Anti-solvent crystallization of sucrose

Jeroen Muller

February 25, 2016

Abstract

In 2011, the Wageningen University discovered and patented a new process for crystallization of sugar. In this process ethanol is added to the sugar solution and water is selectively removed by a zeolite. Royal Cosun renounced the idea of working with zeolites, but remained interested in the concept of anti-solvent crystallization.

The study started out by analyzing the expected benefits of a process based on anti-solvent crystallization. The energy consuming process of water evaporation is no longer needed if only anti-solvent crystallization is applied. However, the concept introduces an energy consuming separation step to recover the anti-solvent.

A literature study was conducted to determine the properties of the anti-solvent (ethanol) and the basic principles behind anti-solvent crystallization. Various models for the solubility, the viscosity and equilibrium data of sucrose mixtures were compared and validated. The model based on the modified UNIQUAC method turned out to be in close agreement with a variety of solubility sources and validated, by the authors, for the expected ethanol concentrations and temperatures used in the process.

Several process designs were considered for the new concept and a selection was made based on criteria provided by Royal Cosun. The selected process design consists of distillation columns to recover the ethanol, a crystallizer suitable for cooling and anti-solvent crystallization and recompression evaporators.

Over the last years the Cosun Food Technology Center (CFTC) developed Matlab/Simulink based models of almost all the components of the sugar factory. These components can be linked together to represent the total sugar production plant. This model was also used for the study, however this meant that certain changes had to be made. Various new process blocks were developed that allow for anti-solvent crystallization.

After several runs of the new model it turned out that only anti-solvent crystallization could not provide a high enough crystal yield. Therefor an additional cooling effect was considered. After optimizing the ratio cooling crystallization/anti-solvent addition it became clear that more cooling crystallization would result in lower energy consumptions.

Finally two concepts were compared to the reference case, the traditional process. The results from the model showed that the new concept had a reduced energy consumption. However, the reduction is not enough to compensate the reduced electricity generation and the investment costs.

Acknowledgements

The completion of this graduation thesis would not have been possible without the support of numerous people. First of all I would like to thank my supervisor Dr.Ir. Herman Kramer for his guidance and advice during this graduation project. I would also like to thank my daily supervisor Ir. Marc van Dijk, not only for the support he gave me continuously throughout this graduation project but also for the many times he cleared his schedule for a meeting with me.

Another word of thanks goes out the the people within the Process Modeling and Energy group of the Cosun Food Technology Centre who made sure all the questions I had were answered while providing a pleasant and cheerful atmosphere. There has not been one disappointing day during my presence at Royal Cosun.

Last but not least I want to thank my partner G. Alfons, family and friends for all the words of encouragement, motivation and above all the love I received which kept me going throughout this graduation thesis.

Contents

Chapter 1

Introduction

1.1 Background

In 2011, the Wageningen University discovered and patented a new process for crystallization of sugar. The patent claimed that the process allowed for more sustainable and profitable sugar beet cultivation and sugar production. To investigate this new process for crystallization of sugar and the opportunities for the sugar production industry, the project entitled "Development of a new method for sugar crystallization" was started in February 2013. Royal Cosun provided data about the sugar production process and partly funded and reviewed the research [1].

Figure 1.1 shows the mass flows of the proposed process by the Wageningen University. In this process ethanol is added to the sugar solution and water is selectively removed by a zeolite. Zeolites are microporous, aluminosilicate minerals commonly used as adsorbents and catalysts. The removal of water and the addition of ethanol causes the sugar to crystallize according to the crystallization principles described in the following chapters.

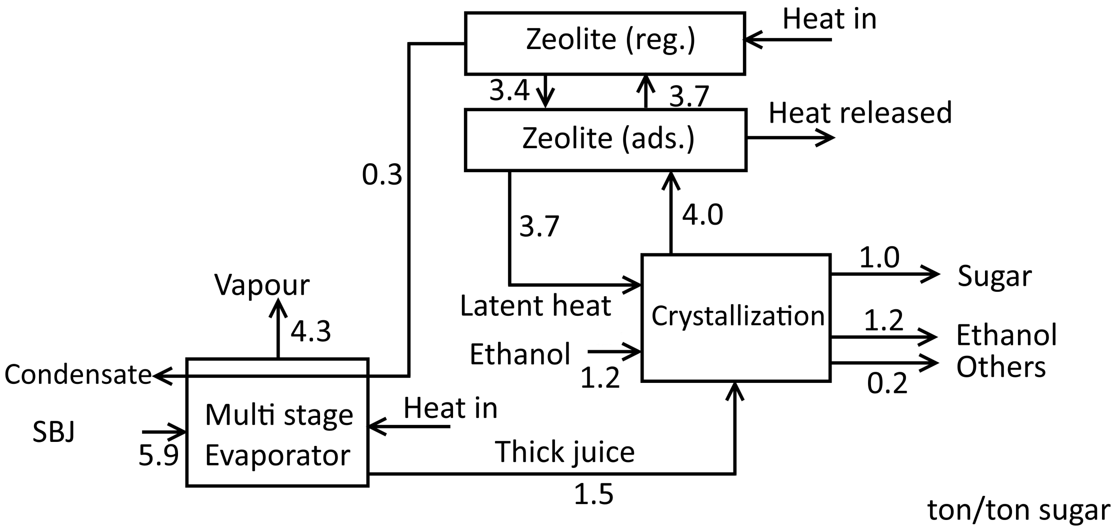


Figure 1.1: Mass flows of the Wageningen concept

The zeolite selectively absorbs the water during which heat is released. After a while the zeolite needs regeneration and this is done by applying heat in the form of superheated vapor. The water leaves the zeolite in the vapor form and is later condensed in the evaporator. The process of water separation with zeolites is similar to evaporation of water, the crystallization principle of traditional sugar production processes, and is highly energy consuming. Royal Cosun renounced the idea of working with zeolites, because it is very similar to evaporative crystallization and does not provide additional benefits. They remained interested in the concept of anti-solvent crystallization if it could replace the traditional evaporative crystallization process. It is obvious that the use of an anti-solvent yields a crystal product without needing to evaporate the solvent, but still requires a separation step to regenerate the anti-solvent [2, p. 4]. The concept could, in theory, reduce the energy demand of the factory. Especially in combination with an ethanol production plant. The residual stream, containing sugar and small amounts of ethanol, can be supplied to the fermentation section. The energy needed for recovery of the anti-solvent can potentially by used in other parts of the plant. The Anklam factory (Germany), owned by Royal Cosun, is such a factory. This study focuses in particular on this factory. In this report, you can read how the concept has been investigated and evaluated.

1.2 Available literature

Anti-solvent crystallization of sugars was investigated by Marco Giulietti and Andre Bernardo [3]. In this study fructose was studied utilizing ethanol, and lactose was studied utilizing ethanol, acetone and isopropanol. They concluded that crystallization of sugars may be improved by adding an organic liquid anti-solvent (as alcohol or ketone) and cooling the system. This addition shuts nucleation hindrance off, as it decreases system viscosity. Simultaneously, the anti-solvent competes with solute for water of hydration, throwing solute out of the solution: promoting crystallization. As the solubility of sugars in the mixture water-organic solvent is much lower than in water only, anti-solvent addition increases the crystallization rate. Cooling the system maximizes the drowning-out effect.

Refining of crystal sugar with ethanol was also investigated by E. R. Asquieri, E. M. de Assis and G.E. Serra [4]. The obtained results show that anti-solvent crystallization of sucrose with ethanol can be applied in the refining of white sugar. The filtering of hydroalcoholic solutions containing sucrose with filter paper, aiming at the elimination of impurities, proved to be efficient on a laboratory bench scale. The secondary nucleation technique, performed by seeding the solution and agitating it during an hour, proved to be applicable to hydroalcoholic solutions containing sucrose. It is also proved to be efficient in relation to the production of sugar with low color and impurities.

The study conducted by Mary An Godshall, Michael Saska et al. [5] and other studies have investigated the effect of ethanol on sucrose solubility and molasses exhaustion. They observed a significant decrease of the massecuite viscosity, however they did not observe a significant increase in molasses exhaustion.

1.3 Problem statement and approach

Literature shows that anti-solvent crystallization of sucrose might improve the production process, however non of the studies provide information about the possible energy reduction of anti-solvent crystallization implemented in an existing sugar plant. It is therefor the aim of this report to answer the following question, which has played a leading role throughout the study:

"What is the feasibility of anti-solvent crystallization from thick juice, applied to an existing sugar factory with bioethanol production".

The research approach which was followed in this study is depicted in figure 1.2. A literature study was conducted for the different kind of crystallization principles that are applied in the current and the new process. Literature about anti-solvent crystallization was gathered to determine what is known on this subject.

After the literature study the properties of the anti-solvent (ethanol) were examined. The examined properties consist of the solubility of the sucrose in the mixture, the excess enthalpy and the handling of the anti-solvent. This study resulted in mathematical models of these properties.

The next step was to select the best process design. Royal Cosun provided an initial process design that was extended and improved by insights gained from the literature study and modeling results. The process design mainly consisted of determining the best way of deploying the energy associated with the flows involved in the process.

Subsequently the computer model, that models the entire sugar plant at Anklam (Germany), of Royal Cosun was explored. Additional process blocks were added to the model library in order to model the selected process design. The created process blocks contain the mathematical models to predict the physical properties of the concerning mixture.

Finally the process was optimized by further improving the process design and the involved parameters like the number of trays in the distillation columns, the reflux ratio, the ratio cooling/anti-solvent addition of the crystallizer.

The main aspects of the anti-solvent crystallization that were examined consist of the potential crystal yield, the recoverability of the anti-solvent and the implementation of anti-solvent crystallization in an existing sugar plant, applying energy (heat) exchange between the new process and the existing part.

1.4 Outline

The remainder of this report has another seven Chapters. Chapter 2 gives an overview of the theoretical background of crystallization as a process and describes the different crystallization principles. The subsequent Chapter 3 reviews the current sugar production process and explains why the new concept could be a promising alternative. In Chapter 4 the main idea of the new concept is explained and the resulting process configuration is described. The physical properties of the anti-solvent are examined in chapter 5 and solubility models are compared and validated. The method of studying the energy consumption of the new concept is described in chapter 6. Here the computer model of the traditional sugar plant is introduced and the adjustments to that model are presented. Chapters 7 discusses the optimization of the concept in order to minimize energy consumption and operating costs, which are presented in chapter 8 together with the equipment investments. The last chapters include the conclusion and a discussion about the results.

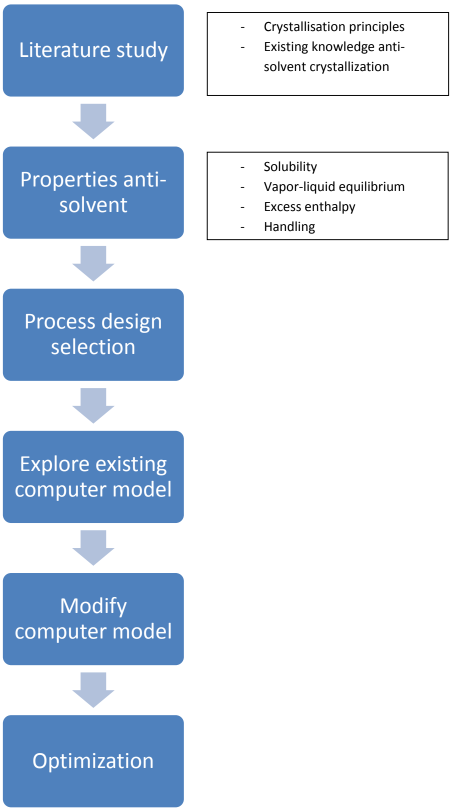


Figure 1.2: Research approach

Chapter 2

Crystallization principles

2.1 Introduction

Crystallization is the second most important separation process in chemical industry after distillation. Crystallization is the (natural or artificial) process of formation of solid crystals precipitating from a solution, melt or more rarely deposited directly from a gas. This solid phase formation occurs in two main steps: the formation of a new thermodynamic phase via self-assembly or self-organization, called nucleation, and the growth of these structures into solid particles, crystals [6, p. 204].

The reverse process of crystallization is dispersion of a solid in a solvent, termed dissolution. The dispersed solid that goes into solution is the solute. As dissolution proceeds, the concentration of the solute increases. The solubility in impure solutions is defined as the maximum amount of solute (in grams) that can be dissolved in 1 g of solution at a given temperature. Given enough time at fixed conditions, the solute will eventually dissolve up to a maximum solubility. Under these conditions, the solution is saturated with solute and is incapable of dissolving further solute under equilibrium conditions.

If the actual concentration is higher than the equilibrium concentration than the difference in concentration is called supersaturation and it is the driving force of crystallization. The growth of the crystal depends on several factors such as temperature, crystal surface area, fluid dynamic conditions and the nature and concentration of the impurities. Supersaturation can be generated in the system by cooling, solvent evaporation, reducing the solute solubility by addition of an anti-solvent, or changing the solute by chemical reaction producing another substance with much lower solubility.

Crystallization is also a chemical solid-liquid separation technique, in which mass transfer of a solute from the liquid solution to a pure solid crystalline phase occurs. In chemical engineering crystallization occurs in a crystallizer.

It might be expected that if a solute is dissolved in a solvent at a fixed temperature until the solution achieves saturation and any excess solute is removed, and the solubility is decreased, the solute would immediately start to crystallize from solution. However, solutions can often contain more solute than is present at saturation. Such supersaturated solutions are thermodynamically metastable and can remain unaltered indefinitely. This is because crystallization first requires formation or nucleation.

Nucleation theory tells us that when the solubility of a solution is exceeded and it is supersaturated, the molecules start to associate and form aggregates (clusters), or concentration fluctuations. If we assume that these aggregates are spherical, we can write an equation (2.1 [7, p. 17]) for the Gibbs free energy change required to form a cluster of a given size

$$\Delta G = 4\pi r^2\sigma - \frac{4\pi r^3}{3V_m}RT\ln(1+S) \tag{2.1}$$

where r is the cluster radius, S the supersaturation ratio, σ is the solid-liquid interfacial tension, and $V_m$is the specific volume of a solute molecule.

The first term is the Gibbs free energy change for forming the surface, and the second term is for the volume. For small numbers of molecules the total Gibbs free energy change is positive. This means that the clusters are unstable and will dissolve. A plot of ΔG as a function of cluster size (figure 2.1) shows that as the cluster size increases, we reach a point where the Gibbs free energy change is negative and the cluster would grow spontaneously. When this happens, nucleation will occur. The reason that supersaturated solutions are metastable is, therefore, because of the need for a critical sized cluster to form [7, p. 17].

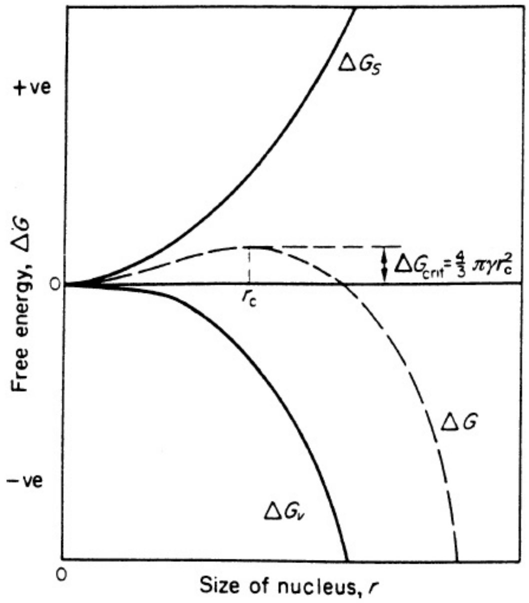


Figure 2.1: Free energy diagram for nucleation

Primary nucleation occurs in the absence of suspended product crystals. Homogeneous primary nucleation occurs when molecules of solute come together to form clusters in an ordered arrangement in the absence of impurities or foreign particles. The growing clusters become crystals as further solute is transferred from solution. As the solution becomes more supersaturated, more nuclei are formed. This is illustrated in figure 2.2 [6, p. 204]. The curve AB in figure 2.2 represents the equilibrium solubility curve. Starting at point 1 in the unsaturated region and cooling the solution without any loss of solvent, the equilibrium solubility curve is crossed horizontally into the metastable region. Crystallization will not start until it has been subcooled to point 3 on the supersolubility curve. Crystallization begins at point 3, continues to point 4 in the labile region and onwards. The curve CD, called the supersolubility curve, represents where nucleus formation appears spontaneously and hence, where crystallization can start. The supersolubility curve is more correctly thought of as a region where the nucleation rate increases rapidly, rather than a sharp boundary due to the fact that nucleation is a statistical event. Primary

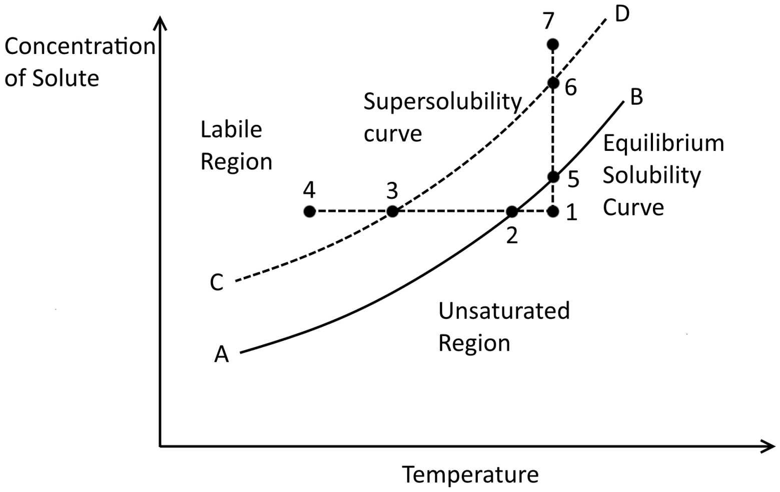


Figure 2.2: Supersaturation in crystallization processes

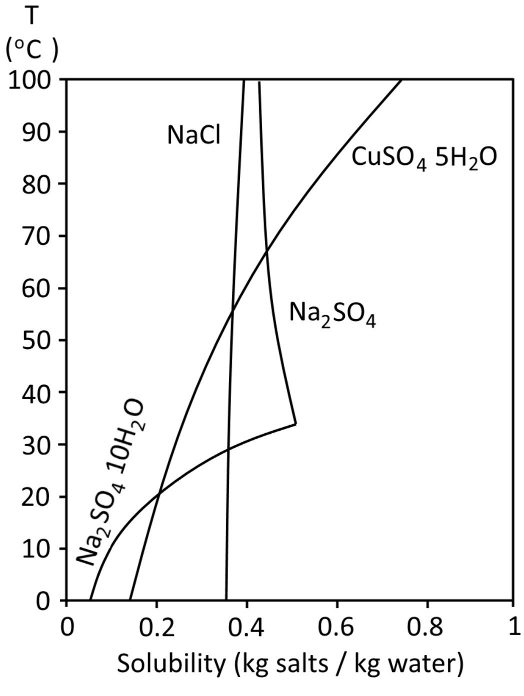


Figure 2.3: Solubility of various salts in water as function of temperature

nucleation can also occur heterogeneously on solid surfaces such as foreign particles [6, p. 204].

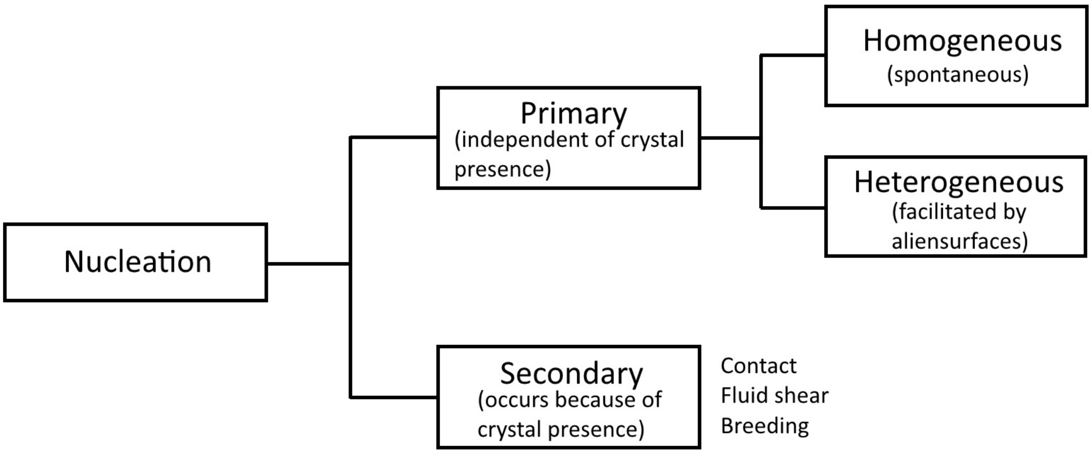


Figure 2.4: Mechanisms of nucleation

Secondary nucleation requires the presence of crystalline product. Nuclei can be formed through attrition either between crystals or between crystals and solid walls. Such attrition can be created either by agitation or by pumping. The greater the intensity of agitation, the greater the rate of nucleation. Another way to create secondary nucleation is by adding seed crystals to start crystal growth in the supersaturated solution. These seeds should be a pure product. As solids build up in the crystallization, the source of new nuclei is often a combination of primary and secondary nucleation, although secondary nucleation is normally the main source of nuclei. Secondary nucleation is likely to vary with position in the crystallization vessel, depending on the geometry and the method of agitation. The classification of the nucleation mechanisms is illustrated in figure 2.4 [3].

One of the conflicting characteristics of crystallization is that the optimal solution conditions for nucleation of the crystals are not the ideal ones to support the crystal growth. This is because spontaneous nucleation is quite simply more likely to occur when the levels of supersaturation are high, whereas slow, ordered growth of large crystals is favored by lower levels of supersaturation. The ideal crystallization therefore must somehow uncouple nucleation from growth to satisfy the distinctly different requirements of the two events. Seeding is a powerful tool for the separation of nucleation and growth. In this technique, previously nucleated crystals are used as seeds and introduced into new drops in equilibrium at lower levels of supersaturation.

Although the formed crystals are likely to be pure, the mass of crystals will retain some liquid when the solid crystals are separated from the remaining liquid. If the sticking liquid is dried on the crystals, this will contaminate the product. In practice, the crystals will be separated from the remaining liquid by filtration or centrifuging. Large uniform crystals separated from a low-viscosity liquid will retain the smallest proportion of liquid. Nonuniform crystals separated from a viscous liquid will retain a higher proportion of liquid. It is common practice to wash the crystals in the filter or centrifuge. This might be with fresh solvent, or with water mixtures.

2.2 Cooling crystallization

Figure 2.3 [6, p. 203] shows the equilibrium solubility of various salts in water. Usually, the solubility increases as temperature increases. The solubility of copper sulfate increases significantly with increasing temperature. The solubility of sodium chloride increases with increasing temperature, but the effect of temperature on solubility is small. The solubility of sodium sulfate decreases with increasing temperature. Such reverse solubility behavior is unusual.

Cooling is probably the most common way of creating supersaturation [7, p. 244]. The principle involves cooling a solution through indirect heat exchange. This is most effective when the solubility of the solute decreases significantly with temperature (see figure 2.3). Rapid cooling will cause the crystallization to enter the labile region. Controlled cooling, perhaps in combination with seeding, can be used to keep the process in the metastable region. Care must be taken to prevent fouling of the cooling surfaces by maintaining a small temperature difference between the process and the coolant. Scraped surface heat exchange equipment might be necessary. In general, solubility is mainly a function of temperature, generally increasing with increasing temperature. Pressure has a negligible effect on solubility. The solubility of sucrose as function of temperature will be discussed in a later chapter.

The yield and economy of cooling crystallization depends on the temperature and concentration of the feed solution to be crystallized, and on whether cooling water or another cooling agent is employed. Typically, a high temperature, concentrated solution is delivered into a jacketed crystallizer equipped with a stirrer and often also a cooling coil to increase the cooling surface area. The solution is stirred, and cold water or cooling agent is pumped through the jacket and, if so equipped, the cooling coil. Such a ”natural” cooling is continued until the temperature of the solution in the crystallizer is near that of the cooling medium [7, p. 244].

An advantage of cooling crystallization can be the low energy consumption compared to other crystallization principles, however the cooling surfaces become quickly covered with layers of crystallizing solute (fouling, scaling, incrustation). This phenomenon is detrimental to the heat transfer efficiency and may bring about a decrease in the rate change of supersaturation [7, p. 244].

2.3 Evaporative crystallization

For substances whose solubility is weakly dependent on temperature or for those with an inverse dependence of the solubility on temperature, a method of choice to create supersaturation is evaporation of the solvent. In practice, evaporative crystallizers usually operate at constant temperature and reduced pressure [7, p. 246].

This way of creating supersaturation is also depicted in figure 2.2 [6, p. 204]. Starting again at point 1 in the unsaturated region, the temperature is kept constant and the concentration is increased by removing the solvent. The equilibrium solubility curve is now crossed vertically at point 5 and the metastable region entered. Crystallization is initiated at point 6 , it continues to point 2 in the labile region and onwards.

Evaporative crystallization is not preferred if the product needs to be of high purity, because in addition to evaporation concentrating the solute, it also concentrates impurities. Such impurities might form crystals to contaminate the product or might be present in the residual liquid enclosed within the solid product. Evaporation of water is a very energy consuming process making this crystallization process less desirable. If the evaporated water can be deployed elsewhere in the process, by condensing, the energy consumption can be reduced.

The traditional sugar production process relies on the principle of evaporative crystallization. This is discussed in detail in a later chapter.

2.4 Anti-solvent crystallization

Anti-solvent crystallization, also known as salting out or drowning out, involves adding an additional substance, called the anti-solvent, which induces crystallization. Anti-solvent crystallization achieves supersaturation by exposing a solution of the product to another solvent (or multiple ones) in which the product is poorly soluble. The anti-solvent must be miscible with the solvent and must change the solubility of the solute in the solvent. The anti-solvent will usually have a polarity different from that of the solvent. For example, if the solvent is water, the anti-solvent might be acetone, or if the solvent is ethanol, the anti-solvent might be water.

Pharmaceutical and fine chemical makers frequently rely on anti-solvent crystallization to generate a solid from a solution in which the product has high solubility [8]. The technique is used for a variety of applications such as polymorph control, purification from a reaction mixture and yield improvement. The process can be semi-batch or continuous. Although this technique has the potential to achieve a controlled and scalable size distribution, it's not without problems. The product requires purification or separation steps to remove the anti-solvent(s).

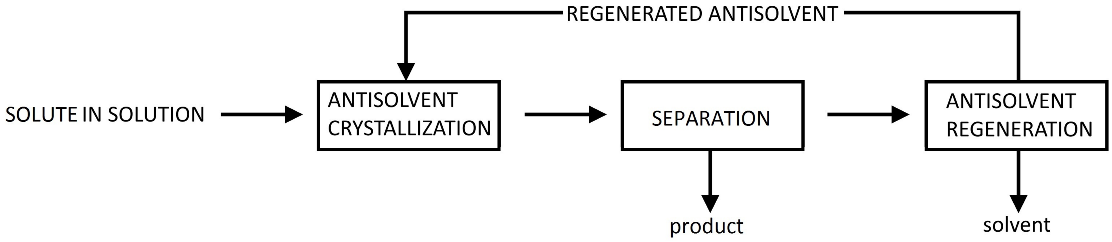


Figure 2.5: Schematic representation of an anti-solvent crystallization process with crystallization, filtration and anti-solvent regeneration

A schematic flow sheet of an ideal anti-solvent crystallization process is given in figure 2.5[2, p. 4]. In the first section of this picture, the solution is mixed with anti-solvent. Due to the anti-solvent's ability to bind water, the solubility of the solute is reduced, resulting in the formation of solid phase either by precipitation or by crystallization. Subsequently, in the separation section, the solid phase is separated from the crystals, either by filtration or centrifugation, leaving a clear filtrate that is sent to the anti-solvent regeneration section where solvent and anti-solvent are separated. Finally, the anti-solvent is recycled to the crystallization section while the water can be used for the dissolution of new material. It is obvious that the use of an anti-solvent yields a crystal product without needing to evaporate the solvent, but still requires a separation step to regenerate the anti-solvent. Solvent (water) and anti-solvent (ethanol) could be separated by simply inducing liquid-liquid phase separation after which both concentrated phases could be recycled within the process. The most common way of separating ethanol from water, to a certain extent, is by distillation.

It is obvious that the feasibility of anti-solvent crystallization is strongly dependent on the properties of the anti-solvent. To mention a few, there are its anti-solving effectiveness, recoverability, long-term chemical stability, toxicity, flammability, environmental stability, costs and acceptability as a trace impurity in the product.

As with all crystallization techniques, seeding may help avoid excessive nucleation. The seed can be added as a powder or in slurry form with the anti-solvent. The latter often is preferred for ease of handling and reduced contamination. Adding seed with the anti-solvent offers an advantage over the traditional method of putting seed in at a single time which poses the risk of adding too soon (seeds dissolve) or too late (nucleation has already occurred). The limited solubility of seed in the anti-solvent means a seed slurry can be prepared beforehand. This mixture normally will represent a small amount of the total anti-solvent charge. It then is added near the saturation point until the metastable zone (MZ) is reached. The anti-solvent in this slurry reduces the solubility, causing the mixture to achieve supersaturation, which is relieved in the presence of the added seeds. The goal is to stay within the MZ, thereby promoting growth with limited nucleation via secondary mechanisms.

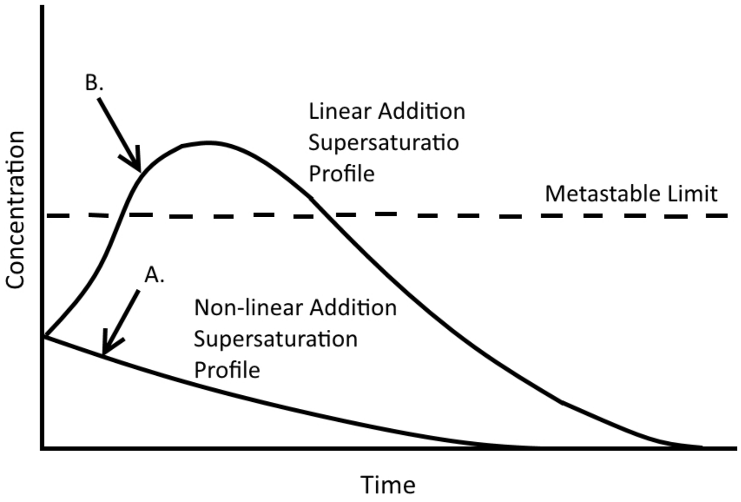


Figure 2.6: Supersaturation profile vs. mode of addition

Often addition takes place at a constant rate. This linear-profile procedure can yield a variable supersaturation whereby the MZ is exceeded early on, resulting in too much nucleation. As figure 2.6 shows (for semi-batch process), an initial slow addition rate followed by a gradual increase in rate can achieve a fairly constant supersaturation within the zone [8]. This non-linear profile is analogous to the ones utilized for batch cooling or evaporative crystallization. The goal is to maintain the supersaturation of the solution consistently within the MZ while achieving growth on existing crystal surface area. As already noted, seeding techniques can help produce this desired outcome.

2.4.1 Batch operation

Figure 2.7 presents typical operating curves for normal addition and a representative equilibrium solubility curve [8]. The metastable zone (MZ) is the area between B-C and D-E. From point A to point B, anti-solvent addition will proceed without crystallization because the concentration of the solution is below the equilibrium solubility. At point B, the solubility curve is reached. As anti-solvent addition continues, supersaturation will

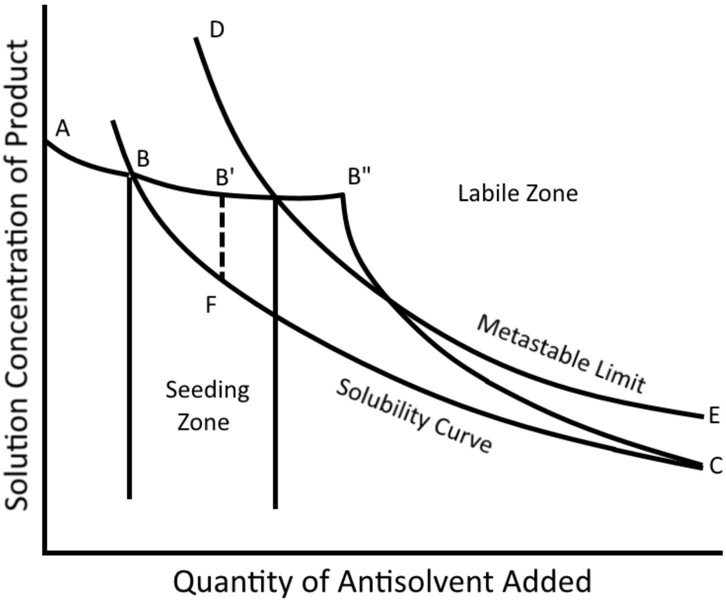


Figure 2.7: Normal addition profile

develop. The amount of supersaturation created prior to nucleation is system specific and depends on the addition rate, mixing, primary or secondary nucleation rate, growth rate, feed location and the amount and type of impurities present in solution.

If the main goal is growth, the presence of a sufficient amount of seed and a slow anti-solvent addition rate may allow the concentration in solution to remain completely in the MZ as crystallization proceeds. The closer the solution concentration profile is to the equilibrium solubility curve (B-C), the higher the possibility of achieving a process with reduced nucleation.

A common procedure for achieving growth while minimizing the possibility for seed dissolution is shown in curve B'-F-C. Anti-solvent addition is stopped and seed is added at point B', where the system is slightly supersaturated. Also, the seed may be added in a slurry with the anti-solvent starting before point B is reached to assure staying within the MZ.

A system without seed or a fast addition rate can develop a high degree of supersaturation, which can result in rapid precipitation or crash out at point B", in the labile zone beyond the MZ. Primary nucleation could be followed by continued nucleation and some growth (B"-C), eventually achieving equilibrium some time after all the anti-solvent is added. If the concentration is allowed to go to point B", the system also is subject to oiling out or agglomeration. Crystallization then is allowed to progress to relieve the supersaturation without the addition of more anti-solvent (B'-F). Given enough time, the solution will closely approach the equilibrium solubility value (point F) while developing adequate surface area to primarily achieve growth during the addition of the remaining anti-solvent. With this increased surface area and a sufficiently slow addition rate, the solution concentration can approach the equilibrium solubility for the remainder of the addition (F-C).

2.4.2 Continuous operation

Some applications require a small mean crystal size and narrow size distribution. Examples include pharmaceutical materials requiring sub-micron or several-micron mean size where the active ingredient has marginal water solubility. Inhalation products also need these attributes. Making such products demands continuous processing via an in-line mixing device or a stirred vessel.

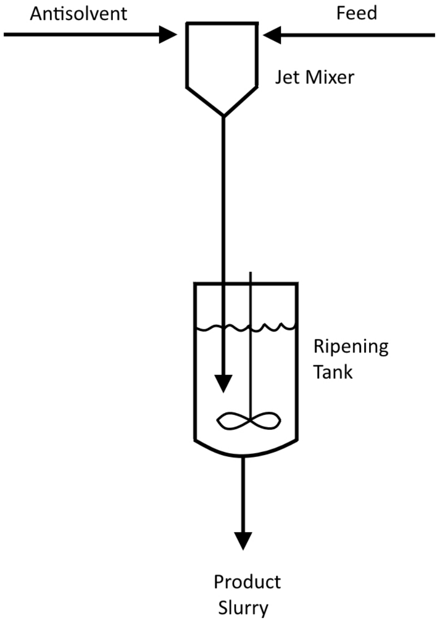


Figure 2.8: PFD for impinging Jet System

In-line mixing equipment for crystallization includes impinging jets, vortex mixers, Y mixers and rotor-stator configurations. The anti-solvent and product solution (which may contain seeds) are mixed in a very small active volume; this yields extremely high supersaturation values that are above the MZ, resulting in the production of a large number of nuclei. The two streams are mixed at the molecular level with excellent micro mixing, with mixing times often being less than the nucleation induction time.

Figure 2.8 depicts a flow diagram for one type of impinging jet configuration [8]. In this case the product is ripened in a stirred tank following contact of the product and anti-solvent streams in the jet mixer. The ripening can be batch or continuous and is designed to facilitate diffusion of the trapped mother liquor in the nucleated solids. Adequate ripening time also is provided to convert amorphous solids into crystalline structures. In some applications seeds are added to the anti-solvent stream or the ripening vessel.

When using such equipment, it's important to recognize that three types of mixing may impact product characteristics: Macromixing, Micromixing and Mesomixing. Macromixing relates to bulk blending in stirred vessels. Micromixing determines the time of blending to a molecular level and the induction time for nucleation. It's influenced by impeller type and speed plus location of the anti-solvent feed pipe. Mesomixing refers to the dispersion of the plume of anti-solvent generated at the feed point as the solvent is added to the slurry. Without proper feed-point location and the right feed device/pipe, pockets of high supersaturation can occur, resulting in undesired nucleation. The time constant for mesomixing depends on the addition rate, feed point and diameter of the feed pipe. Too high a value can lead to premature nucleation.

Feed pipe location, pipe diameter and anti-solvent flow can impact both micromixing and mesomixing times. A change in mean particle size and crystal size distribution (CSD) at different pipe locations would confirm product sensitivity to mixing.

Mesomixing can influence the product when the anti-solvent feed rate is faster than the local mixing rate, resulting in a plume of highly concentrated anti-solvent that isn't mixed at the molecular level. This can yield a high localized nucleation rate; the phenomenon can present scale-up difficulties, requiring a thorough engineering analysis for success.

The shortest mixing time constant occurs at the location of maximum turbulence in the vessel, which is just above the impeller for a down-pumping pitched-blade turbine (PBT), or at the point of discharge flow for a radial flat-blade agitator.

If the anti-solvent is added in a poorly mixed zone such as at or near the surface or a baffle, a number of potentially undesirable results such as crash nucleation or agglomeration may occur.

Subsurface addition of anti-solvent at times can help avoid high levels of supersaturation and nucleation when introduction is made at a zone of intensive micromixing. Results depend on the feed point location plus pipe diameter and anti-solvent feed rate. For example, too large a pipe diameter could prompt a high supersaturation region prior to blending at a molecular level. Reverse flow with potential pluggage also could occur.

Chapter 3

Current process

3.1 Sugar production process - general overview

Sugar production involves cultivation, transportation and processing of sugar beets and residues. Figure 3.1 shows a schematic overview of a sugar production process including several other production units that can be linked to a sugar factory like bio-ethanol production [9]. The process shown in 3.1 is quite similar to the production process of the Anklam sugar factory of Royal Cosun, except for the resin separation for the production of betain and raffinate and the horticulture. Figure 3.2 shows a similar process with sugar production in combination with bioethanol production in more detail using a different presentation [10].

After harvesting and transport, beets are washed and sliced into cossettes. These cossettes enter a diffusion process for sugar extraction. The water temperature in the diffusers is about 70 °C. The sugar passes from the plant cells into the surrounding water. From this process two important substances remain the pulp and the sugar that is in the water, which is known as raw juice.

The raw juice from the diffusion process passes through an important purification stage. Milk of lime (calcium hydroxide) is added to increase the pH of the juice causing precipitation of proteins and removal of invert sugar. Then CO2 gas is added, during which CO2 and milk of lime re-combine to produce calcium carbonate which precipitates out, taking some of the impurities with it. The juice that remains from the purification process is called thin juice.

The next stage in the process, evaporation, is where the water is boiled off in a series evaporator vessels, known as multiple effect evaporators. This process increases the solids content of the juice. The liquid that remains is known as thick juice. A part of the thick juice is diluted to a dry substance content of approximately 67-68 % and stored in thick juice tanks.

Finally this thick juice is concentrated by vacuum pan boiling (evaporative crystallization). Here, sucrose crystals are grown to the required size. After multiple crystallisation steps finally molasses remain as byproduct. In a separate thick juice campaign the thick juice that has been stored is processed to white sugar.

The main product is white sugar. The by-products include tare, pellets, lime, sludge and molasses. At the Anklam factory also ethanol is produced at the accompanying ethanol production plant using thick juice as substrate.

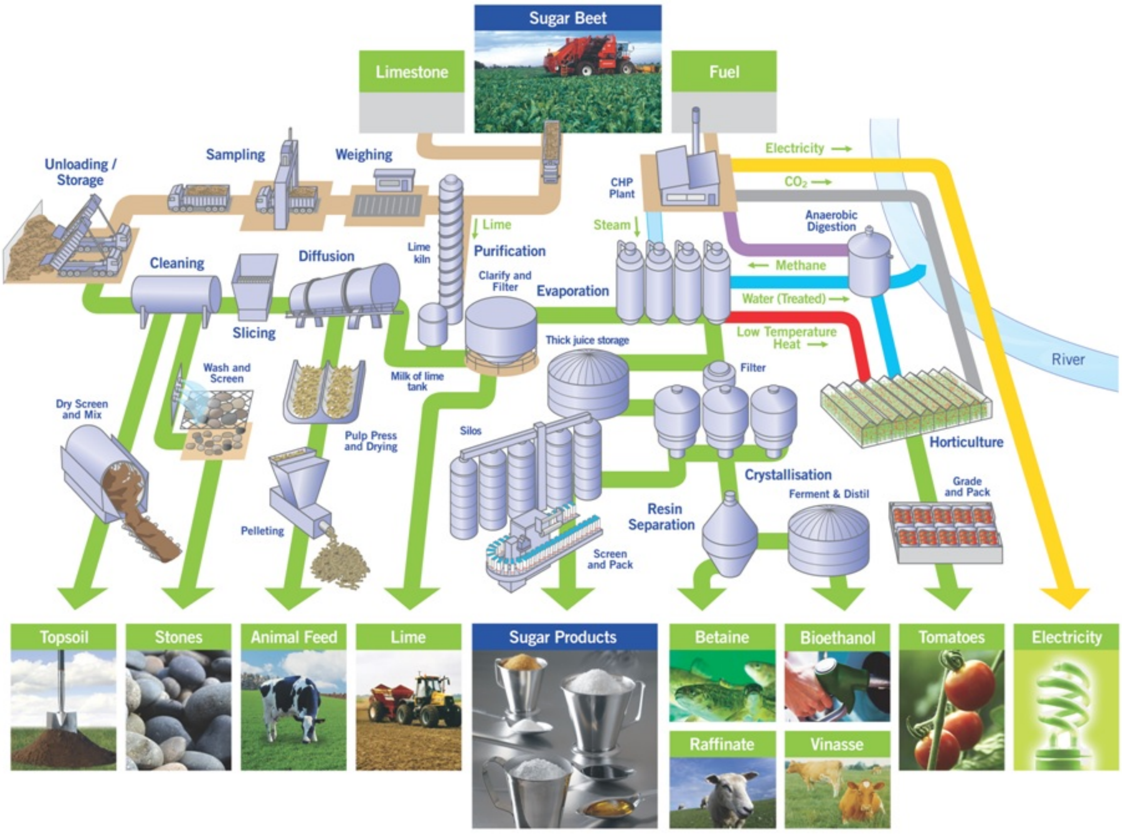


Figure 3.1: Traditional process

3.2 Evaporation

At the Anklam factory the evaporation of water from the thin juice is done by a multistage evaporation system. A multiple-effect evaporator, as defined in chemical engineering, is an apparatus for efficiently using the heat from steam to evaporate water [11]. In a multiple-effect evaporator, water is boiled in a sequence of vessels, each held at a lower pressure than the last. Because the boiling temperature of water decreases as pressure decreases, the vapor boiled off in one vessel can be used to heat the next, and only the first vessel (at the highest pressure) requires an external source of heat. While in theory, evaporators may be built with an arbitrarily large number of stages, in practice the number of stages is limited. Every additional stage is less efficient than the preceding one making a large number of stages financially unattractive.

The evaporation system at Anklam is of the forward-feed kind. Forward-feed operation is shown in figure 3.3 [6, p. 207]. The fresh feed is added to the first stage and flows to the next stage in the same direction as the vapor flow. The reason this method is used is to reduce color formation in the mother liquor. The boiling temperature decreases from stage to stage.

The Anklam factory uses an evaporator with 6 stages and a pre-evaporator on stage 5. The reason a pre-evaporator is used is to reduce the non-condensables and to stabilize the pressure of the evaporative crystallizer. Not all the vapor leaving evaporator 1 is sent to the next stage. Some of the vapor is used for preheating juices in other parts of the plant. The excess vapor leaving the last stage is condensed in the condenser. The thick juice leaving the last stage is sent to the crystallizers, the fermentation (reducing the crystal

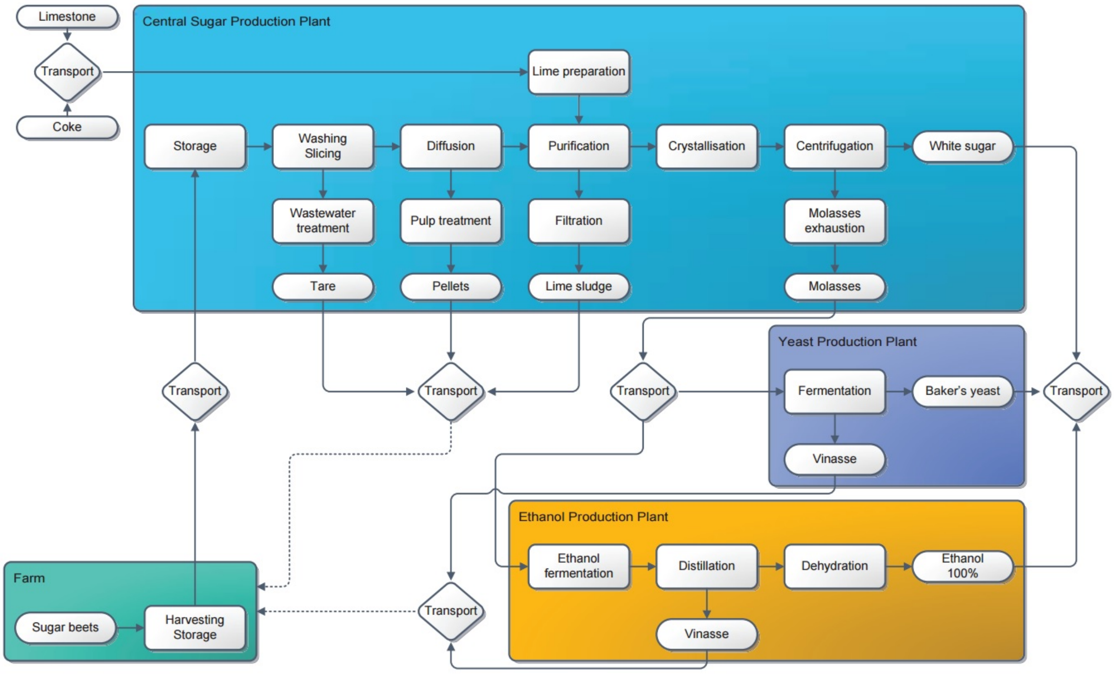


Figure 3.2: Block diagram of the traditional process

sugar yield) or stored in thick juice tanks to be processed later. The process flow diagram of the evaporation station is shown in figure 3.4.

Figure 3.5 shows the vinasse evaporation. Vinasse is a byproduct of the sugar industry. Sugar beet is processed to produce crystalline sugar, pulp and molasses. The latter are further processed by fermentation to ethanol, ascorbic acid or other products. After the removal of the desired product (alcohol, ascorbic acid, etc.) the remaining material is called vinasse. Vinasse is sold after a partial dehydration and usually has a viscosity comparable to molasses. The dehydration is realized by evaporators as can be seen in the figure. The vapor leaving the evaporators is sent to the mash column (stripper column in the bioethanol plant).

3.3 Crystallization

Figure 3.6 shows the sugar house of the Anklam factory. The crystallization principle used at Anklam is of the evaporative kind. The pressure in the crystallizers is kept around 300 mbar, reducing the temperature of evaporation, and heat is applied to the crystallizers. A consequence of this reduced pressure and temperature is that the dry content of the thick juice should be limited in order to prevent supersaturation and premature crystallization or nucleation. The crystallization of sugar in the current situation does not happen in one single step. At the Anklam sugar plant there are three crystallization stations placed in series. The crystallization station consists of several batch crystallizer pans. Only the crystals from the first crystallizer (crystallizer A) are sold as white sugar. The crystals from the other two crystallizers (crystallizers B & C) are again dissolved and transported back to crystallizer A. Crystallizers B & C are actually just additional separation steps to exhaust the syrup. The fact that crystals are produced in these crystallizers has no additional value, besides the separation effect, because these crystals are immediately dissolved after

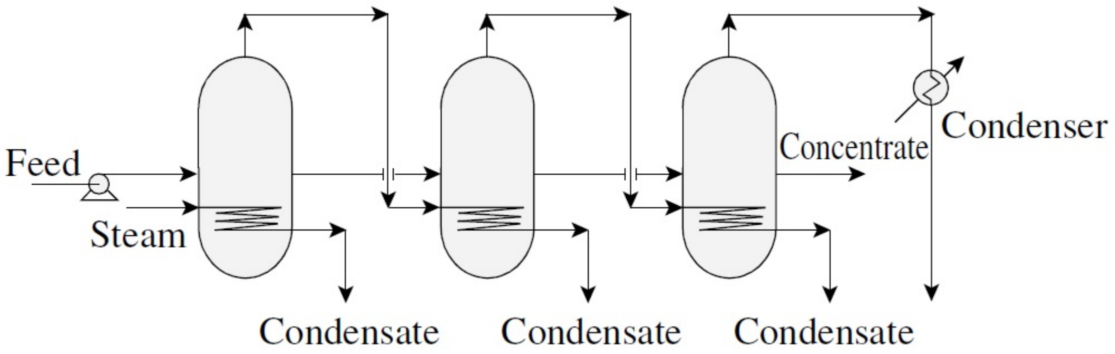


Figure 3.3: Forward feed multistage evaporator system

separation in the centrifuge. The vapor leaving the fifth stage of the evaporator is used as energy source for the crystallizers to evaporate the water. The condensate is used for juice preheating in other parts of the plant.

The magma leaving the crystallizers is transported to the centrifuges. Here the crystals are separated from the mixture and subsequently washed with wash water. The remaining liquid is called run-off and this flow feeds the next crystallizer. The run-off from the last centrifuge is exhausted and called molasses and this stream is not further processed.

At the Anklam factory evaporative crystallization is applied to produce the seedlings used to uncouple the nucleation from crystal growth. A small amount of thick juice is taken from the mean stream going to the crystallizers. This amount enters a separate evaporative crystallizer. Here a slurry is prepared that contains the seedlings. The slurry (magma) is used in crystallizer A to induce controlled crystal growth.

Crystallization in the A, B & C crystallizers at the Anklam factory happens batch-wise, to have a better control of the crystal size and high supersaturations. Batch-wise crystallization consists of the following steps: filling, concentrating, seeding, stabilizing, boiling up, emptying, steam cleaning and ready for the next strike.

The magma leaving crystallizer C first undergoes additional cooling crystallization before continuing to the centrifuges.

3.4 Energy flows

Figure 3.7 shows the most important energy flows of a traditional sugar production plant [12, p. 14]. The energy source is oil or gas that is converted to steam and by CHP into electricity. The turbine exhaust steam is used to evaporate water in the evaporators to create thick juice from thin juice. The evaporated steam is subsequently used for the crystallization of the sucrose by evaporating the water from the thick juice. The water vapor from the crystallizer is sent to the water treatment and cooling section of the plant. Here the energy is transferred to a cooling water stream from a nearby river or evaporated in a cooling tower. This amount of energy is lost to the environment.

The energy demand of the crystallizers mainly consist of steam needed for the evaporative crystallization of sugar. If another crystallization principle would be used, for example anti-solvent crystallization or cooling crystallization, the steam demand would almost completely vanish. This would drastically reduce the amount of heat loss to the environment (waste heat), reducing the energy demand of the whole production plant. This effect is basically the main principle of energy reduction, investigated in this study.

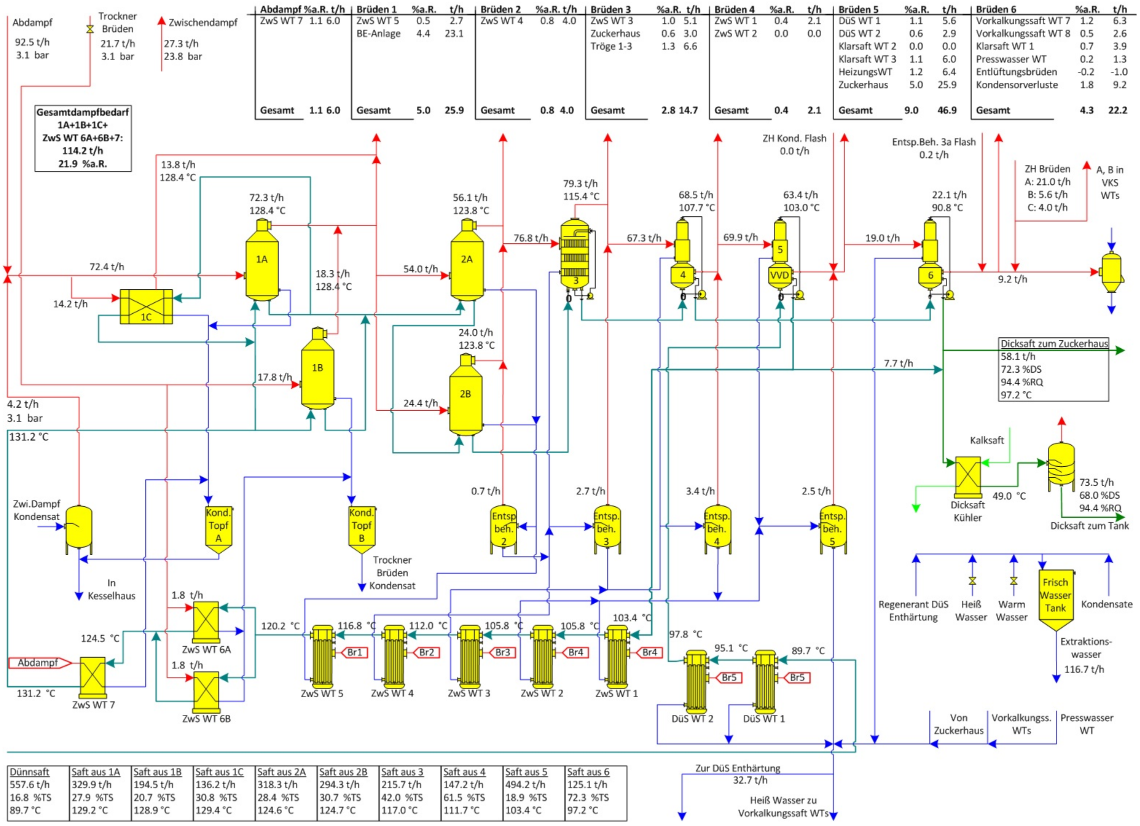


Figure 3.4: Process flow diagram of evaporation station

Reducing the energy demand of the crystallizers requires changing other parts of the process. The steam, needed for evaporative crystallization, comes from the evaporators. The reduced steam demand results in insufficient thickening of the juice and should be resolved by improving the efficiency of the evaporators. Also the regeneration of the anti-solvent requires major changes to the process. This is thoroughly discussed in a later chapter.

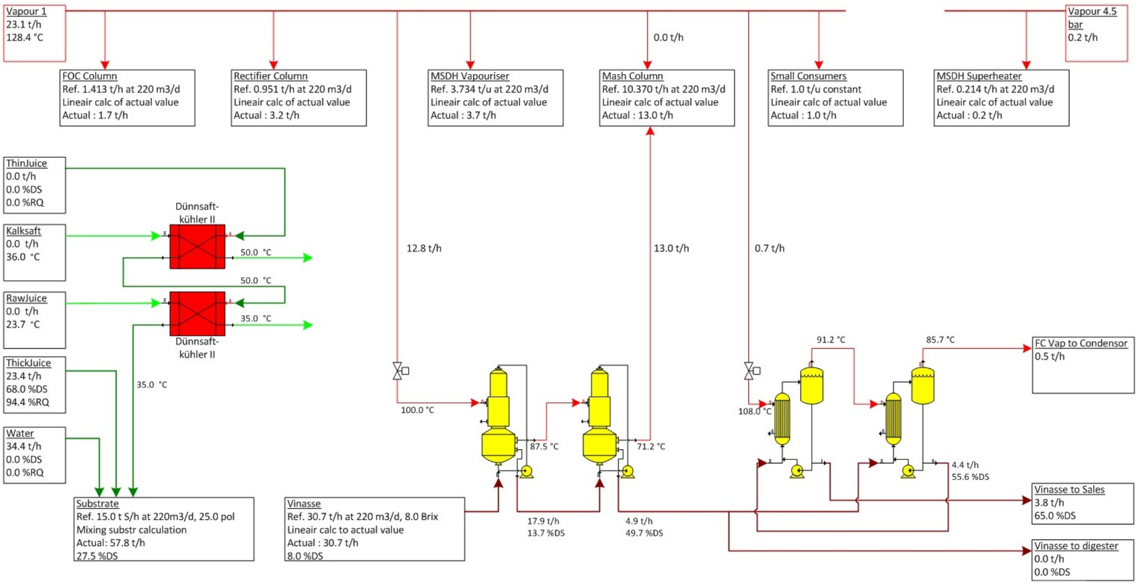


Figure 3.5: Process flow diagram of vinasse evaporation

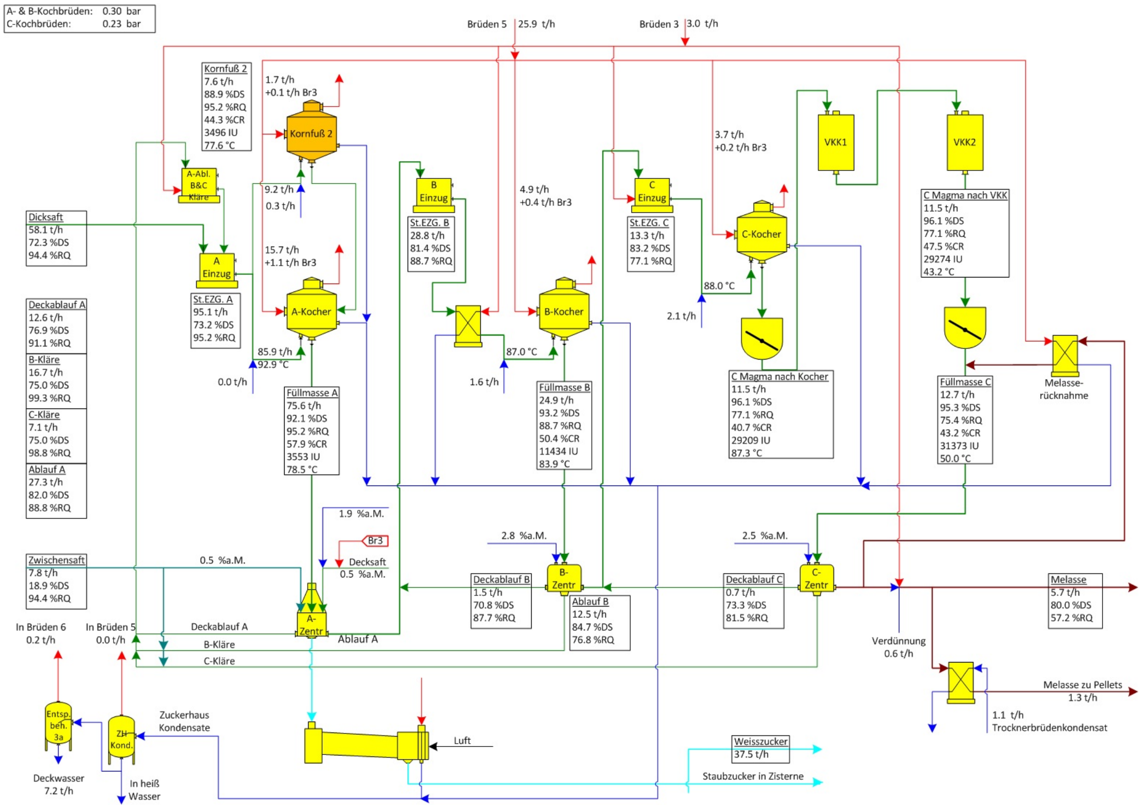


Figure 3.6: Process flow diagram of sugar house

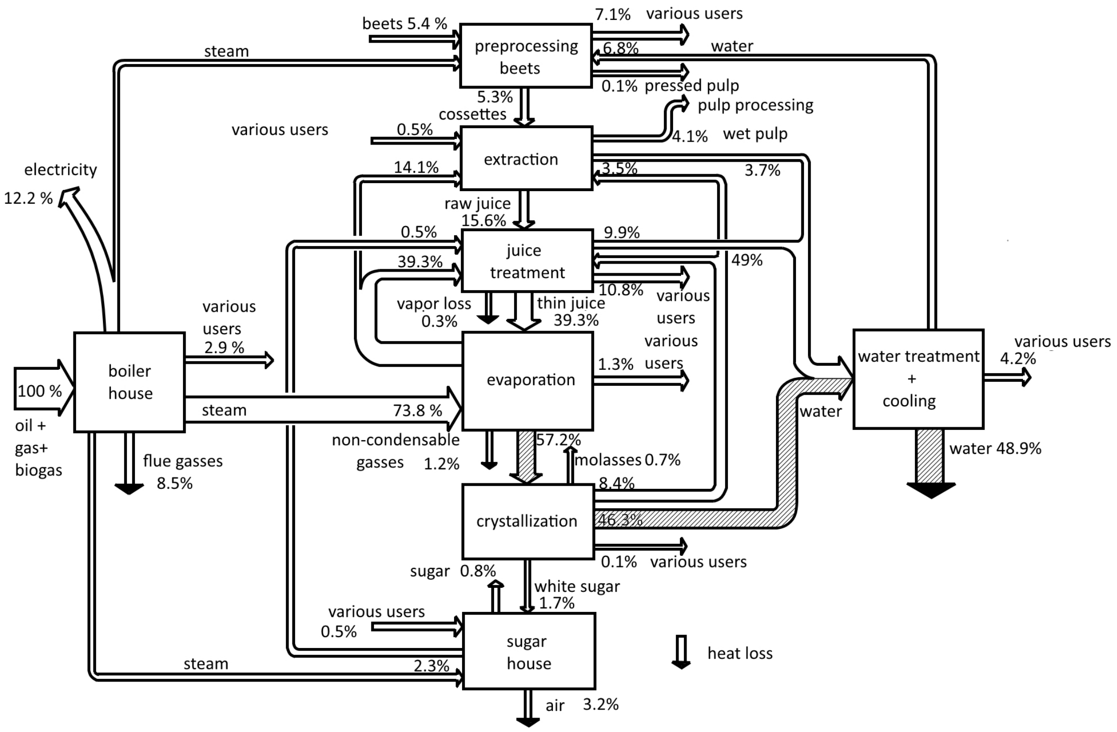


Figure 3.7: Energy flows

Chapter 4

Cosun concept

4.1 Line of thought

As previously mentioned, Royal Cosun renounced the idea of working with zeolites, but remained interested in working with an anti-solvent. The main advantage of working with an anti-solvent would be the reduced steam demand of the crystallizers. This because the water in the thick juice no longer needs to be evaporated. The Wageningen University proposed the use of ethanol as anti-solvent. This also seemed to be a convenient choice for the first concept, without the use of zeolites, investigated by Royal Cosun. Especially with a sugar factory in combination with an ethanol plant, like the one in Anklam Germany. Sugar that does not crystallize from the solution can be sent to the ethanol production plant to be fermented. The ethanol that can not be recovered also ends up in the fermentation process, but does not disturb the process since ethanol is the final product of the fermentation.

Working with anti-solvents demands an additional separation step for the recovery of the anti-solvent. In the case of ethanol most of the industries use distillation to separate the ethanol from the ethanol-water mixture. This is also the way ethanol is concentrated at the Anklam factory after fermentation. Furthermore the distillation process is driven by a temperature gradient; the exhaust heat in the condenser can be further used in the process. That is why distillation was chosen by Royal Cosun, for the new concept, as method to recover the ethanol. In the distillation column heat is supplied to the reboiler and the ethanol concentration in the liquid increases in every successive equilibrium tray. The ethanol-rich vapor leaves the tower at the top of the column and the water-rich liquid leaves at the bottom. The process design regarding the distillation sequence is further discussed in a next chapter.

This way the energy demanding crystallizer, in the original process, is replaced by a less energy demanding crystallizer and an additional energy demanding separation step. However, it became clear that the energy needed for the distillation column can be reused, in the bioethanol plant, by condensing the vapor leaving the top of the column. The expected temperature of the vapor from the column (roughly the boiling temperature of ethanol) is high enough for the bioethanol plant, around 78 °C. The bioethanol plant requires a lot of energy (equivalent to 13 t/h steam) making it the best choice for the deployment of the ethanol vapor. This way it is possible to produce sugar all year round instead of producing in shorter campaigns. All year round production means less storage of raw materials, cheaper equipment (lower capacity) and the advantages of a more continuous process. Also the energy demand of the distillation column is assumed to be less than that of the evaporative crystallizers due to the reduced evaporation enthalpy of ethanol. The temperature of the distillate can be changed by increasing or decreasing the operating pressure of the columns to match the heat sink.

Another aspect of anti-solvent crystallization that should be considered is the effect of the reduced vapor demand of the crystallizers on the evaporation section. The evaporators will lose efficiency due to the new crystallization method. Additionally the anti-solvent crystallization demands a sugar content of the thick juice as high as possible to ensure a sufficient yield of sugar crystals. This is why also changes to the existing multi-effect evaporator should be made in order to make the new concept feasible.

The concept developed by Cosun is based on several key ideas:

1. Crystallization from thick juice with a much higher dry matter content than usual to ensure a sufficient yield of sugar crystals (in the traditional process the thick juice in flashed to saturation conditions due to crystallization under vacuum).

2. Crystallization by anti-solvent addition.

3. The recovery of the anti-solvent (ethanol) can be achieved by distillation.

4. The heat supplied to the reboiler of the distillation column can be reused in the bioethanol plant. This allows for year round sugar production from thick juice being stored during the beet campaign.

5. The streams leaving the bottom of the distillation column can be fermented in the ethanol production plant.

4.2 Initial process design

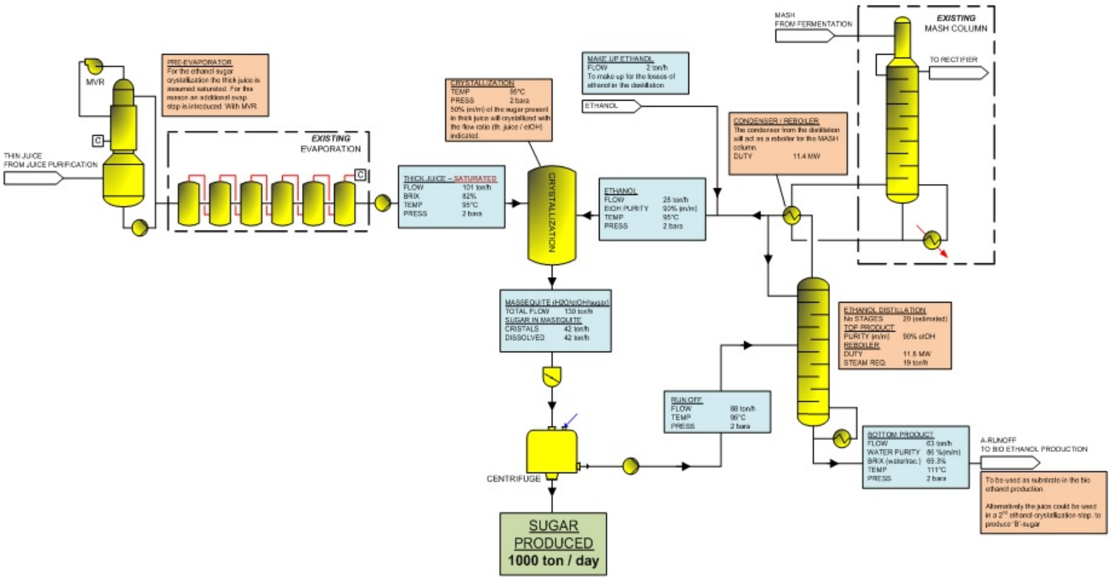


Figure 4.1: Initial Cosun concept

The initial study to determine the feasibility of anti-solvent crystallization was performed with Chemcad (Chemstations). This program is used to simulate the material and energy balances of chemical processing plants by iteratively solving a system of equations. The studied process flow is displayed in figure 4.1.

This process flow contains the modifications to the original process that cope with the key ideas mentioned in the previous section. In this concept the flow first enters a newly added evaporator stage, before continuing to the already existing multistage evaporator. This additional stage is of the vapor-compression kind. In a near subsection the principle behind this kind of evaporation is further discussed.

The highly concentrated sugar-rich juice (thick juice) continues towards the crystallizer. Here the anti-solvent (ethanol) is added to the saturated solution inducing crystallization. The magma leaving the crystallizer is sent to the centrifuge where the sugar crystals are separated. The juice is subsequently transported to the distillation column where the ethanol is recovered from the mixture. The bottom flow goes to the ethanol production plant to be fermented. The ethanol-rich vapor leaving the top of the column is condensed in a condenser. The released heat is used for the reboiler of an already existing distillation column that is part of the ethanol production plant. The condensed ethanol is sent back to the crystallizer.

4.2.1 Distillation

The initial Cosun concept uses continuous distillation as separation method to recover the ethanol from the run-off stream leaving the centrifuge. Continuous distillation is an ongoing distillation in which a liquid mixture is continuously fed into the process and separated fractions are removed continuously as output streams during the operation. Continuous distillation produces a minimum of two output fractions, including at least one volatile distillate fraction, which has been separately captured as a vapor, and then condensed to a liquid.

In principle, by creating a large enough cascade, an almost complete separation can be carried out. At the top of the cascade liquid is needed to feed the cascade. This is produced by condensing vapor that leaves the top stage and returning this liquid to the first stage of the cascade as reflux. Changing the reflux (in combination with changes in feed and product withdrawal) can also be used to improve the separation properties of a continuous distillation column while in operation (in contrast to adding plates or trays, or changing the packing, which would, at a minimum, require quite significant downtime). All of the vapor leaving the top stage can be condensed in a total condenser to produce a liquid top product. Alternatively, only enough of the vapor to provide the reflux can be condensed in a partial condenser to produce a vapor top product if a liquid top product is not desired. Vapor is also needed to feed the cascade at the bottom of the column. This is produced by vaporizing some of the liquid leaving the bottom stage and returning the vapor to the bottom stage of the cascade in a reboiler. The feed to the process is introduced at an intermediate stage, and products are removed from the condenser and the reboiler.

For this study a computer model of a distillation column was developed. The modeling of the distillation column and the employment of the column in the process is discussed in later chapters.

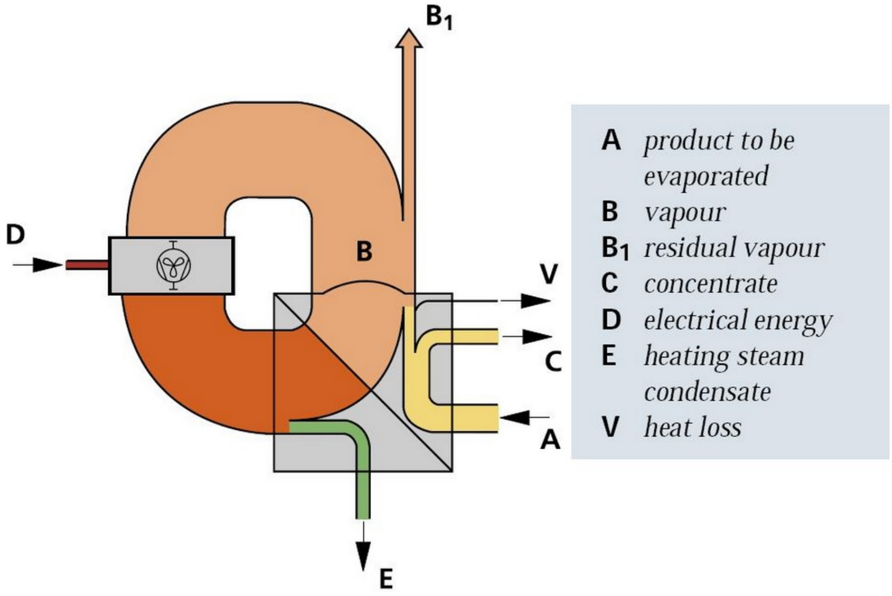


Figure 4.2: Heat flow diagram of an evaporator installation using Mechanical Vapor Recompression.

4.2.2 Mechanical vapor recompression

Figure 4.2 shows the heat flow diagram of an evaporator installation using Mechanical Vapor Recompression [13]. Mechanical Vapor Recompression (MVR) is the evaporation method by which a compressor is used to compress and thus increase the pressure of the steam produced. Since the pressure increase of the steam also generates an increase in the steam temperature, the same steam can serve as the heating medium for the liquid being concentrated from which the vapor was generated to begin with. This makes this evaporation method very energy efficient. Usually the compressor of a MVR is electrical driven. The reasons for using mechanical vapour recompression are [13]:

1. Low specific energy consumption
2. Gentle evaporation of the product due to low temperature differences
3. Short residence times of the product, as a single-effect system is most often used
4. High availability of the plants due to the simplicity of the process
5. Excellent partial load behavior
6. Low specific operating costs

4.3 Final process design

The final process design of the Cosun Concept sugar house, as developed in this study, is displayed in figure 4.3. The main process design selection of this study consists of choosing the best configuration of the flows to reduce energy consumption. This means that paring of process flows was done carefully. The condensate and vapor flows of the new process are coupled with existing flows in such a way that the temperature difference is kept low and that most of the energy can be transfered from one flow to the other. This way the destruction of exergy is limited.

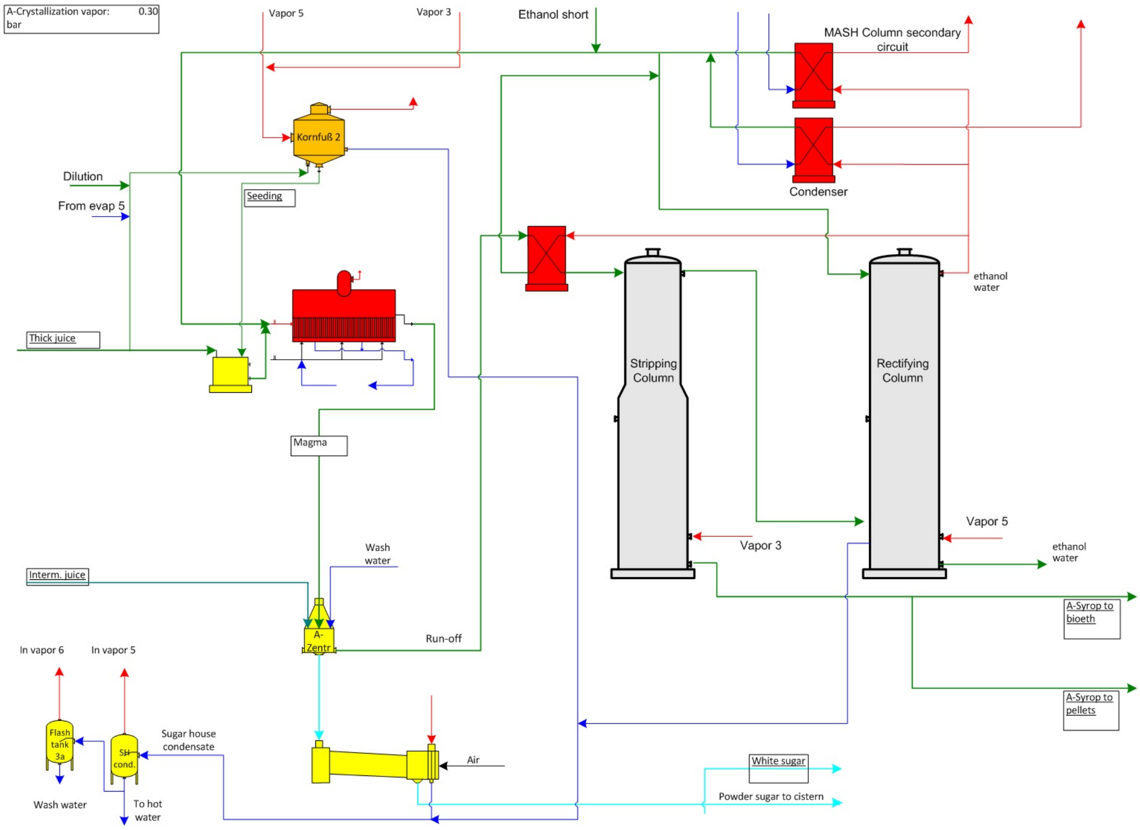


Figure 4.3: Process flow diagram of the Cosun concept sugar house

There are some distinct differences between the initial and the final Cosun concept sugar house:

1. An additional distillation column (two in total)

2. A cooling circuit for the crystallizer.

3. Vinasse evaporation with Mechanical Vapor Recompression

After an extensive literature study it was decided to add a second distillation column to the Cosun concept creating an indirect sequence as displayed in figure 4.4. This decision is based on already existing processes and heuristics that have been proposed for the selection of the sequence for simple distillation columns. In literature the additional distillation column is often referred to as "beer" or "mash" column [25]. In traditional ethanol production this tower takes feed directly from the fermenters complete with all the solids, proteins and sugars. This tower removes all the solids and other potentially fouling agents along with a majority of the water. In the Cosun Concept the sugars are removed in this column and the flow to the next column is reduced, facilitating a better separation of the ethanol. The heuristics are based on observations made in many problems and attempt to generalize the observations [6, p. 212].

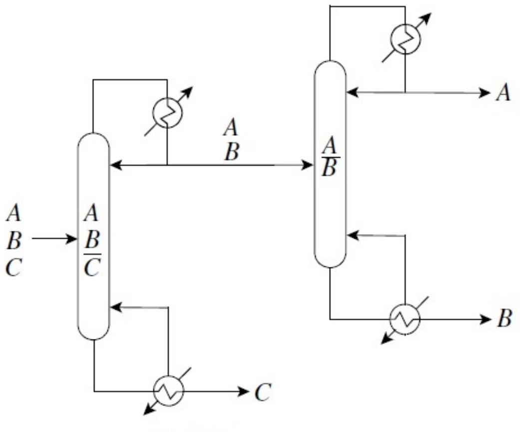


Figure 4.4: Indirect sequence

Heuristic 1. Separations where the relative volatility of the key components is close to unity or that exhibit azeotropic behavior should be performed in the absence of nonkey components. In other words, do the most difficult separation last.

Heuristic 2. Sequences that remove the lightest components alone one by one in column overheads should be favored. In other words, favor the direct sequence.

Heuristic 3. A component composing a large fraction of the feed should be removed first.

Heuristic 4. Favor splits in which the molar flow between top and bottom products in individual columns is as near equal as possible.

The heuristics 1, 3 & 4 apply to this process. Ethanol and water form an azeotrope with each other (further discussed in a later chapter) and the large fraction of sugar, that does not enter the vapor phase, should be removed first to facilitate a better separation of the ethanol.

The first distillation column is a stripper column. A typical stripper is a column where the feed tray enters at the top of the column, with few to zero stages (trays) above the feed tray. The heat source enters the column at the bottom, and the feed trickles down to the bottom trays and is essentially 'stripped' of light material by the vaporized reflux traveling up the column. The light material vaporizes and leaves in the overhead product, and the heavy material is purified all the way down to the heavier product stream. In the second distillation column (the rectifier) the separation of ethanol and water happens. The fact that sugar is no longer present in the product stream means that an efficient reflux can be applied to increase the purity of the ethanol.

The cooling circuit is applied to remove the heat that is generated by the crystallization process and to introduce the option of applying additional cooling crystallization to increase the crystal yield. This is further discussed in a next chapter.

Figure 4.5 shows the new process flow diagram of the vinasse evaporation. Because the vapor from the rectifier is now used for the mash column of the bioethanol a MVR is applied to reduce the steam demand of the vinasse evaporation. Using the vapor of the rectifier column reduces the consumption of higher quality steam.

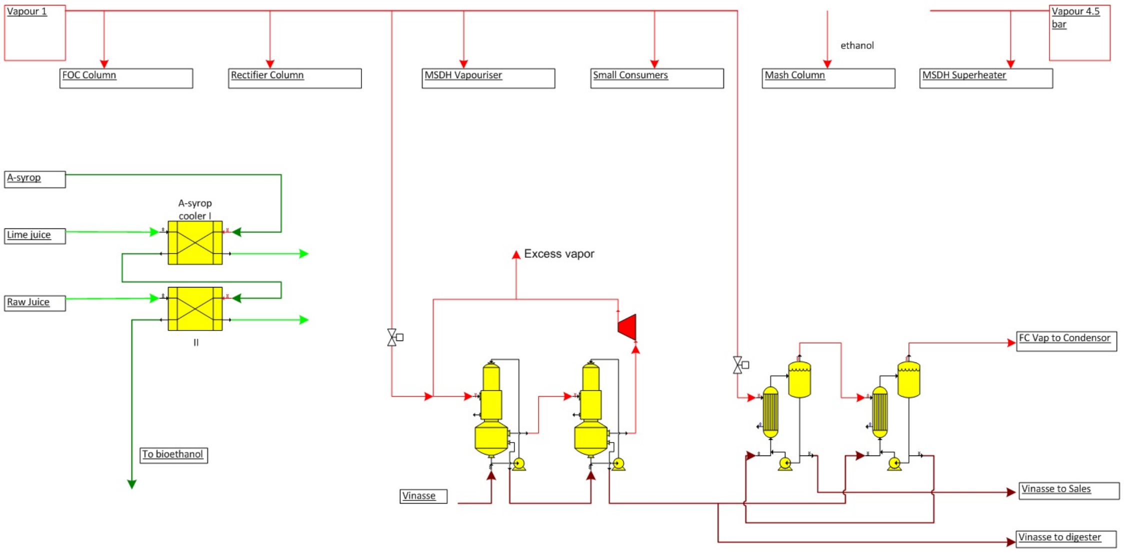


Figure 4.5: Process flow diagram of the vinasse evaporation in the final Cosun concept

The last major change, associated with the final Cosun concept, involves the preheating of the lime juice. In the current process this is done by condensing crystallization vapor, evaporator vapor and cooling down hot condensate as indicated in figure 4.6. In the final Cosun concept there is less crystallization vapor available, but more condensate. In the new concept only one heat exchanger is fed with crystallization vapors (coming from the evaporative crystallizer producing seed crystals) and a new heat exchanger further cools down the condensate.

The thick juice campaign of the Cosun concept only involves the vinasse evaporation, the boiler house, preheating the thick juice from the tank and the sugar house. Only the preheating of the thick juice deviates from the beet campaign. The process flow of the thick juice is included in the attachments and not further discussed here.

4.4 Uncertainties

Several question will arise when confronted with the principle of anti-solvent crystallization. Very obvious questions heard in industrial crystallization are "Isn't it dangerous to use organic compounds, think about flammability or even the risk of an explosion" and "We've been using this evaporative crystallization process for more than 100 years. Is this new process really better (read: cheaper)". Apart from these, several other more fundamental questions can be asked. A brief summary:

1. What are the properties of the anti-solvent: the cost, the stability, the handling and safety with respect to the people and environment?

2. It is known that foreign components in the mother liquor can have an influence on the nucleation and growth mechanisms and rates of the crystals: the relative growth rates of the various faces may change which results in a different particle size distribution and a different morphology of the product. With the anti-solvent, a high concentration of potential habit modifier is present which may vary locally due to mixing effects. How can this influence the crystal size and the crystal habit? And how is the anti-solvent incorporated in the crystals? Are inclusions formed, or occlusions, or are anti-solvent molecules substituted into the crystal structure?

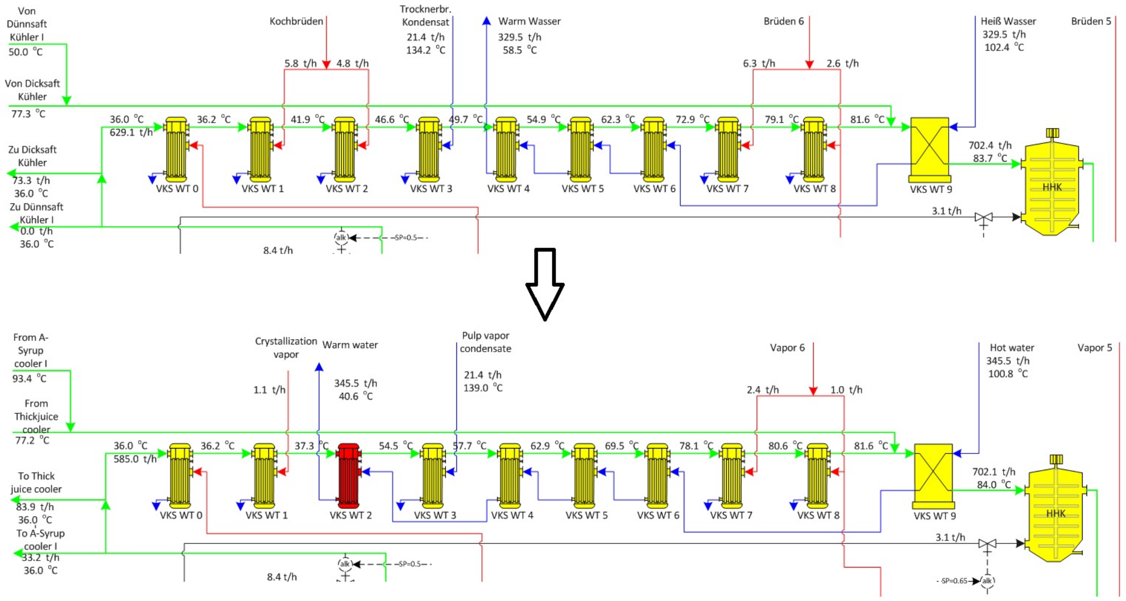


Figure 4.6: Preheating of the lime juice

3. The addition of anti-solvent and the subsequent decrease in solubility of the solute changes the characteristics of the crystallizing system: low solubilities are combined with high supersaturations which are the features of precipitation. It is therefore necessary to know if sufficiently large crystals can still be produced and whether the impurity uptake, which is closely related to the growth rate of the crystals, is not too high.

4. When a satisfactory product can be produced with an anti-solvent that fulfills all requirements, the economic feasibility can be determined more accurately. What investments need to be done and what are the operating costs ? How much energy can actually be saved ?

5. The possible regeneration of the anti-solvent strongly depends on the thermodynamic behavior of the ternary mixture of water, dissolved sugar and anti-solvent. What is known about the system of interest? How does the anti-solvent influence the solubility of the dissolved sugar and how does the dissolved sugar influence the miscibility of the water and the anti-solvent?

6. How does the anti-solvent affect the taste, flavor and smell of the food product or the acceptation of the food product sugar. Think of acceptation for halal or kosher production standards. Is food grade ethanol required to make up the ethanol losses.

Chapter 5

Physical properties

5.1 Solubility

The solubility of a solute in a solvent at determined conditions, such as pressure, temperature and the presence of other substances is the maximum amount of this solute that can be dissolved and stay in solution (saturation); the solute concentration above the saturation concentration is the supersaturation. Depending upon the conditions, either nucleation or growth may predominate, and as a result, crystals with different sizes and shapes are obtained.

5.1.1 Two sources

The equilibrium concentration of the solution ethanol-water-sucrose was examined by H. Schiwek and A. Kolber in their study "Zur Frage der optimalen Ausbilding der Zuckerkruste bei Krustenpralinen" [14]. This study tries to determine the optimal formation of a sugar crust on chocolate candy. The formation of the sugar crust is controlled by the crystallization process of sucrose. The chocolate candy's also contain ethanol and therefore the effect of the ethanol concentration on the solubility of sucrose was examined.

Temperature	Ethanol content W_{Eth} in g/100g solution					
t in °C	0	4	8	12	16	20
15	66.04	62.07	58.10	54.15	50.21	46.28
20	66.72	63.00	59.09	55.20	51.31	47.43
25	67.47	63.96	60.12	56.27	52.43	48.58
30	68.29	64.96	61.18	57.37	53.56	49.74
35	69.17	65.99	62.26	58.50	54.71	50.90
40	70.10	67.04	63.38	59.65	55.88	52.06
45	71.09	68.13	64.52	60.83	57.06	53.23
50	72.12	69.25	65.70	62.03	58.27	54.41
55	73.18	70.41	66.90	63.26	59.49	55.59
60	74.26	71.59	68.14	64.52	60.73	56.77
65	75.37	72.80	69.41	65.80	61.98	57.96
70	76.48	74.05	70.70	67.11	63.25	59.15

Table 5.1: Sucrose content W_s of a saturated solution

The maximum solubility was determined for different ethanol concentrations (0-20 ethanol w%) and temperatures (15-70 °C). Table 5.1 shows the sucrose content of the saturated solutions.

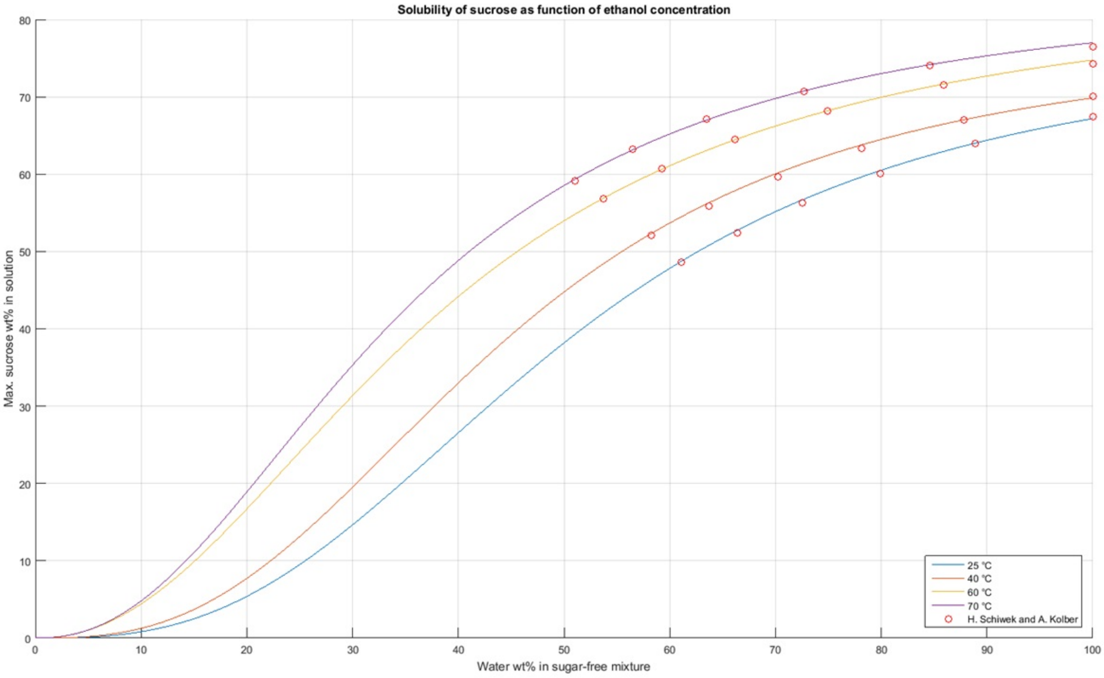


Figure 5.1: Correlated solubility of sucrose

An empirical correlation was suggested by the Wageningen University of the form:

$$S = \frac{a}{1 + (\frac{w}{x})^b} \tag{5.1}$$

where S is the solubility of the sucrose in the solution, W is the water mass percentage in the sugar-free solution and a, b and x are temperature dependent fit parameters [1]. Figure 5.1 shows the set of data and the curves suggested by the Wageningen University. The data and the correlated curves are in good agreement with each other. However the data from H. Schiwek and A. Kolber only gives information about the solubility for a limited amount of ethanol in the solution. For higher concentrations of ethanol the curves are extrapolated introducing uncertainties.
The solubility of sucrose in the mixture of ethanol-water was also examined by Antonio M. Peres and Eugenia A. Macedo. In their publication ”Phase equilibria of D-glucose and sucrose in mixed solvent mixtures: Comparison of UNIQUAC- based models” a UNIQUAC model was proposed to predict the ternary phase equilibria [15]. In the study a comparison between three UNIQUAC based activity coefficient models was carried out taking into account their abilities to describe the vapor-liquid and the solid-liquid equilibria of aqueous solutions containing one or two sugars, as well as the solid-liquid equilibria of one sugar in mixed solvent mixtures at different temperatures. The obtained results clearly showed that only the modified UNIQUAC model is able to give an accurate representation of all the above-mentioned equilibria. Figure 5.2 shows the solubility of the sucrose according to the proposed model. The solid-liquid equilibrium data (obtained by measurements done by the authors) used to find the needed parameters are also depicted in the figure.

It can clearly be seen that Schiweck and Macedo are in agreement about the solubility for water wt% between 60 and 100. At higher temperatures and ethanol wt% the results

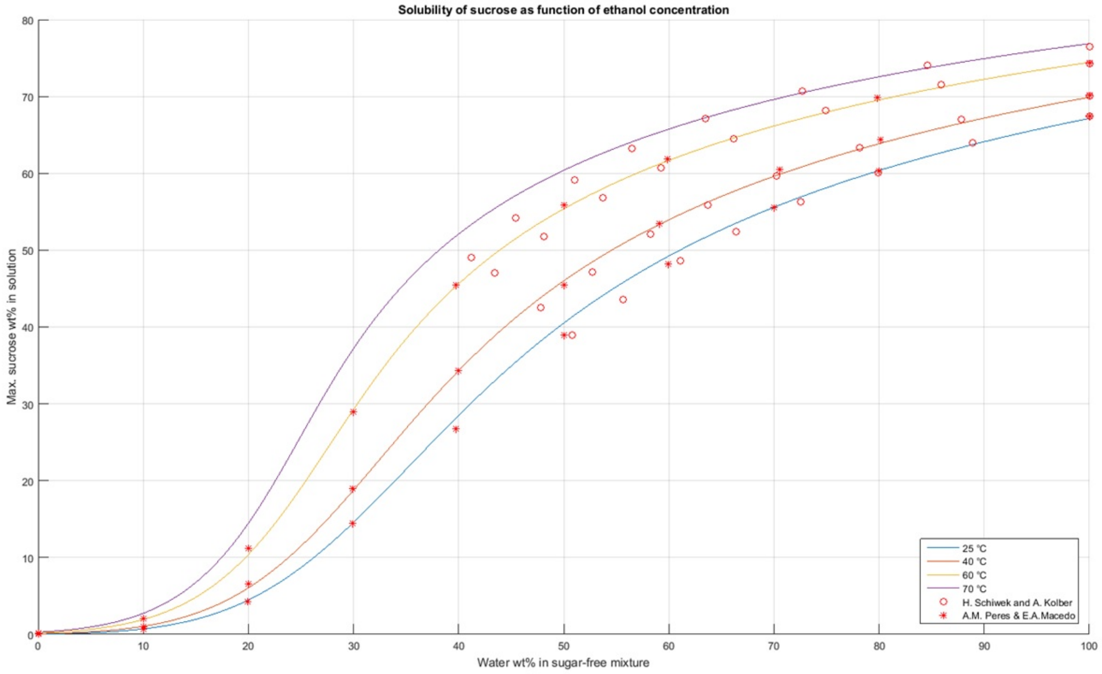


Figure 5.2: Solubility of sucrose UNIQUAC

start to deviate from each other. Extrapolating to higher temperatures will give even bigger deviations.

The range of the ethanol concentration in the measurements conducted by Macedo is wider and therefore more trustworthy for higher ethanol concentrations. However the temperature is only limited to 60 °C. The measurements conducted by Schiweck go up to 70 °C.

Solubility measurements were also conducted by A. Bouchard, G. W. Hofland and G-J. Witkamp [16]. The measurements were conducted at 310 K with varying ethanol concentrations from 0 up to 100 wt%. These measurements are in total agreement with the measurements conducted by by Antonio M. Peres and Eugenia A. Macedo.

The latter two solubility sources are in agreement with each other and the measurements were conducted with ethanol concentration varying over the whole range. For this reason the modified UNIQUAC model, proposed by Antonio M. Peres and Eugenia A. Macedo is used to predict the solubility.

5.1.2 Effect of non-sugars

The juice treatment does not remove all the undesired components in the juice. The thick juice also contains dissolved components that are not water or sucrose. These dissolved components are called non-sugars. The purity of the thick juice is the ratio between the mass of sucrose and the total mass of the dissolved solids. The solution containing only water and sucrose is often referred to as a pure solution and if there are non-sugars present it becomes a technical solution.

The non-sugars influence the solubility of sucrose in the solution. The TDS (total dissolved solids) are tabulated in the ”Sugar Technologists Manual” for different temperatures and varying purities [17, p. 210]. To predict the influence of the purity on the solubility of the ternary mixture including ethanol a study was conducted to the influence of the purity on the solubility of technical solutions not containing ethanol.

The hypothesis is introduced that, for saturation mixtures, the non-sugars do not influence the ratio of sucrose to sucrose and water. Figure 5.3 shows for different temperatures the ratio of sucrose to sucrose plus water as function of purity.

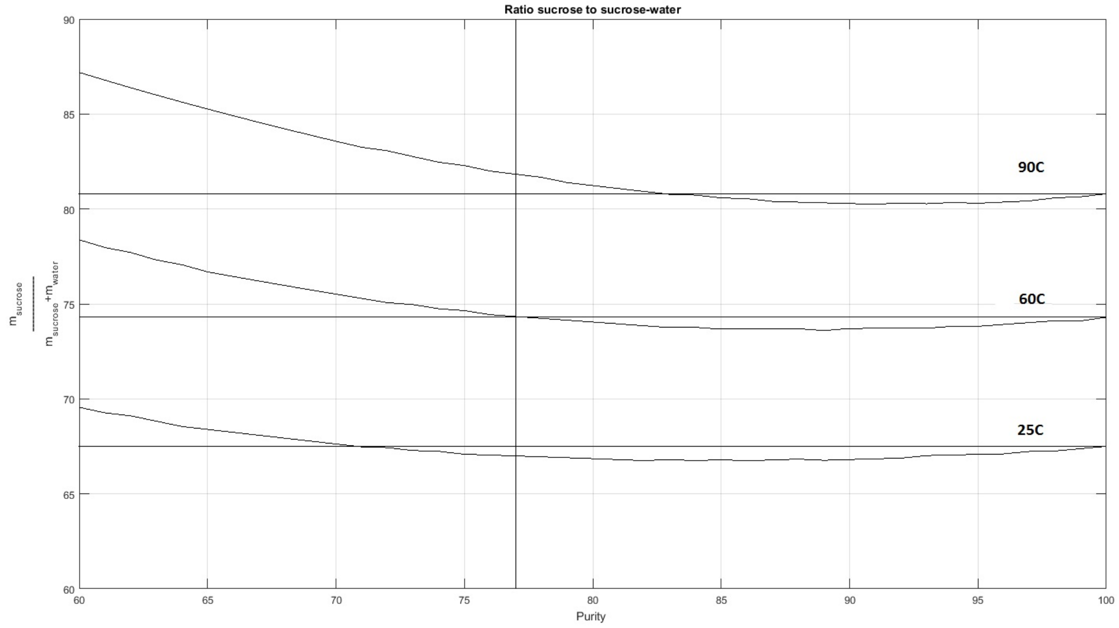


Figure 5.3: Ratio of sucrose to sucrose-water

The horizontal straight lines shown in the graph represent the solubility of sucrose for pure solutions. It can be seen that the hypothesis holds for purities from 77% up to 100% for all the considered temperatures. The purity of the thick juice (92-95 %) and of the A-Syrup leaving the second column (87-89 %) are well in range of the purities for which the hypothesis holds. The non-sugars do not decrease the solubility of the sucrose in the available water, but do decrease the total solubility since it is defined as the mass sucrose divided by the total mass (including the non-sugars). The "total" solubility decreases with decreasing purity, but the "corrected" solubility (without the non-sugars) does not change for high purities.

The assumption is made that this also holds for mixtures including ethanol. In saturated mixtures the ratio sucrose to water plus sucrose plus ethanol does not change for high enough purities.

5.1.3 Crystal recovery

Knowing the solubility of sucrose it becomes possible to determine the crystal recovery as function of temperature and added ethanol. Figure 5.4 shows the crystal recovery as a function of the temperature drop and the ethanol concentration. The crystal recovery is defined as the mass based amount of crystals formed, divided by the total amount of sucrose available. The ethanol concentration is presented as the mass based ratio of ethanol to water (r). At the lower right corner of figure 5.4 the solution is saturated and no crystals are formed yet.

The conclusion can be drawn that only adding ethanol, without cooling down the mixture, would result in a limited crystal recovery. Especially cooling down the first twenty degrees

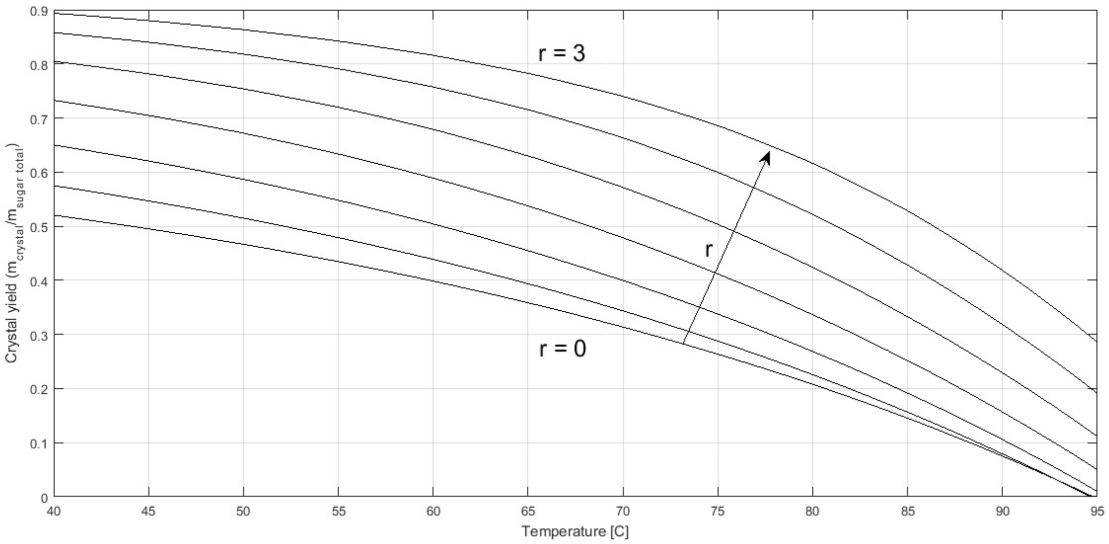


Figure 5.4: Crystal recovery

gives a considerable recovery. Cooling down the mixture without adding ethanol also gives a limited result, however much better compared to only adding ethanol. At this point it is still impossible to determine how far the mixture should be cooled down or how much ethanol should be added. Cooling the mixture will give secondary flows at low temperatures which might be useless in the plant. Adding a lot of ethanol will result in a high energy consumption recovery. The figure does however give an insight into the effect of cooling down and adding ethanol.

5.2 Vapor-liquid equilibrium

As previously mentioned, the recovery of the ethanol is realized by distillation. In this section the vapor-liquid equilibrium of a sugar-ethanol-water mixture is discussed. The vapor-liquid equilibrium is needed to determine the dimensions of the distillation column and the energy needed to recover the ethanol. In figure 5.5 a standard vapor-liquid equilibrium curve of a binary mixture is shown. The way distillation works is indicated in this figure. Point A is the starting point. This point represents a mixture with a certain concentration and temperature below the bubble point curve. Increasing the temperature of the mixture means going straight up in the diagram until the bubble point curve is reached (point B). At this point the mixture starts to evaporate. If the liquid concentration is kept constant then the vapor concentration, in equilibrium with the liquid concentration, can be found by drawing a horizontal line until it intersects the dew point curve (point C). Condensing this vapor and repeating the previous steps results in a complete separation of the two compounds.

However, this is not possible for all binary mixtures. Figure 5.6 shows the vapor-liquid equilibrium of ethanol and water [18]. At the azeotropic point (indicated in the diagram) the vapor and liquid have the same concentration. Once the azeotropic point is reached further distillation is futile. A better separation is not possible without additional modifications to the distillation process.

The equilibrium conditions can be determined by calculating the activity coefficient for the ternary mixture. With the activity coefficient used in equation 5.4 it becomes possible to determine the molar fractions in the vapor phase. With an iterative procedure it is possible to calculate the temperature at the corresponding tray.

$$y_i \ P = \gamma_i \ x_i \ P^{sat} \tag{5.2}$$

with P the pressure, y_i the molar fraction in the vapor, γ_i the activity coefficient, x_i the molar fraction in the liquid and P^{sat} the vapor pressure of the pure component.

The vapor-liquid equilibrium curve was first investigated with Chemcad (Chemstations). After selecting the components of the mixture "Chemcad" proposes an activity coefficient model. For this mixture "Chemcad" advises to use the non-random two-liquid model (NRTL model).

The concept of NRTL is based on the hypothesis of Wilson that the local concentration around a molecule is different from the bulk concentration. This difference is due to a difference between the interaction energy of the central molecule with the molecules of its own kind U_{ii} and that with the molecules of the other kind U_{ij}. The energy difference also introduces a non-randomness at the local molecular level. The NRTL model belongs to the so-called local-composition models. Other models of this type are the Wilson model, the UNIQUAC model, and the group contribution model UNIFAC. These local-composition models are not thermodynamically consistent due to the assumption that the local composition around molecule i is independent of the local composition around molecule j.

Applying this NRTL model, for atmospheric pressure, results in a vapor-liquid equilibrium curve equal to the one displayed in figure 5.6. Also comparing the calculated equilibrium curve to curves from other sources at different pressures confirms the validity of the NRTL model for the binary mixture.

5.3 Viscosity

Adding an anti-solvent without water evaporation could decrease the viscosity of the magma. This has a positive effect on mixing, the crystallization kinetics and the final purity of the sugar crystals. This is why Royal Cosun also required a model to determine the viscosity of the water-ethanol-sucrose solution. The dynamic viscosity η_{12}, of an ideal binary mixture consisting of the components with viscosities η_1 and η_2 obeys the Arrhenius equation 5.3,

$$ln(\eta_{12}) = x_1 ln(\eta_1) + x_2 ln(\eta_2) \tag{5.3}$$

where $x_i (i = 1, 2)$ is the mole fraction of the ith component in the mixture [19].
The viscosity of the varying mixtures of sucrose-water are known and described by correlations provided by the "Sugar Technologists Manual" [17, p. 167]. Taking this viscosity as one of the binary viscosities, in the above mentioned Arrhenius equation, makes it possible to predict the viscosity of the ternary mixture.

The viscosity of the ternary mixture was investigated by H. Schiwek and A. Kolber [14] and by A. Bouchard, G. W. Hofland and G-J. Witkamp [16]. The proposed model was validated using the measurement data from the two sources. The comparison with the values by G-J. Witkamp are shown in table 5.2.

Table 5.2 shows that not all the values are in total agreement with each other. However, the order of magnitude of the viscosity data from the source and the calculated values are the same. The viscosity at 0 wt% ethanol measured by G-J. Witkamp is not in agreement

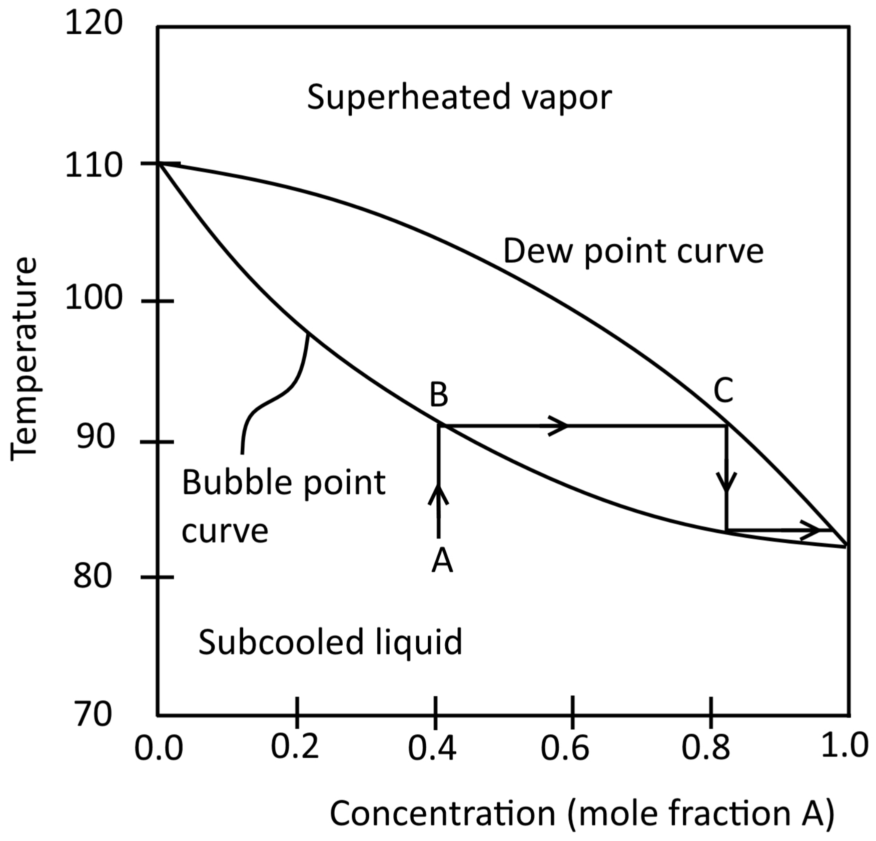


Figure 5.5: A standard vapor-liquid equilibrium curve of a binary mixture

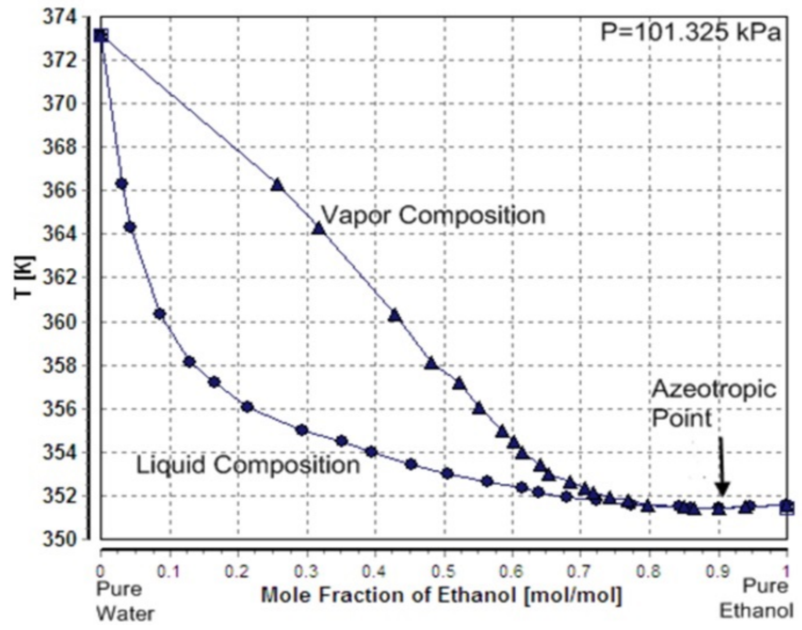


Figure 5.6: The vapor-liquid equilibrium curve of ethanol and water

% ethanol in sugar free solution (w/w)	Viscosity from source (mPa s)	Calculated viscosity (mPa s)
0	91.74	149.24
12.5	91.79	97.34
25	75.32	68.91
37.5	41.03	36.34
50	18.56	14.50
62.5	5.60	4.66
75	2.32	1.50
85	1.37	0.95
95	1.12	0.87
100	0.89	0.88

Table 5.2: Viscosity at 310 K

with the viscosity of the sucrose solution presented by other sources. The correctness of the value, provided by the source, is questionable. The calculated value is in close agreement with the other sources.

% sucrose (w/w)	% ethanol (w/w)	40 °C	50 °C	60 °C	70 °C	80 °C
30	10	3.01/2.15	-	-	-	-
30	20	4.17/2.47	3.06/1.93	1.80/1.55	1.03/1.27	-
40	10	5.94/4.12	3.31/3.12	-	-	-
40	20	6.52/5.22	3.82/3.87	2.81/2.96	1.82/2.32	-
50	10	14.98/10.19	9.24/7.18	6.05/5.25	3.66/3.96	-
50	20	19.74/15.57	12.34/10.50	7.78/7.37	4.85/5.36	3.59/4.03
60	10	46.30/39.52	25.18/24.61	15.97/16.13	11.57/11.06	8.36/7.89
60	15	-	-	22.57/21.37	13.18/14.21	10.89/9.88
60	20	-	-	-	-	14.26/12.71
70	5	-	-	43.4/60.36	32.9/37.05	-

Table 5.3: Viscosity

The comparison with the values from H. Schiwek and A. Kolber are presented in table 5.3. Most of the values from the data presented by H. Schiwek and A. Kolber are well predicted by the Arrhenius equation for ideal mixtures. It is not possible to validate the model for higher concentrations of ethanol and different temperatures due to the limited amount of data available in literature.

For the viscosity of mother liquor containing crystals, for example the magma leaving the crystallizer, equation 5.4 was proposed by the "Sugar Technologists Manual" [17, p. 264].

$$log(\eta_{Ma}) = log(\eta_{MS}) + 0.01326 \cdot W_{DS,Ma} \cdot \frac{W_{CR,Ma}}{85 - W_{CR,Ma}} \tag{5.4}$$

where η_{Ma} is the viscosity of the magma, $W_{DS,Ma}$ the total dry matter content [%], $W_{CR,Ma}$ the crystal content [%] and η_{MS} the viscosity of the mother liquor. The viscosity of the magma, containing ethanol, can be calculated by applying equation 5.3, to determine the viscosity of the mother liquor, and subsequently inserting this viscosity in equation 5.4. It is assumed that this procedure will give a good estimation of the viscosity of the magma, containing ethanol, because equation 5.4 only corrects for the crystal content. However, this could not be validated due to the limited amount of data available in literature. This procedure was used to determine the viscosity of the magma leaving the crystallizer in the Cosun Concept.

5.4 Excess enthalpy

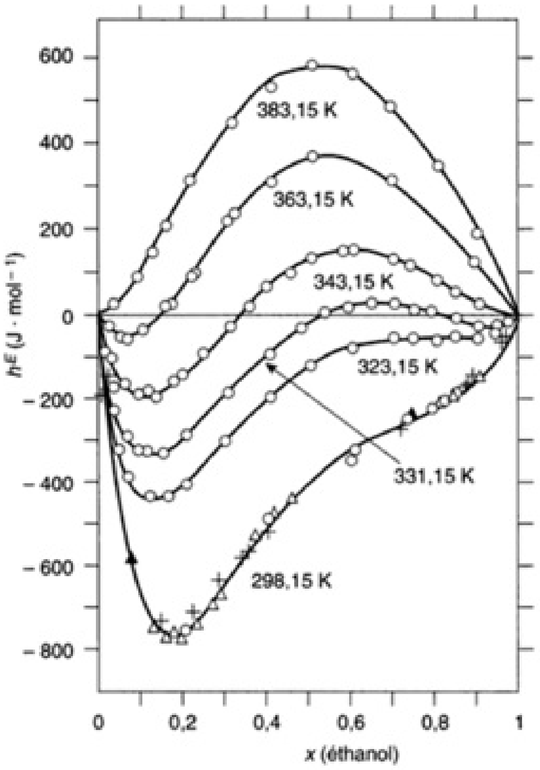


Figure 5.7: Excess enthalpy

Enthalpy of mixing refers to the change in the enthalpy per mole of solution formed when pure components are mixed at the same temperature and pressure. Or in other words the difference between the enthalpy of a mixture and the sum of the enthalpies of its components at the same pressure and temperature. Enthalpy effects on mixing of liquids can be quite large and of considerable importance, especially for the design of absorption and distillation columns.

The excess enthalpy for water-ethanol mixtures was investigated by J.A. Larkin [20]. Figure 5.7 depicts the molar excess enthalpy for different temperatures and varying ethanol mole fraction. Figure 5.7 shows that the excess enthalpy changes in shape dramatically as the temperature is increased. At 298.15 K and 323.15 K the curves are highly skewed with sharp minima near $x = 0.15$ and inflexions near $x = 0.3$ and $x = 0.8$. Mixing is exothermal at all compositions. At temperatures between about 330 K and 370 K H^E has both negative and positive portions with minima at $x = 0.1$ and maxima at $x = 0.6$. At 383.15 K H^E is nearly symmetrical about $x = 0.5$ and is positive at all compositions: the specific molecular interactions which are so marked at 298.15 K have become insignificant at this temperature, except for mixtures rich in water where the excess enthalpy is smaller than would be expected for a mixture with only physical molecular interactions.

The excess enthalpy is used in the calculation of the total enthalpy of the streams entering and leaving the crystallizer. It is assumed that the total enthalpy of a stream equals the sum of the water-sucrose enthalpy, calculated with a correlation from the sugar technologists manual, the enthalpy of pure ethanol and the excess enthalpy. The mole fraction ethanol, used to determine the excess enthalpy, is calculated as if the solution only consists of ethanol and water. The study, conducted by J.A. Larkin, only contains correlations for certain temperatures. The measured data, presented in the paper, are extrapolated with the 2-d lookup table function in Matlab/Simulink. This way is becomes possible to determine the excess enthalpy for all temperatures and mole fractions ethanol.

5.5 Appearance, Handling & Safety

The properties of the anti-solvent regarding the stability, the handling and safety with respect to the people and environment are obtained from the book "Chemiekaarten"[21, p. 555]. The concerning page is included in the attachments.

The appearance of ethanol is a colorless liquid, with a characteristic odor. The vapor mixes well with air and explosive mixtures are easily formed. The chemical dangers include slow reactions with calcium hypochlorite, silver oxide and ammonia, causing fire and explosion hazard. It reacts violently with strong oxidants such as nitric acid, silver nitrate, mercuric nitrate or magnesium perchlorate, causing fire and explosion hazard.

The substance can be absorbed into the body by inhalation of its vapor and by ingestion. A harmful contamination of the air will be reached rather slowly on evaporation of this substance at 20°C. The inhalation of high concentration of vapor may cause irritation of the eyes and respiratory tract. Effect of long-term or repeated exposure include the defatting of the skin. The substance may have effects on the upper respiratory tract and central nervous system, resulting in irritation, headache, fatigue and lack of concentration. Chronic ingestion of ethanol may cause liver cirrhosis.

Acute Hazards include fire and explosion. The liquid is highly flammable and vapor/air mixtures are explosive. The prevention of fire consists op avoiding open flames, sparks, and smoking. The prevention of explosion consists of working with closed systems, ventilation, explosion-proof electrical equipment and lighting. Compressed air for filling should not be used.

Ethanol should be stored fireproof and separated from strong oxidants, acids en light metals (e.g. aluminium).

Chapter 6

Model development

6.1 Introduction to the current model

Over the last years the Cosun Food Technology Center (CFTC) developed Matlab/Simulink based models of almost all the components of the sugar factory. These components can be linked together to represent the total sugar production plant. The steady state model is called "STEM" and this abbreviation stands for "Sugar technological economical model". This model makes it possible to simulate the process and to determine what happens to the output when some changes are made to the process.

The model does not iteratively solve a set of equations as most software packages do. The STEM model reaches steady state in a dynamical way. It can be stated that STEM is a dynamic model, however many components do not have realistic dynamics. Additional fictive accumulators or controllers are applied that do not exist in reality. Only the steady state values should be reviewed. Once the steady state is reached the conservation equations are satisfied.

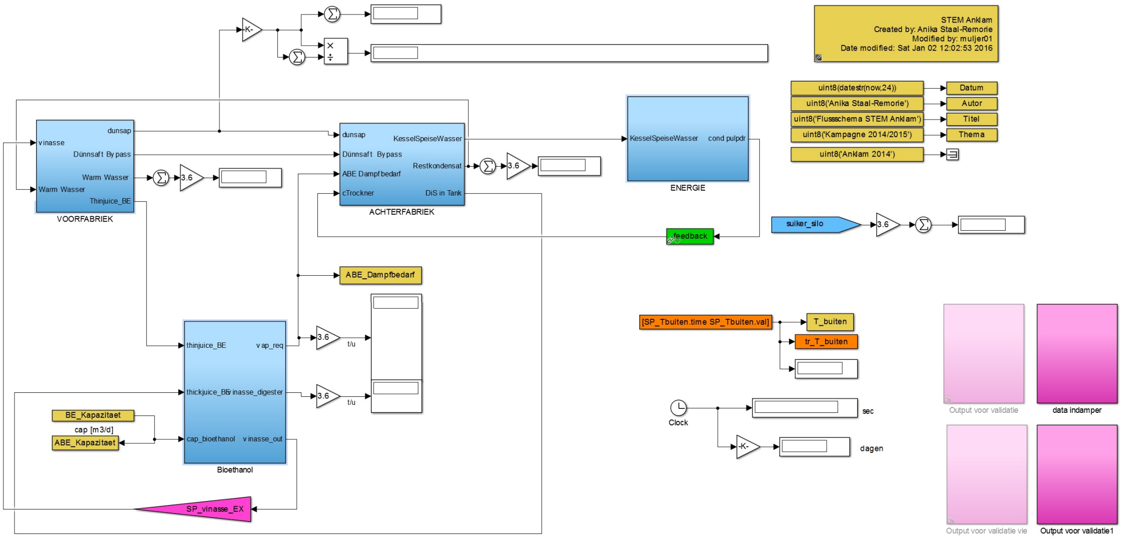


Figure 6.1: Original STEM model of the Anklam factory

Figure 6.1 shows the top layer of the STEM model. The model is divided into four parts: the pre-processing part, the post-processing part, the energy part and the bioethanol part. The pre-processing part consists of the sugar extraction and juice purification. The post-processing part consists of the evaporation and sugar crystallization. In the energy part the calculations for the boiler house are executed. Here the amount of gas, needed for steam production is determined and the amount of generated electricity is calculated. In the last part the steam demand for the bioethanol plant is calculated. The figure also shows the signal lines that induce the interaction between the different parts of the model. The signal lines in the Simulink model consist of multiple signals representing mass flows. In the the post-processing part, the part that undergoes the biggest changes in this study, a signal line consists of the mass flows water, dissolved sugar, non-sugars and sugar crystals. Other process variables, like temperature and pressure, are transmitted by separate lines or via the Matlab workspace.

Process parameters, needed for the models, are imported by means of a Matlab input file. This way all the parameter are clearly displayed and can easily be changed, looked up and validated. The calculated output values are later transported from Simulink to a process flow diagram, created in Visio, to make the results more presentable.

The STEM model was also used for this study, the feasibility study of anti-solvent crystallization, however this meant that certain changes had to be made.

6.2 New process blocks

The following process blocks were created and added to the STEM library in order to make the new model, based on anti-solvent crystallization:

1. A new crystallizer, allowing for cooling and anti-solvent crystallization.

2. A distillation column with variable number of trays and applicable for the separation of water, ethanol and sucrose.

3. A centrifuge, allowing for ethanol flows.

4. A mixing block that allows for ethanol flows.

5. A heat exchanger that allows for ethanol flows.

6.2.1 Crystallizer

The crystal yield of the crystallizer is determined by comparing the amount of sugar dissolved in the mixture, at the start of the process, to the maximum amount of sucrose that can be dissolved at lower temperatures and with added ethanol. The difference between those values equals the crystal yield. The solubility of the sugar in the mixture is determined with the modified UNIQUAC method and parameters previously described [15]. The crystallizer model assumes that the leaving magma is not supersaturated. This is a optimistic estimate, because in reality the magma will always retain a slight supersaturation. The crystallization process is considered as a continuous process, where in practice it can be a batch or semi-batch process using several (semi) batch crystallizers.

The model also calculates the cooling duty. The formation of crystals is accompanied by heat production. This heat production is determined in the model by calculating the enthalpy difference between the flows entering and leaving the crystallizer. The enthalpy is a function of the crystal content, the dry matter and the temperature according to the Sugar Technologists Manual [17, p. 116 & 206]. The heat released due to the excess enthalpy of water and ethanol is also part of the cooling duty of the crystallizer since the ethanol is added in this process step. The last part of the crystallizer model consists of cooling down the mixture to the desired temperature. The total cooling duty is the sum of the three cooling steps

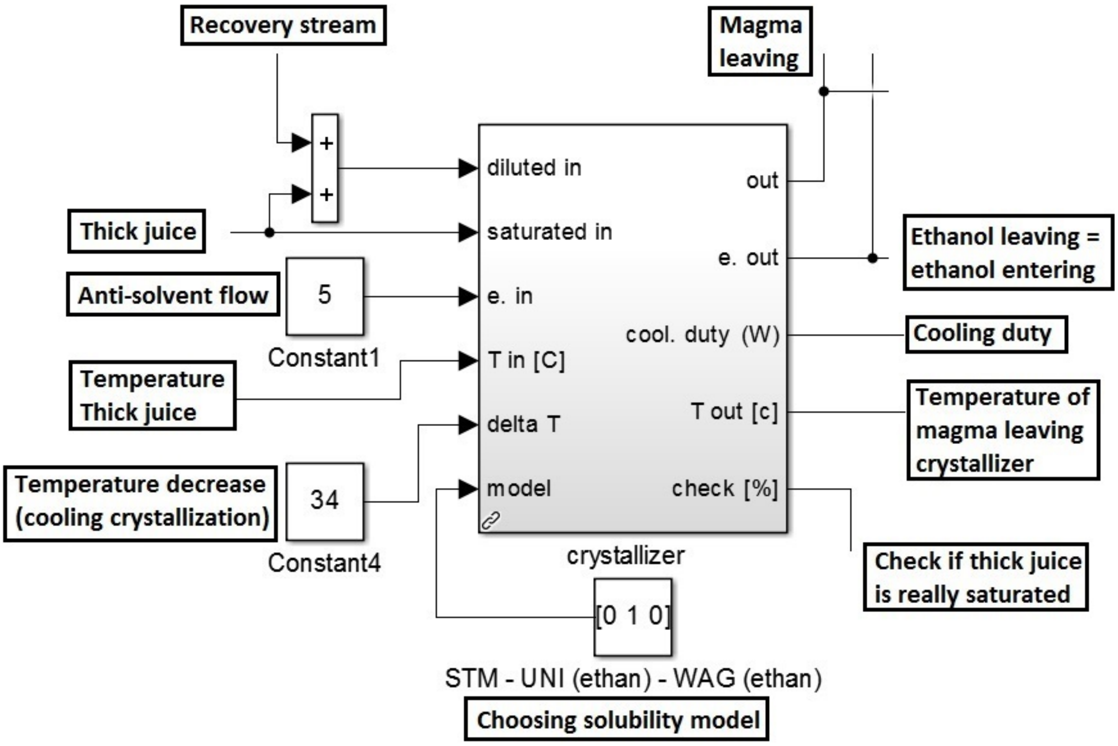


Figure 6.2: The anti-solvent crystallizer model

Figure 6.2 shows the anti-solvent crystallizer model. The bold texts in the boxes indicate what the inputs and outputs represent. The signal lines of the thick juice, recovery stream and the leaving magma include multiple signals (mass flows). The other signal lines only transmit one signal. The possibility is kept to choose one of the other solubility models for the crystallizer. Only the last two (UNI & WAG) support ethanol streams. The first one (STM) uses solubility data from the Sugar Technologists Manual as function of temperature. This model should be used if only cooling crystallization is applied.

Finally there is a built-in check to verify if the thick juice is really saturated before the recovery stream is added. The recovery contains some water (due to the azeotrope of water and ethanol) that dilutes the thick juice, lowering the crystal yield.

6.2.2 Distillation column

The selected method of separation of the ethanol from the solution is distillation. At first the idea was to use Chemcad (Chemstations) as separate model next to the STEM for the distillation, because there was no distillation column available in the STEM library. This however would mean that the outputs of the STEM model and the Chemcad model would have to be iteratively matched. Therefore it was chosen to build a Matlab Simulink library block for the distillation column.

A distillation column consists of multiple equilibrium stages. A single equilibrium stage can only achieve a limited amount of separation [6, p. 157]. With each repeated

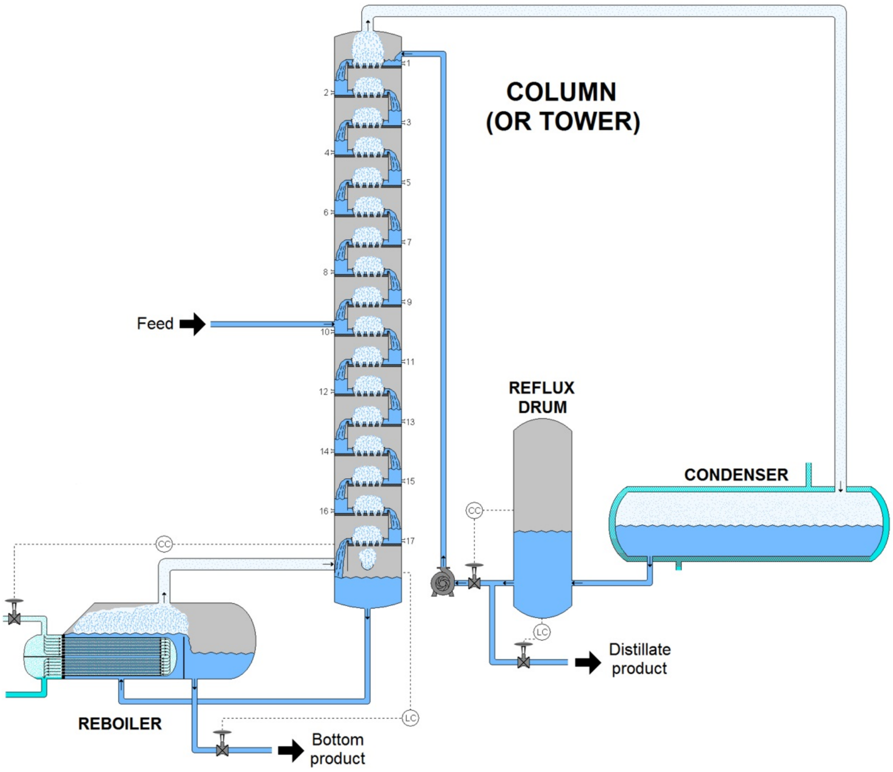


Figure 6.3: Distillation column with reboiler and condenser

condensation and vaporization, a greater degree of separation will be achieved. In practice, the separation to multiple stages is extended by creating a cascade of stages, in the form of trays, as shown in figure 6.3. It is assumed in the cascade that liquid and vapor streams leaving each tray are in equilibrium. Using a cascade of stages in this way allows the more volatile components to be transferred to the vapor phase and the less-volatile components to be transferred to the liquid phase. If each physical tray or plate were 100% efficient, then the number of physical trays needed for a given separation would equal the number of equilibrium stages or theoretical plates. However, that is very seldom the case. Hence, a distillation column needs more plates than the required number of theoretical vaporliquid equilibrium stages.

In the model each tray of the distillation column is balanced individually. For this thermodynamic system, the required equilibrium equations of relevance for the design are summarized using the MESH method [22]. MESH stands for Material balance, Equilibrium, Summation conditions and Heat balance. When using an iterative procedure, the MESH method would result in a complex system of equations for each tray. The mathematical calculation would be very extensive and convergence algorithms would be required. However, this is not the case when using a dynamic approach and a modeling program, like Simulink. The following assumptions for the model are made:

1. Each tray is defined as a thermodynamic system in which the phase equilibrium is reached.

2. No chemical reactions occur.

3. The uptake of liquid drops in the gas phase and the inclusion of gas bubbles in the liquid phase are not considered.

4. The liquid holdup on each tray, the condenser and the reboiler are constant and perfectly mixed.

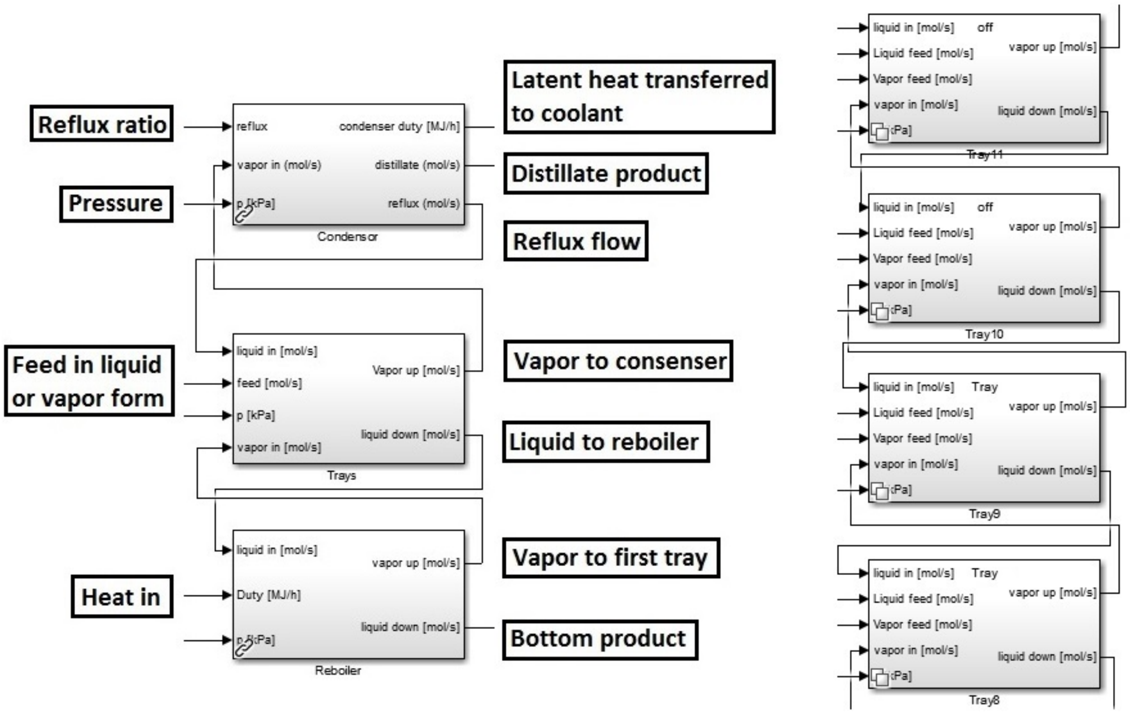


Figure 6.4: Model of the distillation column

Figure 6.4 shows the distillation column model. The column consists of a condenser, a section of trays and the reboiler. The expanded section of trays is also displayed and consists of multiple trays successively connected to each other. The amount of trays, participating in the model, can easily be adjusted by changing a variable in the Matlab input file. The trays that do not participate are still present in the model, but they will only pass the signals unaltered to the following tray. This is indicated by the word ”off”, as displayed in trays 10 and 11 in figure 6.4. The feed point of the distillation can be adjusted by connecting the feed to the appropriate tray. The feed can either be in the vapor or liquid form. Also the pressure in each tray is adjustable, allowing for pressure drops in the column.

The equilibrium between the liquid and the vapor in a tray is calculated in the equilibrium block displayed in figure 6.5. The inputs for the equilibrium calculation are the ethanol and sugar compositions in the liquid (on molar basis) and the pressure in the tray. With the NRTL method it is possible to calculate the ethanol and water concentration in the vapor (in equilibrium with the liquid) and the equilibrium temperature of the tray.

The calculation of the activity coefficients requires the temperature on the tray and the liquid composition. Subsequently the activity coefficients make it possible to calculate the pressure and the ethanol composition in the vapor. This is not the same input and output configuration as the one of the previously described equilibrium block. In order to facilitate the right input-output configuration a feedback controller was implemented.

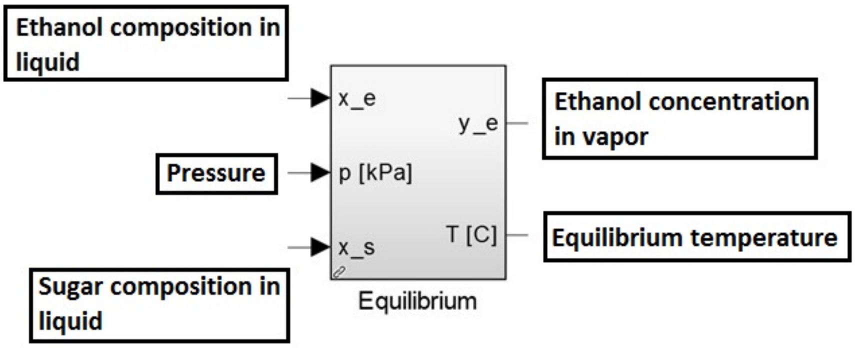


Figure 6.5: Equilibrium block

This is displayed in figure 6.6, one level lower than the equilibrium block.

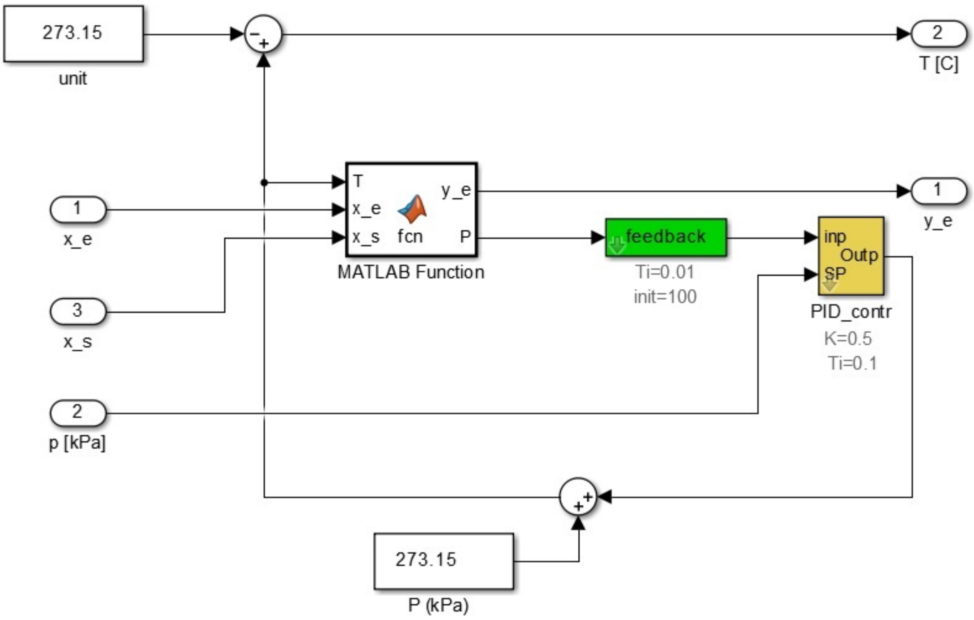


Figure 6.6: Inside equilibrium block

The calculation of the equilibrium temperature and vapor composition proceeds as follows. The calculation starts with an arbitrary temperature and the composition of the liquid in the tray. The Matlab function calculates the activity coefficients, using the NRTL method, and the corresponding pressure. This pressure usually doesn't equal the actual pressure in the tray. A PI controller is used to resolve this problem. The controller controls the pressure by manipulating the temperature. The setpoint for the controller is the predetermined pressure. Once the closed loop system has converged, the equilibrium conditions are known.

In the distillation column a temperature gradient will arise due to the varying liquid composition and the assumption that the vapor and liquid on a tray are in equilibrium. Liquid falling from the overlying tray will have a cooling effect on the lower tray. This is also accounted for in the model. The specific heat of the mixture is calculated and the amount of energy, associated with the cooling effect, is determined. This cooling energy is subtracted from the energy available for evaporating the liquid on the tray. The reflux ratio can be adjusted and is treated the same way as the internal overflow of water from an overlying tray to a lower tray.

The distillation column model was validated using Chemcad (Chemstations). The model was compared with the SCDS column of Chemcad. The SCDS column is one of the rigorous columns that can be used in CHEMCAD. SCDS stands for "Simultaneous Correction Distillation System". It is a very versatile column model that is suited for all rectification processes. When calculating the rigorous SCDS column, a stationary state between liquid-vapour phase or liquid-liquid phase is assumed for each tray [22]. Figure 6.7 shows the distillation column in Chemcad together with the entering and leaving streams. The amount of sugar in the feed stream is set to zero in order to make this model represent the rectifier column. The model is also suitable for a feed stream containing sugar. The same process was modeled with the distillation column in Simulink and the results are displayed in figure 6.8. The stream compositions and other outputs of the two models are very similar, as expected, because the same thermodynamic model and assumptions were used for both models.

An extensive validation was conducted by changing the different equipment parameters and process variables. Parameters and variables like the amount of trays, the feed point position and its composition, the reboiler duty, the reflux ratio and the pressure of the column were considered. Each time the two models were almost in complete agreement with each other.

6.2.3 Centrifuge

The STEM library contains a centrifuge model that separates the sugar crystals from the magma. This centrifuge model consists of three main parts; the flinging part, the substitution part and the rinsing part. The centrifuge model can be used for both batch centrifuges where the different parts actually are different phases in the centrifugation or continuous centrifuges, where different parts really are different locations on the centrifuge. For production of white sugar crystals to the silo usually batch centrifuges are used to prevent fracture or abrasion of the crystals. So here it is probably better to speak of phases. In the flinging part, the mother liquor gets flung until a predetermined dry matter content is reached. A small amount of the crystals leaves the centrifuge together with the syrup. In the new concept an additional stream of ethanol is present in the centrifuge. For the flinging phase this means a simple modification of the dry matter content calculation. In the new situation the ethanol stream is also included in the calculation of the total mass. The filtered crystals continue to the substitution phase. Here a predetermined amount of wash water is sprayed on the crystals to substitute the mother liquor that still adheres to the crystals. The substitution of the mother liquor occurs based on a substitution curve shown in figure 6.9. A Simulink Lookup table, including the curve data, is used to determine the substituted liquor. The input for this Lookup table is the amount of water in the wash water divided by the amount of adhering liquid. The output is a factor indicating the amount of liquor that gets replaced by the wash water. The removed mother liquor is completely replaced by the wash water. For the new concept (with ethanol) it is assumed that the same substitution curve can be used with a modified input to the Lookup table. The difference lies in the additional ethanol in the adhering liquor. It might be possible that the ethanol is easier to expel from the crystals than water, but no data could be found to confirm this. Therefore the assumption was made that the ethanol is similar to water when it comes to expulsion from the crystals.

A small amount of wet sugar remains on the sieve. This sugar is washed away in the rinsing phase of the centrifuge model. The change in the model for the new concept consists of determining the amount of ethanol that remains on the sieve together with the sugar. The amount of ethanol is determined by the ethanol concentration of the sugar. Once the amount of sugar is known the amount of ethanol remaining on the sugar is known.

6.2.4 Mixing

In the process, many process flows eventually get mixed together. In the model the calculation of the resulting temperature happens in the mixing blocks. The mixing blocks contain the temperature dependent specif heats of the involved components. Equation 6.1 shows how the temperature of the final mixture is calculated.

$$\frac{m_1C_1T_1 + m_2C_2T_2}{m_1C_1 + m_2C_2} = T_{out} \tag{6.1}$$

with m the mass flow, C the specific heat and T the temperature. The subscripts indicate the involving component.

This formula does not take into account non ideal mixing effects. This assumption is also used for the additional ethanol stream. For the new concept the specific heat of liquid ethanol is required. These were retrieved from Chemcad (Chemstations) and validated with other sources.

6.3 Applied changes to the model

6.3.1 Evaporation & Mechanical vapor recompression

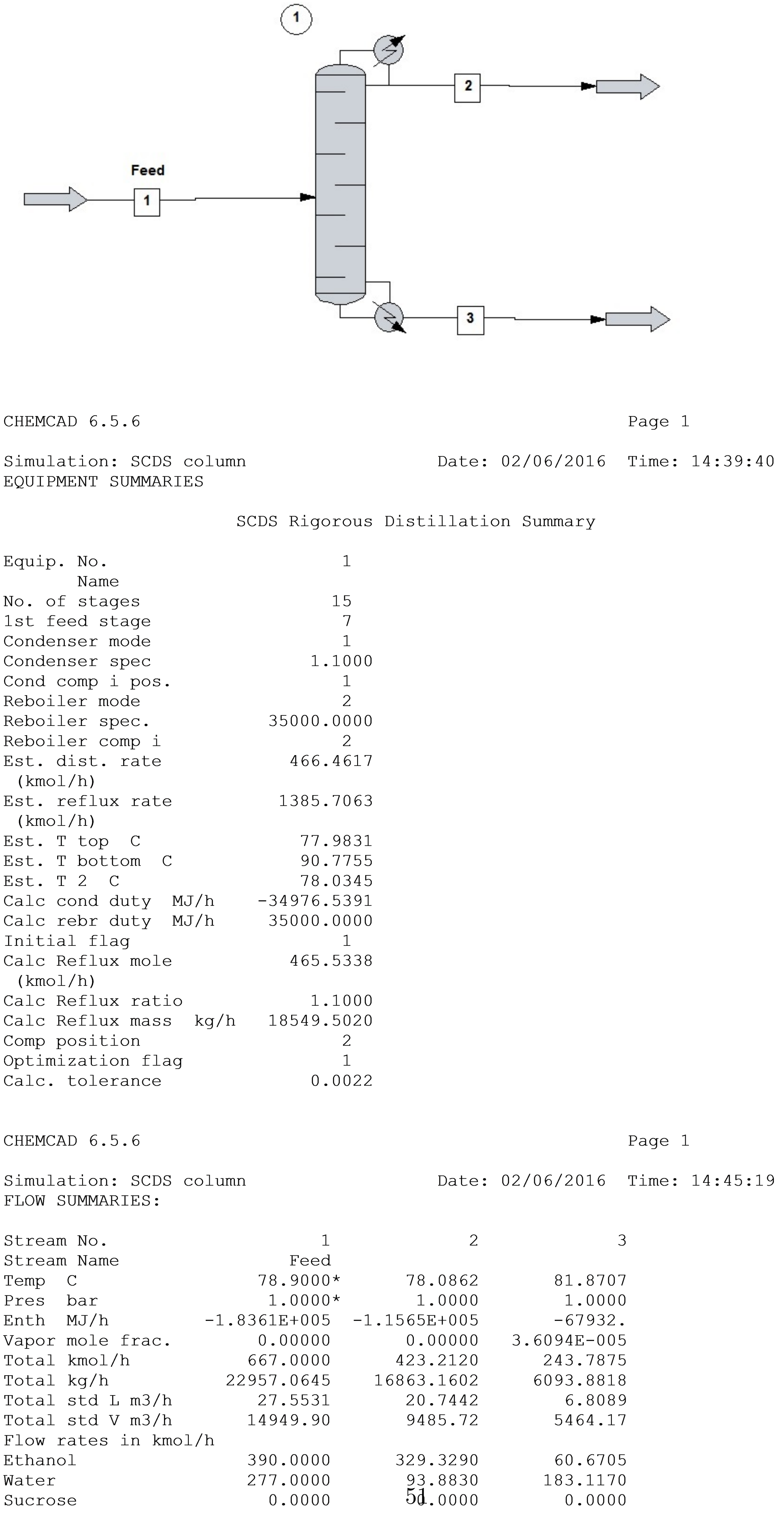
An additional evaporator stage with Mechanical Vapor Recompression (MVR) was added to the modified STEM model in order to achieve a higher dry matter content of the thick juice and to compensate for the reduced steam demand from the crystallization. Both the evaporator block and the MVR block are part of the original STEM library. In the modified STEM model they are connected to each other according to figure 6.10. For the evaporator it is assumed that a falling film plate evaporator is used. The k-value was estimated using a STEM library block to calculate k-values as function of dry matter content, purity and temperature for these type of evaporators.The evaporator surface was sized to have a temperature difference of approximately 7 °C. This to be able to work with fan type compressors.

The amount of evaporated water is chosen in such a way that the condenser losses are minimized. This water vapor enters the MVR block. Here the power, needed for the compressor, is calculated using a polytropic compression equation. The vapor leaving the compressor is superheated. Also the amount of additional vapor resulting from cooling the steam down to the saturation temperature, by water addition, is calculated in this block. The vapor is cooled down to saturation conditions to ensure immediate condensation in the heat exchanger. The model also contains a PI controller. This controller is a fictional one and only exists in the model. The controller changes the temperature of the vapor going to the evaporator and with this the temperature level in the evaporator in order to minimize the excess vapor.

In the current situation the steam coming from the vinasse evaporators is used in the distillation column of the fermentation. In the Cosun concept this is no longer the case since the vapor of the new rectifier column is used. To reduce the amount of vapor needed for the vinasse evaporation a second MVR is applied. The changes to the STEM model are similar to the ones described above.

6.3.2 Electrical energy consumption

Some changes have been made to the way the electrical energy consumption is calculated for the Cosun concept. The previously mentioned MVR's are electrically driven so they are added to the energy consumption. The reduction of the amount of crystallizers also means a decrease in the electrical energy consumption of the sugar house. The decrease is predicted with calculations in a spreadsheet. The spreadsheet is included in the attachments. Here it is assumed that the specific electrical consumption, per ton white sugar, of the current process equals that of the Cosun concept with less crystallizers and additional distillation columns. Because of a lower production capacity of white sugar per hour the electrical energy consumption is reduced with 0.97 MW.



```
CHEMCAD 6.5.6                                              Page 1

Simulation: SCDS column                 Date: 02/06/2016  Time: 14:39:40
EQUIPMENT SUMMARIES

                      SCDS Rigorous Distillation Summary

Equip. No.                       1
       Name
No. of stages                   15
1st feed stage                   7
Condenser mode                   1
Condenser spec              1.1000
Cond comp i pos.                 1
Reboiler mode                    2
Reboiler spec.          35000.0000
Reboiler comp i                  2
Est. dist. rate           466.4617
 (kmol/h)
Est. reflux rate         1385.7063
 (kmol/h)
Est. T top  C              77.9831
Est. T bottom  C           90.7755
Est. T 2  C                78.0345
Calc cond duty  MJ/h   -34976.5391
Calc rebr duty  MJ/h    35000.0000
Initial flag                     1
Calc Reflux mole          465.5338
 (kmol/h)
Calc Reflux ratio           1.1000
Calc Reflux mass  kg/h  18549.5020
Comp position                    2
Optimization flag                1
Calc. tolerance             0.0022


CHEMCAD 6.5.6                                              Page 1

Simulation: SCDS column                 Date: 02/06/2016  Time: 14:45:19
FLOW SUMMARIES:

Stream No.                     1              2              3
Stream Name                 Feed
Temp  C                  78.9000*       78.0862        81.8707
Pres  bar                 1.0000*        1.0000         1.0000
Enth  MJ/h           -1.8361E+005  -1.1565E+005       -67932.
Vapor mole frac.          0.00000        0.00000    3.6094E-005
Total kmol/h             667.0000       423.2120       243.7875
Total kg/h             22957.0645     16863.1602      6093.8818
Total std L m3/h          27.5531        20.7442         6.8089
Total std V m3/h         14949.90        9485.72        5464.17
Flow rates in kmol/h
Ethanol                  390.0000       329.3290        60.6705
Water                    277.0000        93.8830       183.1170
Sucrose                    0.0000         0.0000         0.0000
```

Figure 6.7: The distillation column in Chemcad with flow and equipment summaries.

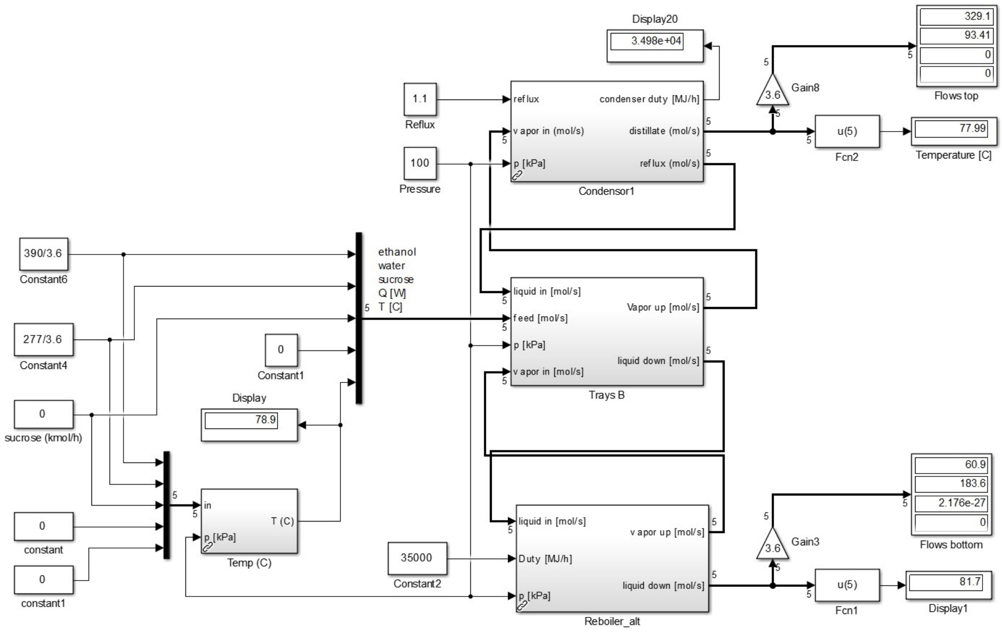


Figure 6.8: The distillation column in Simulink

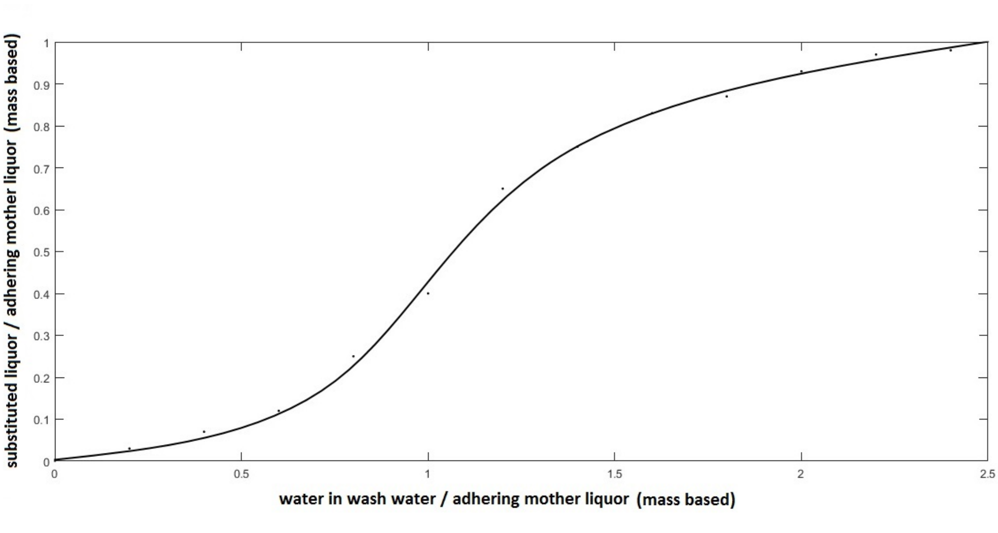


Figure 6.9: The substitution curve

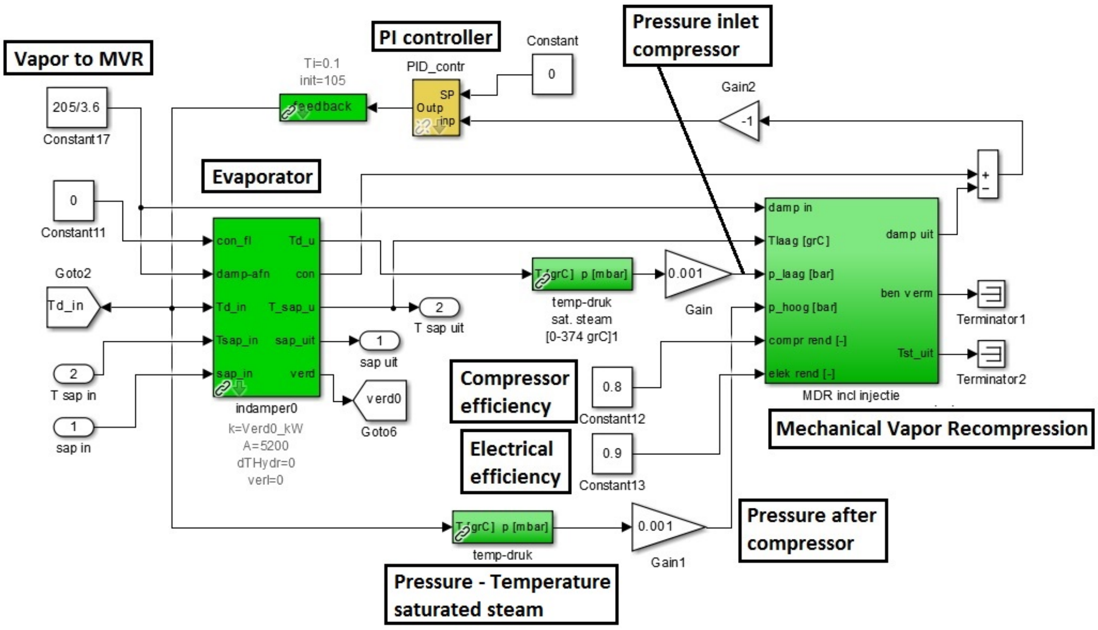


Figure 6.10: Mechanical vapor recompression

Chapter 7

Optimization

7.1 Distillation

In order to determine the most efficient feed point position of the stripping tower the modified STEM model was used. This was done by varying the feed point and minimizing the amount of ethanol leaving the bottom of the column by adjusting the amount of power supplied. The power is supplied in the form of vapor coming from evaporator 3. The vapor is directly injected at the bottom of the column. This way water is added to the product stream, reducing the boiling point elevation. The main aim for the stripper column is to separate the sugar without losing ethanol. All the ethanol should be present in the distillate and all the sugar should leave the column at the bottom together with some water. It became clear that the most efficient feed point is at the top of the column, as expected. Also the amount of stages was determined using the modified STEM model. Increasing the amount of stages increases the efficiency of separation and reduces the amount of energy needed. However, the separation effect per added stage decreases and at a certain amount of added stages the separation does not improve. Adding more stages is futile. For the Cosun concept the amount of theoretical stages was found to be 10. Adding a reflux to the column results is a less efficient separation, therefor no reflux is needed.

The vapor leaving the top of the column is directed towards the rectifier column. In the rectifier column the water and ethanol are separated up to a certain purity. The reboiler is fed by vapor coming from evaporator 5. This vapor has a lower temperature than the vapor used for the stripping column. The reason for this is that the rectifier column does not contain any sugar, so no boiling point elevation occurs, and the ratio ethanol/water is different compared to the stripping column. A temperature of around 100 °C (boiling point water) is sufficient. The vapor is kept separate from the product in order to avoid dilutions and to maximize the separation efficiency.

It is desired that the rectifier column separates the ethanol to a purity (mass based) of around 90 % or higher with a minimum amount of energy supplied. Allowing for too much water in the ethanol would lead to lower crystallization yields increasing again the amount of ethanol or cooling required. The amount of energy required for water/ethanol separation should be preferably lower than the energy demand in the bioethanol. The same procedure, used to determine the configuration of the stripping column, was also applied to determine the configuration of the rectifying column. After an extensive analysis it became clear that the optimal feed point is the bottom tray.

Increasing the purity of the ethanol, leaving the top of the column, can be done by increasing the reflux ratio or the amount of trays. Increasing the amount of trays means increased equipment costs and increasing the reflux ratio results in a higher energy demand during production. The modified STEM model was used to determine how many trays should be applied to reduce the energy demand and still have a significant separation effect on all the trays. It turned out that roughly 20 theoretical trays is sufficient for the rectifier column. More trays will not increase the separation efficiency and will lead to higher equipment costs.

7.2 Ratio cooling/anti-solvent crystallization

As already mentioned in chapter 5 crystallizing with only anti-solvent (ethanol) is not feasible because the crystal yield is simply not high enough. Additional cooling crystallization is considered in this study. Working with two crystallization principles introduces an additional variable that can be changed in order to optimize the process. In order to determine the most energy reducing configuration several ethanol mass flows were imposed and the cooling effect was adjusted in order to get a sufficient crystal yield and low condenser losses. It turned out that the more ethanol was used the higher the energy demand turned out to be. The energy consumption for cooling the crystallizer is very low compared to the energy consumption associated with the ethanol flow. In the final comparison two Cosun Concepts were chosen with ethanol flows that allow for high enough purities of the separated ethanol, the right crystal yield and a realistic temperature drop over the crystallizer allowing for convenient separation in the centrifuges. The process flow diagrams corresponding to the different ratio's are included in the attachments. The crystallizer in Cosun Concept 1 is fed with 5 kg/s ethanol and is cooled down 35.5 degrees. This concept has a significant condenser loss, required to have a high enough purity of the separated ethanol. The Cosun Concept 2 crystallizer is fed with 4 kg/s ethanol and cooled down 40.3 degrees. This concept has zero condenser loss in the sugar house and roughly the same purity of the ethanol.

After the optimization of the ratio cooling/anti-solvent addition it turned out that the cooling water, leaving the crystallizer, is not heated enough to deploy it elsewhere in the sugar/bioethanol plant. The preheating of the process flows in the plant is already achieved by other means or require higher temperatures. Therefor the associated energy of the cooling water should be considered as lost to the environment.

Chapter 8

Results

8.1 Capacities

In order to determine the energy savings a comparison is made between several cases. First a Reference Case is defined. The Reference Case represents the current process with predetermined production capacities. The Cosun concepts represent the new process based on anti-solvent crystallization, for different ratio's of cooling and anti-solvent addition, with the same amount of extracted sugar processed and with similar production capacities.

Reference Case	Beet campaign	Thick Juice campaign	Bioethanol campaign
Campaign length [days]	130	31	169
Beet processing (paid beet) per day [t/d]	12000	0	0
Cosettes processing [t/d]	12526	0	0
Bioethanol production [m3/d]	220.00	220.00	220.00
Sugar to bioethanol [t/d]	360.66	360.66	360.66
Sugar production [t/d]	900.00	900.00	0
Sugar in molasses [t/d]	76.88	62.60	0

Table 8.1: Production capacities Reference Case

Table 8.1 shows the capacities of the Reference Case. There are three campaigns distinguished in the table. Bioethanol is produced during 330 days a year. What is noted in the table as bio-ethanol campaign is the period in which during the reference period only bioethanol is produced. During the beet campaign the beets are processed and sugar, molasses and bioethanol are produced. During the beet campaign not all of the produced thick juice is processed, but some of it is stored in thick juice tanks for later processing to either bioethanol or white sugar in the thick juice campaign. In the thick juice campaign the stored thick juice is processed and sugar, molasses and bioethanol are produced.

The capacities of the Cosun Concepts are shown in table 8.2. For these cases there are only two campaigns distinguished. The Thick Juice campaign is considerably longer compared to the one of the Reference Case. Since all the bioethanol is produced during either the beet campaign or thick juice campaign the separate bioethanol campaign is redundant.

In both cases the amount of sugar processed is equal, but the production of sugar crystals in the new concept is considerably higher than that of the Reference Case. This has to do with the fact that the Reference Case also produces molasses. Molasses is

Cosun Concepts	Beet campaign	Thick Juice campaign
Campaign length [days]	130	200
Beet processing (paid beet) per day [t/d]	12000	0
Cosettes processing [t/d]	12526	0
Bioethanol production [m3/d]	220.00	220.00
Sugar to bioethanol [t/d]	360.66	360.66
Sugar production [t/d]	463.20	463.85
Sugar to pellets [t/d]	15.13	0

Table 8.2: Production capacities Cosun Concept

considered a valuable by-product and the sugar in molasses generally has a more or less comparable value as industrial white sugar. Therefore the comparison is valid. The filtrate (A-syrup) of the Cosun Concepts is used as substrate for the bioethanol plant and is not sold on the market.

8.2 Energy consumption

To determine the energy consumption of the different cases the required data was extracted from the process flow diagrams, generated with Simulink and Microsoft Visio. For the Reference Case only a beet campaign model exist. So it is not possible to generate process flow diagrams of the other two campaigns of the reference case. For the thick juice campaign of the reference case the energy consumption was calculated with specific energy consumption data of a typical thick juice campaign, provided by Royal Cosun. For the bioethanol campaign a more comprehensive calculation was needed, based on data provided by the beet campaign model. The calculations, with detailed explanation, are included in the attachments together with the process flows generated with the computer models. The Cosun Concept has Simulink models for both campaigns, so no additional calculations are needed. The energy consumption of the Reference Case is displayed in table 8.3.

Reference Case	Beet campaign	Thick Juice campaign	Bioethanol campaign
Natural gas to boilers [Nm3/hr]	8990.80	3907.20	1853.40
Electricity production [MW]	16.60	4.31	3.70
Electricity consumption [MW]	13.30	1.88	1.30
Export Electricity [MW]	3.30	2.44	2.40
Energy consumption total [MW]	88.60	37.50	16.50
Energy consumption total [MWh]	276,432	27,900	66,924

Table 8.3: Energy consumption Reference Case

The total energy consumption is based on the summation of the electrical energy and the energy associated with the gas consumption. For a whole year the total energy consumption of the Reference Case comes down to 371,256 MWh.

Cosun Concept 1	Beet campaign	Thick Juice campaign
Natural gas to boilers [Nm3/hr]	5190.20	3093.00
Electricity production [MW]	8.50	6.20
Electricity consumption [MW]	18.60	5.90
Export Electricity [MW]	-10.10	0.30
Energy consumption total [MW]	63.17	31.33
Energy consumption total [MWh]	197,090	150,384

Table 8.4: Energy consumption Cosun Concept 1

During all the campaigns of the Reference Case more electricity is produced than consumed, resulting in a year round export of electricity. For Cosun Concept 1 this is clearly not the case as can be be seen in table 8.4. During the beet campaign a lot of electrical energy has to be imported due to the decrease of electricity generation, caused by the reduced steam production, and the increase of electricity consumption, caused by the mechanical vapor recompression evaporators. However, the total energy consumption in lower than that of the Reference Case beet campaign and comes down to 347,474 MWh. The results for Cosun Concept 2 are displayed in table 8.5. For a whole year the total energy consumption of Cosun Concept 2 comes down to 333,130 MWh. This is a lower energy consumption compared to Cosun Concept 1. This was expected, as already mentioned in chapter "Optimization", due to the shift towards cooling crystallization.

Cosun Concept 2	Beet campaign	Thick Juice campaign
Natural gas to boilers [Nm3/hr]	5,083.90	2,799.30
Electricity production [MW]	8.30	5.60
Electricity consumption [MW]	18.60	5.90
Export Electricity [MW]	-10.30	-0.30
Energy consumption total [MW]	62.28	28.92
Energy consumption total [MWh]	194,314	138,816

Table 8.5: Energy consumption Cosun Concept 2

8.3 Costs

8.3.1 Energy costs

The energy costs of the 3 concepts are displayed in table 8.6. These numbers are based on the cost calculations included in the attachments. It turns out that both Cosun Concepts are more expensive in energy costs than the Reference Case. The energy consumption is lower, but a part of the energy consumption has shifted from natural gas to electricity. Also the amount of generated electricity has reduced compared to the Reference Case. These two factors result in a costly electricity import and a more expensive process.

	Beet campaign	Thick Juice campaign	Bioethanol campaign	Total
Reference Case	8,498,389	795,850	1,811,270.61	11,105,509
Cosun Concept 1	7,282,329	4,433,212	0	11,715,541
Cosun Concept 2	7,217,746	4,245,166	0	11,462,911

Table 8.6: Energy costs

8.3.2 Equipment costs

Not only the energy costs are considered, but also the equipment costs that are coupled with the new process. The new equipment consists of:

1. A new crystallizer, allowing for cooling and anti-solvent crystallization.
2. Two distillation columns.
3. Four heat exchangers for the beet campaign.
4. Two additional heat exchangers for the thick juice campaign.
5. Two compressors for mechanical vapor recompression.
6. One falling film evaporator.

So far there has been no mentioning of the type of crystallizer to be used in the Cosun Concept. The energy analysis does not require the choice of the type of crystallizer, because the choice does not influence the outcome. For the cost estimation however it is relevant to know what kind of crystallizer could be used. Since anti-solvent crystallization is a new technique for the production of sugar this equipment would have to be newly designed for this purpose. Historically batch crystallizers have been mainly used in the sugar industry. However, last decades more and more continuous crystallizers are used for the production of sugar. They allow for more specific heating area, lower liquid volumes over the heating chamber and more continuous operation. Continuous processes are favored in the process industry, because of higher and consistent product quality, reduced manufacturing cost and reduced waste flows. For this reason also for the Cosun Concept a continuous crystallizer is chosen in the cost estimation. The costs of the crystallizer are estimated by summarizing the prices offered in a budget-quotation of a comparable crystallizer. The crystallizer in the budget-quotation has a volume of 224 m^3 resulting in a residence time for the Reference Case of 2.5 hours. The residence time of the crystallizer in the Cosun Concept is estimated to be twice the residence time of the traditional process. However the production capacity of white sugar is halved compared to the reference case. This means that the volume of new crystallizer is roughly the same as the one in the budget-quotation. The total costs of the crystallizer, excluding installation, comes down to 1.5 million euro.

The costs of the heat exchangers are estimated with the "DACE Price Booklet" [23]. For heat exchangers this booklet provides the costs as function of the surface area, material and type of heat exchanger. Table 8.7 provides the specifications of the heat exchangers and the associated costs. Heat exchanger VKS WT 2 is a tube heat exchanger, because the product flow has a fouling tendency. The other heat exchangers are all plate heat exchangers. The area's of the heat exchangers are taken from the modified STEM model. These area's were chosen, together with typical heat transfer coefficients based on experience, in order to facilitate a sufficient heat exchange. Table 8.8 shows the specifications of the heat exchangers and the associated costs for the additional heat exchangers needed for the thick juice campaign.

Name	Type	Material	Area [m^2]	Price [Euro]
VKS WT 2	Tube	AISI316	800	280,000
HEX MASH	Plate	AISI316	340	100,000
HEX COND	Plate	AISI 316	40	23,000
HEX STRIP	Plate	AISI 316	250	59,500

Table 8.7: Equipment costs additional heat exchangers for beet campaign

Name	Type	Material	Area [m^2]	Price [Euro]
HEX SYR	Plate	AISI 316	310	70,000
HEX REG	Plate	AISI 316	92	32,000

Table 8.8: Equipment costs additional heat exchangers for thick juice campaign

According to the "DACE Price Booklet" [23] the cost of a distillation column is a function of the average wall thickness, the diameter and the material of the column. The average wall thickness was estimated with available data of existing distillation columns for the purification of ethanol in the bioethanol plant. The estimated wall thickness of the stripping column is 10 mm and the wall thickness of the rectifying column 14 mm. For the material of the columns AISI 304 was chosen, equal to the material of the existing columns of the bioethanol plant. The diameter of the columns were calculated using correlations provided by the book "Separation Process Principles" [24, p. 225]. The calculations are included in the attachments. The required data was either extracted from the modified STEM model or from other sources, clearly indicated at the calculations. The estimated diameter of the rectifying column turns out to be a little more than 2 meters and the diameter of the stripping column close to 1,5 meters. According to the "DACE Price Booklet" [23] the cost for the rectifier column, without internals, with a diameter of 2,5 meters, a wall thickness of 14 mm and made of AISI 304 would come down to 534,000 euro. For the stripping column, with a diameter of 1,5 meters, a wall thickness of 10 mm and made out of AISI 304 this comes down to 286,000 euro. These prices do not include the sieve trays of the distillation column. The total cost of the sieve trays is a function of the diameter of the trays and the total surface area. The amount of theoretical trays were determined in the chapter "Optimization". The tray efficiency was estimated to be 60% for the stripping column and 70% for the rectifying column. These estimations are based on the configuration of the existing distillation columns of the bioethanol plant at Anklam and literature [25]. The amount of actual trays for the stripping column comes down to 17 and for the rectifying column to 29. The costs for the internals are estimated to be 16,080 euro for the stripping column and 67,237 euro for the rectifying column. The total estimated costs for the distillation columns comes down to 903,317 euro.

The costs of the compressors, needed for the mechanical vapor recompression, were again estimated with budget-quotations. The compressor for the vinasse evaporation is a 3-staged fan. The budget price for a 3-staged fan with a capacity of 10 t/h equals 420,000 euro. The compressor of the Cosun Concept has a capacity of 21 t/h. The price of this compressor is estimated by scaling the budget price with the power law [6, p. 17], using a cost exponent of 0.5. The costs for the compressor turn out to be 609,000 euro. The compressor for the thin juice evaporation has a lower temperature difference (7 degrees), resulting in a lower specific price. A know price for a 5 t/h compressor is 100,000 euro. The compressor of the Cosun Concept has a capacity of 205 t/h. Again the power law was used, using a cost exponent of 0.5. The cost price for this compressor tuns out to be 640,000 euro.

The last equipment is the falling film evaporator. This evaporator has an area of 5200 m^2. A design cost price, provided by Royal Cosun, is 500 euro per square meter. With this design cost price the price for the evaporator becomes 2.6 million euro. This price includes the installation costs.

Equipment	Cost excluding installation [euro]	Cost including installation [euro]
Crystallizer	1,500,000	4,500,000 (3x)
Distillation columns	903,317	1,806,634 (2x)
Heat exchangers	561,500	1,123,000 (2x)
Compressors	1,249,000	2,498,000 (2x)
Evaporator	-	2,600,000
Total	-	12,528,000

Table 8.9: Total equipment costs

The total equipment costs are displayed in table 8.9. The costs in the left column are the first very rough estimates of the total equipment costs. These costs do not cover all the installation costs like piping material, instrumentation, automation, civil and building costs etc. Common practice is to multiply the equipment costs by 2 or 3 in order to get the total installation cost. These costs are also presented in table 8.9.

Chapter 9

Discussion

In chapter 4 some uncertainties were presented that normally arise when confronted with the principle of anti-solvent crystallization. With this study only a few of the uncertainties can be eliminated.

The stability, the handling and safety of the anti-solvent were briefly discussed in chapter 5. The Anti-solvent turns out to be flammable and explosive vapor mixtures can easily emerge. The prevention of explosions consists of working with closed systems and explosion-proof electrical equipment. This means that the investment costs increase due to the properties of the anti-solvent.

The possible regeneration of the anti-solvent and how the anti-solvent influences the solubility of the dissolved sugar has thoroughly been discussed in this report. Models were created to predict the energy consumption linked to the separation of the anti-solvent and several solubility models were examined to predict the influence of the anti-solvent.

The study answers the question what investments need to be done and what the operating costs are. How much energy that can actually be saved. It turns out that energy can be saved, but the reduction is not enough to compensate for the investments. In the Cosun Concept the natural gas consumption is partly compensated by electricity. If another concept would be thought out, that limits the shift to electricity, the concept could become cost effective regarding the operating costs. However, the investments would still tackle the concept.

The crystallization kinetics and the quality of the food product was not examined in this study. The research approach was to first examine the feasibility of anti-solvent crystallization in regard of the energy consumption and operating costs. The crystallization kinetics and the quality would be examined in a successive study when the first study would provide promising results.

Chapter 10

Conclusion

During this study the feasibility of anti-solvent crystallization was investigated. Based on the created models it turns out that the Cosun Concept, without evaporative crystallizers, is possible. The desired amount of sugar beets can be processed and the crystal yield is high enough. Also the energy consumption is slightly reduced. However, this concept is not cost effective. The combination of reduced steam production, causing less electricity generation, and a higher electricity consumption results is a more expensive process.

The results of this study are less promising than the initial estimates made by Royal Cosun. This has to do with the fact that more ethanol is needed to create a high enough crystal yield than previously thought. Also the electricity consumption turns out to be higher than expected, due to the implementation of the compressors to facilitate an efficient thickening of the thin juice and vinasses.

It turns out that unavoidable heat losses remain and that energy is lost to the environment. For example the energy delivered by the crystallizer to the cooling water (1.8 MW) can not be deployed in the process, because there is simply no need for it or the temperature of the cooling water is too low. Also the A-syrup that is used as substrate for the fermentation has a high temperature (117 °C), but the associated energy cannot be deployed usefully.

The last cause why the Cosun Concept is less promising has to do with the fact that more water is sent to the fermentation resulting in a more energy consuming thickening of the vinasses by the recompression evaporators.

Throughout the study the principle of cooling crystallization revealed itself as a potential energy saving concept. The Cosun Concept already heavily relies on this principle and the optimization of the concept turned out positive for this principle. This study gives rise to a follow-up study to determine if cooling crystallization could provide better results.

Bibliography

[1] Ruben C. Kolfschoten, Folpert Douma, Johan P.M. Sanders, Arnoud Togtema, Marieke E, Bruins, *Development of a new method for sugar crystallisation.* Wageningen UR, Wageningen, 2013.

[2] Harald Oosterhof, *Antisolvent crystallization of Sodium Carbonate.* Universal Press Science Publishers, Veenendaal, 1999.

[3] Martine Decloux, Frederique Labatut, Michael Saska and Mary An Godshall, *Effect of ethanol on sucrose solubility and molasses exhaustion.* International Sugar Journal, Vol. 103, 2001.

[4] E. R. Asquieri, E. M. de Assis and G.E. Serra, *Refining of crystal sugar with ethanol.* Alimentaria, Enero-Febrero, Madrid Vol. 38, 2002.

[5] Marco Giulietti and Andre Bernardo, *Crystallization by Antisolvent Addition and Cooling.* Chemical Engineering Department Federal University of So Carlos UFSCar, Brasil.

[6] Robin Smith, *Chemical Process Design and Integration.* John Wiley & Sons, West Sussex, 1nd Edition, 2005.

[7] Albert M. Schwartz and Allan S. Myerson, *Handbook of Industrial Crystallization.* Butterworth-Heinemann, Boston, 2nd Edition, 2001.

[8] Wayne Genck, *Make The Most of Antisolvent Crystallization.* Genck International, Nov 08, 2010.

[9] *Inside a sugar factory (presentation).* British Sugar, 2010.

[10] Ruben C. Kolfschoten, Marieke E. Bruins and Johan P.M. Sanders, *Opportunities for small-scale biorefinery for production of sugar and ethanol in the Netherlands.* John Wiley & Sons, 2014.

[11] R.L. Earle with M.D. Earle, *Unit Operations in Food Processing, Web Edition.* The New Zealand Institute of Food Science & Technology (Inc.), 2004.

[12] *Cursus suikertechnologie CSM - RT.* CSM Suiker BV & Tiense Suikerraffinaderij NV, 1987.

[13] *Evaporation Technology using Mechanical Vapour Recompression (Brochure).* GEA Wiegand GmbH, Ettlingen (Germany), no date.

[14] H. Schiwek & A. Kolber, *Zur Frage der optimalen Ausbilding der Zuckerkruste bei Krustenpralinen.* Susswaren 8, 1975.

[15] Antonio M. Peres, Eugenia A. Macedo, *Phase equilibria of D-glucose and sucrose in mixed solvent mixtures: Comparison of UNIQUAC -based models.* Laboratory of Separation and Reaction Engineering, Porto, 1997.

[16] Andreanne Bouchard, Gerard W. Hofland, Geert-Jan Witkamp, *Properties of Sugar, Polyol and Polysaccharide Water-Ethanol Solutions.* Process Equipment, Delft University of technology, Delft, 2007.

[17] Z. Bubnik, P. Kadlec, D. Urban, M. Bruhns, *Sugar Technologists Manual: Chemical and Physical Data for Sugar Manufacturers and Users.* Bartens, Berlin, 1995.

[18] Wilfried Cordes, *Some Mixture Properties of Ethanol and Water: Vapor-liquid equilibrium of the mixture of Ethanol and Water.* Dortmund Data Bank, 2008.

[19] Boris Zhmud, Ph.D., Assoc.Prof., MRSC, *Viscosity Blending Equations.* Sveacon Consulting (Lube Magazine), Stockholm, 2014.

[20] J. A. LARKIN, *Thermodynamic properties of aqueous non-electrolyte mixtures I. Excess enthalpy for water + ethanol at 298.15 to 383.15 K.* Division of Chemical Standards, National Physical Laboratory, Teddington, U.K., 1974.

[21] Chemiekaarten, *Chemiekaarten, Gegevens voor veilig werken met chemicaliën.* Sdu Uitgevers, Den Haag 30th Edition, 2014.

[22] Lisa Weise, *Rigorous column simulation - SCDS (Tutorial).* Chemstations Europe GmbH

[23] DACE Cost and Value, The Dutch Network and Knowledge Center for Cost Engineering and Value Management, *DACE Price Booklet.* Helene Hartlief, Nijkerk, 31th Edition, November 2015.

[24] J. D. Seader, Ernest J. Henley, D. Keith Roper, *SEPARATION PROCESS PRINCIPLES, Chemical and Biochemical Operations.* John Wiley & Sons, Inc., 3th Edition, 2011.

[25] Daniel R. Summers, P.E., *RECTIFIER DESIGN FOR FUEL ETHANOL PLANTS.* Sulzer Chemtech USA, Inc., San Francisco, November 2006.

Attachments

1. Energy and Costs calculation

2. Reduction energy costs calculation

3. Reference Case PFD

4. Beet campaign Cosun Concept 1 PFD

5. Beet campaign Cosun Concept 2 PFD

6. Thick Juice campaign Cosun Concept 1 PFD

7. Thick Juice campaign Cosun Concept 2 PFD

8. Equilibrium calculation column STEM

9. Phase equilibria of D-glucose and sucrose in mixed solvent mixtures - Comparison of UNIQUAC models

10. Calculation Columns

11. Chemiekaarten - ethanol