

THE VISCOSITY OF MOLLASSES AND MASSECUITE

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Abstract

The factors that affect molasses and massecuite viscosity are discussed and an equation expressing molasses viscosity in terms of dry substance, temperature, purity and reducing sugar/ash ratio is proposed. The effects of shear rate, colloids, dextran and gas which also affect molasses viscosity are neglected. The equations that have been proposed to show the effect of crystal on massecuite viscosity are reviewed and an equation relating the ratio of massecuite viscosity/molasses viscosity to crystal content, crystal size and coefficient of variation is submitted.

Introduction

The viscosity of molasses and massecuite is one of the most important physical properties that affects the operation of pans, crystallizers and centrifugals. A knowledge of the factors that influence it would be of value in optimizing these operations.

Equations for predicting molasses and massecuite viscosity have been developed previously. These equations, however, do not take into account all the variables involved.

The study presented here is a preliminary assessment of the effect of some of the variables, and work in this field is continuing so as to try to improve the accuracy of the equations proposed.

Theory

Viscosity is the resistance of a fluid to flow. Its value may be defined as the ratio of the shearing stress applied to the rate of shear produced. For a Newtonian fluid this ratio is constant, and the proportionality constant, μ , is called the viscosity. It may be represented by the equation

$$\tau = \mu d\gamma/dt \quad (1)$$

Newtonian viscosity for a given fluid depends only on temperature and pressure and is independent of shear.

For non-Newtonian fluids the proportionality constant depends not only on the temperature, but also on the shear rate. For pseudoplastic fluids the ratio, which in this case is called the consistency, falls progressively with shear rate, and becomes constant only at very high shear rates. This relation may be described by the following equation

$$\tau = k(d\gamma/dt)^n \quad (2)$$

where k is a measure of the consistency of the fluid, the higher k the more viscous the fluid, and n is the flow behaviour index which is a measure of the non-Newtonian behaviour. The smaller n is, the more pronounced are the non-Newtonian properties of the fluid.

If the consistency depends not only on the rate of shear but also on the time the shear has been applied, the fluid is said to be thixotropic. In these fluids, there is a progressive breakdown of structure with time until equilibrium is reached, the equilibrium position depending upon the intensity of shear. It is a reversible process and during a period of rest the structure builds up again gradually.

Previous work on molasses viscosity

The variables that affect molasses viscosity include temperature, solubles content (i.e. dry substance), composition of the

solubles, and the insolubles content, such as colloids and gas. In addition, under certain conditions molasses exhibits pseudoplastic properties and its viscosity is thus shear dependent.

The amount of solubles, or dry substance, is the variable that has the greatest influence on molasses viscosity. Its effect can be described by the dry substance/water ratio as proposed by Kolarov and Garcell¹ as follows:

$$\mu_o = A (DS/(100 - DS))^B \quad (3)$$

To a lesser extent it has been shown that molasses viscosity decreases with an increase in purity and is affected by the reducing sugar/ash ratio as well as with the composition of the ash and the presence of dextran.

Temperature has an effect on molasses viscosity which is only second in importance to solubles content. A straight line relationship between viscosity and temperature is given by the following equation which was proposed by Pidoux.²

$$\log \mu_o = A + B (T - 273,15)/T^2 \quad (4)$$

Other factors that increase the viscosity are the amount of colloids and of gas, and their removal results in a significant reduction in viscosity. According to Moritsugu³ the decrease in viscosity caused by surface active agents is primarily the result of decreased gas content.

Molasses is non-Newtonian under certain conditions with a flow behaviour index between 0,85 and 0,96. This value may be lower for degraded cane containing a high level of dextran.

Broadfoot and Steindl⁴ have developed this equation which expresses molasses viscosity in terms of purity, shear rate, dry substance and temperature

$$\mu_o = \frac{0,111e^{\left(\frac{3,7 DS^*}{113,5 - DS^*}\right)}}{(S/DS)^{1,3} (d\gamma/dt)^{0,16}} \quad (5)$$

where

$$DS^* = DS - 0,19 (T - 323,15) \quad (6)$$

The range of variables covered is as follows:

| | |
|-----------------------------|--------|
| Dry substance % | 74-87 |
| True purity, % | 42-80 |
| Temperature, °C | 40-60 |
| Shear rate, S ⁻¹ | 0,2-35 |

The standard error is $\pm 27\%$ with a maximum error of up to 100%.

Previous work on massecuite viscosity

The work of several research workers has shown that the viscosity of massecuite depends upon the crystal content, crystal size, size distribution and shape and on the viscosity of the molasses surrounding the crystals. It has been shown that massecuites are pseudoplastic, thixotropic fluids and thus that their viscosities are shear and time dependent.

The factor which has the greatest influence on massecuite viscosity is the crystal content. The effect of crystal size is reported to be slight, but the crystal size distribution, or coefficient of variation, is recognised as being one of the factors that affects viscosity, a mixture of sizes causing a lowering of the viscosity for the same crystal content.

The viscosity of a two phase mixture such as massecuite is usually expressed as the relative viscosity which is the ratio of its viscosity to that of the molasses surrounding the crystals.

$$\mu_{rel} = \frac{\mu}{\mu_0} \quad (7)$$

Silina (1953)⁵ has proposed an equation which relates massecuite viscosity to the volume concentration of crystals.

$$\mu_{rel} = \frac{1}{1 - 3,8047\theta + 3,6586\theta^2} \quad (8)$$

Kelly⁶ linked the relative viscosity to the volume fraction of crystals by the equation

$$\mu_{rel} = 10^{1,93(L+1)\theta} \quad (9)$$

He added that the equation was of limited application especially from the point of view of particle size variation.

Artyukhov and Garyazha⁷ expressed the relative viscosity as a function of the volumetric ratio crystal/molasses.

$$\mu_{rel} = 1 + 2/(1 - 0,85 V^{2/3})^2 \quad (10)$$

Awang and White⁸ developed an equation in which the relative viscosity is a function of the volumetric ratio crystal/molasses, the crystal size and the coefficient of variation

$$\mu_{rel} = 10^{1,65L^{0,15} V(1 - CV/12)} \quad (11)$$

In this equation the effect of size is less than in Eq (10) and inclusion of the coefficient of variation takes care of the lowering of the viscosity caused by mixed sizes that has been observed.

Ackermann and Shen⁹ have derived an equation based on theoretical considerations for the viscosity of solid-liquid mixtures which agrees well with the experimental results of previous investigations. This equation is:

$$\mu_{rel} = \left[1 - \frac{\pi}{4\alpha^2} \right] + \left[\frac{\pi}{4} - \frac{\pi}{6\alpha} \right] \left[\frac{1}{\alpha^2 - 1} \right] \left[1 + \frac{2}{\sqrt{\alpha^2 - 1}} \tan^{-1} \sqrt{\frac{\alpha + 1}{\alpha - 1}} \right] \quad (12)$$

where $\alpha = \left(\frac{\theta_{\infty}}{\theta} \right)^{1/3} \quad (13)$

It has been found that the maximum volume concentration of solids, θ_{∞} , at which general shearing first becomes possible in a mixture formed of granular solids of uniform size and a surrounding fluid is 0,625.

Experimental Procedure

The molasses samples used in the experiment were first degassed by boiling under vacuum. The samples were then placed in a constant temperature waterbath until equilibrium was reached. Viscosity measurements were made using a Brookfield HBT viscometer with spindle No. 3 and a speed sufficiently high to give adequate readings on the viscometer scale.

Determinations of dry substances, sucrose, reducing sugars and ash contents of the molasses were made using the methods recommended for the South African sugar industry.¹⁰

The procedure used for the measurement of the apparent massecuite viscosity was to mix sugar of known crystal size with degassed molasses, the viscosity of which had been established previously, in such a proportion as to obtain the volumetric ratio of crystal to molasses required. The viscosity of the synthetic massecuite was measured after the mixture had been stirred until homogeneous.

The same viscometer spindle and speed was used as far as possible for all the measurements so as to minimize the effect of the shear rate. In some cases, however, a different speed or spindle had to be used because of the wide range of viscosities encountered.

The data obtained is listed in Table 1.

Correlation for molasses viscosity

A correlation for molasses viscosity was established using sixty-nine measurements obtained in this study and one hundred and six points from a study by Beesley¹¹ on South African molasses. He used a Hoesppler viscometer and measured viscosities of both defecation and sulphitation molasses.

TABLE 1
Data for relative viscosity massecuite/molasses

| Volumetric ratio | Crystal size/mm | Co-efficient of variation | Temperature °C | Visco-meter spindle | Visco-meter speed (rpm) | Relative viscosity |
|------------------|-----------------|---------------------------|----------------|---------------------|-------------------------|--------------------|
| 0,5 | 0,7 | 0,31 | 29 | 3 | 10 | 27 |
| 0,9 | 0,7 | 0,31 | 29 | 3 | 5 | 7,43 |
| 0,9 | 0,7 | 0,31 | 41 | 3 | 10 | 7,4 |
| 1,0 | 0,7 | 0,31 | 29 | 3 | 5 | 9,38 |
| 1,0 | 0,7 | 0,31 | 41 | 3 | 10 | 7,5 |
| 0,317 | 0,64 | 0,36 | 40 | 3 | 10 | 2,22 |
| 0,362 | 0,64 | 0,36 | 40 | 3 | 10 | 2,54 |
| 0,408 | 0,64 | 0,36 | 40 | 3 | 10 | 2,59 |
| 0,468 | 0,64 | 0,36 | 40 | 3 | 10 | 2,80 |
| 0,481 | 0,64 | 0,36 | 40 | 3 | 10 | 3,07 |
| 0,542 | 0,64 | 0,36 | 40 | 3 | 5 | 4,63 |
| 0,317 | 0,144 | 0,25 | 58 | 6 | 1 | 2,84 |
| 0,84 | 0,75 | 0,29 | 50 | 4 | 10 | 6,58 |
| 0,139 | 0,131 | 0,18 | 59 | 6 | 2,5 | 2,54 |
| 0,704 | 0,55 | 0,38 | 51 | 4 | 10 | 7,48 |

The analytical methods used by Beesley were the same as those used in this study except for dry substance which was obtained by vacuum oven instead of by the Karl Fischer method. It has been shown, however, that there is no significant difference between these two methods.^{12, 13}

The range of variables considered in establishing the correlation was as follows

| | |
|---------------------|-----------|
| Dry substances, % | 66-89 |
| True purity, % | 34-68 |
| Temperature, °C | 30-73 |
| Reducing sugars/ash | 0,7-1,4 |
| Viscosity, Pa.S | 0,068-720 |

The best fit to the data was obtained with the equation

$$\mu_0 = \frac{1,03 \times 10^{-17} (DS/(100 - DS))^{5,82}}{\left[\frac{T - 273,15}{T^2} \right]^{4,45} e^{(0,187 (S/NS)^3 + 0,689 (RS/A))}} \quad (14)$$

The results are shown graphically in Fig. 1. The standard error is $\pm 20\%$ with a maximum error of $\pm 108\%$.

Effect of crystal on massecuite viscosity

The five equations that have been proposed for the effect of solids on the viscosity of a slurry that are mentioned in the text are shown graphically in Fig. 2.

This graph shows that, compared with the equation of Ackermann and Shen, the equations of Silina, Artyukhov and

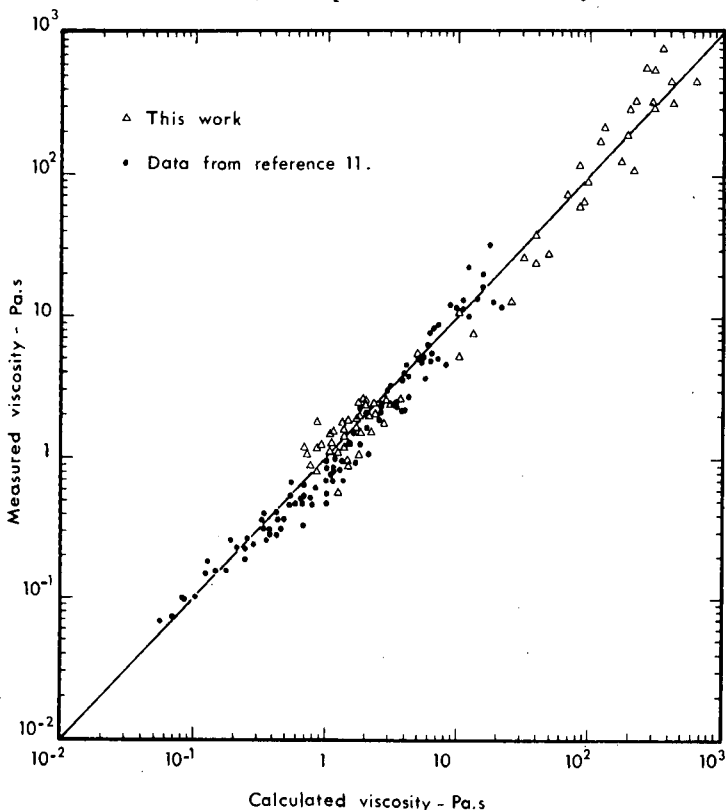


FIGURE 1 Correlation for molasses viscosity.

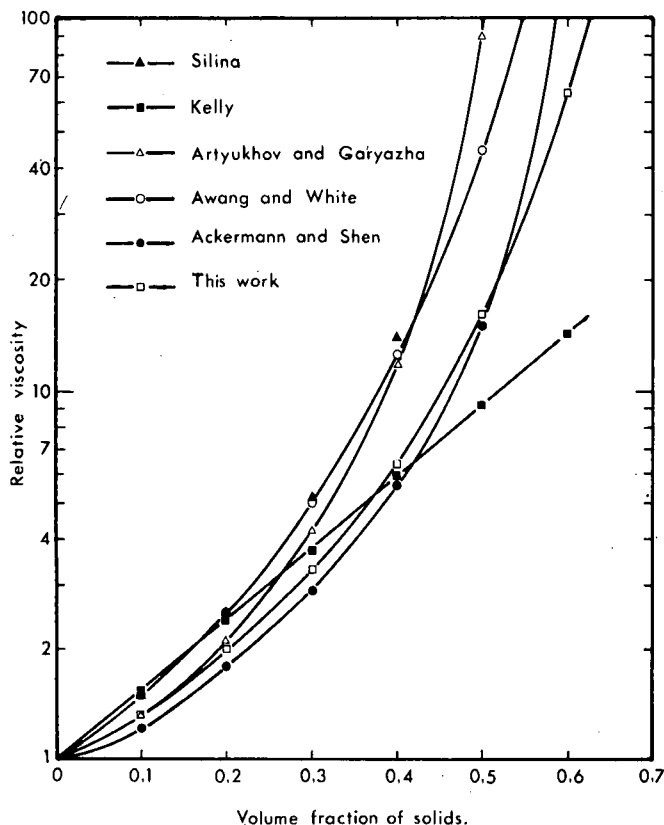


FIGURE 2 Relationship between relative viscosity and volume concentration of crystals.

Garyazha and of Awang and White give high values of relative viscosity, particularly at the higher crystal content such as occurs in A-massecuite.

This was also verified by the measurements taken on massecuite viscosities which are listed in Table 1. Based on this data and data obtained from Reference (8), but neglecting the coefficient of variation, the correlation coefficients given in Table 2 were obtained.

TABLE 2
Correlation coefficients of equations proposed to calculate relative viscosity of suspensions

| Author | Reference | Correlation coefficient |
|-------------------------------|-----------|-------------------------|
| Silina (1953) | (5) | 0,845 |
| Kelly (1958) | (6) | 0,767 |
| Artyukhov and Garyazha (1970) | (7) | 0,796 |
| Awang and White (1976) | (8) | 0,871 |
| Ackermann and Shen (1979) | (9) | 0,918 |
| This work | — | 0,908 |

As can be seen the best correlation coefficient is that of the equation of Ackermann and Shen. This equation, however, is complex and does not take into consideration the effect of crystal size and of the coefficient of variation.

The equation of Awang and White was therefore modified so as to give a better fit to the data. This modified equation is

$$\mu_{rel} = e^{(2,84L^{0.0377} \sqrt{1 - CV/12})} \quad (15)$$

Again neglecting the coefficient of variation this equation has a correlation coefficient of 0,908.

Discussion and Conclusions

Equation (14) for molasses viscosity considers the effect of dry substance, temperature, purity and reducing/sugar ash ratio. It has a standard error of $\pm 20\%$ with a maximum of $\pm 108\%$.

The equation proposed by Broadfoot and Steindl⁴ takes into consideration the effect of dry substance, temperature, purity and shear rate, and has a standard error of $\pm 27\%$ with a maximum of $\pm 100\%$.

It appears therefore that other factors which are not considered in these equations must have an important influence on molasses viscosity. Since the measurements of molasses viscosities were taken on degassed molasses, these factors could include colloids or dextran. Measurements done by the SRI¹⁴ in Australia, have shown that suspended matter in molasses amount to as much as six per cent by weight and that the relative viscosity of molasses with and without suspended matter was as high as 1,87. This was confirmed by Wilkes and Jennings¹⁵ and Bruijn¹⁶ in South Africa. The former found relative viscosities of up to 1,42 and the latter 1,92. It appears therefore that an equation giving an accurate estimation of molasses viscosity should include a correction for suspended matter.

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Nomenclature

The symbols used in the text are listed below:

- A Constant
- B Constant

| | | |
|-------------------|-----------------------------------|-----------------------------------|
| C | Coefficient of variation | |
| DS | Dry solids | |
| k | Fluid consistency index | $\text{kg.m}^{-1}.\text{s}^2 - n$ |
| L | Crystal specific grain size | mm |
| n | Flow behaviour index | |
| RS/A | Reducing sugar/ash ratio | |
| S/NS | Sucrose/non-sucrose ratio | |
| T | Temperature | $^{\circ}\text{K}$ |
| V | Crystal/molasses volumetric ratio | |
| W | Water content | |
| <i>Greek</i> | | |
| α | $(\theta_{\infty}/\theta)^{1/3}$ | |
| dy/dt | Shear rate | s^{-1} |
| μ | Viscosity | Pa.s |
| τ | Shear stress | kg.m.s^{-2} |
| θ | Volume concentration of crystals | |
| θ_{∞} | Maximum attainable concentration | |
| <i>Subscripts</i> | | |
| | Molasses | |
| rel | Relative | |

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