Time-Dependent and Time-Independent Rheological Characterization of Date Syrup

Ibrahim O. Mohamed¹ & Eihab Hassan²

¹ Department of Food Science, College of Food and Agriculture, United Arab Emirates University, UAE
² Emirates Date Factory, Alsaad, UAE

Correspondence: Ibrahim O. Mohamed, Food Process Engineering Consultant, P.O. Box 377004, Deira, Dubai, UAE. Tel: 97-142-544-066. Fax: 97-142-251-700. E-mail: iom106@yahoo.com

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Abstract
The time-dependent and time-independent rheological properties of Barhi date syrup have been investigated. Rheological measurements were performed with a rotational viscometer with parallel plate geometry. The date syrup showed thixotropic behavior and a first order exponential decay model characterized the time-dependent behavior. The rate constant of the structure breakdown was found to be a function of shear rate. The steady shear flow measurements showed that the date syrup is a non-Newtonian material fit the power law model (p <0.001). The Arrhenius model described the effect of temperature on consistency coefficient; the estimated parameters from the Arrhenius equation were used to develop a prediction rheological model for the apparent viscosity. The model accurately predicts the experimental data even when extrapolating beyond parameter estimation temperature range. The time-independent viscosity model was satisfactory for modeling date syrup despite the presence of thixotropic behavior.

Keywords: Rheology, date syrup, Barhi, viscosity, rheological model, activation energy, thixotropy

1. Introduction
The fruit of the date palm (Phoenix dactylifera L.) is one of the most economically important fruit in the Middle East and North African countries. Dates are important for human nutrition because they are a rich source of carbohydrates, proteins, minerals, dietary fiber and some vitamins in addition to being a source of rapid energy (Jasim Ahmed, Almusallam, & Al-Hooti, 2013; Al-Hooti, Sidhu, Al-Saqer, & Al-Othman, 2002; Al-Shahib & Marshall, 2003; El-Nagga & Abd El–Tawab, 2012). Dates are mostly consumed as a whole fruit or in processed form such as date paste or date syrup. Date syrup is one of the major processed forms of the dates. Date syrup is not produced like fruit juice by pressing but produced by the addition of potable water to the dates to dissolve sugars and other components, which is then subjected to a series of purification and concentration steps. Demand for date syrup in the food industry as a natural sweetener packed with nutrients is growing, and there is much potential for new food products that contain date syrup.

Studies on date processing are very limited, Ahmed and Ramaswamy (2005) investigated the effect of temperature on viscoelastic properties and visual color degradation kinetics of dates (Lulu cultivar). Recently Gabbi, Trigui, Barrington, Helal and Taherian (2013) determined the rheological properties of date syrup from three Tunisian cultivars (Menakher, Alligue & Lemsi). The date syrups from the Tunisian cultivars were found to follow the power law with a temperature sensitive flow behavior index. Razavi, Habibi Najafi, & Alaee (2007) investigated the rheological properties of low fat sesame pastes with blended date syrup as well as fat replacement with guar gum, xanthan and starch. They found that all sesame paste/date syrup blends exhibited non-Newtonian pseudoplastic behavior at all temperature and levels of fat substitution. The power law model was the best model that fitted the shear stress and shear rate of dates blended with sesame paste with and without fat replacer.

The rheological behavior of syrup such as molasses is an important factor that affects the efficiency of the various production and refining processes such as boiling, crystallization, separation and pumping (Leong & Yeow, 2002). Rheological properties are an important quality control parameter in food industry during production, they provide insight into the food’s physical properties. This will help in understanding the
underlying mechanisms of momentum and heat transfer (Kaur, Kaler, & Aamarpali, 2002). Information related to the rheological properties of date syrup is quite scarce despite the growth in the date processing industry. The aim of this work is to develop a complete rheological characterization model for date syrup.

2. Materials and Methods

2.1 Materials

Commercially-certified organic date syrup from Barhi dates produced by the Emirates Date Factory (Al-Saad, UAE) was purchased from a local supermarket. The total soluble solids were measured with a digital refractometer at 20 °C.

2.2 Sugars and Minerals Content

Sugars in the date syrup samples were determined using High-performance liquid chromatography (HPLC) on a Waters Alliance 2695 system (Waters Corporation, Milford, MA) using a Waters Refractive Index Detector (Waters 2410) and column μ-Bondapack NH₂ (300 mm length x 3.9-mm id x 10 μm particle size, Waters 084040 ) according to AOAC method 977.20. The mineral contents were determined using inductively coupled plasma atomic emission spectrometry on a Varian ICP-OES model 710-ES (Varian-Vista-MPX; Varian, Inc., Palo Alto, CA, USA) according to the standard operating protocol. Measurements were made in triplicates

2.3 Rheological Measurements

An HR-2 Discovery Hybrid Rheometer (TA Instrument, New Castle, DE, USA) equipped with a Peltier heater was used for all the rheological measurements. Trios v3.0 software controlled the rheometer and was used for data collection and analysis. A parallel plate geometry having 40 mm diameter with a gap of 1000 μm was used for all measurements. Dynamic rheological measurements were performed at 25 °C with a strain of 2%, which was confirmed to be in the linear region by performing strain sweep testing at 10 rad/s. Measurements of yield stress were performed at 25 °C on a concentric cylinder system consisting of a 28 mm vane bob with a length of 42 mm and a cup diameter of 37 mm. The sample was carefully loaded on the cup to minimize any disturbance to the sample structure and allowed to rest for 30 minutes before taking measurements. The rheometer was set at a constant speed of 0.27 RPM and span time of 5 minutes; this system was used to record the shear stress and shear rate. The steady shear flow runs were performed at 15 °C, 25 °C, 35 °C, 45 °C and 55 °C at a shear rate of 2 up to 300 1/s. Temperature sweep testing used steady shear flow at a shear rate of 50 1/s and 150 1/s. Measurements we performed at least in duplicate, and the average value was reported.

2.4 Time-Independent Rheological Model

The shear stress (τ) and shear rate (γ̇) data at various temperatures were fitted to the well-known power law model given by:

$$\tau = k(\dot{\gamma})^n$$

(1)

where $k$ is the consistency coefficient (Pa s^n), and $n$ is the flow behavior index (dimensionless).

The effect of temperature on consistency coefficient was modeled by the Arrhenius equation given by:

$$k = k_o e^{(\Delta E/RT)}$$

(2)

where $k_o$ is a constant, $\Delta E$ is activation energy, $R$ is the universal gas constant and $T$ is the temperature in absolute unit (K). The parameters of Eq. 2 can be easily determined using the following linearized form of Eq. 2

$$\ln(k) = \ln(k_o) + \frac{\Delta E}{RT}$$

(3)

The temperature-dependent of apparent viscosity for a power law fluid can be described by:

$$\eta_a = k_o e^{(\Delta E/RT)} (\dot{\gamma})^{(n-1)}$$

(4)

where $\eta_a$ is the apparent viscosity (Pa.s^n), and $k_o$ is a constant representing the consistency coefficient at a reference temperature.
2.5 Time-dependent Characterization

To study time-dependency, measurements of shear stress and shear rate were carried out in ascending and descending order at 25 °C. Also, measurements of the shear stress at a constant shear rate of 100, 150, 200 and 300 (1/s) were performed at constant temperatures of 25 °C for about 350 sec. Several models have appeared in the literature to describe structure breakdown during constant shearing. These include first order stress decay with zero stress value, first order stress decay with non-zero stress value, the Weltman model or structure kinetics model (Altan, Kus, & Kaya, 2005; Razavi & Karazhiyan, 2009). In this research work based on preliminary testing of the shear stress-time data, the first order stress decay model given below was found to be more appropriate for fitting date syrup data:

\[ \tau = \tau_{eq} + (\tau_o - \tau_{eq})e^{-\beta t} \]  

(5)

where \( \tau_o \) is the shear stress at time \( t=0 \), \( \tau_{eq} \) is the equilibrium shear stress and \( \beta \) is the structure breakdown rate constant.

3. Results and Discussions

3.1 Sugars and Minerals Content

Date syrup is an aqueous extract from date fruits that is concentrated under vacuum commercially to 70 – 78 °Brix. The sample used in this study is 71 °Brix, and the sugar and mineral content of the date syrup sample is shown in Table 1 based on dry basis. Both sugars and minerals were close to what is reported in the literature for Barhi date syrup (Al-Hooti et al., 2002).

Table 1. Sugars and minerals content of Barhi date syrup

<table>
<thead>
<tr>
<th>Components</th>
<th>Value*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sugar</td>
<td>(g/100g)</td>
</tr>
<tr>
<td>Fructose</td>
<td>44.93 ± 1.37</td>
</tr>
<tr>
<td>Glucose</td>
<td>41.73 ± 0.17</td>
</tr>
<tr>
<td>Minerals</td>
<td>(mg/100g)</td>
</tr>
<tr>
<td>Potassium</td>
<td>607.67 ± 24.00</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>82.67 ± 2.13</td>
</tr>
<tr>
<td>Calcium</td>
<td>53.33 ± 1.33</td>
</tr>
<tr>
<td>Magnesium</td>
<td>78.93 ± 1.86</td>
</tr>
<tr>
<td>Sodium</td>
<td>9.33 ± 0.53</td>
</tr>
</tbody>
</table>

*Mean ± standard deviation; n = 3

3.2 Dynamic Flow Measurement

Dynamic flow measurements were performed to examine the viscoelastic behavior of the date syrup. Figure 1 shows elastic modulus (\( G' \)) and loss modulus (\( G'' \)) as a function of frequency. Both \( G' \) and \( G'' \) appear to be frequency dependent with nonlinear behavior with respect to frequency. However, the value of the \( G'' \) is much higher compared to \( G' \) indicating that the date syrup behaves more as a viscous fluid than as an elastic material. The ratio of the loss modulus to storage modulus is given by \( \tan(\delta) \) where \( \delta \) is the phase angle between dynamic stress and strain. A phase angle of 90° indicates perfect viscous behavior with all shearing energy dissipated while a phase angle of 0° indicates perfect elastic behavior with all shearing energy stored. A material with a phase between 0° and 90° shows some viscoelastic behavior. For date syrup, the phase angle \( \delta \) ranged from 45 to 72° at 25 °C, which indicates that the date syrup behaves more as a viscous material than as elastic material.
3.3 Yield Stress Measurement

Figure 2 shows the stress response as a result of shearing at constant velocity; the rheometer is capable of taking measurements with millisecond resolution. Prior to 0.023 second, there are some peaks for both shear stress and
shear rate. These are attributed to inertia effects, and thereafter the date syrup showed continuous shearing effects. The shear stress increase to a maximum value and then decreases to a minimum value followed by a steady rise until it reaches equilibrium. The yield stress in such a situation can be defined at the first maximum value of the shear stress after the syrup exhibited uniform shearing. The yield stress based on the above definition is 0.173 Pa. This is a very low value that indicates that date syrup could fit a non-Newtonian model with no yield stress such as the power law.

3.4 Steady Flow Measurements

Figure 3a shows a steady shear flow curve for the date syrup at different temperatures used in the study. It is clear from the figure that the nonlinearity of the shear stress versus shear rate data shows pseudoplastic non-Newtonian behavior. The effect of temperature is more pronounced at temperatures below 25 °C. In other words, the mean increase in apparent viscosity is quite large at temperatures lower than 25 °C relative to decrease in viscosity at higher temperatures. The shear stress and shear rate data were fitted to the power law model using SigmaPlot software (Systat Software, San Jose, CA). Table 2 shows result of regression analysis, which clearly indicates that the power law model fitted the data very well as evident from the value of the coefficient of determination (R²) that is close to 1.0 and (p<0.001) indicating the appropriateness of the power law model for describing the rheological behavior of the date syrup. Gabsi, et al. (2013) reported that date syrup from varieties Menakher, Alligue and Lemi at concentration 17 – 39 °Brix fit the power law model very well for a shear rate range 10 – 100 l/s used in their study. However, the study of Gabsi et al. (2013) showed that the flow behavior index is sensitive to temperature for a given concentration level that is not the case in this study because the flow behavior index from 0.70 to 0.79 with an average value of 0.75 and a standard deviation of 0.04. The sensitivity of the flow behavior index to temperature in Gabsi et al. (2013) could be due to the higher temperature used 60 – 80 °C that could result in caramelization. Lengyel (2007) reported that; the sugar content of fruits starts to caramelize at temperature as low as 50 °C. Previous studies have shown that the flow behavior index (unlike consistency coefficient) is not temperature sensitive (Hassan & Hobani, 1998; Sopade & Filibus, 1995; Toğrul & Arslan, 2004; Vitali & Rao, 1984)

![Figure 3a](image)
Figure 3. Shear stress versus shear rate: a) at different temperatures b) forward and backward at 25 °C

Table 2. Power law parameters at different temperatures

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>k (Pa.s^a)*</th>
<th>n</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>35.4658 ± 0.4651</td>
<td>0.72 ± 0.00</td>
<td>0.999</td>
</tr>
<tr>
<td>25</td>
<td>11.8695 ± 0.0248</td>
<td>0.75 ± 0.00</td>
<td>0.999</td>
</tr>
<tr>
<td>35</td>
<td>5.3388 ± 0.1143</td>
<td>0.79 ± 0.00</td>
<td>0.999</td>
</tr>
<tr>
<td>45</td>
<td>3.1552 ± 0.0932</td>
<td>0.78 ± 0.00</td>
<td>0.999</td>
</tr>
<tr>
<td>55</td>
<td>2.4537 ± 0.0700</td>
<td>0.73 ± 0.00</td>
<td>0.998</td>
</tr>
</tbody>
</table>

*Mean ± standard deviation; n = 2; values in the same column with different superscripts are significantly different (p<0.05).

3.5 Activation Energy

The effect of temperature on the consistency coefficient can be determined by fitting the linearized form of the Arrhenius equation (Eq. 3) to the data in Table 2. The coefficient of determination (R^2) of the Arrhenius model is 0.959 and the P-value < 0.005 indicating that the model describes well the effect of temperature on consistency coefficient. The model parameter: k_o = 7.34x10^8 (Pa.s^a), and the activation energy is ΔE = 52868.7 (J/mole). The activation energy reported by (Gabsi, et al., 2013) for date syrup at 39 °Brix is lower than the concentration in this study and ranged between 111.941 – 135.337 (J/mole)—an order of magnitude lower than that reported here. This could be due to a mathematical error or could be due to the higher temperature used in their study which could result in caramelization.

The activation energy of honey is to some extent similar to the date syrup in terms of sugar composition reported for some Australian honey that ranged from 66.31 to 99.29 kJ/mole at 50 RPM (Mossel, Bhandari, D'Arcy, & Caffin, 2000). This is within an order of magnitude of the date syrup studied here. In another study by Cohen and
Weihs (2010), the activation energy of honey was found to be 84.7 – 96.9 kJ/mol; Toğrul and Arslan (2004) reported an activation energy for molasses with ethanol ranging between 32.5 – 40.6 kJ/mole. (Recondo, Elizalde, & Buera, 2006) reported an activation energy value for honey, fructose syrup, fructose-glucose syrup and glucose of 82.8, 81.3, 79.9 and 50.3 kJ/mole respectively. The activation energy of the date syrup reported here is close to the activation energy of the glucose and is within an order of magnitude of the fructose and fructose-glucose syrup. However, date syrup contains other components such as fiber and minerals that may contribute to unique value reported here.

3.6 Time-dependent Characterization

Figure 3b shows the flow curves for the forward and backward measurements showing formation of a hysteresis loop that clearly indicates that the date syrup is time-dependent. The enclosed area in the hysteresis loop represents an extended thixotropy. The phenomena of time dependency is very complex for food materials due to the complexity of the structure of food materials and the interaction of the various food material components with each other during shearing. This makes the development of a deterministic model for time-dependent food material quite difficult. Studies of stress decay during constant shearing rate is a common approach often used to describe time dependency. Figure 4 shows the shear stress as a function of shearing time. The shear stress at zero time (τ₀) is taken at the time when the shear rate reached the set value for the measurement in this study or ~0.3 second.

The data shows that the proposed first order model fit the data very well with R² ≥ 0.96. The model showed that the shear stress attained equilibrium (τₑ) in about 120 second for all shear rates. The rate constant increases with increased shear rate similar to other published works employed to study the stress decay model for milled sesame (tahini) (Abu-Jdayil, Al-Malah, & Asoud, 2002), salep solution (Razavi & Karazhiyan, 2009), gilaburu juice (Altan et al., 2005). The equilibrium shear stress is at most 11% less than the shear stress at zero time implying that the time dependency for date syrup was detectable but would not produce significant error if neglected. This is because the ratio of initial to equilibrium viscosity (η₀/ηₑ) is a measure of structure breakdown (Abu-Jdayil 2004). In this study, this corresponds to the ratio of the shear stress (τ₀/τₑ) that does not exceed 11% for the shear rate values studied here.
Furthermore, nearly all thixotropic materials have yield stresses, and the close link between thixotropy and yield stresses have been reported by earlier studies (Mewis & Wagner, 2009). As shown earlier, the measured value of the yield stress for date syrup is very low. This illustrates that although thixotropy is present, its effects might not be of significance for date syrup.

3.7 Time-independent Rheological Model

Because the date syrup was non-Newtonian, the viscosity becomes a function of the shear rate and is better expressed as apparent viscosity. Table 3 showed that the flow behavior index at different temperatures are not significantly different (p < 0.05) therefore an average value was used and incorporated into Eq. 4 resulting in the following model for predicting apparent viscosity of date syrup.

\[ \eta_a = 7.34 \times 10^{-9} e^{(3.35)\beta} (\dot{\gamma})^{-0.25} \]  

Table 3. Parameters of the first order stress decay model (Eq. 5)

<table>
<thead>
<tr>
<th>Shear rate (1/s)</th>
<th>( \tau_o )</th>
<th>( \tau_{eq} )</th>
<th>( \tau_o/\tau_{eq} )</th>
<th>( \beta ) (1/s)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>615.19</td>
<td>579.90</td>
<td>1.06</td>
<td>0.020</td>
<td>0.96</td>
</tr>
<tr>
<td>150</td>
<td>581.19</td>
<td>533.81</td>
<td>1.09</td>
<td>0.025</td>
<td>0.99</td>
</tr>
<tr>
<td>200</td>
<td>1004.91</td>
<td>913.12</td>
<td>1.10</td>
<td>0.035</td>
<td>0.98</td>
</tr>
<tr>
<td>300</td>
<td>938.69</td>
<td>838.61</td>
<td>1.11</td>
<td>0.067</td>
<td>0.99</td>
</tr>
</tbody>
</table>

3.8 Model Validation

Figures 5a) and 5b) show the predicted and measured viscosity as a function of temperature at a shear rate of 50 (1/s) and 150 (1/s) respectively. The model prediction fall very well within the 95% confidence interval over a wide temperature range including outside the parameter estimation temperature range of 15 to 55 °C. The time-independent model predicts viscosity very well despite the presence of thixotropy, which is not significant as explained before. This model could be a useful contribution to food industry because it may help in the design of flow systems and heat transfer operations especially for applications where date syrup is used as an ingredient. Furthermore, such a model could be used in quality control of the date syrup because viscosity is an important food quality parameter. The models have the capability to predict viscosity as a function of temperature and shear rate.
4. Conclusions

Dynamic rheological measurements showed that date syrup exhibited a liquid-like rheological behavior with a loss modulus (\(G''\)) much higher than the storage modulus (\(G'\)); the phase angle was 45 to 72° at 25 °C. Date syrup showed non-Newtonian behavior, and the power law model fit the shear stress and shear rate data from 15 to 55 °C. The Arrhenius model described the effect of temperature on consistency coefficient very well. Date syrup exhibited thixotropic behavior, and the first order stress decay model fit the shear stress/time data very well. The time-independent rheological model developed for apparent viscosity was validated using a temperature from 50 1/s to 150 1/s, the model predicted the apparent viscosity as a function of temperature and shear rate very well versus the measured viscosity at two different shear rates. The time-independent viscosity model showed that the presence of thixotropic behavior does not produce significant error as shown by the good fit of the experimental viscosity data.

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