SUGARCANE COMPONENTS THAT AFFECT EFFICIENCY OF MEMBRANE FILTRATION: IDENTIFICATION AND REMOVAL

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ABSTRACT

Milling of sugarcane (Saccharum officinarum) produces a juice containing sucrose, other soluble materials including high molecular weight polymeric colorants and polysaccharides, and particulates in suspension. The extraneous material in sugarcane juice is implicated in fouling of membranes and loss of efficiency of membrane filtration processes. Studies of the colloidal chemistry of sugarcane juice components, reported herein, have shown that sugarcane juice components may form very high molecular weight aggregates responsible for membrane fouling. Removal of tightly held, colloidally suspended particulates in sugar juices or syrups by physical means before membrane filtration is important to ensure reduction of colorants and crystallization inhibitors. Clarified juice was centrifuged by means of a high speed disk-stack centrifuge to remove membrane fouling materials. The disk-stack centrifuge removed some 65% of colloidal suspended solids from the clarified sugarcane syrup. Flux rates of membrane colloidal filters were increased more than twice with concomitant decrease in cycle times for filtrates. Subfractionation of the centrifuge effluent by membrane nominal molecular weight cutoff types afforded enriched high polymer, and permeates of lower molecular weight colorant or components which were further analyzed by gel permeation chromatography, compositional analysis, and nuclear magnetic resonance spectroscopy.

Keywords: Membranes, ultrafiltration, turbidity, centrifugation, clarifier juice, sugarcane

INTRODUCTION

Preparative membrane chemistry and gel chromatography can be used to both isolate and break apart the tight network of sugarcane polymers that defy technology intended to eliminate interferences in processing streams and improve sugar recovery.

Earlier studies on the chemical composition of materials causing turbidity in clarified sugarcane juice and interference with crystallization established the need to remove such suspended colloids (Fort and Smith, 1954). Using a Sharples supercentrifuge (60,000 x force of gravity) Fort and Smith (1954) were able to reduce the color of clarified juice by 50%. At the same time, these authors removed 60% of ash, 90% of turbidity, and 80% of silica. Pelleted residues from the clarified juice were rich in organics, silica, ash, iron, lipids, protein, and starch. They found that the rate of crystal growth to large grains was much faster after centrifuging the clarified juice. Although Fort and Smith did not think that centrifugation of clarified juice would be practical on a factory scale, present day centrifugation equipment is capable of the high speed feed volume of the juice (thousands of gallons per minute) as well as the efficiency to remove turbidity.

The advantages of improved clarification were also investigated by Roberts et al. (1994) while testing DEAE-modified bagasse as an adsorbent for removing colorant and turbidity. Upon centrifugation of clarified sugarcane juice at 15,000 x force of gravity, Roberts found the sedimentable turbidity to consist of discreet carbohydrate, lipid, and mineral components.
The promise of centrifugal pretreatment for membrane separation of clarified juice has been noted recently (Monclin 1995a and 1995b). The various molecular weight ranges of native sugarcane juice polymers as well as the products generated under the stress of juice evaporation have been examined extensively in previous papers by the Sugar Processing Research Institute, Inc. (SPRI) (Carpenter and Roberts, 1975; Clarke et al. 1984, 1990, and 1992; Godshall et al., 1988; Godshall and Grimm, 1994; and Vercellotti et al., 1996). These co-authors from SPRI have reported chromatographic separations at various stages of the sugar purification process and across the harvest season to characterize polymeric by-products.

In recent papers from the Sugar Processing Research Institute (Vercellotti et al., 1998a and 1998b; and Clarke et al., 1998) membrane and centrifuge treatments were described which separated sucrose from suspended colloidal material, colorant and other molecules in sugarcane juice that interfere with crystallization. That work also explored the composition of components of sugarcane juice which foul or diminish efficiency of ultrafiltration equipment in the sugar industry. Historical perspective of the industrial importance of membrane processing of sugarcane juice was emphasized in these reports (Vercellotti et al., 1998a and 1998b; and Clarke et al., 1998) and the reader is referred to those papers. In this report more detailed analyses of macromolecular components isolated from sugarcane juice that interfere with membrane processes are described. Objectives focused on the following concepts as useful goals to improve processing.

- High speed centrifugal pretreatment of clarified juice or molasses to divert troublesome colloidal suspensions from sugar recovery streams. The significant lowering of turbidity makes the solutions more amenable to subsequent membrane processes and produces economically efficient primary process streams with higher sucrose yields.
- Use of preparative chromatographic and membrane techniques to isolate aggregated components in the juice or syrup which coalesce to clog membrane pores, form evaporator build-up, or impede sugar crystallization during molasses exhaustion.
- Compositional assessment of those indigenous sugarcane juice components, which drastically change membrane flux rates, by physical or chemical means, with the intention of applying remediation techniques to membrane fouling problems by chemical, biochemical or physical processes not yet currently in use.

MATERIALS AND METHODS


Analyses performed by ICUMSA methods were pol, refractometer Brix, apparent purity, pH, color, haze (ICUMSA, 1994), and dry substance solids by heated vacuum oven drying. Dextran was analyzed by the official AOAC Roberts Method. Total polysaccharides and starch were analyzed by SPRI methods. High performance liquid chromatography of sucrose, glucose, and fructose for the Louisiana factory samples was performed on a Dionex PAC-1 column with pulsed amperometric detection using the Dionex AI-450 integrating computer program (AOAC, 1995a).

Gel permeation chromatography of colorant polymers was carried out according to Khan and coworkers (Khan et al., 1994) as well as Saska and Oubrahim (Saska and Oubrahim, 1987).
Application of membrane ultrafiltration to soluble molasses polymer isolation and preparative gel filtration were carried out on high molecular weight colloidal filter retentates of final C molasses as in Vercellotti et al. (Vercellotti et al., 1985; and 1998a).

Industrial centrifuge information, equipment, and trials were obtained from the Alfa Laval Sharples Company, Warminster, PA, U.S.A. An Alfa Laval Model 403 pilot scale disk-stack centrifuge with maximum flow-through of 6 gallons per minute at 8000 x g was used on the stream coming from the clarifier at 200°F.

Nuclear magnetic resonance spectroscopy of Sephadex G-200 fractions was conducted on a Bruker n.m.r. spectrometer with 90 MHz carbon and 360 MHz proton fields using samples saturated in perdeuterated methylsulfoxide (DMSO-d6). Sugars were estimated in the hydrolyzates of fractions as alditol acetates by gas chromatography using an SP 2340 column (Supelco, Bellefont, PA, USA) according to Theander (Theander, 1995; AOAC, 1995) and Englyst (Englyst and Cummings, 1988).

RESULTS AND DISCUSSION

Membrane Separations of Polymers in Final Molasses

Fractionation of sugarcane final C molasses was carried out using colloidal filters as illustrated in Figure 1. In this preparative molasses polymer isolation work, the Sugar Processing Research Institute, Inc., has used both organic and ceramic membranes successfully (Vercellotti et al., 1998a and 1998b). From many years of experience we know that in such a preparative chemistry application it is essential, for both membrane types, to clarify the molasses samples by centrifugation at 7000 or more times gravity as a relative centrifugal force (on our 6 liter, preparative laboratory centrifuge that is about 5000 rpm) to avoid changing properties of the colloidal filter or ultrafilter or foul the membrane so that preparative flow rates are no longer useful. Some 9.3% of the molasses sediments on initial centrifugation, which is not surprising, given the nature of the colloidal material being put forward past dissolved solid materials, filters, or clarifiers, and being concentrated in final molasses as heat induced polymers or coordination networks with ash. The nature of this pelleted material and related substances has been considered in greater detail by Goynes (Goynes et al., 1998) and Ingber (Ingber et al., 1998).
Final C Molasses Separation
Using Membrane Ultrafilters

1 kg/7 l of water
81 °Brix; 810 g solids

Centrifuge 5000 rpm/30 minutes
Save Pallet
78 grams; 9.63 percent

Retentate, >1,000,000 Da.
Dialyzed and concentrated by R/O
5.8 grams; 0.72 percent

Fresenius P25, 0.2 micron
Cross-flow colloidal
filter. M.W. cutoff, ca. 1,000,000 Da.
Continuous dialysis/diafiltration
with Cordes-Dow C-DAK
hollow fiber dialyzers (2),
M.W. cutoff, ca. 1500 Da.

Permeate of colloidal
filter. Range <1,000,000 Da
to >1500 Da

Dialysis/diafiltration with
Cordes-Dow C-DAK
hollow fiber dialyzers (2),
M.W. cutoff, ca. 1500 Da.

Concentrate dialyzed permeate
with R/O; 88 grams; 10.86 percent; >1500 Da.

Disodium Dialyze (78.79 percent
dialyzable)

Fig. 1 : Final C Molasses Separation Using Membrane Ultrafilters
Separation of Aggregate by Preparative Gel Filtration on Sephadex G-200

Final C Molasses Retentate of Colloidal Filter
Separation of Aggregate by Preparative Gel Filtration on Sephadex G-200

<table>
<thead>
<tr>
<th>Retentate, &gt;1,000,000 Da</th>
<th>Permeate of colloidal filter, &gt;1,000,000 Da</th>
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</thead>
<tbody>
<tr>
<td>Dialyzed and concentrated</td>
<td>10.78 g solids (1.075% of Final C Molasses)</td>
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<tr>
<td>&gt;1.3 x 1,000,000 Da</td>
<td>to &gt;1000 Da</td>
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<tr>
<td>5 g solids (0.5% Final C Molasses)</td>
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G-200
2.1 gal 0.05M PO4 5 g Retentate pH 8.0

<table>
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<tr>
<th>Wash on with 450 ml buffer</th>
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<tr>
<th>Fraction 1</th>
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<tr>
<td>750 ml</td>
<td>100 ml</td>
<td>400 ml</td>
<td>550 ml</td>
<td>450 ml</td>
<td>450 ml</td>
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<tr>
<td>1.177 g (23.43%) yellow/grey opalescent</td>
<td>1.278 g (25.55%) orange/grey opalescent</td>
<td>8.5954 g (7.89%) brown/orange</td>
<td>1.346 g (26.57%) dark brown</td>
<td>8.6355 g (13.15%) very dark brown/black</td>
<td>6.2130 g (4.28%) orange/brown</td>
</tr>
<tr>
<td>Mol. wt. range 2 million to 50,000 Da</td>
<td>Mol. wt. range 1 million to 25,000 Da</td>
<td>Mol. wt. range 200,000 to 10,000 Da</td>
<td>Mol. wt. range 10,000 to 10,000 Da</td>
<td>Mol. wt. range 45,000 to 5000 Da</td>
<td>Mol. wt. range 25,000 to 600 Da</td>
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</table>

TOTAL* 3110 ml buffer

*Total 4,6932 g (100%)
Recovery 99.6% from column
To determine the nature of the colloidal retentate of sugarcane final C molasses, the dialyzed retentate was subjected to size exclusion chromatography on the cross-linked dextran, Sephadex G-200, as shown in Figure 2 (Clarke et al., 1990; Clarke et al., 1992). The exclusion limit on Sephadex G-200 is about 1 million Da, with an effective fractionation range of 5000 to 800,000 Da. The retentate was separated into 6 fractions as shown in Figure 1. The column diagram (Figure 1) gives the distribution of molecular weights across the elution volume from Blue Dextran marker (2 million Da, completely excluded) to potassium dichromate (gram formula weight 294, totally included).

The presence of huge aggregates of membrane-fouling materials is postulated from the data in Figure 2. The retentates from molasses membrane separation have a nominal molecular weight cutoff greater than 1,000,000 Daltons, and yet, on size exclusion chromatography, this aggregate was resolved into 6 molecular weight fractions well below that range. Even after extensive dialysis, sucrose was still entrapped in the retentate. This retentate material was highly viscous.

Table 1 gives the distribution of total polysaccharides, dextran, and starch in the gel filtration fractions of the colloidal retentate from final molasses. It was surprising to find that in such a highly pigmented mixture Fraction 1 was nearly colorless. In fact, pigmentation and colorant actually increased going to lower molecular weight (left to right)(Bento, 1995). All the fractions contained significant quantities of polysaccharide, with Fractions 1 and 2 containing most of the dextran, indicating the presence of high molecular weight dextran. The fact that various molecular weight distributions of these polymers is present demonstrates the heterogeneous nature of the plant source from which they derive. The distribution correlates with earlier observations (Carpenter and Roberts, 1975; Clarke et al. 1984, 1990, and 1992; Godshall et al., 1988; Godshall and Grimm, 1994; and Vercellotti et al., 1996) that high molecular weight colorants are selectively occluded in the crystals during crystallization.

Table 1: Distribution of Total Polysaccharides, Dextran, and Starch in Gel Filtration Fractions of Colloidal Retentate (mol. wt.>1,000,000 DA) from Final C Molasses

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Total polysaccharide (%)</th>
<th>Dextran (%)</th>
<th>Starch (%)</th>
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<tbody>
<tr>
<td>Fraction 1</td>
<td>23.00</td>
<td>9.49</td>
<td>0.20</td>
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<tr>
<td>Fraction 2</td>
<td>5.16</td>
<td>1.65</td>
<td>0.25</td>
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<tr>
<td>Fraction 3</td>
<td>17.73</td>
<td>0.61</td>
<td>0.20</td>
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<tr>
<td>Fraction 4</td>
<td>2.04</td>
<td>0.59</td>
<td>0.18</td>
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<tr>
<td>Fraction 5</td>
<td>34.73</td>
<td>0.81</td>
<td>0.16</td>
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<tr>
<td>Fraction 6</td>
<td>8.18</td>
<td>1.61</td>
<td>0.16</td>
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Analytical gel permeation chromatography was performed on each of the Sephadex G-200 fractions using Toyo Soda TSK columns as described in the EXPERIMENTAL (Bento, 1995; Khan et al., 1994; Saska and Oubrahim, 1987; Vercellotti et al., 1996). The very high molecular weight distribution of Fraction 1 was compared with Fraction 2, which lost much of the polymer near the
void volume. Both ultraviolet and refractive index detection were used to detect the relative masses injected on the column and to characterize the aromatic content of each. Comparing Fractions 1 and 2, Fraction 1 contains about a third of the intensity of ultraviolet absorbing material as Fraction 2. Similarly, in Fractions 3 and 4 the intensity of ultraviolet absorbing material is higher than in Fractions 1 or 2. The greatest absorbance is seen in the lowest molecular weight fractions, Fractions 5 and 6, which are coincidentally very highly visibly colored.

The proton nuclear magnetic resonance (n.m.r.) spectra, summarized in Table 2, of final molasses colloidal retentate fractions from gel filtration demonstrated some of the same observations made in the previous paragraph about their analytical gel chromatography (Khan et al., 1994). Protons of anomic carbons in the region 5.2-5.4 ppm, as found in all the fractions, are indicative of an alpha-D-linked polysaccharide and probably can be attributed to dextran ((Khan et al., 1994). In addition to carbohydrate peaks in all of the fractions, aliphatic lipid chemical shifts are apparent across all the fractions separated. Both Fort and Smith (1954) and Roberts et al. (1994) made note of these lipid components in the suspended turbidity residues of clarified juice (as much as 12% by weight). The fact that so much lipid is aggregated with the other polysaccharide and polyphenolic components is very interesting in terms of trying to explain the cohesiveness of the membrane fouling components. Other pyranose ring protons in the 3 to 5 ppm chemical shift range are also typical of such a structure. No obvious aromatic resonances are found in the proton spectrum of Fraction 1, giving the impression that it is predominantly polysaccharide as concluded above. Fraction 2 begins to have aromatic resonances in the chemical shift range of 6 to 9 ppm. Fractions 3 and 4 continue to have polysaccharide character in proton clustering but they indicate much more of the lower energy resonance of more highly substituted aromatic rings, probably polymers from the peak broadening. Fractions 4 and 5 have high intensities of these broad aromatic peaks in the 6 to 10 ppm range. The somewhat lower intensity of aromatic rings and greater resolution of proton chemical shifts at higher energy (aliphatic) would indicate that Fraction 6 is predominantly low molecular weight material of a mixed carbohydrate and substituted aromatic nature. 13C nuclear magnetic resonance spectra of these retentate gel filtration fractions confirm the polysaccharide and aromatic nature of the proton assignments above.
<table>
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<tr>
<th>Sample</th>
<th>10 ppm acidic</th>
<th>9 ppm phenolic</th>
<th>8 ppm benzylic</th>
<th>7 ppm olefinic</th>
<th>6 ppm anomic</th>
<th>5 ppm aromatic</th>
<th>4 ppm proton</th>
<th>3 ppm hydroxylic</th>
<th>2 ppm carboxylic</th>
<th>1 ppm methyllic</th>
<th>0 ppm aliphatic</th>
<th>1 ppm nonpolar</th>
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33
The carbohydrate composition of the fractionated material is shown in Table 3. These data correspond with the proton nuclear magnetic resonance spectroscopy data in Table 2, indicating the presence of carbohydrate in all fractions. As the molecular weight decreases, the amount of carbohydrate (polysaccharide) decreases and the amount of aromatic polyphenolic character increases, as shown by the n.m.r. data. The amount of polyphenolic material correlates with an increase in visible color. The complexity of the polysaccharide composition also increases with decreasing molecular weight.

From all of the above it is clear that a strong aggregate forms composed of high and low molecular weight material in the colloidal filtration of sugarcane final C molasses. Each of the fractions examined were involved in actual processes that fouled membranes. Why these polymers fill the narrow pore size of the membranes even when the viscosity is relatively low and flow rate is quite rapid is not understood. These are transverse flow membranes (cross flow at a 90° angle to the flux) and generally can resist fouling (Cheryan, 1998). Trapped in this aggregate, held together with electrostatic and other hydrophobic or hydrophilic forces, are high molecular weight dextrans, polysaccharides, and polyaromatics which, in turn, build up complex aggregated layers on the membrane surface and eventually cause fouling and diminished flux. Much more work must be done on other insoluble residues carried along in the colloidal filtrate. An unexpected aspect of this treatment was that in the retentate, even after long dialysis, a significant quantity of sucrose was still entrapped in the aggregate. A comparison of the integral role of sucrose in membrane concentration of molasses and its inclusion in the retentate aggregate will be given below.

Table 3: Carbohydrate composition of Sugarcane Final C Molasses Retentate Fraction from Separation on Preparative Gel Filtration Column

| Table 3. Carbohydrate Composition of Sugarcane Final C Molasses Retentate Fractions from Separation on Preparative Gel Filtration Column |
|---|---|---|---|---|---|---|
| Fraction 1 | Fraction 2 | Fraction 3 | Fraction 4 | Fraction 5 | Fraction 6 |
| Percent sugars | Percent sugars | Percent sugars | Percent sugars | Percent sugars | Percent sugars |
| Rhamnitol | 0.38 | 0.56 | 0.00 | 2.31 | 2.75 | 3.27 |
| Arabinolol | 0.83 | 16.60 | 20.95 | 19.72 | 20.07 | 41.92 |
| Xyloolol | 0.60 | 5.12 | 12.85 | 7.81 | 11.47 | 20.45 |
| Mannitol | 3.66 | 3.02 | 8.99 | 4.18 | 5.28 | 12.68 |
| Galactitol | 9.33 | 17.32 | 5.71 | 9.46 | 11.47 | 5.73 |
| Glucitol | 73.68 | 55.38 | 45.99 | 43.77 | 48.97 | 15.95 |
| Total recovery of sugars on hydrolysis(%) | 91.57 | 89.30 | 67.75 | 71.27 | 44.56 | 47.41 |

Centrifugation Studies on Clarified Juice

Prior to membrane filtration, a physical pre-separation system was sought to remove fine suspended solids and other colloidal material that form the above aggregates from sugarcane juices and syrups. Alfa Laval Sharples Centrifuge Corporation (Tumba, Sweden) was consulted. Alfa Laval equipment, of the disc-stack centrifuge type, is used in molasses desludging before molasses fermentation or ion exclusion separator recovery of beet or cane sugar but had not otherwise been employed in sugar manufacture.
Laboratory scale centrifugation trials were conducted at the Alfa Laval Centrifuge Demonstration Laboratory (Warminster, PA), on fresh samples (not frozen) of sugarcane juices. Mixed, crusher and clarified juices and evaporator syrup were transported by S.P.R.I. personnel to the Laboratory. It is important that juices and syrups are not subjected to freezing because the freezing process makes clarification (or separation of solids) from any juice or syrup proceed much more rapidly and efficiently than it does in the fresh state.

Trials were made with both a high speed decanter-separator and a disc-stack centrifuge. Separation of suspended solids from whole mixed juice and crusher juice could not be achieved with either system alone, but required both types of separator in series (decanter first) because of the wide range of particle sizes in mixed or crusher juices. There is a claim in the patent literature that equipment similar to disc-stack centrifuge will achieve this separation (Monclin 1995a and 1995b), but the study described here did not find this to be the case. Cane juice after standard factory clarification (settling clarification with lime and polyacrylamide added to mixed juice) was successfully separated by disc-stack centrifuge alone to remove two-thirds of turbidity. Evaporator syrup could also be successfully separated by disc-stack centrifuge alone, but required too long a treatment time.

The treated juices were tested to determine degree of improvement for subsequent membrane filtration treatments. In the current work, a comparison of the colloidal filtration characteristics (0.2 μ average pore size or approximately 2 million Dalton nominal molecular weight cut-off ceramic filter) of supernatant effluent from a 60-disc continuous flow centrifuge was made for clarified juice at rates of 0.5 and 1.0 gallons per minute at a nominal temperature of 200°F. Both the feed clarified juice and supernatant coming out of the centrifuge were taken in 3.7 liter jugs each. A typical 3.7 liter sample of the discharge/sludge was also taken for examination of contents. The samples were measured for color and turbidity using the ICUMSA method for color (ICU).

Turbidity measurement is determined by subtracting the ICU of the filtered solution from the ICU of the unfiltered solution, both measured at 420 nm in the same cell. Because of the widespread use of measurement of “turbidity” at 720 nm, that wavelength was used also. Since there is only a low baseline of color absorption at 720 nm in the visible range, a direct reading can be made for turbidity as above at 720 nm and the turbidity absorbance units calculated for the suspended particulate alone since color is not the dominant absorbing species. The reading of turbidity at 720 nm is used as an alternative to the 420 nm reading. The latter is preferred because the 720 nm reading may often be negative even when turbidity is visually observed.

Although the Alfa Laval Model 403 disc-stack centrifuge is a small model, running only a few gallons per minute (maximum flow rate 6 gallons per minute at 8000 x g and 200°F), experience has shown that scale-up is effectively linear to 400 gallons per minute. The clarified juice originates from simple settling defecation of mixed juice with lime, phosphoric acid, and water soluble organic polymers. While the flocculation process removes much turbidity from the mixed juice, a large amount of suspended colloidal solids remains which could, heretofore, only be removed by microfiltration. This suspended solid material is measurable by spectrophotometric turbidity measurements. Membrane filtration of this clarified sugarcane juice to reduce color is still not possible without pretreatment. Reduction of the turbidity in clarified juice by high speed centrifugation results in a clarified juice with much less burden of solids to be carried forward to evaporators and pans. This improvement in the quality of the juice results in lowered maintenance costs and higher yields of higher quality crystallized sugar.

Two samples of the highest performance efficiency from the Alfa Laval Model 403 centrifuge were studied for residual turbidity and colloidal solids. Composition of the feed clarifier juice and the effluent from one of the sampling rates (1 gal/min) are shown in Table 4. These had centrifuge effluent (supernatant) rates of 0.5 gal/min and 1.0 gal/min as flow rates of the small pilot unit. At these rates about two-thirds of the dispersed colloidal content of the feed clarifier juice was
removed in one pass. Membrane filtration studies with 0.2\( \mu \)M pore size Applexion ceramic colloidal filters indicated that at that centrifuge efficiency, membrane flux was improved about 2.5 times that over the feed even though some 33% of colloidal solids still remained in the supernatant stream. These samples represented the very best effort by the small Alfa Laval Model 403 versus the sedimentable colloidal content in the feed clarifier juice. All other higher rates of centrifugation streams were less efficient and, therefore, SPRI performed studies on these samples to try and discern what remained in the supernatant even after some’ 8000-10,000 x gravity force was applied.

Table 4 Composition of clarifier juice before and after Disk-Stack centrifugation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Percent Solids</th>
<th>Brix</th>
<th>Turbidity 420nm (ICU)</th>
<th>Dextran (PPM)</th>
<th>Polysaccharides (PPM)</th>
<th>Starch (PPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed clarifier Juice (before centrifuge)</td>
<td>11.18%</td>
<td>12.5</td>
<td>3617</td>
<td>560</td>
<td>3550</td>
<td>265</td>
</tr>
<tr>
<td>Supernatant from centrifuge (after centrifuge)</td>
<td>11.89%</td>
<td>11.96</td>
<td>0</td>
<td>420</td>
<td>2313</td>
<td>196</td>
</tr>
<tr>
<td>Discharge from centrifuge</td>
<td>7.9%</td>
<td>n.a.</td>
<td>190380</td>
<td>33%</td>
<td>61%</td>
<td>8387</td>
</tr>
</tbody>
</table>

Although the lengthy membrane filtration performed on the two samples above and the respective feed clarifier juices (about 1 gallon each) to isolate residual colloids was not possible for all centrifuge rates from 0.3 gal/min to 6 gal/min that were studied, the retained samples were all measured for turbidity loss and ability to pass easily through a 0.2\( \mu \)M membrane on a 2.5 cm Swinny-type adapter and 10 cc syringe. Resistance to filtration began with supernatant effluent from a centrifuge rate of 4 gal/min (less sludge removed than at a slower speed) whereas it was possible to filter the uncentrifuged feed stream only slightly before blockage. At 3 gal/min, however, the centrifuge supernatant was still permeable to the membrane much like at 1.0 gal/min sample. The 3 gal/min sample has turbidity reduction and total colloidal solids content of 50% that of the feedstock as contrasted to 67% for the 1 gal/min. The 4 gal/min and higher flow rate samples resist filtration strongly and contain much more than 50% residual turbidity and total non-sedimentable solids, indicating that these flow rates are much less efficient for proper sedimentation of highly emulsified clarifier juice solids. Membrane flux approaches that of the feed clarifier juice above 3 gal/min indicating little advantage in increasing the Model 403 disk stack centrifuge throughput above 3 gal/min. A maximum centrifugal efficiency coefficient can be calculated from such a pilot scale run and applied to use of the 400 gal/min high flow disk stack units with sugarcane clarifier juice.

Centrifugation brought about 70% to 80% reduction in suspended solids (turbidity) with anticipated decrease in juice viscosity and evaporator scale formation, and should improve processing efficiency by 10% to 20%. Reduction in suspended solids, and corresponding decrease in viscosity, will improve crystallization rate, by an estimated minimum of 10%. The treatment will improve
crystal yield by an estimated 10% to 20%, and will improve sugar quality by reducing turbidity (sediment) by 80% to 90%. Tests of membrane filtration of clarified juice, through a ceramic type filter of 0.2 μM average pore size, showed that centrifugation made an improvement in flux rate of 80% to 100% above that of untreated clarified juice. Cycle times for membranes (between cleanings) should be, therefore, approximately doubled.

CONCLUSIONS

Colloidal chemistry of molasses retentates indicated that affinity of the natural components produces very high molecular weight aggregates which are implicated in membrane fouling and decrease in flux and throughput.

Subfractionation of the above material by membrane nominal molecular weight cut-off types afforded fractions enriched in high molecular weight polymers and permeates of lower molecular weight colorant or components. These were further analyzed by gel permeation chromatography, compositional analysis and nuclear magnetic resonance spectroscopy.

Centrifugation of clarified juice improved flux rate by 80% to 100% above that of untreated clarified juice in tests of membrane filtration on clarified juice.

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REFERENCES


**COMPONENTES DE AZUCAR DE CANA QUE AFECTAN EFICIENCIA DE MEMBRANAS PARA FILTRACION: IDENTIFICACION Y ELIMINACION**

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RESUMEN

La molienda de caña de azúcar (*Saccharum officinarum*) produce un jugo con sacarosa, otros materiales solubles incluyendo colorantes de peso molecular alto; polisacáridos, y partículas en suspensión. El material extraño en el jugo de caña de azúcar es implicado en obstrucción de las membranas y pérdida de eficiencia del proceso de filtración de las membranas. Estudios de los la química coloidal de los componentes de jugo de caña de azúcar reportados aquí, demuestran que los componentes del jugo de cana de azúcar podrían formar agregados de muy alto peso molecular, los cuales causan la obstrucción de la membrana. Eliminación de partículas que están
fuertemente atadas y coloidalmente suspendidas en jugos de azúcar o meladura por medios físicos antes de filtración de membrana es importante para asegurar reducción de colorantes y inhibidores de cristalización. Jugo clarificado fue centrífugado por medio de una centrífuga tipo disco a alta velocidad, para remover el material incrustador de membrana. La centrífuga de disco removió un 65% de sólidos coloidalmente suspendidos en la meladura clarificada. El flujo por unidad de área de filtros de membrana coloidales fue aumentado más del doble y forzando un decenso concomitante en el tiempo de ciclo para el filtrado. Subfraccionación del efluente de la centrífuga por corte del peso molecular nominal de la membrana permitió un concentrado de alto polímero y permeado con colorantes o componentes de peso molecular bajo, los cuales fueron analizados por el método de cromatografía de permeación de gel, análisis composicional, y espectroscopía por resonancia magnética nuclear.

Palabras Claves: Membranas, ultrafiltración, turbidez, centrífugación, clarificador de jugo, azúcar de caña.

LES COMPONENTS DE LA CANNE QUI AFFECTENT L’EFFICIENCE DES MEMBRANES POUR LA FILTRATION: IDENTIFICATION ET ELIMINATION

J.R. Vercellotti et al.

RÉSUMÉ

Le broyage de la canne (Saccharum officinarum) produit un jus qui contient du saccharose, d’autre produits solubles, entre autres de polysaccharides et des colorants de forts poids moléculaires, et aussi des matières en suspension. Les matières étrangères de la canne sont souvent associées à l’encrassement des membranes, et à la perte d’efficience. On présente une étude des composants colloïdaux du jus qui peuvent former des agrégats de poids moléculaire très élevé. L’élimination de ces colloïdes avant la membrane réduit la présence des colorants et des produits qui retardent la cristallisation. Le jus clarifié a été centrífugé pour enlever les composants qui encouragent les membranes. La centrifuge a enlevé 65% des colloïdes. Le flux au membranes a été augmenté par un facteur de deux et le temps de filtration a été réduit. On a traité l’effluent de la centrifuge pour produire des polymères et des permeats; ces produits ont été analysés par chromatographie, pour leur composition et par spectroscopie.