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WHERE DO YOU GO TO, MY SACCHARIDES? A PRELIMINARY SACCHARIDE ANALYSIS OF REFINERY STREAMS

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Abstract

The Sugar Milling Research Institute NPC (SMRI) has a long history of determining minor saccharide constituents in sugar process streams. These include the common monosaccharides (glucose and fructose) and trisaccharides such as kestoses and oligosaccharides. Within a refinery, minor saccharides can not only originate from the incoming raw sugar but can build up due to the use of recycle streams and may also be formed as a result of sucrose deterioration in low brix process streams. The presence of some of these minor constituents can have a detrimental effect on crystal habit. A study was undertaken to determine the fate of some of these saccharides at the Tongaat-Hulett Sugar Refinery. Sampling was conducted over a three-month period during 2016 and analysis of the samples was undertaken using the methods developed by the SMRI. The results showed that not only was a large proportion of the kestoses being recycled but an unequal division of selected kestoses occurred between refined sugar and High Test Molasses. The results also indicated that the commonly assumed pol:sucrose ratio of one is not true for High Test Molasses.

Keywords: refinery, mass balance, kestose, refinery pol:sucrose ratio

Introduction

Saccharide is a general term used for sugars. Most sugar technologists are accustomed to using terms such as glucose and fructose (known as monosaccharides) and sucrose (a disaccharide). A further two groups of saccharides can be defined, viz. oligosaccharides (compounds containing 3-10 monosaccharides) and polysaccharides (often containing 10 or more of monosaccharides joined to form chains). The Sugar Milling Research Institute NPC (SMRI) has a long history of developing chromatographic methods for the analysis of oligosaccharides and investigating their role and fate in sugar processing (Nurok and Reardon, 1975; Morel du Boil and Schäffler, 1990; Morel du Boil, 1991). The four principal oligosaccharides found in South African process streams are 1-kestose, 6-kestose, neo-kestose and theanderose (Figure 1). Sucrose is a disaccharide made up of glucose and fructose. The trisaccharide structures are essentially a sucrose molecule with an additional fructose molecule joined in position 1 on the fructose of the sucrose (1-kestose), or position 6 of the fructose of the sucrose (6-kestose). The addition of fructose on the glucose molecule of the sucrose gives rise to neo-kestose while the addition of a glucose molecule to the sucrose molecule gives theanderose.

Oligosaccharides have been found to be the principal cause of crystal elongation in the South African sugar industry with up to five types of oligosaccharides being reported in factory process streams (Morel du Boil 1985, 1991, 1992, 1995). The main impact of the presence of oligosaccharides is experienced in crystallisation processes. This is due to the sucrose moiety

in the kestoses being able to be incorporated into the growing crystal surface and affecting further growth on that particular axis. Morel du Boil (1998) showed that these oligosaccharides transferred far more readily to the sugar crystal than did monosaccharides (glucose and fructose) and that theanderose transferred preferentially to the refined sugar crystal.

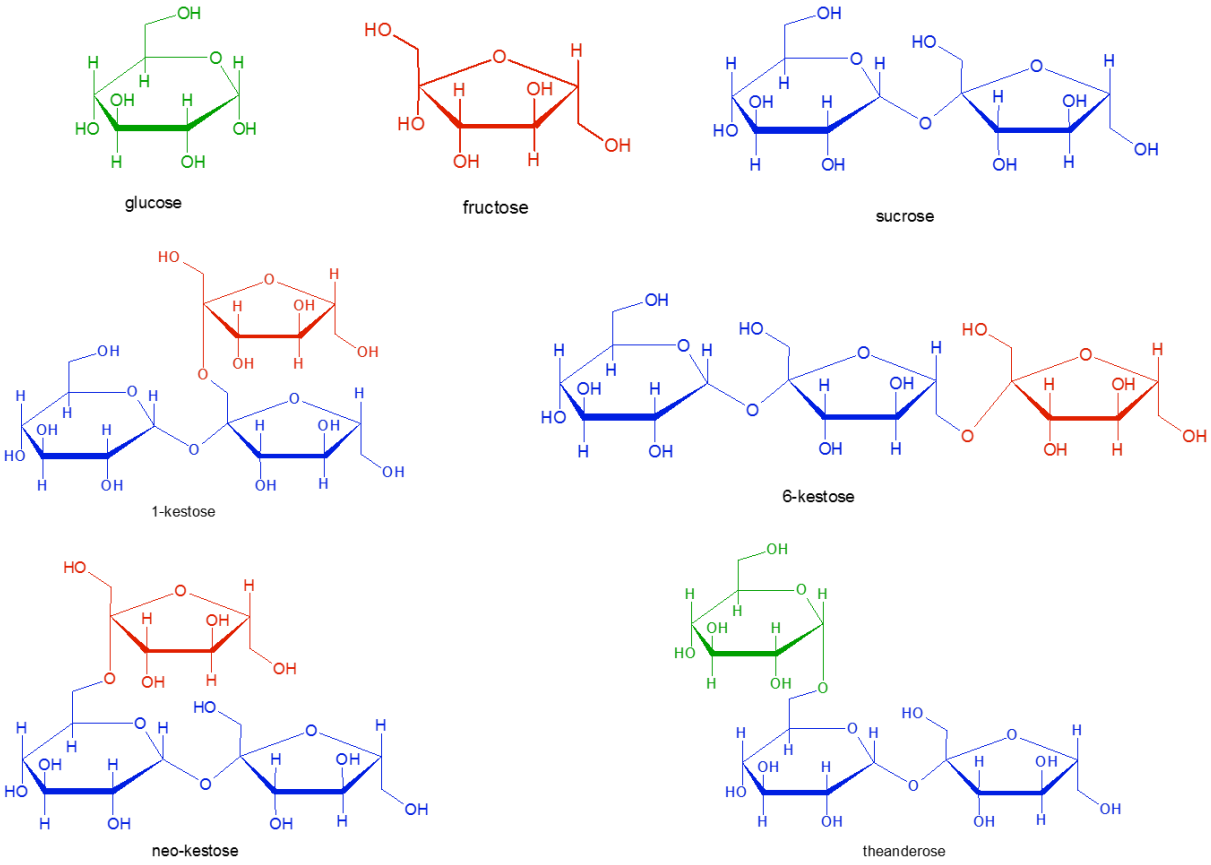

Figure 1. Structures of the mono-, di- and trisaccharides investigated in this study. The common sucrose structure in the trisaccharides is shown in blue.

Tongaat-Hulett Sugar (THS) operates the only standalone refinery in South Africa. Without the benefit of a raw house, the refinery is required to operate a partial recovery house to maximise the recovery of sugar. Consequently, several recycle streams exist, which result in the recycle of impurities present in the incoming raw sugar such as the oligosaccharides. Although investigations have been undertaken into the concentrations of these oligosaccharides in specific refinery streams (du Boil and Walford, 1995), no overall saccharide balance has been reported in a South African refinery.

As part of its research programme, SMRI is currently isolating and preparing pure kestose samples to investigate the transfer of oligosaccharides to crystal sugar. A task within this project calls for a factory experiment to measure kestose concentrations and mass flows around a raw house and refinery. In discussions with THS refinery process staff the opportunity arose to collect samples from the refinery and improve the sampling and analysis methods for future studies within the project. This paper highlights the preliminary results obtained from a three-month continuous investigation during 2016 into an overall saccharide balance (mono-, di- and oligosaccharide) across the THS refinery during 2016.

Experimental

Nine streams were sampled hourly (raw sugar, main melt, sweet water, brown liquor, fine liquor, return syrup, High Test Molasses (HTM), remelt and refined sugar), stored in a freezer, and used to prepare weekly composite samples. The process flow chart showing the sampled streams is shown in Figure 2 (note that not all sources of sweet water are shown in this figure). These composite process stream samples were analysed at the THS refinery for pol and brix and at the SMRI for sucrose, glucose, fructose, 1-kestose, 6-kestose, neo-kestose and theanderose on a weekly basis. The saccharides were analysed using previously described High Performance Anion Exchange Chromatography methods (Walford *et al*, 2004) and the results expressed on an on-sample basis. Factory stream flow data were not measured; average refinery flows for raw sugar, HTM and refined sugar supplied by the refinery staff were used to estimate rudimentary mass balances.

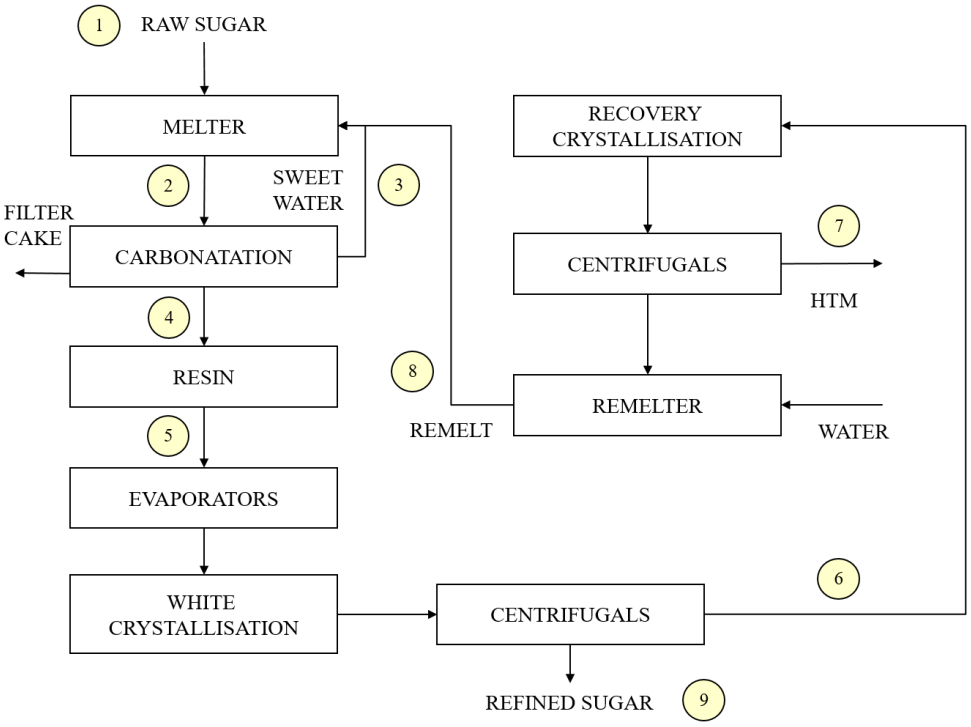

Figure 2. Basic process flow diagram of the Tongaat-Hulett refinery and sampling points used in the study. Numbers refer to sampling points as referenced in Table 1.

Results and Discussion

Mono and oligosaccharide balances

The analyte results for the nine weekly-composite process stream samples were averaged and are shown in Table 1. The brown liquor stream in Table 1 is the outlet from the carbonatation stage (Figure 2), fine liquor is the stream exiting the resin columns and the return syrup is the feed to the recovery crystallisation house.

Previous investigations of the oligosaccharide composition of South African raw sugar showed ranges of 40-250 ppm for 1-kestose, 0-160 ppm for 6-kestose, 70-190 ppm for neo-kestose and 185-350 ppm for theanderose (Morel du Boil, 1996). The average results for the raw sugar entering the refinery in this study are within these reported ranges. Morel du Boil *et al.* (1970) used a carbon-celite column and paper chromatography to isolate and estimate the concentration of two oligosaccharides in refinery molasses (HTM). Although not positively

identified, one of the oligosaccharides was believed to be 1-kestose or neo-kestose with a concentration of approximately 0.5 %. The value of 3 755 ppm for 1-kestose (Table 1) is equivalent to 0.37 %, a value in agreement with the previous work. Theanderose in refined sugar from the THS refinery had been previously measured at between 80 and 145 ppm (Morel du Boil, 1996), and neo-kestose at 95 ppm, values approximately the same as recorded in this study. In a study of oligosaccharides at a South African backend refinery, Morel du Boil and Walford (1995) reported values of 167 ppm for 1-kestose, 86 ppm for 6-kestose, 109 ppm for neo-kestose and 155 ppm for theanderose for fine liquor, again similar to this study. This study showed that none of the 1-kestose and 6-kestose were transferred to the refined sugar crystal from the fine liquor, the same observation reported previously (Morel du Boil, 1996). The similarity of the raw sugar, fine liquor, HTM and refined sugar values reported in Table 1 and the previous studies, gave the authors confidence in the results reported here for the remaining previously unreported streams (sweet water, brown liquor, return syrup and remelt).

Table 1. Average analyte results from nine-weekly composite process stream samples collected over a three month period expressed as on-sample

Sample Point	Process Stream	Analyte[1]							
		Brix (%)	Sucrose (%)	Glucose (%)	Fructose (%)	1-K (ppm)	6-K (ppm)	neo-K (ppm)	Theand (ppm)
1	Raw sugar			0.104	0.098	50	40	119	170
2	Main melt	68.54	67.15	0.30	0.27	135	52	57	63
3	Sweet water	40.62	39.68	0.25	0.20	130	76	60	42
4	Brown liquor	65.92	65.17	0.18	0.16	64	30	39	34
5	Fine liquor	70.73	70.33	0.32	0.26	248	89	104	102
6	Return syrup	71.84	66.32	0.99	0.66	360	186	205	202
7	HTM	76.24	54.33	5.13	3.39	3755	1042	966	485
8	Remelt	54.66	53.26	0.45	0.32	170	55	55	60
9	Refined sugar			87 ppm	128 ppm	ND[2]	ND[2]	80	150

[1]1-K = 1-kestose, 6-K = 6-kestose, neo-K = neo-kestose, Theand = theanderose
[2]ND = not detected

Based on the average refinery throughput, estimates of the average flows into (raw sugar) and out of (refined sugar and HTM) the refinery were made. These values were combined with the sample concentration data (Table 1) to estimate the mass throughput of the mono- and oligosaccharides (Table 2 and Table 3, respectively).

Table 2. Mass balance of the monosaccharides based on the average composition and refinery flow data

Process Stream		Analyte		
		Glucose (kg/hr)	Fructose (kg/hr)	Total (kg/hr)
Raw sugar	In	82.9	78.7	161.6
HTM	Out	51.3	33.9	85.2
Refined sugar	Out	6.6	9.6	16.2

Table 3. Mass balance of the oligosaccharides based on the average composition and refinery flow data

Process Stream		Analyte[1]				
		1-K (kg/hr)	**6-K (kg/hr)**	**neo-K (kg/hr)**	**Theand (kg/hr)**	**Total (kg/hr)**
Raw sugar	In	4.0	3.2	9.5	13.6	30.3
HTM	Out	3.8	1.0	1.0	0.5	6.3
Refined sugar	Out	ND[2]	ND[2]	6.0	11.3	17.3

[1]1-K = 1-kestose, 6-K = 6-kestose, neo-K = neo-kestose, Theand = theanderose
[2]ND = not detected

To complete a mass balance for any of these saccharides, measures of all inputs, outputs, sources of destruction and generation are required. In this study, estimates of mono- and oligosaccharides were made for raw and refined sugar and HTM. While HTM and refined sugar are not the only streams in which mono- and oligosaccharides could exit the factory, they are expected to account for the majority of all the saccharides leaving the factory.

Glucose and fructose are partially destroyed during the carbonatation process and could be produced if sucrose inversion occurs in the evaporators. In this study, no samples were taken between the evaporators and crystal sugar. Therefore, the occurrence of inversion could not be determined during evaporation. The composition of the monosaccharides before and after carbonatation support destruction of the monosaccharides in the high pH unit operation (difference between main melt [sample point 2] and brown liquor [sample point 4] in Table 1). In contrast, oligosaccharides are believed to be stable under refinery conditions. Given that (1) no accurate mass flows were recorded, (2) the refinery was not running optimally due to the drought conditions and raw sugar supply issues, (3) the results are based on composite samples that were averaged over nine weeks, (4) not all process recycle streams were considered, and (5) no filter cake samples were analysed, it is remarkable how closely the in and out total oligosaccharide mass flows correspond. The results clearly show that the 1- and 6-kestoses accumulate in the HTM whilst the theanderose and neo-kestose concentrate primarily in the refined sugar (Table 3), as reported previously (Morel du Boil, 1996). The effect of the oligosaccharides on the crystal habit in the recovery house is seen in Figure 3 which shows typical needle-shaped crystals that are subsequently melted and returned to process.

The THS refinery effectively operates a 6½ pan boiling scheme. The first four boilings are used for refined sugar and the last 2½ to recover sucrose for remelt. The recovery of the sucrose in the recovery house is difficult due to the shape of the crystal, leading to significant sucrose losses through HTM.

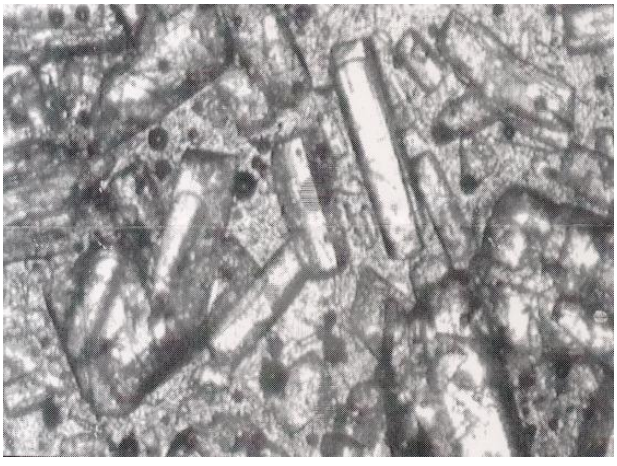

Figure 3. Crystal elongation present in the sugar used for remelt

Refinery pol:sucrose ratio

It is common in refineries to assume that the pol measurement used in refinery control is equivalent to sucrose due to the high purities being processed (a pol:sucrose ratio of 1). The measurement of sucrose in this study has allowed the process staff to check this assumption.

Pol is a measure of the apparent sucrose using the polarimetry method (Anon, 2009). A pol reading is the sum of the specific rotations of all optically active compounds present in the juice relative to their concentrations. Sucrose is a dextrorotatory compound and rotates the plane of a polarised light ray to the right. Fructose is laevorotatory (rotates the plane of a polarised light ray to the left) and has a higher negative specific rotation value ($[\alpha]_D^{20}$ = -92) than the dextrorotatory glucose specific rotation ($[\alpha]_D^{20}$ = +53). The apparent sucrose is based on the sum of these specific rotations which will change dependent on the concentrations of fructose, glucose and other compounds present in the refinery streams which also rotate the plane of polarised light. Given concentrations of sucrose, glucose and fructose, a derived pol can be determined from the specific rotations (Morel du Boil and Schäffler, 1978).

The measured and derived pol:sucrose ratios are compared in Table 4. It can be seen that there is a small difference between the measured pol:sucrose ratio and the pol:sucrose ratio determined from the derived pol and that for process purposes using a pol:sucrose ratio of 1 is justified for all streams other than for HTM as the pol:sucrose ratio for this product is considerably different to 1. Based on the THS refinery throughput, a preliminary estimate of the amount of sucrose in HTM using the measured pol:sucrose ratio is more than 1 % greater than the amount calculated using a pol:sucrose ratio of 1. Further investigation is required to verify this figure.

Table 4. Actual process stream pol:sucrose compared to the 'derived pol' pol:sucrose ratio

Process stream	Measured pol:sucrose	Pol_{deriv}:sucrose
Main Melt	1.004	0.998
Sweet Water	1.005	0.998
Brown liquor	1.000	0.999
Fine liquor	0.997	0.999
HTM	0.981	0.989
Return syrup	0.993	0.998
Remelt	0.991	0.998

Possible future work

This preliminary study has highlighted future possible considerations for tracking and analysing saccharides in a refinery. Some process streams were not included in this study and assumed flow data were used for all streams. Therefore, sampling of the filter cake, sampling after the evaporator station, sampling of all sources of sweetwater and more accurate mass flows of process streams will be required if a mono- and oligosaccharide mass balance study is undertaken. Consideration of sampling all possible sweetwater input streams would help highlight recycle process stream sources of oligosaccharides.

Conclusion

The study presents the first complete set of mono- and oligosaccharide measurements for the majority of process streams in a South African refinery and an estimate of the mass flows of these saccharides entering and leaving the refinery. It has confirmed previous studies that

showed that 1- and 6-kestose preferentially concentrate in the HTM stream and neo-kestose and theanderose concentrate in the refined sugar. Measuring the sucrose and pol for the refinery process streams has shown that the assumption that a pol:sucrose ratio of one can be used for all refinery streams is not valid for HTM. This could have an effect on the amount of sucrose assumed to be leaving the refinery in this product. Unfortunately, this investigation was undertaken in a particularly bad drought year and the incoming raws had very high colours and the refinery was not running at normal throughput due to the high colours which may have resulted in incorrect assumed flows and the consequent mass composition of the composite samples. Consequently, a similar study needs to be considered in a normal year taking into account the suggested sampling refinements.

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