THE CHEMISTRY OF CLARIFICATION

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Abstract

Much energy has been expended in understanding the chemistry of clarification with a view to optimising the process. This paper reviews current practice and considers the mechanisms and chemistry from a practical standpoint and the effect they have on the removal of impurities.

Keywords: Sugarcane, clarification, processing, chemistry

Introduction

Mixed juice is a complex mixture of various components, not only extracted from the cane plant itself, but also brought in as extraneous matter. The clarification of mixed juice is commonly referred to as the 'simple defecation process' in which heat and lime are used to produce a clear juice suitable for further processing. The variability in the composition of the juice as a result of differing geographical location, cane variety and seasonal influence as well as the conditions to which the cane is subjected during harvest and transport, however, complicate this simple process and there is no universal method for producing a good quality clear juice. Furthermore, the chemical reactions which occur have been made more complex by the use of a variety of clarification aids. Each factory is therefore essentially unique and adopts a system of clarification based on the simple defecation process with modifications usually determined by a combination of research and experience.

Systems of liming

Several liming systems have been developed over the years. They include cold liming, hot liming, intermediate liming and fractional liming and double heating, but that which is commonly utilised in South Africa is the method of hot liming. The juice is heated to 100-104°C and milk of lime is then added to give a pH of between 7,4 and 8 such that the clear juice obtained after settling has a pH of between 6,9 and 7,3. Processing of drought cane has necessitated some factories liming closer to pH 8 to reduce turbidity problems ([1]personal communication). A good quality lime is very important and is normally characterised by an available CaO content of 85-90%, and moisture, SiO_2, Fe_2O_3, Al_2O_3, MgO and carbonate levels of approximately 2% each (Chen and Chou, 1993a). At least one South African factory employs saccharate liming to enhance clear juice clarity but this is only when juice colours are high. The findings by Scott (1988) which showed slower settling and increased mud volumes, while achieving a 44% decrease in clear juice turbidity, have possibly detracted from the use of this method in other factories.

Mechanistic and chemical aspects of juice clarification

Zeta potential

It has been shown that particulate matter in raw juice has a negative charge, the outer layer being proteinaceous and with

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a large percentage being mucoid, in which protein is coagulated with a polysaccharide (Bennett, 1957a). The electrostatic repulsion between these particles ensures that spontaneous flocculation of the suspension does not take place (Bennett, 1957b). The raw juice particle is depicted in Figure 1 (Chen and Chou, 1993b).
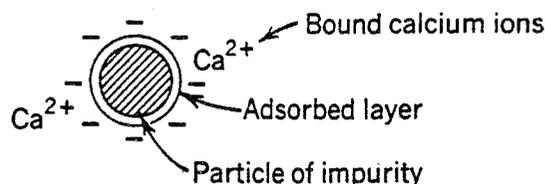

FIGURE 1: The raw juice particle.

The charge lies in the ionizable groups of this outermost adsorbed layer and can be measured in terms of the Zeta potential. Reducing the Zeta potential to zero (the isoelectric point) will result in optimum flocculation. This is achieved partially by the introduction of calcium ions in the form of lime when adjusting the pH. The reaction of organic acids with lime increases lime consumption and reduces the effect on the lowering of the Zeta potential. Under these conditions clarification could be improved by the addition of calcium chloride (Bennett and Ragnauth, 1960).

The role of calcium, phosphate and pH

The mechanism of primary floc formation involves the *in situ* precipitation of calcium phosphate. The Ca^{2+} ions adsorbed at the juice particle surfaces act as nuclei for this precipitation and the impurities become incorporated into the coagulum with the calcium phosphate acting as bridges between the impurity particles (Figure 2) (Chen and Chou, 1993b).
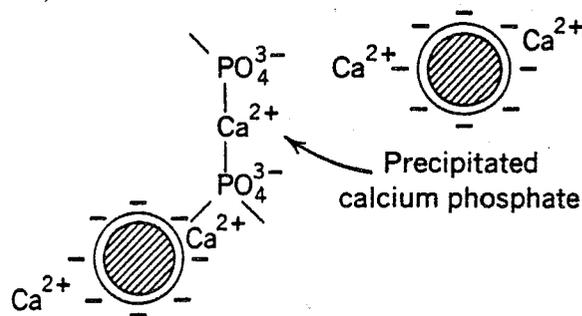

FIGURE 2: Calcium phosphate bridging.

The success of the primary flocculation is dependent upon the extent of the calcium phosphate precipitation and, therefore, on the concentration of the calcium and phosphate ions. Bennett and Ragnauth (1960) have shown that the effects of

calcium and phosphate on the turbidity, settling rate and mud volume are greatest when one or the other is at optimum concentration. Both the optimum calcium and phosphate concentrations increase with the age of the cane. In the commercial process lime addition is determined by pH considerations rather than by calcium concentration and it is assumed that, since the calcium (and magnesium) content after liming is always in excess of that required for complete inorganic phosphate precipitation, the calcium requirement is always satisfied. It is generally accepted that phosphate levels of approximately 300 ppm are required for good clarification, and dosing with 80% commercial phosphoric acid is done when levels are low and processing and clarification problems are experienced. At present dosing is gauged empirically. Much attention is given to pH control since values below seven result in losses due to sucrose inversion while values above eight lead to degradation of reducing sugars which increase colour formation.

The effect of heat

The fact that floc formation can be initiated by heating alone indicates that the effect of temperature has a significant part to play in clarification. This is attributed primarily to protein coagulation. It is generally believed that superheating is not advantageous and that temperatures just above the boiling point (103°C) are the maximum for good practice.

Reaction time and the role of flocculants

Although reaction time is considered to be an important element in the reaction of lime (longer reaction times lead to improved floc formation, better settling rate, lower turbidity, less increase in residual calcium and lower final mud volume) more emphasis is placed on throughput and reduced clarifier residence time. This has been aided by the availability of commercial flocculants.

The functions of good flocculant are:

(a) to increase the settling rate of insoluble solids
(b) to decrease mud volumes
(c) to produce good clarity (low turbidity) clarified juice
(d) to produce good filterability of mud, with good clarity of filtrate.

There are a multitude of flocculants available and the choice is dependent on several factors. Two of the main parameters are the degree of hydrolysis (DH) and the molecular size. The degree of hydrolysis for the commonly used partially hydrolysed polyacrylamide flocculants shown in Figure 3 is defined as:
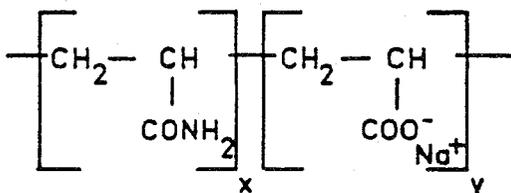
FIGURE 3: The chemical composition of partially hydrolysed polyacrylamides.

For a particular juice sample there exists an optimum DH at which the settling rate of the limed juice is at a maximum. At a similar or slightly higher DH, the turbidity of the resultant clear juice reaches a minimum (Figure 4) (Crees and Whayman, 1974)
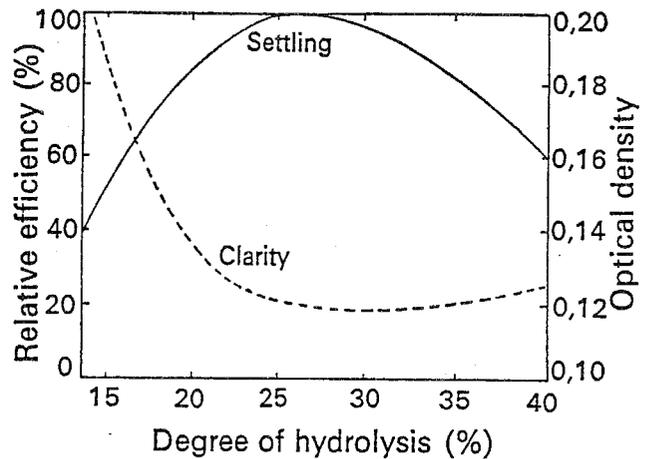
FIGURE 4: Clarity offset from settling peak.

Attempts at the Sugar Milling Research Institute (SMRI) in the 1970s to correlate Zeta potential with settling rate, turbidity or optimum DH were not successful (Shephard, 1978a). The best method of measuring the efficiency of flocculants is by laboratory settling tests as described by Lionnet and Ravnö (1976). Since the juice composition varies with cane age, variety, geographical location and time of year, flocculants should be assessed regularly. Analysis of juice from various South African factories indicated that the normal requirement in the flocculant DH is between 40 and 50% (Shephard, 1980).
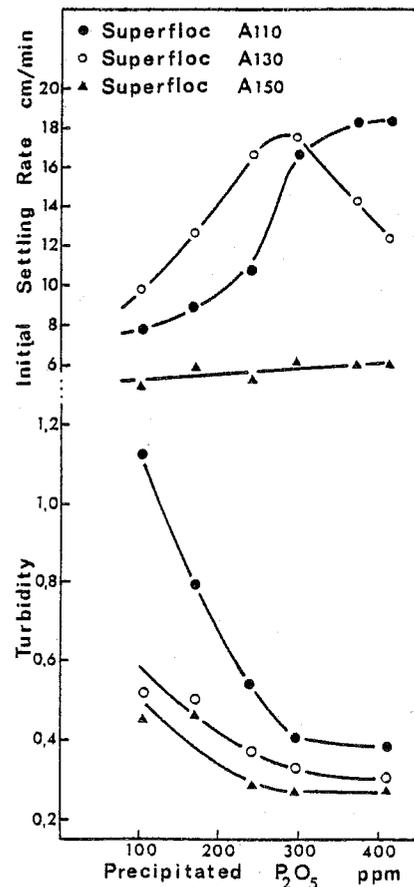
FIGURE 5: The effect of P_2O_5 precipitated on clarification with flocculants of varying DH
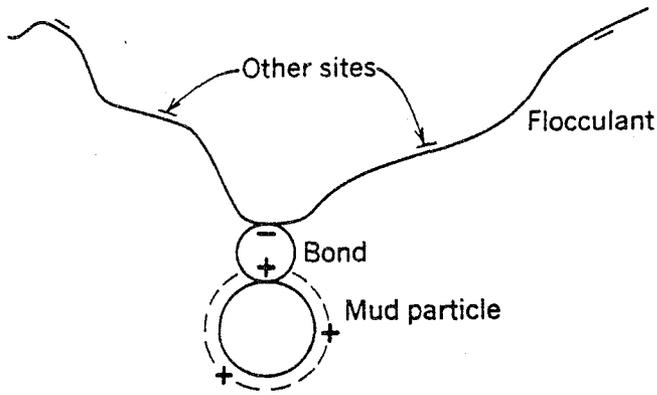
FIGURE 6: Secondary floc formation.

Although the roles played by phosphate and calcium in clarification are well documented, relatively little is known about their interaction with flocculant and the effect on the efficiency. Experiments conducted with three flocculants – Superfloc A110 (DH=30%), Al30 (DH=45%) and Al50 (DH=60%) show the effect on settling rate and turbidity as the phosphate content increases (Figure 5) (Shephard, 1978b).
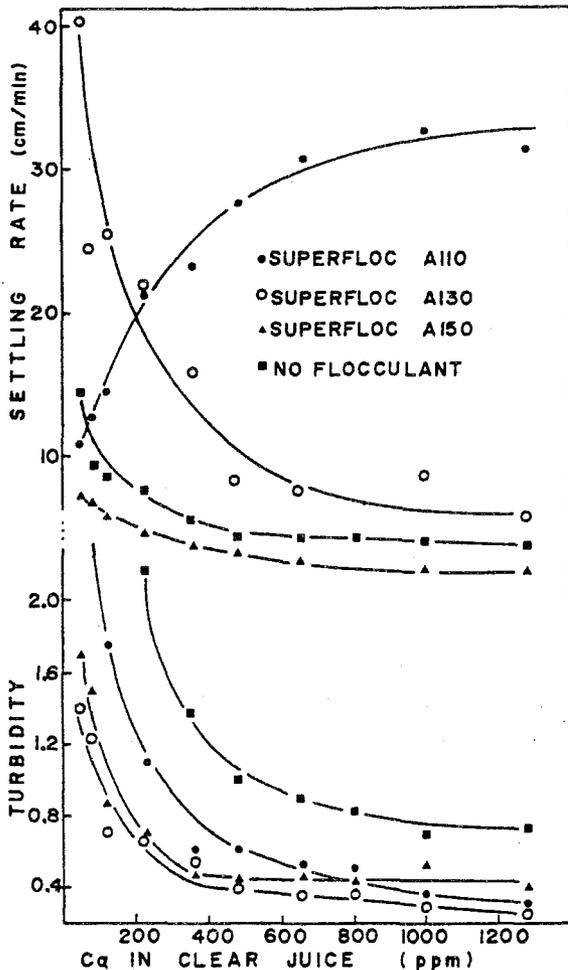

FIGURE 7: The effect of Ca^{2+} on clarification with flocculants of varying DH.

At high levels of phosphate, Superfloc A110 becomes superior to the A130, which is the optimum flocculant for low and intermediate levels of phosphate. The effect of calcium ion concentration on clarity is equally interesting since the mechanism of secondary floc formation involves the attachment of the flocculant (via the acrylate) to the juice particles via adsorbed calcium ions (Figure 6) (Chen and Chou, 1993b).

While holding the phosphate content constant at 320 ppm, the calcium ion content was increased and, at 450 ppm, 90% of the phosphate had precipitated. The behaviour of the Superflocs A130 and A150 parallels that of the suspension without flocculants, whereas Superfloc A110 shows an anomalous response in becoming by far the best at high calcium concentration (Figure 7) (Shephard, 1980).

The shift in DH needed for optimum settling is brought about by increasing amounts of calcium adsorption which promotes the binding of the flocculant to the particle surface. This results in an overbound intermediate DH flocculant (A130) and an optimum for the low DH A110 flocculant. The overbound state is depicted in Figure 8.
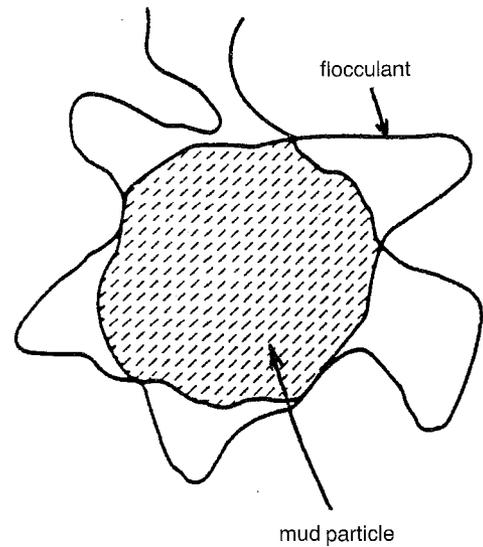

FIGURE 8: Overbound flocculant.

From the above observations it is clear that the type of flocculant needs to be chosen carefully. Dosage rates are normally 2-4 ppm on mixed juice and may very often be a combination of flocculants. Inevitably a significant amount of flocculant will remain in the clear juice. At normal dosage rates the filterability will not be affected but, at higher dosages, the effect may be quite severe (Crees et al. 1977). Figure 9 shows the standard curve using flocculant A110 prepared for use in estimating the residual flocculant in clear juice by measurement of the filterability. The carry-over of flocculants A110, A120, A130 and A140 at varying dosages is shown in Figure 10. In addition, although the sedimentation rate may increase with dosage, suspended solids in the juice may also increase (Crees and Whayman, 1983) (Figure 11).

Equally as important as the choice of flocculant is the method of preparation. A stock solution of 0,1-0,5% is usually prepared, as below 0,05% a rapid decrease in flocculant efficiency occurs (Shephard, 1978b). Dissolution should be brought about by gentle stirring in condensate water for at

least two hours. Temperatures above 50°C should be avoided in order to prevent thermal degradation.
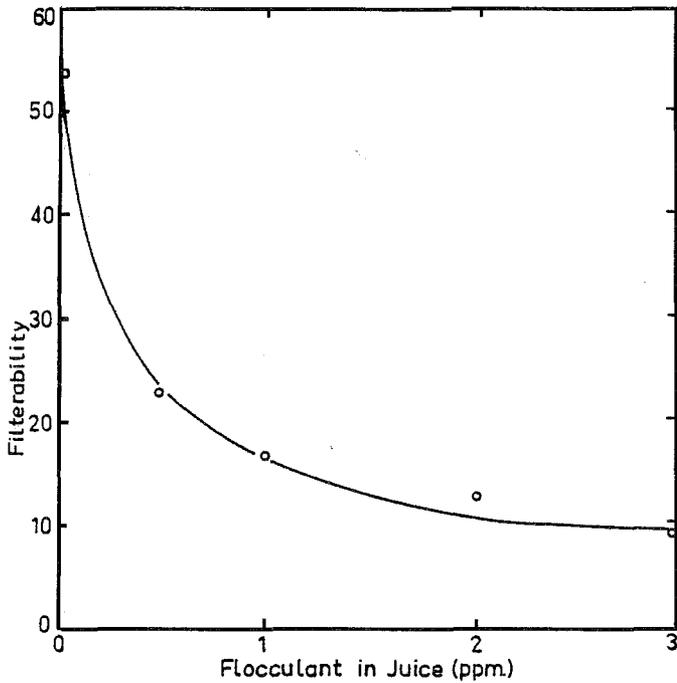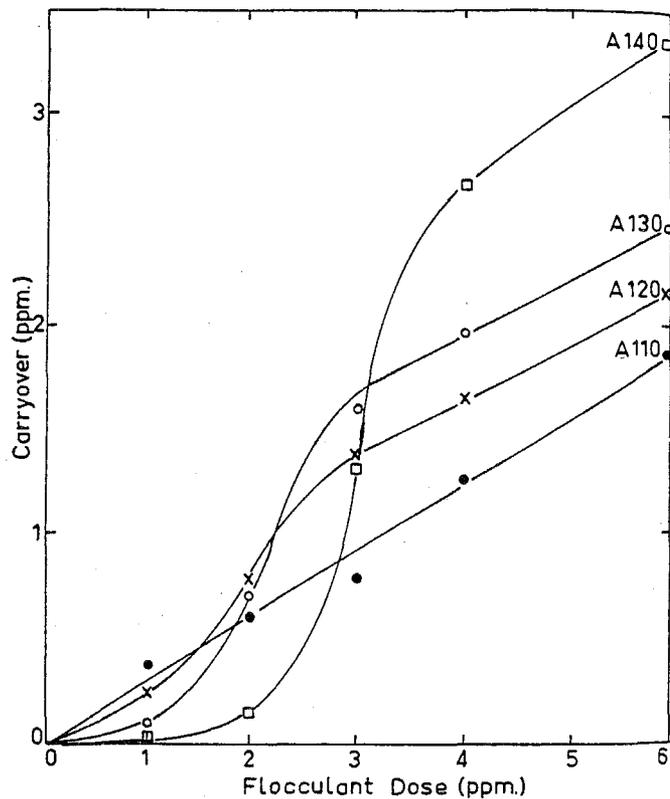

FIGURE 9: Standard curve for A110.

FIGURE 10: Variation of flocculant carry over with dose for selected flocculants.
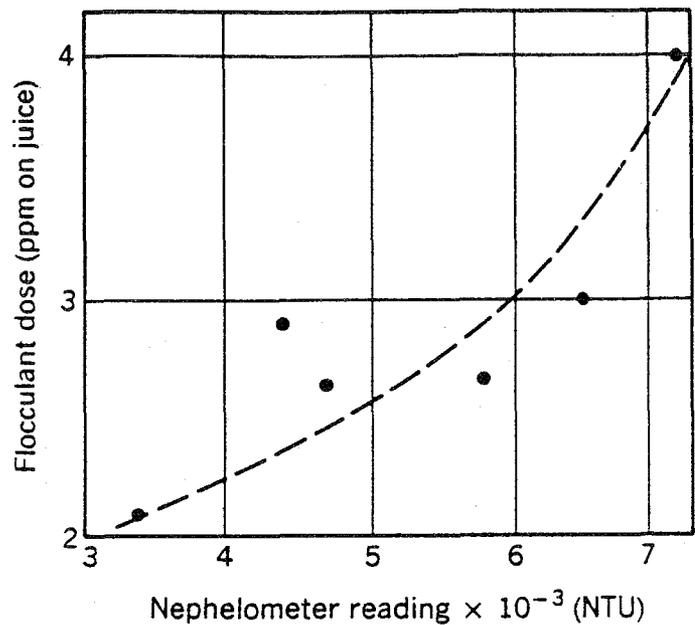

FIGURE 11: Flocculant dosage versus nephelometer reading.

The removal of impurities by clarification

Having 'optimised' the clarification process, it is interesting to note the effect on the impurities present in the mixed juice. The components of mixed juice can be divided conveniently into four categories: non-crystallisable sugars, mineral non-sugars, organic non-sugars and foreign matter. Only the first three are discussed here.

Non-crystallisable sugars. Reducing sugars occur in mixed juice in amounts second only to those of sucrose. They are undesirable from the point of view that they undergo degradation at alkaline pH forming organic acids (which utilise lime), and highly coloured condensation complexes. Oligosaccharides and polysaccharides originate from the metabolic activities of the plant and from the activities of micro-organisms and include starch, cellulosans, hemicelluloses, pectins, sarkaran, indigenous cane polysaccharide, dextrans and levans. Clarification eliminates about 10-15% of these and is improved by a higher liming pH (Honig, 1964). Many are colloidal in nature and, due to their great surface activity, have a physical effect on the mixed juice system out of proportion to their quantity. Although the amount eliminated is not large, the partial removal of these substances is an important result of the clarification process.

Mineral non-sugars (salts). The quantities of cations and anions in mixed juice vary with plant age and material brought in with foreign matter. Potassium, sodium and chloride levels remain unchanged by the clarification process, but iron and aluminium are almost completely removed at pH 8. There is a lack of fundamental knowledge on the removal of silica in clarification, but it is most probably present in the soluble colloidal or suspended forms and as silicates. Most of the suspended material is removed by liming, leaving a clarified juice which contains 0,030-0,075% (on solids). The sulphate content of juice is highly variable and the results of Honig (1964) show less than 20% removal with ordinary liming. Polyvalent trace elements such as manganese, zinc and cobalt are almost completely removed. High levels of magnesium may influence clarification, and its precipitation

is dependent on pH. Above pH 7 increased magnesium precipitation results in increased calcium in solution, possibly impacting on the settling rate of calcium phosphate.

Organic non-sugars. These are composed of various molecules including colourants, organic acids, nitrogen compounds, waxes, fats and phospholipids. Colourants can be divided into those of natural origin and those formed during the manufacturing process. Of the naturally occurring colourants only the anthocyanins are of significance since they are soluble polyphenolic compounds which react with iron to form darkly coloured compounds. Anthocyanins are not precipitated except in strongly alkaline conditions. Of the organic acids, aconitic acid is probably the most important since it occurs in the greatest concentration, although very little is precipitated unless liming to high pH is practised. Nitrogen compounds include proteins such as albumen and free amino acids. Protein is removed mostly by the action of heat and lime, but any that remains is highly deleterious due to its action as a protective colloid. The amino acids and amides are stable under the conditions of clarification, and impact on the clarification process only by complexing calcium ions which result in increased calcium levels in the clear juice and through the 'browning', or Maillard, reaction with reducing sugars. The effects of waxes and fats on clarification are principally physical. They are generally removed in the scum (due to their lower density), with some being carried down in the calcium phosphate precipitate. Some colloidal material may nevertheless be found suspended in the clear juice.

Conclusions

Crees *et al.* (1973) suggested that the measurement of juice colloid Zeta potential may in the future lead to fine-tuning of the clarification process. Although the measurement of Zeta potential has found application in the purification of water, no inroads have been made in the sugar industry. The intro-duction into several factories of the juice clarity meter developed at the SMRI has offered a means of monitoring the efficiency of the clarification process, but there is still scope for further improvements. Perhaps the introduction of membrane filtration will bring about a step change in the clarification process.

Acknowledgements

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