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ANALYTICAL STUDY OF GUMS FOUND IN FINAL MOLASSES FROM SIX SOUTH AFRICAN MILLS FOR THE 2011/2012 MILLING SEASON

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Abstract

Gums are high molecular weight carbohydrates which are precipitated from sugar processing solutions with acidified alcohol. Previous research reported that gums found in sugar processing streams contribute to processing problems and reduced sugar recoveries. Gums arise from the metabolism within the sugarcane plant and from external microbial activity during both cane handling and cane processing, and concentrate in final molasses (FM) streams.

An investigation of gums found in the FM from six South African sugarcane mills was conducted by the Sugar Milling Research Institute NPC on weekly samples received during the 2011/2012 milling season. The gums were isolated from the samples and their composition and structure were determined by gas chromatography mass spectroscopy. Other analyses reported on the FM samples include the measurement of pol, brix, dry solids, sugars, ash, target purity difference and viscosity.

This study details how the composition and structure of the FM gums differs within and between the mills investigated over the 2011/2012 season. Also highlighted are differences in the gums between mills processing irrigated cane and those that process rainfed cane.

Keywords: gums, final molasses, composition, structure, GC-MS, viscosity

Introduction

Sucrose loss in final molasses (FM) accounts for double the amount of sucrose lost to other components (bagasse, filter cake and undetermined loss) and results in a major financial loss to the industry (Love and Muzzell, 2009; Saska *et al.*, 2010). At a process level, sucrose loss is minimised by maximising exhaustion from the process streams. Exhaustion is defined as a process which aims to recover the maximum amount of sucrose in the minimum time, with only the economically unrecoverable sucrose lost to FM (Davis and Schoonees, 2006).

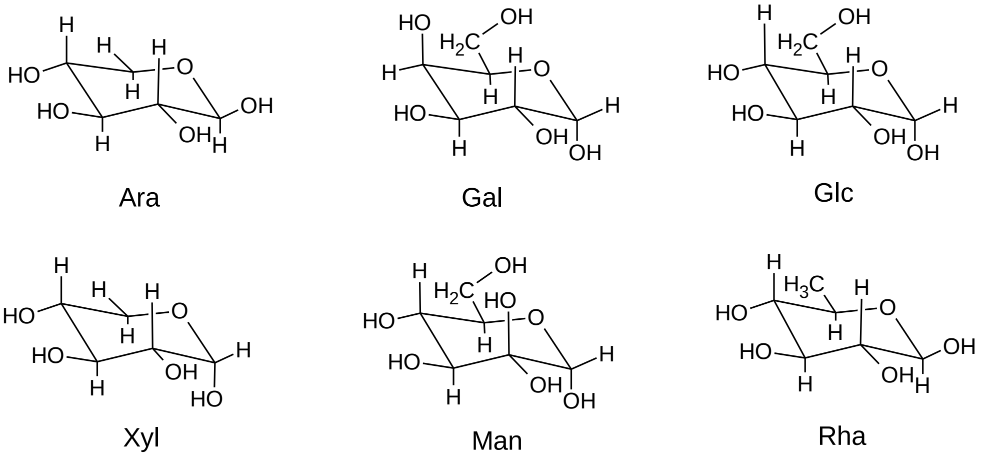
Factors which affect exhaustion include operational conditions, and the composition and physical properties of massecuites. Operational processes which can be optimised for sucrose exhaustion in the C-station include seed preparation, boiling, cooling, reheating and centrifugation (Love and Muzzell, 2009). Compositional aspects of massecuites which affect sucrose exhaustion include the concentration of non-sugars such as reducing sugars, ash and gums. The viscosity of massecuites is said to be a great limiting factor in the exhaustion of sucrose (MacGillivray and Matic, 1970). Gums in massecuites and FM are believed to contribute to viscosity (Morel du Boil, 2000a; Cuddihy Jr *et al.*, 2001; Figueira *et al.*, 2010).

This paper aims at quantifying and characterising the gums isolated from six South African sugarcane mills studied by the Sugar Milling Research Institute NPC (SMRI) over the 2011/2012 season, with respect to the composition and structure of the gums. A novel approach is taken in looking at the predominant structural features of the gums in assessing if variations in the structure arise due to seasonal, agricultural and/or geographical differences, and whether these variations alone show any correlation with FM viscosity and/or sucrose exhaustion. FM was used in this study because impurities, including gums, concentrate in this process stream.

Overview of gums and effects on sucrose exhaustion

Gums

'Gums' is a collective term used to describe polysaccharides (PS) found in sugar processing streams. Polysaccharides are carbohydrate chains comprised of 10 or more monosaccharides. The monosaccharides that make up polysaccharides are numerous and can include arabinose (Ara), galactose (Gal), glucose (Glc), xylose (Xyl), mannose (Man) and rhamnose (Rha), as depicted in Figure 1.



Ara = arabinose   Gal = galactose   Glc = glucose
Xyl = xylose   Man = mannose   Rha = rhamnose

Figure 1. Pyranose (six-member ring) forms of various monosaccharides that can be found in different gums.

The physical characteristics (including solubility and solution viscosity) of different polysaccharides arise due to the types of monosaccharides present (composition), the manner in which the monosaccharides are linked in the chain (structure/linkages), the degree of branching (number of side chains of monosaccharides off the main chain) as well as the chain length (molecular weight, MW) (du Clou and Walford, 2010).

Polysaccharide structure is largely determined by a method of chemical modification (permethylation) and degradation (hydrolysis) of the carbohydrate chains into discreet monosaccharidic units, followed by derivatisation and analysis by gas chromatography mass spectroscopy (GC-MS). The specific degradation products arise due to the manner in which each monosaccharide was linked in the original polysaccharide chains. For instance, a polysaccharide of alpha (α) Gal mono-saccharides linked from the carbon in the one position (Figure 2) on a Gal molecule to the carbon on the six position of the next Gal molecule, will give rise to penta-*O*-methyl-6-*O*-(tetramethylsilyl)-α-galactopyranoside (Gal6) units. For further details on the mechanism of the preparation, nomenclature and abbreviations of the arising degradation products, refer to the paper by du Clou and Walford (2010).

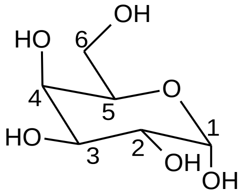


Figure 2. Labelled carbons of the galactose monosaccharide (hydrogens have been omitted for clarity).

The types of polysaccharides which have been identified in sugar processing streams result from either the metabolism within the sugarcane plant (metabolic) or from external microbial activity (microbial) during cane harvesting and handling (Morel du Boil, 2000a). Soluble polysaccharides such as indigenous sugarcane polysaccharide (ISP) and starch occur naturally in the sugarcane plant (Clarke *et al.*, 1986; Godshall *et al.*, 2001; Figueira *et al.*, 2010). Dextran and sarkaran (pullulans) are polysaccharides that arise as a result of microbial activity (Clarke *et al.*, 1986; Morel du Boil, 2001b).

ISP is a soluble cell wall polysaccharide. It is classified as a type of hemicellulose arabinogalactan which may contain up to 8% glucuronic acid. The backbone of the PS is made up of beta 1,3-linked Gal units with side chains of Gal, Ara or glucuronic acid linked in the six position (Clarke *et al.*, 1986). The major structural units determined in ISP include Gal6 (from the Gal branches linked at carbon six position off the backbone), Gal1,3,6 (arising from the backbone units containing branches) as well as Ara1 and Glu1 (as the branches of arabinose and glucuronic acid, respectively).

Starch is a common component of sugar solutions and comprises of amylose (20-30%) and amylopectin (70-80%) (Figueira *et al.*, 2010). Amylose consists of linear α-1,4 linked Glc units (Glc4) whilst amylopectin consists of Glc4 units with α-1,6 linked Glc (Glc6) branch points (Gidley, 1985). Analysis of starch identifies Glc4 and Glc6 as the primary structure units. Starch levels vary widely between different cane varieties and growing conditions (Figueira *et al.*, 2010). Average starch levels in South African FM are 1340 ppm on brix (or 0.2% on non-sucrose) (Sahadeo and Lionnet, 1999). Starch influences massecuite viscosity, co-crystallises with sucrose and can be found within raw sugar crystals, and it reduces purity. Starch levels above 250 ppm in raw sugar are said to cause problems within refineries (Morel du Boil, 2000b).

Dextran in sugar processing streams arises primarily from the microbial activity of *Leuconostoc* species on cane during harvesting and handling (Clarke *et al.*, 1986; Morel du Boil, 2001b). Infection of cane occurs whenever factors including borers, burning, frost, hail, or cutting causes damage to the stalk (Morel du Boil, 2001b). Dextran is also a Glc-based polysaccharide consisting of a Glc6 backbone with either α-1,2-, α-1,3- and/or α-1,4 linked Glc branches (Cui and Wang, 2006). Dextrans can range in chain length and are thus classified as either being low in molecular weight (LMW) or high in molecular weight (HMW). Dextrans are implicated in processing problems in the raw house, particularly at the end of the crushing season (Morel du Boil, 2000b).

Sarkaran is a polysaccharide which belongs to a family known as pullulans. Pullulans are linear glucans primarily made up of maltotriose (three α-1,4 linked Glc units) linked to a variable amount of maltotetraose (four α-1,4 linked Glc units) via α-1,6 linkages (Morel du Boil, 2000a). As with starch, the analysis of pullulans identifies Glc4 and Glc6 as the primary structure units. Sarkaran is reportedly associated with drought-stressed, frost-affected, stale and carryover cane (Morel du Boil, 2000a; Morel du Boil *et al.*, 2005). Sarkaran is generally linked with high viscosity processing streams (Morel du Boil *et al.*, 2005).

Other gums associated with sugar streams include hemicelluloses, levan, pentosans, pectins, phytoglucan (Cuddihy Jr *et al.*, 2001), and galactomannans (Clarke *et al.*, 1986). Gums lower the purity of streams and reduce sucrose exhaustion due to increased viscosities and modification of crystal growth (Cuddihy Jr *et al.*, 2001). Gums concentrate in FM.

Sucrose exhaustion

Target purity difference

Target purity difference (TPD) is a measure of sucrose exhaustion and indicates factory performance (Matthesius and Mellet, 1976). TPD is the difference between the true purity and target purity (TP) of FM. Whilst the true purity is a measure of the actual purity and is expressed as a percentage of sucrose to dry solids, the TP refers to the theoretical level of sucrose that should remain for a fixed level of non-sucrose substances in the solution. TP is calculated empirically as a function of the reducing sugars (fructose and glucose) and ash content in the sample according to equation 1 (Smith, 1995),

$$\text{Target purity (\%)} = 43.1 - 17.5\left(1 - e^{-0.74\left(\frac{F+G}{A}\right)}\right) \qquad (1)$$

where F is fructose, G is glucose and A is ash (% m/m) in the molasses sample.

Target purity is correlated to the equilibrium purity (EP) of FM. The EP is the experimentally determined sucrose:dry solids ratio of a FM that has been fully exhausted. The FM is fully exhausted in a procedure where the sample is concentrated under vacuum, crystallised with castor sugar, and extracted in a Nutsch filter. Theoretically, the calculated TP should give the same value as the EP (Sahadeo, 1998). The TPD therefore allows for mill performance to be measured in terms of sucrose lost to FM. Generally, Southern African mills with good sucrose exhaustion have seasonal average TPD values of 2-3 units (Davis and Schoonees, 2006), with most mills achieving averages of between 3-7 units (Sahadeo and Lionnet, 1999).

Factors affecting sucrose exhaustion

In practice it is difficult to achieve fully exhausted FM in a mill due to operational conditions. The use of steam and water in centrifugation cause sucrose to redissolve from the massecuite into the FM (Davis and Schoonees, 2006). FM sucrose crystals that are not sufficiently large (>120 microns) pass through C-centrifuge screens, resulting in a purity rise (Love and

Muzzell, 2009). Factors which impede sucrose exhaustion (melassigenic) include high levels of reducing sugars, certain inorganic ash constituents, gums and the overall viscosity of FM. Reducing sugars decrease sucrose solubility in FM. Inorganic ash constituents of alkali metal salts have been found to either decrease or increase sucrose solubility. Potassium, sodium, calcium and magnesium ($K^+ > Na^+ > Ca^{2+} > Mg^{2+}$, respectively) were found to be melassigenic in decreasing order of power in beet molasses (Day-Lewis, 1993). However, Sahadeo (1998) found that for cane molasses the least powerful melassigenic component is K^+, whilst Na^+ is the most powerful. Chlorides, phosphates and inorganic salts that form stable hydrates are also considerably melassigenic (Gupta *et al.*, 1973; Broadfoot and Steindl, 1980; Day-Lewis, 1993).

Gums and sucrose exhaustion

Gums including starch and dextran have previously been investigated for their melassigenic nature. Sahadeo (1998) spiked molasses samples with both potato starch and dextran. Starch revealed no measureable effect on sucrose exhaustion. At levels of 8 000-20 000 mg/kg dry solids, dextran largely affected the EP (and exhaustion); however, it could not be confirmed whether the difference between the EP and the TP was due to the gum effect alone, or the associated increase in viscosity and related kinetic effects. Later it was shown that there is a strong correlation between gum concentration (between 20 000 and 50 000 mg/kg dry solids) and TPD (Sahadeo, 1999).

Gums and final molasses viscosity

Besides their melassigenic nature, gums in FM have been shown to affect viscosity (Sahadeo, 1998, 1999; Sahadeo and Lionnet, 1999). Viscosity, in turn, directly affects the time required for FM to reach maximum sucrose exhaustion. FM viscosity is affected by the temperature, degree of supersaturation, and concentration of the various non-sucrose components (ash and gums). On an operational level, viscous massecuites are physically more difficult to handle, require longer residence times in the crystallisers and limit the degree to which the FM can be concentrated (brix level). Low crystallisation rates result as the migration of dissolved sucrose to growing crystal surfaces is physically impeded. Viscous massecuites are generally heated to improve handling; however, this not only results in higher energy costs but an overall increased loss of sucrose (as sucrose solubility increases with temperature) (Davis and Schoonees, 2006). HMW dextran has been found to increase viscosity (Morel du Boil, 2000b). Bruijn and co-workers (1980) found that concentrations of gums in molasses above 4% had a significant effect on viscosity. Sahadeo and Lionnet (1999) showed that 0.5-4% (based on non-sucrose) of both total gums and dextran have a direct effect on FM viscosity.

Materials and Methods

Final molasses samples

Table 1 details the FM samples analysed from six South African mills. The samples were collected and composited on a weekly basis for each mill over the 2011/2012 sugar milling season. Mills which process either primarily rainfed or irrigated cane were selected based on their geographical location.

Table 1. Description of mills from which weekly final molasses samples were collected over the 2011/2012 sugar milling season.

Mill	Abbreviation	Geographical region	Irrigated/ Rainfed	Mill/Diffuser
Komati	KM	Inland (Northern)	Irrigated	Diffuser (2 tandem)
Pongola	PG	Inland (Northern)	Irrigated	Diffuser (1 tandem)
Noodsberg (Refinery)	NB	Inland (Natal Midlands)	Rainfed	Mill (1 tandem)
UCL	UC	Inland (Natal Midlands)	Rainfed	Diffuser (1 tandem)
Darnall	DL	Coast (North of Durban)	Rainfed	Mills (1 tandem)
Sezela	SZ	Coast (South of Durban)	Rainfed	Diffusers (2 tandem)

Final molasses analyses

The FM samples collected from the respective mills were composited and subjected to the routine SMRI weekly analyses including pol, brix, fructose, sucrose, glucose, dry solids, ash and TPD. In addition, the FM sample viscosity, consistency and flow behavior index were determined with a Brookfield cone and plate viscometer at 30°C, at a constant shear rate at variable speeds (six measurements), with a CP51 spindle with a 1.565° angle and 2.4 cm diameter. A certified silicone Brookfield viscosity standard (a Newtonian fluid) of 59.2 Pa.s was run alongside the FM samples (Barker, 1998).

Isolation of gums

The method to isolate gums from FM is adapted from the SMRI method (Anon, 2006). A 10.0 ± 0.1 g sample of well mixed molasses was weighed into a 250 mL Nalgene centrifuge bottle. Deionised water (dH_2O) was added to give a final mass of 100.00 ± 0.02 g and the sample was mixed until all the molasses completely dissolved. The sample was centrifuged at 4800 rpm for 10 minutes to remove insoluble material and then 25.00 ± 0.01 g of the supernatant liquid was weighed into a separate 250 mL Nalgene centrifuge bottle. To this solution 120 mL of a chilled solution of 83% ethanol acidified to 8.3% with an HCl solution was added. The bottle was capped and allowed to cool in the refrigerator for 15 minutes. The sample was centrifuged at 4800 rpm for 10 minutes and the supernatant decanted. The precipitate was washed with 50 mL of 80% ethanol to remove residual sugars, and centrifuged at 4800 rpm for 10 minutes. The washings were discarded and the wash step repeated. After discarding the second washings, the precipitated gums were dissolved in 5-10 mL boiling dH_2O and quantitatively transferred to a pre-weighed round bottom flask. The sample was freeze-dried. Freeze-dried gums were then prepared and analysed for composition and structure.

Analysis of isolated gums

The gums from the FM samples were isolated, and then prepared and analysed by GC-MS for monosaccharide composition and linkage information according to the method detailed in du Clou and Walford (2010).

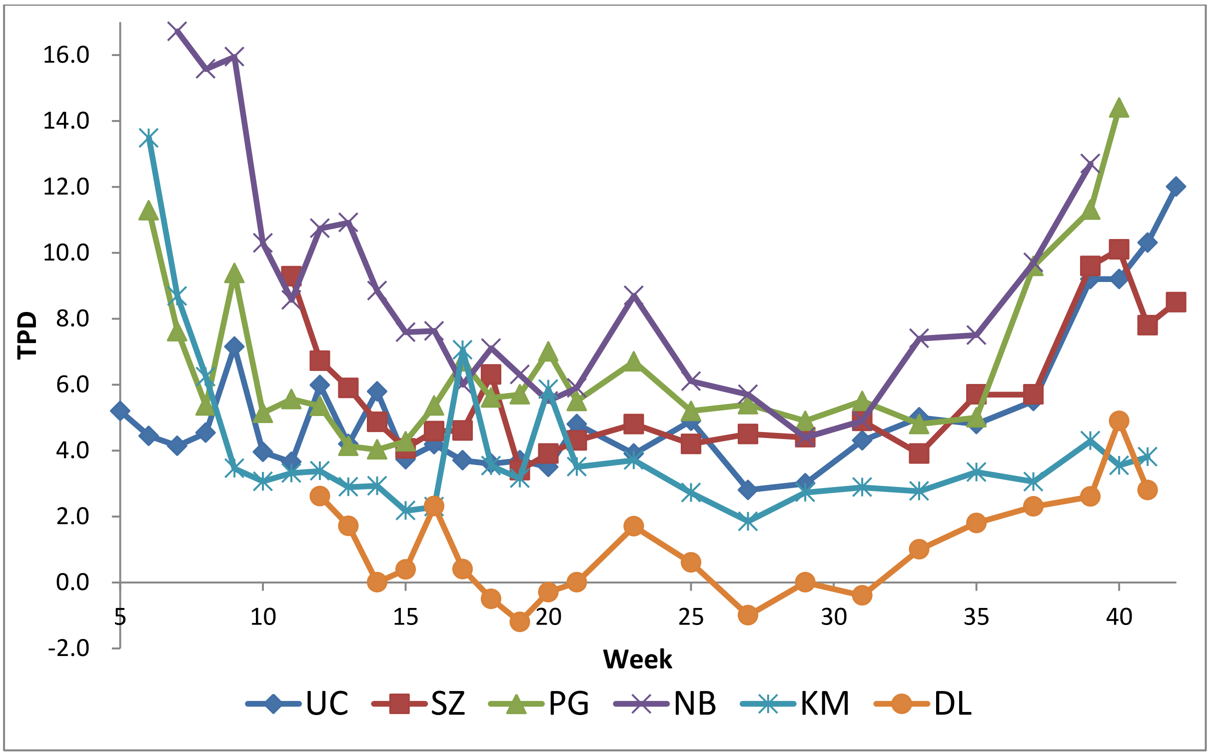
Composite molasses control sample

A composite of molasses samples from the 2010/2011 sugar milling season was prepared. This composite molasses (COMP) was used as a control sample with each batch of FM isolations, preparations and analyses. The results obtained for the samples analysed to date covering the 2011/2012 sugar milling season are reported herein.

Results and Discussion

Target purity difference

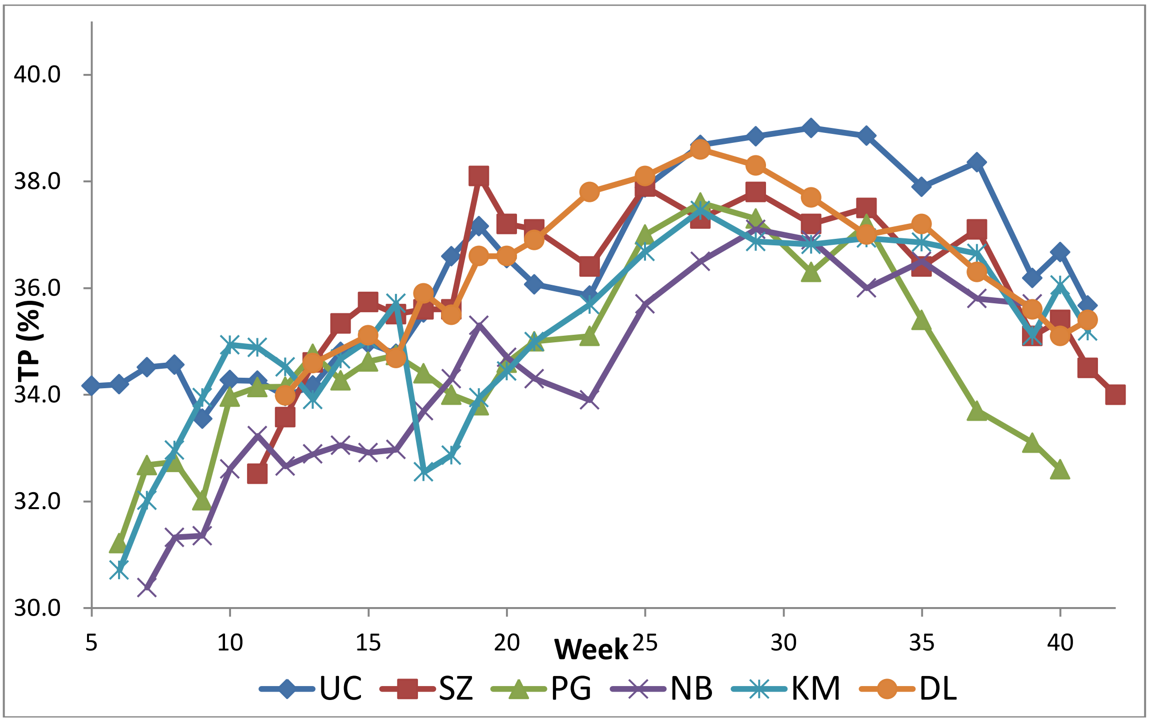
Figure 3 reveals a general trend in the TPD values for the six mills studied over the 2011/2012 season. At both the beginning and end of the season there was an overall rise in TPD for NB, KM, PG and SZ (TPD of 8-17 units). On the other hand, UC began the season with an intermediate TPD of 5 units, whereas DL started and ended the season with a TPD of less than 3 units. At the end of the season UC experienced a steep rise in TPD to 12 units. Through the middle of the season (weeks 11-24) UC, SZ, PG and KM had TPD values generally within the industry average of 3-7 units (Sahadeo and Lionnet, 1999). Over the same period NB had the highest average TPD value (9 units), whilst DL had the lowest (1 unit).



UC = UCL SZ = Sezela PG = Pongola NB = Noodsberg KM = Komati DL = Darnall

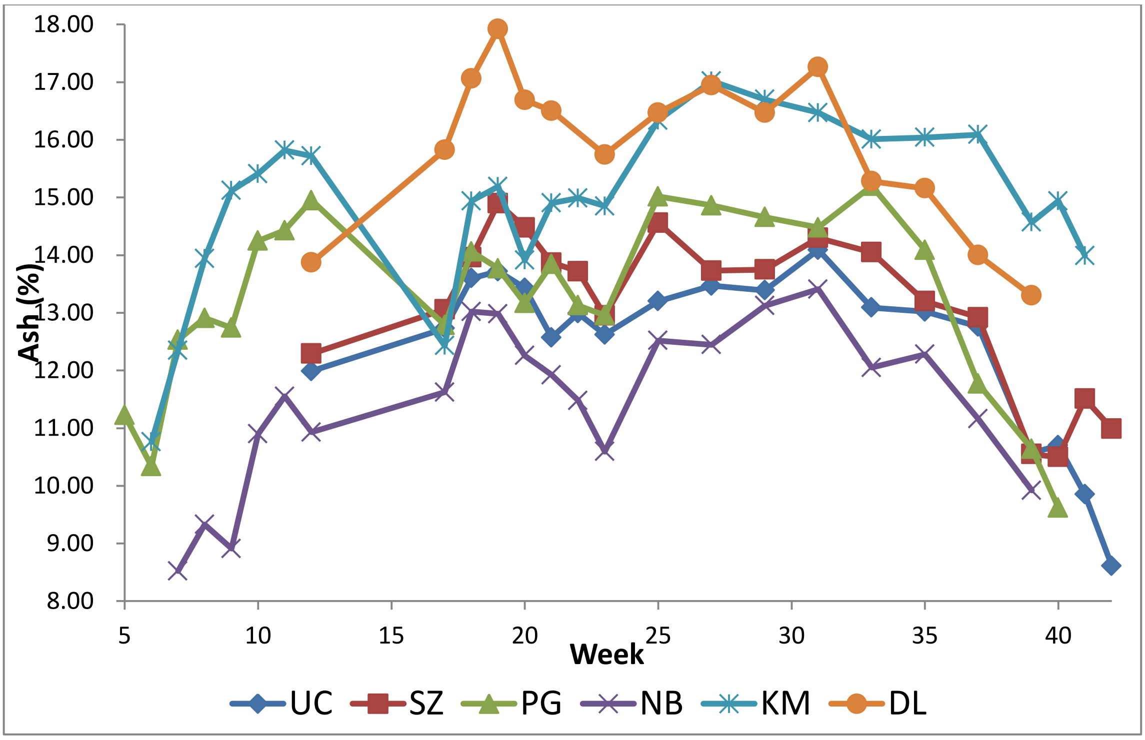
Figure 3. Target purity difference (TPD) values for final molasses for six South African mills investigated over the 2011/2012 season.

The TP and ash content is also plotted for the six mills over the season in Figures 4 and 5, respectively, and the data reflects the trend as generally experienced for Southern African mills. Refer to Appendix A for the summarised data for all the FM samples analysed.



UC = UCL SZ = Sezela PG = Pongola NB = Noodsberg KM = Komati DL = Darnall

Figure 4. Target purity (TP) values for final molasses for six South African mills investigated over the 2011/2012 season.

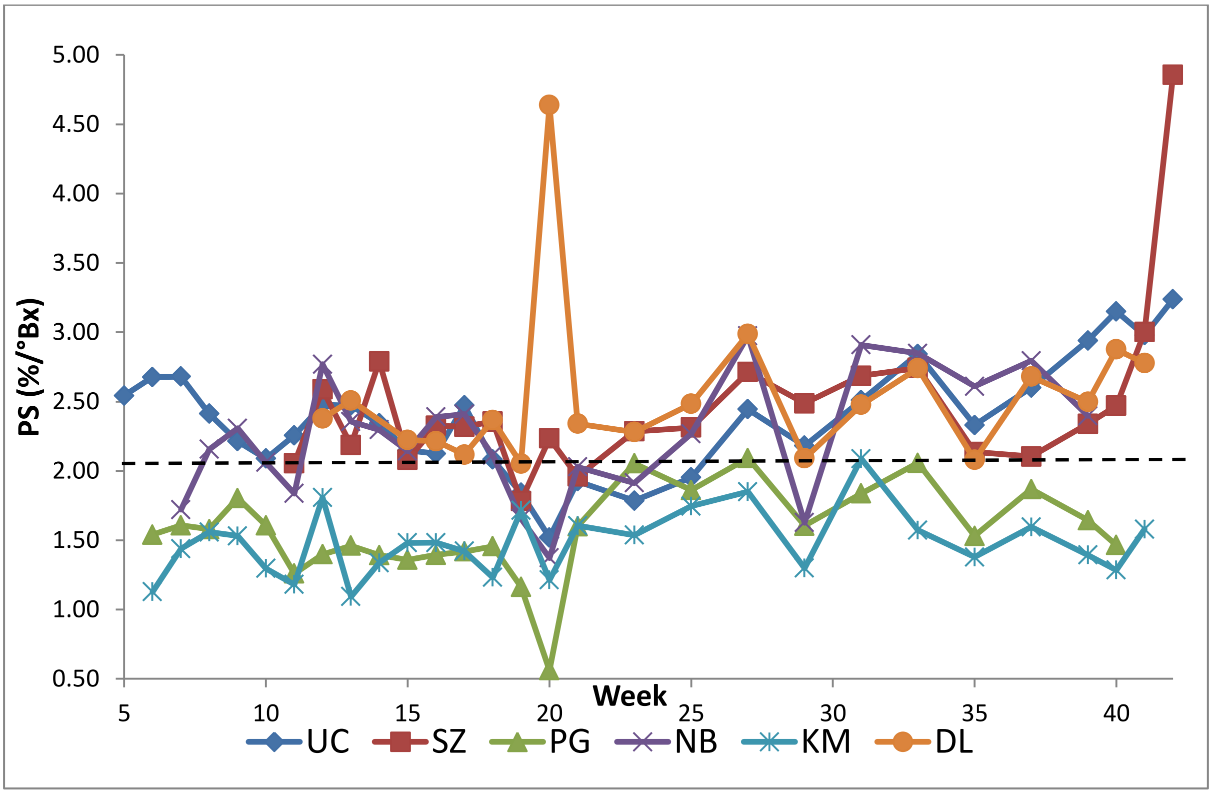


UC = UCL SZ = Sezela PG = Pongola NB = Noodsberg KM = Komati DL = Darnall

Figure 5. Ash values for final molasses for six South African mills investigated over the 2011/2012 season.

Gum quantity effect on sucrose exhaustion

Figure 6 depicts the change in gum concentration in the FM samples studied over the season. Whilst there is no clear seasonal trend in the quantity of gums in FM, and no correlation to TP (or TPD) was established, it is important to note that the majority of the analysed samples (99%) contain gums below 4% based on brix (%/°Bx). Bruijn and co-workers (1980) made note that gums between 1-4% in molasses did not affect sucrose exhaustion. The two samples that did have gums in excess of this level had markedly different TPD and ash values (Table 2). This difference calls for factors including the FM viscosity and makeup of the gums to be considered to determine whether gums in significant quantities directly affect TPD.



UC = UCL SZ = Sezela PG = Pongola NB = Noodsberg KM = Komati DL = Darnall

Figure 6. Gums (polysaccharides) isolated from final molasses samples for six South African mills over the 2011/2012 season.

Table 2. Final molasses sample results for gums above 4%/°brix.

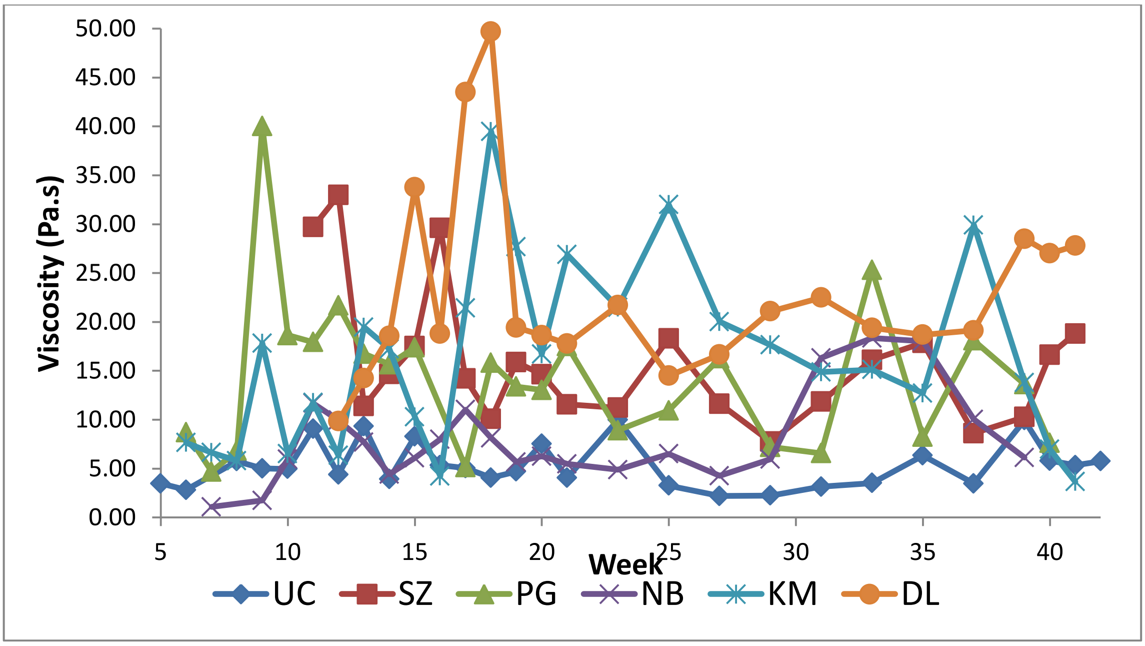
Mill	Week	Target purity difference	Ash (%)	PS (%/°brix)	Viscosity (Pa.s)
Darnall	20	-0.3	16.69	4.64	18.64
Sezela	42	8.5	10.99	4.86	3.48

What the data in Figure 6 does show is that the gum concentration is found in the normal range (less than 5% on brix) as reported for South African FM samples studied in 1955 (Douwes Dekker, 1957) and again in 1970 (MacGillivray and Matic, 1970) across the 2011/2012 season. This reveals that the level of gums in FM has remained fairly consistent in the South African sugar industry over the past 65 years.

An interesting trend evident in Figure 6 is the distinction in gum quantity found in FM of mills that process cane from irrigated fields (<2.1 %/°Bx; KM and PG) and those that process cane from predominantly rainfed fields (>2.1 %/°Bx; UC, SZ, NB and DL). Cane that is grown in rainfed areas includes that which comes from KwaZulu-Natal coastal areas (DL and SZ) and the KwaZulu-Natal Midlands (NB and UC). The higher gums experienced in the FM from the rainfed cane are likely due to the drought conditions experienced over the period 2009 to 2012, coupled with bouts of high frost (NB and UC), hail damage (UC), and higher no-cane stops due to cane shortages (Anon, 2010, 2011; Smith *et al.*, 2011; Anon, 2012). Gums arising are likely to include higher levels of pullulan-like polysaccharides, which are more prone in drought-stressed cane (Morel du Boil, 2001a; Morel du Boil *et al.*, 2005). In cases where cane was damaged due to frost and/or hail (NB and UC) or where delays in milling drought-affected cane occurred due to challenges with cane supply from growers and hauliers (SZ), higher levels of dextran are likely (Morel du Boil, 2000a; Anon, 2011).

Gums and final molasses viscosity

Whilst the levels of gums determined across the season were relatively low and no discernible correlation between gum concentration and TPD was determined, the impact of the gums on the FM viscosity was also investigated. Figure 7 illustrates the change in viscosity for the FM samples of the mills over the season. No trend was evident in any of the mills studied over the 2011/2012 season. No correlations between gum quantity and viscosity were established either. Bruijn and co-workers (1980) commented that, in addition to having an effect on sucrose exhaustion, only gum quantities above 4% affected an increase in FM viscosity. The samples which satisfy this criterion, however, had contrasting viscosities (Table 2). One sample had a relatively high viscosity (DL20 = 18.64 Pa.s), and the other did not (SZ42 = 3.48 Pa.s). Analysis of the composition and structure of all the gums was then carried out to determine whether the type of the gum present had a higher impact on FM viscosity compared to gum quantity alone.



UC = UCL SZ = Sezela PG = Pongola NB = Noodsberg KM = Komati DL = Darnall

Figure 7. Measured viscosity of final molasses for six South African mills over the 2011/2012 season.

Gums composition and structure

The composition and structure of the gums isolated from the FM samples of the six mills were analysed in conjunction with the COMP sample, as summarised in Tables 3 and 4. The method for isolation, treatment and analysis of the gums composition and structure is validated by the consistency of the COMP results for both sets of analyses (standard deviation, SD, of ≤ ±4%).

Table 3. Summarised statistical data for the compositional analysis of gums isolated from the composite final molasses (FM) (2010/2011 season) and FM for six mills analysed over the 2011/2012 season.

Sample	Value	Ara (%)	Gal (%)	Glc (%)	Man (%)	Rha (%)	Xyl (%)
COMP	Mean (±SD)	12(2)	18(3)	56(4)	4(1)	1(0)	9(1)
	Min-Max	8-16	10-22	50-69	0-6	1	5-11
KM	Mean (±SD)	13(3)	18(4)	55(7)	3(1)	1(0)	10(2)
	Min-Max	9-18	9-23	44-66	2-5	0-1	6-14
PG	Mean (±SD)	9(3)	12(3)	67(8)	3(1)	1(0)	8(2)
	Min-Max	5-16	6-18	54-81	2-4	0-1	4-12
NB	Mean (±SD)	11(5)	13(3)	64(6)	4(1)	1(0)	7(1)
	Min-Max	5-27	8-19	53-74	0-6	1	5-9
UC	Mean (±SD)	9(3)	14(4)	64(9)	4(1)	1(0)	8(3)
	Min-Max	4-17	7-19	52-83	2-7	0-1	0-11
DL	Mean (±SD)	13(3)	19(3)	51(4)	6(1)	1(0)	10(1)
	Min-Max	8-21	12-23	44-57	5-8	1	7-12
SZ	Mean (±SD)	9(3)	13(4)	64(7)	5(2)	1(0)	9(1)
	Min-Max	5-18	0-20	47-82	0-7	0-1	6-11

Ara = arabinose Gal = galactose Glc = glucose Man = mannose Rha = rhamnose Xyl = xylose
COMP = composite molasses SD = standard deviation
KM = Komati PG = Pongola NB = Noodsberg UC = UCL DL = Darnall SZ = Sezela

The compositional data in Table 3 shows that the major monosaccharide composition includes:

$$\text{Glc} > \text{Gal} > \text{Ara} > \text{Xyl} > \text{Man} > \text{Rha}.$$

Compositionally, the gums isolated from all the mills showed a fair amount of consistency, with SD values of five or less units about the mean quantity of most of the major monosaccharides. Glc is both the major monosaccharide in all the gums, and the component with the highest variability in concentration (SD ±4% to ±9%), both within the mills and between the mills over the 2011/2012 season. DL experienced the least overall variation in gum composition over the season, whilst the UC gum composition varied the most. An increase in gum Glc ratios indicate an increase in PS arising from higher starch levels or increased microbial activity (dextrans and pullulans). The Gal, Ara, Xyl, Man and Rha monosaccharides are most likely due to ISP, hemicelluloses and other soluble metabolic PS from the sugarcane plant. On average SZ, NB, UC and PG all contained Glc levels above 64%, whilst KM and DL had average levels of 55% or less. It is indicated that KM and DL were least affected by microbial activity over the 2011/2012 sugar milling season.

Table 4. Summarised statistical data for the linkage analysis of gums isolated from the composite final molasses (FM) (2010/2011 season) and FM from six mills analysed over the 2011/2012 season.

Sample	Value	Xyl1,2,4+Xyl1,3,4 (%)	Glc4 (%)	Glc6 (%)	Gal6 (%)	Gal1,3,6 (%)
COMP	Mean (±SD)	9(1)	45(3)	11(2)	5(1)	27(4)
	Min-Max	6-12	39-54	6-15	4-7	19-36
KM	Mean (±SD)	11(2)	45(7)	12(6)	5(5)	25(8)
	Min-Max	7-16	30-57	3-30	3-13	6-43
PG	Mean (±SD)	9(2)	48(7)	19(19)	3(1)	18(5)
	Min-Max	4-13	35-60	10-38	2-6	11-28
NB	Mean (±SD)	8(2)	49(5)	17(6)	4(4)	20(5)
	Min-Max	5-13	40-60	11-32	3-5	13-31
UC	Mean (±SD)	8(3)	49(7)	18(10)	4(1)	18(5)
	Min-Max	1-12	31-63	10-45	2-8	9-26
DL	Mean (±SD)	11(2)	37(4)	15(6)	5(1)	28(5)
	Min-Max	9-16	31-42	5-25	4-8	22-39
SZ	Mean (±SD)	9(3)	50(7)	17(6)	3(1)	16(4)
	Min-Max	2-13	38-68	10-33	1-6	3-20

Xyl = xylose Glc = glucose Gal = galactose
COMP = composite molasses SD = standard deviation
KM = Komati PG = Pongola NB = Noodsberg UC = UCL DL = Darnall SZ = Sezela

The structural data in Table 4 shows that the major linkages include:

Glc4 > Gal1,3,6 > Glc6 > Xyl1,2,4+Xyl1,3,4 > Gal6.

The structural analysis of the isolated gums revealed more variability in gums structure compared to the composition over the season. Glc4 and Glc6 together make up the Glc component in the gums, and reflect the quantities determined from the compositional analyses. Glc4 was the most abundant structural unit in all the samples, with mean quantities ranging from 37-50%. Whilst Glc6 was detected in mean quantities of 11-19%, this structural feature varied most across the season (SD ±6 to ±19%). Gal1,3,6 was the second most abundant of the major linkages in the samples, and which also had moderate variability (SD ±4% to ±8%). Compositional analysis indicated that both KM and DL had high levels of metabolic PS as opposed to infection PS. Structural analyses support these findings. KM and DL both had the lowest average quantity of Glc4 (37-45%) and Glc6 (12-15%) linkages, and both had moderate SD values for these linkages through the season (±4 and ±7%, respectively). This indicates that a small proportion of the gums consisted of pullulans and/or starch (predominantly Glc4 in nature), and that dextran (Glc6) levels were generally low. Higher levels of ISP, hemicelluloses and other metabolic PS from the plant are indicated, as the concentration of Gal and Xyl linkages were highest. Both mills contained the highest amounts of ISP, indicated by the high Gal1,3,6 ratios. Compositional analysis of SZ, NB, UC and PG suggested that the cane processed by these mills experienced higher levels of microbial activity due to the higher propensity of Glc present. This is further supported by the structural analysis. Since the mean Glc6 levels were found to be highest in these samples (17-19%) a higher likelihood of dextrans is suspected. The higher mean Glc4 levels (48-50%) indicate a greater presence of possible pullulans and/or starch. Conversely, Gal1,3,6 was found in substantially smaller mean quantities (16-20%) indicating less ISP is present compared to the PS from infection in these mill samples over the season.

Rainfed cane is more likely to be affected by drought conditions, and thus gums such as sarkaran are expected to be more prevalent. FM from mills that process this cane is expected to contain an increased ratio of gums due to microbial activity compared to the metabolic gums. The opposite is expected of gums in FM from mills that process irrigated cane. As such, KM and PG are expected to have similar compositional and structural features in their FM gums. However, the structural features of PG's gums were more similar to the rainfed mill FM gums of UC, NB and SZ. Furthermore, the FM gums from DL (rainfed) had similar compositional and structural ratios to KM (irrigated). It was reported in the 2011 Local Grower Council Report for PG that harvesting was hampered by consistent rains at the end of the 2010/2011 season, and that the mill performed below average resulting in carryover cane of about 50 000 tons (Anon, 2011). It is likely that these factors contributed to higher incidents of microorganism-related PS in the cane in the ensuing milling season. In the same report, various climatic conditions and handling problems explained why UC, NB and SZ would have experienced higher incidents of microbial activity compared to DL. It was further reported that there were problems associated with frost (NB and UC) and hail (UC) in 2010 (Anon, 2011) as well as high incidents of cane delivery delays (UC) at the beginning of the 2011 season due to cane shortages (Dickey, 2011). These factors may have contributed to higher incidents of microorganism-related PS development in the cane processed at NB and UC. Whilst the coastal mills were not exposed to frost and hail conditions like their Midlands counterparts, SZ reported problems with cane quality due to the wet conditions on the drought-affected cane at the end of the 2010/2011 season. SZ also experienced problems with cane deliveries from both growers and hauliers (Anon, 2011). Cane deliveries were also diverted from the Umzimkulu mill, which was closed over the 2011/2012 season. Although exposed to the same drought stresses and cane delivery problems, microbial infection at DL appears to have been minimised, as indicated by the greater ratio of Gal1,3,6 containing PS found in the FM samples.

Whilst the composition and linkage types determined for the different gums correlate to environmental and/or poor handling factors for all the study mills except DL, correlations between these gums on the FM viscosity and sucrose exhaustion could not be established on the current data. The two samples displaying the highest gum levels were further compared (Tables 2 and 5). DL20 had a high viscosity (18.64 Pa.s) and high ash value (16.69%) with a favourable TPD (-0.3 units). High viscosities can be attributable to the presence of HMW dextran. Dextran is indicated by high levels of Glc6, however, DL20 had a low propensity of Glc6 (8%) compared to the level of linkages arising from ISP and other metabolically derived PS of the sugarcane plant. Further investigation is required to determine whether the MW of the predominant PS in this FM is the major cause of the high viscosity. It should also be investigated whether the combination of constituents in the FM has resulted in any difference between EP and TP values, and if this has given rise to a more favourable TPD. In the case of SZ42, the sample had a relatively low viscosity (3.48 Pa.s), low ash content (10.99%) and a relatively high TPD (8.5 units). Structural analysis of SZ42 revealed a high level of dextran and pullulan/starch linkages (Glc6 = 24%), and low ISP linkages. It is possible that the dextran content is of LMW, as the viscosity of the sample was not affected. LMW dextran is indicated by the high incidence (6%) of terminal Glc residues (GlcT). Similar to the DL20 sample, it needs to be determined whether the MW of the predominant PS has caused the favourable viscosity.

Table 5. Linkage analysis of the two final molasses samples with a gums concentration of greater than 4%/°brix.

Mill	Week	Xyl1,2,4 + Xyl1,3,4 (%)	Glc4 (%)	Glc6 (%)	Gal6 (%)	Gal1,3,6 (%)	GlcT (%)
Darnall	20	10	36	8	6	39	1
Sezela	42	8	46	24	3	13	6

Xyl = xylose   Glc = glucose   Gal = galactose

From the summary of seasonal data (Appendix A) we see that DL and UC represent two extremes. Although both mills had high average gum quantities, DL had on average a high viscosity, a high ash content, yet low TPD values. On the other hand, UC had on average low viscosity, low ash and yet moderate TPD values. The analysis of the data accumulated on the FM samples to date has not shown conclusive evidence that any one factor, including gum quantity or gum type, has a direct effect on viscosity or sucrose exhaustion. To better understand which factors affect sucrose exhaustion, further studies on gum MW and ash components (and possible interactive effects with specific gums) should be investigated alongside EP determinations.

Conclusions

The quantity of gums isolated from the six mills over the 2011/2012 season were found to be in the normal range (<5% on brix) as first reported by Douwes Dekker in 1957. This study reveals that mills processing irrigated cane had an overall lower quantity of gums compared to mills processing predominantly rainfed cane. This difference is attributed to the widespread drought conditions experienced over the period of cane maturation in the respective geographic regions. Variations in composition and structure were established. A minority of the samples contained high levels of metabolic PS, whereas the majority of samples contained PS indicative of infectious microbial activity. The increase in microbial activity was attributed to both the negative climatic conditions and handling factors. Climatic factors included drought stress, and damage from hail and frost. Handling factors included cane shortages, harvest delays, poor mill performance and carryover cane. Correlations between gum quantity and structure against FM viscosity and sucrose exhaustion could not be established. Future work would also include the analysis of the FM gum MW and related ash components to determine which of the factors (in isolation or combination) have a more deleterious effect on sucrose exhaustion.

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APPENDIX A

Table A. Data including the mean, standard deviation (±SD), range (min-max) and number of samples (n) are detailed for the final molasses samples analysed across six South African mills over the 2011/2012 sugar milling season. The means are colour-coded to illustrate the degree of the value (low, medium or high).

Mill	Value	Pol (°Z)	Bx (°brix)	DS (%)	TPD	Ash (%)	PS (%/°brix)	PS (mg/kg DS)	Viscosity (Pa.s)
KM n=27	Mean	27.2	84.3	79.5	4.1	15.0	1.48	15665	16.08
	±SD	2.1	1.5	1.4	2.4	1.4	0.24	2532	9.28
	Min-Max	24.4 - 32.4	81.1 - 86.9	76.0 - 82.2	1.8 - 13.5	10.8 - 17.0	1.09 - 2.09	11647 - 22320	3.65 - 39.48
PG n=26	Mean	30.1	83.9	79.1	6.6	13.4	1.56	16566	14.24
	±SD	2.3	1.4	1.4	2.6	1.5	0.32	3393	7.68
	Min	26.9 - 36.6	81.6 - 86.1	76.9 - 81.9	4.0 - 14.4	9.6 - 15.2	0.56 - 2.09	5955 - 22284	4.68 - 40.02
NB n=24	Mean	30.6	80.5	76.0	8.8	11.4	2.25	23806	7.99
	±SD	2.5	2.1	1.6	3.5	1.3	0.43	4636	4.59
	Min	27.4 - 36.0	75.3 - 83.9	72.0 - 78.7	4.4 - 16.7	8.5 - 13.4	1.37 - 2.97	14586 - 31718	1.08 - 18.35
UC n=29	Mean	28.5	80.1	75.0	5.2	12.3	2.39	25474	5.45
	±SD	2.4	1.7	1.6	2.3	1.2	0.41	4310	2.30
	Min	25.8 - 33.8	75.6 - 82.6	71.6 - 77.8	2.8 - 12	8.6 - 14.1	1.52 - 3.24	16240 - 34139	2.20 - 9.98
DL n=21	Mean	27.7	83.8	79.0	1.1	15.4	2.54	26947	22.92
	±SD	2.0	1.3	1.0	1.6	1.6	0.56	5990	9.56
	Min	24.9 - 30.8	81.3 - 86.6	77.2 - 80.9	-1.2 - 4.9	12.1 - 17.9	2.05 - 4.64	21793 - 49301	9.86 - 49.70
SZ n=23	Mean	30.9	82.8	77.8	5.7	13.0	2.47	26278	15.43
	±SD	1.8	1.0	0.9	2.0	1.3	0.60	6276	7.16
	Min	28.1 - 35.6	81.1 - 84.8	76.4 - 79.9	3.4 - 10.1	10.5 - 14.9	1.78 - 4.86	19123 - 51344	3.48 - 32.98

Key	low	medium	high

KM = Komati PG = Pongola NB = Noodsberg UC = UCL DL = Darnall SZ = Sezela