Modeling of Rheological Behavior of Egyptian Cane Molasses

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Abstract

The rheological properties of Egyptian cane molasses were studied at a temperature range of 30-60°C at a shear rate of 1.1 to 5.5 sec^{-1} for solid concentrations 60%,70%, 75% and 80%. Results indicated that the power law model fitted well the shear stress-shear rate data. The molasses behaved as a shear-thinning fluid with a flow behavior index less than one. Dependence of the apparent viscosity on the temperature was related through the Arrhenius model for which the values of activation energy of molasses were estimated at investigated shear rates. The Krieger-Dougherty model, for concentration–viscosity relationship, fairly fitted the viscosity data. A hysteresis loop between forward and backward cycle of the flow curve indicated thixotropic behavior and was quantified by Weltman model. Other two models were applied, based on analytical approach using time-independent power law models modified to include a structural parameter, λ. These models were used to account for time-dependent effects as well as reproduce experimental results of shear rate-viscosity to evaluate their validity. Finally, the values of λ with time were plugged in Tiu and Boger kinetic model to obtain the constants of that model.

Keywords

Rheology of molasses; Thixotropy of food; Modeling; shear rate; Apparent viscosity

1. Introduction

In the production of sugar crystals, sugar cane juice is concentrated and crystallized repeatedly. The liquor at the end of the concentration stage of this multi-stage process is referred to as molasses. Molasses contains 20% water, 8% inorganic matters, 72% sugar and non-sugar organic substances such as organic acids, lipids and inorganic salts, invert sugar, macromolecules of high molecular weight (starch, cellulose, hemicellulose, legnin, pectin, tannin) [Kaur et al, 2002].

Molasses is used in production of ethanol and baker's yeast, as an additive in animal feed industry [Anon, 2002], as a binder to develop activated carbons from agriculture byproducts, as a complex carbon source in β-carotene production by means of fermentation from industrial wastes, and for reduction of SO_2 emissions caused by domestic heating [Buzzini & Martini, 2000].

The rheological behavior of molasses is important as it provides information on its physical properties and helps in understanding the underlying mechanisms of momentum and heat transfer processes such as boiling, crystallization, centrifugal separation and pumping [Leong & Yeow, 2002]. In animal feed industry, viscosity is one of the most important parameters required in the design of process with relation to mixing of molasses [Togrul & Arslan, 2004].

Studies regarding the rheological properties of molasses were carried out by different investigators [Leong & Yeow, 2002 and Kaur et al, 2002] but thixotropic behavior of molasses, to the best of our knowledge, was not examined. Thixotropy is an active research area in theoretical rheology and it is also a difficult property to measure. This is related to effect of the sample treatment history on its present rheological state. Thixotropic fluids have been defined as having inelastic properties, a shear stress which instantaneously reaches a maximum value that declines with time to equilibrium stress. They have shear stress which recovers when shearing is ceased. It is suggested that the change in rheological parameters with time is probably due to structural change within the fluid [Amemiya & Shoemaker, 1992 and Altay & Ak, 2005].

The primary objective of this study was to obtain rheological data on Egyptian cane molasses as a function of concentration (Brix) and temperature. The data were obtained at temperatures between (30-60°C) so that they can be used in design of systems handling molasses. A second objective was to determine applicable models that can describe the rheological data as a function of shear rate, temperature and concentration as well as to model the flow of molasses, a product exhibiting time- dependent viscosity behavior. Therefore, the emphasis in this study was to develop relationships useful in engineering applications.

2. Materials and Methods

2.1 Preparation of samples

A sample of molasses was collected from Sugar Company, Giza, Egypt. The Brix was determined by Abbemat Refractometer (Leica Mark). Brix is the measure of total dissolved or dissolvable solids (including sucrose, glucose and fructose, salts and plant material), expressed as a percentage of the total mass of molasses.

$$brix\% = \frac{mass\ of\ brix\ in\ molasses}{mass\ of\ total\ solids} \times 100\% \tag{1}$$

In the molasses sample the Total solids was 82.5%, initial Brix was 80%. Delivery brix (80%) was adjusted to the desired production brix (Y) by adding a quantity of hot water (X) calculated as follows:

$$water\ required,\ X(\%) = \left(\frac{Delivery\ brix}{Y} \times 100 - 100 \right)\% \ m/m\ water\ per\ molasses \tag{2}$$

In addition to delivery brix of 80% three other samples were prepared by diluting with hot water, 60, 70 and 75%.

2.2 Rheological measurements

Rheological characteristics (shear stress, shear rate, and apparent viscosity) of molasses were recorded directly from the rheometer for different brix values (80, 75, 70 and 60%) at various temperatures (30, 40, 50 and 60°C). Samples were sheared using five different rotational speeds at an increasing order. Rotational speeds (5, 10, 15, 20 and 25 rpm) were selected for the flow behavior determination as well as temperature and concentration dependence, while rotational speeds (0.5, 3, 5.5, 8 and 10.5 rpm) were selected for the time dependence investigation.

A Brookfield Rheometer, model DVIII, V 3.0 LV, Programmable Rheometer with a small sample adapter (stainless steel) closed tubes system of sample volume 8 ml and spindle code SC4-25 was used. The water at a given temperature was circulated in water jacket. The sample was kept in water bath

for 5 to 10 minutes for temperature equilibrium and stress relaxation to be attained before the reading was recorded.

As for time-dependent measurements, the shear rate was increased from 0.11 to 2.31 sec^{-1} (six ascending shear rates) during 6 minutes, remained constant at 2.31 sec^{-1} for 2 minutes . Then it was decreased from 2.31 to 0.11 s^{-1} during 6 minutes. A hysteresis loop was obtained when shear stress was plotted against shear rate as will be shown in the results. Other curves were obtained for thixotropic behavior by measuring the shear stress and shear rate in the time range (0-360 seconds) at temperature 30°C for 80% brix at different shear rates (0.11, 0.66, 1.21, 1.76 and 2.31sec^{-1}). The experimental data were described by Weltman model [Juszczak et al, 2004] and Tiu and Boger model [Tiu and Boger,1974]

3. Theoretical Considerations

Butler and O'Donnell, 1999 developed a simple approach to characterize time-dependent viscosity behavior in foods by modifying the flow behavior model to include a structural parameter, λ, to account for the time-dependent effects. Their equation of state was:

$$\tau' = \lambda \tau \tag{3}$$

For the present work the basic equations of state were found to be:

$$\tau = K \dot{\gamma}^{n} \tag{4}$$

and,

$$\mu = K \gamma^{n-1} \tag{5}$$

where, τ is the shear stress (Pa), τ' is the shear stress as a function of time (Pa), γ the rate of shear (s^{-1}), K the consistency index (Pa.s), n the flow behavior index which is a measure of the departure from Newtonian flow, and μ is viscosity of molasses (Pa.s).

The structural parameter, λ, was described by a kinetic equation developed by Tiu and Boger, 1974:

$$\frac{d\lambda}{dt} = -k(\lambda - \lambda_e) \text{ for } \lambda \rangle \lambda_e \tag{6}$$

The structural parameter, λ, ranges from an initial value of unity at maximum shear stress time to an equilibrium value, λ_e that is less than unity. The rate constant k is function of shear rate.

4. Results and Discussion

4.1 Rheology model

The shear stress-shear rate data obtained during experimentation is fitted well to the power law model (pseudoplastic) which agrees with the work of Kaur *et al*, 2002 and Togrul & Arslan, 2004 on molasses.. This is to be expected, since the principal factor rendering these fluids non-Newtonian and so distinguishing them from Newtonian pure sugar solutions is the presence of polysaccharides, components known to induce pseudoplasticity and elasticity [Lapasin and Pricl,1995]. Equation (4) is the constitutive equation of this model. Curves of shear stress against shear rate have been presented in Figs. 1-4.

Apparent viscosity in general was found to decrease with an increase in rpm indicating a shear thinning behavior.[Fig. 5]
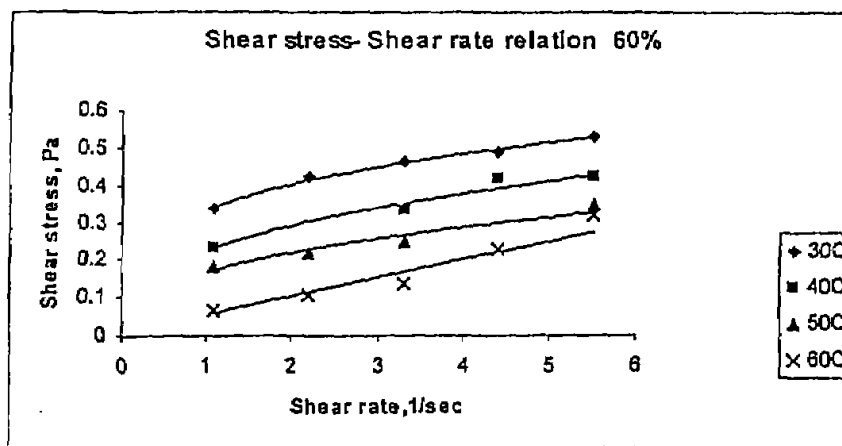

Fig. 1 Shear rate- shear stress at 60% solid concentration and different temperatures
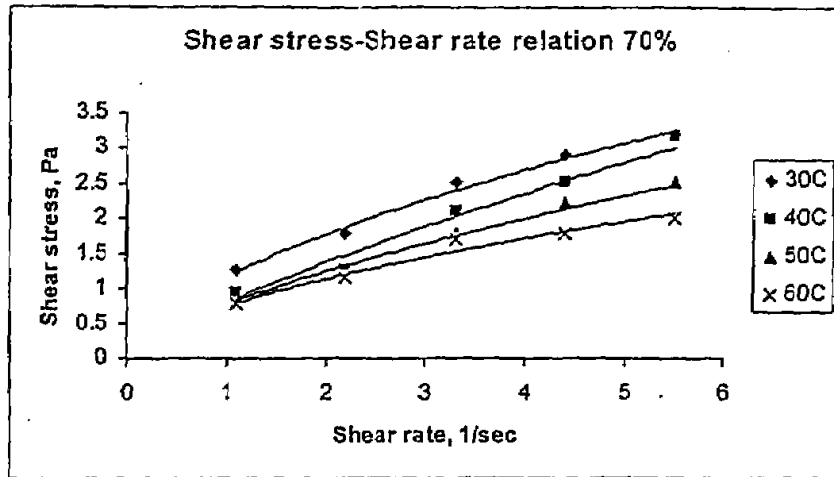
Fig. 2 Shear rate- shear stress at 70% solid concentration and different temperatures
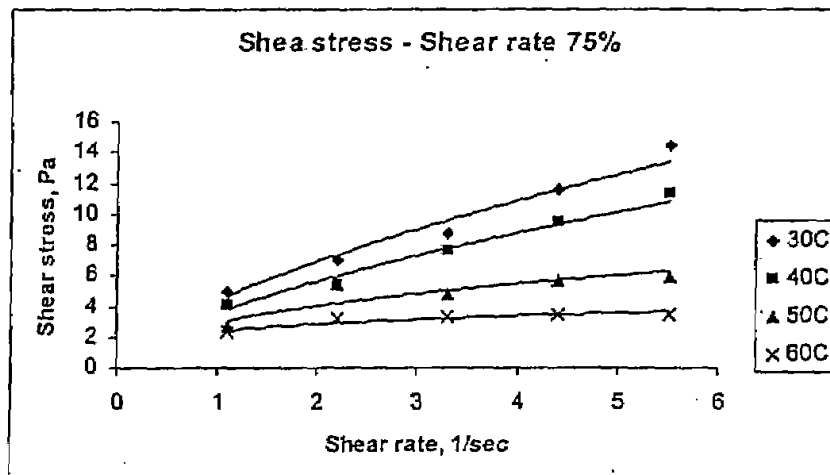

Fig. 3 Shear rate- shear stress at 75% solid concentration and different temperatures
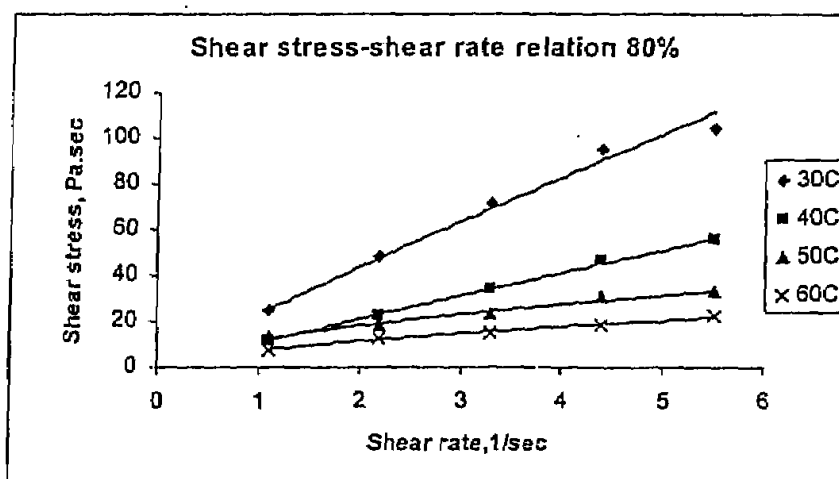

Fig. 4 Shear rate- shear stress at 80% solid concentration and different temperatures
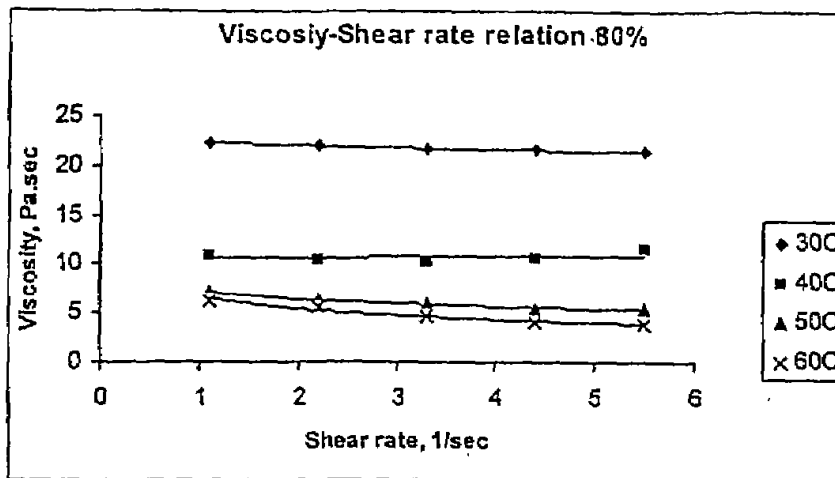
Fig. 5 Shear rate- viscosity at 80% solid concentration and different temperatures

4.2 Effect of Concentration

The apparent viscosity (Pa s), shear stress (Pa) and shear rate (s^{-1}) at different rpm and at four given temperatures were recorded. The viscosity of molasses increases rapidly with increase in solid content. Although various molasses may differ greatly in viscosity at a given solids content, the rate of change with change in solids is similar. The relation between viscosity and concentration was described by the Krieger – Dougherty model [Mancini &Moresi, 2000, Altay & Ak, 2005]:

$$\mu = \mu_o \left(1 - \frac{C}{C_{max}} \right)^{-AC_{max}} \tag{7}$$

where, C is the fraction of dissolved solids, C_{max} is the maximum fraction, μ is the viscosity of the solution, μ_o is the viscosity of the continuous phase and A is a constant. It was possible to estimate μ_o and A by plotting (μ) versus ($1-C/C_{max}$) on logarithmic scale. Figure 6 represents this fitting for shear rate 5.5 sec^{-1}, the other shear rates showed the same fitting trend. Table 1 shows the values of A and μ_o at different shear rates.
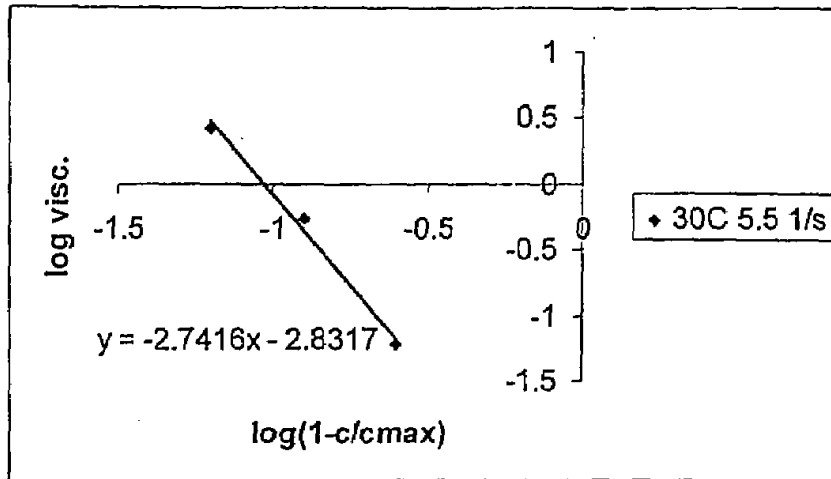
Fig. 6 Krieger- Dougherty model at 30°C and 5.5 s^{-1}

Table 1 Values of empirical constants of Eq. (7) at different shear rates

Shear rate(γ), sec^{-1}	A	μ_o x 10^3
1.1	2.3	21.5
2.2	3	5
3.3	3	4
4.4	3.25	2.5
5.5	3.375	1.4

4.3 Effect of Temperature

The temperature-dependent behavior of apparent viscosity over the temperature range of 30- 60°C was recorded. The experimental data were described by the Arrhenius equation [Kaur et al, 2002 and Togrul & Arslan, 2004]:

$$\mu = \mu_\infty e^{E/RT} \tag{8}$$

where μ is the apparent viscosity (Pa.s), μ_∞ is a parameter that is considered as the viscosity at infinite temperature (Pa.s), E is the activation energy (J/mol.), R is the molar gas constant ((J/mol.K) and T is temperature in K.

The viscosity of molasses decreases sharply with rise in temperature as thermal energy of the molecules increases and molecular distances develop due to reduction of intermolecular forces and hence viscosity of the fluid decreases [Arslan et al, 2005]. This is shown in the curves of Figs. 7-10. Although the slope of the temperature-viscosity lines for different shear rates varies, it will be noted that all the curves are smooth and without any abrupt changes in slope.

Values of activation energy at different shear rates for concentration of 80% are shown in Table 2. In general, higher shear rates appear to have higher activation energies; they are more temperature sensitive in relation to viscosity. This agrees with findings of Crandall *et al*, 1988.

Table 2 Activation energy values at different concentrations and shear rates

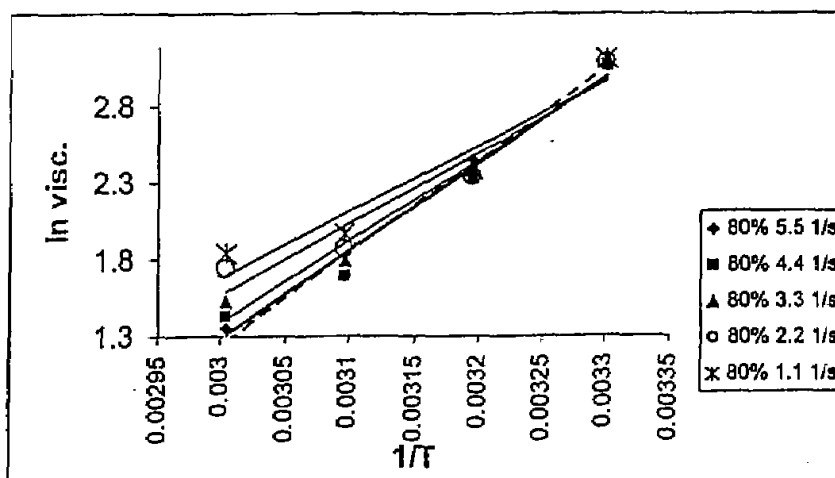| Concentration%	Shear rate(γ), sec^{-1}	Activation energy x 10^{-3}, J/mol
80	5.5	49.7
	4.4	47.4
	3.3	44.1
	2.2	38.4
	1.1	35.8
75	5.5	40.8
	4.4	34.4
	3.3	28.6
	2.2	21.9
	1.1	16.4
70	5.5	15.1
	4.4	14.5
	3.3	10.7
	2.2	11.6
	1.1	5.6
60	5.5	26.7
	4.4	22.8
	3.3	22.7
	2.2	12.9
	1.1	16.4

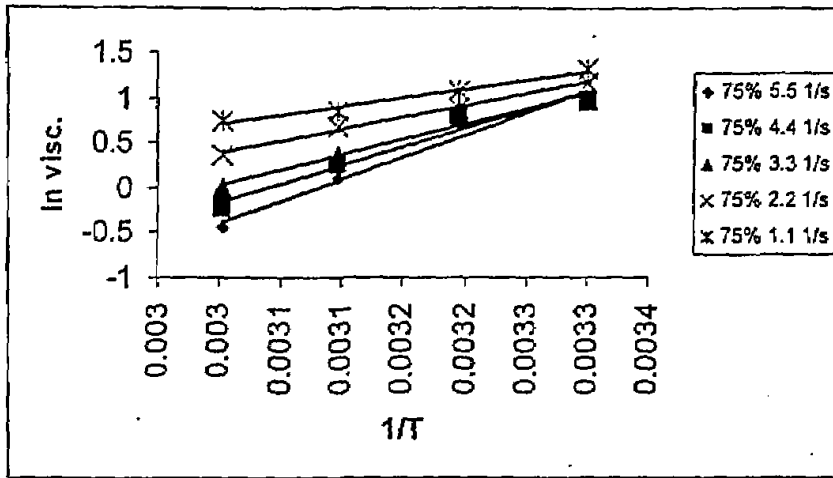Fig. 7 Arrhenius model at 80% solid concentration

Fig. 8 Arrhenius model at 75% solid concentration

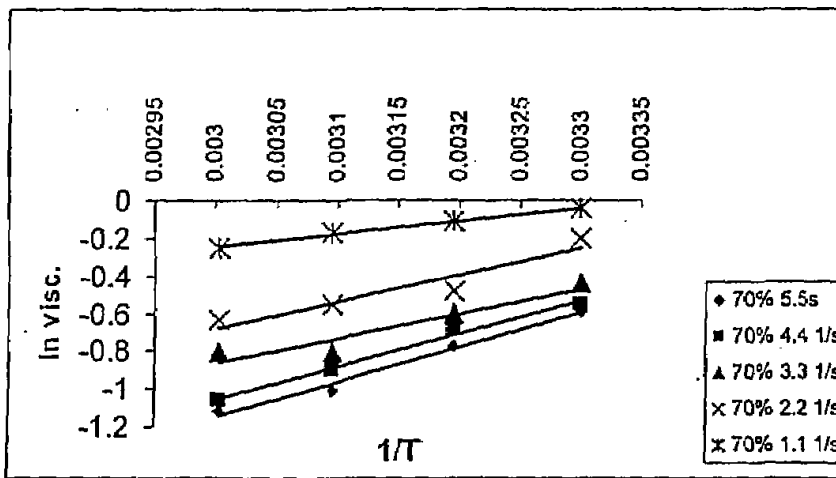

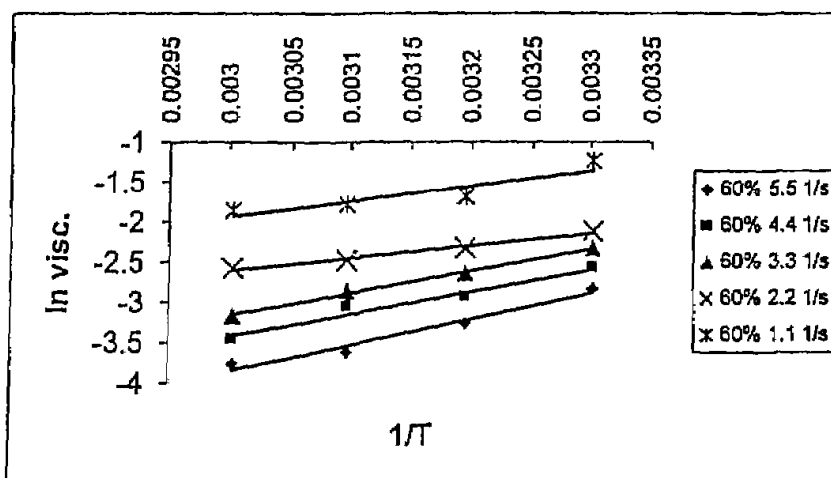Fig. 9 Arrhenius model at 70% solid concentration

Fig. 10 Arrhenius model at 60% solid concentration

4.4 Characterization of Time-Dependent Viscosity Behavior

The viscosity of molasses was found to exhibit time-dependent behavior. Figure 11 shows the hysteresis loop obtained from plotting shear stress against shear rate for forward and backward shear rate ramps. Its flow results from Brookfield viscometer was modeled using four approaches. The first model used to quantify the time-dependent shear stress; the variation of shear stress with time of shearing was fitted to Weltman model:

$$\tau = a - b \ln t \qquad (9)$$

where, τ is shear stress, Pa and t is time, second.

In Fig. 12 the shear stress was well fitted with time according to Weltman model (Eq. 9) for different shear rates at 30°C and 80%. The lines are almost parallel with a constant slope of $b \approx 12$. The relation between constant (a) in equation (9) and shear rate was fitted well to the following constitutive equation:

$$a = -45\gamma^3 + 213.6\gamma^2 + 278.5\gamma + 186.1 \qquad (10)$$
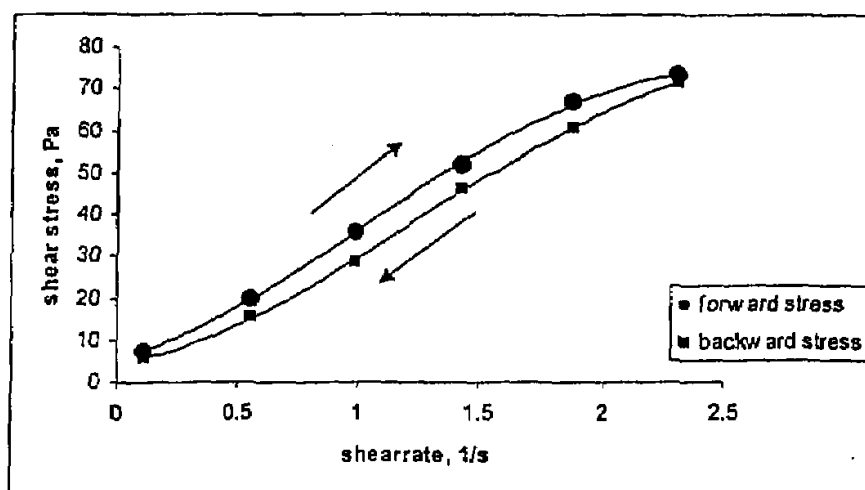

Fig. 11 Hysteresis loop in shear rate–shear stress (Thixotropic behavior) at 30°C & 80% concentration. Arrows indicate forward and backward shear rate ramps.
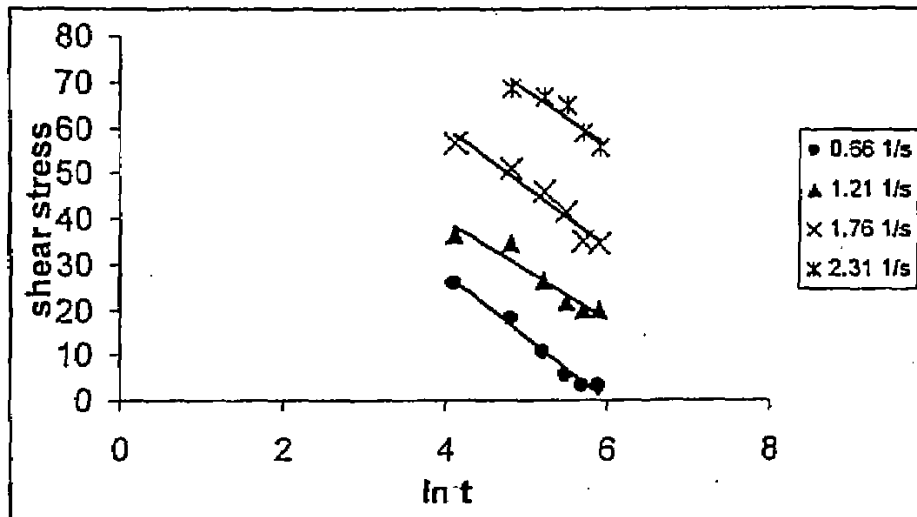
Fig. 12 Weltman model (ln t -Shear stress)

Figure 13 presents the shear stress versus time from which t_o is specified (the time at maximum value of shear stress after which a breakdown of the molasses structure starts).

Other two models (Eqs. 3, 4 &5) were based on analytical approach using time-independent power law models to characterize a structural parameter λ, to account for the time-dependent effects, and compare the predicted viscosity, using λ, with the experimental viscosity to evaluate the validity of estimated values of λ.

Table 3 shows the values of λ at different time values. Figure 14 compares experimental time-viscosity data (1.21 sec^{-1}, 30°C & 80%) with time-viscosity values as predicted by:

$$\mu' = \lambda K \gamma^{n-1}$$

where, μ' is viscosity at time t, Pa.s.

Agreement was best in the middle and high shear time. The maximum error was 13%. It seems that the model underestimated the fall in viscosity in the first 60

seconds. This indicated that the structural parameter λ did not decrease rapidly enough with time in the early period of shearing.
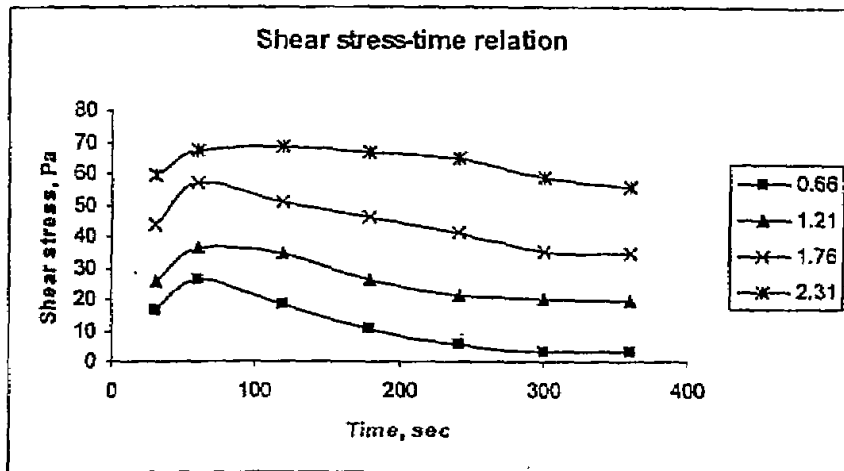
Shear stress-time relation

Fig. 13   Time - Shear stress at different shear rates

Table 3 Values of $\lambda(t) = \tau(t) / \tau_0(t)$; to is time at maximum τ, at $30^{\circ}C$, 80% concentration and different shear rates

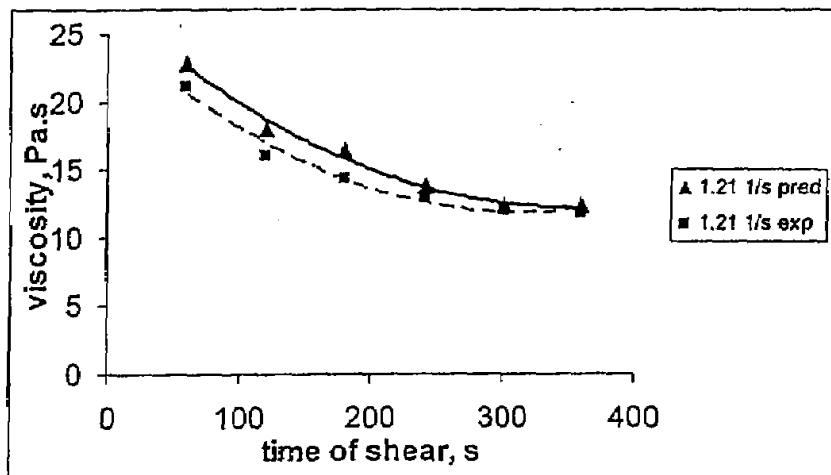| γ, sec^{-1} time, sec	0.66	1.21	1.76	2.31
60	1	1	1	-
120	0.7	0.95	0.897	1
180	0.4	0.72	0.81	0.97
240	0.22	0.6	0.73	0.94
300	0.13	0.54	0.62	0.86
360	0.12	0.54	0.6	0.81

Fig. 14   Predicted results and experimental data of viscosity as a function of time at $30^{\circ}C$ & 80%concentration

The fourth model (Eq. 6) used estimated values of λ to find the constants of this model (k & c). When Tiu and Boger model for λ description was integrated the following equation was obtained:

$$\ln(\lambda - \lambda_e) = -k(t - t_o) + c \tag{12}$$

The values of λ against time, t in Table 3 were used in the fitting of integrated model (Eq. (12)) to obtain the constants k and c of the model at different shear rates as shown in Table 4. A linear relation between k and shear rate is obtained with 0.91 regression:

$$k = 0.006\gamma - 0.002 \tag{13}$$

Table 4 Empirical constants of Eq. (12) at 30°C and 80% solid concentration

γ, sec^{-1} constant	0.66	1.21	1.76	2.31
k	0.0179	0.0116	0.0114	0.007
c	-0.37	-0.51	-0.56	-1.07

5. Conclusions

Molasses samples are pseudoplastic fluids. The power law model can be used to describe the shear rate-shear stress data. The Arrhenius model described well the effect of temperature on the apparent viscosity. The effect of concentration on the apparent viscosity can be described by the Krieger – Dougherty model.

Molasses showed thixotropic behavior which indicated time-dependent breakdown in its structure. Thixiotropic behavior was quantified by the Weltman model. The predicted viscosity, using a modified model of shear rate – viscosity [Butler and O;Donnell], almost comply with experimental results obtained for viscosity with time with error 13% in the early time of shearing. This modified model considers the time-dependent behavior by plugging a structural parameter in the basic equation of state.

Notation

A	Constant of Krieger-Dougherty model	α	Constant of linear regression
a	Weltman constant	β	Constant of linear regression
b	Weltman constant	γ	Shear rate, sec-1
C	Fraction of dissolved solids	λ	Structural parameter
C_{max}	Maximum fraction of dissolved solids	λ_e	Equilibrium structural parameter
		μ	Viscosity of molasses, Pa.s
E	Activation energy, J/mol	μ_0	Viscosity of continuous phase of molasses, Pa.s
K	Consistency index, Pa.s		
k	Specific kinetic constant	μ_∞	Viscosity of molasses at infinite temperature, Pa.s
n	Flow behavior index		
R	Molar gas constant, J/mol.K	μ'	Viscosity at time t, Pa.s
T	Temperature, K	τ	Shear stress, Pa
t	Time, second	τ'	Shear stress at time-t, Pa
t_0	Time at maxim shear stress, second		

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