Modelling of rheological behaviour of pummelo juice concentrates using master-curve

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\textbf{A B S T R A C T}

The rheological behaviour of freeze-dried-concentrated pummelo juice was modelled to investigate the effects of temperature and concentration on its fluid type and viscosity using a rotational viscometer at shear rates ranging from 1 to 400 s\textsuperscript{-1}. The effect of concentration measured by its total soluble solids content resulted in the juice concentrates behaving towards shear thinning or pseudoplastic behaviour with flow behaviour index values, $n < 1$. Temperature increase from 6 to 75 °C produced a reversing effect of the shear thinning behaviour from the increase of $n$ values at all three investigated concentrations, 20, 30 and 50°Brix. The consistency coefficient decreases with temperature but increases with total soluble solid contents. Modelling the rheological behaviour of pummelo juice concentrates using the master-curve yielded results over a range of temperature to overlap on a single line, which allows generalisation of flow behaviour and characteristics. The master-curve plots confirmed that the juice viscosity and pseudoplasticity increase with concentration with high regression coefficients, $R^2 > 0.98$.

1. Introduction

The processing of commercial fruit juices such as heat sterilization, evaporation or pasteurization is favoured in terms of preserving the juice for a longer period of time. However, vitamin C, a water-soluble antioxidant vitamin which is important in forming collagen, a protein that gives structure to bones, cartilage, muscle, and blood vessels, is very sensitive to heat and will be easily destroyed during heat treatment. The development of concentrated fruit juice in the form of dehydrated fruit juices or frozen concentrates serves as an alternative method for maintaining more nutrients and volatile properties of the fresh fruit. Juices obtained by removal of a major part of their water content by vacuum evaporation of fractional freezing are known as concentrated juice (Lozano, 2006).

The processing of commercialized juice is subjected to tight supervision because its properties, such as viscosity, concentration, and temperature vary during processing. The flow properties and behaviour of processed juice products are important in determining the power requirements for pumping and sizing of pipes in its processing (Kimball et al., 2004; Sestak et al., 1983; Telis-Romero et al., 1999). In the design and operations, it is important to determine the type of flow, such as turbulent or laminar in heat exchangers (Gratão et al., 2006). An assumption of simple Newtonian flow can result in error in the estimation of holding time. The changes in properties are also important in the selection of equipment and type of processing. For example, the film type evaporators are generally used in concentrating juices. Due to the importance of liquid properties during processing, rheological models are frequently constructed to aid processing. Rheological properties, such as viscosity arise from studies of flow and deformation of a matter (Barnes et al., 1993). Besides playing an important role during processing, such as in plant design, flow processes, quality control, storage, it is also referred for measurement of processing stability and for predicting texture (Davis, 1973). A parameter of juice quality which is related to rheology is known as the mouthfeel. Matz (1962) defines mouthfeel as the mingled experience deriving from the sensation of the skin of the mouth after ingestion of a food or beverage and that it relates to density, viscosity, surface tension and other physical properties of the material being sampled. The physical properties of fruit juices have begin to gain importance as textural dimensions of fruits juices have been developed and quantified (Ingate and Christensen, 2007).

Various mathematical models have been used to represent the flow behaviour of non-Newtonian fluids (Rao, 1999). Following Rao (1999), there are Power law model, Herschel–Bulkey model, Bingham model, Cross-model, Carreau model, Casson model, and the Heinz Casson model. Crandall et al. (1982) used the Power law model to study concentrated orange juice at 42.5 °Brix while Ibarz et al. (1992) studied clarified peach juice from 40 to 60 °Brix. Although the physical properties such as viscosity, flow behaviour
index and density of many tropical fruit juices have been studied, most of the investigations are at low concentrations. Among them are fruits juices such as guava juice at 9 and 11 °Brix (Zainal et al., 2000, 2001), mango juice at 12–26 °Brix (Azoubel et al., 2005), pineapple juice at 12–13 °Brix (Shamsudin et al., 2007) and pummelo juice at 8 and 10 °Brix (Chua et al., 2008). Rheological studies on juice concentrates were mainly on sub-tropical fruits such as clarified apple juice at 12–70 °Brix (Constenla et al., 1989), pear juice at 10–70 °Brix (Ibarz and Miguelansz, 1989), apple juice at 14–39 °Brix (Bayindirli, 1992), grape juice at 20–80 °Brix (Bayindirli, 1993), peach juice at 40–69 °Brix (Ibarz et al., 1992), cherry juice (Giner et al., 1996) and clarified peach and orange concentrates at 60 °Brix (Ramos and Ibarz, 1998).

The present study uses modelling to investigate the effect of temperature and juice concentration on the rheological properties and flow characteristics of pummelo juice concentrates. The pummelo fruit is gaining popularity since studies showed that it contains antioxidant capacity as extracts of carotenoids, phenolics, vitamin C, lycopene, and anthocyanins were found in them (Tsai et al., 1997; Jayaprakasha et al., 2008). An advantage of using concentrated pummelo juice sample is that it has a low pH value (Chin et al., 2007). An advantage of using concentrated pummelo juice sample is that it has a low pH value (Chin et al., 2007) and it is known that a pH value less than 3.7, bacteria will not multiply and only a short time pasteurization process is necessary (Arthey and Ashurst, 1996). The rheological properties were superposed along the stress axis using shift factors at a chosen arbitrary reference temperature in a stress—temperature superposition (Harper and El Sahrigi, 1965; Rao et al., 1981; Vitali and Rao, 1984; Speers and Tung, 1986; Steffe, 1996; Udyarajan et al., 2007).

2. Materials and methods

2.1. Preparation of Juice

Fresh harvest of pummelo fruits, Citrus grandis (L.) Osbeck, were obtained from the same cultivation batch from a farm as raw materials. The pummelo fruits were stored in a refrigerator at 10 °C for a few days until the peeling process for juice sample extraction. The thick fruit skin was peeled away after incision of longitudinal cuts with a sharp knife onto the spongy skin to reveal the juicy segments. The fruit was separated into individual segments and the inner skin of each segments was peeled and discarded, including any seeds found. Most of the bitter component, the naringin and limonin found in the white membrane were completely removed. Using the cold peel method, the peel was stripped off manually to remove both albedo and the outer membrane of each segment (Arthey and Ashurst, 1996). The juice was extracted by using a home kitchen juice blender (HR2027, Philips, Malaysia) and filtered using nylon to remove its pulps from the juice. The physico-chemical compositions of fresh pummelo juice at moisture content of 85.32 ± 1.52% is at about 10 °Brix (Chin et al., 2008). About 2 l of juice, sampled into 200 ml each, was dry concentrated by using a laboratory vacuum freeze dryer (Model SB4, Pump Model RV8, Edward High Vacuum International, Crawley Sussex, England) or 24 h with a dying temperature programmed from 25 to −40 °C. During the freeze drying process, the juice was frozen and the frozen solvent was removed by sublimation under vacuum. The sublimed ice was pulled from the vacuum chamber by vacuum pumps. The freeze-dried concentrated juice was then diluted to three concentrations, 20, 30 and 50 °Brix with distilled water for rheological test.

2.2. Rheological measurements

The rheological properties investigation of pummelo juice concentrates were performed using a computerised rotational viscometer (Rotovisco RT 20, Haake, Germany) using the concentric cylinder geometry, Z40 DIN Ti. The sample volume of the geometry was 85 cm³. The viscometer consists of high rotor speeds with a powerful drive motor, enabling it to be operated at a wide shear rate range of 0.1–1000 s⁻¹. The viscometer is equipped with an electric temperature controlled system (DC 50) to control the experimental temperature to ±0.1 °C. The system consists of a hybrid base with an electric heater and connectors for thermal liquid cooling. Data was recorded from the interface software, RheoWin Job Manager. Concentrated pummelo juice samples were measured at six levels of temperatures, i.e., 6, 20, 30, 40, 60 and 75 °C for each concentration level of 20, 30 and 50 °Brix from 1 to 400 s⁻¹ at a continuous increasing shear rate manner.

2.3. Analysis and modelling

The experiments were conducted in triplicates. Mean and standard deviation were calculated using Microsoft Excel 2003 (XP Edition, Microsoft Corporation, USA). The error bars in the graphs are the standard deviation of means from three replications. Analysis of variance (ANOVA) at alpha level of 0.05 was performed using the statistical tool in Microsoft Excel. Curve fitting was perform using the solver function in Microsoft Excel adopting the generalised reduced gradient (GRG2) nonlinear optimization code to determine the rheological parameters, K and n in the Power law model (Eq. (1)). The best fitted line with minimum sum of square errors (SSE) was used as the sole criteria during curve fitting. The goodness of fit, R² was calculated as R² = 1 − SSE/SST, where SST is the total corrected sum of squares (Walpole et al., 2002). In determining the effects of temperature and concentration on rheological parameters, the Arrhenius (Eq. (3)) and a power type equation (Eq. (4)) were linearised by taking the logarithmic terms to obtain the constants and coefficients.

2.3.1. Modelling of fluid flow behaviour using Power law

The fluid behaviour of pummelo juice concentrate was the modelled using the Power law:
\[ \sigma = K \dot{\gamma}^n \]  \hspace{1cm} (1)

where \( \sigma \) is the shear stress exerted by the fluid (Pa), \( K \) is the consistency coefficient, \( \dot{\gamma} \) is the shear rate (s\(^{-1}\)) and \( n \) is the flow behaviour index. \( n \) does not equal to 1 for non-Newtonian fluids and it determines the type of fluid category it belongs to. For non-Newtonian fluids, the apparent viscosity, \( \eta_{app} \) is reported as a function of shear rate. For this work, a shear rate of 100 s\(^{-1}\) was chosen because 10–100 s\(^{-1}\) approximates the shear rate of tumbling and pouring while 100–1000 s\(^{-1}\) approximates the shear rate of home mixers (Bourne, 2002):

\[ \eta_{app} = f(\dot{\gamma}) = \frac{\sigma}{\dot{\gamma}} = K(\dot{\gamma})^{n-1} \]  \hspace{1cm} (2)

2.3.2. Effect of temperature on rheological model

The dependence of consistency coefficient, \( K \), on temperature is described using the Arrhenius relationship

\[ K = K_0 \exp \left( \frac{E_a}{RT} \right) \]  \hspace{1cm} (3)

The data on consistency coefficient from Eq. (1) was used to obtain constants, \( K_0 \) and \( E_a \), known as the frequency factor and activation energy, respectively. Eq. (3) was linearised by taking the logarithm on each term. The constants, \( K_0 \) and \( E_a \) were obtained from the y-intercept and the slope of the linearised equation.

2.3.3. Effect of concentration on rheological model

The dependence of consistency coefficient, \( K \), on concentration is modelled using the power type relationship where both constants of the \( K_1 \) and \( n_1 \) values were determined from the y-intercept and the slope of the linearised equation

\[ K = K_1(C)^{n_1} \]  \hspace{1cm} (4)

2.3.4. Modelling fluid flow using master-curve equation

Eq. (5) shows that a rheogram at any temperature in the interested range can be generated by utilising constant values obtained from Eqs. (1) and (3), such as the average flow behaviour index, \( n \), frequency factor, \( K_0 \) and activation energy, \( E_a \). When expressed in terms of shear stress, the combined effect of shear rate and temperature in a single expression is as follow (Harper and El Sahrigi, 1965):

![Fig. 1. Rheograms showing shear stress versus shear rate plots for pummelo juice concentrates at 6 °C (.), 20 °C (□), 30 °C (○), 40 °C (○), 60 °C (△), and 75 °C (▲) for concentration at (a) 20, (b) 30, and (c) 50 °Brix. Lines are calculated model values using parameters given in Table 1.](image-url)
\[ \sigma = f(T, \dot{\gamma}) = K_0 \exp \left( \frac{E_a}{RT} \right) (\dot{\gamma})^n \]  

Concurrently, the master-curve was also developed to allow prediction of rheological behaviour that covers the entire range of temperature and shear rates. As such, the rheological behaviour of pummelo juice concentrate at six different temperatures was further interpreted using the master-curve technique. The shear rates were horizontally shifted at \( \sigma = 2.5 \) Pa using Eq. (1) to obtain the dimensionless shift factors, \( a_T \), defined as the ratio of shifted shear rates with a selected reference temperature of 20 \(^\circ\)C. The master-curve was then plotted using original shear stress versus original shear rates divided by the dimensionless shift factors. The horizontal shifting causes data to overlap on a single line. Finally the master-curves at various concentrations were fitted to the original Power law equation to present a single description of flow behaviour in terms of consistency coefficient, \( K' \) and flow behaviour index, \( n' \).

3. Results and discussion

The rheograms in Fig. 1 shows plots of shear stress versus shear rate of pummelo juice concentrates at three concentration levels.
measured at temperatures from 6 to 75 °C. The values of consistency coefficient, \( K \), and the flow behaviour index, \( n \), were obtained by curve fitting using least square method and presented in Table 1 showing high goodness in fitting with high regression coefficients, \( R^2 \), from 0.9972 to 1.000. A close observation on each of the \( n \) value shows that pummelo juice concentrates exhibited a shear thinning, non-Newtonian behaviour and behaves pseudoplastically \( (n < 1) \) at all concentration levels. The pseudoplastic behaviour increases with concentration of juice while the effect of temperature seems to reduce its pseudoplasticity at each concentration level. The juice concentrates at 20 °Brix (double the concentration of fresh juice) shows a characteristic approaching Newtonian when heating or holding time in flow lines during pasteurization at recommended temperature will be longer for juices with higher total soluble solids, which is in the order of \( 6 \)–\( 10 \) °Brix. It was reported that high pulp levels and soluble components can contribute to the apparent viscosities (Kimball, 1986). The calculated apparent viscosity of pummelo juice concentrates at 100 s\(^{-1}\) as presented in Table 1 showed an agreeing trend to the consistency coefficient with respect to the effect of temperature and concentration levels. Both analysis on \( n \) and \( K \) values are important in juice processing. For example, the increase in consistency coefficient will decrease the flowing rate of juice in the pipe due to more resistance flow (Earle, 1985). This means that heating or holding time in flow lines during pasteurization at recommended temperature will be longer for juices with higher total soluble solids for the same pressure drop.

Table 2 lists the results of constants, \( K_0 \) and \( E_a \) obtained through linearization of Eq. (3). The \( K_0 \) values which are in the order of tenth power of negative 4–8 are in the range of those reported by Ibarz et al. (1992) on clarified peach juices at 40–69 °Brix with the range from tenth power of negative 6–11. The maximum activation energy, \( E_a \) of 42.06 (kJ/mol) occurred at the concentration of 30 °Brix. This activation energy value is in a reasonable range for juice products (Rao, 1986). There are inconsistent reports about changes of activation energy with concentration as increase with concentration is reported in Ibarz et al. (1994), Giner et al. (1996), Singh and Eipeson (2000), Kaya and Belibagli (2002), Altan (1993). It was reported that high pulp levels and soluble components can contribute to the apparent viscosities (Kimball, 1986). The calculated apparent viscosity of pummelo juice concentrates at 100 s\(^{-1}\) as presented in Table 1 showed an agreeing trend to the consistency coefficient with respect to the effect of temperature and concentration levels. Both analysis on \( n \) and \( K \) values are important in juice processing. For example, the increase in consistency coefficient will decrease the flowing rate of juice in the pipe due to more resistance flow (Earle, 1985). This means that heating or holding time in flow lines during pasteurization at recommended temperature will be longer for juices with higher total soluble solids for the same pressure drop.

Table 2

<table>
<thead>
<tr>
<th>Total soluble solids (°Brix)</th>
<th>Activation energy, ( E_a ) (kJ/mol)</th>
<th>Constant in Arrhenius equation, ( K_0 ) (Pa s(^n))</th>
<th>Coefficient of determination, ( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>34.02 ± 1.042</td>
<td>3.023E – 08 ± 4.311E – 10</td>
<td>0.9437</td>
</tr>
<tr>
<td>30</td>
<td>42.06 ± 4.412</td>
<td>9.512E – 08 ± 9.486E – 09</td>
<td>0.9684</td>
</tr>
<tr>
<td>50</td>
<td>22.12 ± 1.360</td>
<td>3.632E – 04 ± 1.534E – 05</td>
<td>0.9693</td>
</tr>
</tbody>
</table>

Table 3

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Constant in power equation, ( K_1 )</th>
<th>Constant in power equation, ( n_1 )</th>
<th>Coefficient of determination, ( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>2.7271E – 07 ± 1.3756E – 08</td>
<td>4.0366 ± 1.223</td>
<td>0.9768</td>
</tr>
<tr>
<td>20</td>
<td>1.8578E – 07 ± 1.4278E – 08</td>
<td>4.4302 ± 0.2507</td>
<td>0.9713</td>
</tr>
<tr>
<td>30</td>
<td>6.3311E – 08 ± 6.0751E – 09</td>
<td>4.9370 ± 0.4018</td>
<td>0.9947</td>
</tr>
<tr>
<td>40</td>
<td>8.9958E – 09 ± 8.2446E – 10</td>
<td>5.3585 ± 0.4961</td>
<td>0.9930</td>
</tr>
<tr>
<td>50</td>
<td>4.8587E – 10 ± 2.0668E – 11</td>
<td>5.5167 ± 0.0928</td>
<td>0.9780</td>
</tr>
<tr>
<td>75</td>
<td>1.7647E – 09 ± 1.6099E – 10</td>
<td>5.2690 ± 0.2992</td>
<td>0.9826</td>
</tr>
</tbody>
</table>
and Maskan (2005) and Belibagli and Dalgic (2007) while a decrease by Dak et al. (2007). Saravacos (1970) reported that the activation energy decreases with the presence of suspended particles in the fruit juice.

Modelling using Eq. (4) presents the parameters as listed in Table 3. Constant, $K_1$ decreases but $n_1$ increases with temperature increase (Fig. 4). The values of $R^2$ calculated were from 0.9713 to 0.9930 suggesting good fitness and accuracy in the constants obtained. An observation of the slight decrease of flow behaviour index at the highest temperature of 75°C could be due to the effect of high heat which may have resulted in biochemical changes of the juice concentrate.

In giving an overall picture of the flow behaviour of pummelo juice concentrate, disregard of its temperature, the master-curve technique was used to model the rheological behaviour to obtain a general fluid characterisation. With a reference temperature of 20°C and a 2.5 Pa basis of shear stress, the master-curve was developed through the determination of shift factor, $\alpha_T$. Fig. 5 shows the plot of original shear stress as $y$-axis while $x$-axis is the shifted shear rates divided by the shift factors in logarithmic scales yielding a linear line for each concentration due to the horizontal shifting of data which caused an overlap. Table 4 presents the results of Power law model fitting of the master-curve data displaying $K_0$ values which increases and $n_0$ values which decreases with concentration thus confirms the earlier analysis suggesting that both juice viscosity and pseudoplasticity increase with concentration. The absolute values of flow behaviour index via this method were about 9–25% lower compared to the average flow behaviour index. Nonetheless, these master-curves are still recommended when comparing data from different products of juice and solving engineering problems such as those requiring prediction of fluid velocity profile or pressure drop during fluid flow (Steffe, 1996).

**Table 4**

<table>
<thead>
<tr>
<th>Total soluble solids (°Brix)</th>
<th>Consistency coefficient, $K_0$</th>
<th>Flow behaviour index, $n_0$</th>
<th>Coefficient of determination, $R^2$</th>
<th>Average flow behaviour index, $\bar{n}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.0351</td>
<td>0.7949</td>
<td>0.9932</td>
<td>0.8956</td>
</tr>
<tr>
<td>30</td>
<td>0.5380</td>
<td>0.4830</td>
<td>0.9887</td>
<td>0.6438</td>
</tr>
<tr>
<td>50</td>
<td>2.9774</td>
<td>0.4729</td>
<td>0.9981</td>
<td>0.5254</td>
</tr>
</tbody>
</table>

Fig. 4. Dependence of (a) constant ($K_1$) and (b) constant ($n_1$) on temperature in °C.

Fig. 5. Master-curves showing stress–temperature superposition with reference temperature at 20°C for pummelo juice concentrates at 6°C (■), 20°C (●), 30°C (●), 40°C (•), 60°C (▲), and 75°C (△) at three concentrations, 20, 30 and 50 °Brix.
4. Conclusions

Modelling of the rheological behaviour of pummelo juice concentrates showed that it is non-Newtonian fluid, and that it possesses characteristics which is pseudoplastic or shear thinning. The effect temperature and concentration both are significant towards the consistency coefficient and index behaviour such that viscosity decreases with temperature but increases with total soluble solid contents. Modelling the rheological behaviour using the master-curve also presented an increase of viscosity and pseudoplasticity with concentration. This technique is useful for reporting the behaviour with respect to any working temperature hence allows convenient comparison of different juice products.

References