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EVAPORATIVE CRYSTALLISATION

DISCUSSION ON BATCH AND CONTINUOUS BOILING TECHNIQUES

by

J. C. de C. THELWALL

Fletcher Smith Ltd
Derby - DE1 1NU, England

BATCH and CONTINUOUS BOILING TECHNIQUES

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Introduction

In order to optimise the performance of any piece of process equipment, it is important to understand the process objectives and the fundamental principles. The purpose of this paper is to compare some of the difference in the boiling techniques used for both batch and continuous boiling of vacuum pans.

Theoretical considerations

The Noyes and Whitney's[1] formula below for crystallisation is used to review the basic control parameters of the crystallisation process.

Rate of Mass (Sugar) deposited $$\frac{dm}{dt} = Kd \times A \times Cs \times (S.S. - 1)$$

Kd = Diffusion Coefficient of the mother liquor.

A = Total surface area of the crystal.

Cs = Mother liquor concentration at saturation point. (Ratio of the weights of sucrose/water)

S.S. = Degree of Supersaturation.

The diffusion coefficient Kd is directly affected by liquor temperature, the purity of the mother liquor and its viscosity, the nature of the impurities in the mother liquor, and the degree of agitation at the crystal surface. If we now look at this formula, the rate at which sugar is deposited will increase with any increase in the surface area available, the mother liquor's saturated sucrose concentration Cs, an the supersaturation of the mother liquor.

Of these factors, the most significant for the operator is supersaturation, and this can be considered as the driving force for crystallisation. From the formula it is apparent that the higher the supersaturation, the greater is the crystal deposit rate, but excessive supersaturation does have three potential dangers:-

i. False grain may be created, if the supersaturation rises into the metastable zone.

ii. There is a potential to form conglomerate type crystals in high purity massecuites during the early stages of the boiling.

iii. With continuous pans, the encrustation rate will increase, which can be a problem when handling higher purity massecuites.

A final very important parameter, which is hidden in the Kd value of the formula, is the mother liquor viscosity, this viscosity has an appreciable effect on both the crystallisation rate and the pan circulation. The increasing mother liquor viscosity has a very significant effect in slowing the whole process down during the cooling crystallisation stage.

Crystal Content

A very important factor, which is not expressed by the Noyes and Whitney's formula, is that of the crystal content of the massecuite. To appreciate the effect of crystal content in the boiling process, consider two crystals separated by a distance 2 λ shown in the top illustration of figure 1, and the local boundary layers around the crystal surface, in the illustration below.

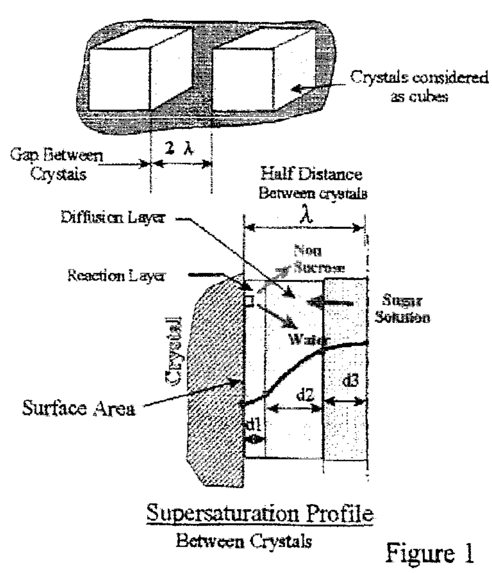


Figure 1

The first boundary layer, the reaction layer d_1, at the crystal surface, has the least supersaturation, as sugar had been removed from the solution and deposited on the crystal. The second boundary layer is the main diffusion layer d_2, here there are two different flows in opposite directions. The one is non-sucrose material and water from the exhausted reaction layer moving away from the surface and back to the main body. The other flow is fresh mother liquor, which is moving towards the crystal. The thickness of these two layers will not vary greatly, during the boiling cycle for a constant agitation. However, the viscosity of the mother liquor does have an important influence on the crystallisation rate, especially in the second boundary layer, as the higher viscosities will reduce the speed of the molecular movement to and from the crystal surfaces.

The third and final layer d_3, is the main body of the mother liquor and is the source of the sucrose for further deposition.

If we increase the crystal content, the gap between the crystals will decrease, reducing the volume of the mother liquor present. There will come a point where the increase overall crystal surface area and the reduced volume of mother liquor per unit volume of massecuite will start to have a major influence on the overall supersaturation. This is because there is now insufficient sugar available in the third boundary layer, to match the sugar deposit rate, forcing the supersaturation to drop until it reaches an equilibrium value.

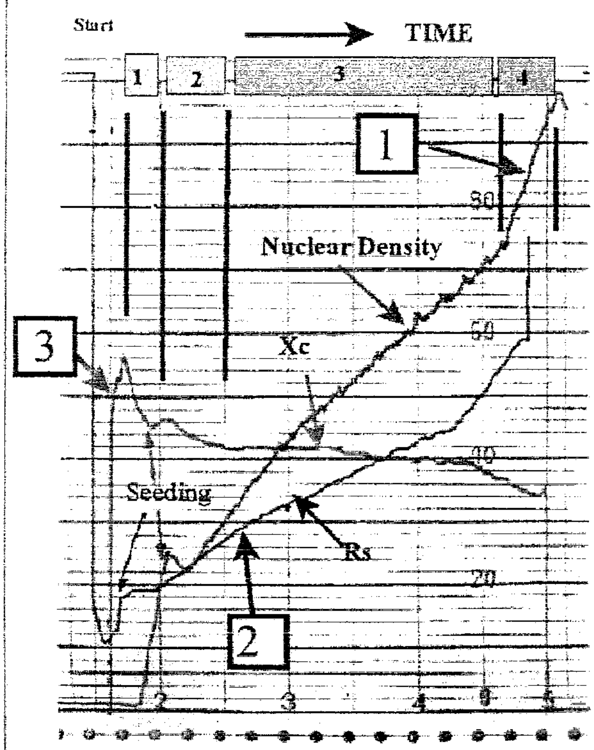
In order to appreciate the effect of the minimum safe crystal content, a number of authors have expressed this critical factor in different ways. Kelly[2] expresses this as the point at which false grain is unlikely to be formed and gives a relationship based on the surface area of crystals per unit weight of mother liquor and mother liquor purity. Genie[3] considered the sugar crystal as simple cubes of the same volume as shown in figure 1, and calculated the half distance, λ, between two cubes when evenly distributed. He proposes a value for λ of 0.1mm or less for the pan to be easy to control, while at 0.2mm it is very difficult. While Chien-Jan Lu[4] gives a limiting ratio of crystal to syrup volumes of 0.143, or the volume of crystal must be maintained above one seventh of the mother liquor. An excessively high crystal content can also reduce the boiling rate, due to the increasing massecuite viscosity, and also the reduction in amount sugar available in the mother liquor. In practice, the maximum crystal content of the massecuite is a compromise between a high crystal content and good circulation.

Supersaturation is a result of the removal of water from the mother liquor, and is affected by the evaporation rate. If the evaporation rate is increased and the massecuite crystal content is maintained, then the supersaturation will rise to find a new equilibrium point.

Batch Pan Operation

Consider now a batch pan boiling cycle for a high purity massecuite. Figure 2. below, shows recorded chart readings for three massecuite sensors boiling a beet white product pan. The chart travels in time from left to right, and records readings from three massecuite sensor signals during one cycle in the process. (Note that the traces are slightly displaced in time so as to allow for pen movement).

The No. 1 (blue) trace is the control signal from a "nuclear density probe", which follows the massecuite density. The other two monitoring signals, Rs, trace 2 and Xc trace 3, are from a Fletcher Smith Duotrac Radio Frequency probe. The black 'Rs' trace 2 is the series resistance signal, and follows a similar pattern to the nuclear density value. The red 'Xc' trace 3 is a capacitance signal[5], and tends to follow the mother liquor brix, but its reading is shown inverted on the chart (i.e. the higher the brix the lower is its numerical value).



Massecuite signals for Batch Pan Boiling Beet WS

Nuclear Density Signal Controlling Signal **Figure 2**

The actual boiling cycle can be subdivided into 4 separate stages, neglecting the filling and discharging of the pan.

1. <u>Concentrating and Seeding</u>

   Steam is fed to the calandria to commence water evaporation, raising the sugar concentration in the pan. This can be seen on all three charts by a rapid change in readings, indicating a rapid rise of syrup brix. The capacitance signal Xc, which has an inverted value on the chart, shows a drop in numerical value. At a predetermined syrup supersaturation value, the pan is seeded with a fixed quantity of very fine crystals. This point is shown on all three traces by an arrow.

2. <u>Establishing Grain</u>

   This next stage is the most critical and difficult part of the whole boiling cycle, because of the very high evaporation rate and low crystal content. To control any excessive rise in mother liquor supersaturation, a drink of water has been given to this pan, and this can be seen by a change in direction on all three traces in the early part of stage two.

The mother liquor supersaturation has now reduced and only gradually rises, best seen in the capacitance curve 3, while the crystal content increases steadily, seen by the increase in density in curve 1.

Excellent circulation is essential during this early phase so as to ensure an even distribution of crystals and a uniform supersaturation throughout the pan.

3. Main Growth

There comes a point where the crystal content has reached a sufficiently high value, which will enable an acceptable control of the mother liquor supersaturation. The syrup feed will now be more adjusted to match the evaporation rate, and it is here that the main crystal growth period commences. There is a gradual increase in crystal content, as shown by the increasing massecuite density in curve 1, while at the same time the evaporation rate will have decreased due to the rising hydrostatic head. However, the mother liquor concentration, which is indicated by the No 3 Xc (red) trace, remains relatively flat, indicating constant supersaturation, and only increases slightly with decreasing mother liquor purity and the slight rise in massecuite temperature.

4. Thickening up

The prime purpose of the boiling operation is to produce crystals, so it is necessary to maximise the final crystal content and not purely maintaining a specific supersaturation. The final fourth stage therefore concentrates on thickening to maximise the crystal content, and its effect is seen in all three traces by a rapid change. The red Xc capacitance signal shows the rise in brix and thus supersaturation for a final drive for growth. The evaporation rate also drops off rapidly, due to the increasing massecuite viscosity reducing the circulation.

Comments on operation

During the first two stages, supersaturation of the mother liquor is of paramount importance, as too high a supersaturation can cause major problems, and the evaporation rate is high. It is important to drop the level of supersaturation during the period of establishing of grain, so that the crystal deposit rate matches the equivalent evaporation rate, which ensures a safe mother liquor concentration.

During the remaining stages, crystal content becomes the major control parameter for two reasons. Firstly in order to achieve the final objective of maximising the quantity of crystal sugar, and secondly, the crystal content has a better control of the supersaturation within the required limitation.

With batch pans, the overall boiling procedure is defined by the geometry of the pan, where the initial charging volume at the commencement of the boiling cycle is approximately a third of the final strike volume. During this initial period, the heating surface to volume ratio is very high and the hydrostatic head is low, giving the potential for the highest evaporation rate. But unfortunately, the overall crystal surface area available for sugar deposition is extremely low. During the final stages of boiling the crystal surface area is at its highest but the evaporation rate has reduced to its minimum due to the increase in hydrostatic head.

Continuous Pans

There are a number of different types of continuous vacuum pans on the market, which may have different control philosophies, and so the general comments made in this paper are based on a multi-cell pan with good boiling and plug flow characteristics.

Figure 3, below, shows a typical crystal growth profile along a 12 celled continuous pan, with seed massecuite or magma being fed into the cell 1. The first difference, which is immediately apparent, between batch and continuous pans is that continuous pans are fed with a seed massecuite or magma and not boiled down from a syrup charge. The seed flow quantities are normally about 20 or 33% of the final massecuite flow. The reason for this is a subject on its own and not discussed here. Continuous pans can therefore be considered to be starting from the equivalent position of the batch pan's third stage. As all further growth will be on the seed crystal provided, it is important that the incoming seed material is of the correct size and with a low size variation. The crystal content should be constant and close to the required value at the commencement of the boiling. Experience has shown that the seed massecuite is not always to specification, and with the multi-cell design, the first two cells can then be used to condition the seed, within limitations.

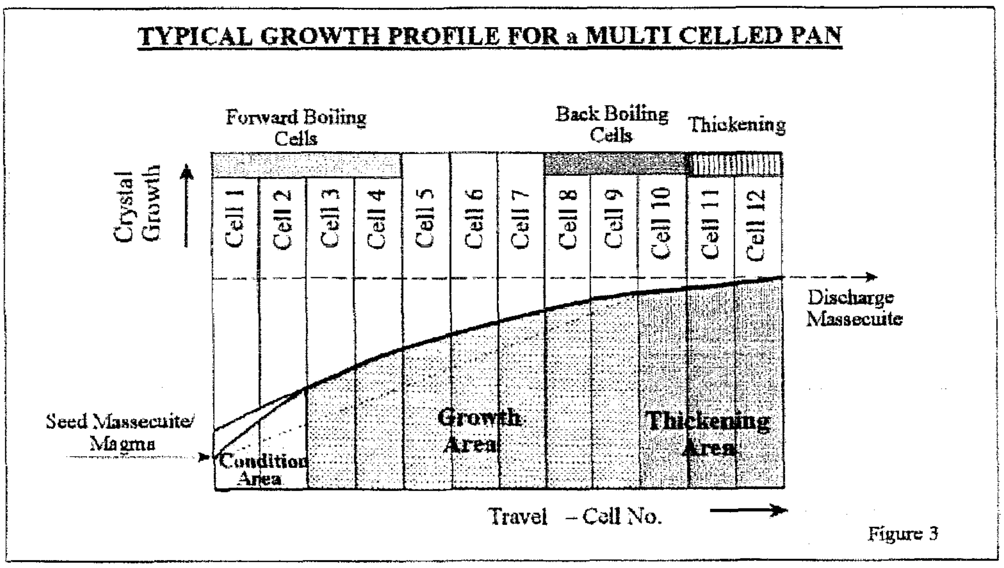


Figure 3

Main Growth

The next stage is the Main crystal growth period shown in the centre section in figure 3. A slightly different approach is required to handle variations in massecuite throughputs between the two types of pan. With a batch system, each pan is operated as an individual batch or strike, which is normally boiled to the optimum or minimum boiling time. Any required reduction in throughput will be accommodated by the variation in the rest time between strikes.

With continuous pans, the whole operation must be sped up or slowed down as required to meet the factory load. As the driving force in the crystallisation process is supersaturation, then this should theoretically be varied, so as to speed up or slow down the process to match the requires crystallisation rate, as the overall crystal area, (that is in effect the crystal content), remains constant.

Boiling Profile

As with the batch pans the initial stages of the boiling are operated at a lower crystal content but well within the safety range. However, this must be gradually raised so as to optimise exhaustion at the pan discharge. There should be no rapid change to the crystal content as this can produce false grain, which means in practice a gradual increase to thickening.

There is no simple direct method of measuring crystal content, and it is therefore more common with low purity massecuites to monitor the conditions in each cell by measuring the massecuite brixes. For high purity massecuites, the variation in brix across the pan is small and a Gillet[6] type meter, as shown in figure 4, is often used to set up a boiling profile. This type of meter measures an apparent crystal volumetric content, which is obtained by determining volumetric change of a sample of massecuite by compression. This is achieved by using a simple cylinder and piston as shown in figure 4 below, and draining out the displaced liquor through a screen at the bottom. This instrument is sufficiently accurate to set up a profile through the pan, and also has the advantage that the pan boiler can obtain a repeatable reading in a few minutes.

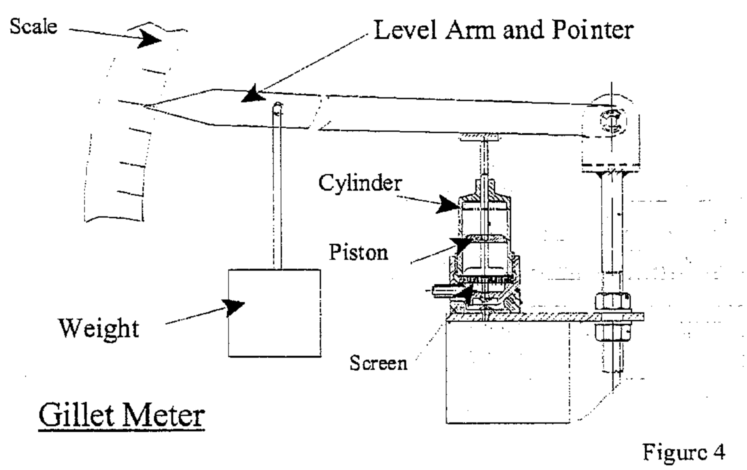


Figure 4

Thickening Stage

The thickening up stage is very important for maximising exhaustion, and it is in this area that continuous boiling offers the opportunity for better control. With batch pans the evaporation rate during the thickening stage is low, due to the high hydrostatic

In the graph on the left, the Y-axis shows the mother liquor apparent purity, and is this value is compared along the X axis to the measured massecuite spindle brix value, the estimated dry massecuite solids value is shown on the lower X axis. The other graph, on the right, shows the thickening rate for the same four conditions. The X axis gives the time after commencement of thickening, and the Y axis the corresponding values of the massecuite measured spindle brix and the estimated massecuite dry solids.

The (red) curves (1) demonstrates the effect of rapid thickening of the massecuite, and this is shown by the steep gradient of the red curve in the right hand graph, while the effect on the exhaustion is shown by the highest mother liquor apparent purity in the left hand set of graphs.

Whalley's 'C' Massecuite Results

Massecuite App Purity 62 – True Purity 68.5

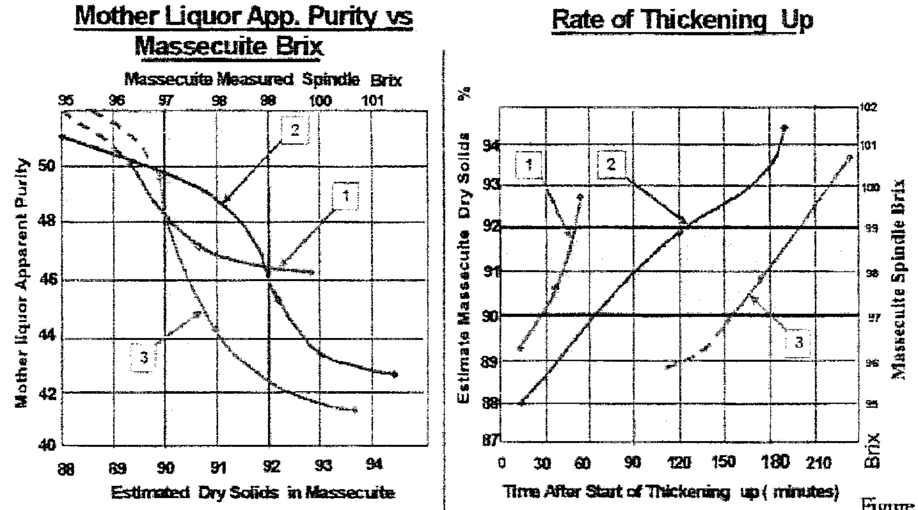


Figure 5

The (blue) curves (2) shows a longer thickening period, at a reduced rate, with the initial massecuite conditions at a lower brix, and the massecuite is now taken to a higher final brix. Although the massecuite brix is raised at a fairly uniformly rate, there is a period where the sugar deposition rate increases, between the massecuite dry solids values of 91 and 92.5, and then the rate slows down to a very low value. With this method, a lower mother liquor purity has been achieved.

The (brown) curves (3) has the longest overall thickening up period, with initially very slow thickening, and this period is not shown in the graph, but changes as shown by the curve (3) to a similar thickening rate used for the second curve. This method has also developed a similar period of a higher sugar deposition between the massecuite dry solids values of 90 and 92. It has also produced a further lowering of the mother liquor purity when compared to the others.

From these curves, it is apparent that to obtain good exhaustions, it is not only necessary to have a high discharge brix, but it is also important to control the rate of thickening. Culp[8] provides an explanation to why, with low purity mother liquors, the crystallisation rate slows down, or produces false grain, when the mother liquor supersaturation reaches a certain high value. He explains that for each sugar molecule to remain stable in a solution, four water molecules are required to be loosely bonded

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Effective control, during this thickening up stage, is more important with continuous pans, because higher evaporation rates are possible, allowing the supersaturation to be raised to too high a level. It is often better to control the supersaturation during the very final stages by the addition of a very small quantity of water, as this forces the remaining sucrose out of the mother liquor. If a syrup feed is used, sucrose will be deposited from the incoming feed. A small amount of water vapour is always necessary to provide good circulation.

Continuous pans like batch pans are able to boil two syrups of different purities. The higher purity syrup is fed during the early stages of the boiling, such as in cells 1, 2, 3 and 4, when the mother liquor purity is still high. If a low purity syrup is to be added, this can be added to the later cells such as 8, 9 and 10, where the mother liquor purity has dropped. The final thickening up is carried out in the final cells, where the feed rate is virtually nothing, and in some installations only a very small dribble feed of water is given.

Continuous Pan Control Philosophies

Two quite different control philosophies have been developed for continuous pans, direct and predictive.

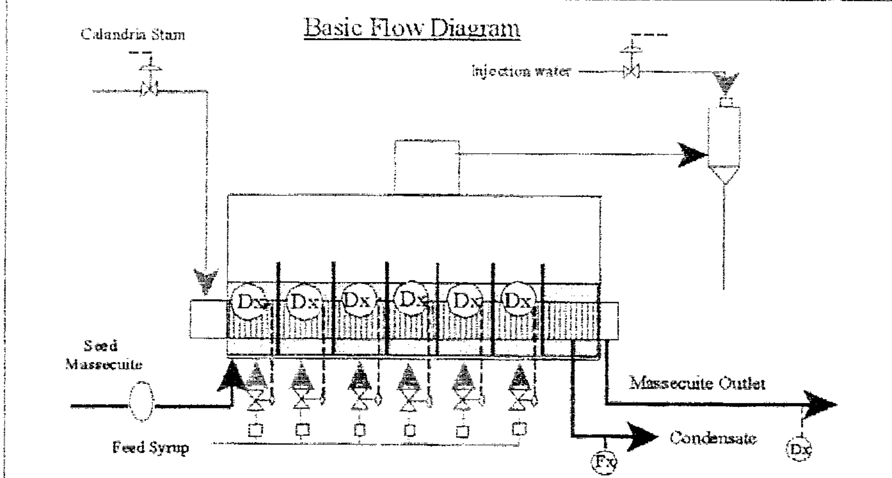

Figure 6

CVP Direct Control

The basic sketch in figure 6 shows a simple flow diagram of a direct control system. The seed massecuite is pumped into the first cell using a variable speed metering pump. The actual flow rate is a function of the ratio of the seed massecuite crystal size to the final crystal size discharged from the pan. The massecuite throughput is controlled by varying the calandria steam pressure. The higher the pressure the greater is the evaporation rate, and the greater is the syrup feed to maintain the same massecuite condition. The vacuum in the vessel is maintained at a constant absolute pressure, using a conventional control system.

With direct control, the massecuite in each cell is controlled to a fixed brix or crystal content using individual signals from probes in each cell. There are a number of different types of probes used in batch pans, but none of them is ideal as they don't measure the crystal content directly.

Probes, which monitor the mother liquor, such as refractometers and methods using boiling point elevation, are more useful during the early stages of the boiling, when the crystal content is low, but not really appropriate for continuous pans, where monitoring the crystal content is more important. Other probes, which monitor the massecuite conditions are much more suitable, such as:- Nuclear density, conductivity and radio frequency probes, are successfully used in batch pans and to some extent monitor crystal content, but are not the ideal.. A third type of probe, which has recently come on to the market is the microwave probe. This measures the overall water content, which is directly related to the massecuite brix, and is in turn indirectly related to crystal content.

Unfortunately all the above probes, when used in continuous pans, must be subjected to some form of regular cleaning to remove any sugar encrustation. The rate of encrustation increases with increasing purity.

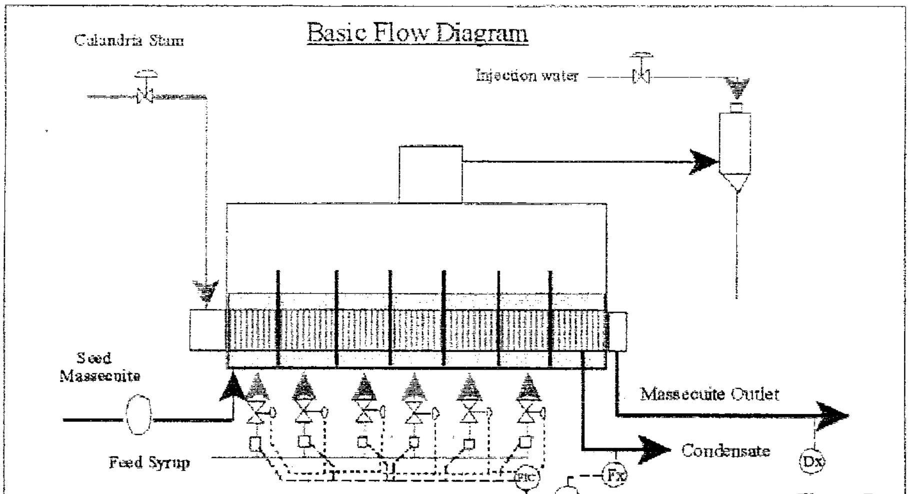

Figure 7

Predictive Control

The alternative method to the conventional direct control is 'predictive control', and the object of this system is to avoid the use of probes and their requirement for cleaning. A basic Flow diagram is shown in figure 7.

For this type of control to operate successfully, it is necessary to operated with steady massecuite flow rates as any changes will take some time to stabilise. It is also most important that the crystal content of the seed massecuite entering the pan is constant. Provided these two conditions are met, predictive control can be used successfully. The massecuite flow rate through the pan is controlled as with the previous direct method by adjusting the steam pressure.

Predictive control is not an accurate method of monitoring the quality of massecuite, because the actual product conditions within a pan are not being measured. It relies on predicting the incoming syrup flow from the calculated the mass flows measurements in and out of the system, and then balancing the conditions within the pan. The seed massecuite flow can be calculated from the metering pump speed, and the condensate flow measurement is used to estimate the water evaporation rate.

This system is able to operate, because under the design conditions the mother liquor supersaturation is being controlled by the crystal content. Difficulties will only arise if massecuite crystal content is allowed to either drop too low to encourage false grain or rise too high to reduce circulation. It is, however, common to trim the overall control by providing a signal of the final brix of the massecuite leaving the pan and transmitting this information back to the controls.

For this type of control to work successfully, it is important that all the flows into and out of the system are accurately measured. It is very important for the crystal content of the incoming seed to be constant, because there is no simple means of monitoring this change and taking the required corrective action.

Overall stability is important with any predictive controlled system, and any short term temporary disturbance to the pan, such as a change of vacuum, will not be accounted for, as the actual massecuite conditions within the pan are not being monitored. Predictive control has been successfully used in many continuous pan installations.

The evaporation rate, which is influencing the supersaturation, is affected by the pans design and operation, and controlled in continuous pans by the temperature difference between the calandria and the massecuite. It is also in this respect that there is a difference between batch and continuous pans in that the CVP can be designed to operate with larger heating surfaces areas, which are effective throughout the whole boiling period. These pans also operate at a much lower hydrostatic head, reducing the temperature profile over the pan, and giving the opportunity to operate with lower massecuite and calandria steam temperatures.

This is an important feature, because the massecuite throughput in continuous pans is controlled by the evaporation rate, which in turn is regulated by the calandria steam pressure, requiring the calandria to operate with a greater variation in low steam pressures.

Conclusion

Although the crystallisation chemistry used for both batch and continuous boiling is the same, the pan boiling characteristics are different, and therefore slightly different control philosophies are used. The modern multi-cell continuous pan has proved to be ideally suited to handle the main crystal growth period providing in many cases significant benefits over the traditional batch pans. It allows the boiling operation to be easily subdivided into a number of simple separate stages, which can be controlled to a predetermined massecuite profile. It does offer the opportunity of a better control of the final thickening stage to achieve good exhaustions, and the benefit of operating at lower boiling temperatures.

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