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Audubon Sugar Institute Contact Information:

Audubon Sugar Institute, LSU AgCenter
3845 Highway 75
St. Gabriel LA, 70776
Office: (225) 642-0135
Fax: (225) 642-8790

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STALK COLD TOLERANCE OF COMMERCIAL VARIETIES AT ARDOYNE FARM DURING THE 2016-2017 HARVEST SEASON*

M. J. Duet¹, B. L. Legendre², E.O. Dufrene¹, H. Birkett², J. Stein², J. R. Todd¹

¹USDA-ARS, Sugarcane Research Unit, Houma, LA

²Audubon Sugar Institute, St. Gabriel, LA

INTRODUCTION

Sugarcane is produced in 79 countries, with exposure to damaging frosts occurring in over 20 of them. The mainland of the United States is most frequently affected, specifically the Louisiana sugarcane growing region. The potential for winter freezes has forced Louisiana to adapt to a short growing season (7-9 months) and short milling season (about 3 months). To measure post-freeze deterioration of stalks of commercial and experimental varieties, a collaborative study was conducted at the USDA-ARS Ardoyne Farm in Schriever, LA between USDA-ARS, Sugarcane Research Unit at Houma, LA and the LSU Agcenter, Audubon Sugar Institute, St. Gabriel, LA.

MATERIALS AND METHODS

Each year variety trials designed to estimate stalk cold tolerance are established on a Sharkey clay soil at the USDA-ARS Ardoyne Farm. Commercial varieties of known cold tolerance are grown as controls. They include HoCP 04-838 for good cold tolerance and the Argentine variety TucCP 77-42 for poor cold tolerance. In general, a variety is considered to have “good” cold tolerance if sugar will crystallize from the juice of the variety four weeks after a freeze event with temperatures between 24-26°F. Crystallization would be hindered in a variety with “poor” stalk tolerance at the same temperature range. Between 8 to 12 commercial and experimental varieties, including the control varieties, are planted in a randomized complete block design with 4 replications; each plot is 3 rows wide (18 feet), and 32 feet long, with a 5 foot alley between plots. Plots are cultivated and fertilized according to recommended practices; insecticides are applied as required. When a hard freeze occurs (26°F or lower for over four hours), a field inspection is done to verify the severity of the freeze and determine if testing should be initiated. Samples are cut from the second row of each plot prior to or immediately following a damaging freeze to provide a baseline for comparison. Depending on the severity of the freeze and post-freeze weather conditions, the test is sampled weekly for 1 to 5 weeks post-freeze. Each sample consists of 10 stalks cut at the base by hand but not stripped of leaves or tops. Harvested samples are weighed to estimate stalk weight (lb/stalk) and processed at the USDA’s Juice and Milling Quality Laboratory using the pre-breaker/-press method. Juice samples are analyzed for Brix by refractometer and sucrose by polarization. The pressed sample residue (bagasse) is weighed, dried, and weighed again to determine moisture content. The Brix,

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sucrose, purity and fiber content of the cane was estimated from these values. This data were used to estimate sucrose content (lbs/ton of cane). Mean stalk weight is calculated from sample weight divided by the number of stalks. To evaluate the effect of freezing temperatures on cane quality, the following analyses were done. Juice samples are analyzed to determine pH, titratable acidity, total soluble polysaccharides, and dextran. Dextran analysis was performed on a subsample of juice using the ASI (Audubon Sugar Institute) Method II. Data were analyzed using the PROC MIXED procedure (SAS 9.4) to determine statistical differences among varieties at each sampling date and across sampling dates.

This experiment included eight commercial varieties (TucCP 77-42, HoCP 96-540, HoCP 00-950, L 01-283, L 01-299, HoCP 04-838, Ho 07-613 and HoCP 09-804) planted at the Ardoyne Farm on October 15, 2015. There were no experimental varieties included in the study.

RESULTS AND DISCUSSION

The first freeze of the 2016-2017 harvest season occurred on the nights of January 7 and 8, 2017. The minimum temperature at the test site was 24.2°F on both nights. On January 7 subfreezing temperatures occurred for 10 hours, with temperatures dipping below 26°F for 3 hours, 30 minutes. Temperatures dropped below 32°F for 14 hours on January 8 and below 26°F for 6 hours, 30 minutes. A field inspection on the morning of January 8 showed evidence of internal stalk damage on some varieties along with damage to the terminal buds of all varieties. There were no visible freeze cracks; however, weeping eyes were observed on many of the varieties. Daytime temperatures following the freeze event were above average, with a high of 81°F on January 10 and 12. Typically, warmer temperatures following a freeze event increase the rate of deterioration and cause a greater degree of deterioration within the varieties.

Samples were harvested on the mornings of January 10, 17, 24, 31 and February 6, 2017. Results for purity (%), sucrose content (lbs/ton), pH, titratable acidity (ml 0.1 N NaOH/10 ml juice to pH to 8.3), and total soluble polysaccharides are shown in Tables 1-5.

HoCP 04-838 and L 01-283 showed no significant reduction in purity for the duration of the sampling period (Table 1). One week following the freeze, TucCP 77-42 and L 01-299 each showed a significant drop in purity. The remaining varieties had significant decreases at one week and 4 weeks post-freeze, with HoCP 96-540 also showing a significant decrease at three weeks, and HoCP 09-804 showing a significant decrease at two weeks. Numerically, TucCP 77-42 had the largest decrease in purity followed by Ho 07-613; the smallest purity decrease was observed in HoCP 04-838.

Three varieties, L 01-283, HoCP 04-838 and HoCP 09-804 had no significant reduction in sucrose content after the initial sampling date (Table 2). At one week and four weeks post-freeze, HoCP 00-950 showed a significant decrease in sucrose content. The remaining varieties, TucCP 77-42, HoCP 96-540, L 01-299 and Ho 07-613 showed a significant decrease in sucrose content one week after the initial sampling. Both TucCP 77-42 and Ho 07-613 exhibited the

greatest decrease in sucrose content, while HoCP 04-838 and HoCP 09-804 showed the smallest decrease.

Only one variety, TucCP 77-42, showed no significant decrease in pH of juice across all sample dates (Table 3). A significant decrease in juice pH at four weeks post-freeze was recorded in L 01-299, HoCP 04-838 and HoCP 09-804. At three weeks post-freeze, HoCP 96-540, HoCP 00-950, L 01-283 and Ho 07-613 showed significant decreases in juice pH. Although TucCP 77-42 showed no significant decrease in juice pH across sample dates, it had the largest overall decrease in pH followed by Ho 07-613. Similar to other criteria, L 01-283, HoCP 04-838 and HoCP 09-804 showed the smallest decrease in juice pH.

Five varieties, HoCP 00-950, L 01-283, L 01-299, HoCP 04-838 and HoCP 09-804 exhibited no increase in titratable acidity compared to the initial sample date (Table 4). Three weeks post-freeze, both TucCP 77-42 and Ho 07-613 showed significant increases in titratable acidity, while HoCP 96-540 didn't show a significant increase until four weeks post-freeze. The largest increase in titratable acidity occurred in TucCP 77-42, nearly doubling three weeks after the initial sample date. The smallest increase occurred in HoCP 09-804 which showed no significant increase.

HoCP 04-838 was the only variety which did not have a significant increase in total soluble polysaccharides across harvest dates (Table 5). The remaining varieties showed an initial significant increase at one week post-freeze, but only TucCP 77-42 and Ho 07-613 showed a continued increase at two weeks post-freeze followed by a decrease at three weeks. By four weeks post-freeze, all varieties showed a reduction in total soluble polysaccharides when compared to the initial sample date. At four weeks post-freeze, HoCP 96-540 and HoCP 09-804 showed a significant decrease in total soluble polysaccharides from the initial sample date.

Using the five criteria to measure stalk cold tolerance, varieties were ranked based on the % change over the sampling period. Rankings were summed to provide an overall ranking for each variety (Table 6). Based upon this data it appears HoCP 09-804 and L 01-283 performed similar to the cold tolerant check variety HoCP 04-838. These varieties are classified as "Resistant or Very Good". HoCP 96-540, HoCP 00-950 and L 01-299 are classified as "Intermediate or Good". The remaining varieties; TucCP 77-42 and Ho 07-613 are classified as "Susceptible or Poor". These rankings are similar to those from previous test with the exception of L 01-283, which is usually listed in the Intermediate or Good category. Also this is the first time cold tolerance data was collected for HoCP 09-804, although a comparable test conducted in 2013 at the LSU AgCenter Sugar Research Station provided a similar ranking.

This was the first freeze event of the year, therefore the growing point and canopy was still intact for all varieties sampled. These factors can provide some level of protection from sub-freezing temperatures. The erectness of the cane can also affect stalk cold tolerance because cold air settles lower to the ground; therefore, lodged cane would be in closer proximity with colder temperatures for a longer duration than standing cane. The varieties in the above test

were mostly erect at the time of the freeze event. It is likely these factors affected the rate and extent of deterioration over the sampling period.

ACKNOWLEDGEMENTS

We would like to thank Dr. Michael Grisham, Research Leader, Jeannette Adams, juice lab coordinator and USDA-ARS staff from the breeding and weed science departments for making this collaborative project possible.

Table 1. Post-freeze changes in purity (%) of 8 commercial varieties in the plant-cane crop following sub-freezing temperatures on January 7 (24.2°F) and 8 (24.2°F), 2017 at the USDA-ARS, Sugarcane Research Unit's Ardoyne Farm in Schriever, Louisiana.

USDA ARS, Sugar Cane Research Unit, ARS John R. Porter, Louisiana							
	Purity (%)					Actual and percent change during harvest	
	Harvest Dates ¹						
Cultivar	1/10	1/17	1/24	1/31	2/6	change ²	(%)
TucCP77-42	86.86	77.94 -	73.18 -	70.35 -	<u>69.76</u> -	-17.10	-19.7
HoCP96-540	89.74	85.65 -	85.75	84.24 -	<u>81.84</u> -	-7.91	-8.8
HoCP00-950	90.81	85.56 -	87.02	86.36	<u>81.82</u> -	-8.99	-9.9
L01-283	90.07	87.76	87.97	<u>84.75</u>	85.76	-5.32	-5.9
L01-299	91.00	85.79 -	86.92 -	86.22 -	<u>84.46</u> -	-6.53	-7.2
HoCP04-838	89.93	<u>87.35</u>	89.65	89.52	87.73	-2.58	-2.9
Ho07-613	91.22	86.99	83.73 -	82.59 -	<u>80.02</u> -	-11.19	-12.3
HoCP09-804	90.17	86.77 -	87.38 -	87.42	<u>85.16</u> -	-5.01	-5.6
Averages by date	89.97	85.48	85.20	83.56 -	82.07 -	-11.51	-12.8

¹Statistically significant ($P = 0.05$) differences from first harvest date are denoted with a plus (+) or minus (-) sign.

²Represents the difference between initial sampling date and date with the lowest or highest value underlined in the following tables.

Table 2. Post-freeze changes in sucrose content of 8 commercial varieties in the plant-cane crop following sub-freezing temperatures on January 7 (24.2°F) and 8 (24.2°F), 2017 at the USDA-ARS, Sugarcane Research Unit's Ardoyne Farm in Schriever, Louisiana.

Cultivar	Sucrose content (lbs/ton)					Actual and percent change during harvest	
	Harvest Dates ¹					change ²	(%)
	1/10	1/17	1/24	1/31	2/6		
TucCP77-42	230	178 -	160 -	152 -	<u>146</u> -	-84.52	-36.7
HoCP96-540	261	231 -	239 -	235 -	<u>222</u> -	-39.41	-15.1
HoCP00-950	277	232 -	257	255	<u>232</u> -	-45.16	-16.3
L01-283	264	242	255	<u>237</u>	239	-27.32	-10.3
L01-299	276	<u>230</u> -	248 -	240 -	238 -	-45.81	-16.6
HoCP04-838	248	<u>228</u>	252	253	238	-19.47	-7.9
Ho07-613	279	249 -	227 -	224 -	<u>208</u> -	-70.77	-25.4
HoCP09-804	252	235	243	249	<u>229</u>	-22.72	-9.0

Averages by

date	261	228 -	235 -	229 -	<u>219</u> -	-41.90	-16.1
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¹Statistically significant ($P = 0.05$) differences from first harvest date are denoted with a plus (+) or minus (-) sign.

²Represents the difference between initial sampling date and date with the lowest or highest value underlined in the following tables.

Table 3. Post-freeze changes in juice pH of 8 commercial varieties in the plant-cane crop following sub-freezing temperatures on January 7 (24.2°F) and 8 (24.2°F), 2017 at the USDA-ARS, Sugarcane Research Unit's Ardoyne Farm in Schriever, Louisiana.

Cultivar	pH					Actual and percent change during harvest	
	Harvest Dates ¹					change ²	(%)
	1/10	1/17	1/24	1/31	2/6		
TucCP77-42	5.40	5.27	4.90	5.48	<u>4.57</u>	-0.82	-15.3
HoCP96-540	5.53	5.67	5.30 -	5.09 -	<u>4.99</u> -	-0.55	-9.9
HoCP00-950	5.55	5.65	5.28 -	5.06 -	<u>4.99</u> -	-0.56	-10.0
L01-283	5.54	5.74	5.35 -	<u>5.22</u> -	5.24 -	-0.33	-5.9
L01-299	5.54	5.54	5.35	5.13 -	<u>4.97</u> -	-0.58	-10.4
HoCP04-838	5.57	5.75	5.68	<u>5.18</u> -	5.36 -	-0.39	-6.9
Ho07-613	5.58	5.56	5.33 -	5.02 -	<u>4.91</u> -	-0.67	-12.0
HoCP09-804	5.54	5.64	5.49	5.24 -	<u>5.19</u> -	-0.36	-6.4

Averages by

date	5.53	5.60	5.33 -	5.18 -	<u>5.03</u> -	-0.50	-9.1
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¹Statistically significant ($P = 0.05$) differences from first harvest date are denoted with a plus (+) or minus (-) sign.

²Represents the difference between initial sampling date and date with the lowest or highest value underlined in the following tables.

Table 4. Post-freeze changes in titratable acidity of 8 commercial varieties in the plant-cane crop following sub-freezing temperatures on January 7 (24.2°F) and 8 (24.2°F), 2017 at the USDA-ARS, Sugarcane Research Unit's Ardoyne Farm in Schriever, Louisiana.

USDA ARS, Sugarcane Research Unit & Phylog Farm in Belmeyer, Louisiana.							
Cultivar	Titratable acidity (ml 0.1 N NaOH/10 ml juice)					Actual and percent change during harvest	
	Harvest Dates ¹					change ²	(%)
	1/10	1/17	1/24	1/31	2/6		
TucCP77-42	3.17	3.52	4.40	5.48 +	<u>6.24</u> +	3.07	96.7
HoCP96-540	2.17	2.04	2.36	2.57	<u>3.00</u> +	0.83	38.2
HoCP00-950	2.11	2.16	2.14	2.50	<u>2.61</u>	0.50	23.5
L01-283	2.23	1.80	1.93	<u>2.57</u>	2.22	0.34	15.3
L01-299	2.01	2.23	2.14	2.41	<u>2.76</u>	0.75	37.3
HoCP04-838	2.29	1.82	1.74	<u>2.71</u>	1.74	0.42	18.2
Ho07-613	1.64	1.57	1.85	2.30 +	<u>2.30</u> +	0.66	40.2
HoCP09-804	2.20	1.94	2.04	2.20	2.20	0.00	0.0

Averages by

date	2.22	2.13	2.32	2.84 +	<u>2.88</u> +	0.67	30.1
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¹Statistically significant ($P = 0.05$) differences from first harvest date are denoted with a plus (+) or minus (-) sign.

²Represents the difference between initial sampling date and date with the lowest or highest value underlined in the following tables.

Table 5. Post-freeze changes in total soluble polysaccharides of 8 commercial varieties in the plant-cane crop following sub-freezing temperatures on January 7 (24.2°F) and 8 (24.2°F), 2017 at the USDA-ARS, Sugarcane Research Unit's Ardoyne Farm in Schriever, Louisiana.

Cultivar	Total Soluble Polysaccharides (ppm/brix)					Actual and percent change during harvest	
	Harvest Dates ¹					change ²	(%)
	1/10	1/17	1/24	1/31	2/6		
TucCP77-42	9693.1	<u>17275.0</u> +	19586.0 +	12827.0	8678.9	9892.9	102.1
HoCP96-540	7448.0	<u>10724.0</u> +	9472.9	8002.5	6827.9	3276.0	44.0
HoCP00-950	6465.3	<u>10301.0</u> +	7894.9 +	6584.6	5291.6 -	3835.7	59.3
L01-283	6603.1	<u>9579.5</u> +	8335.0	8664.3	5087.7	2976.4	45.1
L01-299	5882.6	<u>10376.0</u> +	9189.6 +	7345.1	6747.5	4493.4	76.4
HoCP04-838	6247.1	<u>9898.6</u>	7390.3	9568.4	5180.9	3651.5	58.5
Ho07-613	4294.5	6954.7 +	<u>7178.2</u> +	5789.9 +	3728.6	2883.7	67.1
HoCP09-804	7427.8	9834.3 +	8706.7	6718.1	5186.5 -	2406.6	32.4

Averages by

date	6757.7	<u>10618.0</u> +	9719.2 +	8187.5	5841.2	3860.3	57.1
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¹Statistically significant ($P = 0.05$) differences from first harvest date are denoted with a plus (+) or minus (-) sign.

²Represents the difference between initial sampling date and date with the lowest or highest value underlined in the following tables.

Table 6. Reaction of commercial sugarcane varieties to sub-freezing temperatures during the 2016-2017 harvest season¹.

Resistant	Intermediate	Susceptible
HoCP 04-838 (9)	HoCP 96-540 (23)	Ho 07-613 (35)
HoCP 09-804(9)	HoCP 00-950 (25)	TucCP 77-42 (40)
L 01-283 (12)	L 01-299 (27)	

¹Varieties were ranked for performance within each of the five parameters used; the number in parenthesis is the sum of these rankings. The lower the number, the better the stalk cold tolerance.

MILLING, BOILERS AND EXCESS BAGASSE

Harold Birkett and Jeanie Stein

Mill performance tests and boiler efficiency and compliance tests are conducted almost every year at the request of individual factories. Progress continues to be made in both milling and boiler operations. Results from testing over the 2016 crop follow. Reasons for the large quantity of excess bagasse produced during the 2016 crop are discussed.

MILLING

Seven mill performance tests were requested during the 2016 crop. Results provided to factories included preparation index, pol % cane and bagasse, individual mill extraction and overall tandem extraction. Seven mini-mill tests were conducted in conjunction with testing of a new detrasher system at one factory and are included below.

Table 1. Prepared cane analyses for all mill tests.

Factory	Moisture % Prep Cane	Fiber % Prep Cane	Pol % Prep Cane	Ash % Prep Cane
G	72.77	13.39	10.62	1.09
C	68.58	14.91	12.51	1.44
D	73.26	13.51	13.01	1.48
D	70.28	14.98	13.37	1.42
C	74.27	14.12	12.28	1.38
B	68.70	13.89	14.91	1.61
B	68.02	15.31	14.81	1.60
K	68.65	13.29	14.07	1.88
B	67.91	15.85	15.26	1.43
B	67.17	15.11	15.27	1.62
A	70.28	13.79	10.94	4.64
B	66.91	15.46	14.82	1.01
B	71.04	14.47	14.69	1.04
B	69.60	13.92	15.53	0.99
AVG:	69.82	14.43	13.72	1.62

Table 1 above shows prepared cane analyses for moisture, fiber, pol and ash. Moisture % prepared cane averaged 69.82 and varied from 66.91 to 74.27. True fiber % prepared cane averaged 14.43 with a low of 13.29 and a high of 15.85. Pol % prepared cane ranged from 10.62 to 15.53 with an average of 13.72. The ash of the incoming cane averaged 1.62% and ranged from 0.99% to 4.64%.

Table 2 below presents first mill bagasse analyses for moisture, open cells and pol extraction. Moisture % first mill bagasse averaged 58.85 and varied from 55 to 62. Open cells % first mill bagasse ranged from 87 to 92.7 and averaged 90. The actual pol extraction of the first mill ranged from 59 to 67 and averaged 65.

Table 2. Analytical results from first mill.

Factory	Moisture % 1st Mill Bagasse	Open Cells % 1st Mill Bagasse	Pol Extraction %, 1st Mill
G	61.37	90.76	64.78
C	55.55	87.10	66.32
D	62.15	91.88	59.53
C	59.01	88.42	67.30
K	56.19	92.67	67.09
AVG:	58.85	90.17	65.00

Table 3 presents results from the analyses of last mill bagasse along with overall pol extraction. Bagasse moisture varied from a low of 44% to a high of 58% and averaged 49.52%. Pol % bagasse averaged 2.31 and varied from 2.02 to 2.78. Last mill bagasse was analyzed for the amount of open cells. Results range from 98.54% to 99.33% and averaged 98.84%. The average bagasse ash was determined to be 2.90% and varied from 1.92% to 6.11%. The overall tandem pol extraction averaged 94.34%, ranging from 91.57% to 95.82%. Reduced pol extraction varied from 92.47% to 96.83% and averaged 95.16%.

Table 3. Results from analyses of last mill bagasse along with extraction.

Factory	Moisture % Bagasse	Pol % Bagasse	Open Cells % Bagasse	Ash % Bagasse	Tandem Pol Extraction, %	Reduced Pol Extraction, %
G	52.68	2.54	99.12	3.66	91.87	92.48
C	58.00	2.16	98.67	2.03	93.06	94.34
D	50.88	2.50	99.02	2.65	94.04	94.55
D	51.52	2.44	--	2.37	93.77	94.95
C	53.41	2.31	98.76	1.97	93.52	94.37
B	46.85	2.35	98.73	2.85	95.44	95.96
B	48.19	2.27	98.63	2.98	95.06	96.10
K	47.56	2.16	99.33	3.93	95.59	95.89
B	45.08	2.02	98.93	2.66	95.82	96.83
B	44.01	2.78	98.54	3.07	94.49	95.58
A	57.31	2.14	--	6.11	91.57	92.47
B	46.40	2.16	98.78	1.95	95.40	96.41
B	45.77	2.16	98.83	2.46	95.59	96.28
B	45.68	2.41	98.77	1.92	95.51	96.03
AVG:	49.52	2.31	98.84	2.90	94.34	95.16

--No sample

BOILERS

This past crop (2016) assistance was given to eight factories who were required to compliance test eleven specific bagasse boilers as permitted by the Louisiana Department of Environmental Quality. Another factory also requested assistance in determining the efficiency of all five of their bagasse boilers. In all, forty-one boiler tests were conducted. Operating conditions and results provided included preheated air temperature, flue gas temperature, bagasse moisture, bagasse ash, oxygen % flue gas, excess air %, efficiency % and pounds steam produced per ton

of bagasse burned (Table 4). The effective moisture has also been calculated and is shown in Table 4.

Table 4. Temperatures and results of bagasse boiler testing.

Factory	Preh. Air, °F	Flue Gas, °F	Moist. % Bag.	Ash % Bag.	Effec. Moist., %	O ₂ , %	Excess Air, %	Effic, %	Lbs Steam/Lb Bag.
K	480	426	49.21	3.75	51.13	10.05	91.43	61.22	2.39
K	489	412	47.10	2.47	48.29	10.29	95.73	63.51	2.67
K	496	389	45.73	2.59	46.95	10.22	94.47	65.47	2.82
S	404	366	51.36	3.89	53.44	6.30	42.64	65.30	2.30
S	401	365	52.25	3.56	54.18	6.18	41.47	65.04	2.26
S	401	368	52.25	2.85	53.78	6.40	43.57	65.16	2.30
S	331	294	52.84	2.32	54.10	9.53	82.80	66.20	2.32
S	332	295	54.48	1.78	55.47	9.33	79.65	65.33	2.24
S	332	295	53.53	2.04	54.64	9.64	84.57	65.70	2.29
S	450	364	53.11	2.12	54.26	9.26	78.52	63.43	2.21
S	452	366	53.20	3.41	55.08	8.62	69.26	63.24	2.13
S	450	368	52.94	3.22	54.70	8.61	69.14	63.44	2.16
S	336	348	52.38	4.79	55.02	9.54	82.89	62.73	2.09
S	357	365	51.42	4.26	53.71	9.68	85.13	62.86	2.16
S	365	354	52.43	3.40	54.28	9.97	90.03	62.79	2.15
G	442	338	51.83	5.02	54.57	8.57	68.68	63.50	2.26
G	455	340	52.90	6.85	56.79	8.42	66.66	61.81	2.04
G	456	339	53.56	3.85	55.70	8.45	67.05	62.59	2.19
H	393	410	50.42	1.94	51.42	10.49	99.51	61.19	2.31
H	405	413	52.06	2.14	53.20	9.90	88.86	60.50	2.20
H	410	413	52.20	2.06	53.30	10.02	90.94	60.23	2.20
A	517	475	53.39	4.60	55.96	10.40	97.67	55.03	1.99
A	540	484	53.39	4.60	55.96	10.31	96.03	54.76	1.98
A	480	450	53.39	4.60	55.96	7.76	58.28	58.90	2.13
A	510	439	53.39	4.60	55.96	9.96	89.87	57.30	2.07
A	515	408	53.39	4.60	55.96	6.39	43.37	61.46	1.90
J	527	427	52.25	1.92	53.27	9.80	87.14	61.10	2.35
J	540	425	52.18	1.71	53.09	9.69	85.36	61.40	2.37
J	544	425	52.33	1.81	53.29	9.60	83.89	61.33	2.35
F	525	422	50.67	2.22	51.82	9.34	79.74	62.99	2.49
F	525	430	50.20	2.24	51.35	8.71	70.54	63.33	2.53
F	525	424	48.00	2.08	49.02	8.94	73.79	64.79	2.71
D	520	432	49.33	3.08	50.90	10.24	94.88	61.72	2.50
D	513	427	48.77	3.43	50.50	10.81	105.81	61.51	2.51
D	519	435	47.69	2.84	49.08	10.51	99.89	62.31	2.63
C	421	397	49.28	5.28	52.03	9.71	85.65	62.26	2.35
C	421	395	48.98	5.24	51.69	9.56	83.20	62.63	2.37
C	420	393	49.57	6.17	52.83	9.35	79.92	62.11	2.28
S	404	374	52.10	3.39	53.93	9.01	74.81	62.66	2.21
S	411	380	51.16	2.99	52.74	9.68	85.21	62.34	2.27
S	414	388	50.73	3.94	52.81	10.11	92.52	62.02	2.24
AVG:	448	392	51.40	3.41	53.22	9.25	80.01	62.27	2.29

Table 4 gives the results of all boiler tests conducted during the 2016 crop. Preheated air temperature varied from 331° to 544°F and averaged 448°F. Flue gas temperatures ranged from a

low of 294°F to a high of 484°F and averaged 392°F. Bagasse samples were collected during each test run and analyzed for moisture and ash. Moisture % bagasse averaged 51.40 (ranging from 45.73 to 54.48) while the ash % bagasse averaged 3.41 (and ranged from 1.71 to 6.85). Because bagasse fuel content is so critical to boiler efficiency, it is useful to look at its effective moisture (which is the moisture taking the ash into account). The effective moisture % bagasse averaged 53.22, almost 2% higher than the regular moisture. Oxygen levels varied from 6.18% to 10.81% and averaged 9.25%. Excess air levels ranged from 41% to 106% and averaged 80%. Efficiency ranged from 55% to 66% and averaged 62%. Each pound of bagasse burned produced between 1.90 and 2.82 pounds of steam, averaging 2.29, for the crop. This number has increased since the early days of boiler testing when the average pounds steam produced per pound of bagasse burned hovered around 2.00.

EXCESS BAGASSE

In recent crops most factories have had a large quantity of surplus bagasse while previously there was little surplus bagasse produced. There are several reasons for the current surplus:

1. Reduced steam usage by the factories.
2. Increased bagasse boiler efficiency.
3. Increased true fiber content of the cane.

Reduced Steam Usage by Factories

The steam requirement of most of the Louisiana sugar factories is controlled by the exhaust steam requirement of the boiling house. Typically, the exhaust steam produced by the factory turbines is insufficient to supply the boiling house and live steam make-up to exhaust is required. Over the years the factories have been employing more evaporator schemes that reduce the exhaust steam requirement of the factories. Initially, the move was from simple triple effect evaporators to quadruple effect evaporators. More recently, several factories have increased their use of first and second effect vapor for juice heating and sugar boiling. Both of these changes have reduced the exhaust steam requirement of the boiling house which in turn reduced the live steam make-up to exhaust and thus the total quantity of live steam required to operate the factory.

Increased Bagasse Boiler Efficiency

Over the last twenty years bagasse boiler efficiency has increased from about 55% to the current level of about 60%. This increase in boiler efficiency is attributable to better boiler operations, lower moisture bagasse and to the installation of new more efficient boilers. For a factory that was self-sufficient on bagasse, the increase in boiler efficiency from 55 to 60% would result in a 9% bagasse surplus.

Increased True Fiber Content of Cane

The steam generating potential is primarily determined by the fiber content of the cane. Figure 1 shows the true fiber content of the cane for the 1988 to 2016 period. From 1988 to 2012 the true fiber content of the cane delivered to the factories averaged 12.18%, while for the last four crops the average increased to 13.42%. The state's factories essentially became self-sufficient on

bagasse in 2010 with only about 1% of the factory's steam being supplied by natural gas as shown in Figure 2.

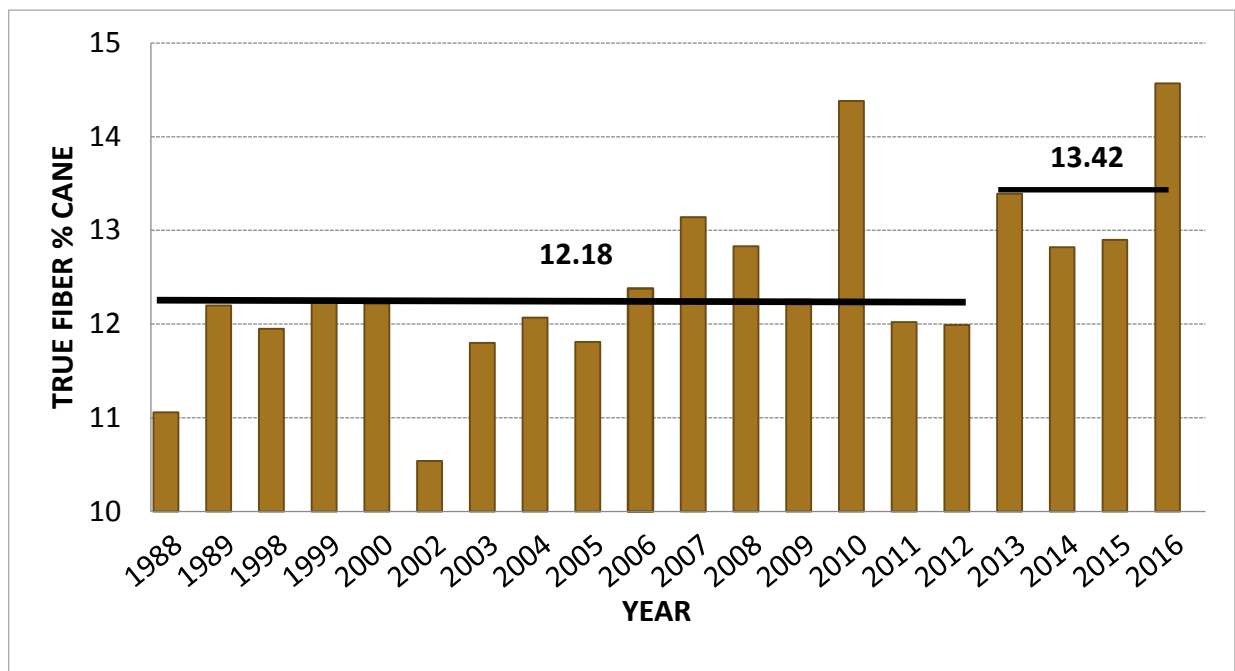


Figure 1. True fiber content of cane from 1988 to 2016.

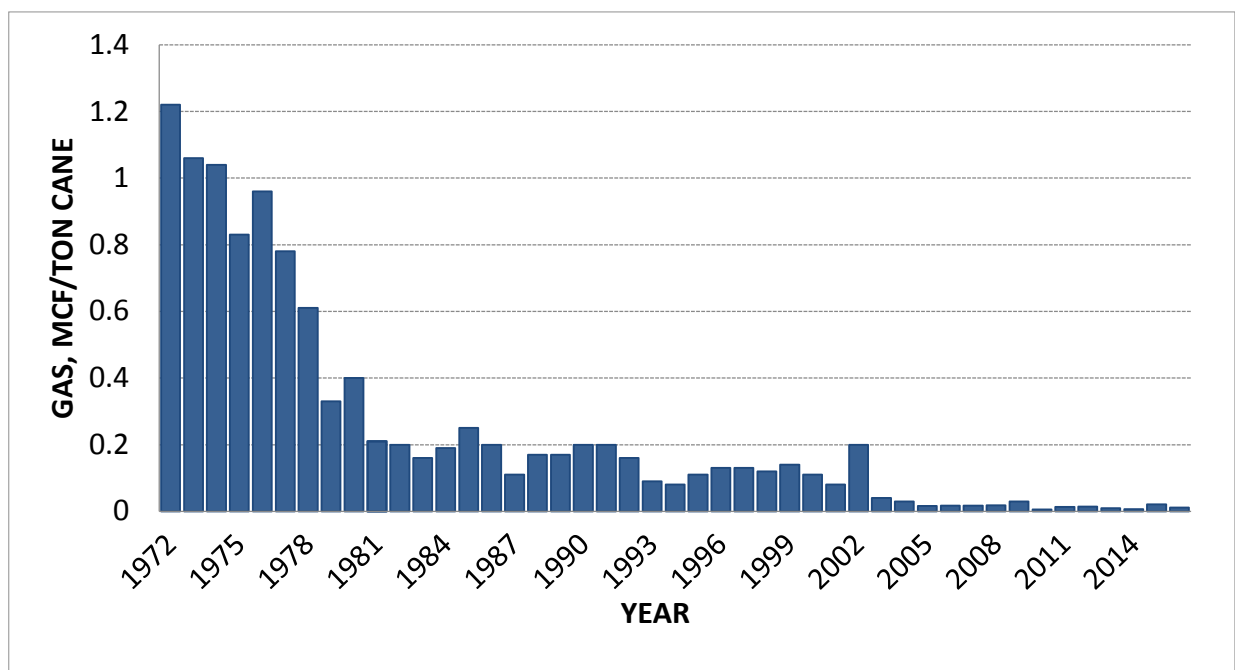


Figure 2. State gas consumption from 1972 through 2016.

For a factory that is self-sufficient on bagasse when the fiber content of the cane was 12.18% true fiber, the processing of cane with a true fiber content of 13.42% would be expected to result in a bagasse surplus of about 10%.

The high true fiber content of the cane processed in recent years is primarily due to dry harvesting conditions. Most of the commercial cane varieties in Louisiana have a true fiber content of about 12% in normal years although some recently released varieties such as HoCP 04-838 have a true fiber content of about 13.7%.

The combination of the reduced steam consumption of the factories, the increased boiler efficiency and the higher fiber content of the cane can easily explain a surplus bagasse quantity of 20%.

Summary

Milling efficiency and boiler efficiency has been steadily improving in Louisiana. In recent years, the dry harvesting weather conditions have contributed to increased true fiber content of the cane. Factory steam self-sufficiency was achieved in 2010, thus the increased true fiber content of the cane and the improved boiler efficiency have contributed to a surplus bagasse condition at all factories – particularly in 2016.

Crystal Size Analysis for Louisiana Sugar Mills

2016/17 Season

Franz Ehrenhauser, Cy Gaudet, Iryna Tishechkina, Daira Aragon

Crystal size analysis has been provided to Louisiana sugar mills since 2007 at the Audubon Sugar Institute (ASI). The crystal size analysis of A-, B-, C-sugars, massecuites and seed slurries is conducted at ASI with a Cilas 1180 laser diffraction particle size analyzer, which enables the quick turnaround of samples and allows the measurement of thousands of particles, which if done manually under an optical microscope would be impossible to accomplish in reasonable time. During the 2016/17 season 519 different samples were analyzed. As a continuing effort of previous years C-sugars were collected and analyzed from every mill and evaluated for their size and distribution.

C-SUGAR SAMPLES

As a continuance of last year's effort on assessing C-sugar size, 247 C-sugar samples were analyzed during the 2016 crop. Table 1 shows the overview of the last two years of C-sugar samples. The average diameter was 214 microns with a 10-percentile of 32 microns and a 90-percentile of 409 microns. Overall C-sugar crystal size increased compared to the 2015 crop. The mean crystal size increased from 203 to 214 microns. This change was mainly caused by increase of the 10 percentile (D10%) from 32 to 41 microns, whereas D90% only increased on average by 4 microns. This development is also reflected in an improved CV of 0.65 compared to the 2015 crop's value of 0.71. Considering the data of the last two years there seems to be currently an upper limit for the D90%, as the highest values for both years center around 440 microns.

Figure 1 shows the median value of the C-sugars sampled with data reaching back to 2011. Over the last two years the numbers have stabilized, indicating the adjustment to new boiling schemes at the factories. The average median value is 202 microns, which is lower than literature recommends (typically 250 to 300 microns), but likely to reflect Louisiana typical processing limitations in the boiling house. Larger crystals with lower CV purge better in the centrifugal machines; however, smaller crystals provide more specific surface area, allowing for higher throughput.

Figure 2 and Figure 3 show the average 10-percentile (D10%) and 90-percentile (D90%) for all Louisiana sugar mills during the 2015 and 2016 crops, respectively. The 10-percentile seemingly changed significantly for two mills (V and VI); however, in both cases improved sampling procedures (top of the centrifuge) might be the true cause. All mills had increased D10% except for two, where the change though was not significant. Considering that grain typically has a larger crystal size than 32 microns, it is clear that there is still room for improvement on the 10-percentile. The 90-percentile exhibits a similar picture, with a general trend to slightly larger D90%. Three mills are having lower average values than in 2015, though the values are not significantly different.

Figure 4 shows the average CV-values for the crops from 2011 to 2016. Due to the increase in the D10% and the lesser increase in the D90% a slight improvement, i.e. a decrease in CV is visible for all mills. The best historic mark of 0.52 (Mill IV in 2011) has yet to be achieved again and indicates further improvement is possible.

ACKNOWLEDGEMENTS

The authors would like to thank the American Sugar Cane League and the Louisiana sugar mills for their support and contributions to this research.

Table 1. 10-percentile, median and 90-percentile, Mean and CV-values of C-sugars during the 2015 crop. (Average values \pm standard deviation)

Mill	# of samples		D 10% [μm]		D50% [μm]		D90% [μm]		Mean [μm]		CV	
	2015	2016	2015	2016	2015	2016	2015	2016	2015	2016	2015	2016
I	49	46	37 \pm 17	40 \pm 14	186 \pm 36	174 \pm 36	393 \pm 34	372 \pm 46	203 \pm 29	192 \pm 29	0.66 \pm 0.07	0.65 \pm 0.09
II	61	38	35 \pm 10	44 \pm 11	188 \pm 32	209 \pm 30	416 \pm 18	427 \pm 14	208 \pm 20	223 \pm 17	0.69 \pm 0.06	0.65 \pm 0.06
III	22	19	47 \pm 14	39 \pm 9	228 \pm 38	173 \pm 26	429 \pm 18	387 \pm 29	233 \pm 23	195 \pm 20	0.61 \pm 0.07	0.67 \pm 0.04
IV	18	18	33 \pm 15	39 \pm 16	206 \pm 52	218 \pm 45	420 \pm 26	421 \pm 48	217 \pm 32	223 \pm 34	0.68 \pm 0.09	0.64 \pm 0.07
V	36	22	14 \pm 5	41 \pm 17	100 \pm 36	214 \pm 73	330 \pm 67	412 \pm 73	140 \pm 38	218 \pm 56	0.92 \pm 0.11	0.69 \pm 0.20
VI	11	13	20 \pm 6	54 \pm 25	147 \pm 34	209 \pm 39	383 \pm 26	416 \pm 19	174 \pm 28	224 \pm 29	0.77 \pm 0.08	0.61 \pm 0.10
VII	61	34	38 \pm 9	41 \pm 10	196 \pm 28	225 \pm 26	415 \pm 26	436 \pm 8	213 \pm 20	230 \pm 14	0.67 \pm 0.05	0.64 \pm 0.05
VIII	20	13	22 \pm 8	40 \pm 20	201 \pm 45	243 \pm 51	428 \pm 16	443 \pm 15	213 \pm 22	241 \pm 29	0.72 \pm 0.07	0.63 \pm 0.10
IX	16	11	22 \pm 9	39 \pm 15	159 \pm 49	184 \pm 44	406 \pm 25	415 \pm 22	191 \pm 27	208 \pm 27	0.78 \pm 0.08	0.69 \pm 0.10
X	58	17	29 \pm 15	29 \pm 9	190 \pm 49	220 \pm 46	417 \pm 23	435 \pm 15	209 \pm 30	224 \pm 22	0.71 \pm 0.10	0.69 \pm 0.07
XI	25	16	40 \pm 22	49 \pm 24	208 \pm 44	189 \pm 39	419 \pm 26	400 \pm 29	220 \pm 31	209 \pm 31	0.65 \pm 0.10	0.64 \pm 0.10
Overall	377	247	32\pm15	41\pm16	184\pm50	202\pm47	405\pm41	409\pm44	203\pm35	214\pm34	0.71\pm0.11	0.65\pm0.10

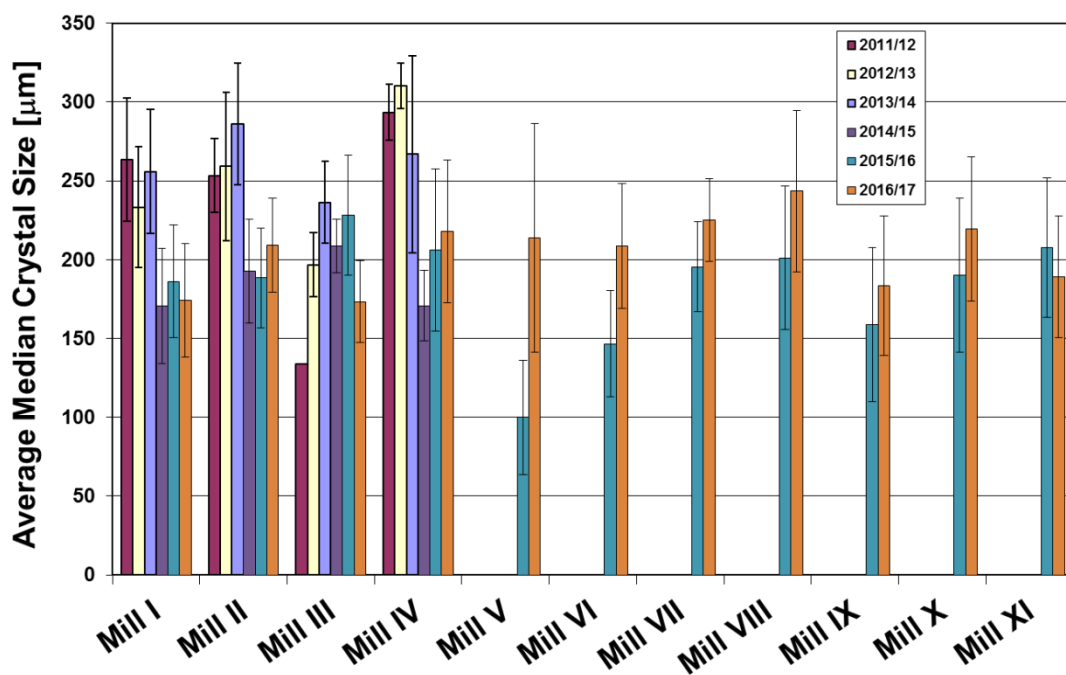


Figure 1. Average median crystal size of C-sugar during the 2011-2016 crops.

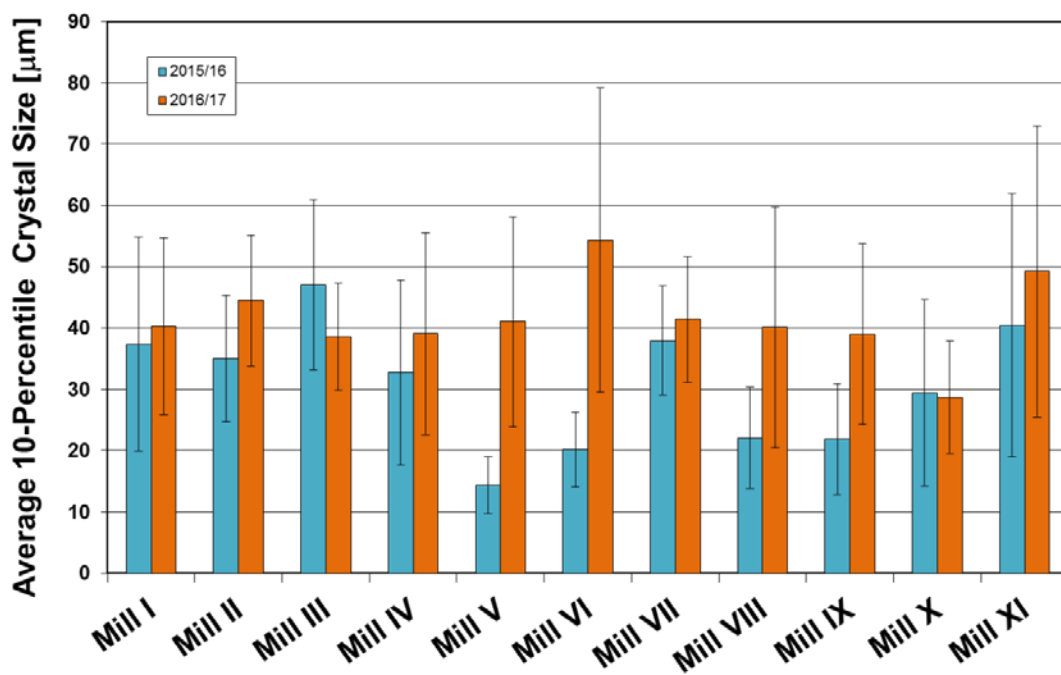


Figure 2. Average 10-percentile of C-sugar crystal size during the 2015 and 2016 crops.

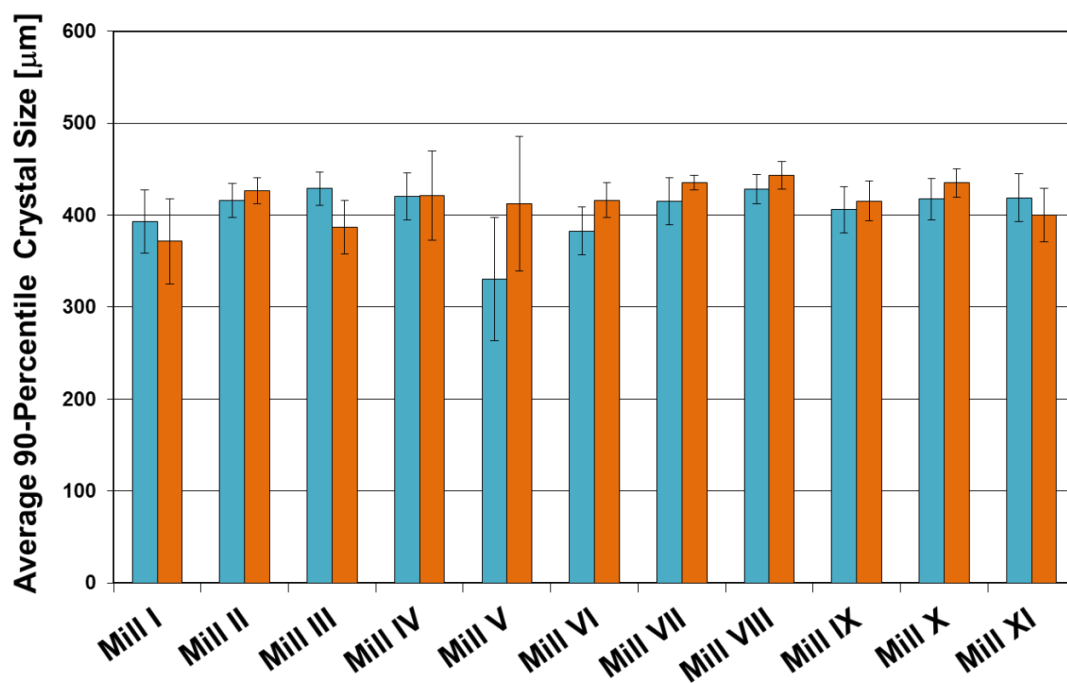


Figure 3. Average 90-percentile of C-sugar crystal size during the 2015 and 2016 crops.

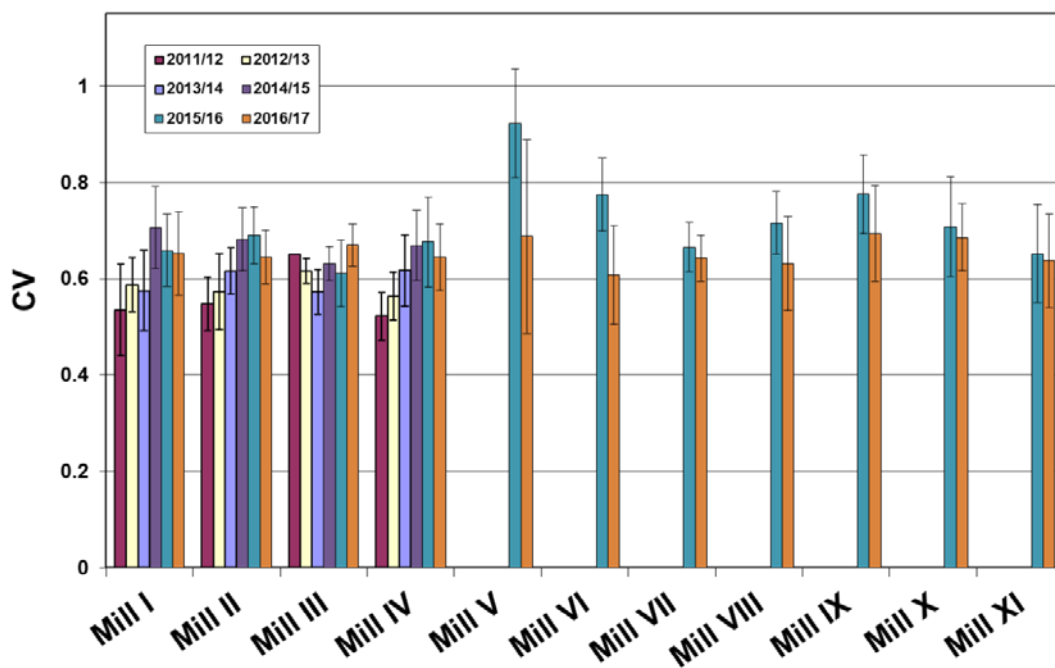


Figure 4. Coefficient of variation (CV) for C-sugar during the 2011-2016 crops

Ammonium in Sugar Cane Juice

Franz Ehrenhauser, Cy Gaudet

During the 2015 crop an unusual ammonia smell was observed at the mixed-juice incubation tank at the St. Mary factory. This excessive ammonia level had detrimental effects on boiling house performance and was only alleviated after taking the tank offline. Systematic sampling was not undertaken as the tank was quickly liquidated and only one sample could be obtained. For typical pH values of pH 5 to pH 8 in sugar cane processing ammonia is predominantly found as ammonium and was therefore analyzed for. The obtained sample from St. Mary showed an ammonium level of 30.8 mg/L and was compared to another mill's sample which had below 2 mg/L. While it is well-known that ammonium is present in sugar cane juice naturally, its "normal" level is unknown. As a follow up, a project was initiated to investigate the ammonium concentration in sugar cane juice before and after clarification as well as in syrup and investigate the possibilities of mill-suitable methods for ammonium measurement.

POTENTIAL ORIGINS OF AMMONIUM

Ammonium could come from two sources, either directly from soil/fertilizer application or from the sugar cane plant itself. Fertilizer can contain nitrogen either in form of ammonium or in form of nitrate. Nitrate can be microbially transformed to ammonium under oxygen depleted soil conditions and is therefore another potential precursor to ammonium in sugar cane juice. The other source of ammonium is the sugar cane itself or more precise the proteins and amino acids in sugar cane. Under heat these nitrogen containing compounds decompose to yield ammonia. pH values either in the acidic or alkaline region catalyzes the reaction. This is the most likely source of ammonium as asparagin is the dominant amino acid in sugar cane juice and easily releases ammonium. The amino acid concentration in sugar cane is the highest in the top and the bottom portion of the cane, as such e.g. detashing will reduce incoming amino acid load, but not prevent it completely. Ammonium can therefore be considered an omnipresent sugar cane impurity.

AMMONIUM MEASUREMENT

Ammonium can be measured through photometric assay (with ninhydrin or phenolic assay), by strips similar to pH-measurement strips, by ion chromatography and by ion-selective probe. The photometric assay was developed for water analysis and is rather unsuitable for sugar juices as primary and secondary amines react as well and the natural color of the juice interferes with the determination. The strips do not allow for proper quantification and ammonium is basically always present within their measuring range. Ion chromatography is fairly expensive and not suitable for Louisiana's routine labs, which operate only three month a year. The ion selective probe works similar to a pH probe; however, suffers from interference of potassium ions (100 parts potassium react as 1 part ammonium). While the interference for e.g. water samples is manageable, it is too much for sugar cane juices, where the typical potassium to ammonium ratio is 300 to 1. The ammonium probe is though quite suitable for condensate analysis, where ammonium is the dominant cation. Because of the potassium-rich nature of sugar juices ion chromatography was chosen as analysis and is now readily available at ASI.

AMMONIUM VALUES IN MIXED JUICE, CLARIFIED JUICE AND SYRUP

A total of 46 samples of mixed juice, clarified juice and syrup were collected during the 2016 crop from all Louisiana sugar mills. The samples were flash frozen in dry ice to prevent decay and analyzed for refractometric dry substance (RDS, ICUMSA GS4-13), conductivity ash (ICUMSA GS1/3/4/7-27) and cations with a Dionex ion chromatograph (20 µL injection volume, sample diluted to 1- 5 Bx, 0.2 µm-filtered, 0.4 mL/min, 30°C, 30 mM methanesulfonic acid, 50 mA cationic suppression,

10 mg/L Li internal standard, Dionex Ionpac CS16 3×250mm with 3×50 mm guard column). Table 1 shows an overview of the measured values.

Table 1. Average refractometric dry substance (RDS), ash and ammonium levels measured in mixed juice, clarified juice and syrup.

Stream	# samples analyzed	RDS [°Bx]	Ash [%/°Bx]	Ammonium [ppm/°Bx]
Mixed juice	6	14.7±1.0	3.5±0.35	42.5±19.6
Clarified juice	45	14.7±1.2	3.2±0.3	78.2±29.1
Syrup	46	61.6±5.7	3.2±0.4	32.8±13.8

Table 1 shows the average refractometric dry substance, ash and ammonium levels in mixed juice, clarified juices and syrups. A normal level of ammonium in mixed juice centers around 42.5 ppm/°Bx. For comparison the level measured in St. Mary's 2005-crop sample can be estimated at 200 ppm/°Bx. During the 2016 crop no comparable levels were observed. The ammonium level increases in the clarified juice, indicating the thermal decomposition of amino acids as a likely cause for the ammonium. This is so far surprising as at the higher temperature some removal is expected in the flash tank; however, only the application of vacuum reduces the ammonium content in the syrup to similar values as they are found in the mixed juice.

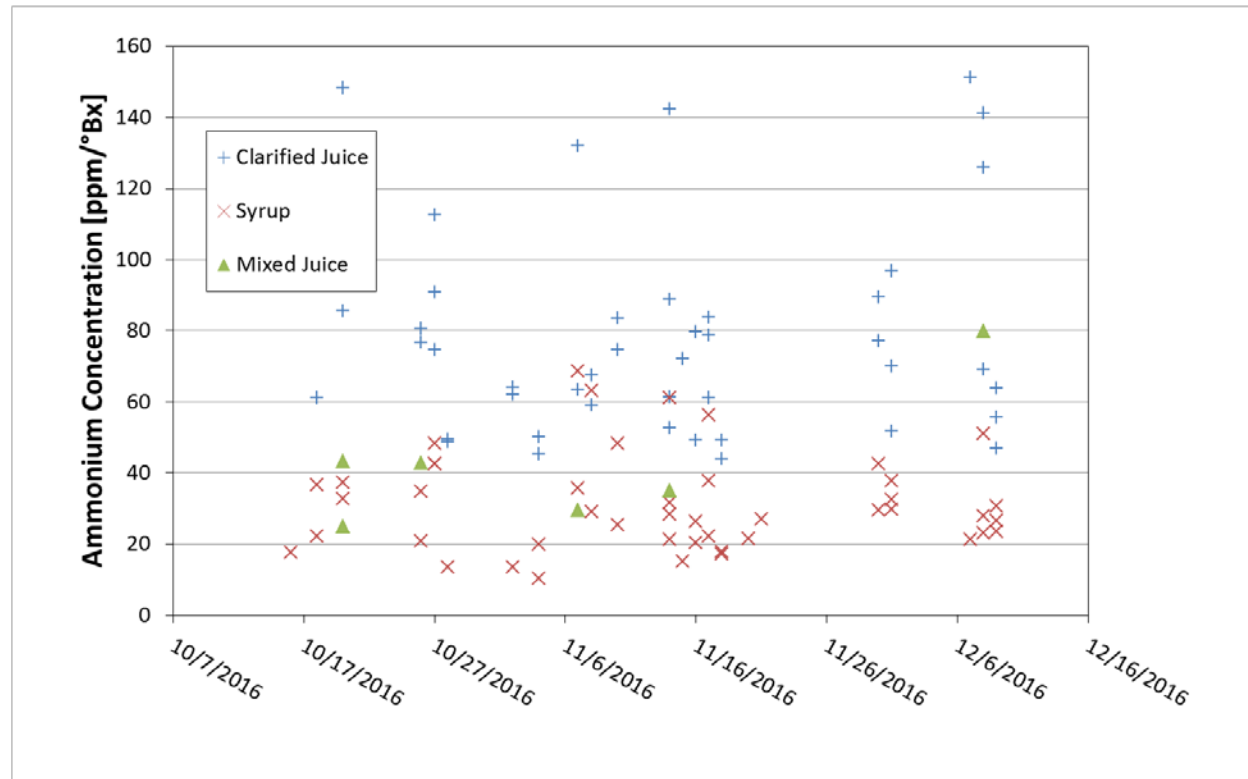


Figure 1. Ammonium levels in mixed juice, syrup and clarified juice during the 2016 crop.

Figure 1 shows the individual ammonium values for the 2016 crop. The values stray quite a bit and no general trend was recognizable, except for syrup and mixed juice having similar levels and clarified juice having an elevated level. Based on literature higher ammonium levels would be expected at the beginning of the season where more immature cane is expected; however, this was not confirmed in the current study. As such ammonium levels in the factory and with it ammonia is a rather omnipresent issue, without great dependence on cane quality changes due to different maturities.

The authors would like to thank all Louisiana sugar mills and their personnel for their support, as well as the American Sugar Cane League for funding this research.

THE 2016 MOLASSES SURVEY

C. Verret & C. Wall

INTRODUCTION

The loss of sugar in molasses is generally the largest loss suffered by a sugar mill. It is important that reliable data on molasses exhaustion be obtained. The Audubon Sugar Institute (ASI) undertook analyses of molasses samples for the mills in Louisiana from 1980-1997. It was briefly discontinued after the 1997 season and reintroduced in 2000 and is currently providing this service to the Louisiana sugar industry.

Since 2001, the Audubon Sugar Institute has analyzed the molasses provided weekly by each of the Louisiana raw sugar factories. The results of our analyses are used to calculate a “target purity (TP) and a true purity for the molasses. The TP is the theoretical concentration of sucrose (sugar) where, regardless of effort, no further sugar can be crystallized. The model that is used to calculate the TP originates from South Africa (Rein, 2007), and has been confirmed as representative of the Louisiana industry (Saska et al., 2010).

The true purity is determined by HPLC and is free of the interferences (reducing sugars) that can offset the accuracy of polarimetric determinations (particularly in molasses where purities are very low). The formula for TP is given below, where *RS* is the total reducing sugar (glucose + fructose) via HPLC (ICUMSA, 2002) and *Ash* is the approximate sulfated ash via conductivity (Saska et al., 1999).

$$TP = 33.9 - 13.4 \cdot \log_{10} \frac{RS}{Ash}$$

The TP is subtracted from the true purity to give a target purity difference or TPD. The TPD is used by the factories to determine how well they are recovering sugar from their massecuite (which is reflected by residual sugar in the molasses). “True purity” is the sum of the non-crystallizable sugar and that which was crystallized, but was lost across the centrifugals. For this reason, the nutsch should be assayed in order to determine how much sugar is lost across the centrifugals. Generally, a lower TPD indicates greater efficiency as it relates to recovery of sugar.

MATERIALS AND METHODS

Composite samples of final molasses (seven day) were sent to us weekly from each of the 11 mills in Louisiana. The 2016 survey season stretched from 09-25-16 until 01-01-17. A total of 159 molasses and syrup samples and 10 juice samples were analyzed in duplicate for the 2016 season. Including standards, this totaled 554 samples for 2016. Analyses included:

1. Refractometer Brix (ICUMSA GS4-13)
2. Sucrose, glucose and fructose by HPLC (ICUMSA GS7/4/8-23)
3. Sucrose via polarimetry*
4. Conductivity ash (ICUMSA GS1/3/4/7/8-13)

*Because we measure sugar using HPLC, we perform a direct polarization of molasses, syrup and juice samples are clarified using Octapol™ (Baddley Chemical) so that we can obtain a pol/sucrose ratio.

Double-blind quality control (QC) was performed each week. Briefly, a large sample of molasses is collected during the first week of the season. This sample is sub sampled into enough small containers to last the season (approximately 28-30 samples). Each week, two of these subsamples are pulled and included randomly into the weekly sample set. Each sample in the weekly set is mixed thoroughly and subsampled into containers identical to those used for the QC. A number is applied to each container, and the identity of each sample is kept in confidence until the analyses are complete.

RESULTS/DISCUSSION

The 2016 season operated for 15 weeks. The 2016 season maximum TPD weekly average was 12.5 and the minimum was 7.1. Throughout the season, the TPDs demonstrated the usual trend of decreasing TPD. The Industry average TPD for 2016 was 8.2. (Figure 1)

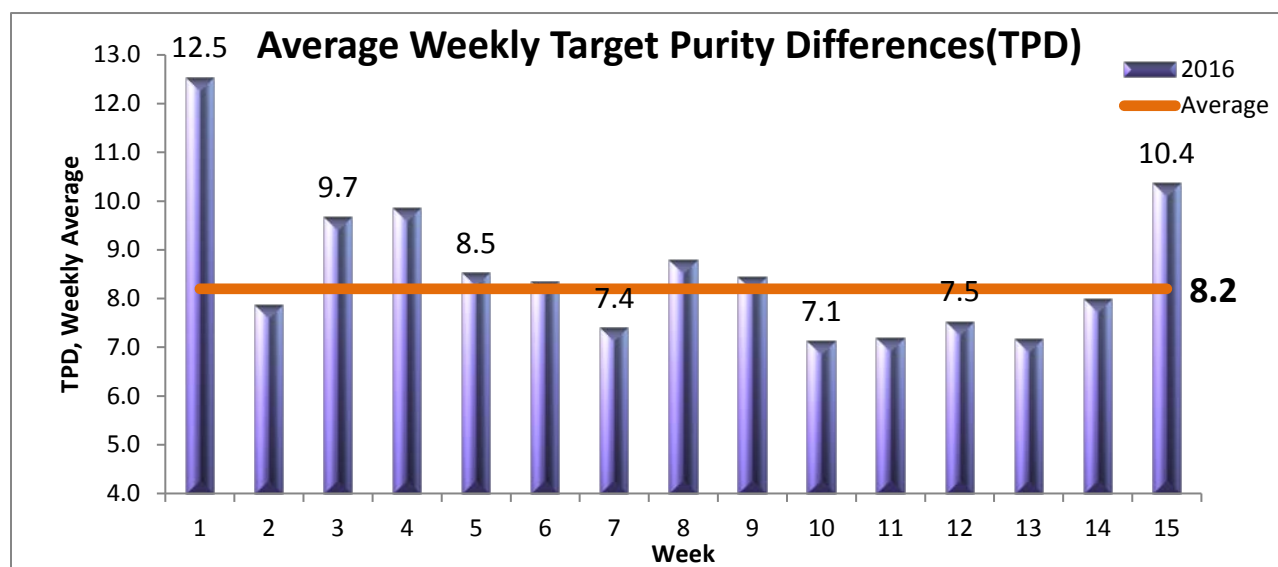


Fig. 1 – 2016 Average Weekly Target Purity Difference

The conductivity ash component for the 2016 season started at the minimum value of 12.6. As the season continued the ash increased to the maximum value of 17.1. The conductivity ash average was 15.5. (Figure 2)

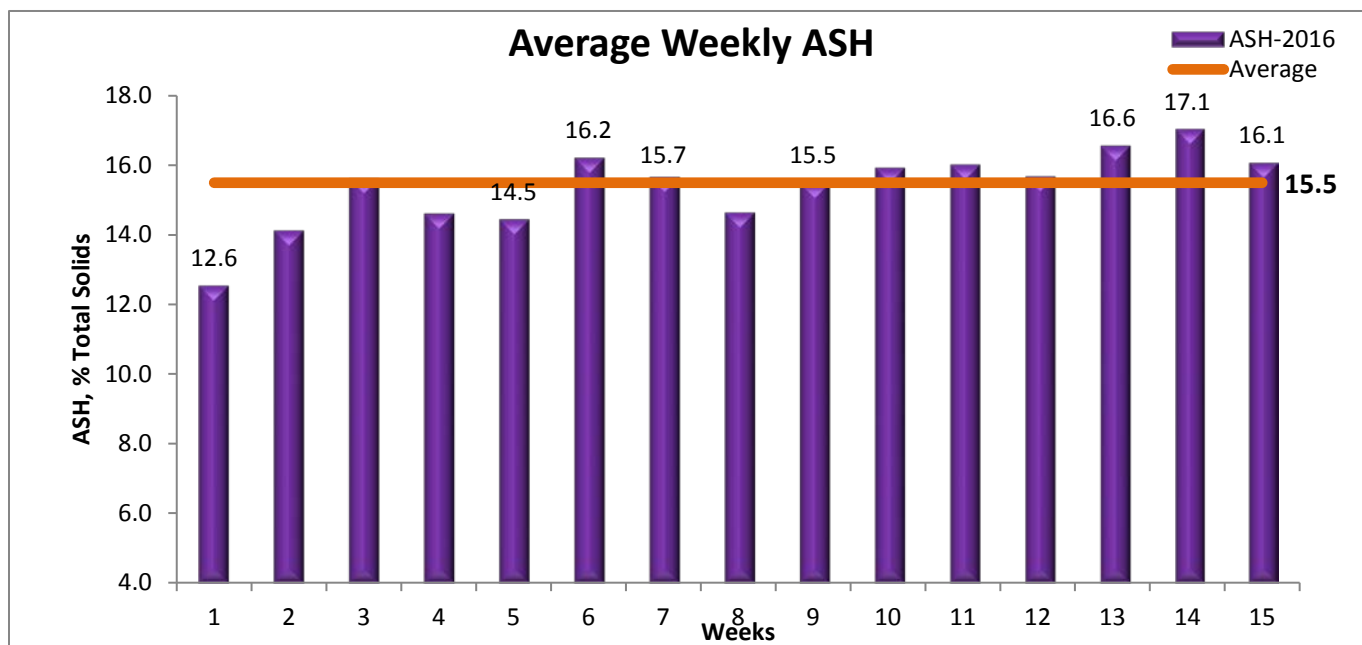


Fig. 2 – 2016 Average Weekly Conductivity Ash

In general, there has been a significant downward trend, relative to time, in the amount of reducing sugar in final molasses. In the 2016 season, the reducing sugars was up and down throughout the season. The maximum was 17.1 and the minimum occurred towards the end with 8.5. (Figure 3)

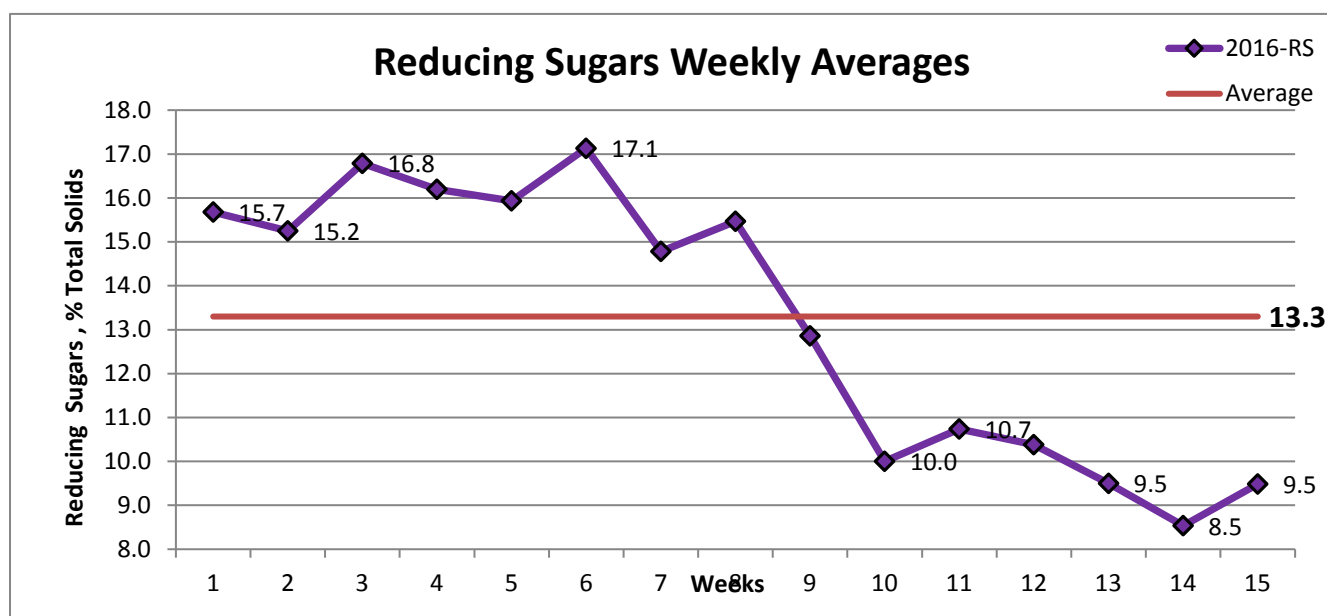


Fig. 3 –2016 Reducing Sugars Weekly Averages

Comparing the results from the 2016 season to the results from the 2012, 2013, 2014 and 2015 seasons showed the yearly average TPD decreased. This is demonstrated in **Figure 4**. The 2016 season maximum TPD was 9.5. The minimum TPD for 2016 was 6.5. (Table 1)

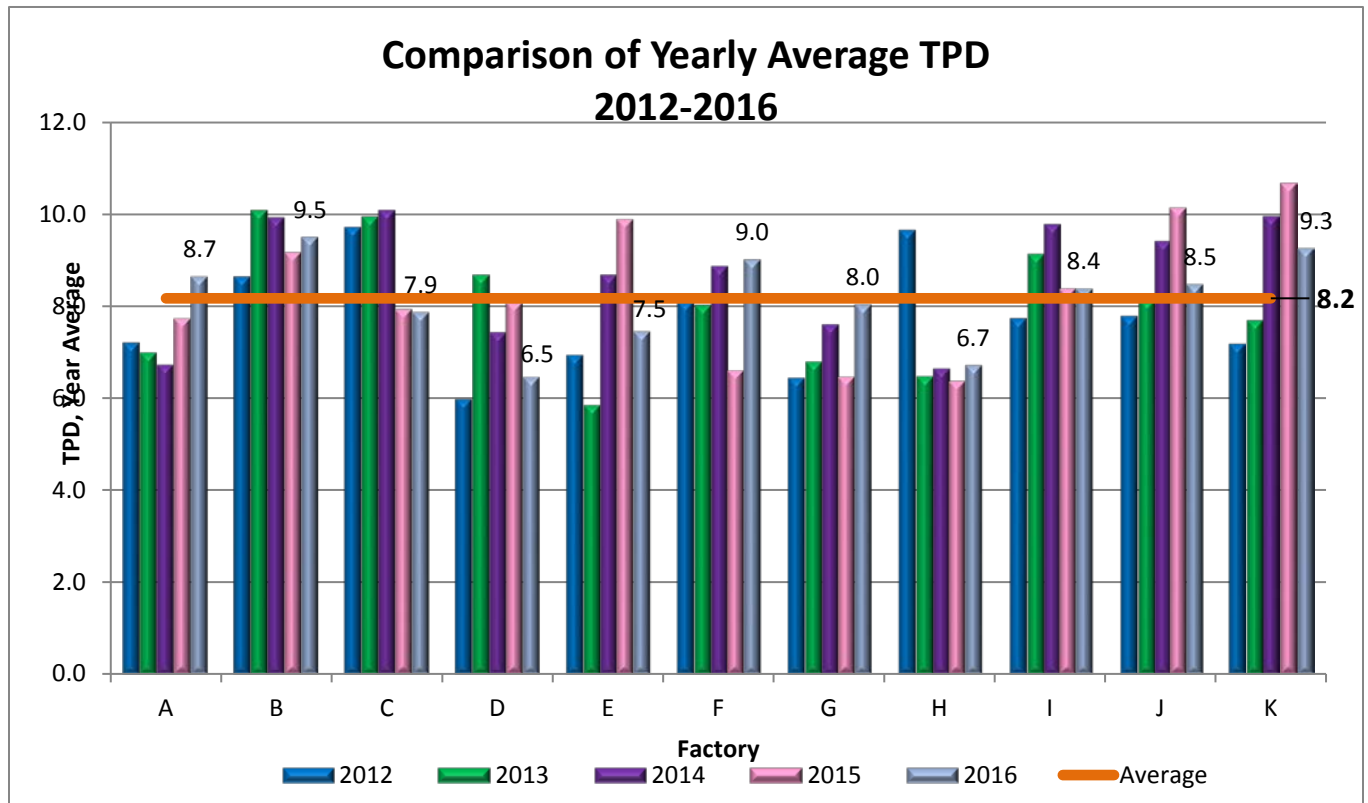


Fig. 4 – Comparison of Yearly Averages TPD 2012-2016

TPD Data Summary for 2012-2016			
Year	TPD Minimum	TPD Maximum	TPD Average
2012	6.0	9.7	7.8
2013	5.8	10.1	8.0
2014	6.6	10.1	8.6
2015	6.4	10.7	8.3
2016	6.5	9.5	8.2

Table 1 – Summary of Yearly TPD 2012-2016

The sugar cane juice from the sugar mill has been analyzed for the past 7 years. In **Table 2**, shows the summary from the analysis. Over the last seven seasons, the average brix is 14.5%, a true purity average of 88.9% and reducing sugars 5.1%.

Juice Survey Summary for 2010-2016			
Year	Ref. Brix (%Juice)	True Purity (% Juice)	Reducing Sugars (%Juice)
2010	14.5	89.3	3.8
2011	15.1	87.2	5.0
2012	14.6	88.1	3.6
2013	14.1	91.1	10.8
2014	14.8	88.7	4.1
2015	13.5	88.9	3.2
2016	15.1	88.9	5.2
Average	14.5	88.9	5.1

Table 2 – Summary of Juice Survey 2010-2016

CONCLUSIONS

The seasonal average TPD was 8.2 for the 2016 season, which was a slight decrease from the 2015 season. The ash decreased for the 2016 season to 15.5%. The reducing sugars increased for the 2016 season to 13.3% from 11.9% from the previous season.

The differences can be attributed to a wide range of factors which included weather conditions and harvest conditions, cane maturity and increased awareness at the cane delivery/mill level.

The mills are conscious of their TPD and are continuing to improve.

For the 2016 season, the juice had an average brix of 15.1%, a true purity of 88.9% and reducing sugars of 5.2%.

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Monitoring Crystal Growth along the CVP

Daira Aragon and Iryna Tishechkina

Introduction

Crystallization in the C strike can be performed in batch pans or in continuous pans. In batch pans, the massecuite is boiled until the desired volume (cu.ft.) and desired size. If the size has not been achieved even though the final volume has been reached, the massecuite is “cut” by sending some of it into a different pan to continue growth. On the other hand, grain and molasses are introduced continuously in a continuous vacuum pan (CVP), where massecuites move, and crystals grow, from one cell to the next one. Ideally, the massecuite flow within a CVP would be of plug flow, where all crystals stay in the CVP for the same time, and no stagnant volume would exist (Rein, 2007). Advantages of a CVP include more uniform crystallization conditions. Therefore, a well-run CVP should theoretically produce a good crystal size distribution. Monitoring the crystal growth along the cells of a CVP can aide in determining potential issues with flow patterns and improvements on seeding procedures. This paper presents the evolution of the C grain in CVP pans and compares with a batch pan.

Procedure

Samples of C grain and massecuite from several cells along the CVP and from the discharge point were collected in Styrofoam containers at a sugar factory in 2016. Samples were transported after collection to the Audubon Sugar Institute where crystal size distribution was measured shortly after arrival to minimize the time between sampling and analysis. Additionally, samples of C grain and C massecuites from a batch pan were collected at another factory in 2016 and analyzed in a similar manner to the CVP samples. Crystal size distribution from massecuite samples along a CVP at a different factory, taken in 2015, were also included in the results for comparison purposes.

Results and Discussion

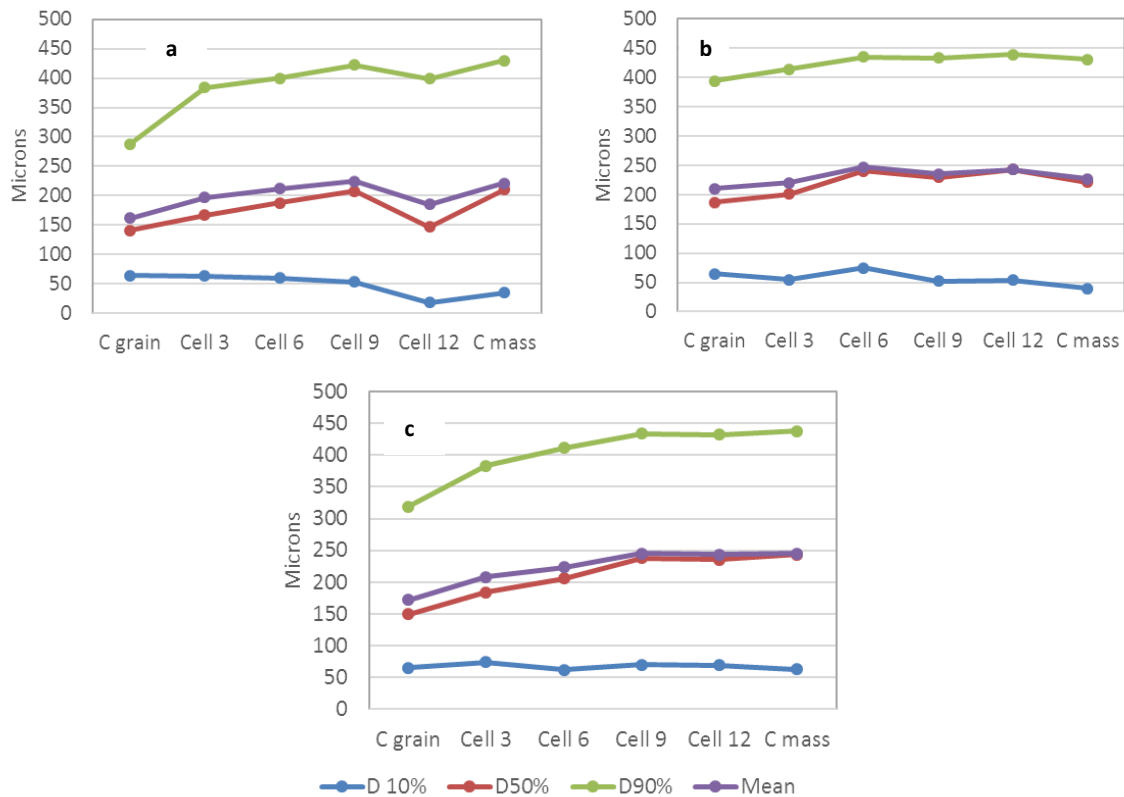
Continuous Vacuum Pan (CVP)

Table 1 shows the average distribution for C grain and C massecuite at the discharge of the CVP. In addition to the overall average, samples were separated depending on whether they were taken at the beginning of the season (first three weeks of grinding), middle of the season and end of the season (last three weeks of grinding). Results in Table 1 show that, overall, the mean crystal size grew from 181 to 233 microns, a total of 52 microns or 28% growth. The D90%, which indicates the amount of largest crystals, grew from 346 to 436 microns, a total of 90 microns or 26% growth. On the other hand, the D10% changed from 63 to 48 microns, suggesting that the relative amount of small crystals is higher in the final massecuite. Table 1 also shows that crystal size distribution of C grain and C massecuite was somewhat consistent during the season, only having significant variations at the beginning of the season. CV values of C grain and C massecuites were comparable to those usually obtained in Louisiana for C sugars. The maximum growth from C grain to C massecuite in samples analyzed was 49% for D90% and 51% for the mean. The crystal size distribution of this CVP during 2016 was very good.

Table 1. Average C grain and C massecuite crystal size distribution for a CVP in 2016

Sample		D 10%	D50%	D90%	Mean	CV
C grain	All samples	63	155	346	181	0.61
	Begin of season	64	141	288	162	0.57
	Middle of season	64	158	360	186	0.62
	End of season	62	157	348	182	0.61
C massecuite	All samples	48	230	436	233	0.62
	Begin of season	35	210	430	221	0.67
	Middle of season	50	233	437	236	0.61
	End of season	52	232	437	236	0.61

The crystal growth along the CVP for three different days during the 2016 season are shown in Fig. 1. There was growth along the CVP in all three samples, although the last cell did not show as much growth as the other. In some cases, such as Fig. 1a, there was an increase in smaller crystals in the last cell of the CVP, which in turn, lowered the D50%, D90% and the mean. Sample illustrated in Fig. 1b showed little growth, particularly because the C grain entering the CVP was already big (mean of 210 microns and D90% of 394 microns). The results for the CVP analyzed in 2016 contrast with those from a CVP at a different factory, taken during 2015, in which there is no growth along the CVP (Fig. 2). The C grain entering the CVP from Fig. 2 showed a mean and D90% of 243 and 439 microns, respectively, leaving no room for additional growth in the pan.

**Fig. 1** Crystal growth along CVP-1 for individual samples at the beginning of the 2016 season (a), middle of the season (b) and end of the season (c)

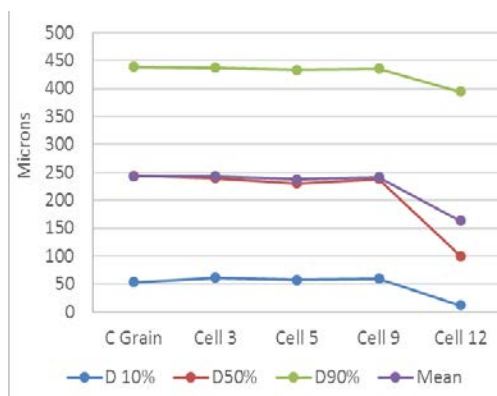


Fig. 2 Crystal growth along CVP-2 at a different factory during the middle of the 2015 season

Batch pan

Average crystal size distribution obtained for a batch pan in 2016 are shown in Table 2. C grain distribution is somewhat consistent throughout the season, while C massecuites present more variation. For this pan, there was a decrease in crystal size for all samples, primarily because of higher amounts of fine crystals, with D10% changing from an overall value of 56 microns for C grain to 15 microns for C massecuites. Larger crystals, however, grew consistently from overall D90% value of 338 to 391 microns, a total of 53 microns or 16% growth. This behavior was observed in each individual sample. Overall mean decreased from 178 to 168 microns, with some individual samples showing improvements while others didn't. Maximum growth for D90% and Mean were 36% and 22%, respectively. Coefficients of variation (CV) for C grain are comparable to those for C sugar and for CVP-1, while CV for C massecuite are higher due to more fines present in the samples.

Table 2. Average C grain and C massecuite crystal size distribution for a batch pan

Sample		D 10%	D50%	D90%	Mean	CV
C grain	All samples	56	158	338	178	0.61
	Begin of season	61	173	368	194	0.59
	Middle of season	57	141	300	162	0.61
	End of season	52	168	361	187	0.63
C massecuite	All samples	15	120	391	168	0.89
	Begin of season	8	64	380	138	1.10
	Middle of season	22	163	389	185	0.75
	End of season	12	106	398	167	0.92

Results presented in this study showed that it is possible to obtain a good crystal size distribution in a CVP. Special attention on the C grain size is needed so that it can grow further in the pan; when grain is too big with mean sizes and D90% above 200 and 350 microns, correspondingly, there could be no growth in the pan translating into loss in time and capacity. Compared to a batch pan, relative crystal growth in the CVP was up to 29 percentage points higher than in the batch pan. The CVP also had less fine crystals and less size variations throughout the grinding season.

Acknowledgments

The authors would like to thank personnel from sugar factories in Louisiana for providing access to samples, Dr. Franz Ehrenhauser and Mr. Cy Gaudet assisting with sampling and the American Sugar Cane League for providing funding for this project.

PRODUCING LOW PURITY FINAL MOLASSES WHEN PRODUCING HIGH POL SUGAR FROM HIGH PURITY SYRUPS

Harold Birkett and Jeanie Stein

In recent years local sugar refineries have been paying premiums for very high pol (VHP) sugar and requiring that their suppliers produce VHP sugar. The premiums being paid make the production of VHP attractive. The need to produce VHP sugar has resulted in a shift from the conventional three boiling system to the double magma system. In the double magma system where all of the C sugar is used in the B strike, and where all of the B sugar is used in the A strike results in higher B and A massecuite purities in comparison with the previously common three boiling scheme. Louisiana syrup purities have been increasing over the years and current crop average syrup purities are about 88 as shown in Figure 1, with individual factories obtaining 89 to 90 purity syrup during the crop as shown in Figure 2. Figure 2 shows the factory with the highest crop average syrup purity together with the factory with the lowest syrup purity during the last two crops (2015 and 2016).

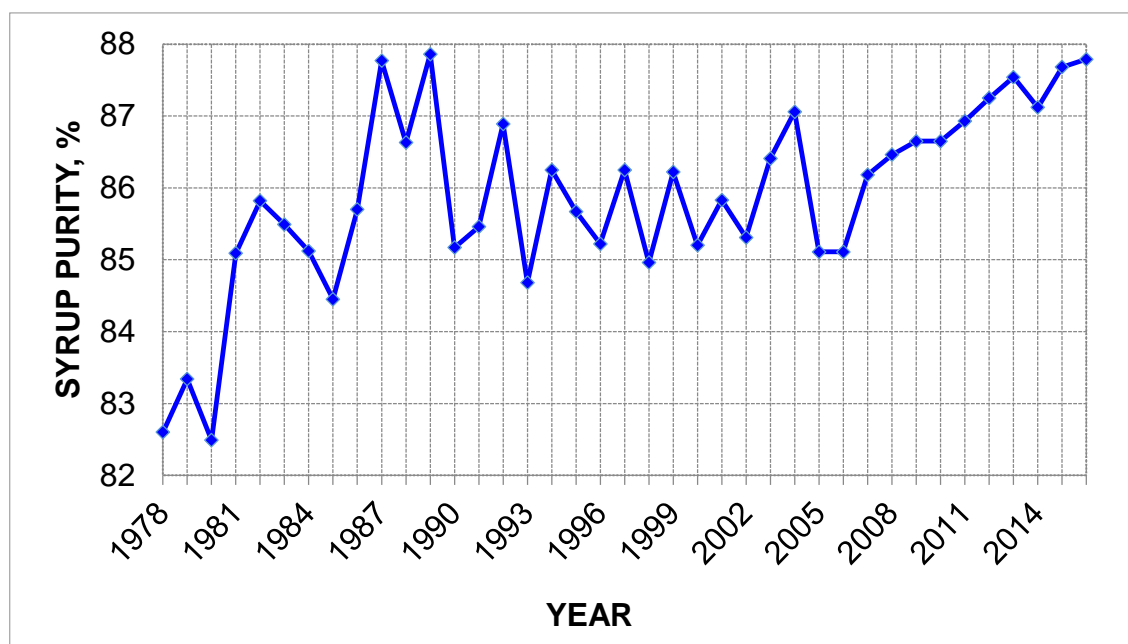


Figure 1. Yearly average syrup purities from 1968 through 2016.

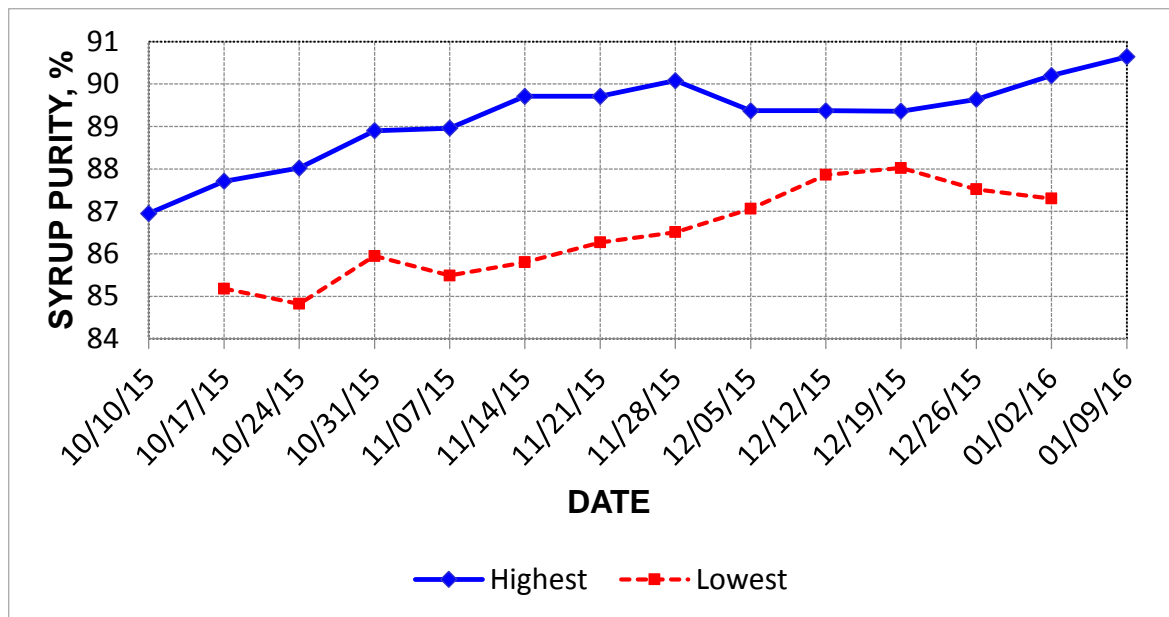


Figure 2. Syrup purities for the factory with the highest crop average along with syrup purities for the factory with the lowest crop average.

High purity syrups processed using the double magma boiling scheme result in high purity massecuites (A, B and C massecuite). High purity C massecuites result in high purity final molasses thereby reducing sugar recovery. Purity data for massecuites and their corresponding molasses for the last two crops (2015 and 2016) are shown in Table 1. Figure 3 shows the relationship between C massecuite purity and the corresponding final molasses purity using data taken from Table 1.

Table 1
Syrup, Massecuite and Molasses Purities - 2015 Crop Average

Factory	Syrup	A Massecuite	A Molasses	B Massecuite	B Molasses	C Massecuite	Final Molasses
8	87.75	87.89	74.17	74.91	55.95	58.00	38.08
11	87.86	85.77	69.72	70.86	49.95	50.97	32.38
15	89.20	84.85	68.47	70.93	51.36	53.62	37.67
20	88.59	88.98	75.20	71.95	55.33	54.26	37.04
23	86.96	87.91	73.19	76.34	57.62	60.26	39.40
24	86.60	86.61	70.96	75.05	54.42	56.03	35.60
25	87.30	87.73	72.11	78.66	60.35	60.52	37.88
26	87.96	84.78	65.42	74.30	53.71	55.39	34.73
27	86.42	88.54	73.88	75.62	54.93	56.89	35.23
28	88.53	85.72	66.33	75.70	56.97	58.78	35.29
29	87.32	87.21	70.57	73.40	52.87	54.80	33.31
Average	87.68	86.91	70.91	74.34	54.86	56.32	36.06

Syrup, Massecuite and Molasses Purities - 2016 Crop Average

Factory	Syrup	A Massecuite	A Molasses	B Massecuite	B Molasses	C Massecuite	Final Molasses
8	87.85	88.30	73.34	73.94	52.89	55.79	37.08
11	87.55	85.29	68.64	70.71	49.91	51.77	32.64
15	88.17	85.26	67.41	70.47	49.16	51.48	34.23
20	87.95	85.54	68.71	70.52	50.95	51.74	35.31
23	87.71	89.08	75.29	77.75	57.84	58.80	36.92
24	88.46	87.84	72.39	75.44	56.10	57.33	36.70
25	88.29	88.07	72.87	79.60	60.54	60.13	37.08
26	87.94	85.25	66.69	75.44	56.25	57.46	36.46
27	86.62	86.83	72.48	75.38	54.33	55.99	35.38
28	88.54	88.36	72.43	73.34	51.68	53.28	32.46
29	86.64	87.97	72.47	74.06	54.18	56.23	35.80
Average	87.79	87.07	71.16	74.24	53.98	55.45	35.46

Data for Factories with C Massecuite Purity below 52

Factory	Syrup	A Massecuite	A Molasses	B Massecuite	B Molasses	C Massecuite	Final Molasses
11	87.86	85.77	69.72	70.86	49.95	50.97	32.38
11	87.55	85.29	68.64	70.71	49.91	51.77	32.64
15	88.17	85.26	67.41	70.47	49.16	51.48	34.23
20	87.95	85.54	68.71	70.52	50.95	51.74	35.31
Average	87.88	85.47	68.62	70.64	49.99	51.49	33.64

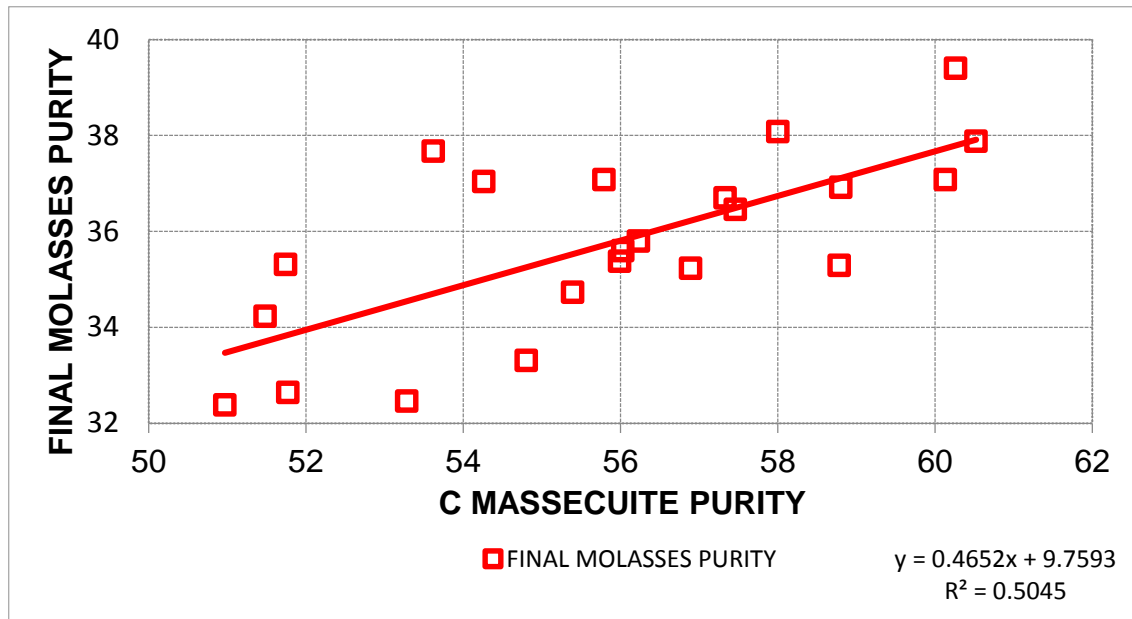


Figure 3. C Massecuite purity versus final molasses purity for 2015 and 2016.

The purity of molasses that can be expected from a massecuite depends on the crystal yield that can be expected. Crystal yield is defined as the 100% pure sugar crystal present in a massecuite expressed as a per cent of the solids in the massecuite. The crystal yield can be calculated from the following equation:

$$\% \text{ Crystal Yield} = \frac{(\text{Massecuite Purity} - \text{Molasses Purity}) \times 100}{(100 - \text{Molasses Purity})}$$

The relationship between massecuite purity and crystal yield is shown in Figure 4 using the data presented in Table 1. The equation that best fits the data is:

$$\% \text{ Crystal Yield} = 0.7609 \times \text{Massecuite Purity} - 11.693$$

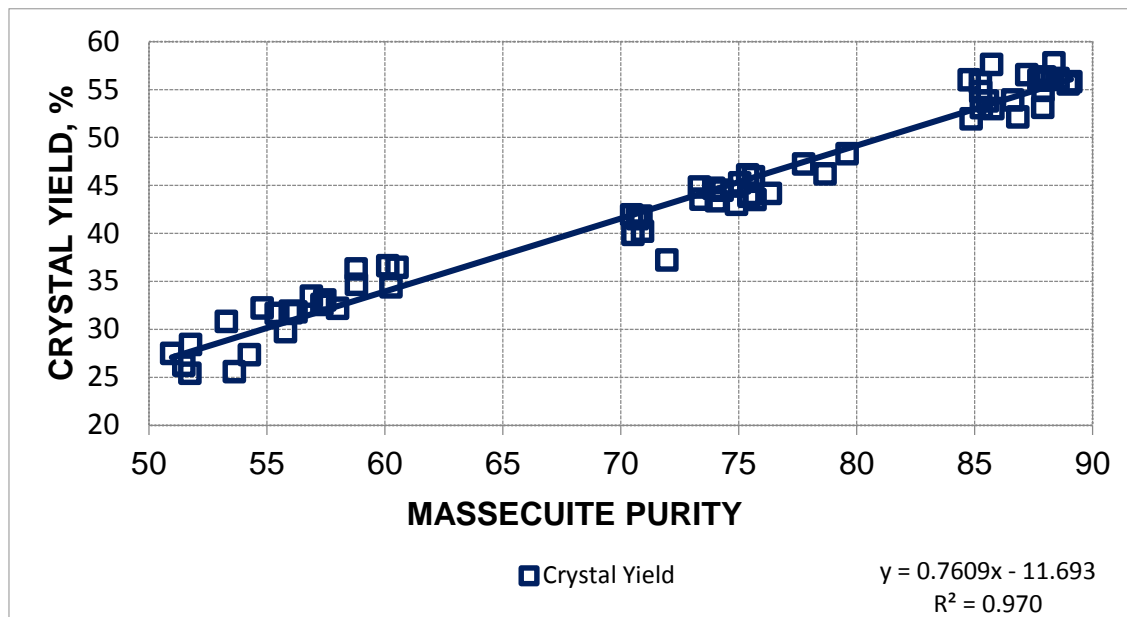


Figure 4. A-B-C Massecuite purity versus crystal yield for the 2015 and 2016 crops.

Reducing the Purity of the Final Molasses

The data shown in Table 1 and Figure 3 indicates that low purity C massecuites generally produce low purity final molasses, i.e. a low purity C massecuite purity is a necessary but insufficient requirement for obtaining low purity final molasses. The state average C massecuite purity for the 2015 and 2016 crops was about 56 purity, while the factories achieving the lowest final molasses purity produced massecuite of about 52 purity. Assuming a goal of producing C massecuites of no more than 52 purity typically requires B molasses of no more than 50 purity.

Based on achievable crystal yields a B massecuite purity of no more than 71 is required to produce a B molasses purity of 50. Similarly, to produce a B massecuite of 71 purity requires an A molasses purity of about 68. To achieve an A molasses purity of 68 requires an A massecuite purity of 85. In the standard double magma system, the A massecuite is produced from a B sugar magma and syrup, but as the B magma typically has a purity of 92, while the average syrup purity is 88, achieving an A massecuite purity of 85 is impossible with the standard double magma system.

The above analysis demonstrates that under Louisiana conditions modifications to the standard double magma boiling scheme is required. To achieve 52 purity C massecuites several options are available including, but not limited to, the four options listed below that are considered in this discussion:

1. Top off A massecuites with A molasses.
2. Top off B massecuites with B molasses.
3. Top off C massecuites with final molasses.
4. Utilize the 4 boiling version of the double magma scheme.

Alternate cases such as combining options 1 and 2 listed above are not included in this discussion.

To compare the pan requirements, centrifugal requirements, steam requirements and molasses recirculation differences between the four boiling schemes considered the data for a typical Louisiana factory was used in the evaluation. Rigorous material and energy (steam) balances were prepared for each of the four cases assuming syrup purities of 84, 85, 86, 87, 88, 89 and 90. The data used is summarized in Table 2.

Table 2
ASSUMPTIONS

<u>Stream</u>	<u>Brix</u>	<u>Purity</u>
A Massecuite	92	85
A Molasses	65	68
B Massecuite	93.5	71
B Molasses	65	50
C Massecuite	95.5	52
Final Molasses	80	33.5
B Magma	91	92
C Magma	92	83.5
C Grain	90	63
A Sugar Pol	99.8	99.2
Syrup	65	84 to 90
Cane, TCD	14,000	
Cane, TCH	583.33	
Cane, % pol	13.56	
Cane, % fiber	14.5	
Pol Extraction	94	
Pol in Syrup, lb/hour	147,000	
Lbs 96 sugar/ton cane		
For 84 Syrup Purity	238.04	
For 85 Syrup Purity	239.89	
For 86 Syrup Purity	241.71	
For 87 Syrup Purity	243.48	
For 88 Syrup Purity	245.21	
For 89 Syrup Purity	246.91	
For 90 Syrup Purity	248.56	
Strike Boiling Time, hours		
A strikes	2	
B strikes	3	
C Strikes	4	

The calculated volumes of A, B, C and total (A + B + C) massecuite produced by the four boiling schemes considered are shown in Tables 3, 4, 5 and 6 respectively. In the case of the 4 boiling double magma scheme where both low (A2) and high purity (A1) A massecuites are produced, their respective volumes are shown in Table 7.

Table 3
A Massecuite Production, cu. ft./hour

<u>Syrup Purity</u>	<u>Three Boiling Double Magma Top off A strike with A Molasses</u>	<u>Three Boiling Double Magma Top off B strike with B Molasses</u>	<u>Three Boiling Double Magma Top off C strike with Final Molasses</u>	<u>Four Boiling Double Magma No top off of any strike</u>
84	2,896	2,841	2,841	2,900
85	2,919	2,830	2,830	2,913
86	2,941	2,820	2,819	2,921
87	2,962	2,808	2,809	2,924
88	2,983	2,796	2,797	2,922
89	3,004	2,787	2,786	2,916
90	3,024	2,774	2,774	2,904

Table 4
B Massecuite Production, cu. ft./hour

<u>Syrup Purity</u>	<u>Three Boiling Double Magma Top off A strike with A Molasses</u>	<u>Three Boiling Double Magma Top off B strike with B Molasses</u>	<u>Three Boiling Double Magma Top off C strike with Final Molasses</u>	<u>Four Boiling Double Magma No top off of any strike</u>
84	1,316	1,564	1,484	1,312
85	1,216	1,589	1,474	1,212
86	1,118	1,615	1,463	1,115
87	1,023	1,637	1,450	1,020
88	930	1,658	1,436	927
89	839	1,681	1,419	836
90	750	1,699	1,400	747

Table 5
C Masecuite Production, cu. ft./hour

<u>Syrup Purity</u>	<u>Three Boiling Double Magma Top off A strike with A Molasses</u>	<u>Three Boiling Double Magma Top off B strike with B Molasses</u>	<u>Three Boiling Double Magma Top off C strike with Final molasses</u>	<u>Four Boiling Double Magma No top off of any strike</u>
84	717	717	851	717
85	663	663	859	663
86	610	610	862	610
87	558	558	859	558
88	507	507	850	507
89	457	457	835	457
90	409	409	815	409

Table 6
Total (A + B + C) Masecuite Production, cu. ft./hour

<u>Syrup Purity</u>	<u>Three Boiling Double Magma Top off A strike with A Molasses</u>	<u>Three Boiling Double Magma Top off B strike with B Molasses</u>	<u>Three Boiling Double Magma Top off C strike with Final Molasses</u>	<u>Four Boiling Double Magma No top off of any strike</u>
84	4,929	5,122	5,176	4,929
85	4,798	5,082	5,163	4,788
86	4,669	5,045	5,144	4,646
87	4,543	5,003	5,118	4,502
88	4,420	4,961	5,083	4,356
89	4,300	4,925	5,040	4,209
90	4,183	4,882	4,989	4,060

Table 7
Four Boiling Double Magma, A1, A2 and Total A Masecuite Production, cu. ft./hour

<u>Syrup Purity</u>	<u>A1</u>	<u>A2</u>	<u>Total A1 + A2</u>	<u>A1 % Total</u>
84	414	2,486	2,900	14.28
85	616	2,297	2,913	21.15
86	808	2,113	2,921	27.66
87	992	1,932	2,924	33.93
88	1,166	1,756	2,922	39.90
89	1,332	1,584	2,916	45.68
90	1,488	1,416	2,904	51.24

The quantity of molasses recycle necessary for each of the boiling schemes are shown in Table 8. For all of the boiling schemes employing top-offs the quantity of molasses recycle necessary is about 40% for syrup purities of 88 and reaches 50% for syrup purities of 90.

Table 8
Molasses Recycled, % of Molasses Production

<u>Syrup Purity</u>	<u>Three Boiling Double Magma Top off A strike with A Molasses Recycle</u>	<u>Three Boiling Double Magma Top off B strike with B molasses Recycle</u>	<u>Three Boiling Double Magma Top off C strike with final molasses Recycle</u>	<u>Four Boiling Double Magma No top off of any strike A+B+C Molasses Recycle</u>
84	11.42	14.80	15.75	0
85	18.34	22.01	22.86	0
86	25.09	28.99	29.26	0
87	31.68	35.58	35.07	0
88	38.10	41.93	40.39	0
89	44.36	48.13	45.27	0
90	50.44	53.93	49.84	0

Based on the volumes of massecuite produced and assuming strike boiling times of 2 hours for A strikes, 3 hours for B strikes and 4 hours for C strikes, the vacuum pan requirements are calculated and shown in Table 9.

Table 9
Pan Capacity Required, cu. ft.

<u>Syrup Purity</u>	<u>Three Boiling Double Magma Top off A strike with A Molasses</u>	<u>Three Boiling Double Magma Top off B strike with B Molasses</u>	<u>Three Boiling Double Magma Top off C strike with Final Molasses</u>	<u>Four Boiling Double Magma No top off of any strike</u>
84	16,853	17,616	18,177	17,287
85	16,220	17,352	18,161	16,596
86	15,602	17,100	18,104	15,909
87	14,998	16,836	18,010	15,225
88	14,407	16,579	17,875	14,544
89	13,830	16,341	17,692	13,866
90	13,266	16,079	17,464	13,187

Table 10
Exhaust (or Vapor) Required for Pans, lbs/hour

<u>Syrup Purity</u>	<u>Three Boiling Double Magma Top off A strike with A Molasses</u>	<u>Three Boiling Double Magma Top off B strike with B Molasses</u>	<u>Three Boiling Double Magma Top off C strike with Final Molasses</u>	<u>Four Boiling Double Magma No top off of any strike</u>
84	198,107	195,899	196,989	191,665
85	193,862	194,054	195,741	187,489
86	189,715	192,309	194,232	183,211
87	185,664	190,430	192,492	178,828
88	181,705	188,594	190,473	174,323
89	177,835	186,944	188,116	169,715
90	174,051	185,027	185,461	164,931

Table 10 shows the steam requirements of the pans for the four cases considered at syrup purities from 84 to 90. Steam requirements are lowest for the 4 boiling double magma scheme.

OPTIMIZATION OF LIQUID AMMONIA PRETREATMENT BY RESPONSE SURFACE METHODOLOGY

Saeed Oladi and Giovanna M. Aita

INTRODUCTION

A pretreatment process is needed to disrupt the recalcitrant nature of lignocellulosic biomass. Unless some type of pretreatment is performed prior to enzymatic hydrolysis, no more than 20% cellulose digestibility can be achieved [1]. Ammonia-based pretreatment technologies are versatile in terms of applied temperature, residence time and ammonia to biomass ratio. Ammonia-based pretreatments can increase the porosity and surface area of the biomass due to swelling while generating less non-sugar by-products (i.e., furans, carboxylic acids, phenolic compounds). Furthermore, ammoniation of the methoxyl groups present in lignin prevents the lignin from non-productively binding to cellulases. Response surface methodology (RSM) has become a practical method for optimizing different chemical and biochemical processes. The main advantage of RSM is minimizing the number of experimental trials required to evaluate the effect of multiple variables as well as their interactions. This study is the first one to evaluate the interactive effect of liquid ammonia pretreatment variables including temperature, residence time and ammonium hydroxide to biomass ratio on the glucose and xylose yields from energy cane bagasse. Subsequently, these variables were optimized for maximum sugar yield (glucose, xylose) using RSM modeling technique.

MATERIALS AND METHODS

Biomass

Energy cane non-commercial variety Ho 02-113 was bred in Houma, LA through collaboration between the United States Department of Agriculture-Agricultural Research Service (USDA-ARS) and the Sugar Research Station at Louisiana State University Agricultural Center in St. Gabriel, LA. Energy cane was harvested at the Sugar Research Station and the entire plant was milled three times using a roller press to extract the juice. The bagasse was oven dried at 45 °C overnight and stored at -20 °C until further use.

Experimental design and statistical analysis

Central Composite Design (CCD) was employed utilizing the software Design-Expert 9.0.3 (State Ease Inc., Minneapolis, MN) to assess the effect of temperature, residence time and ammonium hydroxide to biomass ratio on the sugar yield of pretreated energy cane bagasse. A total of 20 experiments were performed in duplicate and are shown in Table 1. Center points of the design were replicated six times to estimate the pure error sum of squares. A quadratic polynomial equation (Equation 1) was assumed to approximate the true function.

$$Y = \beta_0 + \sum_{i=1}^3 \beta_i X_i + \sum_{i=1}^3 \beta_{ii} X_i^2 + \sum_{i=1}^2 \sum_{j=i+1}^3 \beta_{ij} X_i X_j + \epsilon_i \quad (1)$$

Where Y, response variable; X_i and X_j , the explanatory variables; β_0 , constant coefficient; β_{ij} , two-factor interaction coefficient; ϵ , random error. Significance of each coefficient was evaluated with analysis of variance (ANOVA). Xylose yields collected from experimental data were used to statistically optimize the pretreatment conditions for maximum xylose yield (independently from glucose yield) using the software Design-Expert 9.0.3.

Table 1. Coded level of independent variables in the central composite design (CCD).							
Variables	Unit	Coded level					
		Coding	$-\alpha^a$	-1	0	+1	$+\alpha^a$
Temperature	°C	A	160	172	190	208	220
Residence Time	min	B	30	36	45	54	60
Ammonium Hydroxide ^b to Biomass Ratio	v/w	C	0	0.10	0.25	0.40	0.50
^a Axial distance = $\sqrt[4]{N}$, where N is the number of experiments of the factorial design.							
^b NH ₄ OH, 28% v/v solution.							

Liquid ammonia pretreatment

Liquid ammonia pretreatment of energy cane bagasse was carried out in a 4 L stirrer reactor (Autoclave Engineers, Erie, PA). Experiments were carried out at ammonium hydroxide (NH₄OH, 28% v/v solution, Fisher Scientific, Pittsburgh, PA) to dried biomass to water ratio of 0-0.5:1:20. Pretreatment temperatures ranged from 160 to 220 °C and residence times ranged from 30 to 60 min. The solid fraction was used for chemical composition analysis and enzymatic hydrolysis assessments.

Chemical composition analysis and enzymatic hydrolysis

Untreated energy cane bagasse and liquid ammonia pretreated energy cane bagasse samples were analyzed following NREL Laboratory Analytical Procedures (LAP TP-510-42618, 42619, 42622). Spezyme CP at 30 FPU/g glucan (Genencor, Danisco US Inc., Rochester, NY, USA) and Novozyme 188 at 30 CBU/g glucan (Sigma–Aldrich, Inc., St. Luis, MO, USA) were used during enzymatic hydrolysis following NREL LAP TP-51043629. A biomass loading of 5% (w/v) was mixed with 0.1 M sodium citrate buffer (pH 4.8) and incubated at 50 °C in a shaker incubator (Amerex Instruments Inc., Lafayette, CA) at 150 rpm for 72 h. Samples were taken at 0 h (before the addition of enzymes), 24 h, 48 h, and 72 h. Samples were frozen at -20 °C until further analysis. All collected samples from enzymatic hydrolysis were centrifuged at 10,000 rpm (Spectrafuge 24D, Labnet International Inc., Woodbridge, NJ) for 5 min and filtered (0.2 µm Syringe Filters, Environmental Express Inc., Mt. Pleasant, SC). Properly diluted samples were analyzed for sugars by high performance liquid chromatography (HPLC) (Agilent 1200 Series) with a BioRad Aminex HPX-87P (P), lead form, 3000 × 7.8 mm (ID), 9 µm column and a differential refractive index detector (G1362A Agilent). Equations described in NREL LAP TP-510-43630 were used to calculate the percent theoretical yield for cellulose and hemicellulose. Glucose and xylose yields were reported as the mass of glucose or xylose released per 100 g of untreated biomass after enzymatic hydrolysis.

RESULTS AND DISCUSSION

Composition analysis of samples

Results from the compositional analysis of energy cane bagasse before and after pretreatment are shown in Table 2. Untreated energy cane bagasse was composed of $40.14 \pm 0.16\%$ glucan, $24.23 \pm 0.51\%$ xylan, $2.76 \pm 0.04\%$ arabinan, $24.41 \pm 0.37\%$ lignin (5.97 ± 0.16 acid soluble, 18.44 ± 0.21 acid insoluble), 3.76 ± 0.62 extractives, and $4.7 \pm 0.04\%$ ash (dry weight). Ammonium hydroxide to biomass ratio had a significant ($p < 0.01$) positive effect on solid recovery. However, our model showed that temperature had the most significant ($p < 0.01$) effect on recovered solids. The interaction effect of temperature and ammonium hydroxide to biomass ratio as well as the interaction effect of residence time and ammonium hydroxide to biomass ratio had a significant ($p < 0.01$) effect on lignin removal. A positive correlation was observed between xylan loss and lignin removal meaning that more xylan was being solubilized as more lignin was removed. Temperature was the only variable with a significant ($p < 0.01$) effect on hemicellulose loss. Cellulose sensitivity to temperature is less as compared to hemicellulose and lignin. However, the more severe the ammonia pretreatment the more cellulose is removed. As compared to the losses observed with xylan and lignin, only a small amount of glucan (4.49% to 12.95%) was lost during pretreatments with ammonium hydroxide.

Model fitting and sugar yields

Glucose yield was used to fit the model using Design–expert 9.0.3. The quadratic model was chosen due to the observed high adjusted R-squared and predicted R-squared values (Table 3). Credibility of the fitted quadratic model was confirmed by lack of the fit test (Table 3). Coefficients of the second order polynomial equation (Equation 1) for glucose yield were calculated by Design–expert 9.0.3 and the final equation (Equation 2) is presented below.

$$\text{Glucose yield} = +27.51 + 3.64A + 0.83B + 1.64C - 2.04AB - 1.05A^2 - 1.24B^2 \quad (2)$$

Where, A: Temperature ($^{\circ}\text{C}$), B: Time (min), C: Ammonium hydroxide to biomass ratio.

All the pretreatment variables had a significant effect on glucose yield ($p < 0.01$). Among the variables, temperature had the highest correlation (0.77). As illustrated in Figure 1, the combination of a higher temperature and a shorter residence time improved the glucose yield (larger slope of the response line) as compared to the combination of a lower temperature and a longer residence time. Increasing the ammonium hydroxide to biomass ratio also improved cellulose digestibility (Figure 2). A quadratic model was fitted ($p < 0.01$) based on the xylose yield of our samples with $R^2 = 0.95$ and adjusted $R^2 = 0.91$. Pretreatment temperature had a negative and close to linear relationship with xylose yield (correlation of -0.79) (Table 2). The opposite was observed for pretreatment temperature and glucose yield having a strong positive correlation (0.77).

Experimental Variables														
Samples	Temperature (°C)	Time (min)	^a Ratio	Recovered Solids (% w/w)	Glucan (% w/w)	Xylan (% w/w)	Lignin (% w/w)	Cellulose Digestibility (% w/w)	Hemicellulose Digestibility (% w/w)	Glucose Yield (g/ 100 g of untreated biomass)	Xylose Yield (g/ 100 g of untreated biomass)	Glucan Loss (% w/w)	Xylan Loss (% w/w)	Lignin Removal (% w/w)
Untreated	^b N/A	N/A	N/A	100	40.14	24.23	24.41	9.27	4.36	4.13	1.22	0	0	0
1	208	54	0.3:1:20	62.74	61.10	2.20	23.52	69.36	57.43	29.54	0.91	4.49	94.18	66.85
2	190	45	0.5:1:20	63.50	58.41	8.69	22.32	72.54	68.51	29.91	4.29	7.59	76.77	64.23
3	190	30	0.25:1:20	67.09	54.57	14.89	13.98	55.66	49.30	22.65	5.63	8.77	57.93	42.85
4	208	54	0.1:1:20	55.50	63.19	2.06	16.86	66.05	52.86	25.74	0.71	12.62	95.19	42.74
5	190	45	0.1:1:20	59.22	59.08	18.39	16.61	59.56	28.28	23.12	3.50	12.95	56.13	44.88
6	208	36	0.1:1:20	56.81	62.07	6.57	18.11	76.11	79.83	29.82	3.40	12.14	84.29	46.86
7	190	45	0.25:1:20	64.34	56.33	16.79	17.14	71.75	58.67	28.89	7.22	9.71	54.50	50.22
8	190	45	0.25:1:20	62.90	57.62	15.57	17.85	67.45	61.00	27.16	6.81	9.71	58.77	51.11
9	220	45	0.25:1:20	56.42	64.70	1.77	23.77	74.34	52.02	30.15	0.65	9.06	95.79	60.83
10	190	45	0.25:1:20	62.34	58.11	12.60	17.09	66.21	59.43	26.65	5.31	9.75	66.92	48.54
11	172	54	0.4:1:20	69.11	52.33	20.74	15.79	64.73	46.15	26.02	7.48	9.89	39.63	49.69
12	208	36	0.4:1:20	62.91	58.20	7.81	19.90	75.20	75.35	30.59	4.23	8.78	87.26	56.86
13	172	36	0.1:1:20	68.63	54.00	17.78	12.54	41.77	36.76	17.20	5.11	7.67	48.59	39.40
14	190	60	0.25:1:20	67.65	54.02	14.06	18.56	62.01	53.56	25.18	5.78	8.95	59.95	57.01
15	172	54	0.1:1:20	72.88	48.01	14.90	12.38	57.13	51.86	22.21	6.42	12.83	54.26	41.27
16	190	45	0.25:1:20	65.86	55.25	14.70	16.45	65.08	54.52	26.31	6.04	9.34	59.24	49.35
17	160	45	0.25:1:20	74.01	48.60	23.12	11.97	46.89	37.07	18.74	7.19	10.37	27.94	40.51
18	172	36	0.4:1:20	71.09	50.65	22.39	11.02	48.19	42.55	19.28	7.74	10.30	32.96	35.96
19	190	45	0.25:1:20	63.29	57.03	15.93	17.86	67.75	56.85	27.17	6.46	10.08	57.55	51.43
20	190	45	0.25:1:20	63.67	56.99	15.25	18.45	71.78	58.71	28.94	6.53	9.60	59.12	53.41

^a Ammonium hydroxide (NH₄OH, 28% v/v solution): bagasse (dry weight): water.

^b Not applicable.

Note: Data shown represent the mean values (Standard error < 5%).

Optimization of process conditions and experimental validation

Based on the conditions defined above, the optimum pretreatment parameters for maximum glucose yield were 208 °C for 36 min and at an ammonium hydroxide to biomass ratio of 0.4:1. The predicted value for glucose yield was 30.77 ± 0.93 g glucose/100 g (dry weight) untreated biomass.

Table 3. Analysis of variance (ANOVA) for response surface quadratic model for the effect of pretreatment variables on glucose yield g/ 100 g (dry weight) of untreated biomass.						
Source	Sum of Squares	Degree of Freedom	Mean Square	F Value	p-value Prob > F	
Model	297.45	9	33.05	38.52	< 0.0001	significant
A-Temperature	180.79	1	180.79	210.69	< 0.0001	
B-Time	9.50	1	9.50	11.07	0.0077	
C-Ammonium Hydroxide	36.62	1	36.62	42.67	< 0.0001	
AB	33.46	1	33.46	38.99	< 0.0001	
AC	0.084	1	0.084	0.098	0.7607	
BC	2.27	1	2.27	2.64	0.135	
A ²	15.82	1	15.82	18.43	0.0016	
B ²	22.11	1	22.11	25.76	0.0005	
C ²	1.45	1	1.45	1.69	0.2223	
Residual	8.58	10	0.86			
Lack of Fit	2.21	5	0.44	0.35	0.8644	not significant
Pure Error	6.37	5	1.27			
Std. dev.	0.93			R-squared	0.972	
Mean	25.74			Adj R-squared	0.947	
Coefficient of Variation%	3.60			Pred R-squared	0.915	
PRESS	26.1			Adeq precision	20.73	

Based on our model for xylose yield, the maximum xylose yield within our experiment design range was predicted as 9.10 g xylose/100 g (dry weight) untreated biomass at 160 °C for 60 min and at an ammonium hydroxide to biomass ratio of 0.31:1. However, the glucose yield obtained under these conditions was 23.34 g glucose/100g (dry weight) untreated biomass. Experimental results fell within the 95% confidence interval of the predicted value which supported the reliability and robustness of our model (Table 4).

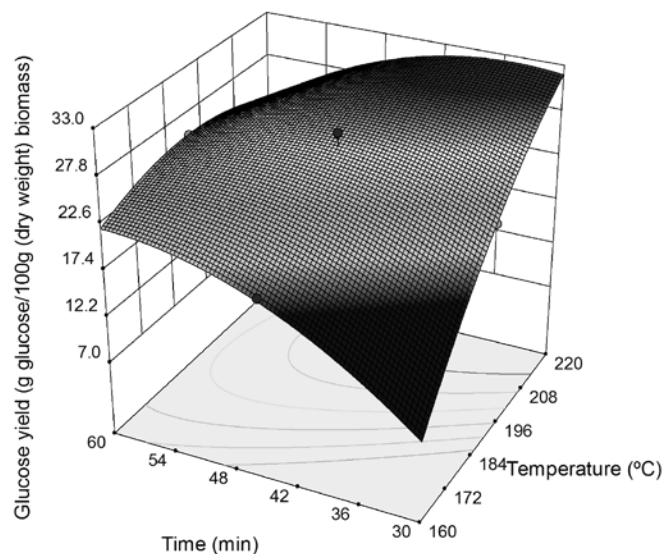


Figure 1. 3D response surface plot of the effects of pretreatment, temperature and residence time on glucose yield (g glucose/ 100 g (dry weight) untreated biomass) at ammonium hydroxide to biomass ratio of 0.25:1.

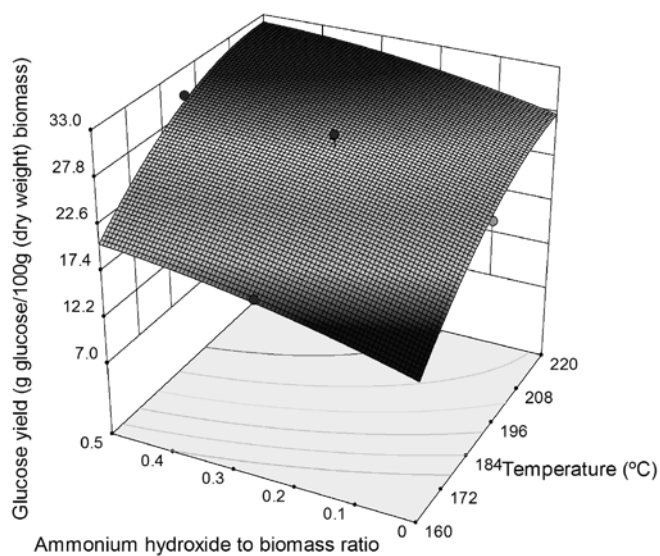


Figure 2. 3D response surface plot of the effects of ammonium hydroxide to biomass ratio and pretreatment temperature at 45 min residence time.

Table 4. Predicted versus experimental results.						
Response	Predicted Mean	Observed	Std. Dev.	SE Pred.	95% PI low	95% PI high
Glucose Yield (g/100 g (dry weight) untreated biomass)	30.77	30.62	0.96	1.20	28.10	33.43
Xylose Yield (g/100 g (dry weight) untreated biomass)	3.99	4.20	0.66	0.84	2.12	5.87
Recovered Solid (%)	63.71	62.51	1.23	1.59	60.17	67.24
Glucan Loss (%)	8.76	9.01	0.24	0.32	8.12	9.45
Xylan Loss (%)	83.27	84.14	7.48	8.25	65.54	100.28
Lignin Removal (%)	59.18	60.26	3.05	3.91	50.73	67.63
Note: Data shown represent the mean values (Standard error < 5%).						

CONCLUSIONS

Temperature was found to be the most effective variable having the greatest impact on the response followed by ammonium hydroxide to biomass ratio. The highest glucose yield was predicted to be 30.77 g glucose/ 100 g (dry weight) untreated biomass with a xylose yield of 3.99 g xylose/100 g (dry weight) untreated biomass obtained at 208°C for 36 min and at an ammonium hydroxide to biomass ratio of 0.4:1. A separate quadratic model (P value < 0.01) was fitted for the experimental values of xylose yield. Based on the model, the maximum xylose yield was predicted to be 9.10 g xylose/100 g (dry weight) untreated biomass obtained at 160°C for 60 min and at an ammonium hydroxide to biomass ratio of 0.31:1. However, these pretreatment conditions resulted only in a predicted glucose yield of 23.34 g glucose/ 100 g (dry weight) untreated biomass. The low xylose yields observed in this study can be attributed to the substantial amounts of xylan being lost during pretreatment due to solubilization. Results of actual experiments carried out at the optimal points from our models fell within 95% confidence interval of the predicted value.

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LIGNOCELLULOSIC SYRUP PRODUCTION FROM ENERGY CANE BAGASSE

Fang Deng and Giovanna M. Aita

INTRODUCTION

Lignocellulosic biomass is a promising renewable energy resource that can be used in the production of biofuels and bio-products. A flexible, year-round supply of lignocellulosic biomass to biorefineries can be extremely challenging due to the seasonality of the crops and harvest times. Lignocellulosic syrup, obtained from the concentration of sugars from hydrolysates of pretreated lignocellulosic biomass, is a promising fermentable sugar feedstock that can improve the logistics associated with long-distance transportation, long-time storage and year-round supply of biomass. Dilute ammonia pretreatment followed by enzymatic hydrolysis has been extensively studied in Dr. Aita's Laboratory and proven to be highly efficient in converting polysaccharides (i.e., cellulose and hemicellulose) to fermentable monosaccharides (i.e., glucose and xylose) [1-3]. However, a major challenge is the interference from non-sugar compounds (organic acids, furaldehydes and phenolic compounds) generated during the processing of lignocellulosic biomass (i.e., pretreatment and enzymatic hydrolysis) [4]. If recovered, these non-sugar compounds can serve as building blocks for chemicals in multiple industries. Thus, the removal and/or recovery of these non-sugar compounds can not only improve the productivity of lignocellulosic biofuels and bio-products, but also provide additional value-added products [5]. In this work, non-sugar compounds present in dilute ammonia pretreated energy cane enzymatic hydrolysates were recovered using flocculants and activated carbon (AC), and the purified hydrolysates were processed into a lignocellulosic syrup.

MATERIALS AND METHODS

Energy cane (HO 02-113) was collected from the Sugar Research Station in St. Gabriel, LA and milled at the Audubon Sugar Institute in St. Gabriel, LA. Energy cane bagasse was pretreated with ammonium hydroxide (28% v/v solution) and water at a ratio of 1:0.5:8 at 160 °C for 1h in a 4L reactor (Parker Autoclave Engineers, Erie, PA). Compositional analysis was conducted for both untreated and pretreated bagasse following NREL Laboratory Analytical Procedures (LAP TP-510-42618, 42619, 42620, 42621, 42622). Pretreated energy cane bagasse was then enzymatically hydrolyzed using a combination of commercially available enzymes, Cellic® CTec2 and HTec2 (Novozymes, Franklinton, NC). Post hydrolysis, solids were removed by passing through a 0.2 µm filter and the hydrolysate liquor was collected and kept in a -20°C freezer for further separation studies. For the separation of non-sugar compounds, flocculants (PEI and pDADMAC) or activated carbon (powdered and granular) were added to the hydrolysate. Treatment parameters including dose, hydrolysate pH and contact time were evaluated to determine the optimum conditions for maximum non-sugar compounds removal and minimum fermentable sugar losses. Sugars, organic acids and furaldehydes were analyzed by High Performance Liquid Chromatography. Total phenolic compounds concentration was determined by UV absorbance at 280 nm [6]. Purified hydrolysate was concentrated to 65°Brix by a rotary vacuum evaporator (Cole-Parmer, Vernon Hills, IL). The collected syrup was then stored for further quality analysis.

RESULTS AND DISCUSSION

A sugar concentration of 25.43 g/L was achieved post enzymatic hydrolysis. Glucose was the predominant sugar (15.74 g/L) detected, while the xylose concentration was much lower (9.69 g/L). This can be attributed to the loss of hemicellulose during pretreatment. The highest concentration of organic acids resulted from formic acid (3.57 g/L), followed by acetic acid (2.38 g/L) and levulinic acid (1.31 g/L). Furaldehydes including furfural (0.04 g/L) and 5-Hydroxymethylfurfural (0.06 g/L) and total phenolic compounds (0.51 g/L) were also detected in the hydrolysate. Results for each separation method (flocculant or AC) are summarized in Table 1. Soluble polyelectrolyte flocculants were able to remove the majority of non-sugar compounds (>50%) with less than 10% fermentable sugar losses. At optimized conditions, flocculants removed almost all furaldehydes and phenolic compounds. When comparing the adsorption efficiency between the two flocculants, PEI outperformed pDADMAC with higher percent non-sugar compounds removal and less fermentable sugar losses. It is also noteworthy to mention that xylose was more susceptible to flocculation treatment than glucose. Activated carbon treatments were more efficient than flocculant treatments and resulted in the removal of all non-sugar compounds with minimum sugar losses. Similar results were observed at optimum conditions for powdered and granular AC. However, a higher dose and longer contact time was needed for granular AC. Lignocellulosic syrup production was conducted using the powdered AC-treated hydrolysate due to its efficiency, lower dose and contact time. A comparison on the chemical composition of commercially available syrup and lignocellulosic syrup from energy cane bagasse is presented in Table 2.

Table1. Sugar losses and non-sugar compounds removal by flocculants or activated carbon.

	Sugar Losses		Non-Sugar Compounds Removal		
	Glucose	Xylose	Organic Acids	Furaldehydes	Phenolic Compounds
PEI	Low	Moderate	Moderate	High	High
pDADMAC	Low	Moderate	Low	High	High
Powdered AC	Low	Low	High	High	High
Granular AC	Low	Low	Moderate	High	High

Table 2. Chemical composition of commercially available syrup and lignocellulosic syrup.

	Cargill Clearsweet® 95% Corn Syrup	lignocellulosic Syrup from Energy Cane Bagasse
Glucose (% Dry Basis)	95	60
Other Sugars (% Dry Basis)	5	40 (Xylose)
Total Solids (%)	70.5-71.5	65
Acetic Acid (mg/L)	5.6	N.D.
Formic Acid (mg/L)	3.2	N.D.
Lactic Acid	142.9	N.D.
Total Phenolic Compound (mg/L)	-	N.D.
Furaldehydes (mg/L)	-	N.D.
pH (1:1)	4.5	4.0

N.D. None Detected.

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