INFLUENCE OF RAW SUGAR QUALITY ON THE PHOSPHATATION PROCESS

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Abstract

Some impurities occurring in raw sugar have been examined with respect to the phosphatation flotation process. It is confirmed that turbidity removal can be achieved by a process based on dissolved air provided the air : solids ratio is favourable. In addition the process reduces the level of other impurities such as starch and colour but has no effect on the ash content of the solution. Starch has a major influence in that it can cause high phosphate levels in clarified liquor. Although both major starch components, viz. amylose and amylopectin contribute to this phenomenon, it is shown that amylopectin has the major influence.

Introduction

The precipitation of calcium phosphate in a raw sugar melt followed by the flotation of the resultant coagulum forms the basis of a defecation process widely practised within the sugar refining industry. In theory the entrapment of all colloidal and suspended matter (0,1 μm to 200 μm) by the coagulation network together with effective air flotation should provide a liquor which is turbidity-free: a prerequisite element for an efficient decolorising process. The phosphatation process has often proved difficult to control and has led some workers[4, 6, 7] to innovate in an attempt to overcome certain inherent deficiencies. Further, those factors associated with raw sugar quality which are important with reference to the phosphatation process are imprecisely understood. The work reported in this paper deals with the effect of suspended matter, colour, starch, ash and gums on the coagulation process and their influence on the quality of clarified liquor. In particular, the role of starch has been found to be anomalous and may be compared with the effect starch has on the refinery carbonatation process.

Phosphatation comprises three important operations: coagulation,* aeration and flotation. Laboratory work at SMRI strongly indicated that, at least for experimental purposes, aeration must take place before coagulum formation. Saranin[8] has emphasized the desirability of utilising the "dissolved air" concept by use of pressure rather than merely dispersing air in the system by use of a sheering device. It has been noted in this laboratory that use of the latter technique for aeration invariably results in lack of control of two very important process parameters: coagulum stability and air bubble size. Production of bubbles of diameter > 200 μm leads to a decrease in flotation potential and the creation of a detrimental stirring action within the flotation vessel. Dissolution of air by the use of pressure provides for precise regulation of the amount of air introduced into the system prior to coagulation. This technique has been adopted for the laboratory investigation.

Experimental

(i) *Apparatus*

The laboratory bench unit consists basically of two vessels: one for pressurising the melt and one for reaction/flotation. (Fig. 1)

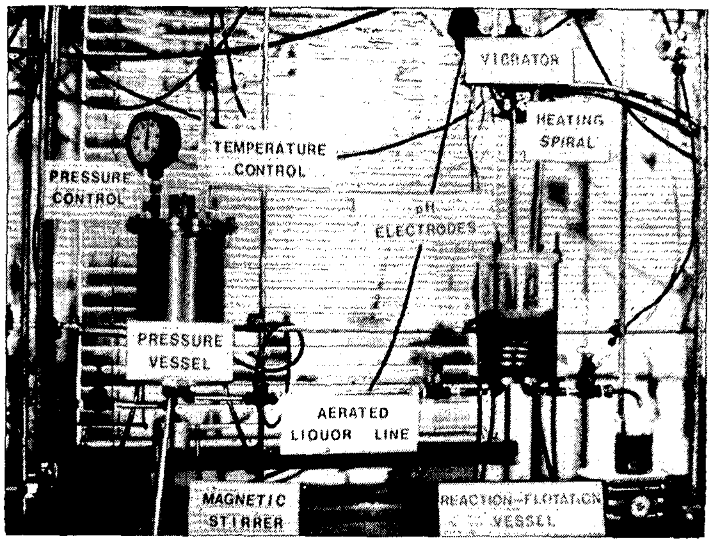

FIGURE 1

The stainless steel pressure vessel (capacity = 5ℓ) is equipped with a 1 500 W electrical heater and has a magnetic stirrer incorporated to facilitate air dissolution. It is capable of withstanding pressures of up to 1 500 kPa. The perspex reaction/flotation vessel (capacity 4ℓ) is equipped with a glycerol-heated coil heater to enable the flotation temperature to be reached quickly. Control of pH is maintained by use of an Ag/AgCl high stability electrode system.

Raw melt (2 ℓ, 60° Bx) together with calcium phosphate seed (0,2 ml) — prepared by precipitation of calcium phosphate in a pure sucrose solution at 60°Bx and 75°C — is introduced into the pressure vessel and the temperature raised to 75°C. The solution is now pressurised to 500 kPa with the magnetic stirrer on to ensure efficient air dissolution. After 15 minutes the pressure is released and the aerated liquor passes to the other vessel. The drop in pressure from 500 kPa to atmospheric pressure causes the formation of a myriad of tiny air bubbles throughout the whole solution. However, the average bubble size is so small that upward movement, i.e. floating action is arrested for some considerable time. Phosphoric acid (≡ 0,025% P_2O_5 on solids) and calcium saccharate are added and mixed very rapidly (30 secs.) using a vibrator. The temperature is now raised from 75°C to 85°C in four minutes which provides for faster and more efficient flotation by creating a drop in solution viscosity of approximately 25%. Flotation is largely complete after four minutes at 85°C. Sampling of the clarified underflow liquor may then take place. The final pH of clear liquor is 7,2 at 20°C.

(ii) *Liquor quality assessment*

(*a*) *Analysis:* Standard analytical tests as used by the SMRI were used to determine the quantity of suspended matter, starch, colour, gums and ash removed by the process.

Difficulties were incurred in obtaining raw sugar where the starch content exceeded 200 ppm. After careful testing, potato starch was found to be an adequate

* Although some authorities refer to phosphatation as a flocculation process, in fact, it is probably more accurate to describe it as depending on a coagulation mechanism.

substitute and this was added to create high starch conditions. Amylopectin and amylose, which are the two major components of starch, were also added.

(*b*) *Filterability:* To assess the efficiency of the coagulation reaction the filtering properties of clarified liquor were measured. A method based on estimating the standard blocking of a membrane filter by residual particles in the liquor was adopted.[3] Standard blocking occurs when the particle size of the insoluble material is very much smaller than the pores of the filter. A progressive restriction is caused by particle adsorption onto the pore walls which creates a build-up within the body of the filter.

The equation which describes this phenomenon is:

$$\frac{t}{V} = kt + \text{const.}$$

where "t" is the cumulative time of filtration, and "V" is the cumulative filtrate volume.

From Sullivan,[9] $K = 10^4 k$ where K is referred to as a filterability constant.

The laboratory procedure for calculating K consists of taking an aliquot (250 ml) of the clarified liquor and filtering it at 70 kPa pressure through a 1,2 μm membrane filter (Sartorius) at 80°C. The cumulative volume "V" in ml is noted against time "t" in secs. and a plot of

$$\frac{t}{V} \text{ versus t is drawn.}$$

K, which is time-independent, may then be calculated.

Results

A selection of refined and raw sugars of widely varying quality were processed using the laboratory phosphatation unit. The percentage removal of impurity by the process was noted in each case together with the change in P_2O_5 content. A measurement of the filterability constant, K, was made for each clarified liquor. The results are shown in Table 1.

The primary aim of refinery defecation is the complete removal of all colloidal and suspended matter from the raw melt and the production of clarified liquor which is essentially turbidity-free. As the results in Table 1 show, this is achieved to a great extent in nearly every sugar sample studied. Th removal of colour and starch is substantial but gum remova is somewhat less. The conductivity ash percent value does not appear to be influenced positively by the process.

Measured values of K, the filterability constant, show wide variation viz. from <20 to >300 as can be seen from a plot of $\frac{t}{V} \sim t$ for some samples (Fig. 2). It is noted that the

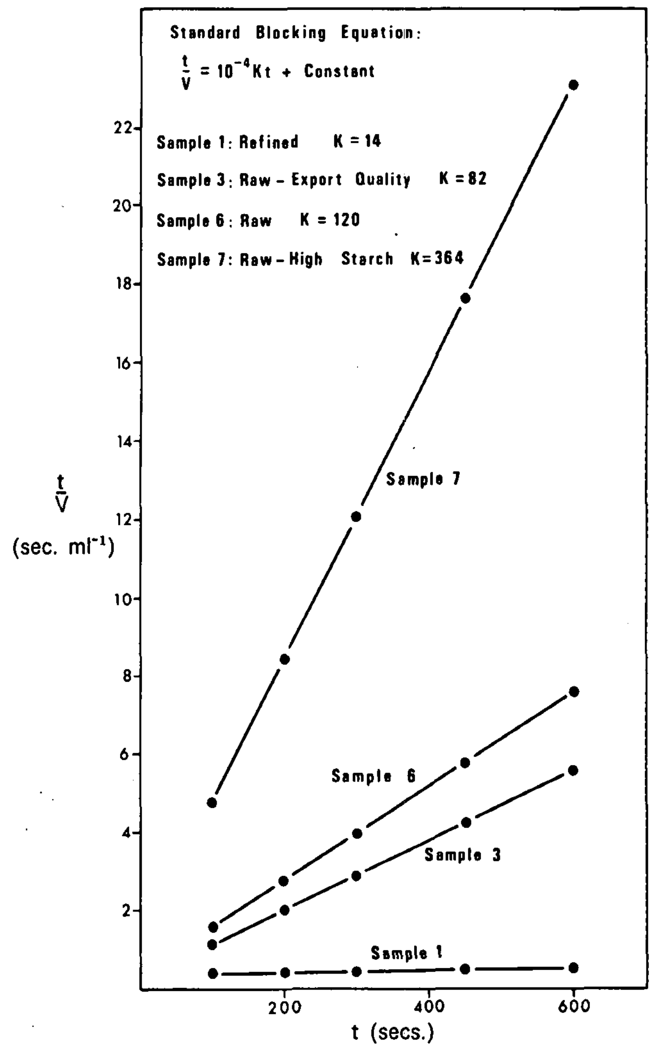

FIGURE 2 Filterability constant by a standard blocking equation.

TABLE 1

Analysis of sugar melt samples and % removal of impurities on processing

Sample No.	Sugar Quality	Turbidity		Colour		Gums		Cond. Ash %		P_2O_5 Content		Starch		Filt. Const. 'K' of Clarif. Liquor
		Melt a* c 720 nm @ pH 7,0	% Removal	Melt a* c 420 nm @ pH 7,0	% Removal	Melt ppm	% Removal	Melt %	% Removal	Melt ppm	Clarified Liquor ppm	Melt ppm	% Removal	
1	Refined	0,00	—	0,00	—	150	10	0,005	0	0	0	0	—	14
2	Raw: export quality	0,15	100	0,80	20	850	5	0,18	0	15	15	50	30	60
3	Raw: export quality	0,16	100	0,76	20	750	15	0,11	0	35	30	95	25	82
4	Raw: export quality	0,16	100	0,77	25	650	10	0,12	0	35	35	85	30	93
5	Raw: local refinery quality	0,43	99	0,90	30	1 000	15	0,11	0	25	45	125	35	107
6	Raw: high suspended matter	0,36	98	1,35	25	1 000	15	0,18	0	40	50	135	30	120
7	Raw: poor quality high starch	0,30	95	0,95	25	1 200	15	0,20	0	15	70	280	30	364

lower the value of K, the greater is the filtration rate of the clarified liquor. Most refined sugars processed have a value of K < 20, due to the almost complete absence of either suspended matter originating from the refined melt or residual calcium phosphate which has not been removed by the flotation process. Export quality raw sugars yield K values within the range 50 - 100. Lesser quality raws which just fail to meet export specifications and which are refined locally generally have K values in the range 90 - 140. Very poor quality raw with high starch (250 ppm) may have a K value in excess of 300.

The results in Table 1 suggest that the value of K is independent of the amount of suspended matter (as measured by turbidity) in the unprocessed melt. This, in fact, is the case if the phosphatation unit is run at a favourable air: floatable solids ratio ($\nless$ 0,02) which according to Saranin[8] is the main factor governing the efficiency of suspended solids removal. That K is independent of suspended solids content of the raw sample is understandable since the process yields an almost turbidity-free clear liquor. Only when incomplete removal of suspended solids is achieved due to an excessively high turbidity, will K be influenced by suspended matter.

The particles in clear liquor responsible for the blocking of the filter during the determination of K do not contribute measurably to clear liquor turbidity since high K values can be found in turbidity-free liquors. This is probably a consequence of the colloidal size of these particles and hence their inability (at the concentration found in clear liquor) to scatter significant amounts of incident light as measured by the absorption at 720 nm.

True colour removal (at 420 nm) is, on average, 25%. It is probable that the main mechanism by which colour is removed is one of adsorption of the negatively charged colour bodies onto the calcium phosphate micro-crystalline precipitate via a calcium linkage. Although the surface area of phosphate for potential colour adsorption is so large it is possible that the coagulation/flotation reaction proceeds too quickly for all colour to become attached. In addition some colour bodies are uncharged and would not readily be adsorbed. Colloid destabilisation of colour bodies by use of a surface active agent is an effective method of enhancing colour removal and is practised in the Talofloc process.[2] Some investigations are presently being carried out with the laboratory phosphatation unit using positively charged polymers in an effort to increase colour adsorption.

Removal of gums (average — 12%) is less than that of colour. The mechanism by which it is accomplished is probably one involving entrapment by the coagulum as it is formed. Gums do not appear to adsorb strongly onto the calcium phosphate surface. Conductivity ash analysis before and after the process indicates that a negligible quantity of dissolved ionic material is removed. Bennett[1] has compared this phenomenon with the removal of ash by the carbonatation refinery process.

It is obvious from the data in Table 1 that of the impurities in raw sugar which have been examined in this study starch has by far the greatest influence on the value of K. High starch values invariably result in high K values, i.e. poor filterability. Its presence causes the formation of large very dense coagules which are difficult to float at an adequate upward velocity. The scum which is formed tends to compress slowly to form a dense, thixotropic layer which is difficult to handle.

Incremental addition of starch to a raw sample followed by phosphatation can be used to measure quantitatively the effect starch has on the value of K. Figure 3 shows this relationship for one sample studied.

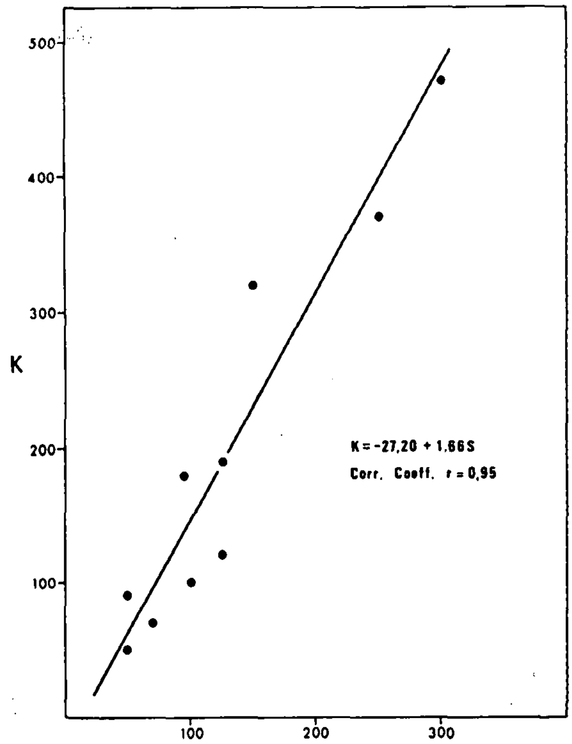

FIGURE 3 Relationship between the filterability constant K of clarified liquor and the concentration of starch S (ppm) in the process liquor.

The data contained in Figure 3 illustrates that there is a significant relationship between raw sugar starch content and the K value of clarified liquor (correlation coeff. "r"=0,95). That the small particles responsible for the variation in K values contain calcium phosphate was shown by centrifuging (at 20 000 rpm and 25°C) a sample of clarified liquor. The resulting precipitate was spot tested and showed the presence of both calcium and phosphate. Hence starch appears to be capable of adversely modifying the precipitation and coagulation of calcium phosphate. The more starch which is present the higher will be the residual phosphate content (measured as P_2O_5) of the clarified liquor. That the phosphate content is particulate can be seen both from conductivity ash percent figures (Table 1) which show no increase from raw melt to clarified liquor as they would if this excess phosphate were in ionic (i.e. soluble) form and also from filtration data. To measure the K value, clarified liquor is filtered through a 1,2 μm membrane filter. If the filtrate is analysed it shows a drop in P_2O_5 content together with a concomitant drop in starch concentration. This suggests that starch and residual phosphate may perhaps be associated with each other in solution. To examine this hypothesis experimentally a comprehensive series of runs was made where starch was added in increments to the raw melt. Both clarified liquor starch content and phosphate content were measured and the results expressed graphically (Figure 4).

The results in Figure 4 provide evidence to support the theory of association between calcium phosphate particles and starch molecules in the clarified liquor. Starch must be capable of preventing a small fraction of the phosphate particles formed from taking part in the coagulation reaction. The starch molecule possibly wraps around the calcium phosphate crystallite and stops it from being incorporated into the growing coagulum. In this manner, the large starch molecules act as a protective colloid and stabilize small crystallites in suspension, thus preventing complete coagulation. This action of starch is not permanent, however, because if the clarified

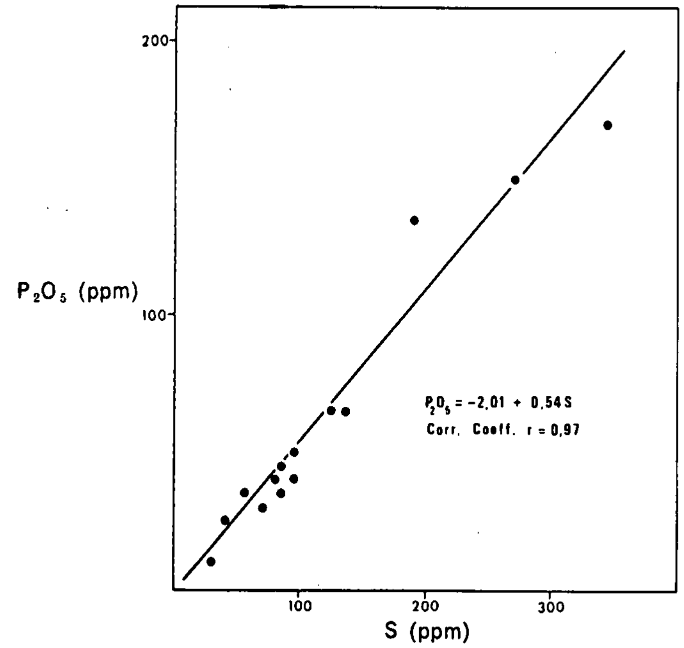

FIGURE 4 Relationship between starch concentration S and calcium phosphate concentration (as P_2O_5) in clarified liquor.

liquor is allowed to age there invariably occurs a secondary precipitation. This is probably caused by a flocculation reaction in which the starch present acts as a bridging flocculant. This phenomenon occurs when phosphate is present at a concentration of 70 ppm P_2O_5 or greater together with a substantial amount of starch (> 150 ppm) in the clarified liquor. In this light, it is obvious that starch is an undesirable raw sugar impurity with reference to the phosphatation refining process.

Starch consists mainly of two different polysaccharides viz. amylose and amylopectin. In order to understand the mechanism by which starch acts as a protective colloid, a series of runs was performed in which amylose and amylopectin were independently added to a raw sugar melt. The results are shown in Figure 5 in which the amount of added

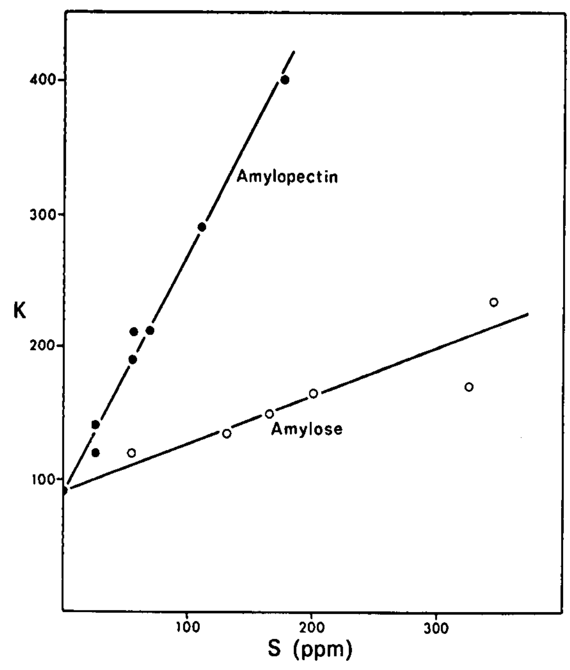

FIGURE 5 Relationship between filterability constant K of clarified liquor and concentration S (ppm) of additional amylose or amylopectin added to the process liquor.

polysaccharide is plotted against the K value of the resulting clear liquor and in Figure 6 in which the P_2O_5 content of clarified liquor is plotted against the amount of added polysaccharide remaining after processing. The raw sugar used for these experiments had a residual 35 ppm P_2O_5 in clarified liquor after phosphatation.

It is evident from Figure 5 that of the two major starch components, amylopectin is the one responsible for the greatest decrease in filterability of clarified liquor. By comparison, amylose gives rise to a relatively small increase in K value. Hence from the above hypothesis regarding the protective colloid action of starch, it is clear that amylopectin is the major factor in stabilizing calcium phosphate crystallites in suspension. Figure 6 shows the relationship between the amylopectin and P_2O_5 concentrations in clear liquor. Amylose, which influences K to a far lesser extent, also causes only a relatively small increase in the phosphate concentration of clarified liquor (Figure 6).

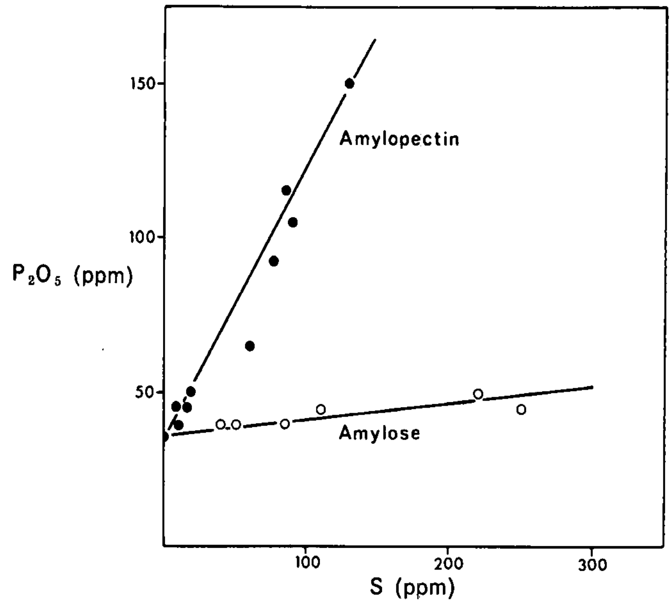

FIGURE 6 Relationship between calcium phosphate concentration (as P_2O_5) and concentration S of additional amylose or amylopectin remaining in clarified liquor.

The reason for the differing behaviour of the two components of starch is presumed to lie in their respective chemical structures. Amylopectin is ideally suited to act as a protective colloid for calcium phosphate particles as it possesses charged phosphate ester groups which can bind chemically to the surface of the calcium phosphate crystallite. Thus this large branched chain macromolecule (Mol Wt 10^7 - 10^8) can wrap around the particle to which it is firmly bound. This coated particle is now hindered from coagulating with the bulk of the calcium phosphate precipitate. The after-precipitation observed at high starch and phosphate levels is due to a chemical rearrangement on the surface of the suspended crystallites in which the amylopectin can act as a bridging flocculant.

In contrast to amylopectin, amylose is a straight chain molecule with molecular wt of 10^5 - 10^6. Due to its uncharged chemical structure, amylose can only adsorb to the calcium phosphate crystallite by relatively weak physical adsorption or by weak complex formation between the hydroxyl groups on the polysaccharide and the calcium ions in the particle surface. This weaker adsorption is not as effective in its protective colloid action as is the chemical binding of amylopectin, i.e. amylose adsorbed on the surface does not hinder coagulation to the same extent as amylopectin.

It is thus the amylopectin component of starch which is mainly responsible in the phosphatation-flotation process for increased phosphate levels in clarified liquor and which gives rise to poor filterability. It is interesting to compare these results with those obtained for the influence of the starch components on the carbonatation process[5] in which it was found that amylopectin has little influence on the reaction while amylose was mainly responsible for poor crystal agglomeration and subsequent bad filterability of the calcium carbonate slurry. Although these results appear contradictory they are in fact complementary when one considers the basic chemical differences between the two defecation processes. The phosphatation-flotation process involves the precipitation of small calcium phosphate crystallites which then may form a coagulum with each other and with impurities which bind to the precipitate via calcium ion bridges. In the carbonatation process, crystals of calcium carbonate are grown in the sugar melt and impurities which can form insoluble calcium salts or which can bind to the crystal via calcium bridges (eg. anionic colour bodies) are incorporated into the growing crystal. In both these processes, amylopectin can bind chemically to the surface of a small crystallite. In the case of phosphatation, precipitation of a large number of crystallites is complete within seconds and surface amylopectin can act to prevent coagulation which is the basis of the defecation process. Thus a small particle is stabilized in suspension. In the carbonatation process, complete reaction takes far longer ($\pm$ 60 minutes) and thus the crystallite continues to grow around the adsorbed amylopectin which is now incorporated into the crystal in a similar manner to other impurities. Thus amylopectin has little effect on the carbonatation reaction, while it exerts a deleterious influence on the phosphatation-flotation process.

In both these defecation processes, amylose is weakly adsorbed onto the respective crystallites. In phosphatation, it acts to a small degree, as a protective colloid in much the same manner as amylopectin. During the time allowed for crystal growth in the carbonatation reaction, the amylose concentration on the crystal surface increases. Here again it acts as a protective colloid and suppresses the growth of agglomerates. The net result is a slurry containing small single crystals which yield a poor filterability. The influence of amylose on carbonatation is relatively greater than on phosphatation due to the time available in carbonatation for the surface concentration of amylose to increase.

In conclusion, this work indicates that the phosphatation flotation process is capable of removing up to 100% of the turbidity of a raw cane sugar melt provided a suitable air: solids ratio is employed. Low retention times can be achieved with this process without the aid of a flocculating agent provided the process parameters are right. The process also removes significant amounts of colour, starch and gum. In contrast to the carbonatation reaction, no drop in the ash content of the liquor was observed in these experiments. It was found that starch, during the phosphatation reaction, is capable of stabilizing small calcium phosphate crystallites by a protective colloid action. The effect of this phenomenon is to raise the P_2O_5 content of clarified liquor which can result in an undesirable secondary precipitation. Further, it is shown that although both amylose and amylopectin can contribute to this phenomenon, amylopectin has the greater effect. This difference between the major components of starch can be related to their respective chemical structures.

Acknowledgements

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