Flow behavior of clarified pear and apple juices at subzero temperatures

Article in Afinidad -Barcelona- · April 2013
Impact Factor: 0.08 · DOI: 10.1111/j.1745-4549.2011.00630.x

CITATION
1

READS
78

4 authors, including:

Victor Falguera
AKIS International
50 PUBLICATIONS  541 CITATIONS
SEE PROFILE

Manuel Vicente
University of Barcelona
24 PUBLICATIONS  372 CITATIONS
SEE PROFILE

Albert Ibarz
Universitat de Lleida
168 PUBLICATIONS  2,631 CITATIONS
SEE PROFILE

Available from: Albert Ibarz
Retrieved on: 09 May 2016
FLOW BEHAVIOR OF CLARIFIED PEAR AND APPLE JUICES AT SUBZERO TEMPERATURES

VÍCTOR FALGUERA1,2,3, MANEL VICENTE2, ALFONSO GARVÍN1 and ALBERT IBARZ1

1Departament de Tecnologia d’Aliments, UPV-XaRTA, Universitat de Lleida, Avda. Rovira Roure, 191, 25198 Lleida, Spain
2Departament d’Enginyeria Química, Universitat de Barcelona, Martí i Franquès, 1, 08028 Barcelona, Spain

The flow behavior of clarified pear and apple juices has been studied at subzero temperatures (between −1 and −18°C), using a concentric cylinder rheometer. The results indicated that these clarified and depectinated juices behave as Newtonian fluids. As the soluble solids content increases, rheological measurements could be performed at lower temperatures because of the freezing point falling. The variation of viscosity with temperature could be quantified using an Arrhenius-type equation, and its change with soluble solids content was described by an empirical exponential expression. Flow activation energy was evaluated in a range of 41–91 kJ/mol for pear juice and of 39–88 kJ/mol for apple juice, for concentrations between 50 and 70 Brix.

PRACTICAL APPLICATIONS

The manufacturing of fluid products includes numerous processing operations from the raw material to the final product. It is necessary to know how viscosity changes with temperature and soluble solids content. These parameters will be of essential importance in the handling and calculation of all the operations involved in processing, especially those based on heat transfer and momentum transfer. In order to avoid the loss of organoleptic and nutritional properties caused by thermal concentration, alternative technologies such as cryoconcentration are being developed. In this way, rheological properties of food fluids just above their freezing point must be investigated to ensure an optimum design of the new cryoconcentration equipment.

INTRODUCTION

Pear and apple are two fruits with the most important production in the area of Lleida (Spain). For this reason, there is a very significant production of these fruit juice concentrates because of the existence of surpluses. The concentrated juices are obtained by extraction or pressing, and later clarification and concentration. The first step produces a juice of about 12 Brix and, after concentration, a final product of about 70 Brix is obtained. During this process, soluble solids content continuously change, and the juice is subjected to different temperatures during processing and storage. Therefore, its properties are also constantly changing, because they depend on the concentration and temperature.

The manufacturing of fluid products includes numerous processing operations from the raw material up to the final product. Involved processes include transportation, by passing the product through pipelines, pasteurization, filtration, evaporation and sterilization, and other processes to maintain the shelf life, such as refrigeration and freezing. It is necessary to know the relationship between the viscosity and density with temperature and soluble solids content. These parameters will be of essential importance in the handling and calculation of all the operations involved in processing (especially those based on heat transfer and momentum transfer) in order to predict the engineering parameters required for processing and performance, and also to contribute to the design of efficient equipment. An appropriate design of unit operations is necessary for optimum processing, to prevent overdimensioned facilities and to subsequently reduce or prevent the wasteful use of natural resources. Moreover, viscosity also influences product acceptance by consumers.
Concentrating operation is usually carried out by means of some evaporation stages. However, this process affects the sensorial and nutritional quality of the juice, causing nutritional losses and nonenzymatic browning reactions that deteriorate the final product. Because evaporation produces undesirable changes in the juice, other concentration processes such as reverse osmosis and cryoconcentration are being explored. The first one of these alternatives has certain practical limitations, mainly because of the required high pressure (Ibarz et al. 2009).

Cryoconcentration is an operation that can be used for concentrating this kind of flowing foods. This technology is in a study phase, but with very promising perspectives. One of the cryoconcentrators used is made up of plates, where the flowing food descends forming a thin layer on a cold plate, at freezing temperatures. A layer of ice is formed on the surface of the plate, and a concentrated fluid flow is obtained. This concentrate is recycled and descends again over the plate, repeating the recirculation process until concentration around 30 Brix is reached (Raventós et al. 2007). One of the limitations of this technology is that the more concentrated the juices are, the greater the viscosity, and the drive through the plate becomes more and more difficult. To obtain a cryoconcentrator device with an efficient design, it is necessary to know the viscosity of the samples that flow down on the surface of the plates.

In the case of fruit juices, this knowledge is limited, because most existing information in the bibliography refers to juices at temperatures that usually range between 5 and 80°C. Thus, the main aim of the present study was to determine the rheological behavior of clarified and depectinated pear and apple juices with different soluble solids contents, at temperatures just above their freezing point in order to provide new data that may be useful for cryoconcentration processes and equipment design.

**MATERIALS AND METHODS**

The study was carried out from samples of 70.0 Brix concentrated and clarified juices, supplied by a juice processing industry located in Mollerussa (Spain). This commercial concentrated juice was obtained in an industrial process consisting of depectination, pulp removal and concentration by evaporation. From this concentrated juice, the samples containing different soluble solids concentration were obtained by dilution with distilled water. These were the samples selected for the study of flow behavior at different temperatures, on which the freezing point depends on the soluble solids content in the juice. As the soluble solids content increases, the freezing point falls down. This study always worked above the freezing point of each sample. Studies have been performed in the range of −18° to −1°C, taking the temperature just above the freezing point of each sample as the lowest one.

**Soluble Solids Content**

Soluble solids were determined by refractometry using an Atago RX-1000 refractometer (Atago-Bussan Co., Tokyo, Japan) at a temperature of 20°C. The soluble solids concentration is expressed in °Brix.

**pH**

A Crison pH-meter (Crison Instruments S.A., Alella, Spain) was used to measure the pH of the concentrated juices.

**Sugars**

Sugar content was measured by the reduction of the Fehling reagent by reducing the sugars of the sample, according to the method of the IFFJP (1972). The Cu²⁺ ions contained in the Fehling reagent are responsible for the blue color of the solution and are converted into Cu⁺ ions by the reduction of the sugars. These ions, associated with oxygen, form Cu₂O, which gives a reddish precipitate. The Fehling reagent becomes progressively discolored until the equivalence is reached when its blue color disappears. To measure the total sugars it is first of all necessary to perform an acidic hydrolysis of the nonreducing sugars in the juice sample. These measurements were carried out on dilutions 1:6 of the concentrated juices, which were mixed with HCl 1 M and placed in a water bath at 70°C for 5 min. After that, the samples were placed in an ice bath until they reached room temperature and neutralized up to pH 6.0 with NaOH.

**Rheological Measurements**

Rheological measurements were carried out using a HAAKE RS-80 RheoStress Rheometer (Karlsruhe, Germany), equipped with coaxial cylinders sensor system Z40-DIN (radii ratio 1.0847). For the control of temperature, a Thermo HAAKE C25 P bath was used, using glycol-water solution (50% w/w) as coolant fluid, which allows the temperature to be set with an interval variation of ±0.2°C.

In order to evaluate the possible thixotropic behavior, the samples were sheared at a constant shear rate (100/s), and the variation of the shear stress with time was measured. To obtain the flow behavior, the samples were sheared previously at 200/s for 3 min. Later, two ramps were carried out for ascending and descending shear rate values. From these data, it is possible to build the rheogram and consequently to obtain the flow behavior parameters of the different assayed samples.

**Statistical Analysis**

The experimental results obtained in this work were fitted to different kinetic and mathematical models using the
StatGraphics Plus 5.1 (STSC Inc. Rockville, MD) statistical data processing software. All the reported values correspond to the estimated parameters and the limits of the 95% confidence level interval.

RESULTS AND DISCUSSION

Regarding the pH of the used samples, concentrated pear juice had a pH value of 3.85, and apple juice of 3.39. Dilution 1:6 of the concentrated pear juice contained 30.2 g/L of reducing sugars and 38.7 g/L of nonreducing sugars. In apple juice, values were 40.2 g/L of reducing sugars and 20.1 g/L of nonreducing ones, also for the dilution 1:6.

First of all, the samples were sheared at a constant rate at the lowest temperature that they reached without freezing, and it was noted that the value of the shear stress did not change with shearing time. Thus, the samples did not present thixotropic behavior. The rheograms have been carried out at shear rate intervals that depend on the soluble solids content.

All the obtained rheograms correspond to a straight line that passes through the origin of coordinates as in the case of a Newtonian fluid, not to a characteristic curve of a pseudoplastic fluid (if the yield stress is null) or Herschel–Bulkley one (if the yield stress is different from zero), as it is usual in the juices that have pulp and pectin (Falguera and Ibarz 2010; Falguera et al. 2010). Figures 1 and 2 show the rheograms that were obtained with clarified pear and apple juices with different soluble solids concentration at the temperature of −1°C.

In all the cases studied in this piece of work, it was observed that the variation of the shear stress with the shear rate was fitted by a straight line, being the slope value the viscosity of the sample according to Newton’s equation:

\[ \sigma = \eta \cdot \dot{\gamma} \]  

where \( \sigma \) is the shear stress, \( \dot{\gamma} \) the shear rate and \( \eta \) the viscosity.

Tables 1 and 2 summarize viscosity values for pear and apple juices data. The first aspect that can be easily seen is that the higher the soluble solids content, the lower the freezing
TABLE 1. VISCOSITY OF CLARIFIED PEAR JUICE AS A FUNCTION OF TEMPERATURE AND SOLUBLE SOLIDS CONTENT

<table>
<thead>
<tr>
<th>T(C)</th>
<th>10 °Brix</th>
<th>20 °Brix</th>
<th>30 °Brix</th>
<th>40 °Brix</th>
<th>50 °Brix</th>
<th>60 °Brix</th>
<th>70 °Brix</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>η (Pa·s)</td>
<td>R²</td>
<td>η (Pa·s)</td>
<td>R²</td>
<td>η (Pa·s)</td>
<td>R²</td>
<td>η (Pa·s)</td>
</tr>
<tr>
<td>-1</td>
<td>0.0069 ± 0.0004</td>
<td>0.9429</td>
<td>0.0082 ± 0.0005</td>
<td>0.9281</td>
<td>0.0123 ± 0.0008</td>
<td>0.9299</td>
<td>0.01598 ± 0.00015</td>
</tr>
<tr>
<td>-3</td>
<td>0.0126 ± 0.0008</td>
<td>0.9311</td>
<td>0.01752 ± 0.00014</td>
<td>0.9990</td>
<td>0.04687 ± 0.00006</td>
<td>0.9999</td>
<td>0.2192 ± 0.0011</td>
</tr>
<tr>
<td>-6</td>
<td>0.02017 ± 0.00012</td>
<td>0.9994</td>
<td>0.05708 ± 0.00003</td>
<td>0.9999</td>
<td>0.2834 ± 0.0015</td>
<td>0.9995</td>
<td>8.3 ± 0.3</td>
</tr>
<tr>
<td>-9</td>
<td>0.07063 ± 0.00013</td>
<td>0.9999</td>
<td>0.3805 ± 0.0018</td>
<td>0.9996</td>
<td>12.440 ± 0.009</td>
<td>0.9999</td>
<td></td>
</tr>
<tr>
<td>-12</td>
<td>0.08840 ± 0.00021</td>
<td>0.9999</td>
<td>0.4744 ± 0.0014</td>
<td>0.9999</td>
<td>19.674 ± 0.013</td>
<td>0.9999</td>
<td></td>
</tr>
<tr>
<td>-15</td>
<td>0.6484 ± 0.0017</td>
<td>0.9999</td>
<td>30.153 ± 0.038</td>
<td>0.9999</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-18</td>
<td>0.8597 ± 0.0034</td>
<td>0.9997</td>
<td>67.3 ± 1.9</td>
<td>0.9871</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Significance level: α = 0.05.

TABLE 2. VISCOSITY OF CLARIFIED APPLE JUICE AS A FUNCTION OF TEMPERATURE AND SOLUBLE SOLIDS CONTENT

<table>
<thead>
<tr>
<th>T(C)</th>
<th>10 °Brix</th>
<th>20 °Brix</th>
<th>30 °Brix</th>
<th>40 °Brix</th>
<th>50 °Brix</th>
<th>60 °Brix</th>
<th>70 °Brix</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>η (Pa·s)</td>
<td>R²</td>
<td>η (Pa·s)</td>
<td>R²</td>
<td>η (Pa·s)</td>
<td>R²</td>
<td>η (Pa·s)</td>
</tr>
<tr>
<td>-1</td>
<td>0.0070 ± 0.0004</td>
<td>0.9420</td>
<td>0.0082 ± 0.0006</td>
<td>0.9270</td>
<td>0.0121 ± 0.0008</td>
<td>0.9337</td>
<td>0.0152 ± 0.0003</td>
</tr>
<tr>
<td>-3</td>
<td>0.0125 ± 0.0008</td>
<td>0.9306</td>
<td>0.01657 ± 0.00016</td>
<td>0.9986</td>
<td>0.04601 ± 0.00006</td>
<td>0.9999</td>
<td>0.1967 ± 0.0011</td>
</tr>
<tr>
<td>-6</td>
<td>0.01865 ± 0.00012</td>
<td>0.9993</td>
<td>0.05126 ± 0.00003</td>
<td>0.9999</td>
<td>0.2569 ± 0.0021</td>
<td>0.999</td>
<td>5.095 ± 0.015</td>
</tr>
<tr>
<td>-9</td>
<td>0.06490 ± 0.00007</td>
<td>0.9999</td>
<td>0.3308 ± 0.0017</td>
<td>0.9996</td>
<td>7.189 ± 0.016</td>
<td>0.9999</td>
<td></td>
</tr>
<tr>
<td>-12</td>
<td>0.07951 ± 0.00016</td>
<td>0.9999</td>
<td>0.4315 ± 0.0038</td>
<td>0.9988</td>
<td>11.615 ± 0.011</td>
<td>0.9999</td>
<td></td>
</tr>
<tr>
<td>-15</td>
<td>0.630 ± 0.013</td>
<td>0.9933</td>
<td>19.36 ± 0.08</td>
<td>0.9997</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-18</td>
<td>0.895 ± 0.020</td>
<td>0.9921</td>
<td>34.25 ± 0.24</td>
<td>0.9992</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Significance level: α = 0.05.
temperature of the sample. In addition, it is plain to see how, as expected, in both cases the viscosity grows with increasing soluble solids concentration and with decreasing temperature. The obtained values are similar to those obtained in previous research (Ibarz et al. 2009) for clarified orange juice at similar temperatures and soluble solids content. Moreover, when soluble solids content is high, temperature has a greater effect on viscosity. In this way, for low concentrations (until 40 Brix) viscosity values slightly increase with lower temperature. But in the case of the 50-Brix sample, lowering the temperature from −1 to −12°C produces an increase in viscosity of 116% for the pear juice and almost 85% in the case of apple, i.e., there is almost a double effect in the viscosity values. Pear and apple values are similar in samples with soluble solids content below 60 Brix. However, 70-Brix samples of pear juice have a higher viscosity than apple juice ones at any studied temperature.

**Effect of Temperature**

The variation of viscosity with temperature can be described by an Arrhenius-type equation (Saravacos 1970; Rao et al. 1984; Ibarz et al. 1994, 1996):

\[ \eta = K_0 \exp \left( \frac{E_a}{RT} \right) \]  

(2)

where \( \eta \) is the viscosity; \( K_0 \) is a constant,

\( E_a \) is the flow activation energy, \( R \) is the gas constant and \( T \) the absolute temperature. Because a minimum of four data points are required to evaluate the effect of temperature, it has only been carried out for the samples with high soluble solids content (above 50 Brix), as it was possible to build rheograms until lower temperatures without sample freezing. Data from Tables 1 and 2 were fitted to Eq. (2) by means of a nonlinear regression in order to find the values of its parameters that minimize the sum of squared residuals by StatGraphics software. Table 3 shows the parameters resulting from these adjustments.

Flow activation energy increases with the soluble solids contents, and the constant \( K_0 \) shows an inverse trend. This tendency is similar to that of other clarified juices (Saravacos 1970; Khalil et al. 1989; Ibarz et al. 2009). Thus, the effect of temperature in decreasing the viscosity of clarified depectinated pear and apple juices is more pronounced as soluble solids content increases. In this way, a decrease from −15°C to −18°C leads to an increase of 33% in 60 Brix pear juice and of 42% in 60 Brix apple juice, but the same temperature change produces an increase of 123% in the 70 Brix pear sample and of 77% in the 70 Brix apple one.

The same behavior was observed by Ibarz et al. (1994) in their study about the flow behavior of clarified orange juice in a concentration range from 30.7 to 63.5 °Brix, and temperatures between 5 and 70°C. In that case, activation energy values were lower. These variations can be attributed to the difference in the temperature range used in the present work (−1/−18°C), because from the standpoint of energy, \( E_a \) is the energy that must be overcome to start a reaction or a process, and the viscosity is the resistance of a fluid that is being deformed. In this way, if the viscosity increases, the activation energy must increase. Saravacos (1970) also showed that the presence of suspended solids and long-chain polysaccharides has a decreasing effect on flow activation energy. This effect has also been reported by several other researchers (Rao 1977; Hernandez et al. 1995). In this way, the slight differences between activation energy values of pear and apple juices are probably due to the variations in reducing and nonreducing sugar content.

As it has been mentioned, pear juice has a higher concentration of nonreducing sugars, while apple juice has a higher content of reducing sugars (monosaccharides and some disaccharides). These differences in their sugar profiles may affect the flow activation energy depending on the temperature. It is known that viscosity is affected by the molecular weight of the sugars contained in the sample, and that even different monosaccharides compositions may have different effects on this parameter. As an example, Cui and Yang (2008) showed that the viscosity of an amylopectin solution was affected in a higher degree by different sugars in this order: sucrose, maltose, glucose, galactose and fructose.

**Effect of Soluble Solids Content**

As it has been already commented, soluble solids content has a definitive effect on viscosity. In this way, the viscosity of clari-
fied pear juice increases from 0.0069 Pa·s in the 10-Brix sample to 4.70 Pa·s in the 70-Brix one, and the increase in clarified apple juice is from 0.0070 to 2.625 Pa·s for the same concentration values. In order to quantify this effect, data from Tables 1 and 2 have been fitted to an exponential empirical model (Ibarz et al. 2009):

\[ \eta = \eta_0 \exp(aC) \] (3)

where \( \eta \) is the viscosity (Pa·s), \( \eta_0 \) is the viscosity when the soluble solids content is 0 Brix, \( a \) is a constant and \( C \) is the concentration (°Brix). Again, as four data points are needed, these fittings have only been carried out at temperatures of \(-3^\circ C\) and \(-1^\circ C\). Data from 70-Brix samples has not been used in these fitting because of their scale difference with other data. The results of these fittings appear in Table 4. When using this expression, other researchers (Rao et al. 1984; Ibarz et al. 1996, 2009) have found that a constant decreases as temperature increases, meaning that at higher temperatures, the viscosity will increase more slowly when the soluble solids content increases. This trend has been also observed in the present work when comparing the two regressions carried out for both pear and apple juices.

**CONCLUSIONS**

Clarified and depectinated pear and apple juices behave like Newtonian fluids in the range of studied temperatures (\(-18\) to \(-1^\circ C\)) and soluble solids content (10–70 Brix). The effect of temperature on the juices can be described with an Arrhenius-type equation. Flow activation energy was found to be in a range between 41 and 91 kJ/mol for pear juice and between 39 and 88 kJ/mol for apple juice, for concentrations between 50 and 70 Brix. The effect of the soluble solids content can be described by an empirical exponential-type equation. The parameters calculated from this equation show that at higher temperatures, the viscosity will increase more slowly when the soluble solids content increases.

**REFERENCES**


**TABLE 4. EFFECT OF SOLUBLE SOLIDS CONTENT ON JUICES VISCOSITY**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Soluble solids range (°Brix)</th>
<th>( \eta_0 ) (Pa·s)</th>
<th>( a ) (°Brix(^{-1}))</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pear</td>
<td>–1</td>
<td>10/60</td>
<td>0.00073 ± 0.00022</td>
<td>0.08 ± 0.05</td>
<td>0.9533</td>
</tr>
<tr>
<td></td>
<td>–3</td>
<td>30/60</td>
<td>0.000067 ± 0.00005</td>
<td>0.09 ± 0.07</td>
<td>0.9465</td>
</tr>
<tr>
<td>Apple</td>
<td>–1</td>
<td>10/60</td>
<td>0.00079 ± 0.00021</td>
<td>0.08 ± 0.04</td>
<td>0.9614</td>
</tr>
<tr>
<td></td>
<td>–3</td>
<td>30/60</td>
<td>0.00077 ± 0.00005</td>
<td>0.09 ± 0.07</td>
<td>0.9515</td>
</tr>
</tbody>
</table>

Significance level: \( \alpha = 0.05 \).