BOILING RATE, HEAT TRANSFER AND VISCOSITY OF TECHNICAL SUGAR CANE LIQUORS

By

MICHAEL SASKA

Audubon Sugar Institute, Louisiana State University Ag Center, St Gabriel, Louisiana, USA
msaska@agcenter.lsu.edu

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Abstract

INCIDENTS of extremely slow sugar boiling were experienced in 2002 by Louisiana mills following periods of prolonged wet weather. Based on the testing at Audubon that followed these observations, they were ascribed to severely reduced heat transfer rates in the vacuum pans. Surprisingly, though, this was found to be unrelated to viscosity effects or polysaccharide levels but rather due, to all indications, to deposition on the heat transfer surface during sugar boiling of a water soluble layer of as yet unknown chemical nature. These presumed deposits were found to be pH-sensitive, and small additions of hydrochloric acid were effective in restoring normal boiling. In the continued testing in 2003, boiling heat transfer coefficients of cane molasses were determined in a pilot vacuum pan under identical conditions to those in 2002, viz. 15.2 kPa.a (4.5"Hg) absolute pressure, 69 kPa.a (10 psi.a) steam pressure, and 80% to 90% dry solids content. With some deviations, a linear relationship of the form HTC = Ax (%RDS) - B between the boiling heat transfer coefficient and dry solids content was found satisfactory, unlike in 2002 when inverted S-shaped curves were required to adequately describe the rapid drop of HTC in the 79–81% RDS range for the refractory materials. The consistency of the same molasses as used in the HTC measurements was measured over the 80–90% dry solid content and an equation for the overall heat transfer coefficient as a function of the molasses viscosity (cP) at standard conditions (50°C, 2/sec) HTC (W/m²°C) = 75176 (μ)⁻⁰·⁵²⁹ was developed. Surprisingly, molasses viscosity at standard conditions did not show any correlation to its dextran or starch content. It is suspected that this observation is related to an incomplete hydrolysis of dextran by dextranase under industrial conditions and the nature of the monoclonal antibody assay. Of the three main cations, no correlation was found between viscosity of molasses and its K and Mg levels, and only a limited one with its Ca level.

Introduction

Detailed analysis of the factors involved in heat transmission in vacuum pans was presented in a series of papers by the Braunschweig Sugar Institute group (Bruhns and Schliephake, 1996). In the sugarcane literature, the industrial data of Webre are still in use (Honig, 1959; Hugot, 1972) as are the more recent measurements of Rouillard (1985). Obviously, the throughput or productivity of a vacuum pan is mainly determined by the time that is required to produce sugar crystals of acceptable size. That in turn, at least in principle, depends on both the water evaporation and sucrose crystallisation rates.

In industrial pans with correctly sized heating surface, the former should not be limiting and the rate of crystal growth determines the overall rate of sugar boiling. The evidence of that in commercial operations is the danger and occasional occurrence of exceeding the workable supersaturation range and formation of false grain.

Scale formation on either side of the heating surface can drastically reduce the heat transfer rate and reduce the evaporation rate to the extent that it becomes rate-limiting. Of the bulk fluid properties, consistency of the crystal-liquor suspension is well known to be the main factor determining the overall crystallisation rate as it affects both the rate of water evaporation as well as the rate of crystal growth.
Rarely, though, are the three related, yet distinct factors, viz. the concentration (dry solids content) of the mother liquor, crystal content and viscosity of the mother liquor considered separately. The fairly frequent yet mostly anecdotal accounts in the sugarcane literature of incidents of boiling difficulties following microbial infection in stale cane are usually interpreted as the effects of polysaccharides on the molasses viscosity and, in turn, on sugar crystallisation.

In the following, an account is given of the recent observations in Louisiana of the occasional but severe difficulties with boiling sugar, and the measurements at Audubon Sugar Institute that followed.

**Rate of boiling and heat transfer rates measurements: 2002–2003 testing**

Following a report in 2001 from one of the mills of difficulties with boiling sugar and unsuccessful efforts to improve the situation by application in the pan of various additives, a series of viscosity measurements was done with final molasses, as is, and after various treatments (Figure 1).

None of the additives, chemicals, or specialty surfactants was found to be effective in reducing molasses viscosity, but a distinct increase, presumably from dextran-causing infection, was noted after the dilute molasses was intentionally ‘spoiled’ by keeping it at ambient temperature for 48 hours at ~ 40% RDS.

Comparison of the very slow boiling syrup A, with a ‘normal’ syrup B, with pure sucrose and with a final molasses (Figure 2) indicated only a moderate increase of viscosity, if any, over the normal syrup, and identical viscosity on the same RDS basis, in the relatively low range of RDS for pure sucrose, cane syrup and final molasses.

In 2002, following periods of heavy and prolonged rains, several mills reported intermittent but severe difficulties with sugar boiling. In the follow-up testing at Audubon that was described in some detail in a recent publication (Saska, 2003), it was determined that the problems were due to severely reduced overall heat transfer coefficients and, consequently, water evaporation rates, rather than to an effect on the crystallisation rate of sucrose.

For the refractory, ‘hard-to-boil’ molasses (the curves in Figure 3 labelled ‘SM “A” molasses and IB “A” molasses’), the heat transfer coefficient dropped rapidly at 79–80% RDS down to the 50–100 W/m²°C range, while a more steady decline and HTC some eight times higher (at 85% RDS) were found for the ‘normal’ molasses (sample SJ “A” in Figure 3).
A sample of final molasses was also tested at that time for comparison and found to fall in the intermediate range but still some four-times higher (at 85% RDS) than the 'hard-to-boil' ‘A’ molasses. A sample of a ‘B’ massecuite followed the trend for the ‘A’ molasses from which it was produced.

This steep drop in heat transfer rate was interpreted as an onset in the 79–81% RDS range of fouling on the molasses side of the heating surface that appeared to be readily reversed by contact with water and therefore unlike the common hard scale found in the vacuum pans and evaporators. The viscosity of the difficult SM ‘A’ molasses (Figure 4) again showed only a modest elevation in the 83% to 85% RDS range where the heat transfer rate was some eight times lower than for the normal SJ ‘A’ molasses.

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**Fig. 2**—Natural logarithm of viscosity of pure sucrose, measured and from the literature (Bubnik et al., 1995), cane syrup and cane final molasses, at 30°C.

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**Fig. 3**—Boiling HTC of ‘A’ molasses, ‘C’ molasses and ‘B’ massecuites from various sources. Note the sudden drop in HTC at higher dry solids levels of the ‘hard-to-boil’ SM and IB molasses.
Fig. 4—Natural logarithm of viscosity (cP) of two 'A' molasses samples, the normal boiling SJ and refractory SM molasses from Figure 3.

None of the common analytical parameters, (monoclonal antibody) dextran (Rauh et al., 2003), starch (the SMRI method), suspended solids, invert sugars, common cations and anions were found to relate to the observed phenomenon. Of the numerous treatments that were attempted, only acidification with small amounts of hydrochloric acid added directly in the vacuum pan was found to lead to an immediate and full restoration of good boiling (Figure 5). The overall conclusion was that minor components of juice, of as yet undetermined chemical nature, and their pH-dependent interactions with other components of the molasses were responsible. These components appeared to be of low molecular weight and likely to be products of microbial or fungal deterioration of cane during prolonged periods of warm, humid and wet weather.

Fig. 5—Summary of the acidification tests. A seven-fold increase of HTC by addition of 1% HCl was obtained, while pH was reduced to about 5. A 'hard-to-boil' molasses IB 'A' from Figure 3.
Heat transfer and viscosity characteristics of final molasses, 2003—2004 testing

Unlike in 2002, the weather was dry and generally very favourable for most of the 2003 season and no boiling problems were reported.

In order to provide more insight into the factors affecting the heat transfer and rate of sugar boiling, a series of heat transfer and viscosity measurements was performed, following, in general, the same procedures as in the previous tests.

The description of the equipment and other details can be found in the literature (Saska and Rein, 2001; Saska, 2002; Saska, 2003).

In the course of the 2003 season, eleven final molasses samples were collected in 55 gal. drums at different Louisiana mills, at different times, then transported to Audubon and subjected to testing of their heat transfer and viscosity behaviour, and their composition.

Consistent with absence of any boiling difficulties reported by the mills, the heat transfer coefficients were found to fall within a narrow range, with the exception of the Alma 10/7 sample that, at higher RDS levels, displayed a noticeably higher HTC.

It is interesting to note that this was the earliest sample collected, just days after start up of harvesting, and from the most-northerly mill in Louisiana. None of the molasses displayed the inverted S-shaped HTC curves associated with the refractory materials studied in 2002—2003.

Linear correlations

\[ \text{HTC (W/m}^2\text{°C)} = a \times (\%\text{RDS}) - b \]

appeared to be adequate (Figure 6) to represent the experimental data where a and b are the constants listed in Table 1.

Table 1—Parameters a and b of the heat transfer coefficient equation (HTC in W/m$^2$°C). Other parameters are as in Figure 6.

<table>
<thead>
<tr>
<th>Name</th>
<th>A</th>
<th>B</th>
<th>R$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alma 10/8</td>
<td>5251</td>
<td>52.6</td>
<td>0.940</td>
</tr>
<tr>
<td>Alma 11/11</td>
<td>7514</td>
<td>80.5</td>
<td>0.949</td>
</tr>
<tr>
<td>Alma 12/12</td>
<td>9409</td>
<td>101.9</td>
<td>0.806</td>
</tr>
<tr>
<td>Lafourche</td>
<td>9352</td>
<td>102.6</td>
<td>0.908</td>
</tr>
<tr>
<td>Enterprise</td>
<td>8623</td>
<td>93.9</td>
<td>0.922</td>
</tr>
<tr>
<td>St. Mary</td>
<td>11622</td>
<td>128.6</td>
<td>0.610</td>
</tr>
<tr>
<td>Cora</td>
<td>10590</td>
<td>118.0</td>
<td>0.916</td>
</tr>
<tr>
<td>Cinclaire</td>
<td>8947</td>
<td>99.0</td>
<td>0.832</td>
</tr>
<tr>
<td>Lula</td>
<td>10404</td>
<td>115.6</td>
<td>0.786</td>
</tr>
<tr>
<td>St. James</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Westfield</td>
<td>11026</td>
<td>122.9</td>
<td>0.823</td>
</tr>
</tbody>
</table>

The viscosity of the samples was measured (Figure 7 and Table 2) with a Brookfield HBTDV-II cone-and-plate viscometer, with CP-42 and CP-52 cone spindles.

Most of the measurements were done at our ‘standard’ conditions, chosen before as 50°C and a shear rate of 2/sec, so as to make the data comparable with the exhaustion criteria of Miller et al. (1998).

Viscosities at other temperatures and shear rates were measured as well, but are not reported here. As all molasses was found to be slightly shear-thinning, the viscosity is not strictly a constant.

It is recognised therefore that the term consistency may be preferable, but both are used interchangeably in this report.

It should be noted that samples for the viscosity measurements were taken from the vacuum pan in the course of the heat transfer measurements, during boiling under vacuum, and were therefore presumed to be free of the interference from entrained air.

Dry solids were determined (as throughout this work) with a standard refractometer after 1:1 dilution and this has to be considered when comparing with viscosity data reported by others.
Fig. 6—Boiling heat transfer coefficients of Louisiana final molasses of different origin, measured at 15.2 kPa.a (4.5 in.Hg) absolute pressure, 69 kPa.a (10 psi.a) steam pressure and 200 r/min stirrer speed. Temperature range ~ 63 to 68°C, increasing with % RDS and the boiling point elevation.

Table 2—Parameters A and B of the viscosity (cP) equation, ln (μ) = A x (%RDS) − B. Other parameters are as in Figure 7.

<table>
<thead>
<tr>
<th>Name</th>
<th>A</th>
<th>B</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alma 10/8</td>
<td>0.356</td>
<td>21.3</td>
<td>0.987</td>
</tr>
<tr>
<td>Alma 11/11</td>
<td>0.378</td>
<td>22.9</td>
<td>0.937</td>
</tr>
<tr>
<td>Alma 12/12</td>
<td>0.568</td>
<td>39.6</td>
<td>0.977</td>
</tr>
<tr>
<td>Lafourche</td>
<td>0.542</td>
<td>36.9</td>
<td>0.984</td>
</tr>
<tr>
<td>Enterprise</td>
<td>0.419</td>
<td>26.9</td>
<td>0.995</td>
</tr>
<tr>
<td>St. Mary</td>
<td>0.435</td>
<td>27.9</td>
<td>0.994</td>
</tr>
<tr>
<td>Cora</td>
<td>0.546</td>
<td>37.5</td>
<td>0.961</td>
</tr>
<tr>
<td>Cinclare</td>
<td>0.648</td>
<td>46.7</td>
<td>0.916</td>
</tr>
<tr>
<td>Lula</td>
<td>0.532</td>
<td>36.7</td>
<td>0.977</td>
</tr>
<tr>
<td>St.James</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Westfield</td>
<td>0.539</td>
<td>36.6</td>
<td>0.858</td>
</tr>
</tbody>
</table>

A fairly good correlation was found between the boiling heat transfer coefficient (HTC) and the logarithm of molasses consistency (Figure 8).
The relationship has the form:

\[ HTC (W/m^2 \cdot ^\circ C) = 75.176 (\mu)^{-0.5295} \]

where \( \mu \) is the molasses consistency in cP, measured at the standard conditions. This relationship can be used to calculate the overall boiling heat transfer coefficient at the conditions typical of sugar boiling.

Obviously, consistency is primarily a reflection of the dry solids content, but it was of interest to see if other compositional factors could be related to the observed consistency variations (at same dry solids contents).

To that effect cations (by ion chromatography) and polysaccharides, starch and dextran (monoclonal antibody method) were determined. Surprisingly and contrary to expectation, no correlations were found between viscosity and polysaccharides, and of the three major cations, only calcium showed a modest correlation.

It should be noted that in Figures 9 and 10 in order to compare the various molasses on the same dry solids basis (86%, 88%, 90% and 92% RDS), the values of viscosity were calculated from the correlations obtained and illustrated in Figure 7 and Table 2.
Fig. 8—Calculated boiling heat transfer coefficients of final molasses, conditions as in Figure 3, v. natural logarithm of molasses viscosity (cP) at standard conditions. Correlations from Table I and II for the nine molasses samples, at 86%, 88% and 90% RDS were used. All data 'Alma.10/7' were left out of the graph and the correlation as well as those at 90% RDS that were outside the range of HTC measurements.

Fig. 9—Molasses viscosity calculated from the correlation in Table II, as a function of the three main cations of sugarcane.
Effects of dextran on viscosity of sucrose solutions have been amply demonstrated in the literature, but frequently in tests that involved adding large doses of commercial dextrans of well-defined molecular weight distribution (e.g. Leong et al., 2002) and at overall dry solids levels well below, and consequently at viscosities one to two orders of magnitude lower than those encountered in low-grade sugar boiling (e.g. Drago and Delavier, 1967; Cortis-Jones et al., 1963; Geronimos and Greenfield, 1978; Koster et al., 1992; Sahadeo and Lionnet, 2001).

While both of these factors render the testing always easier and the results frequently more readily interpretable, it has been recognised (e.g. Cortis-Jones et al., 1963) that it is the complex interactions of the polysaccharide molecules with those of sucrose, water, and the other components of the industrial liquors that cause the viscosity effects, and justification for the extrapolation to the process conditions should not be tacitly assumed.

Furthermore, the intricacies of dextran chemical structure and methods of its determination must be considered when interpreting the results, and it is suspected that the lack of correlation seen in our tests between viscosity and dextran content is at least in part due to this factor.

<table>
<thead>
<tr>
<th>Name</th>
<th>Starch, ppm RDS</th>
<th>Dextran, ppm RDS</th>
<th>Ca</th>
<th>K</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alma 10/8</td>
<td>6453 6476 5852</td>
<td>6260</td>
<td>1007 932 970</td>
<td>0.84</td>
<td>4.78</td>
</tr>
<tr>
<td>Alma 11/11</td>
<td>3829 3878 4123</td>
<td>3943</td>
<td>1719 1641 1680</td>
<td>1.12</td>
<td>5.02</td>
</tr>
<tr>
<td>Alma 12/12</td>
<td>1993 1755 1680</td>
<td>1809</td>
<td>349 392 371</td>
<td>1.16</td>
<td>4.98</td>
</tr>
<tr>
<td>Lafourche</td>
<td>4746 4688 4411</td>
<td>4615</td>
<td>1763 1908 1836</td>
<td>0.96</td>
<td>3.85</td>
</tr>
<tr>
<td>Enterprise</td>
<td>4287 4152 3742</td>
<td>4060</td>
<td>235 343 289</td>
<td>1.04</td>
<td>5.72</td>
</tr>
<tr>
<td>St. Mary</td>
<td>7335 7402 7020</td>
<td>7252</td>
<td>760 959 860</td>
<td>0.81</td>
<td>5.51</td>
</tr>
<tr>
<td>Cora</td>
<td>3238 3208 3008</td>
<td>3151</td>
<td>1964 1783 1874</td>
<td>0.96</td>
<td>3.82</td>
</tr>
<tr>
<td>Cincinare</td>
<td>3054 2682 2725</td>
<td>2820</td>
<td>8592 6378 7485</td>
<td>0.96</td>
<td>3.13</td>
</tr>
<tr>
<td>Lula</td>
<td>4521 3480 4442</td>
<td>4148</td>
<td>250 260 255</td>
<td>1.53</td>
<td>6.13</td>
</tr>
<tr>
<td>St. James</td>
<td>4507 4347 4035</td>
<td>4296</td>
<td>1399 1373 1386</td>
<td>1.27</td>
<td>3.90</td>
</tr>
<tr>
<td>Westfield</td>
<td>3081 3146 2914</td>
<td>3047</td>
<td>575 605 590</td>
<td>1.15</td>
<td>5.55</td>
</tr>
</tbody>
</table>
Adding dextranase to juice or syrup has become routine in Louisiana and it is very likely that at least some of the molasses samples came from a process that employed dextranase. It is plausible that during the limited contact time in the mill between the enzyme and the juice before the enzyme becomes deactivated by high temperatures or dry solid levels in the process, the polysaccharide undergoes only a partial hydrolysis (Figure 11), thus effectively merely shifting its molecular weight distribution towards lower values. This will lead to the desired reduction of viscosity, but the detected residual amount (after application of dextranase) will differ based on the detection method.

Merely a 30% reduction of dextran in laboratory tests has been observed with the antibody test while a nearly complete ‘disappearance’ in the same test was found when the traditional ‘haze’ test is applied (Day, 2004, pers. comm.). This is illustrated in Figure 11: the antibody test ‘sees’ a wider molecular weight range than the ‘haze’ test and with incomplete hydrolysis detects a higher residual dextran and lower removal than the haze test that responds primarily to the very high MW range.

Clear correlations exist between the starch viscosity and its degree of hydrolysis (e.g. White and Johnson, 2003). As with dextranase, the use of amylase in Louisiana mills has become commonplace and similar considerations to those regarding dextran may apply to the interpretation of the viscosity v. starch data.

Unlike for dextran though and despite frequent claims, no reliable data exist in the literature on possible correlations between viscosity of the technical sugar solutions and their starch contents. Recent data for final molasses from various geograpical regions (Sahadeo and Lionnet, 2001) found no correlation between starch and viscosity.

Neither K nor Mg ion levels were expected to relate to the molasses viscosity and this was confirmed (Figure 9). Magnesium and calcium were presumably found to raise viscosity of pure sucrose solutions and dilute beet molasses in a detailed laboratory study (Drago and Delavier, 1967). Complex reactions and in some cases gel formation of calcium with polysaccharides are known and might be related to the correlation albeit weak observed here between the viscosity and calcium in low grade molasses.

The inverse power dependence of the overall boiling heat transfer coefficient on solution viscosity has been reported before for sugar liquors, with coefficients ranging from -0.25 to -0.7 for low viscosity liquors to about 200 cP (Perry and Green, 1997).

The effect of crystals on heat transfer was not studied here but the very limited tests with massecuities (Figure 3) did not indicate any drastic effect of crystals. At the same Reynolds number and for pure sucrose, crystals were actually found to enhance heat transfer (Bruhns and Schliephake, 1995) presumably by disturbing the laminar layer of the mother liquor (molasses) adjacent to the heat transfer surface. The reported values of HTC in low grade continuous pans (Rein and Msimanga, 1999) fall within the 50 to 150 W/m² °C range. Although the dry solid content of the mother liquor was not given, this can be

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**Fig. 11**—The approximate molecular weight range of the sugarcane dextran before and after industrial application of dextranase and the effective range of the two analytical techniques.
assumed to be in the 88% to 92% RDS range. As our correlations (Figures 6 and 8) do not extend beyond about 90% RDS and 100 000 cP (measured at the standard conditions), it appears that HTC at dry solid levels in low grade pans must level off as it may be enhanced in pans by direct injection of steam and feeding of dilute molasses.

It is concluded that, for a specific pan configuration, the rate of sugar boiling is generally related to the consistency of the mother liquor. This is turn is predominantly a function of dry solids content, but the effect of polysaccharides must be considered. If industrial enzymes are employed as is increasingly the case in the sugarcane industry, the situation is further complicated by the incomplete hydrolysis of the polysaccharides and specifics of the analytical techniques.

In isolated cases though, other factors than mother liquor viscosity control the rate of boiling. Clearly, the observations in Louisiana of ‘hard-to-boil’ molasses are unrelated to the viscosity but rather stem from reduction of heat transfer from fouling of the heat transfer surface.

The specific nature of the foulants is yet unknown but is related likely to products in the cane from atypical deterioration after extended periods of wet and warm weather, much unlike the much more frequent and better understood dextran-generating microbial infections.

REFERENCES


