

## Insights to the Clarification of Sugar Cane Juice Expressed from Sugar Cane Stalk and Trash

C. C. D. Thai, H. Bakir, and W. O. S. Doherty\*

Centre for Tropical Crops and Biocommodities, Queensland University of Technology, Brisbane, QLD 4000, Australia

**ABSTRACT:** Processing of juice expressed from green sugar cane containing all the trash (i.e., tops and leaves, the nonstalk component) of the sugar cane plant during sugar manufacture has been reported to lead to poor clarified juice (CJ) quality. Studies of different liming techniques have been conducted to identify which liming technique gives the best clarification performance from juice expressed from green cane containing half of all trash extracted (GE). Results have shown that lime saccharate addition to juice at 76 °C either continuous or batchwise gives satisfactory settling rates of calcium phosphate flocs (50–70 cm/min) and CJ with low turbidity and minimal amounts of mineral constituents. Surprisingly, the addition of phosphoric acid ( $\leq 300$  mg/kg as  $P_2O_5$ ), prior to liming to reduce juice turbidity ( $\leq 80\%$ ), increased the Mg ( $\leq 101\%$ ) and Si ( $\leq 148\%$ ) contents particularly for clarified GE juices. The increase was not proportional with increasing phosphoric acid dose. The nature of the flocs formed, including the zeta potential of the particles by the different liming techniques, has been used to account for the differences in clarification performance. Differences between the qualities of the CJ obtained with GE juice and that of burnt cane juices with all trash extracted (BE) have been discussed to provide further insights into GE processing.

**KEYWORDS:** trash, clarification, sugar cane juice, flocculation, sugar manufacture, calcium phosphate

### ■ INTRODUCTION

In the sugar cane industry, there are a number of byproducts that have the potential to be used as feedstock for the production of platform chemicals and industrial products. An example is the fibrous residue of sugar cane exiting the sugar milling process, called bagasse. Bagasse is burned in sugar boilers to produce steam and electricity to supply the needs of the factory, with excess electricity sold as additional revenue for the factory. Surplus bagasse not used in this process can be used for cogeneration or used for the production of industrial products (e.g., cellulosic ethanol and biofuels), thus the sustainability of the sugar cane industry and its long-term economic viability can be assured. Edye et al.<sup>1</sup> showed that the revenue (AU\$/tonne of sugar cane) from producing ethanol and lignin from bagasse was 4 times the revenue generated from producing electricity via cogeneration using high pressure boilers. This has led to a trend toward a change from burnt to green sugar cane (containing trash) harvesting for the manufacture of raw sugar. Also, to increase the amount of surplus bagasse, ways to harvest, transport and deliver large supplies of trash to the factory gate are currently being investigated in Australia.<sup>2</sup> Eggleston et al.<sup>3</sup> revealed that more than one-third of potential fiber on a dry basis was derived from trash from Louisiana sugar cane. McGuire et al.<sup>4</sup> recently reported the processing of whole crop (i.e., the entire cane plant) in the Condong and Broadwater districts in Queensland, Australia, resulting in an 83% increase in fiber compared to conventional burnt cane harvesting.

The effect of whole crop processing on the operation and performance of a sugar mill based on laboratory and factory trials has been conducted across the globe: Scott et al.,<sup>5</sup> Reid and Lionnet,<sup>6</sup> Bernhardt et al.<sup>7</sup> and Muir et al.<sup>8</sup> in South Africa; Moller et al.,<sup>9</sup> Eggleston et al.<sup>3</sup> and Saska<sup>10</sup> in Louisiana, USA; Kent et al.,<sup>11</sup> McGuire et al.<sup>4</sup> and Thai and Doherty<sup>12</sup> in

Australia. All these studies reported poor clarification performance when processing whole crop. The measurements conducted on a laboratory scale are only used as an estimate as there would be an absence of soil and sand compared to trials based in the factory, since the dense trash harvested would trap a fair amount of soil and sand. Even for factory trials, success is reliant on the district harvest contractors supplying cane to the required specification.

Clarification is the process where maximum removal of suspended and non-sucrose impurities (e.g., minerals, proteins, polysaccharides) are removed to obtain clarified juice (CJ) with high purity and low turbidity. Effective clarification results in good sugar quality and high sugar yield. This is because the quantity and type of impurities present in CJ will affect sugar purity, while the impurity to sucrose ratio affects the viscosity of molasses and the crystallization process, and as a consequence the sugar yield.

The clarification process used in Australian sugar cane factories is simple defecation. In this process, lime saccharate is added to primary juice (PJ) to raise the pH from  $\sim 5.0$  to 7.6–7.8 to react with inorganic phosphate to form calcium phosphate flocs. The flocs settle via gravity, sweeping suspended impurities from CJ. Most sugar cane factories worldwide employ the addition of milk of lime rather than lime saccharate, and the addition of lime may be batchwise rather than continuous, and to cold juice (35–40 °C) to intermediate juice (72–76 °C) or hot juice (100 °C).<sup>8–16</sup> The intermediate liming technique is commonly employed in Australian sugar cane factories. Variations in the clarification process influence

**Received:** December 6, 2011

**Revised:** February 21, 2012

**Accepted:** February 24, 2012

**Published:** February 24, 2012

the calcium solubility, reaction time and temperature.<sup>17</sup> An acrylamide–sodium acrylate copolymer is added at the feed launder in the clarifier to enhance settling of calcium phosphate flocs. Since the phosphate level in juice improves clarification performance, phosphate in the form of superphosphate and phosphoric acid can be added to mixed juice prior to heating.<sup>17,18</sup>

Despite the amount of factory and laboratory clarification trials and research conducted to date regarding green sugar cane stalk and trash, there is little published information relating to the differentiation between the clarification of juice expressed from green cane containing half of all trash extracted (GE) and burnt cane with all trash extracted (BE).

To gain further insight into the clarification of juice expressed from GE cane, this paper reports on laboratory clarification experiments conducted on-site at Condong sugar mill, NSW, Australia, using variants of the simple liming technique. For comparison, clarification was also conducted with BE juices from Condong sugar mill. As both sets of GE and BE juices did not all originate from the same cane (i.e., variety, maturity, location and soil type), statistical analysis using least-squares means (ANOVA) was used to establish the preferred liming technique. Chemometrics analysis [Pearson's correlations and principal component analysis (PCA)] was also used to determine which component and/or parameter influences good clarification performance.

## MATERIALS AND METHODS

**Materials.** Primary juices obtained from GE cane were collected from the processing lines at Condong sugar mill, NSW, Australia, during the 4 week period the factory was investigating the effect of trash on factory operations. A mechanical cane harvester (model 3520, John Deere, Moline, IL, USA) was used to harvest the sugar cane stalk, and the speed of the harvester's fan was adjusted such that approximately half of the trash was collected. Composite PJ obtained from BE cane was also collected from the same processing lines at Condong sugar mill during the period of normal processing operations before and after the 4 week trial of processing juice expressed from GE

cane. Table 1 shows the number of sugar cane varieties harvested during the trials to indicate that the juices originating from these varieties will each vary in composition, and why it was necessary to collect composite samples. Sampling of juices was conducted every 0.5 h and a composite made after every 2 h. It was necessary to maintain the PJ temperature of collected juices in order to avoid changes in the juice properties. A total of 29 BE and 56 GE composite juice samples were analyzed.

The mineral content, polysaccharides, proteins, starch and electrical conductivity (EC) of composite PJs, collected during the period work described in this article was conducted, were determined by Thai and Doherty,<sup>12</sup> and the results are presented in Table 2.

**Clarification Tests.** All clarification tests were conducted on-site at Condong sugar mill, and PJs (pH 5.0 ± 0.5) were collected and clarified immediately in a laboratory on-site. All juices are independent samples obtained within the same period. Various clarification tests were conducted in random order and sampled during different periods to account for changes associated with cane variety (Table 1), soil type, harvesting conditions, maturity and location.

Phosphoric acid solution, 10 wt %, was prepared with an analytical reagent (AR) chemical (Chem-Supply, Gillman, Australia) and Milli-Q water with a resistivity of 18.2 MΩ cm, which was purified from a Milli-Q purification system (Millipore, Bedford, MA, USA).

Lime saccharate was obtained from the factory, and constitutes a mixture of 100 g of a 200 g/kg solution of calcium oxide and 100 g of 68 brix factory syrup.

The pH of the juice samples was measured using a portable pH meter (Hach HI160, Loveland, CO, USA) with a glass probe (model 93×218814, Eutech Instruments, Singapore) and high temperature probe (EC-FG-7350401B, Eutech Instruments).

Clarification experiments were conducted using lime saccharate, and the juice was boiled and allowed to settle in standard settling tubes [each tube of 1 L capacity with a dimension of 460 mm (h) × 55 mm (i.d.)] in an Australian Sugar Research Institute (SRI)-designed heated illuminated clarification test kit. Despite the fact that these PJs contain endogenous phosphate, it was necessary to add phosphoric acid to assist in reducing juice turbidity. Prior to clarification experiments, known amounts of phosphoric acid (up to 300 mg/kg as P<sub>2</sub>O<sub>5</sub>) were added to the juices. For BE juices, phosphoric acid dosages of up to 100 mg/kg were added to II and CI limed juices as these dosages were adequate for low juice turbidity. A dose equivalent to 5 or 7 mg/kg of a mixture of two flocculants, Superfloc 2115 and Superfloc 2120 with a weight ratio of 1:2, was added before settling the juice particles and flocs. Both Superflocs 2115 and 2120 have a similar molecular weight of 23 × 10<sup>6</sup>, with a degree of hydrolysis of 26% and 30% respectively. These flocculants (polyacrylamide-co-sodium acrylate polymer) were supplied by Cytec, Australia. The flocculant mixture and dosage were found to be most effective for the clarification of juice at Condong sugar mill. Typically, sugar mills use one type of flocculant and at a dosage of between 2 and 3 mg/kg.

Since the settled juice particles (i.e., mud) were unstirred, the mud heights were not indicative of values obtained in commercial clarifiers. The mud heights were recorded after 30 min of settling. The methods of clarification used are listed in Table 3. Cold liming was not included in this study because it resulted in the highest proportion of calcium and phosphate ions in CJ compared to other liming techniques.<sup>19</sup> Cold/hot liming (i.e., juice at 50 °C, limed to a pH of 6.2, heated to 100 °C and then limed to the final pH) was also not included in the present study because of the very high amount of lime saccharate

**Table 1. Details of the Sugarcane Varieties of GE and BE Cane Harvested**

variety	code name
202	Q202
203	Q203
205	Q205
210	Q210
211	Q211
5	CONCORD
26	MXD/OTHR
51	Q151
93	Q193
94	BN81–1394

**Table 2. Composition of GE and BE Primary Juices<sup>12</sup>**

	mg/kg on dry solids <sup>a</sup>							EC <sup>a</sup> (μS/cm on dry solids)
	P	Ca	Mg	Si	protein	polysaccharide	starch	
GE	930	1005	1655	274	5843	10872	1126	20880
BE	560	873	1120	256	4245	8328	601	20106

<sup>a</sup>Error in the analysis ±5%.

Table 3. Details of the Clarification Methods

liming technique	description
intermediate (I)	PJ (76 °C), lime saccharate to pH 7.8, heat to 100 °C, add flocculant and clarify.
intermediate/intermediate (II)	PJ (76 °C), lime saccharate to pH 6.2, maintain at 76 °C, add lime to pH 7.8, heat to 100 °C, add flocculant and clarify.
cold/intermediate (CI)	PJ (50 °C), lime saccharate to pH 6.2, heat to 76 °C, add lime to pH 7.8, heat to 100 °C, add flocculant and clarify.

required to achieve neutralization.<sup>20</sup> Samples of CJ were siphoned from the settling tubes for storage and subsequent analysis.

The settling rate of calcium phosphate flocs were determined by measuring the level of the mud interface at 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 min. The initial settling rate (cm/min) was obtained from graphical analysis of the initial linear slope.

The turbidity of CJ was determined by measuring the absorbance (A) at 900 nm in 1 cm cells against Milli-Q water.<sup>21</sup> The absorbance was obtained using a Cintra 40 double-beam UV–visible absorption spectrometer (GBC Scientific Equipment Pty. Ltd., Braeside, VIC, Australia), and the turbidity was defined as 100A.

**Light Microscope Imaging.** An Olympus BX41 System light microscope equipped with an Olympus DP71 microscope digital camera (Olympus, Melville, NY, USA) was used to examine the calcium phosphate floc structure and shape at a magnification of  $\times 10$ .

**Compositional Analyses.** Clarified juices obtained from both GE and BE juice types at Condong sugar mill were stored at  $-20$  °C and thawed prior to compositional analysis.

**Brix.** Brix is a measure of total soluble solids (percent sucrose content) in an aqueous sugar solution. The brix of the samples was measured at ambient room temperature using a Bellingham and Stanley RFM 342 digital refractometer (Tunbridge Wells, Kent, U.K.) accurate to  $\pm 0.01$  °Brix. Triplicate measurements were taken to obtain the mean brix.

**Mineral Content.** The mineral contents of the sugar juice samples and reagents (phosphoric acid and lime saccharate) were determined using a Varian Vista-MPX CCD simultaneously inductively coupled argon plasma optical spectrometer (ICP-OES, Varian Inc., Mulgrave, VIC, Australia). To reduce the interference of the organic sugar matrix, the juice samples were diluted to a sucrose concentration of  $\sim 2$  wt %. The measurements were conducted in triplicate.

**Zeta Potential.** The charge (zeta potential) of juice particles was measured on the basis of the electrophoretic mobility of particles in

suspension using a Zetasizer Nano ZS instrument (Malvern Instruments, Inc., Southborough, MA, USA). Particle charge measurements were conducted using a disposable capillary zeta cell.

The different liming techniques outlined in Table 3 were conducted on GE and BE PJ samples on a laboratory scale to measure the zeta potential of suspended particles after boiling and 15 min sedimentation.<sup>22</sup> For this study, no flocculant was added.

In a separate set of experiments, sugar cane juices were also heated at a temperature of  $52 \pm 2$  °C and  $76 \pm 2$  °C and adjusted to pH 7.8 using lime saccharate. The charge of the suspended particles was measured after 15 min of sedimentation.<sup>22</sup> All measurements were conducted in triplicate.

The juice aliquots were diluted to 4-fold (to avoid burning the electrodes on the capillary cell and produce good quality phase plots<sup>23</sup>) in a matrix of 15 brix sucrose solution and a concentration of 0.004 M of KCl (the major components in a juice solution<sup>12</sup>). A lower KCl concentration was used since a higher ionic strength will influence the state of dispersion of particles and result in the attractive force between particles to become dominant over the repulsive force.<sup>24</sup>

To determine the charge of the suspended juice particles without dilution, sample aliquots were diluted using different ratios (up to 10-fold) and the particle charge recorded. A linear curve ( $R^2 = 0.97$ ) from the data points was generated, and extrapolation to zero dilution gives the particle charge of juice. For subsequent analyses, juice aliquots diluted 4-fold were measured and the slope of the linear curve was used to determine the particle charge of juice without dilution. The results obtained using this approach were similar to those of Crees.<sup>25</sup>

**Statistical Analysis.** Chemometrics analysis (Pearson's correlations and PCA), analysis of variance (ANOVA) and tests of significance were performed using Minitab version 16.1.1 (State College, PA, USA) with a confidence level of 95%.

## RESULTS AND DISCUSSION

**Clarification of GE Juices.** Table 4 shows the clarification parameters and the main mineral contents of GE CJ. This reveals that I liming gave the fastest settling rate (70 cm/min) without phosphoric acid addition. Kent et al.<sup>11</sup> obtained values of between 10 cm/min and 30 cm/min for juice particles originating from whole sugar cane crop and higher values of 50 cm/min with juice particles originating from green sugar cane stalk showing the effect of trash. Eggleston et al.<sup>14</sup> measured the settling behavior of mud particles with juice processed from stalk and trash using milk of lime for a hot liming process. The juice was observed to foam during the clarification process, and

Table 4. Clarification Parameters and Clarified Juice Composition<sup>a</sup> of GE Juice Samples

liming	phosphoric acid dose, mg/kg	init settling rate, cm/min	final mud level, %	turbidity per 100 brix	Minerals, mg/kg on dry solids			
					P	Ca	Mg	Si
I	0	70.0 a	15.7 de	175.9 a	88 b	2208 a	608 bc	112 f
I	75	49.6 ab	22.5 abc	149.5 ab	238 ab	2872 a	1277 ab	332 abc
I	100	60.6 abcd	18.9 bcde	132.2 bcd	240 ab	2698 a	1193 abc	313 abcd
I	200	62.7 abc	22.3 abc	102.9 cde	219 ab	2705 a	867 abc	238 bcde
I	300	56.3 bcde	24.0 ab	43.0 f	158 ab	2281 a	1062 abc	226 de
II	0	30.8 b	19.1 bcde	154.2 ab	117 b	2728 a	599 c	136 f
II	75	49.5 e	16.1 cde	141.3 abc	291 a	2866 a	1295 ab	320 abcd
II	100	38.0 f	26.0 a	144.3 ab	219 ab	2937 a	1229 ab	329 abc
II	200	63.9 ab	20.8 abcd	100.7 de	235 ab	2967 a	990 abc	249 cde
II	300	55.1 cde	24.0 ab	49.8 f	205 ab	3018 a	1298 ab	310 abcd
CI	0	50.8 de	13.2 e	169.9 ab	132 ab	3302 a	814 bc	194 ef
CI	75	54.4 cde	19.4 abcde	161.4 ab	284 a	2933 a	1271 ab	334 ab
CI	100	53.0 cde	21.7 abcd	147.0 ab	242 ab	2920 a	1248 ab	318 abcd
CI	200	62.5 abc	20.0 bcd	104.7 d	206 ab	2962 a	1056 abc	261 abcde
CI	300	53.3 cde	21.0 abcd	69.7 ef	218 ab	3037 a	1527 a	349 a

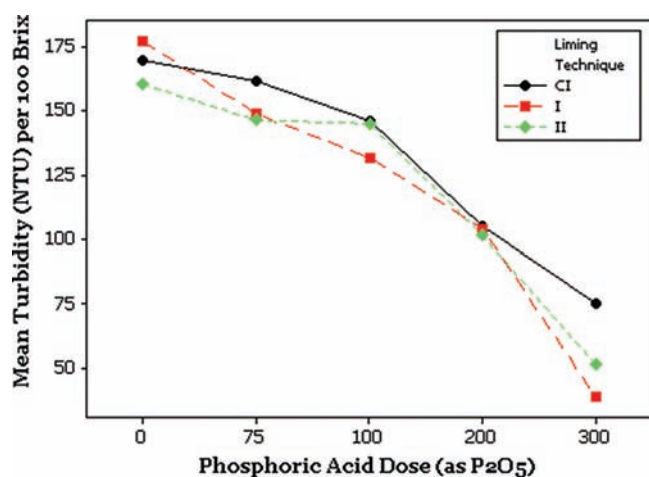
<sup>a</sup>For each clarification parameter and clarified juice composition, figures with the same letters are not significantly ( $P > 0.05$ ) different.



the settling rate was slightly variable compared to juice processed from clean stalk. Foaming is probably due to an increase in the proportion of proteins, polypeptides, polysaccharides and surface active agents.<sup>27,28</sup> The higher level of impurities present in juice derived from cane stalk and trash in comparison to juice derived from clean stalk would impact negatively on the coagulation and flocculation process because of the magnitude of charge of the juice particles (refer to the section Particle Stability) and the type of calcium phosphate flocs formed.

In comparison to the II and CI liming techniques, I liming generally tends to give lower turbidity and lower mineral contents when no phosphoric acid was added to the juice. The higher values obtained with I liming without phosphoric acid addition may be because it has the fastest settling rate. There were no significant differences ( $P < 0.05$ ) in the final mud volumes after 30 min of settling (13.5% to 26%). The differences in final mud volumes are because of the addition of phosphoric acid, which increased the amount of calcium phosphate formed. The mineral contents varied in the P (80–290 mg/kg on dry solids), Mg (600–1550 mg/kg on dry solids), Si (100–350 mg/kg on dry solids) and Ca levels (2200–3300 mg/kg on dry solids). Of significance in these results is the definite increase in Mg and Si levels with CJ obtained from phosphoric acid addition. This effect is true for all liming types.

A plot of the CJ turbidity (per 100 brix) vs phosphoric acid dosage (as  $P_2O_5$ ) is shown in Figure 1. The results show that,



**Figure 1.** The effect of phosphoric acid dose (as  $P_2O_5$ ) on the turbidity of clarified juice.

irrespective of liming technique, CJ turbidity decreases linearly with increasing phosphoric acid dosage (Table 4). This is due to the formation of increasing amounts of calcium phosphate flocs which adsorb and sweep up suspended solids during the settling process. Also, the initial addition of acid lowers the juice pH, causing the precipitation of proteins (and other organics), because the isoelectric points of these compounds would have been reached.

Higher phosphate levels are obtained with CJ processed from juices in which phosphoric acid was added (Table 4). This may typically be an equilibrium effect from the increased amount of insoluble calcium phosphate formed. However, the increased amount of residual phosphate in CJ may be due to other factors. Typically, during the clarification process, calcium ions

from lime saccharate react directly with inorganic phosphate present in juice to form calcium phosphates. However, in the situation with added phosphoric acid, calcium ions from lime saccharate will preferentially react with the added phosphate ions before reacting with any endogenous phosphate ions to satisfy the stoichiometry necessary for the formation of the calcium phosphate phases. The preferential reaction that occurs with the added phosphoric acid may be because the phosphate in juice is relatively more associated and hence less readily available. The outcome from this is that an increased amount of residual phosphate would remain in juice. So, while the addition of phosphoric acid to juice reduces CJ turbidity, it increases the amount of phosphate present in CJ and subsequently increases the amount of phosphate scale formed in the evaporators. This has implications not only in the performance of the evaporators and pans (as scale formation reduces the heat transfer coefficient) but also in increases in the costs associated with evaporator cleaning. The cost of evaporator cleaning becomes significant if phosphate scale coprecipitates with calcium oxalate and amorphous silica in the No. 4 and 5 evaporators of a quintuple evaporator set, as a combination of cleaning chemicals and longer cleaning times will be required.<sup>29</sup> An increase in phosphate level in CJ also reduces raw sugar filterability.<sup>30</sup>

Surprisingly, CJs obtained with phosphate addition (despite having lower turbidities) were significantly higher in Mg ( $\leq 101\%$ ) and Si ( $\leq 148\%$ ) concentrations (Table 4) in comparison to juice with no phosphoric acid addition. These higher concentration values cannot be accounted for from the amount present in the added phosphoric acid (ca. 5 mg/kg Si and 3 mg/kg Mg) and lime saccharate (ca. 0.5 mg/kg Si) as impurities. Increasing the dose of phosphoric acid did not proportionately increase the Mg and Si contents, because the juice contains a fixed amount of these metal ions in both the associated and dissociated forms. The increase in these metal ions in CJ must be related to reactions occurring during clarification in the presence of added phosphoric acid. When dissolved in water, silica is weakly ionized and exists in the form of undissociated silicic acid,  $H_4SiO_4$ , up to pH  $\sim 8.0$  according to the following equation:



The solubility of silica, to a certain extent, increases with increasing pH and increasing temperature.<sup>31</sup> The addition of phosphoric acid would reduce juice pH and consequently reduce silica solubility and result in the formation of colloidal silica. Divalent (e.g., magnesium) and trivalent (e.g., iron) cations lead to a reduction in silica solubility due to the formation of an insoluble metal silicate layer at the silica surface.<sup>32,33</sup> So, it is probable that insoluble silica–magnesium species are formed during clarification with added phosphate. They later dissolve during the clarification process where high temperature and pH favor their dissolution.<sup>34</sup> Work by East et al.<sup>31</sup> identified a silicate scale consisting mainly of Si and Mg present in a sugar mill heat exchanger tube deposit, probably implying the presence of a silica–magnesium complex in CJ. In the absence of phosphoric acid, silica precipitation may still occur, though to a lesser extent because of the higher initial juice pH. Some magnesium removal would occur both in the presence and in the absence of phosphoric acid via precipitation as calcium magnesium phosphate.

The mean differences in the results of CJ obtained by various chemometrics analyses as well as statistical analysis by least-

Table 5. Clarification Parameters and Clarified Juice Composition<sup>a</sup> of BE Juice Samples

liming	phosphoric acid dose, mg/kg	init settling rate, cm/min	final mud level, %	turbidity per 100 brix	minerals, mg/kg on dry solids			
					P	Ca	Mg	Si
I <sup>b</sup>	0	54.6	17.3	73.3	158	2042	970	180
II	0	66.4 a	16.0 d	78.0 b	147 b	1696 c	890 a	256 a
II	75	60.8 ab	19.5 c	59.0 c	146 b	2348 a	881 a	232 a
II	100	57.2 ab	24.8 a	49.0 c	113 c	2009 b	727 a	152 b
CI	0	57.4 ab	14.8 d	74.4 b	93 c	1321 d	683 a	234 a
CI	75	53.2 ab	22.4 b	93.9 a	142 b	2184 ab	851 a	288 a
CI	100	65.0 ab	18.0 c	74.4 b	203 a	2229 ab	928 a	256 a

<sup>a</sup>For each clarification parameter and clarified juice composition, figures with the same letters are not significantly ( $P > 0.05$ ) different. <sup>b</sup>Average value: insufficient data to perform ANOVA.

squares means in Table 4 show that the best juice quality (with regard to settling rate, P, Ca and Mg levels) is achieved with I liming followed by II and CI. The differences observed between the various liming techniques may be related to differences in the type and form of the calcium phosphate phases formed. When cold juice is limed to raise the pH to 6.2, prior to subsequent liming and heating to 100 °C, it contains a larger proportion of unreacted calcium and phosphate ions than I/II.<sup>19</sup> This is because calcium phosphate solubility increases with decreasing temperature. So, with CI liming the reaction between higher levels of calcium and phosphate ions will follow different reaction pathways that probably result in different proportions of the calcium phosphate phases.<sup>34</sup>

**Clarification Performance Comparison between GE and BE Juices.** Clarification experiments were conducted not only to identify the best liming technique for GE but also to ascertain why the clarification performance of BE has been reported to be better than that of GE. Table 5 gives a summary of the least-squares means of the clarification parameters and CJ composition when BE juices were clarified. In comparison to the data obtained from GE juice clarification in Table 4, the results show that the settling rate of calcium phosphate particles and mud heights are similar. The CJs produced from BE are of better quality than CJs from GE in terms of turbidity, phosphate and mineral ion concentrations. Since juice expressed from the inclusion of trash contains a higher proportion of non-sucrose impurities, this will affect clarification performance (e.g., coagulation and flocculation efficiency) and clarified juice quality (e.g., juice turbidity).

The Pearson's correlations were used to assess the clarification parameters and mineral contents of GE and BE CJ ( $P < 0.05$ ). There were highly positive correlations between CJ turbidity and four mineral components (P, Mg, Ca and Si),  $P < 0.03$ . However, there were highly negative correlations between the initial settling rate of flocculated mud impurities, turbidity and Ca content ( $P < 0.05$ ). There was correlation between P, Mg, and Si levels ( $P < 0.0001$ ), in agreement with the aforesaid statement that increases in Mg and Si contents particularly with clarified GE juice occur when phosphoric acid is added. The phosphoric acid dose was significantly correlated ( $P < 0.001$ ) with juice turbidity (Figure 1).

In order to identify the patterns in the clarification results and the variable/s which are influential between the clarifications of GE and BE juices, principal component analysis (PCA) was used. The use of PCA was carried out using the data presented in Tables 4 and 5, and it was established that two principal components (PC) were significant for explanation of total variability of GE and BE juices. The PC1 and PC2 account for 40.8% and 17.6% of total 100% variability,

respectively. The more significant loadings for PC1 were associated with P, Mg and Si levels. For PC2, the most influential variables were the initial settling rate and Si levels.

The score plots enable the differentiations among juices of independent origins. The score plot in Figure 2 shows that the

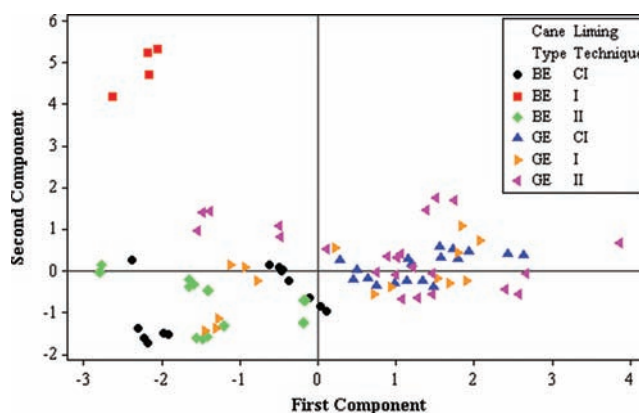
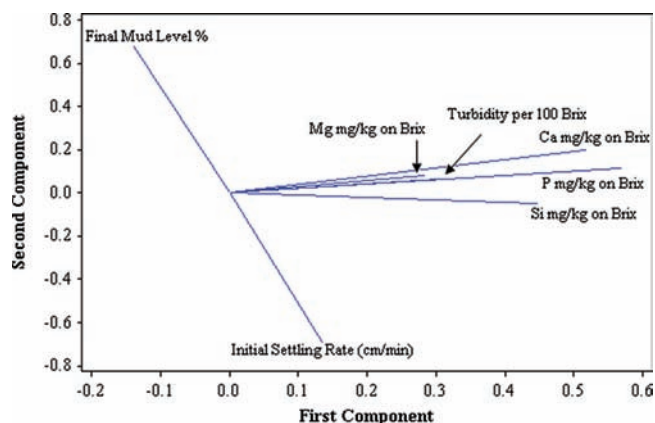


Figure 2. Score plots on clarification variables of GE and BE juice clarification on the first two principal components (PC1 versus PC2).

clarification parameters and CJ compositional analyses obtained from the clarification of GE and BE juices resulted in two distinct clusters assigned into groups of GE and BE juices. Hence, it could be said that, based on the variables, the identification of the type of juice, either GE or BE, can be clearly determined. The majority of scattered points characteristic of GE juices are shown in quadrants PC1 > 0, and for BE juices, the points are shown in PC1 < 0.

The loading plot in Figure 3 shows the correlation between the variables and the components (i.e., GE and BE scatter points) and the variance of each variable based on the length of the vector/loading plot rays. Figure 3 shows that the turbidity and the mineral components are positively correlated with GE juices (i.e., the scatter points observed in quadrants PC1 and PC2 > 0 of the score plot in Figure 2), which also agree with the data obtained from using Pearson's correlations. The loading plot also shows that the final mud level and initial settling rate of the flocculated mud impurities load heavily on the clarification of BE juices.

**Particle Stability.** The effectiveness of the clarification process is closely related to the type and morphology of the calcium phosphate phases formed, the juice composition (including suspended and dissolved compounds), the amounts of soluble inorganic phosphate, organic acids, proteins and polysaccharides, the liming technique, and the type of



**Figure 3.** Loading plot on variable on the first two principal components (PC1 versus PC2).

interactions between juice constituents. Thus, to explain the differences obtained between CJs originating from BE and those originating from GE the physicochemical properties of the juices were examined.

The zeta potential (i.e., charge) of sugar cane particles provides a good indication of the most efficient clarification method on the basis of particle stability and the removal efficiency of impurities. The closer the charge is to zero, the more likely the particles will coagulate and separate from the liquid phase. The zeta potential of limed GE and BE juice to pH 7.8 at 52 and 76 °C is presented in Table 6. Also shown in

**Table 6.** Zeta Potential of GE and BE Juice Particles Limed to pH 7.8

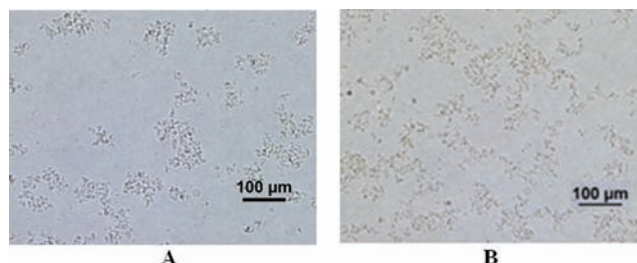
	particle charge <sup>a</sup> (mV)	
	GE	BE
I liming	-3.2	-2.5
II liming	-3.3	-2.6
CI liming	-3.4	-2.8
52 °C	-3.8	-3.2
76 °C	-4.5	-3.7

<sup>a</sup>Error in the analysis  $\pm 5\%$ .

Table 6 is the zeta potential of juices clarified using the various liming techniques without the addition of a flocculant. The charge on the particles resulting from GE is more negative than that on the BE particles, implying that the particles are more stable and would remain suspended in solution. This would result in higher juice turbidity as evident in Tables 4 and 5.

There appears to be a difference when liming at 52 and 76 °C, though the charge for GE at 52 °C is less negative than juice at 76 °C. So, cold liming is likely to result in lower CJ turbidity. However, liming at a lower temperature results in a higher Ca level in CJ which would increase the scaling intensity in the evaporators.

Figure 4 shows the light microscopic examination of calcium phosphate flocs formed from GE and BE without flocculant addition. The floc aggregates formed in BE juice are less compact than those formed with GE juice and so will have a better chance of trapping suspended solids during settling, improving the juice turbidity. A recent study by Thai and Doherty<sup>12</sup> revealed that PJ derived from BE cane resulted in a slightly lower electrical conductivity (20106  $\mu\text{S}/\text{cm}$  on dry solids), as shown in Table 2, than GE PJ (20,880  $\mu\text{S}/\text{cm}$  on dry



**Figure 4.** Light micrograph of calcium phosphate flocs formed in BE juice (A) and GE juice (B) in the absence of a flocculant.

solids), which may have impacted the floc structure shown in Figure 4.

The higher calcium and phosphate levels shown in Table 2 were also reported on GE PJ in comparison to BE PJ,<sup>12</sup> and again this would imply that the CJs derived from them should have lower turbidities than CJs obtained from BE. This is because calcium ions tend to foster flocculation<sup>35</sup> and hence reduce CJ turbidity, while phosphate ions, as seen in this and other studies, reduce juice turbidity. Recently, Doherty<sup>18</sup> acknowledged the vital role played by the initial calcium and phosphate concentrations in sugar cane juice clarification. Using calcium ion-selective electrode, Doherty<sup>18</sup> showed that the amounts of “free” calcium ions are six times lower than the values obtained by ICP-OES. The implication of this is that a proportion of calcium in juice is bound and not readily available to react with phosphate during clarification. It is also probable that some of the phosphate (as phosphorus) in juice exists in a complex and/or as an organic compound. Kampen<sup>35</sup> reported that the amount of organophosphorus in sugar cane juice, where phosphorus is covalently bonded, is ca. 30%.

As proteins and polysaccharides (including starch) are polar, there is evidence that shows sucrose has a solubilizing effect on proteins. It is likely that these materials tend to adsorb and therefore form the major interface between the juice particles and the bulk phase.<sup>36</sup> So the charges on these materials influence not only the EC but also the particle charge which dictates coagulation properties of juice particles. Thus, polysaccharides and perhaps proteins will indirectly contribute to CJ turbidity. Thai and Doherty<sup>12</sup> reported that proteins, polysaccharides and starch are higher in GE PJ than in BE PJ (Table 2). Eggleston et al.<sup>3</sup> also reported significantly high levels of starch and polysaccharides in juice expressed from green leaves in comparison to the cane stalk. Eggleston et al.<sup>37</sup> noted the present of starch, polysaccharides causes processing difficulties to the sugar cane factory and refinery and ultimately affect the quality of raw sugar. Hence, these studies show that the additional impurities from trash account for the relatively poorer quality of clarified GE juices.

Results from the present study have shown that sugar factories can successfully process juice expressed from green cane containing a reasonable proportion of trash (i.e., up to half) without significantly changing operating conditions using I liming. Phosphoric acid addition is deemed necessary (unlike with BE juices) in order to reduce CJ juice turbidity to acceptable levels. The addition of phosphoric acid, though, leads to a higher residual phosphate, Mg and Si in CJ. An attempt to explain why there was an increase in Mg and Si levels, when phosphoric acid was added, considered silica solubility under acidic conditions and the formation of silica–magnesium complexes. The use of superphosphate which does



not lower the juice pH was not examined in this study, as it may behave differently from phosphoric acid and so not elevate the Mg and Si contents. Particle charge and the nature of the particles, the juice composition, and the floc structure have been used to explain differences in clarification performance between juices expressed from GE and those juices expressed from BE. The study has also shown that more than one compound is responsible for the clarification behavior of juices expressed from sugar cane stalk and trash. Chemometrics analysis was useful to determine the clarification parameters which were most influential between GE and BE juice types. Information derived from the present study is currently being used to identify an effective clarification procedure for sugar cane juice expressed from whole green cane (i.e., cane stalk and all trash).

## AUTHOR INFORMATION

### Corresponding Author

\*Tel: +61 7 3138 1245. Fax: +61 7 3138 4132. E-mail: w.doherty@qut.edu.au.

### Funding

The authors wish to thank Sugar Research Limited, Queensland University of Technology, and Sugar Research and Development Corporation for financial assistance in the project.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors thank Condong sugar mill for supplying the sugarcane juices.

## REFERENCES

- (1) Edey, L.; Doherty, W. O. S.; Blinco, J. A.; Bullock, G. E. The sugarcane biorefinery: energy crops and processes for the production of liquid fuels and renewable commodity chemicals. *Proc. Aust. Soc. Sugar Cane Technol.* **2005**, *27*, 9–22.
- (2) DeltaElectricity, Delta Sustainability Report. 2010.
- (3) Eggleston, G.; Grisham, M.; Tew, T.; Triche, R.; Antoine, A. Potential biomass quantity and sugar processing quality of trash and stalk tissues by different US sugarcane varieties. *Int. Sugar J.* **2009**, *111*, 108–118.
- (4) McGuire, P. J.; Inderbitzin, M.; Rich, B.; Kent, G. A. The effect on whole crop harvesting on crop yield. *Proc. Aust. Soc. Sugar Cane Technol.* **2011**, *33*, 1–12.
- (5) Scott, R. P.; Falconer, D.; Lionnet, G. R. E. A laboratory investigation of the effects of tops and trash on extraction, juice quality and clarification. *Proc. S. Afr. Sugar Technol. Assoc.* **1978**, *52*, 51–53.
- (6) Reid, M. S.; Lionnet, G. R. E. The effects of tops and trash on cane milling based on trials at Maidstone. *Proc. S. Afr. Sugar Technol. Assoc.* **1989**, *63*, 3–6.
- (7) Bernhardt, H. W.; Pillay, V.; Simpson, A. Impacts on greencane harvesting on sugar factory operation at Sezela. *Proc. S. Afr. Sugar Technol. Assoc.* **2000**, *74*, 369–372.
- (8) Muir, B. M.; Eggleston, G.; Barker, B. The effect of green cane on downstream factory processing. *Proc. S. Afr. Sugar Technol. Assoc.* **2009**, *82*, 164–199.
- (9) Moller, D. J.; Broadfoot, R.; Bell, S.; Bakir, H. Whole crop processing at Broadwater mill: impacts on process operations. *Proc. Aust. Soc. Sugar Cane Technol.* **2010**, *32*, 573–587.
- (10) Saska, M., Composition of non-stalk components of sugarcane and field residues and their effects on composition of industrial mixed juice, in International Society of Sugarcane Technologists Workshop. 2008: Reunion Island.
- (11) Kent, G. A.; Moller, D. J.; Scroope, P. D.; Broadfoot, R. The effect of whole crop processing on sugar recovery and sugar quality. *Proc. Aust. Soc. Sugar Cane Technol.* **2010**, *32*, 559–572.
- (12) Thai, C. C. D.; Doherty, W. O. S. The composition of sugarcane juices derived from burnt cane and whole green cane crop. *Proc. Aust. Soc. Sugar Cane Technol.* **2011**, *33*, 1–9.
- (13) Eggleston, G.; Monge, A.; Pepperman, A. Preheating and incubation of cane juice prior to liming: A comparison of intermediate and cold lime clarification. *J. Agric. Food. Chem.* **2002**, *50*, 484–490.
- (14) Eggleston, G.; Grisham, M.; Antoine, A. Clarification properties of trash and stalk tissues from sugar cane. *J. Agric. Food. Chem.* **2010**, *58*, 366–373.
- (15) Eggleston, G.; Monge, A.; Ogier, B. E. Sugarcane factory performance of cold, intermediate, and hot lime clarification processes. *J. Food Process. Preserv.* **2003**, *26*, 433–454.
- (16) Paley, L. A. CLarification and treatment of sugar juice. United States Patent, 1976, 3,994,743.
- (17) Doherty, W. O. S.; Edey, L. A. An overview on the chemistry of clarification of cane sugar juice. *Proc. Aust. Soc. Sugar Cane Technol.* **1999**, *21*, 381–388.
- (18) Doherty, W. O. S. Improved sugar cane juice clarification by understanding calcium oxide-phosphate-sucrose systems. *J. Agric. Food. Chem.* **2011**, *59*, 1829–1836.
- (19) Doherty, W. O. S.; Greenwood, J.; Pilaski, D.; Wright, P. G. The effect of liming conditions in juice clarification. *Proc. Aust. Soc. Sugar Cane Technol.* **2002**, *24*, 443–451.
- (20) Doherty, W. O. S., Personal communication. September 6, 2010.
- (21) BSES Laboratory Manual for Australian Sugar Mills, Method 10. Vol. 2; Bureau of Sugar Experiment Stations: Indooropily, QLD, Australia, 2001.
- (22) Wu, X.; Ge, X.; Wang, D.; Tang, H. Distinct mechanisms of particle aggregation induced by alum and PACl: floc structure and DLVO evaluation. *Colloids Surf, A* **2009**, *347*, 56–63.
- (23) Malvern. Concentration Limits for Zeta Potential Measurements in the Zetasizer Nano. [cited 2011; Available from <http://www.iesmat.com/Lectura%20recomendada/Productos-MAL/DLS-Concentration%20Limits%20for%20Zeta%20Potential%20Measurements%20in%20the%20Nano.pdf>.
- (24) Jiang, J.; Oberdorster, G.; Biswas, P. Characterization of size, surface charge, and agglomeration state of nanoparticle dispersions for toxicological studies. *J. Nanopart. Res.* **2009**, *11*, 77–89.
- (25) Crees, O. L. The flocculation of cane sugar muds in Australian raw sugar factories. 1988, Thesis (PhD), James Cook University of North Queensland, Department of Chemistry and Biochemistry.
- (26) Doherty, W. O. S.; Fellows, C. M.; Gorjian, S.; Senogles, E.; Cheung, W. H. Flocculation and sedimentation of cane sugar juice particles with cationic homo- and copolymers. *J. Appl. Polym. Sci.* **2003**, *90*, 316–325.
- (27) Cheng, H. T.; Lin, W. F. Studies on the foam-causing substances in raw cane sugar. *Proc. Int. Soc. Sugar Cane Technol.* **1983**, *18*, 129–137.
- (28) Doherty, W. O. S.; Simpson, R. F.; Rackemann, D. W. Enhanced performance of caustic soda used for the removal of scale in sugar mill evaporators. *Proc. Aust. Soc. Sugar Cane Technol.* **2007**, *29*, 411–419.
- (29) Doherty, W. O. S. Personal communication. November 16, 2010.
- (30) Bennett, M. C.; Regnauth, J. M. The effects of calcium and phosphate in cane juice clarification. *Int. Sugar J.* **1960**, *62*, 13–16.
- (31) East, C. P.; Doherty, W. O. S.; Fellows, C. M.; Yu, H. Characterization of sugar juice heat exchanger tube deposit. *Surf. Interface Anal.* **2011**, *43* (9), 1231–1239.
- (32) Iler, R. K. *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry*; Wiley: New York, 1979.
- (33) Patterson, R. E. Influence of silica properties on performance of antifoams in pulp and paper applications 2. In-situ hydrophobing. *Colloids Surf, A* **1993**, *74*, 115–126.

(34) Deben, J. G. The chemistry of calcium phosphate precipitation in cane sugar juice clarification, Parts I, II and III. *Int. Sugar J.* **1976**, *78* (35–39), 73–75.

(35) Kampen, W. H. Improved clarification with a cationic flocculant. *Int. Sugar J.* **1997**, *99*, 353–360.

(36) Bennett, M. C. Behaviour of adsorbed protein in cane sugar juice. *J. Colloid Sci.* **1957**, *12*, 434–451.

(37) Eggleston, G.; Viator, R. P.; Grisham, M. Glyphosate ripener effects on the processing quality of different sugarcane tissues. *Proc. Int. Soc. Sugar Cane Technol.* **2007**, *26*, 1460–1467.