

BOILING OPTIMIZATION PROGRAM

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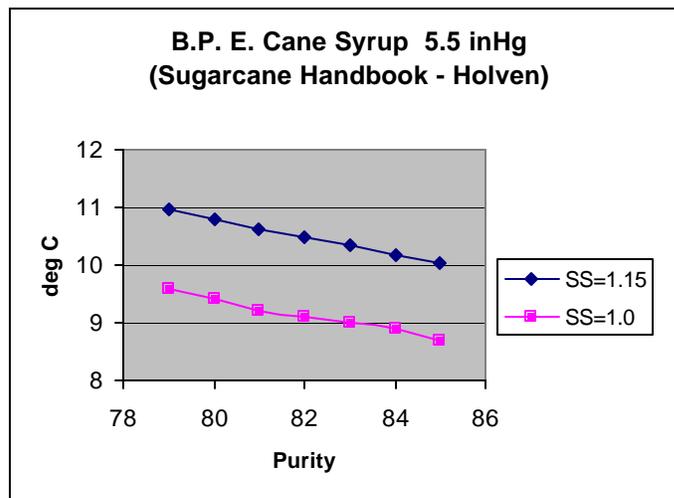
This is to report on the activities related to the boiling program from August, 2000 to February 2001. A brief account is given of the accomplishments as well as comments where the actual work deviated from the tentative plans.

Accomplishments / Comments

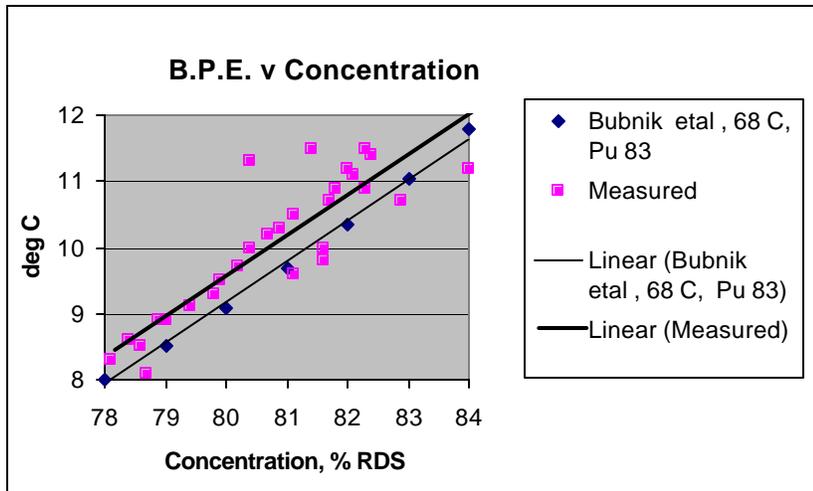
1. “Development of a standard boiling protocol – Pan No. 1”

A number of repeat boilings with syrup brought to ASI from the Cinclaire factory were performed in ASI Pan No. 1 with the objective of developing the standard boiling protocol for syrup boiling. This testing extended throughout the 2000 grinding season, but is now considered completed. Some of the difficulties that were encountered had to do with correct determination of the boiling point elevation at which to seed the pan, and apparently, at times, inconsistent readings from the Dynamic Systems conductivity sensor. Main points follow:

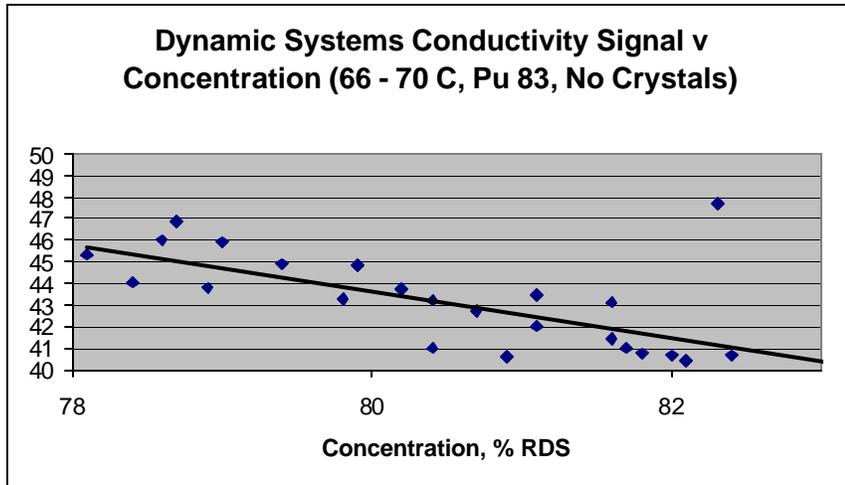
- BPE tables of Holven / Sugarcane Handbook were reviewed because the values previously used at ASI (as per H. Birkett) at supersaturation 1.15 were found too high, leading to excessive false grain formation. The data appear suitable for seeding, at ss value of 1.00 to 1.05,



- A literature equation (Sugar Technologists Manual, Bartens, 1995) for BPE of industrial sugar liquors was reviewed and found to agree with the experimental data from Pan No. 1.



- the conductivity sensor appeared suited for A massecuite boilings, but it is realized in retrospect that the limited sensitivity experienced may have been caused by the way the probe was calibrated before the season's start.
- the automated boiling with the Foxboro I/E system, from start (brixing up the 60 Bx syrup) – BPE control, through seeding , growing of crystals (conductivity control) and “tightening up” - stirrer power control were accomplished.
- standard procedure involved conditioning of the massecuite overnight in a temperature controlled crystallizer at 60 C.
- centrifugation, 1% was water on sugar was found to produce sugar of color comparable to factory raw sugar.
- response of the Dynamic Systems' conductivity probe to syrup Brix and massecuite crystal content was measured .



Based on the more recent experience with the same probe on Pan No. 2, it is expected that the sensitivity can be increased by recalibration that will be performed before the next round of tests on Pan No. 1.

2. Impurity Transfer in sugar boiling

All feeds and sugar produced in the series of boiling trials were analyzed among others for color, ash, polysaccharides, dextran and starch (the latter analyses were performed at SPRI laboratory). The results were tabulated and expressed in terms of the elimination coefficients of the individual impurities, viz. Color, dextran, etc. A sample of the results is below:

Summary of Boiling Tests - Non Filtered (Conventional)

Color (Icu units)

Test No.	Feed	Sugar		Elimination		
		Whole	Affined	Feed-Wh	Feed-Aff	Whole-Aff
2	14,600	430	75	97.1	99.5	82.6
3	11,000	1,121	145	89.8	98.7	87.1
4	11,400	1,607	215	85.9	98.1	86.6
5	12,300	1,505	164	87.8	98.7	89.1
6	9,400	1,617	182	82.8	98.1	88.7
Average	11,025	1,463	177	86.6	98.4	87.9

More detail on these findings is available in the February 2001 ASSCT presentation authored by M. Saska, S. Goudeau, and M. A. Godshall.

3. Effect of ethanol on molasses exhaustion

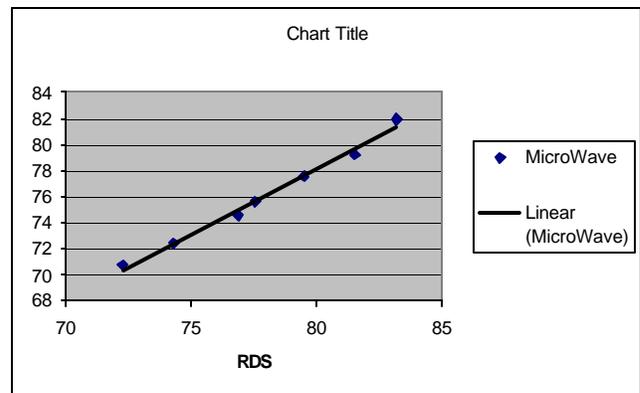
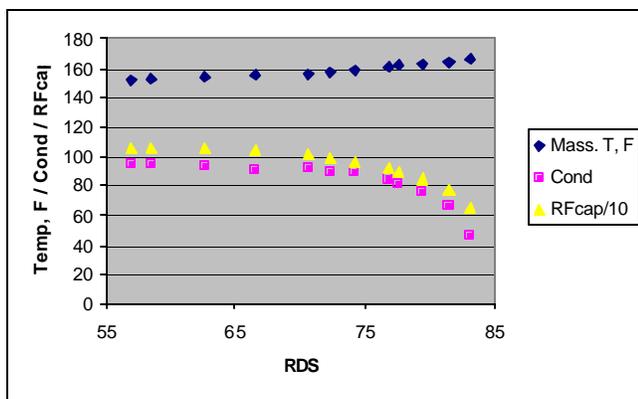
This program, led by Dr. M. Decloux, a visiting researcher at SPRI, was performed in the ASI facilities and was completed by performing several tests with beet molasses supplied by three U.S. beet processors. The results were consistent with previous tests with cane molasses. Very small or nil effect of ethanol addition on molasses exhaustion, and an approx. ten-fold drop in mother liquor viscosity. These somewhat surprising results are being summarized into a publishable form by M. Decloux.

4. Boiling of membrane treated refinery liquors

Several runs of concentrating 100 L quantities of dilute permeates from membrane filtration of refinery liquors and boiling in pan No. 1 of the concentrated permeates were accomplished by Dr. Iqbal of SPRI in the ASI facilities and under supervision and assistance from ASI personnel.

5. Instrumentation and testing of Pan No. 2

The pan has now been instrumented with conductivity, microwave, and RF supersaturation sensors, and a Honeywell UMC controller has been installed. To date the automatic control of absolute pressure and steam pressure have been implemented. The automatic control of the syrup feed valve and stirrer power meter are yet to be implemented pending purchase of an additional I/P, frequency controller, and load cell. The calibration and setup of the three supersaturation sensors are under way. The preliminary results indicate good performance of the conductivity and microwave probes. The RF probe performance is still being tested. An interesting similarity of the RF-capacitance and Dynamic Systems conductivity signals has been noted and is illustrated below. The linearity of the microwave signal has been confirmed.



CANE WASHING LOSSES AT LOUISIANA FACTORIES

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SUMMARY

Cane and cane wash water were sampled at several Louisiana sugar factories during the 2000 crop. Sugar losses caused by cane washing averaged 6 lb/ton cane. Washing efficiency averaged 37%, and the amount of entrained wash water entering the factory with the cane averaged about 7%.

INTRODUCTION

This was the final year of a three year study to investigate cane washing. Sugarcane arrives at the factory with extraneous matter (leaves, dirt) and must be washed before processing. Objectives of this project were to:

- (1) Determine amount of sugar lost when washing cane.
- (2) Determine washing efficiency of existing equipment.
- (3) Determine amount of entrained water entering the factory with the washed cane.

PROCEDURES

Cane Washwater Losses

Incoming and outgoing cane wash water samples were collected with two Omega variable speed peristaltic metering pumps. Sample collection times ranged from 15 minutes to 3 hours. Samples were preserved using a few drops of Clorox (5.25% sodium hypochlorite), filtered through 0.45 micron filters and placed on ice. Samples were analyzed as soon as they reached the lab using the phenol-sulfuric acid method for determining sugar concentration.

A Polysonics Doppler flow meter was purchased for the 2000 crop to measure the cane washwater flow rate. Values given by this meter are considered minimal since the meter, despite comparing favorably with similar instruments from the manufacturer, on several occasions gave readings much lower than thought to be realistic by factory personnel and on two occasions gave readings lower than those physically measured. Therefore, if the meter is considered to be in error, cane washing losses reported should be considered as a minimum.

This project was funded by grants from the American Sugar Cane League.

Washing Efficiency and Entrained Water

Cored cane (directly from incoming loads of sugarcane) and washed prepared cane samples were collected throughout the sampling periods of 30-60 minutes. Standard methods were used to determine fiber and ash content of all samples. The calculations used were as follows:

Washing Efficiency, % =

$$\frac{[(\text{Ash \% Fiber Cored Cane} - \text{Ash \% Fiber Prepared Cane})]}{(\text{Ash \% Fiber Cored Cane} - \text{Ash \% Fiber Clean Cane})} \times 100$$

Entrained Wash Water, % =

$$[(100 \times \text{Fiber \% Cored Cane}) / \text{Fiber \% Prepared Cane}] - 100$$

RESULTS

Table 1 shows cane processed per hour along with the quantity of water used for washing. Sugar losses, based on the meter's flow rate and 2 physically measured flow rates, range from a low of 2.49 lb/ton cane to a high of 9.91 lb/ton cane. Average losses were 6.15 lb/ton cane and should be considered a minimum for the reason stated earlier.

A summary of ash in cane before and after washing is presented in Table 2. Also shown is the variability in washing efficiency, ranging from about 5% to 78%. Entrained washwater is also given and averaged 7.5% during the 2000 crop.

A comparison of washing efficiency, entrained cane washwater and sugar losses for the past three years is presented in Table 3.

References

Chen, J.C.P. and C.C. Chou. 1993. Cane Sugar Handbook. New York: John Wiley & Sons, Inc.

SASTA. 1985. Laboratory Manual for South African Sugar Factories. South African Sugar Technologists' Association.

Table 1. Summary of pounds sugar lost in cane washwater per ton of cane.

Factory	Tons Cane/Hr	Cane Wash- water, Gal/Min	Sugar Losses, Lb/TC
S	375	897	6.52
K	322	3,565	9.46
K	322	3,457	9.23
K	318	3,698	8.12
A	380	10,500	9.35
H	500	5,200	6.59
P	280	5,160	3.13
E	275	11,725	4.42
S	325	897	7.09
A	400	10,500	3.49
P	275	7,082	2.49
G	438	4,941	3.37
D	430	4,882	3.71
D	430	4,864	5.68
S	350	1,048	5.49
S	350	1,048	5.27
D	325	4,952	4.83
D	325	4,901	7.31
D	420	4,800	3.22
D	415	4,755	8.19
D	380	5,314	9.82
D	380	3,270	4.80
D	375	5,365	9.91
AVG:	365	4,905	6.15

Table 2. Summary of ash in cane before and after washing along with washing efficiency and entrained cane washwater.

Factory	Ash % Corer Cane	Ash % Washed Cane	Fiber % Corer Cane	Fiber % Washed Cane	Ash % Fiber Cane	Ash % Fiber Washed	% Washing Efficiency	Entrn. CWW, %
S	1.45	0.96	11.36	11.13	12.76	8.65	49.16	2.07
K	1.88	1.36	11.67	11.08	16.07	12.28	32.43	5.32
K	1.88	1.37	11.67	11.62	16.07	11.79	36.66	0.43
K	1.80	1.25	11.90	10.92	15.08	11.48	33.70	8.97
A	3.23	2.76	13.55	12.09	23.87	22.84	5.29	12.08
H	7.04	5.21	12.17	10.59	57.86	49.17	16.25	14.92
S	3.38	1.58	12.95	10.48	26.13	15.08	50.88	23.62
A	3.95	3.10	12.47	12.71	31.65	24.40	26.62	-1.89
S	4.07	1.27	11.80	11.50	34.49	11.03	77.98	2.62
S	4.18	3.43	11.96	10.50	34.94	32.67	7.46	12.35
S	4.45	1.46	11.88	11.56	37.46	12.63	75.11	2.77
AVG:	3.39	2.16	12.13	11.29	27.85	19.27	37.41	7.57

Table 3. Comparison of washing efficiency, entrained cane washwater and cane washing losses for the past three years.

Year	Washing Efficiency, %	Entrained Cane Washwater, % Cane	Sugar Losses, Lb/TC
1998	45.55	9.66	8.22
1999	58.93	5.08	8.03
2000	37.16	7.57	6.15

FALLING FILM PLATE EVAPORATOR

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Audubon Sugar Institute

Both rising film plate evaporators and falling film plate evaporators have very compact plate evaporator designs and high rates of heat transfer. None of these units are in use in the Louisiana sugar industry. Fear of high rates of fouling and blockages exist. A rising film version (Alpha Laval) was tested successfully in 1999 at the Cora-Texas Sugar Company in White Castle. The falling film version was tested at the Raceland Sugar Company toward the end of the 2000 grinding season.

Balcke Durr donated the distributor for an operating feed range of 8.3 to 16.0 GPM and the plate pack with a heat exchange surface area of 10 square meters or 130.7 sq.ft.

Housing, valving, piping, and instrumentation were provided by the Audubon Sugar Institute, and the unit was installed with the assistance of Raceland. The unit was only ready for manual operation by December 12, 2000. The average data obtained during three days of manual operation were: $> 16 \text{ lbs/(h)(sq.ft.)}$ of evaporation at an overall heat transfer coefficient of $748 \text{ Btu/(h)(sq.ft.)(}^\circ\text{F)}$. It is intended to operate the unit continuously and automatically during this year's grinding season so that the effects of fouling can be established.

ELECTROCOAGULATION TO MINIMIZE EVAPORATOR SCALING

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Audubon Sugar Institute

This project is a continuation from last year's project at Cora-Texas Sugar Manufacturing Company. A new and improved reactor (open design, two stage) was rented from Kaselco of Shiner, Texas. The unit contains sacrificial steel plates, to which a DC-current with changing polarity is applied, which is treating the clarified juice. At the anode, for each mole of iron going into solution, one ferric ion and one electron are formed. The latter reacts with water molecules at the cathode forming hydrogen and hydroxyl ions. The end result is the formation of colloidal ferric hydroxide, which in turn forms the nuclei for mineral aggregates of impurities consisting of mainly silicon (dioxide), calcium, magnesium, and phosphorus. Because of the formation of small amounts of oxygen (1 mg for every mg of Fe into solution) as well as dissolved gases in the juice, these aggregates float to the top. By gentle stirring and the use of a flocculent, they rapidly settle. The settled "mud" can be pumped to the filters for sugar recovery. The clear supernatant goes to the evaporators.

By optimizing the current and the juice flow rate, small amounts of iron are added to the juice (up to 15 - 20 ppm), while silicon dioxide levels are reduced from 350 - 400 ppm to some 25 ppm. Calcium, magnesium, and phosphorus levels are reduced by 10 to 40%. Hence, the removal of scale formers is highly significant. The treatment cost is < 0.02 cents per pound of sugar and the estimated cost of a complete electrocoagulation unit for a 12,000 TCD factory is \$ 300,000. Expectations are that the evaporator cleaning interval can be increased significantly. In the new reactor, Reynolds numbers for flow are around 12 (hence strongly laminar), and the superficial velocity was around 0.075 ft/sec. Residence time per stage was 50 seconds. Current levels were 30 DCA at 5 DCV.

Drums of clarified juice (as is and treated with electrocoagulation) have been stored in the freezer for further processing in small evaporators at ASI. A quadruple effect is being simulated, and the scale from each stage will be collected. The syrups will be boiled into sugar. This work is in progress.

Additionally, several dirty tubes from each effect of a quadruple effect evaporator at Iberia Sugar Coop have been obtained for scale analysis as well as scale removal tests with chelates (BASF) and a special acid (Jamison Chemical Company). Scale samples from the last catch-all at the Iberia Sugar Coop are also being processed. This work is in progress as well.

PROSPECTS FOR THE USE OF NIR MEASUREMENTS IN THE LOUISIANA INDUSTRY

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What is NIR?

Near-Infra Red spectroscopy (commonly referred to as NIR) uses recently developed techniques to measure the absorbance of wavelengths of light in the near infrared region, either by measuring transmission through the sample or by reflectance from the sample.

All substances of plant and animal origin are composed of constituents possessing functional groups of atoms such as -CH, -OH, and -NH- that absorb in the NIR region (700 to 2500nm). Their characteristic absorbance pattern can be traced down the spectra as overtones (simple multiples of the fundamental frequencies) and combination bands (the result of the interaction of two fundamental frequencies) (Petersen 1999). The wavelength of an absorption band often reveals the nature of the chemical bonds responsible for the absorption, and quantitative measurements can be made based on the Beer-Lambert law.

Modern chemometrics software packages analyze the information present in the NIR spectra and develop mathematical models which can be used to provide quantitative results based on the spectra of unknown samples. The vibrated modes for sucrose molecules were examined by Clarke et al. (1993) using a saturated sucrose solution and were found to display unique absorptions at 2088nm and 2272nm, with HOH groups absorbing at 1435nm and 1940nm.

Why is it of advantage to pursue this technique?

Schäffler (2000) has been studying the feasibility of using NIRS for analyzing raw sugar factory process streams. As he notes, the technique is theoretically capable of monitoring multiple analytes quickly and conveniently. It gives results rapidly, within a minute or two, and requires very little labor.

The same instrument can be used for all product streams in a factory, with no sample preparation required, other than perhaps dilution.

It can be said that it can supply more accurate answers, more quickly, without chemicals and using less labor than any other methods. Better results at lower cost are possible.

NIR has been shown to be a valid assessment of cane quality; the method is far more precise and the error in the method is much less than in the conventional Louisiana cane analysis method (Edey and Clarke 1996).

It should be possible to use the technique for analysis of solid materials, cane, and bagasse, using a reflectance measurement technique. One analysis should be able to give a full analysis (moisture, fiber, brix, and pol).

A considerable amount of work has been done on this technique, in Australia, South America, South Africa, and North America. The time may now be appropriate for us to capitalize on previous work.

The experience gained elsewhere should be used to help achieve the improvements in measurement accuracy at reduced cost.

What are the pitfalls?

If it is not done correctly, it could be the quickest way to get the wrong answer!

It is a secondary measurement technique in that it relies on being calibrated against other measurements. The accuracy of the answers is no more accurate than the primary analyses on which the calibrations are based.

Selecting appropriate samples for use in an effective database and developing practical equations are demanding tasks. Many spectra and results have been discarded thus far in various investigations (Schaffler 2000).

Global calibrations have not yet been developed, and calibrations still need to be updated routinely. An operator or supervisor experienced in the techniques and sensitive to the analyses is still crucial to keep NIR errors to a minimum (Johnson 1999; Schaffler and Meyer 1996).

Dirt in cane affects the accuracy of fiber analyses (Staunton et al 1999)

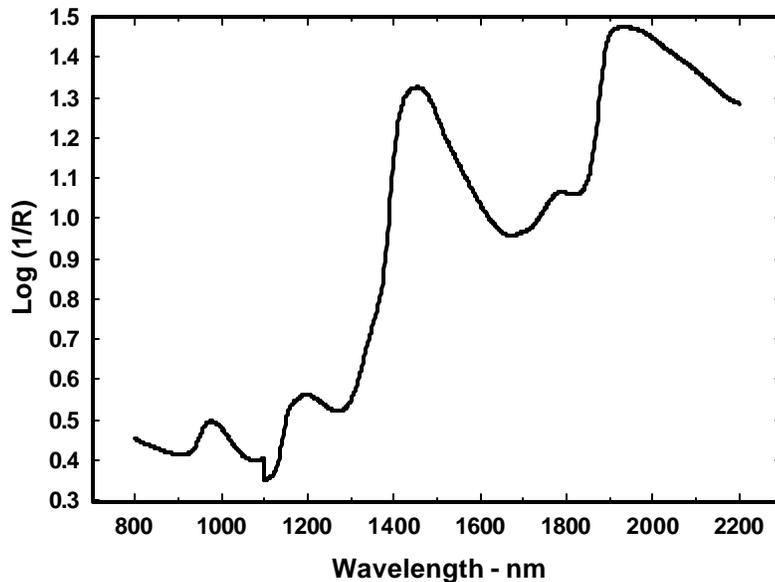
Where are these techniques currently being used?

NIR has been used routinely for cane variety assessment over many years in Australia (Brotherton and Berding 1998) and in South Africa (Meyer 1997, Meyer 1998).

At the American Crystal Sugar Company uses include: on-line NIR determination of sucrose, RDS (refractometer Brix) and betaine levels in the molasses desugarisation plant; the use of AOTF (acousto-optic tuneable filter) equipment; the measurement of key parameters of factory juices by both scanning and AOTF machines; and use of NIR in the factory laboratories (Jacobson *et al* 2000).

Techniques for analysis of liquid products are already well established (Schaffler 1997, Schaffler 2000) and can be totally automated.

Figure 1. Mean spectrum of samples in fibrated mature-stalk sugarcane (n=1764), from Berding and Brotherton (1999).



Fully automatic NIRS analysis of a number of components including sugar and total solids and purity in liquid process samples is used in CSM beet factories in Holland (de Bruijn 1997).

NIR is used for juice analysis for cane payment purposes in some Florida mills (Johnson 2000).

During the 1994 sugar cane harvest season in Sao Paulo, Brazil, the NIR technique was field tested by COPERSUCAR and the results led to the approval of NIR as an acceptable technique for the analysis of pol and Brix in cane juice. Today, the technique is in use for cane payment by factories in the state of Sao Paulo (Petersen 1999).

Attention is now being given to the direct analysis of cane in both Australia and South Africa (Meyer 1997, Brotherton & Berding 1998). Sample preparation and presentation to the instrument are still important issues receiving attention. A typical spectrum of fibrated cane (Fig. 1) shows the dominance of the moisture peaks ($\approx 1,440$ and $1,920$ nm) and portions of the spectrum with reflectance values ($\log (1/R)$) higher than 1.3 that tend to non-linearity.

NIR has been used on-line in the chute of the first mill at Mulgrave in Australia for on-line analysis of fiber (Staunton et al 1999)

What is the way forward for Louisiana and Audubon Sugar Institute?

Audubon Sugar Institute has the necessary analytical capability for the accurate measurement of sugars in any process streams via chromatographic techniques. In addition ASI has on loan an NIR instrument which is being applied to the analysis of molasses. The next step would be to install the instrument at a mill and establish the practicality of its use on a comprehensive basis. Method development has been studied by others, but proving work would

still be required in a Louisiana mill. Initial work has just been completed at St. James mill. This would take probably two crushing seasons to establish its viability. Thereafter the practicability and cost savings can be properly evaluated.

A visit to the Sugar Milling Research Institute in South Africa has already been undertaken to assess progress and make contact with the researchers. In Australia in September 2001, the opportunity will be taken to assess progress in the Australian industry. Thereafter the implications for the adoption of these techniques in Louisiana would need to be evaluated.

Foss has approached Audubon Sugar Institute with a proposal to install a system to measure cane quality on line, and this will be pursued in the coming season.

REFERENCES

Brotherton GA and Berding N. Near infra-red spectroscopic applications for milling; prospects and implications. *Proc Aust Soc Sugar Cane Technol.* (1995) 17, 21

Brotherton GA and Berding N. At-line analysis of mill-prepared cane using near infra-red spectroscopy. *Proc Aust Soc Sugar Cane Technol.* (1998) 20, 34

Clarke, M. A., ER. Arias and C. McDonald-Lewis. Near infrared (NIR) analysis in the sugarcane factory. *Proc Int Soc Sugar Cane Technol.* (1993) 21, 829

Clarke, M. A. , L. A. Edye and W. S. Patout III. Sugar cane crop analysis by NIR. *Proc Int Soc Sugar Cane Technol.* (1996) 22, 114

de Bruijn JM (1997) Development and application of automatic NIRS in factory laboratories. *Zuckerind.* 122, 878-882.

Edye, LA and MA Clarke. (1996) Sugarcane quality analyses by near infrared spectroscopy. *Proceedings South African Sugar Technologists' Association* 70, 127-130

Jacobson, B.J., Wallevand, J.H., McGillivray, TD and Fischer, CG (2000). Overview of the development and application of near infrared spectroscopy at American Crystal Sugar Company. *Conf. Sugar. Proc. Res. Inst.*, Porto, Portugal (in press).

Johnson TP (2000) Cane juice analysis by near infrared (NIR) to determine grower payment. *Conf. Sugar. Proc. Res. Inst.*, Porto, Portugal (in press).

Meyer JH. (1997) Review of near-red spectroscopy research in the South African Sugar Industry. *Proc. S Afr Sugar Technol Ass.* 71, 33

Meyer, J.H. (1998) Near infrared spectroscopy (NIRS) research in the South African sugar industry. *International Sugar Journal* 100, 279-286.

Petersen JC. (1999) Near infrared (NIR) technology in the sugar and alcohol industries. *Second Int. NIR Users Mtg. for Sugar and Alcohol Industries*. Sao Paulo.

Schaffler, K.J. (1997) Rapid near infra-red estimation of multi-components in mixed juice and final molasses: the possibility of day-to-day control of raw sugar factories using NIR. *Proc. S Afr Sugar Technol Ass.* 71, 153

Schaffler, K.J. (2000) The trials and tribulations of implementing NIRS for raw sugar factory liquors. *Proc. S Afr Sugar Technol Ass.* 74 in press

Staunton, SP, P.J. Lethbridge, S.C. Grimley, R.W. Streamer, J. Rogers, and DL Macintosh (1999) On-line cane analysis by near infra-red spectroscopy. *Proceedings Australian Society Sugar Cane Technologists* 21, 20-27.

A SURVEY OF MOLASSES EXHAUSTION IN LOUISIANA MILLS

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ABSTRACT

The results of the survey of analyses of weekly molasses samples from the Louisiana mills for the 2000/01 season are presented. These are related to the South African target purity equation, which is considered to be the most appropriate as a benchmark. This is supported by laboratory exhaustion tests. The results indicate that, on average, significant reductions in molasses purity can be achieved, with substantial savings for the industry. The analyses of monosaccharides indicate the widespread occurrence of Maillard reaction in the massecuites, which hampers good molasses exhaustion.

INTRODUCTION

The loss of sugar in molasses is generally the largest loss suffered by a sugar mill. It is therefore important that reliable data on molasses exhaustion be obtained. The normal measurements used in a sugar mill laboratory are not accurate enough at the low purities associated with final molasses. Chromatographic methods of measurement of sugars content in molasses are now well developed and can be relied upon to give accurate and reliable answers.

In the past, Audubon Sugar Institute undertook analyses of molasses samples for the mills in Louisiana. This was discontinued after the 1997 season, but it was considered to be important to reintroduce the analyses of weekly composite molasses samples to provide the mills with reliable information on how well the molasses is being exhausted.

To assess the degree of exhaustion achieved, a benchmark is necessary. This is generally available in the form of a “target purity” equation. A number of these have been proposed in the past, and it is necessary to choose the most appropriate for Louisiana conditions.

Background to target purity equations

A number of different target purity equations have been proposed over the years. Essentially they have been derived by laboratory trials on various molasses samples under controlled conditions, establishing in essence equilibrium purity under specified conditions.

A target purity can be thought of in two ways, either the lowest molasses purity achievable in a lab (equilibrium purity) or the target realistically achievable in a factory. The former is preferred, since it is an objective standard related to what can be achieved and is not dependent on a subjective assessment of what is acceptable. The difference between actual and target purities is referred to as the Target Purity Difference (TPD) and gives an indication of potential improvement; obviously this should be as small as possible.

The target purity is significantly affected by the measurement methods used in the process of deriving the formula. The effect of analytical methods makes it essential to specify the methods used for each target purity equation. Those which have been used in the past are shown in Table 1.

Table 1. Target purity equations proposed in the literature.

Reference	Equation	Analytical Method			
		Dry Solids	Sucrose	Monosaccharides	Ash
Foster 1960	$40.7-17.8\log(RS/A)$	Drying	Double pol	L & E	Sulfated
Miller et al 1998	$39.4-10.6\log(RS/A)$	Drying	Double pol	HPLC	Sulfated
Bruijn et al 1972	$39.9-19.6\log(RS/A)$	Drying	L & E	L & E	Sulfated
Rein & Smith 1981	$37.7-17.6\log(RS/A)$	Drying	L & E	L & E	Sulfated
Rein & Smith 1981	$33.9-13.4\log(RS/A)$	Drying	GLC	GLC	Sulfated
Smith 1995	$43.1-17.5[1 - \exp(-0.74RS/A)]$	Drying	GLC	GLC	Sulfated
ASI 1993	$42.4-12.3\log(RS/A)$	RDS Correlation	HPLC	HPLC	Conduct.

The monosaccharides fructose and glucose are most accurately measured by GLC (gas liquid chromatography) or HPLC (high performance liquid chromatography). They are commonly referred to as reducing sugars (RS) and measured by the Lane & Eynon method (L & E). Reducing sugars decreases the solubility of sucrose in molasses, while most inorganic components, which constitute the ash, tend to increase the solubility. These target purity equations all take these two effects into account in the ratio of reducing sugars to ash (RS/A). This is a convenient approach, leading to a simple form of target purity equation. High values of RS/A will generally enable lower molasses purities to be achieved.

Choice of Target Purity Equation as a Benchmark

The ASI (Audubon Sugar Institute) equation was derived originally simply by fitting the lower range of factory molasses purities and is now considered too lenient (Saska et al 1999). The South African formula (Rein and Smith 1981) was assumed to be the most appropriate for the following reasons:

- It is based on an extensive experimental program.
- It makes use of the most accurate and reliable measurements (GLC).
- It has been used extensively in Southern Africa for 20 years, and has been reliable under all conditions.
- Subsequent laboratory exhaustion work on molasses from other cane-producing areas has confirmed its general applicability, generally within one unit of purity (Sahadeo 1998).
- A recent survey of molasses from around world shows TPD values in the range of 3 to 7 units, in the expected range, confirming its general applicability (Sahadeo 1999).

The use of HPLC techniques has now been shown to give accuracy similar to the use of GLC, on which the equation was derived. HPLC is a much easier technique to use and is accepted for use with this equation.

It has been shown that in the Tongaat-Hulett mills in South Africa, the TPD values recorded are very similar to the purity rises measured on curing (Smith 1995). This indicates that the massecuite is well exhausted after the crystallizers and provides further evidence for the suitability of this formula.

In practice therefore it is very unusual for a factory to achieve a zero TPD. The best factories will report a TPD of around two to three units, roughly equal to the rise in mother liquor purity across the centrifugals.

PROCEDURE FOR THE ANALYSES OF WEEKLY MOLASSES SAMPLES

Sample handling and preparation:

Upon arrival each sample is number coded and the mill name blacked out. A key is made to identify the sample numbers with the factories. The samples are then mixed and a portion separated for analyses. Each week, one to three samples of a control sample are coded and mixed in with factory samples. The original samples are stored for future analyses if required. After thorough mixing, 30 grams or more of the sample are weighed and diluted with an equal amount of warm deionized water. The diluted samples are then mixed for five minutes using a Burrell Shaker. From the diluted samples, 26 and 4 grams are weighed into 200 ml volumetric flasks for Pol and conductivity ash analyses, respectively. A 15 ml centrifuge tube is filled with the diluted sample for Brix and HPLC analyses.

After analyses the remainder of the diluted sample in the centrifuge tube is frozen and retained for the season. A portion of the coded sample is saved until the end of the season when they are combined into two composites for each factory, one for each half of the crop, for elemental analysis. The remainder of the coded sample is discarded.

The data from the analyses are entered into a spreadsheet and associated with the appropriate factory or control. Weekly results are reported to each mill by fax and the results are posted on the ASI's website.

Procedures:

Pol: Twenty-six grams of the 1:1 diluted sample is weighed in a 200ml volumetric flask and diluted to volume with deionized water. The solution is then transferred to a glass jar and two teaspoons of Octapol are added. The sample is shaken well filtered and read on the saccharimeter.

Brix: The diluted sample is read directly on the refractometer. True solids were not measured directly, but were calculated from a relationship developed by Matthesius and Mellet (1976):

True Solids = $100 / ((101.3 / \text{Refractometer Brix}) + (.932 / \text{True Sucrose}))$.

Conductivity Ash: A 1% molasses sample is prepared by diluting four grams of 1:1 sample solution to 200 ml in a volumetric flask. The sample is then brought to 20°C in a water bath and the conductivity is read in μS on a conductivity meter. The ash is calculated using the following formula:

Conductivity Ash = $9.224 \times K \times C + 2.5119$
K = cell constant ($.99 \text{ cm}^{-1}$).
C = measured conductivity in μS

This formula was derived from data collected over three (1990-1993) seasons on 405 samples.

Sugars by HPLC: Approximately one gram of the diluted sample is weighed into a 100ml volumetric flask. The sample weight is recorded to a minimum of three decimal places. The sample is then diluted with Type I water and filtered through a $0.45 \mu\text{m}$ filter into a sample vial. The sample vial is placed into the auto sampler and the true solids weight, calculated from the Brix reading of the 1:1 solution, is entered into the integrator along with the sample number. Standards are ran at the beginning and end of each sample set and every five to six samples to verify accuracy.

Equipment used for analyses:

Apparent Purity:

Bellingham and Stanley Limited RFM90 Refractometer.
Rudolph Research Autopol IIS Saccharimeter.

Conductivity Ash:

Radiometer Copenhagen CDM3 Conductivity Meter.

Sugars by HPLC:

Column: Bio-Rad HPX-87K 300 X 7.8mm.
Column Heater: Waters Column Heater Module at 85°C.
Solvent: 0.01 M K_2SO_4 at 0.6 ml/min.
Detector: Waters 410 Differential Refractometer.
Integration: Spectra-Physics SP4270 Integrator.
Auto Sampler: Bio-Rad AS100 HRLC with 20 μl sample loop and temperature control at 5°C.
Pump: Waters Model 510.

Verification of Methods and Instrument Accuracy:

Several of the methods are similar to the ICUMSA methods procedures, but they vary from the ICUMSA method in the amount of sample used or the amount of dilution. Comparison studies using ASI and ICUMSA methods will be conducted to determine if the differences between the methods are significant. The ICUMSA methods will be used for the following

seasons. As mentioned above, the True Solids calculation will be evaluated using the data collected in the NIR study.

Providing a more stable temperature for ASI's instruments is of great concern. ASI will be looking into the current locations, conditions, capabilities, and calibration procedures for equipment so that ASI can assure the best accuracy possible is provided for our customers.

Season survey results, 2000/01

The average values for the analyses for the season for all mills are given in Table 2 and the TPD values are shown in Figure 1. Note that some mills provided only a few samples during the season, in particular Factory J. Average values for each week of the season for all mills are given in Table 3. The averages for each week of the season are shown in Figure 2, as well as the variation during the season of the average monosaccharide / ash ratio.

The monosaccharide / ash ratio shows the expected trend during the season, starting at a higher than average value, dropping as the season commences, and rising toward the end of the season. The TPD values in Figure 1 show higher values at the beginning and end of the season, reflecting startup and liquidation problems at the end of the season. An unusual peak in mid-November is evident. This is caused mainly by high values recorded in the southern most mills and is thought to be associated with the heavy rain experienced at the time. This introduces additional delays in harvesting and transport, leading to massecuites which are difficult to process.

Of interest is the performance of one of the mills, Factory Q, which is generally known as an efficient processor. A graph of its TPD is shown in Figure 3. Initially it showed a very high TPD value of around 12 units; midway through the season it made some substantial improvements, and the TPD dropped to a very respectable number of around 5 units.

Laboratory exhaustion trials

A previous lab exhaustion trial gave results which supported the applicability of the target purity equation being used (Saska et al 1999). With the apparent exhaustion problems at Factory Q, samples of molasses from that factory were collected and subjected to exhaustion trials at ASI. The procedures and the equipment used are described elsewhere (Saska et al 1999). The molasses was concentrated up in a 150 L pilot pan, seeded with fine sugar, concentrated up to the required consistency, and cooled down to 40 C in pilot crystallizers. Samples were taken periodically for analysis of mother liquor purity. The results as a function of cooling time are shown in Figure 4.

Two sets of runs were undertaken, with a high and a low brix after concentration being used in each set of runs. The two lower graphs in Figure 4 represent the high brix case and show that, after about 50 hours, very little extra exhaustion is achieved. The target purity predicted by the equation for this massecuite is 36.0, and it can be seen that this purity is achieved.

Figure 5 shows the final purities achieved as a function of mother liquor brix. This emphasizes the importance of concentrating up the massecuite to as high a level as possible to achieve good exhaustion.

DISCUSSION

The weakness of this work lies in the fact that true solids were not measured but were inferred from refractometer brix. However it is unlikely that this simplification affects the true purity by more than one unit, within the accuracy of the whole determination. Further work will be done on these samples, specifically to investigate the use of NIR as a routine measurement for this purpose.

Dextran affects the viscosity of massecuites, and, above levels of about 10 000 ppm on brix (roughly twice the normal Louisiana level), the target purity should be increased by one unit or more (Sahadeo 1998). In times of long delays, therefore, when dextran levels rise, TPD values are expected to be higher.

The value of the fructose/glucose ratio (F/G) is of considerable interest. The F/G ratio was measured at 1.17 in mixed juice on some samples from Factory R, but averaged 1.6 for the industry in molasses, with a range of values 1.4 to 2.0. The variation in these values is shown in Figure 6. In general the value in juice should be close to one, and it is the occurrence of Maillard reaction which causes this ratio to change. In South Africa in 1999, values of 1.2 - 2.0 with an average of 1.4 were reported (Lionnet 2000). The higher the value of F/G, the greater the extent of the reaction.

Maillard reaction is a reaction between reducing sugars and amino nitrogen. It results in the formation of color and aerates the massecuite, significantly increasing viscosity (Newell 1979). It is also known as the phenomenon which causes molasses swelling in crystallizers and explosions in molasses tanks, since it is exothermic (Wong et al 1996). It destroys reducing sugars, forming additional impurity and increasing molasses losses. Glucose is consumed preferentially in the reaction, which leads to values of F/G higher than one, although some fructose also reacts. The RS/ash ratio is reduced, affecting massecuite exhaustion. High concentrations and high temperatures promote the reaction, with a 5 C increase in temperature leading to a doubling of the reaction rate. The reaction can be minimized by boiling pans at as low a temperature as possible. In general, particularly with C massecuites, to minimize the reaction temperatures should be kept below 63 C (145 F) at strike and cooled as quickly as possible. Molasses backblending also may help.

CONCLUSIONS

The new target purity formula does seem to represent Louisiana conditions. Some work needs to be done on refining and updating analytical techniques. Further work will be done using NIR on these molasses samples. Molasses purities on average are 5 units higher than they could be. This is worth 2.5 units of overall recovery, or \$20 million a year to the Louisiana industry. Efforts to reduce molasses purities would be assisted by reducing the prevalence of Maillard reactions.

REFERENCES

- Bruijn J, Fitzgerald J.R, MacGillivray A.W.and Koenig S. (1972) Exhaustion of South African final molasses. *Proc S Afr Sugar Technol Ass* 46:103-109.
- Foster DH (1960) A final molasses exhaustion formula. *Sugar Res Inst Internal Report*.
- Lionnet GRE (2000) Annual review of Factory Operations. *Proc S Afr Sugar Technol Ass*. 74:.
- Matthesius, G.A. and Mellet P (1976) An exhaustion formula for South African molasses *Proc S Afr Sugar Technol Ass*. 50:206 – 207.
- Miller KF, Ingram GD and Murry JD (1998) Exhaustion characteristics of Australian molasses. *Proc. Aust. Soc. Sugar Cane Technol*. 20, 506-513.
- Newell, G.M. (1979) A preliminary investigation into factors affecting gas formation in massecuite and molasses *Proc S Afr Sugar Technol Ass* 53: 62.
- Rein, P.W and Smith I.A. (1981) Molasses exhaustibility studies based on sugar analysis by gas-liquid chromatography. *Proc S Afr Sugar Technol Ass* 55:85 – 91.
- Sahadeo P (1998) The effect of some impurities on molasses exhaustion. *Proc S Afr Sugar Technol Ass* 72:285-289.
- Sahadeo P (1999) An analytical survey of final molasses from fifteen cane producing countries. *Proc Int Soc Sugar Cane Technol* 23:92 – 103.
- Saska M, Goudeau S and Andrews L (1999). Molasses exhaustion and target purity formulas. *Sugar J* 62:20-24.
- Smith IA (1995) Exhaustibility of molasses with very low reducing sugar levels. *Proc S Afr Sugar Technol Ass* 69:163 – 165.
- van Staden LF, Rungasamy C and Simpson R (1999) Use of conductivity ash for calculating target purity difference (TPD). *Proc S Afr Sugar Technol Ass* 73:257-262.
- Wong Sak Hoi L and Chasteau de Balyon JC (1996). Maillard reaction in molasses storage tank. *Proc S Afr Sugar Technol Ass* 70:.

Table 2. Weekly averages for all Louisiana mills.

Week Ending	Ref. Brix	True Solids	App. Purity	True Sucrose	Ratio pol /sucrose	True Purity	Fructose F	Glucose G	Cond. Ash	(F+G)/ Ash	Target Purity	T. P. Diff.	F/G Ratio
09/30/00	80.8	78.1	36.7	34.8	0.85	44.6	8.6	5.3	15.5	0.91	34.6	9.9	1.62
10/07/00	81.4	78.7	35.1	34.8	0.82	44.2	7.6	4.9	16.2	0.77	35.5	8.7	1.55
10/14/00	81.1	78.3	36.1	33.4	0.87	42.7	7.4	4.9	16.6	0.74	35.7	7.0	1.52
10/21/00	80.6	77.9	35.7	33.5	0.86	43.0	7.4	5.1	16.8	0.74	35.7	7.4	1.46
10/28/00	80.7	78.0	36.6	34.2	0.86	43.9	7.2	4.8	16.8	0.72	35.9	8.0	1.51
11/04/00	80.8	78.2	37.5	35.3	0.86	45.2	6.8	4.8	16.7	0.69	36.1	9.1	1.43
11/11/00	80.2	77.6	37.3	36.0	0.83	46.4	6.8	4.4	16.7	0.67	36.3	10.1	1.54
11/18/00	80.6	78.0	37.6	35.8	0.85	45.9	6.3	4.1	17.7	0.59	37.0	8.9	1.55
11/25/00	80.8	78.2	36.9	35.6	0.84	45.5	6.6	4.1	17.8	0.60	36.9	8.6	1.61
12/02/00	81.2	78.5	33.5	35.3	0.77	45.0	7.8	4.8	17.6	0.72	35.8	9.2	1.61
12/09/00	81.6	78.9	34.1	36.0	0.77	45.6	7.2	4.3	18.0	0.64	36.6	9.0	1.68
12/16/00	81.5	78.9	34.4	36.4	0.77	46.2	7.5	4.1	17.8	0.65	36.4	9.8	1.81
12/23/00	80.9	78.2	35.4	36.8	0.78	47.0	7.1	4.0	17.7	0.63	36.6	10.4	1.79
12/30/00	81.8	79.1	36.2	37.1	0.80	46.9	7.1	3.9	17.4	0.64	36.6	10.3	1.79
01/06/01	82.0	79.3	36.9	37.5	0.81	47.2	7.2	3.7	16.8	0.65	36.4	10.8	1.92
01/13/01	83.4	80.7	38.8	37.7	0.86	46.7	7.5	4.3	14.9	0.79	35.3	11.4	1.75
Average	81.2	78.5	36.2	35.6	0.83	45.4	7.2	4.5	16.9	0.70	36.1	9.3	1.63

Table 3. Seasonal average values for each factory.

Factory	Ref. Brix % mol.	True Solids % mol.	App. Purity %	True Sucrose % mol.	Ratio pol /sucrose	True Purity %	Fructose F % mol.	Glucose G % mol.	Cond. Ash % mol.	(F+G)/ Ash	Target Purity %	T. P. Diff.	Ratio F/G
A	80.7	78.0	37.2	36.0	0.84	46.1	6.9	4.4	17.2	0.65	36.4	9.7	1.58
B	79.3	76.7	35.8	34.7	0.82	45.3	6.4	4.0	17.7	0.58	37.1	8.2	1.60
C	80.0	77.4	35.5	35.0	0.81	45.2	6.6	3.5	17.3	0.59	37.0	8.2	1.90
D	82.1	79.4	35.1	35.7	0.81	45.0	7.1	4.2	17.3	0.66	36.4	8.6	1.68
E	83.7	80.9	35.1	35.4	0.83	43.7	7.7	5.6	17.7	0.75	35.6	8.2	1.36
F	82.0	79.3	36.5	36.1	0.83	45.5	7.5	5.3	16.4	0.79	35.4	10.1	1.42
G	79.5	76.9	37.2	35.5	0.83	46.2	7.1	5.2	16.9	0.72	35.8	10.4	1.37
H	82.2	79.4	34.8	35.4	0.81	44.6	7.5	4.6	17.5	0.69	36.1	8.5	1.62
I	80.5	77.9	37.5	35.9	0.84	46.1	8.2	6.3	16.5	0.88	34.6	11.5	1.31
J	83.5	80.7	34.0	36.7	0.77	45.5	7.5	3.7	17.5	0.64	36.5	9.0	2.01
K	80.7	78.0	35.3	34.6	0.83	44.3	7.2	4.4	17.4	0.68	36.3	8.0	1.64
N	81.4	78.6	34.3	34.4	0.81	43.8	7.5	4.2	17.3	0.68	36.2	7.6	1.79
O	79.5	76.9	36.1	35.2	0.82	45.8	7.3	4.3	16.0	0.73	35.8	10.0	1.70
P	78.3	75.7	35.1	33.7	0.81	44.6	6.6	3.6	17.4	0.59	37.0	7.6	1.82
Q	82.4	79.7	36.2	36.7	0.81	46.1	7.2	4.4	18.3	0.64	36.6	9.5	1.64
R	79.0	76.4	37.5	35.1	0.85	45.9	6.8	4.7	17.1	0.68	36.2	9.7	1.46
S	83.5	80.8	37.4	37.0	0.84	45.8	7.0	4.0	16.2	0.68	36.2	9.7	1.76
W	82.2	79.4	34.3	34.3	0.82	43.2	7.5	4.5	17.3	0.70	36.0	7.2	1.65
Average	81.1	78.4	35.8	35.4	0.82	45.2	7.2	4.5	17.2	0.69	36.2	9.0	1.60

MICROBIOLOGICAL ASPECTS OF CANE WASHING SYSTEMS: EFFECTS ON JUICE QUALITY AND SUGAR LOSSES

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In Louisiana, the rapid shift from whole stalk harvesting to billet harvesting has resulted in unanticipated alterations of traditional processing systems in the sugar factories. One such alteration has been higher sugar losses on cane washing. Increased amounts of sugar have gone into wash pond systems designed to handle lower BOD inputs. It would be expected that higher sugar would bring about concomitant increases in both microbial and organic acid loading of wash waters. Day and Birkett (2001) reported a 10-15 % carry-through of washwater from cane washing to the juice. An increase in organic acid loading in the mixed juice may cause processing problems ranging from increased scale formation, higher lime usage, and higher sugar losses to more rapid equipment corrosion. This study documented both the types and amounts of organic acids carried through to the sugar process streams due to cane washing and as well the carry through to mixed juice.

The objective of this project was the establishment of baseline data on organic acid levels present in washwaters in and around the wash tables at Louisiana sugar mills and organic acid carry through to mixed juice.

METHODS

Organic Acids in Washwaters: The sugar factories tested were grouped according to rate or water recycle in their wash systems. Those with a rapid turnaround of their washwater (less than 24 hours) and minimal treatment are group A; those with a very long washwater recycle time (more than 30 days) are group B; those with a rapid turnaround, but extensive aeration, are group C; and those with an intermediate time and treatment regime are group D. Washwaters entering and exiting the wash tables were analyzed for pH, Brix, lactic, formic, and acetic acids. These acids were chosen because they are primary products of anaerobic microbial action on sugars (Sokatch 1969). Brix analysis was conducted by refractometry after mud removal by centrifugation. Organic acids were analyzed by HPLC.

RESULTS AND DISCUSSION

Solids Loss on Washing: Average Brix increase in washwater across wash table was 0.21 Brix (range 0.1 - 0.7). There was no relationship between loss and type of wash system. This is an estimated loss of 0.017 lb. soluble solids/gal of washwater (at 5,000 gpm this amounts to 122,000 lb./day of solids), and is well in line with previous reports. A significant portion of this is probably recoverable sugar. This loss should be factored in when the cost of cane washing is calculated.

Organic Acid Levels: Concentrations of lactic, formic, and acetic acids were determined in water going onto the wash tables and categorized according to wash pond treatment and in the mixed juice produced at the same time (Table1).

Table 1. Organic acids in cane washwater and mixed juice.

Group A* Sample Day	washwater			mixed juice		
	lactic (ppm)	acetic (ppm)	formic (ppm)	lactic (ppm)	acetic (ppm)	formic (ppm)
1	1233	301	119	124	31	6
5	548	766	271	134	46	7
12	661	320	302	382	76	20
27	161	274	8	62	42	8
32	2	215	18	34	28	7
Group B						
5	1	0.5	0	69	49	7
12	0.7	0.1	0.2	109	2	8
Group C						
8	4	0.3	0.5	36	62	7
12	1.6	0.2	0.5	133	241	21
25	5.3	0.5	0.2	56	17	6
Group D						
19	141	56	55	62	160	32
25	500	221	208	56	51	7

*Mills grouped according to washwater recycle and treatment. Acid concentrations are given as ppm on volume.

The concentration of organic acids in the washwater reflected the state of the wash pond. Levels were low with once through, or well-aerated water, and high where the holding time was very short or aeration was inadequate (Figure 1). The organic acid which was most prevalent was lactic acid. It also was the most responsive to changes in wash pond conditions. Where lime was used to control the pH of the wash system (Group A), the concentrations of lactic acid dropped, presumably because of formation of calcium lactate. A similar effect was seen with formic acid concentrations, but acetic acid levels did not appear to change in tandem with the other two test acids.

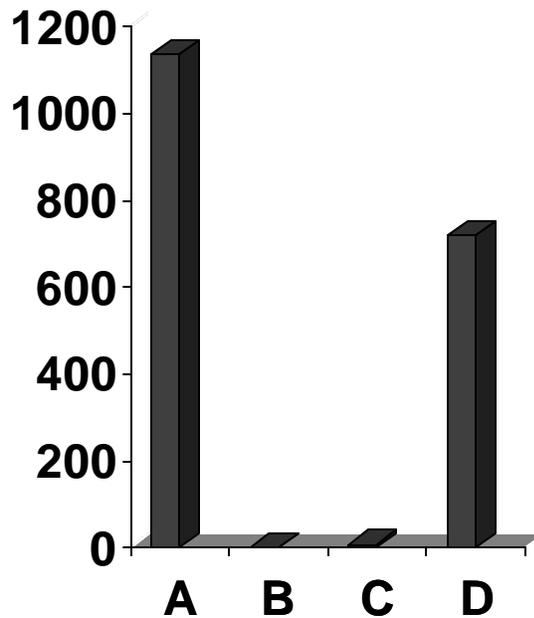


Figure 1. Average organic acid levels in washwater as a function of pond treatment. Values are for lactic, acetic, and formic acids over a one-month period.

Organic Acid Carry-through: There was concern that corrosion found within the factory may be caused by acid carry over from cane washing. A comparison of the lactic acid levels in cane wash and in mixed juice showed no correlation. In some cases high levels in the juice had low levels in the wash or the reverse. On average there was a relatively constant concentration of organic acids found in mixed juice, around 60 ppm on volume (Figure 2). This was independent of the type of washing or concentration of the organic acids in the washwater. It is likely that mixed juice organic acid levels are more a reflection of cane deterioration than cane washing.

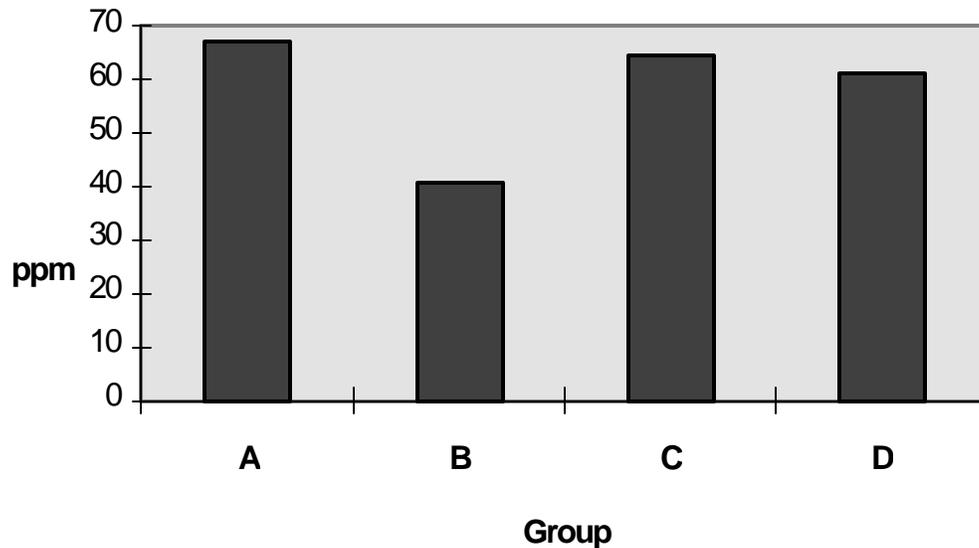


Figure 2. Average organic acid (lactic, acetic, formic) concentrations in mixed juice. Values are given as ppm on volume.

It is probable that the levels of organic acid found in the juice are a reflection of the amount of deterioration in the cane and that there is little or no increase in acid juice levels because of the washing system. However, there are fluctuating but significant amounts of acids found in the juice, which may have deleterious effects on downstream processing.

REFERENCES

Day, Donal F. and Harold Birkett, 2001. Investigation into Washing and Biological Losses in Cane Wash Systems. Annual Meeting, American Society of Sugar Cane Technologists, Louisiana Division, Baton Rouge, La. Feb 6-7.

Sokatch, J. R. 1969. Bacterial Physiology and Metabolism. Academic Press, New York.