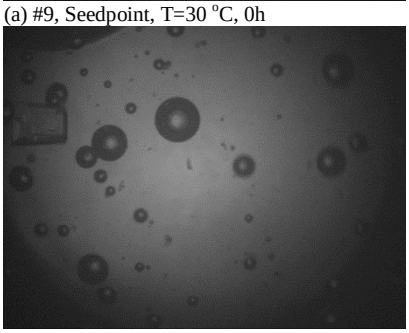


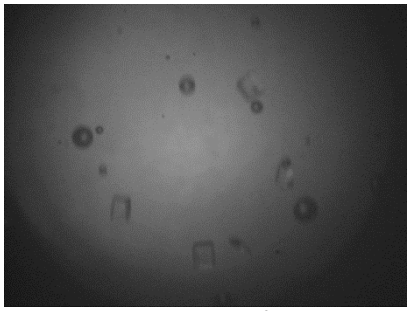
Figure 7.8: CSD of experiments #9 and #10



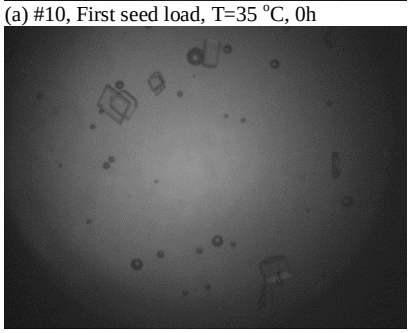
(a) #9, Seedpoint, T=30 °C, 0h



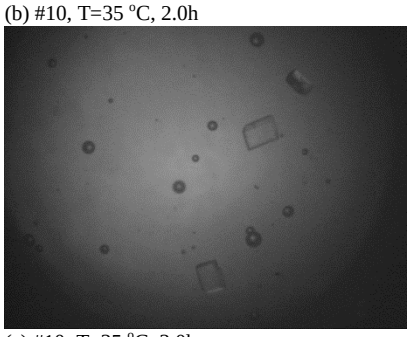
(b) #9, end of experiment, T=30 °C, 2.5h



(a) #10, First seed load, T=35 °C, 0h

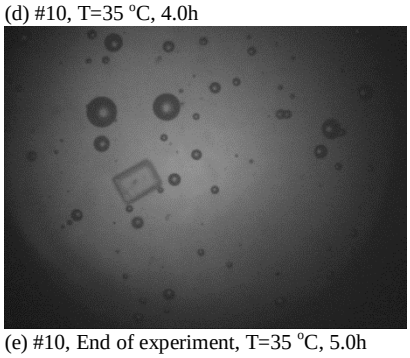


(b) #10, T=35 °C, 2.0h



(c) #10, T=35 °C, 3.0h

(d) #10, T=35 °C, 4.0h



(e) #10, End of experiment, T=35 °C, 5.0h

Figure 7.9: Images of experiments #9 and #10 taken from the PVM

In Figure 7.8 CSD measurement of experiment #9 shows a greater variation in CSD compared to experiment #10, possibly due to a short operating time. The slope of the solubility line between 30 ^{o}C and 35 ^{o}C, and 35 ^{o}C and 40 ^{o}C is similar. Therefore, no significant difference in product quality is expected. However, the nucleation and growth kinetics might be slightly different. Images taken with the PVM in both experiments, #9 and #10, show a clear solution with grown crystals.

The main peak in the CSD measurement is at 352 µm in both the experiments #9 and #10. Additional experiments are required to explain this peak. In the continuous operation, the product is removed continuously from the airlift crystallizer and transported to the make-up vessel. Note that samples for CSD measurement were taken from the bottom of the airlift crystallizer, because the sample point (V308) assembled on the product line (PL304) showed a low volume fraction of crystals during the experiments #9 and #10.

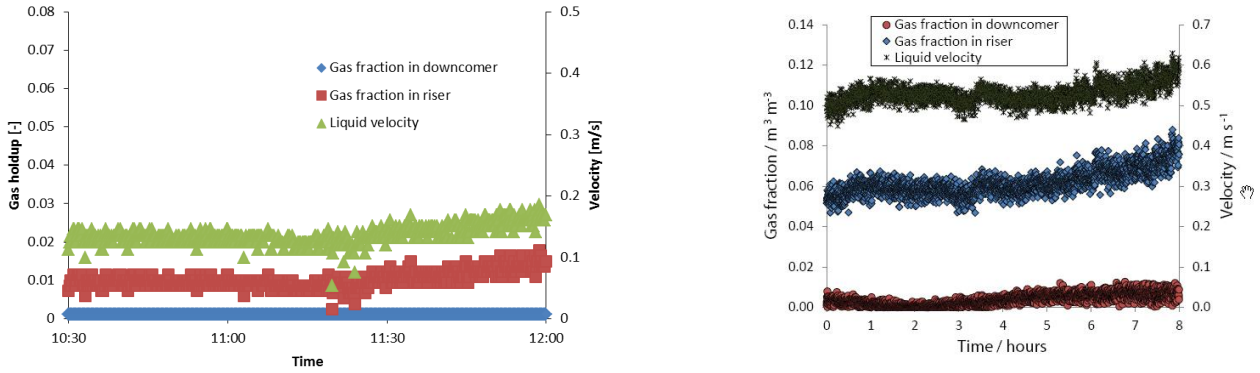
To give better and reliable analysis on product quality from a continuous process, it is recommended to take samples from the product line and the bottom of the crystallizer, and to compare these results. Sampling of the product line can be achieved by installing a filtration unit after the mass flow meter (FT303). Crystal properties can then be validated with future experiments.

Comparison cooling batch versus continuous cooling operation

Batch experiments with the aforementioned process conditions produced larger crystals, with a greater CV value (broader CSD), while continuous processes have the ability to produce narrower CSD. Influence of secondary nucleation was possibly suppressed in the cooling batch operation, while no nucleation was observed during the continuous operations. The CSD in continuous mode depends on process conditions, such as the feed and product flow rate, operating temperature and circulation velocity of the crystallizer. The choice of the circulation velocity determines the size of the crystals. Based on the circulation velocity, it is expected that smaller crystals stay in suspension until the size is large enough to settle at the bottom. The influence of increased or decreased feed flow rate is not studied. Before proceeding with a sensitive analysis, it is recommended to design experiments, where larger amounts of samples can be collected for better analysis, as well as from the bottom of the crystallizer, as from the product line.

Liquid circulation velocity

During the continuous process of experiment #10 the liquid circulation velocity is calculated with data achieved by the pressure transmitters and the equations (2-31) to (2-42). The liquid circulation velocity is calculated for the time before crystallization was started (in the absence of crystals). In this case the equations are simplified for a two-phase system. The pressure difference measured by PI301 (downcomer) is used to calculate the gas holdup in the downcomer, and the pressure difference measured by PI302 is used to calculate the gas holdup in the riser. The calculated gas holdup and the liquid circulation velocity are shown in Figure 7.10.
In the work of Lakerveld et al. [5] the liquid circulation velocity was calculated with only water and a gas flow rate of 1000 l/h was used. In this research, the liquid circulation velocity is calculated for L-ascorbic acid and a gas flow rate of 400 l/h is used. Therefore, these results cannot be compared to each other. The results of both the experiments, in this research with L-ascorbic acid and in the research of Lakerveld et al. with water, are shown in Figure 7.10.



(a) (b)

Figure 7.10: (a) Circulation velocity L-ascorbic acid, (b) circulation velocity water from the work of Lakerveld et al. [5]

As can be seen from Figure 7.10, the measured gas fraction in the downcomer is approximately 0% in this research. However, during the experiment, a low fraction of gas bubbles were visible on the screen of the PVM camera. A possible reason for this is the formation of crystals on the tubes of the pressure transmitters. Note that the tubes of the pressure transmitters are currently not traced (electrical wire for temperature control). As the solution is kept for several hours in the reference column, the crystals might be formed at the inlet and outlet of the pressure transmitters. This blockage may influence the measured pressure. During filling and draining of the airlift crystallizer, air is possibly not fully escaped from these tubes. It is recommended to clean and trace the tubes of the pressure transmitters and reproduce the experiment with water for validation.

7.3 Continuous Membrane-assisted Crystallization

The operating conditions for the membrane module are adapted from the results achieved by K. Mathew Thomas [13] and are given in Table 6.1. The air flow rate of the sweeping gas is kept on 3000 l/h and the feed flow rate on 552 l/h for both the experiments #11 and #12. Based on the information given in the report of K. Mathew Thomas [13], the value of the membrane flux for L-ascorbic acid is assumed to be 0.26 l/hm^2. Both the experiments, #11 and #12, were designed to operate at a crystallizer temperature of 38 ^{o}C (40 ^{o}C at saturated condition). Experiment #12 was performed the day after experiment #11, and the same solution was used. Unfortunately, the solution was undersaturated at 40 ^{o}C during experiment #12, and it was chosen to proceed the experiment with a crystallizer temperature of 32 ^{o}C.

Density measurements

During the experiments the density of the solution in the buffer vessel, as well as the density of the solution in the crystallizer was measured, see Figure 7.11. The density of the solution in the feed vessel was only measured two hours before starting the experiments. In addition, the density at saturated conditions is also given in Figure 7.11 for the feed temperature, as well as for the crystallizer temperature.

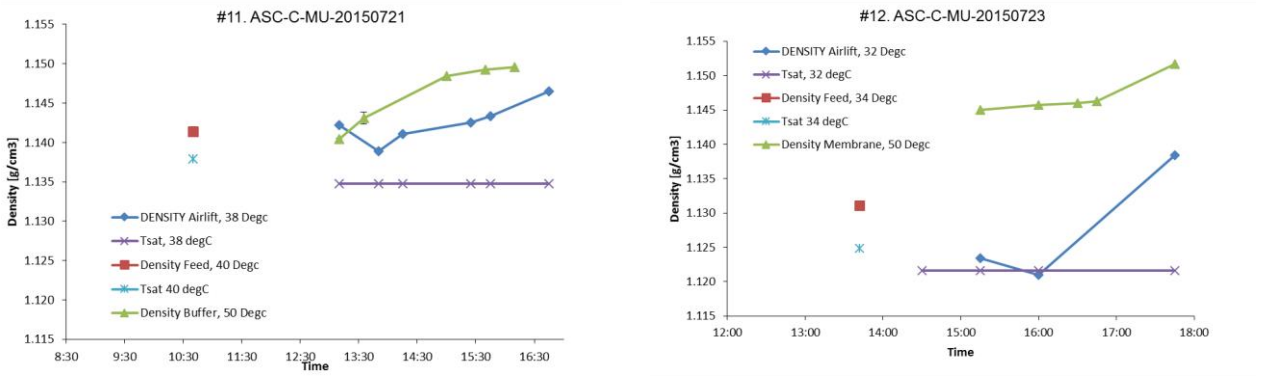


Figure 7.11: Density measurements MaCC experiments

The density measurement of the feed vessel shows that the solution was possibly already supersaturated. Note that only one sample was taken for the density measurement. Therefore, this observation cannot be validated. After the preparation of the solution, saturated at 40 ^{o}C, in the make-up vessel, a small layer of solute was visible on the bottom. This indicates that the solution is saturated and no more solute can be dissolved in the solution. The density measurements of the solution from the crystallizer show in both the experiments #11 and #12 an increasing behaviour. As discussed in the section of continuous cooling crystallization, an increasing behaviour indicates that the generation of supersaturation is greater than depletion. An increasing trend in density measurements can be seen for the solution in the buffer vessel. This is also expected based on the results achieved by K. Mathew Thomas [13].

Product quality MaCC

The product quality and CSD of the experiments #11 and #12 are respectively shown in Table 7.3 and Figure 7.12. Images taken from the PVM are shown in Figure 7.13.

Table 7.3: Results MaCC experiments

Exp. ID # 	Mean size [µm]	Median size [µm]	CV (X_{90}/X_{10}) [-]	Feed flow rate membrane [l/h]	Air flow rate membrane [l/h]	N_2 flow rate airlift [l/h]	Residence time [h]	Operation time [h]
11	349.5	324.9	1.2	552	3000	400	3.0	4.0
12	335.2	306.4	1.3	552	3000	400	3.0	2.0

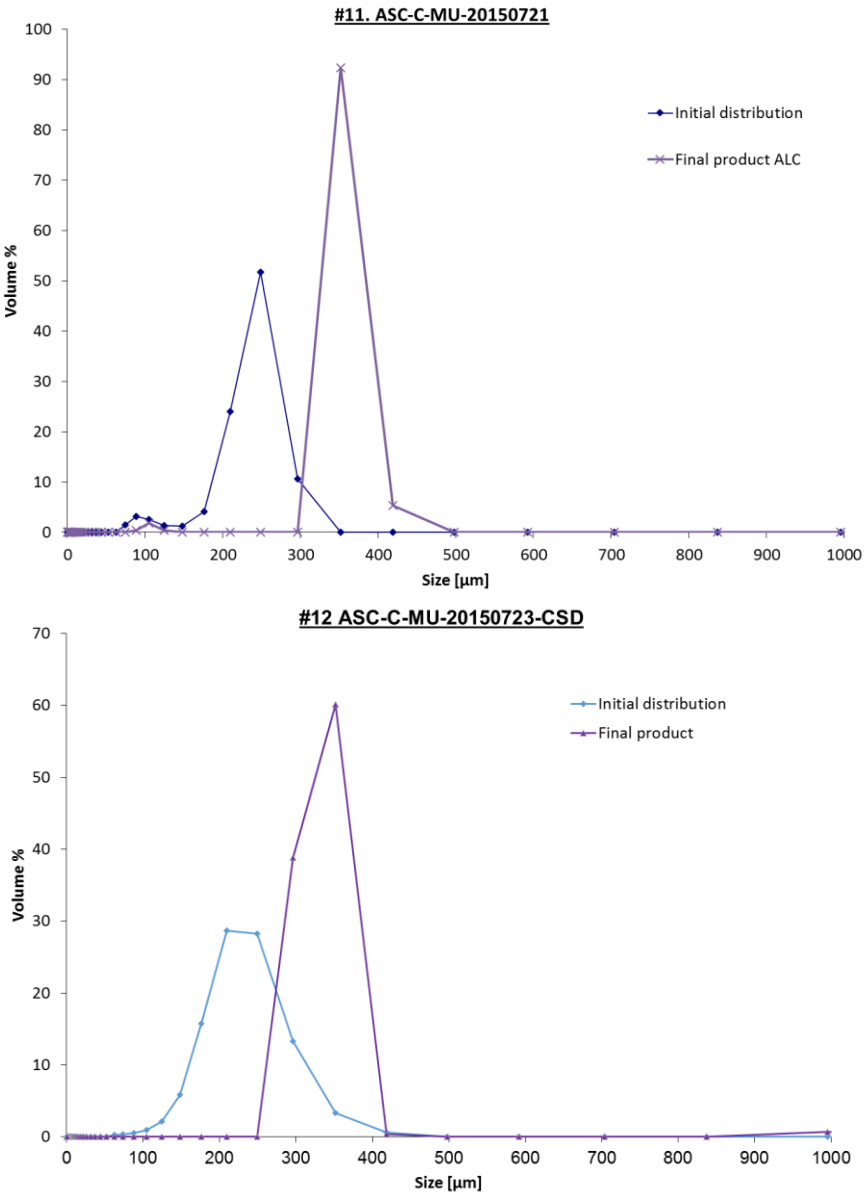
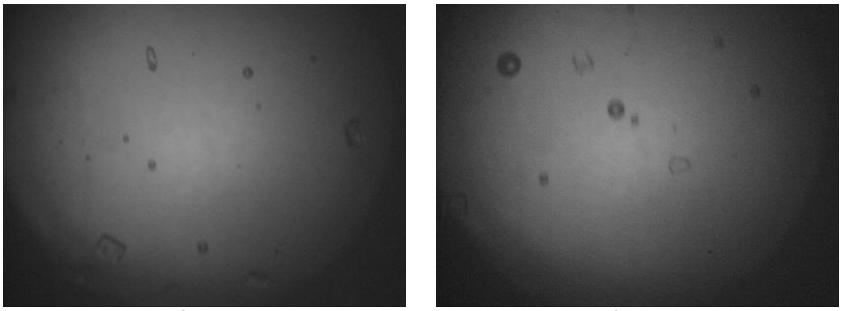
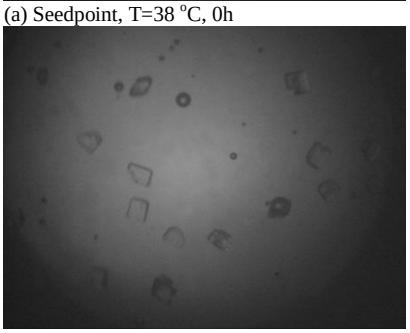


Figure 7.12: CSD of experiment #11 and #12

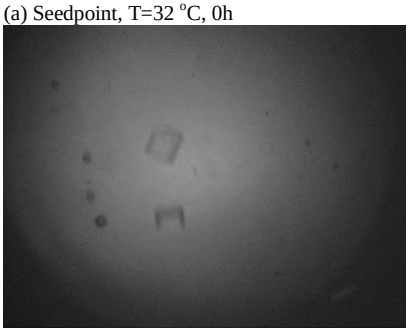


(a) Seedpoint, T=38 °C, 0h

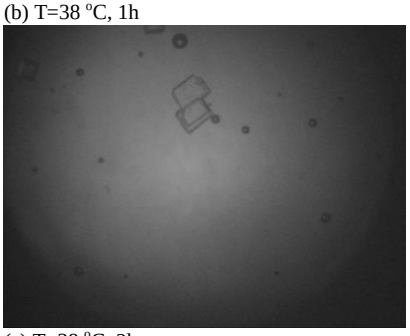
(a) Seedpoint, T=32 °C, 0h



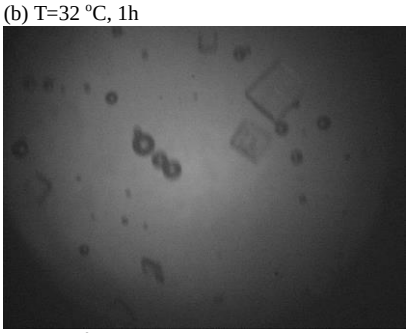
(b) T=38 °C, 1h



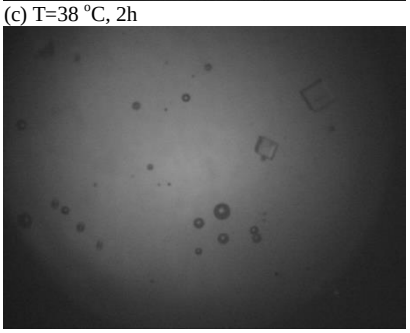
(b) T=32 °C, 1h



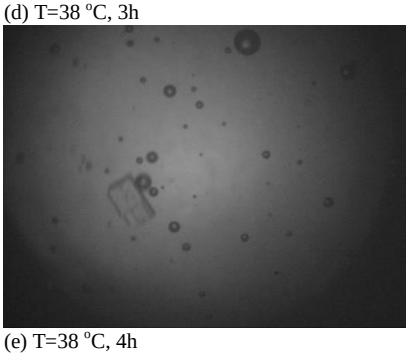
(c) T=38 °C, 2h



(c) T=32 °C,



(d) T=38 °C, 3h



(e) T=38 °C, 4h

Figure 7.13: Images of experiment #11 and #12 taken from the PVM

In Figure 7.8 CSD measurement of experiment #12 show a slightly greater CSD variation compared to experiment #11, possibly due to a short operating time. Even though, experiment #12 had an operating time of 2 hours, it showed crystal sizes equal to experiment #11. Possible reasons for fast growth are lower operating temperatures and possible supersaturated conditions at the start point of the experiment. It is recommended to take more samples in future experiments and to analyse the product crystals under a microscope, to give a better analysis of product quality. Furthermore, it is recommended to design and perform more experiments with the combination of the airlift crystallizer with the membrane unit, to analyse final product quality. The design should allow higher product mass to collect enough samples in a short time.

Comparison MaCC versus continuous cooling operation

Based on the results achieved from the performed experiments, the airlift crystallizer integrated with the membrane module (MaCC) has the potential to achieve a narrower CSD compared to continuous cooling operation. The main peak in the CSD measurement is at 352 µm in both the experiments #11 and #12, similar to experiments in the continuous cooling operation. As discussed in the section of the continuous cooling operation, samples were only taken from the bottom of the crystallizer. To give better and reliable analysis on product quality from a continuous process, it is recommended to take samples from the product line, and from the bottom of the crystallizer, and to compare these results. As well as from the experiment in the continuous cooling experiments, as with the MaCC operation, an increasing behaviour of the density is observed in the crystallizer, which indicates that the generation of supersaturation is greater than the depletion. Additional experiments are required to find optimal conditions.

The flux of the membrane unit was not measured during the experiments. Due to a pressure drop in the tubing from buffer vessel to airlift crystallizer, the speed of pump P301 gives a different flow rate than pump P304. Therefore, it is difficult to conclude whether the variation of the level in the buffer vessel is caused by membrane flux or pressure drop in the tubing. In future experiments, the pressure drop should be validated with the measured flow (from buffer vessel to airlift crystallizer).

Pressure drop

The residence time of all the continuous processes was three hours. The product flow rate was set to 100 ml/min (43 rpm) and a feed flow rate of 115 ml/min (50 rpm) for both the feed to the buffer vessel and the crystallizer. During the experiments, it was observed that the level in the crystallizer was decreasing with time. This indicates that the flow rate of the buffer vessel to the airlift crystallizer is lower than expected. After trial-and-error the feed flow rate was finally set to 74 rpm to maintain a constant level in the crystallizer. According to the description of the manufacturer and the test results in chapter 5, the pump speed of 74 rpm is related to a flow rate of 170 ml/min. However, no flow rate of 170 ml/min was measured by the flow meter (FT304). The measured flow rate was lower than the low limit value of the flow meter. This indicates a drop in pressure.

The pressure drop in the tubing between the membrane unit and the airlift crystallizer is calculated using the Darcy Weisbach equation:

$$\Delta p = \frac{f \cdot L \cdot v^2}{2d/\rho_L} \qquad (7\text{-}1)$$

Where:
v is the velocity of the medium [m/s]
f is a friction factor [-]
L is the length of the tube [m]
d is the inner diameter of the tube [m]

ρ_L is the density of the solution [kg/m^3]

The friction factor is approximated with the Swamee-Jain equation:

$$f = \frac{0.25}{log_{10}\left(\frac{\varepsilon}{3.7D} + \frac{5.74}{Re^{0.9}}\right)^2} \quad (7\text{-}2)$$

Where:
ε is the roughness height [m]
D is pipe diameter [m]
R_e is the Reynolds number

The relation between the pressure drop and the volume flow rate is shown in Figure 7.14. The pressure drop due to the height difference is included in the graph.

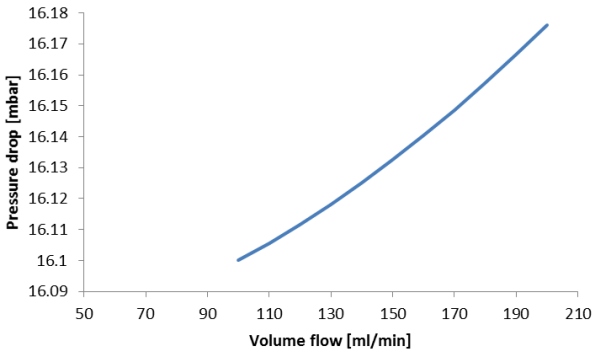


Figure 7.14: Pressure drop between membrane unit and crystallizer

It is recommended to validate the pressure drop in future experiments.

8

Conclusions and recommendations

8.1 Conclusions

A new experimental setup, called Membrane-assisted Crystallization (MaC), is designed, constructed and automated in this research to disentangle crystallization phenomena, such as primary and secondary nucleation, growth, dissolution, attrition and agglomeration, and to investigate these phenomena independently for further optimization and improvement of crystal properties, such as purity, shape of crystals, polymorphic form and CSD. The experimental setup is designed and constructed in a modular way to perform experiments with standalone units, both in batch and continuous operation, as well as in combined modes in which the crystallizer is connected to a membrane unit. Experiments with the new MaC setup have shown that it is possible to perform batch and continuous operated cooling and membrane-assisted crystallization experiments, in both the airlift crystallizer, as well as in stirred tank crystallizer.

Furthermore, it can be concluded that useful data is recorded and monitored by the control unit, which is designed and tested in this research. Process conditions, such as maintenance of flow rates in continuous processes, temperatures of the solution in the different vessel and setting a cooling profile during cooling batch operation, are automated in this research. Furthermore, pipelines are kept on temperature during experiments with the use of tracing. The safety of the plunger pump P306 is automated by a level switch (LI303) in the buffer vessel.

Test experiments with L-ascorbic acid showed that the Marprene tube, which is not traced, will be blocked if the flow is stopped and the solution is not removed from the tubing. This same problem occurred in the volume flow meter and the mass flow meter. The conclusion here is that a continuous flow is required to prevent clogging, or if the crystallizer is operated in batch mode, this sensible parts has to be by-passed.

It can be concluded that oxidation of L-ascorbic acid is dependent on temperature and surface area. The higher the operating temperature and the larger the surface area, the faster the oxidation of the L-ascorbic acid solution takes place. To prevent very fast oxidation, it is recommended to use distilled water for the solution, to strip the oxygen from the distilled water before preparing the solution and, to keep a blanket of nitrogen in all the vessels during experiments.

Experiments with L-ascorbic acid were performed in batch and continuous mode. The continuous mode was divided into continuous cooling and membrane-assisted continuous crystallization. The cooling batch experiments have shown a significant difference in the final product quality between a low and a high gas flow rate in the crystallizer, and between a linear and third-order cooling profile. The conclusion here is that using a high gas flow rate and third-order cooling profile, gives comparable results to previous research.

During the continuous cooling crystallization, narrower CSD and no influence of secondary nucleation were observed, compared to the cooling batch operation.
During the continuous membrane-assisted crystallization, narrower CSD was measured compared to continuous cooling crystallization. Peaks of maximum 352 µm were observed in the continuous operations. An overall conclusion is that this size can be possibly controlled by the liquid circulation velocity in the continuous processes. Additional experiments and sensitive analysis in continuous cooling mode and continuous membrane-assisted operations are required to check the influence on final crystal properties.

8.2 Recommendations

To extract reliable data from the pressure transmitters, to calculate the gas holdup, it is recommended to clean the tubes of the pressure transmitters, and to trace this tubes. Another recommendation is the replacement of the pressure transmitter which is measuring the pressure difference between the riser and ambient pressure. With this difference, the level in the airlift crystallizer can be estimated. This pressure transmitter has an operating limit between 0 mbar and 75 mbar. For a system with only water, the 75 mbar corresponds to 75 cm. The height difference between the overflow and the location of this pressure transmitter exceeds 80 cm. Therefore, during experiments, this pressure transmitter shows only a constant trend and the value shown on the control system is not valid. To measure a valid level in the airlift crystallizer, it is recommended to place this transmitter higher, or replace it with the 0 – 125 mbar transmitter.

The density measurements during this research gave a lot of errors, possibly due to the method of measurement. Air bubbles may entrap in the syringe, or crystals may form at the wall of the syringe and the density measurement equipment. It is recommended to filter the samples before measuring the density, and to keep the samples at temperature by using a simple warm bath. It is also recommended to measure the concentration of the solution, and to compare and calibrate the results with the density measurements. This will also help to prevent undersaturated or supersaturated solutions at the start of an experiment. It must be noted that the concentration of the solute may change after an experiment, due to solution removal, solvent removal, rinsing, etc. If this solution is saved for another experiment, it is important to bring this again in a saturated condition.

The sample point at the bottom of the crystallizer is lower than the product stream, see Figure 8.1. In the continuous mode, crystals are continuously removed from the airlift crystallizer and transported to the make-up vessel via the product line. When the valve of the sample point is closed, crystals may settle at this point, due to gravity, and CSD measurements may result in a different profile. It is recommended to design continuous experiments with a higher production rate, and collect samples from the bottom of the crystallizer, as well as from the product line to compare these results. As mentioned earlier, additional experiments are required. In this way a reliable analysis on the product quality can be made. For the samples from the product line, it is recommended to design a filtration system, just after the mass flow meter, to collect the product crystals which are transported from the crystallizer.

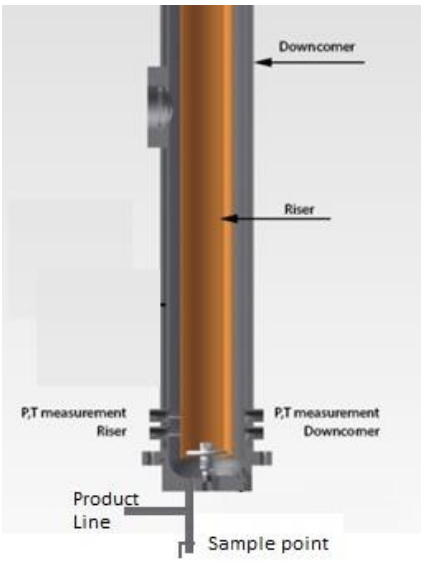


Figure 8.1: Sample point and product line at bottom of airlift

Note that the new eTape level sensor in the feed vessel is not accurate and it starts measuring beyond the 2 cm level. The problem of the inaccuracy is still unknown. It is recommended to use another type of level sensor.

During experiments, solvent and solution is removed from the system. Especially during continuous membrane-assisted operations, solution is lost during the rinsing of the buffer vessel. The amount of lost solution is difficult to determine during the experiments. When the solution is stored for another experiment, it is important to have enough solution, based on the design. Therefore, it is recommended to place a level sensor in the make-up vessel.

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Glossary

List of abbreviations

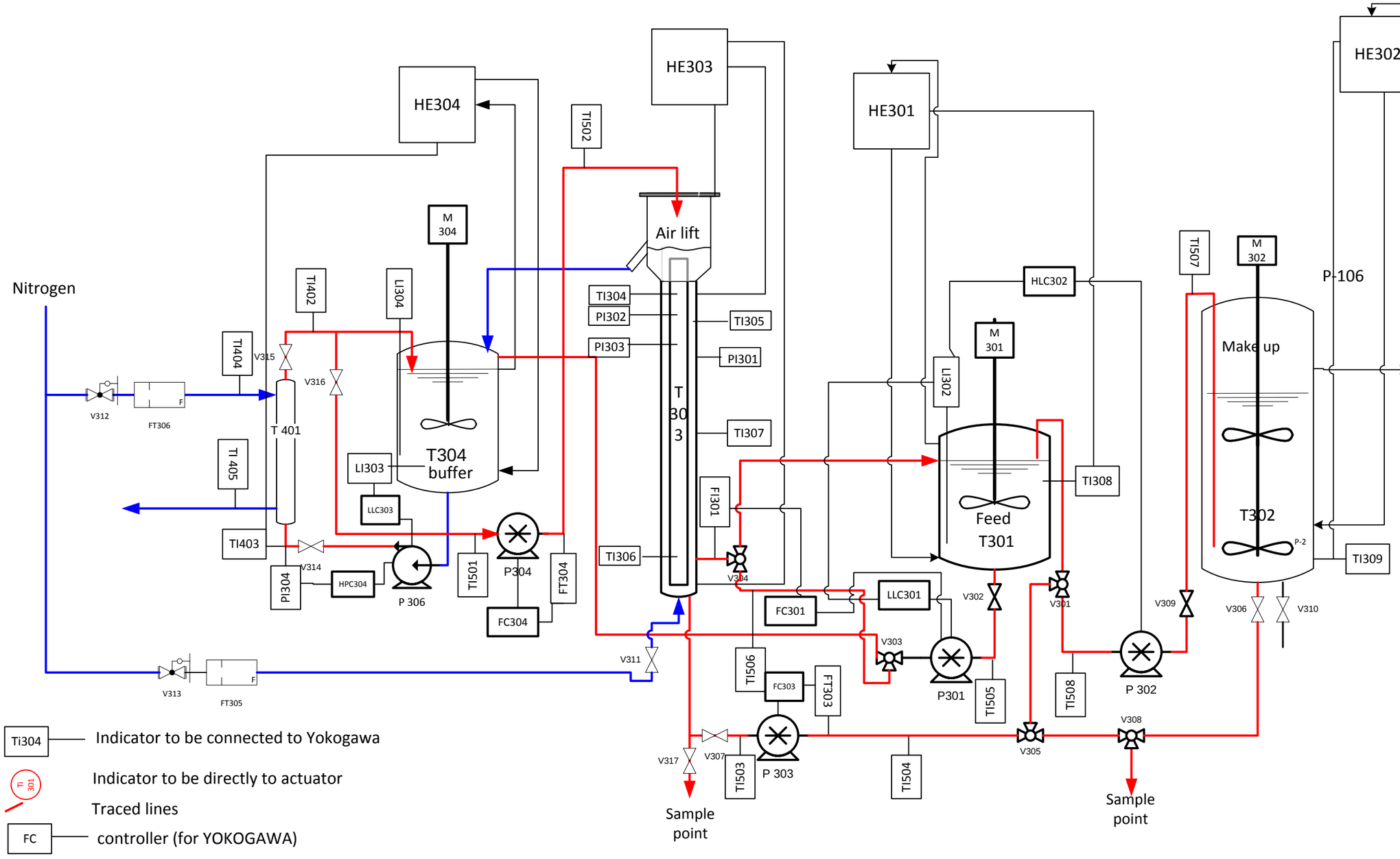
AGMD	Air Gap Membrane Distillation
ALC	Airlift crystallizer
API	Active Pharmaceutical Ingredients
ASC	L-Ascorbic acid
CSD	Crystal size distribution
DCMD	Direct Contact Membrane Distillation
DCS	Distributed Control Station
ENG	Engineering station
FCS	Field Control Station
HIS	Human Interface Station
MaC	Membrane-assisted Crystallization
MaCC	Continuous Membrane-assisted Crystallization
MD	Membrane Distillation
MSZW	Meta Stable Zone Width
MU	Membrane Unit
PFD	Process Flow Diagram
SGMD	Sweeping Gas Membrane Distillation
X_i	Quantile at percentile i
VMD	Vacuum Membrane Distillation

List of symbols

A	Cross section	[m^2]
c	Real concentration of a solution	[kg/kg]
c*	Saturation concentration	[kg/kg]
C_p	Heat capacity	[kJ/kg K]
H	Enthalpy	[kJ/kg]
L	Particle length	[m]
$\dot{m}_a$	Mass flow rate of air	[kg/s]
$\dot{m}_f$	Mass flow rate of feed	[kg/s]
m_s	Seed mass	[kg]
M_T	Total crystal mass	[kg]
N	Membrane distillation flux	[l/m^2 h]
p	Pressure	[bar]
P	Production rate	[kg/s]
R_e	Reynolds number	[-]
t	Time	[s]
T	Temperature	[^oC]
V	Crystallizer volume	[m^3]
ε	Liquid fraction	[-]
ξ	Friction factor	[-]
α_g	Gas fraction	[-]
α_s	Solid fraction	[-]
ϕ_v	Volumetric flow rate	[m^3/s]
μ	Chemical potential	[J/mol]

η	Dynamic viscosity	[Pa s]
ρ	Material density	[kg/m^3]
τ	Residence time	[s]
ω	Mass fraction	[-]
ν	Velocity	[m/s]

Appendix A – Process flowsheet and description of the processes


Nitrogen
HE304
HE303
HE301
HE302
TI502
M 304
Air lift
TI304
PI302
PI303
TI305
PI301
TI307
T 30 3
FI301
TI306
V304
FC301
LLC301
HLC302
M 301
LI302
TI308
Feed T301
V302
V301
TI507
M 302
P-106
Make up
T302
P-2
TI309
V309
V306
V310
TI402
LI304
TI404
V315
V316
V312
FT306
T 401
TI 405
LI303
T304 buffer
LLC303
TI403
V314
PI304
HPC304
P 306
TI501
P304
FT304
FC304
V311
V313
FT305
TI506
FC303
FT303
V303
P301
TI505
TI508
P 302
V308
V305
V317
V307
P 303
TI503
TI504
Sample point
Sample point
Ti304 — Indicator to be connected to Yokogawa
Indicator to be directly to actuator
Traced lines
FC — controller (for YOKOGAWA)

A.1 Preparation of the solution

The experiment starts with preparing the solution. First the required volume of the solvent and the solute is calculated to prepare a saturated solution. The total volume is dependent on the desired experiment. For cooling batch experiments, minimum 18 L is required, for cooling continuous operations, minimum 30 L is required and for continuous membrane-assisted crystallization, minimum 40 L is required. If the solution is used for more than one experiment, it is preferred to prepare minimum 5 L extra since solution might lose during rinsing. The valves V306 and V310 at the bottom of the make-up vessel (T302) are closed. Set first a temperature on the Yokogawa unit, then switch on the thermostatic bath HE302, on the hardware. In this stadium it is preferred to operate the controller manually. The solvent is added in the make-up vessel, followed by adding nitrogen (if needed) and starting stirrer M302 with the button on the electrical cabinet. The speed of the stirrer is set on the control unit. For safety reasons, the stirrer starts operating at 20% of the total speed range. This corresponds to 250 rpm on the Yokogawa unit. During stripping of the oxygen from the solvent, the stirrer can be operated at low speed (300 rpm). For L-ascorbic acid solutions, stripping of oxygen are performed for approximately 4 hours. Once the solvent is on temperature, the PID controller is changed to the automatic mode and solute is added gradually to the solvent. The speed of the stirrer is gradually increased to 1200 rpm, to make sure that all the solute will dissolve and to prevent settling of the solute at the bottom of the make-up vessel (T302). After the preparation of the solution, M302 is operated between 300 and 500 rpm, and the designed experiment can be started.

A.2 Cooling batch experiments

The cooling batch operation is performed with the airlift crystallizer (T303) as a standalone unit. The make-up vessel (T301) is needed for the preparation of the solution. The experiment starts with switching on HE303 on the hardware, and setting a temperature by the Yokogawa unit. It is preferred to transport the solution from T302 to T303 from the product line, by bypassing the mass flow meter FT303. The product flow of T303 is closed. Tracing TI503 and TI504 are switched on from the Yokogawa unit. The valves V306, V308, V305 and V307 in PL304 are opened, while V317 is closed. Air or nitrogen is added to the airlift on a low pressure (2 bar) and a low flow rate (150 l/m). The equalizer valve of pressure transmitters PI301 and PI302 are opened, and the pump P303 is starting to transfer the solution from T302 to T303. Prior to the transfer, V306 is opened. During the filling of T303, the gas flow to T303 is stopped shortly, to deaerate the tubes of the pressure transmitters. After the level in T303 is beyond the top tube, the equalizer valves are closed, and the gas flow is turned on again. Pump P303 is running until all the solution is transported to T303. P303 is stopped after transportation of the solution, and V307 is closed. The Marprene tube of P303 is disconnected from the PL304, and hot water is immediately transported to PL304 by starting P303. PL304 is rinsed for a couple of minutes to prevent blockage. After rinsing, the Marprene tube is connected again. HE301, TI503, TI504 and M302 are switched off. Now the experiment can start by increasing the gas pressure of T303 to 7 bar and increasing the gas flow rate to the desired value. A cooling profile is set on the Yokogawa unit, followed by changing the operation mode to cascade.

If the solution is going to be saved for a next experiment, all the crystals should be dissolved in the crystallizer by increasing the temperature. The solution is then transported from T303 to T302 through PL304, by opening V307 and starting P303. After the solution is transported, valve V306 is

closed immediately. HE302 is maintaining the temperature of the solution in T302, and M302 is set to a low speed (300 rpm). The airlift crystallizer (T303) is filled with hot water and rinsed. The direction of V308 is changed to also clean the tubing.

If the solution is not saved after an experiment, this can be removed directly from T303, and T303 is rinsed with hot water. A small amount of water is kept in the vessels and the tubes after rinsing.

A.3 Continuous cooling crystallization

For preparation of the solution, see section A.1, a temperature for preheating T301 and T303 is set on the Yokogawa unit, followed by switching on HE301 and HE303, on the hardware. During start-up, the PID controllers are operated manually. Valves V309 and V301 in PL301, V303 and V304 in PL305 and V307, V308 and V306 in PL304 are opened in the correct direction. Tracing TI507, TI508, TI505, TI506, TI503 and TI504 are switched on from the Yokogawa system. Before starting with the transport of solution, it is advised to first check if the product flow on the bottom of T302 is not blocked. This can be done by disconnecting the Marprene tube from PL304, and starting a reverse flow. Nitrogen is added to T301 and T303. P302 is started to transport the solution from T302 to T301. Mixer M301 should be started manually when there is enough solution in the feed tank T301. Air or nitrogen is added to the airlift on a low pressure (2 bar) and a low flow rate (150 l/m). The equalizer valve of pressure transmitters PI301 and PI 302 are opened, and pump P301 is started to transfer the solution from T301 to T303. During the filling of T303, the gas flow to T303 is stopped shortly, to deaerate the tubes of the pressure transmitters. After the level in T303 is beyond the top tube, the equalizer valves are closed, and the gas flow is turned on again. The PID controllers of T301 and T303 can now be changed to automatic mode. After filling T303, pump P303 is started. Now there is a continuous flow between T301, T303 and T302. The experiment can start now. The gas pressure to the crystallizer (T303) is increased to 7 bar and the gas flow rate to the desired value.

If the solution is saved after an experiment, first the tube inside T302 is slided to above the level in T302, to make sure that all the solution in PL301 is removed. Pump P302 is stopped when no solution is left over in PL301. If T301 and PL305 are empty, pump P301 is stopped. When the crystallizer T303 and product line P304 is empty, pump P303 is stopped, and V306 at the bottom of the make-up vessel (T302) is closed. All the used vessels and tubes are rinsed with hot water, by adding water in T301 and T303 and circulating the water through the pipelines. Unused thermostatic baths, stirrers, pumps, nitrogen and tracing are stopped.

If the solution is not saved after an experiment, this can be removed from T303 and T302. After rinsing, a small amount of water is kept in the vessels and tubes.

A.4 Continuous membrane-assisted crystallization

For preparation of the solution, see section A.1. A temperature for preheating T301, T303 and T304 is set on the Yokogawa unit, followed by switching on HE301, HE303 and HE304, on the hardware. During start-up, the PID controllers are operated manually. The valves V309 and V301 in PL301, V303 and V304 in PL305 and V307, V308 and V306 in PL304 are opened in the correct direction. It must be noted that the buffer tank T304, can be either filled from the overflow (PL303) of T303 or directly from the feed tank (T301). All the tracing are switched on from Yokogawa. Before starting with the transport of solution, it is advised to first check if the product flow on the

bottom of T302 is not blocked. This can be done by disconnecting the Marprene tube from PL304, and starting a reverse flow. Nitrogen is added to T301 and T303. P302 is starting to transport the solution from T302 to T301. Mixer M301 is started manually when there is enough solution in the feed tank T301. Air or nitrogen is added to the airlift on a low pressure (2 bar) and a low flow rate (150 l/m). The equalizer valve of pressure transmitters PI301 and PI 302 are opened, and pump P301 is starting to transfer the solution from T301 to T303. During the filling of T303, the gas flow to T303 is stopped shortly, to deaerate the tubes of the pressure transmitters. After the level in T303 is beyond the top tube, the equalizer valves are closed, and the gas flow is turned on again. When all the vessels have enough solution, the PID controllers of T301, T303 and T304 can be changed to automatic mode. After filling T303, pump P303 is started. Valves V314 in PL401 and V315 in PL402 are opened, followed by starting pump P306 (from the electrical cabinet) and P304. The speed of P306 is set on the Yokogawa unit. To operate at 50 Hz frequency, the speed should be set to 560 rpm on Yokogawa. Now there is a continuous flow between T301, T303, T304, T401 and T302. The experiment can start now. The gas pressure to the crystallizer (T303) is increased to 7 bar and the gas flow rate to the desired value.

If the solution is saved after an experiment, first the tube inside T302 is slided to above the level in T302, to make sure that all the solution in PL301 is removed. Pump P302 is stopped when no solution is left over in PL301. If T301 and PL305 is empty, pump P301 is stopped. The solution of the buffer vessel is removed from a valve on P306. Pump P304 is topped to stop the flow between T304 and T303. The buffer tank is rinsed by adding hot water into the tank and keep removing, until the tank and the membrane module is solution free. Then pump P306 is stopped, and valves in PL401 and PL402 are closed to keep water in the membrane module (T401). Pump P304 is operated shortly to rinse PL403 and FT304. When the crystallizer T303 and product line P304 are empty, pump P303 is stopped, and V306 at the bottom of the make-up vessel (T302) is closed. All the used vessels and tubes are rinsed with hot water, by adding water in T301 and T303 and circulating water through the pipelines. Unused thermostatic baths, stirrers, pumps, nitrogen and tracing are stopped.

If the solution is not saved after an experiment, this can be removed from T303, T304 and T302.
After rinsing, a small amount of water is kept in the vessels and tubes.

Appendix B – List of the equipment

Table B.1: List of input and output of the Yokogawa unit

Slot	1		2		3		4		5		6		7		8	
Type	RTD		RTD		RTD		DI/O		AI		AI/O		AI/O		AI/O	
Card Nr.	1AAR145-S		2AAR145-S		3AAR145-S		4ADV859-P		5AAI141-S		6AAI841-S		7AAI841-S		8AAI841-S	
Nr. adr.	16		16		16		32		16		16		16		16	
	In	TI 402	**In**	TI501	**In**		**In**	LI303	**In**	FT303	**In**	PI 301	**In**	HI301A	**In**	
	In	TI 403	**In**	TI502	**In**		**In**		**In**	FT304	**In**	PI 302	**In**	HI301B	**In**	
	In	TI 404	**In**	TI503	**In**		**In**		**In**		**In**	PI 303	**In**	HI302A	**In**	
	In	TI 405	**In**	TI504	**In**		**In**		**In**	LT302	**In**	PI304	**In**	HI302B	**In**	
	In	TI 304	**In**	TI505	**In**		**In**		**In**	LT304	**In**		**In**	HI303A	**In**	
	In	TI 305	**In**	TI506	**In**		**In**		**In**	FT301	**In**		**In**	HI303B	**In**	
	In	TI 306	**In**	TI507	**In**		**In**		**In**		**In**		**In**	HI304A	**In**	
	In	TI 307	**In**	TI508	**In**		**In**		**In**		**In**		**In**	HI304B	**In**	
	In	TI 308	**In**		**In**		**In**		**In**		**Out**		**Out**	HO301A	**Out**	
	In	TI 309	**In**		**In**		**In**		**In**		**Out**		**Out**	HO301B	**Out**	
	In		**In**		**In**		**In**		**In**		**Out**		**Out**	HO302A	**Out**	
	In		**In**		**In**		**In**		**In**		**Out**	P306	**Out**	HO302B	**Out**	
	In		**In**		**In**		**In**		**In**		**Out**	FC 301	**Out**	HO303A	**Out**	
	In		**In**		**In**		**In**		**In**		**Out**	FC 303	**Out**	HO303B	**Out**	
	In		**In**		**In**		**In**		**In**		**Out**	FC 304	**Out**	HO304A	**Out**	
	In		**In**		**In**		**In**		**In**		**Out**	M302	**Out**	HO304B	**Out**	
							Out	TR501								
							Out	TR502								
							Out	TR503								
							Out	TR504								
							Out	TR505								
							Out	TR506								
							Out	TR507								
							Out	TR508								
							Out	LLC301								
							Out	HLC302								
							Out	LLC303								
							Out	HPC304								
							Out									
							Out									
							Out									
							Out									

Table B.2: Explanation of the tagnames

TAG	Explanation	Criteria					
	Vessels	**Volume [L]**	**Diameter [m]**	**Height [m]**	**Material [-]**		
T301	Feed tank	10	0.3	0.45	glass		
T302	Make-up tank	70	0.3	1	SS 3.16		
T303	Airlift crystallizer	20	0.13	1.42	SS 3.16		
T304	Buffer-tank	30	0.3	0.39			
T401	Membrane unit		0.15	0.2			
T402	Batch crystallizer	2	0.09	0.3	glass		
	Pumps	**Type**	**Control type**	**Yokogawa power**	**Power connection**	**Speed**	**Inputs**
P301	Pump from feed tank to airlift crystallizer	Watson Marlow 323 U/D	Analog	0-10 V	Outlet	3-400 rpm	FT301
P302	Pump from Product tank to feed tank	Watson Marlow 504U	On/off		Outlet	4-400 rpm	
P303	Pump from airlift to product tank	Watson Marlow 323 U/D	Analog	0-10 V	Outlet	3-400 rpm	
P304	Pump from membrane to airlift	Watson Marlow 323 U/D	Analog	0-10 V	Outlet	3-400 rpm	FT304
P306	Pump from buffer tank to membrane unit	Plunger 5CP6221	Frequency	0-50 Hz	Elec. cabinet	560-1410 rpm	LI303
	Temperature sensors (PT100)	**Type**	**Yokogawa power**	**Power connection**	**Control**		
TI304	Temperature indicator for riser in top of airlift	RTD 3 thread	4-20 mA	Yokogawa	HE303		
TI305	Temperature indicator for downcomer in top of airlift	RTD 3 thread	4-20 mA	Yokogawa	HE303		
TI306	Temperature indicator for riser in the bottom of airlift	RTD 3 thread	4-20 mA	Yokogawa	HE303		
TI307	Temperature indicator for downcomer in the bottom of airlift	RTD 3 thread	4-20 mA	Yokogawa	HE303		
TI402	Temperature indicator for membrane out	RTD 3 thread	4-20 mA	Yokogawa			
TI403	Temperature indicator for membrane in	RTD 3 thread	4-20 mA	Yokogawa	HE304		
TI404	Temperature indicator for air in membrane	RTD 3 thread	4-20 mA	Yokogawa			
TI405	Temperature indicator for air out membrane	RTD 3 thread	4-20 mA	Yokogawa			
TI 308	Temperature indicator feed vessel	RTD 3 thread	4-20 mA	Yokogawa	HE301		
TI 309	Temperature indicator make-up vessel	RTD 3 thread	4-20 mA	Yokogawa	HE302		
TI 501	Temperature indicator for tracing membrane to airlift	RTD 3 thread	4-20 mA	Yokogawa	TR201		
TI 502	Temperature indicator for tracing membrane to airlift	RTD 3 thread	4-20 mA	Yokogawa	TR502		
TI 503	Temperature indicator for tracing product to airlift	RTD 3 thread	4-20 mA	Yokogawa	TR503		
TI 504	Temperature indicator for tracing product to airlift	RTD 3 thread	4-20 mA	Yokogawa	TR504		
TI 505	Temperature indicator for tracing feed to airlift	RTD 3 thread	4-20 mA	Yokogawa	TR505		
TI 506	Temperature indicator for tracing feed to airlift	RTD 3 thread	4-20 mA	Yokogawa	TR506		
TI 507	Temperature indicator for tracing product to feed	RTD 3 thread	4-20 mA	Yokogawa	TR507		
TI 508	Temperature indicator for tracing product to feed	RTD 3 thread	4-20 mA	Yokogawa	TR508		

	Level indicators/controller	Type	Yokogawa power	Power connection	Control	Measuring
LI301	Level indicator feed tank	12" eTape	4-20 mA	Yokogawa	P301	0-30 cm
LI303	Level indicator low liquid level buffer vessel	Sp conductivity	On/off	Yokogawa	P306	
LI304	Level meter buffer vessel	ultrasound	4-20 mA	Yokogawa		-9 – 294 mm

	Flow meters	Type	Yokogawa power	Power connection	Control	Measuring
FT301	Flow meter in feed line	Magnetic FMG82	4-20 mA	Yokogawa	P301	0.114-11.365 l/min
FT303	Density mass flow meter in product line	Coriolis M15	4-20 mA	Yokogawa		0.6-30 kg/h
FT304	Flow meter in buffer return flow	Magnetic FMG82	4-20 mA	Yokogawa	P304	0.114-11.365 l/min

	Pressure sensors	Type	Yokogawa power	Power connection	Measuring
PI301	Pressure diff. indicator over downcomer	Siemens DSIII	4-20 mA	Yokogawa	0-125 mbar
PI302	Pressure diff indicator over riser	Siemens DSIII	4-20 mA	Yokogawa	0-125 mbar
PI303	Pressure difference indicator riser - ambient	Siemens DSIII	4-20 mA	Yokogawa	0-75 mbar
PI304	Pressure sensor membrane				

	Thermostatic baths	Type	Yokogawa power	Power connection	Inputs	Bath volume [L]
HE301	Thermostatic bath for feed tank	Lauda RE415 Gold	4-20 mA	Outlet	TI308	4
HE302	Thermostatic bath for make-up tank	Lauda RE1050 Gold	4-20 mA	Outlet	TI309	10
HE303	Thermostatic bath for airlift crystallizer	Lauda RE1050 Gold	4-20 mA	Outlet	TI304-TI307	10
HE304	Thermostatic bath for buffer tank	Lauda RE415 Silver	4-20 mA	Outlet	TI403	4

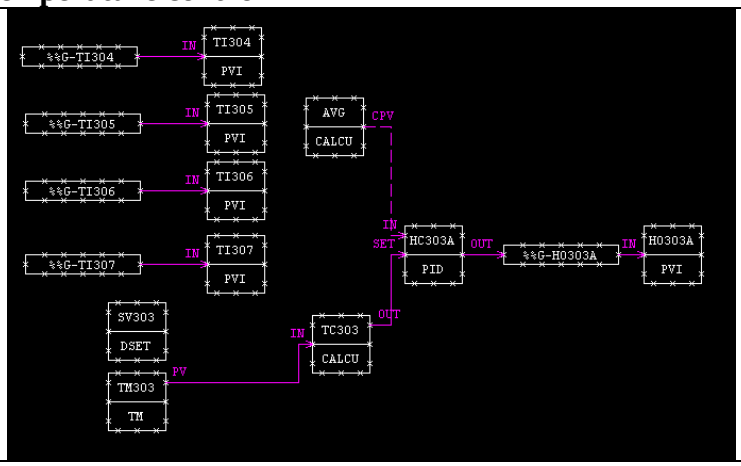
	Stirrer motors	Type	Power connection	Inputs	Speed
M301	Motor of feed tank stirrer	Heidolph RZR2021	Outlet		40-2000 rpm
M302	Motor of make-up tank stirrer	Lightnin Mi5P1	Outlet	Frequency	250-1500 rpm
M304	Motor of buffer tank stirrer	Heidolph RZR2051	Outlet		50-2000 rpm
M402	Motor of batch crystallizer stirrer	Heidolph RZR2051	Outlet		50-2000 rpm

	Tubes	Material	Internal diameter [mm]	Tracing
PL301	Pipeline from make-up to feed tank	Stainless steel	8	Y
PL302	Pipeline from feed tank, back to feed tank	Stainless steel	8	N
PL303	Overflow from airlift to buffer tank	PFA	10	N
PL304	Pipeline from airlift to make-up tank	Stainless steel	8	Y
PL305	Pipeline from feed tank to airlift	Stainless steel	8	Y
PL306	Pipeline from feed tank to buffer tank	Stainless steel	8	N
PL401	Pipeline from membrane to buffer tank	Stainless steel	10	N
PL402	Pipeline from buffer tank to membrane	Stainless steel	10	N
PL403	Pipeline from buffer tank to airlift	Stainless steel	8	Y

	Valves	Type
V301	Valve in feed line between P302 and feed tank T301	3-way
V302	Valve to close bottom of feed tank	Open-close
V303	Valve between P301 and airlift/buffer	3-way
V304	Valve between V303 and T303/T301	3-way
V305	Valve in product line between P303 and V301	3-way
V306	Valve to close bottom of make-up tank	Open-close
V307	Valve to close product flow from T303	Open-close
V308	Valve in product line between P303 and V305	3-way
V309	Valve in product line between P302 and T302	Open-close
V310	Valve in bottom T302 for draining	Open-close
V311	Valve for air supply at bottom airlift	Open-close
V312	Control valve for air supply membrane unit	Open-close
V313	Control valve to air supply air lift crystalliser	Open-close
V314	Valve for feed inlet membrane unit between P306 and T401	Open-close
V315	Valve for membrane outlet	Open-close
V316	Valve between membrane and P304	Open-close
V317	Valve for product samples at bottom of airlift	Open-close
V318	Valve for rinsing feed flow of airlift	Open-close

Examples from Yokogawa control system

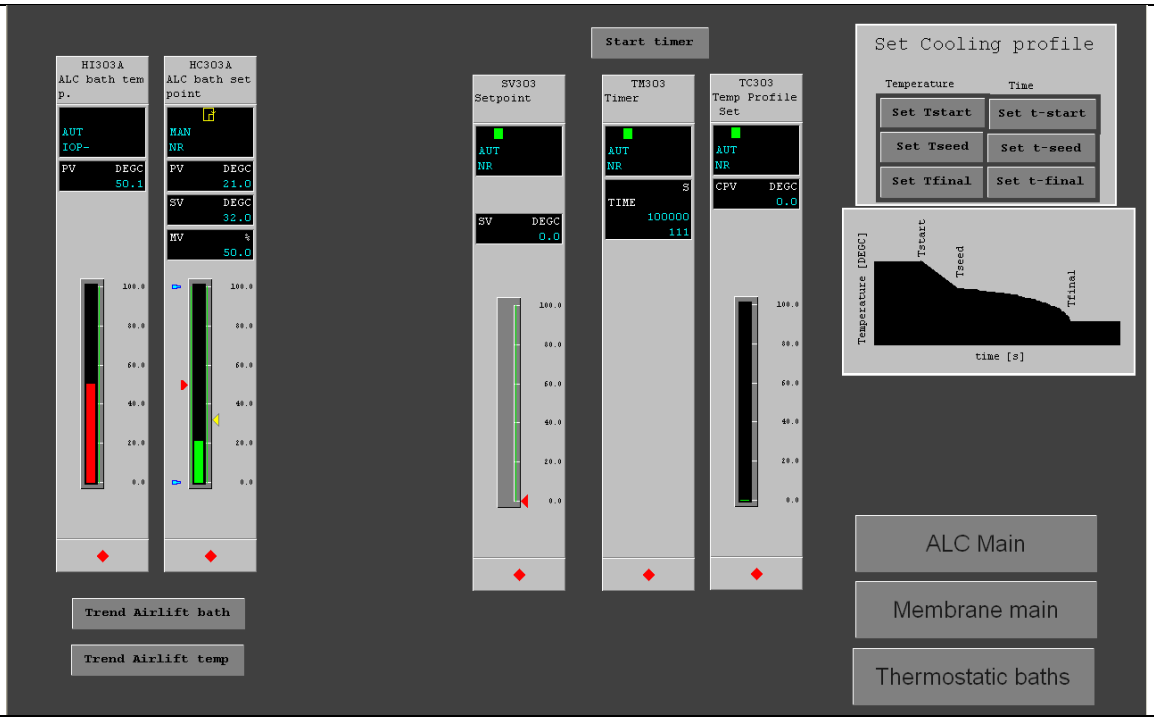
Airlift crystallizer temperature control



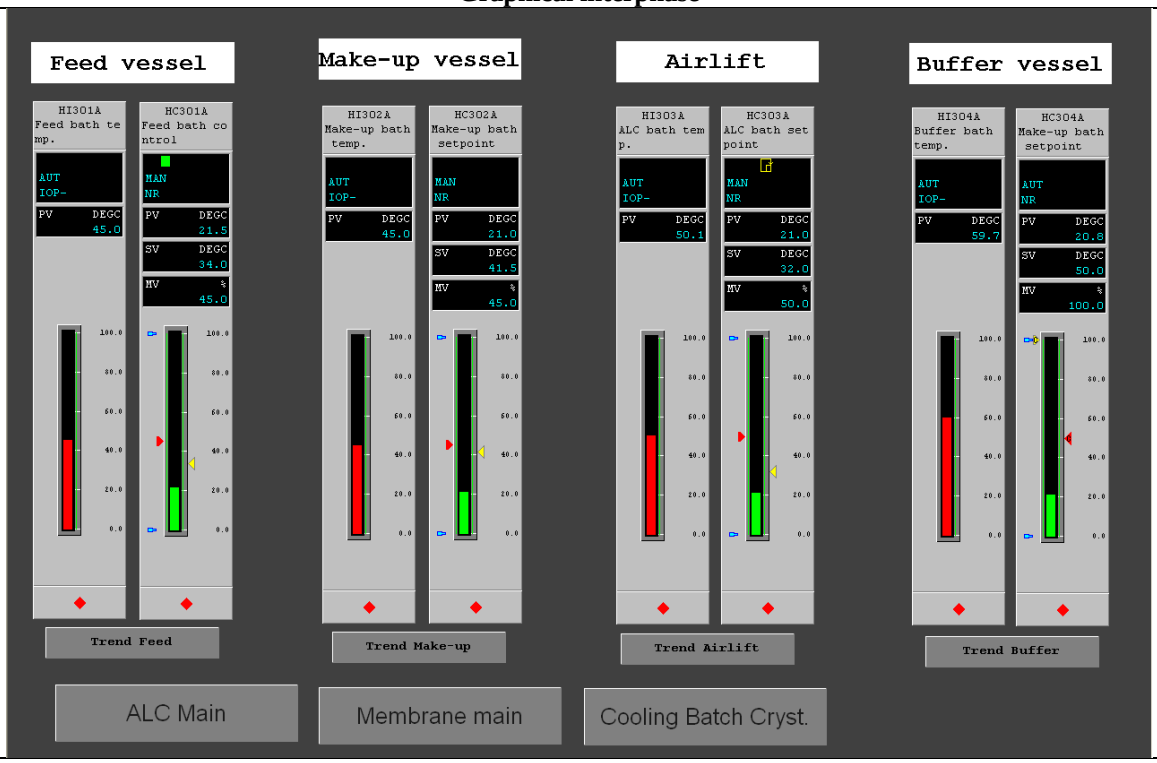
Calculation block for cooling profile – cooling batch only

```
 1|program
 2|
 3|#Define Tt CPV          ! Output of calculation block
 4|#Define T1 P01          ! Lineair temp. profile to seedpoint
 5|#Define Ts P02          ! 3rd order profile from seedpoint to final
 6|#Define Tf P03          ! Final temperature
 7|#Define tm1 P04         ! Time at start (T1)
 8|#Define tms P05         ! Time at seed (Ts)
 9|#Define tmf P06         ! Time at final (Tf)
10|
11|
12|Alias tm TM303.PV       ! timer is known as tm
13|Alias SP SV303.SV       ! setpoint value is known as SP
14|#Define TEMP AVG.CPV    ! average temperature in airlift
15|
16|if (tm<=tm1) then
17|  Tt = T1
18|end if
19|
20|if(tm > tm1)and (tm <= tms) then
21|  Tt = Ts+((T1-Ts)*(tm-tms)/(tm1-tms))
22|end if
23|
24|if (tm > tms) and (tm <=tmf) then
25|!  Tt = Tf+((Ts-Tf)*(tm-tmf)/(tms-tmf))
26|
27|  Tt = Ts-(Ts-Tf)*((tm/tmf)*(tm/tmf)*(tm/tmf))
28|end if
29|
30|if (tm>tmf) then
31|  Tt = Tf
32|end if
33|
34|If (tm>tmf+10) then
35|  TM303.BSTS = STOP
36|  Tt = SP
37|end if
38|
39|end
40|
```

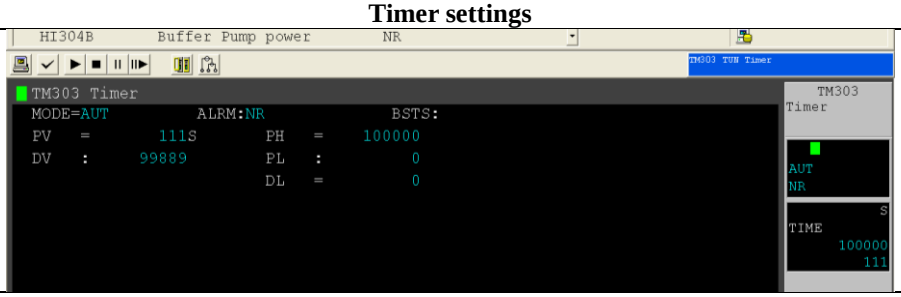
(HC303A)



Graphical interphase

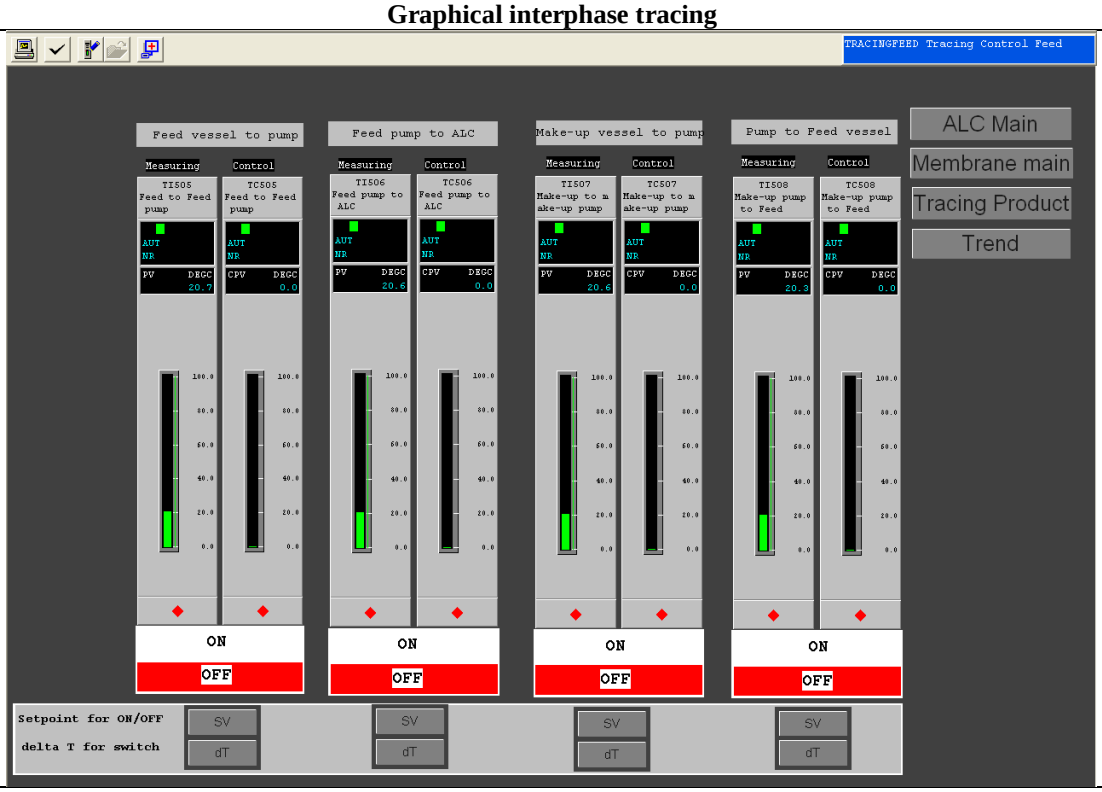


Timer settings



Tracing control

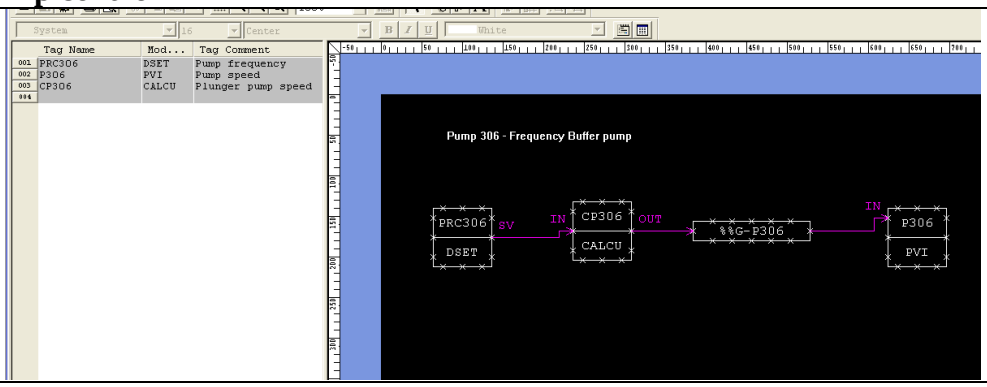
Graphical interphase tracing



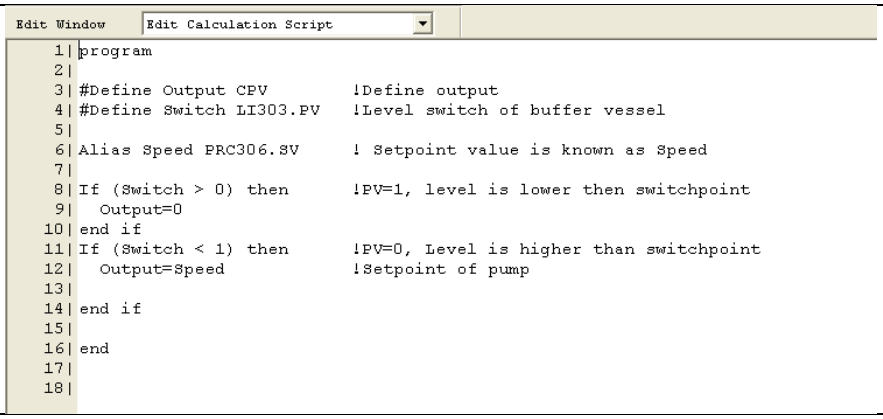
Calculation block for on-off

```
program

#Define SwitchP P01    !P01 is the setpoint value
#define deltaT P02     !P02 is temperature tolerance for on and off

#define Output CPV

Alias Temp TI502.PV    !The measured temperature of pt100
Alias HEX TR502.PV     !The output value (0=off, 1=on)

If (Temp > SwitchP +deltaT ) then
    HEX = 0
end if
If (Temp < SwitchP -deltaT ) then
    HEX = 1
end if

Output = SwitchP

End
```

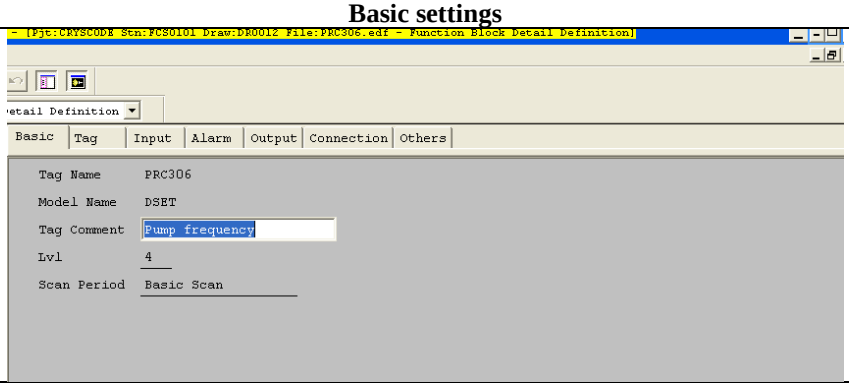
Plunger pump control



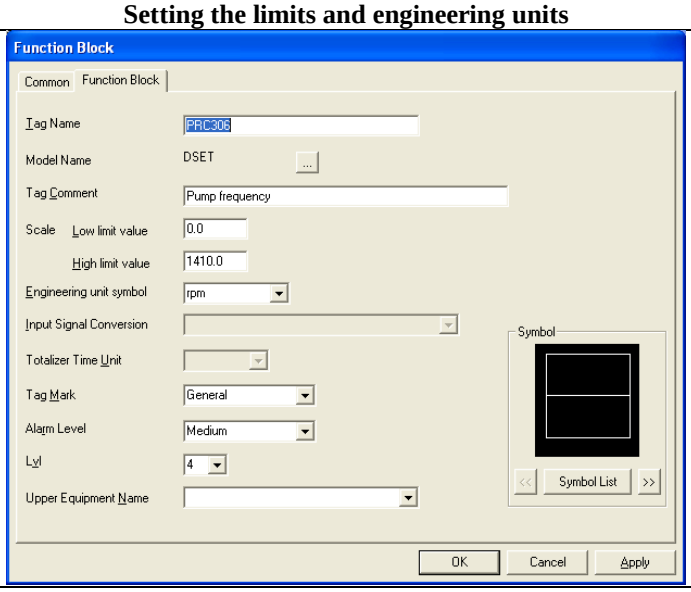
Calculation block for switch



Basic settings



Setting the limits and engineering units



Appendix C – Flowsheet for experiments

Membrane-assisted Crystallizer (MaC)

Make up

Feed

Airlift

Buffer

Membrane

Process

Notes:

Vessels:
- T301: Feed vessel
- T302: Make up vessel
- T303: Airlift crystallizer
- T304: Buffer vessel
- T401: membrane unit

Thermostatic baths:
- HE301: Thermostatic bath for T301
- HE302: Thermostatic bath for T302
- HE303: Thermostatic bath for T303
- HE304: Thermostatic bath for T304

Pumps:
- P301: From T301 to T303/T304
- P302: From T302 to T301
- P303: From T303 to T302
- P304: From T401 to T303
- P306: From T304 to T401

Mixers:
- M301: mixer for T301
- M302: mixer for T302
- M303: mixer for T304

Pipelines:
- PL301: From T302 to T301
- PL302: From T301 to T301
- PL303: From T303 to T304
- PL304: From T303 to T302
- PL305: From T301 to T303
- PL306: From T301 to T304
- PL401: From T401 to T304
- PL402: From T304 to T401
- PL403: From T304 to T303

Tracing:
- TI501: Tracing T401 to P304
- TI502: Tracing P304 to T303
- TI503: Tracing T303 to P303
- TI504: Tracing P303 to T302
- TI505: Tracing T301 to P301
- TI506: Tracing T301 to T303
- TI507: Tracing T302 to P302
- TI508: Tracing P302 to T301

[1]. Prepare solution in T302:
- Add N2 and switch on HE302 (T from Yokogawa)
- Close valves in PL304
- Add solvent
- Start M302 from Yokogawa (minimum 250 rpm)
- Bring solvent on temperature and strip oxygen
- Add solute gradually and bring on temperature

During a continuous process:
- Turn off M302 at end of experiment
- Wait untill crystals are settled for samples
- Turn on M302 and dissolve left over crystals

Is the solute dissolved?

No → Wait untill all crystals are settled, Keep mixing and check visual for disollution

Yes

[2]. Fill the feed vessel T301:
- Add N2 and switch on HE301 (T from Yokogawa)
- Open valves in PL301
- Switch on TI507 and TI508 from Yokogawa
- Start P302
- Start M301
- Check level in T301 and prevent overflow

Recycle:
- Open valves in PL302
- Turn on P301

Recycle feed flow? Yes → Recycle

No

Level in T301 >75%? No → [2]. Fill the feed vessel T301

(extra check)

Yes

[3]. Fill the Airlift T303:
- Add N2 and switch on HE303 (T from Yokogawa)
- Open valves in PL305
- Switch on TI505 and TI506 from Yokogawa
- Start P301
- Stop N2 and deaerate pressure transmitters during filling
- If level is beyond the top transmitter, add N2
- Check level in T303 (from top or through PL404 (overflow))

Crystallization including the membrane unit?

Yes → [4]. Fill the buffer T304:

Option 1. From T301:	Option 2. From overflow:
• Add N2 and Switch on HE304 (T from Yokogawa) • Open valves in PL306 • Check if P301 is running • Start M303	• Add N2 and Switch on HE304 (T from Yokogawa) • Fill through PL404 (keep filling T303) • Check if P301 is running • Turn on M303

Level in T304 >75%? No → [4]. Fill the buffer T304

Yes

[5]. Generate supersaturation:

No → Cooling cryst. Batch:
- Stop P302 and P301
- Close valves in PL304
- Measure concentration
- Set a cooling profile for T303
- Operate according to experimental design
- Rinse T301 and T302 and tubes to prevent clogging

Sampling:
- Open V317 (bottom T303) to take samples

At the end of the process:
- Take samples for CSD from V317
- Dissolve crystals in T303
- Open valves in PL304
- Start P303 to transport solution to T302
- Stop P303 if T303 is empty
- Clean according to cleaning flowsheet
- Check on pumps, tracing, thermostatic baths, stirrers and air/nitrogen

Yes → Cooling cryst. Continuous:
- Open valves in PL304
- Turn on P303
- Measure concentration
- Set a cooling profile for T303
- Operate according to experimental design

Sampling:
- Open V317 (bottom T303) to take samples

At the end of the process:
- Take samples for CSD from V317 (bottom T303) and/or V310 (bottom T302) and or V308 (sample point)
- Stop P302 to keep filling T301
- Stop P301 after T301 is empty
- Stop P303 if T303 is empty
- Clean according to cleaning flowsheet
- Check on pumps, tracing, thermostatic baths, stirrers and air/nitrogenSend the solution to T302

Cooling crystallization

MaC Batch:
In the batch process there is a flow from T304 to T401 via P306, T401 to T304, T304 to T303 via P304 and T303 to T304 via overflow.

Process:
- Open valves in PL401, PL402 and PL403
- Start P306 and P304
- Add air to T401
- Stop P301
- Check if product flow is closed (PL304)
- Set airflow rate
- Measure concentration in T304 and T303
- Operate according to experimental design
- Check level in T304

Sampling:
- Open V317 (bottom T303) to take samples

At the end of the process:
- Take samples for CSD from V317
- Dissolve crystals in T303
- Open valves in PL304
- Start P303 to transport solution to T302
- Stop P304 if level in T304 is below level switch LI303
- Stop P303 if T303 is empty
- Start rinsing T304 and T401
- After rinsing, stop P306
- Close valves in PL401 and PL402
- Proceed with cleaning according to cleaning flowsheet
- Check on pumps,tracing, thermostatic baths, stirrers and air/nitrogen

MaC Continuous:
In the MaCC process there is flow to all the vessels

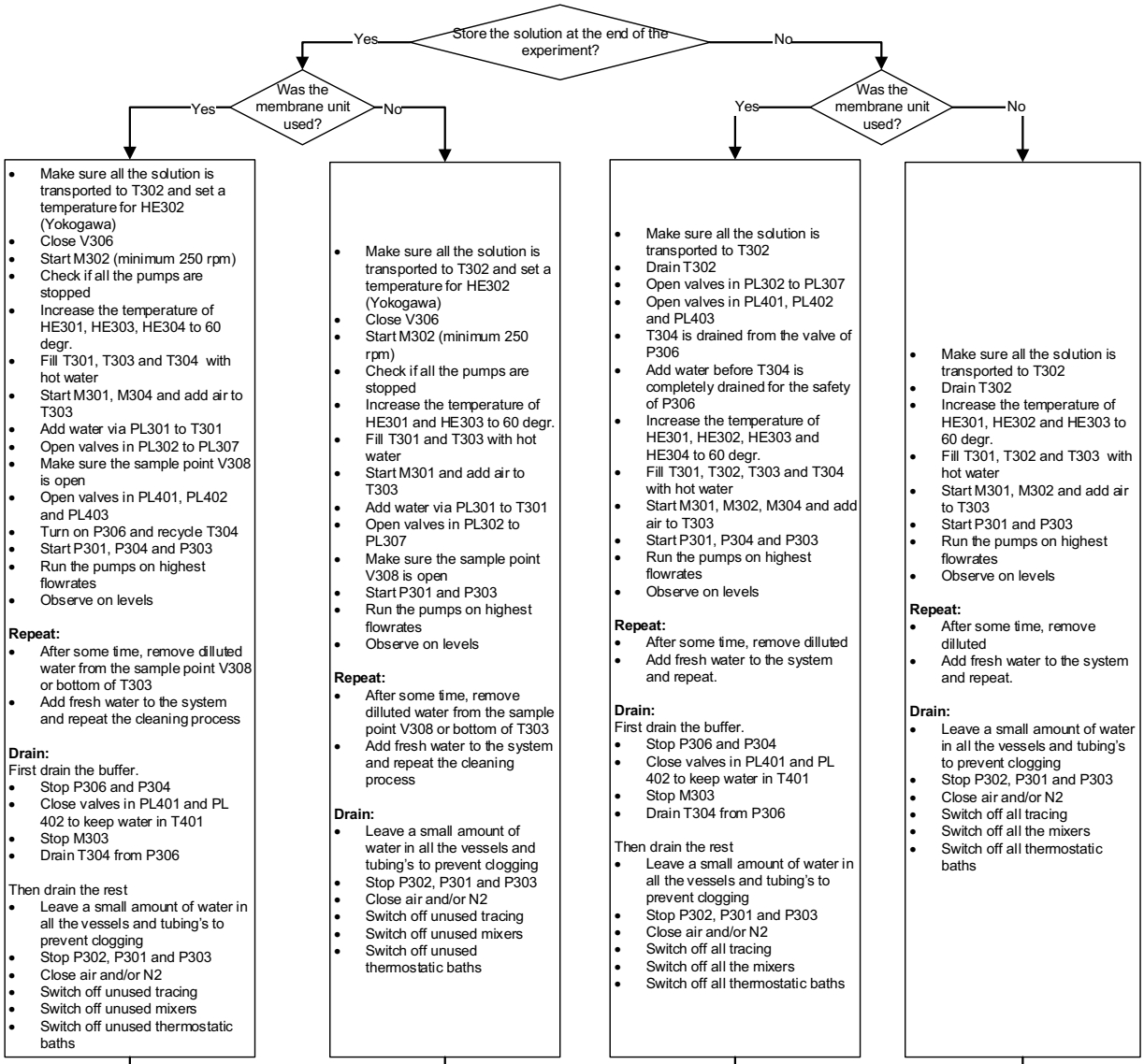
Process:
- Open valves in PL401, PL402, PL403 and PL304
- Start P306, P304 and P303
- Add air to T401
- Measure concentrations
- Operate according to experimental design
- Observe levels in vessels, leakages, flowrates.

Sampling:
- Open V317 (bottom T303) to take samples

At the end of the process:
- Take samples for CSD from V317 (bottom T303) and/or V310 (bottom T302) and or V308 (sample point)
- Stop P302 to keep filling T301
- Stop P301 after T301 is empty
- Stop P304 if level in T304 is below LI303
- Stop P303 if T303 is empty
- Start rinsing T304 and T401
- After rinsing, stop P306
- Close valves in PL401 and PL402
- Proceed with cleaning according to cleaning flowsheet
- Check on pumps, tracing, thermostatic baths, stirrers and air/nitrogen

Appendix D – Flowsheet for cleaning

Cleaning of the MaC



Werin Mohangoo

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Department: Process & Energy, Faculty 3mE
Section: Intensified Reaction & Separation Systems

Graduation committee:
Dr. ir. H.J.M. Kramer
F. Anisi, MSc.
Prof. dr. ir. A.I. Stankiewicz
Dr. ir. A.J.J. Straathof