Rheology of microfiltrated prickly pear (Opuntia sp.) juices

M. Ennouri, E. Bourret, S. Baklouti, K. Damak, A. Rebaï, H. Attia

RÉSUMÉ
Étude rhéologique des jus de figue de Barbarie (Opuntia sp.) microfiltrés
Le jus de figue de Barbarie a été clarifié par microfiltration tangentielle sur une membrane de type minéral. Le flux de filtration a été réduit de 50 % après 60 min de fonctionnement et s’est stabilisé autour de 40 l/hm². La clarification du jus s’est traduite par un jus plus translucide et l’accentuation de la couleur jaune. Le comportement rhéologique du jus microfiltré a été étudié en fonction de la concentration (12-58 °Brix) et de la température (10-70 °C) à l’aide d’un viscosimètre avec un système de mesure de type cylindres coaxiaux. Notre étude montre que dans cet intervalle de température et pour toutes les concentrations étudiées, les concentrés de jus de figue de Barbarie microfiltrés ont un comportement Newtonien. L’effet de la température sur la viscosité des jus s’est traduit par une équation de type Arrhenius. L’effet de la concentration sur la viscosité suit une relation de type exponentiel pour toutes les températures. Les constantes rhéologiques des modèles de type Arrhenius et exponentiel ont été calculées et un modèle mathématique traduisant l’effet combiné de la température et de la concentration a été trouvé.

Mots clés
figue de Barbarie, microfiltration, clarification, rhéologie.

SUMMARY
A prickly pear juice was filtered through microfiltration mineral membrane. The flux decreased of about 50% in the first 60 min and stabilised at 40 l/hm². The clarification was illustrated by a more translucent juice and the accentuation of yellow colour. Then the rheological behaviour of micro filtrated prickly pear juice with different soluble solids content (12-58°Brix) was studied at a wide range of temperatures (10-70°C) using a viscometer with coaxial cylinders measuring system. The results indicated

2. Laboratoire de Physique Moléculaire et Structurale – Faculté de Pharmacie de Montpellier – BP 14491 – 34093 Montpellier cedex 5 – France.
5. Unité de Bioinformatique – Centre de Biotechnologie de Sfax – BP 3038 – Sfax – Tunisie.
* Corresponding author: Tél.: +216-98-278-684 – Fax: +216-74-221-160 – e-mail address: monia.ennouri@enis.rnu.tn (M. Ennouri)
that the clarified juices behave always as Newtonian fluid. The effect of temperature on their viscosity may be described by an Arrhenius-type equation. The effect of concentration on viscosity followed an exponential relationship whatever the temperatures applied. The rheological constants for the Arrhenius and exponential models were calculated and mathematical model traducing the combined effect of temperature and concentration was given.

Keywords
prickly pear, microfiltration, clarification, rheology.

1 – INTRODUCTION

In Tunisia, prickly pear fruit of Opuntia sp. grow spontaneously; it is consumed exclusively as fresh fruit. Only a small quantity being used for processing; so, there is need to create a better outlet for seasonally surplus fruits which otherwise go to waste. The available data have been especially concerned with the general physico-chemical composition of the pulp and seeds (EL KOSSORI LAMGHARI et al., 1998; ENNOURI et al., 2005). However, few reports have been published on the industrial uses of prickly pears (HOFMANN, 1980; HAMDI, 1997; SAEZ, 2000). The ability of technologies transformations have been limited to the analysis of volatile constituents of pulp (DICESARE and NANI, 1992), use of pulp in juice production (ESPINOSA et al., 1973), production of alcoholic beverage (BUSTOS, 1981), jam production (SAWAYA et al., 1983), production of natural liquid sweetener from cactus pear (SAENZ et al., 1996), and production of cocoa butter equivalents from prickly pear juice fermentation (HASSAN et al., 1995). Our study aim to improve marketability of prickly pear by producing value added products from the fruits, which are disposable for the production of juice, by studying chemical and rheological characterization of clarified prickly pear juice by tangential filtration.

Membrane separation has been applied successfully in the clarification of many fruit juices (DELOUX and PROTHON, 1998; VAILLANT et al., 2001). This process offers the advantages to process at low temperature and minimise the formation of fouling in the membrane surfaces (GIRARD and FUKUMOTO, 2000). The juices clarified with membrane treatment include that of apple (RAO et al., 1987), pear (KIRK et al., 1983), kiwi (LOZANO et al., 1986), orange and lemon (CAPANNELLI et al., 1994), pineapple (JIRARATANANON et al., 1997), passion fruit (CHIANG and YU, 1987), and starfruit (SULAIMAN et al., 1998) etc.

By microfiltering the prickly pear fruit juice, we aim to reduce the pulp and macromolecules present in the juice for producing a limpid fruit juice concentrates, which can be consumed in state or used like ingredient able to be added advantageously to many products such as ice creams, fruit syrups, jellies and fruit juices beverages (DELOUX and PROTHON, 1998; OLLE et al., 2002).

In the present paper, we tried to test the ability of prickly pear fruit juice to be clarified by tangential microfiltration process and follow the rheological behaviour of obtained permeates as a function of both temperature and concentration. These data of rheological behaviour are of great interest for the industrial process and the sensory quality.
2 - MATERIALS AND METHODS

2.1 Sample preparation

Mature prickly pear fruits of *Opuntia ficus indica* were collected in August from local varieties of Sfax (Tunisia). The fruits were washed with running water, hand-peeled, and pulped with a domestic pulper (Moulinex). The extraction of juice was performed with a textile cloth.

2.2 Tangential microfiltration of juice

Essays of microfiltration were carried out on a monotube mineral membrane (Carbosep) with a total effective filtration area of 75 mm² and 0.14 μm average pore diameter. The schematic diagram of the equipment is shown in figure 1. The system allowed the precise control of applied pressure and feed flow rate. Heating of the feed tank was assumed by the heat plate.

The following conditions, which were the optimal conditions established earlier (unpublished data), were used: average transmembrane pressure, 0.18 MPa; tangential flow velocity, 2.35 m.s⁻¹; temperature, 50°C; volume concentration factor (FCV), 1.

The MF membrane was carefully cleaned after each experiment in order to recover the original permeability. The pilot unit was rinsed with hot water (50°C). Then a 1% sodium hydroxide solution was recirculated (80°C/30 min with filtration). After rinsing with running water, a 0.5% nitric acid solution at 60°C was used during 30 min. Finally, the circuit was rinsed with distilled water.

All results presented are an average of three experiments differing by only ~ 5% for fluxes.

![Diagram of MF pilot laboratory](image-url)
2.3 Concentration of the clarified juice

The obtained permeates by microfiltration were concentrated under vacuum at 40°C to 58°Brix using a Buchi evaporator. Then, samples of 45, 35, 25, and 12°Brix were obtained by diluting this concentrated juice (58°Brix) with deionised water.

All the samples were flushed with nitrogen and kept at –20°C until analysis.

2.4 Physico-chemical analyses

Soluble solids contents of concentrates were determined at 20°C using an Abbe-Zeiss refractometer, they are expressed in °Brix. The pH was measured with a pH-meter (Mettler Toledo MP 220). Titrable acidity was determined by titration with NaOH 0.1N solution using phenolphthalein as indicator according to the standard procedures (AOAC, 1990). Reducing sugars in the juice were determined using the 3,5 dinitro salicylic acid (DNS) method (Miller, 1959) using glucose as standard.

2.5 Colour measurement

Colour was measured using a Labscan spectrocolorimeter. This instrument determined colorimetric parameters L*, a* and b* referred to illuminant D65, where L* is the lightness, a* is the red-green dimension and b* is the yellow-blue dimension. The values of a* and b* permit the calculation of hue (H* = tan⁻¹ b*/a*) and chroma [C* = (a*² + b*²)⁰.⁵].

2.6 Rheological measurements

The rheological measurements were carried out using a StressTech Reologica rheometer (Reologica Instruments AB, Lund, Sweden) with a coaxial cylinders measuring system (inner diameter 25 mm and outer diameter 27 mm). The flow curves were determined at a gradient shear rate from 1 s⁻¹ to 700 s⁻¹. A thermostatic bath was used to control the working temperature ranging from 10 to 70°C.

2.7 Statistical methods

Regression parameters were estimated using linear regression procedure (after suitable transformations of variables) in SPSS version 10. The plot in three dimensions was determined using Matlab 6.

3 – RESULTS AND DISCUSSION

3.1 Physico-chemical characteristics of the juice

The juice reconstituted to 12°Brix presented a pH of 6.50, an acidity of 1.33 g of citric acid/l of juice and reducing sugar content of 8.85 g/l (table 1). The pH indicated a low acidity in good agreement with previous results of STINTZING et al. (2003) concerning Opuntia ficus indica cultivar bianca juices. The acidity, expressed as citric acid, was higher and reducing sugars lower than values reported in the study mentioned above. The sugar-acid ratio, which characterizes sensorial qualities, was 6.65:1 lower than sensorial criterion of pleasant sweet-sour taste situated at 10:1 to 18:1. This may have been due to particle retention by microfiltration process.
3.2 Microfiltration of juice

3.2.1 Performance

Variation of microfiltrate flux related to time is given in figure 2. Flux was reduced by 50% in approximately 60 min. The initial flux of 80 l.h⁻¹.m⁻² decreased and tended to stabilise around 40 l.h⁻¹.m⁻². The obtained steady-state showed that the external fouling occurred progressively. This suggested an important heterogeneity of macromolecules (pectin, cellulose, hemicellulose...) which participate to the establishment of fouling. Similar stabilized flux (41 l.h⁻¹.m⁻²) has been observed by CHAMCHONG and NOOMHORM (1991) with a membrane of 0.2 µm nominal pore diameter for the clarification of tangerine fruit juice.

![Figure 2](image-url)

Change in permeate flux with filtration time for the prickly pear juice. Microfiltration was performed without concentration at 50°C with average transmembrane pressure of 0.18 MPa and a tangential flow velocity of 2.35 m.s⁻¹.

3.2.2 Clarification

The juice colour was determined for raw and microfiltrated juice, the parameters of colour are presented in table 2. Microfiltrated juice was more translucent than the raw juice (value of L higher; 45.53 versus 36.66), this is confirmed visually. The decrease of the a* component (red) underline that the microfiltrated juice lost few of red colour than the raw juice. On the other hand the b* component (yellow), increased in the microfiltrated juice.
juice which give to the juice an accented yellow colour. The quantitative analyses put in evidence the loss of the red colour and the accentuation of the yellow colour.

Table 2
Colour components of the raw and microfiltrated juice Lightness (L*), Chroma (C*), hue (h°), red-green dimension (a*) and yellow-blue dimension (b*).

<table>
<thead>
<tr>
<th>Colour parameters</th>
<th>Raw juice</th>
<th>Microfiltrated juice</th>
</tr>
</thead>
<tbody>
<tr>
<td>L*</td>
<td>36.66 ± (0.02)</td>
<td>45.53 ± (0.07)</td>
</tr>
<tr>
<td>C*</td>
<td>67.29 ± (0.06)</td>
<td>76.58 ± (0.23)</td>
</tr>
<tr>
<td>h°</td>
<td>66.16 ± (0.08)</td>
<td>78.31 ± (0.06)</td>
</tr>
<tr>
<td>a*</td>
<td>34.1 ± (0.10)</td>
<td>25.59 ± (0.15)</td>
</tr>
<tr>
<td>b*</td>
<td>58.01 ± (0.01)</td>
<td>72.18 ± (0.19)</td>
</tr>
</tbody>
</table>

1. Mean values of triplicate measurements; (±SD)=standard deviation.

3.3 Rheological behaviour

3.3.1 Flow curves

The rheological behaviour of microfiltrated prickly pear juice was studied over a wide range of concentration (12-58°Brix) and wide range of temperature (10-70°C). The experimental results as shear rate versus shear stress plots showed that all the concentrates, i.e. 12-58°Brix, exhibited Newtonian behaviour (figure 3):

\[ \tau = \eta \gamma \]  

where \( \tau \) is the shear stress (Pa), \( \gamma \) is the shear rate (s\(^{-1}\)) and \( \eta \) is the coefficient of viscosity (Pa s).

Previously the flow of concentrated prickly pear juice was reported pseudoplastic, depending on the type of juice, pulped or pressed, and on the degree of concentration. The rheological behaviour changed to Newtonian in low levels of solid contents (SAENZ and COSTELL, 1990). The Newtonian flow of present prickly pear juice may be related to pulp and pectin content which are partially stopped by the microfiltration membrane.

3.3.2 Effect of temperature

The rheograms at different temperatures are given in figure 4. The influence of temperature on the viscosity of liquid fruit products has been described by an Arrhenius-type relationship (RAO et al., 1984; IBARZ et al., 1989; KHALIL et al., 1989):

\[ \eta = \eta_0 \exp \left( \frac{E_a}{RT} \right) \]  

where \( \eta \) is the coefficient of dynamic viscosity (Pa.s), \( \eta_0 \) is a constant (Pa.s), \( E_a \) is the activation energy for flow (kcal g-mol\(^{-1}\)), \( R \) is the gas constant (1.987 cal g-mol\(^{-1}\)) and \( T \) is the absolute temperature (K). Table 3 lists the rheological constants for the Arrhenius model. The general tendency for the activation energy is to increase with the soluble solids concentration.
Table 3

<table>
<thead>
<tr>
<th>C (°Brix)</th>
<th>( \eta_0 ) (Pas)</th>
<th>( E_a ) (kcal/mol)</th>
<th>( r^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>( 7.11 \times 10^{-6} )</td>
<td>3.20</td>
<td>0.9466</td>
</tr>
<tr>
<td>25</td>
<td>( 13.44 \times 10^{-6} )</td>
<td>3.10</td>
<td>0.9740</td>
</tr>
<tr>
<td>35</td>
<td>( 9.03 \times 10^{-6} )</td>
<td>3.60</td>
<td>0.9738</td>
</tr>
<tr>
<td>45</td>
<td>( 9.88 \times 10^{-6} )</td>
<td>3.97</td>
<td>0.9874</td>
</tr>
<tr>
<td>58</td>
<td>( 1.29 \times 10^{-6} )</td>
<td>5.95</td>
<td>0.9600</td>
</tr>
</tbody>
</table>

Figure 3

Flow curves for prickly pear juice concentrates at 10°C. Concentrations (♦ 12°Brix, • 25°Brix, △ 35°Brix, × 45°Brix and ο 58°Brix).

Figure 4

Prickly pear juice rheograms at 58°Brix as a function of temperature (♦ 10°C, × 25°C, △ 40°C, ο 55°C and + 70°C).
3.3.3 Effect of concentration

Two types of equation describing the change in viscosity coefficient with the soluble-solids content are reported in the literature (VITALI and Rao, 1982): power law and exponential type equation:

\[ \eta = \eta_i (C)^{b_1} \]  
\[ \eta = \eta_2 \exp(b_2C) \]

In both equations, \( \eta_i \) and \( b_i \) are constants, \( C \) is the concentration in °Brix and \( \eta \) is the viscosity. Both models were applied by many authors for clarified banana juice (KHALIL et al., 1989), clarified orange juices (IBARZ et al., 1994), and clarified cherry juices (Giner et al., 1996). Table 4 lists the values of the parameters for the power-law and the exponential relations [equations (3) and (4)]. According to the values of obtained correlation coefficient, it seems that exponential model gives better fit than power-law model. However, the following form of exponential type equation gives the best fit at all temperatures:

\[ \eta = \eta_3 \exp (AC + BC^2) \]

Where \( \eta_3, A \) and \( B \) are constants. The values of the parameters are listed table 5. This model was previously used with success for clarified pear juice (IBARZ et al., 1989).

Table 4
Effect of concentration (C) on the viscosity of Opuntia ficus indica juices, at different temperatures (T) (\( \eta_i, \eta_2, b_1, b_2 \) constants ; \( r \) correlation coefficient).

<table>
<thead>
<tr>
<th>T°C</th>
<th>( \eta_1 ) (Pa.s)</th>
<th>( b_1 )</th>
<th>( r^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>7.24 × 10^-4</td>
<td>2.73</td>
<td>0.9402</td>
</tr>
<tr>
<td>25</td>
<td>10.26 × 10^-4</td>
<td>2.46</td>
<td>0.9503</td>
</tr>
<tr>
<td>40</td>
<td>16.62 × 10^-4</td>
<td>2.23</td>
<td>0.9534</td>
</tr>
<tr>
<td>55</td>
<td>8.31 × 10^-4</td>
<td>2.39</td>
<td>0.9438</td>
</tr>
<tr>
<td>70</td>
<td>1.61 × 10^-4</td>
<td>2.65</td>
<td>0.9826</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T°C</th>
<th>( \eta_2 ) (Pa.s)</th>
<th>( A ) (Brix^-1)</th>
<th>( B ) (Brix^-2)</th>
<th>( r^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.1125</td>
<td>0.106</td>
<td>0.9972</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0.1686</td>
<td>0.086</td>
<td>0.9972</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>0.2188</td>
<td>0.074</td>
<td>0.9960</td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>0.1097</td>
<td>0.0860</td>
<td>0.9955</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>0.1979</td>
<td>0.0642</td>
<td>0.9966</td>
<td></td>
</tr>
</tbody>
</table>

Table 5
Effect of concentration (C) on the viscosity of Opuntia ficus indica juices, at different temperatures (T) (K, A and B are constants; \( r^2 \) correlation coefficient).

<table>
<thead>
<tr>
<th>T°C</th>
<th>( \eta_3 ) (Pa.s)</th>
<th>A (Brix^-1)</th>
<th>B (Brix^-2)</th>
<th>( r^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2.907</td>
<td>-0.0310</td>
<td>0.0014</td>
<td>0.9997</td>
</tr>
<tr>
<td>25</td>
<td>1.435</td>
<td>-0.0072</td>
<td>0.0009</td>
<td>0.9999</td>
</tr>
<tr>
<td>40</td>
<td>1.205</td>
<td>-0.0028</td>
<td>0.0008</td>
<td>0.9996</td>
</tr>
<tr>
<td>55</td>
<td>0.9904</td>
<td>-0.0016</td>
<td>0.0008</td>
<td>0.9998</td>
</tr>
<tr>
<td>70</td>
<td>0.6117</td>
<td>0.0116</td>
<td>0.0005</td>
<td>0.9994</td>
</tr>
</tbody>
</table>
3.3.4 Combined effect of temperature and concentration

It is interesting to obtain a single expression including the effect of temperature and soluble solids contents on the rheological behaviour. For *Opuntia ficus indica* juice it is assumed (GINER *et al.*, 1996; IBARZ *et al.*, 1996) that viscosity varies with temperature and concentration according to an exponential equation of the type:

\[ \eta = \eta_3 \exp \left( \frac{E_a}{RT} + b_3 C \right) \]  

**Model 1**  

\[ \eta = \eta_4 \exp \left( \frac{E_a}{RT} + b_4 C + b_5 C^2 \right) \]  

**Model 2**

in which \( \eta_3, \eta_4 \) and \( b_3, b_4, b_5 \) are the parameters to be determined, \( E_a \) is the activation energy of flow, \( T \) is the absolute temperature. The variation of viscosity with temperature and concentration was fitted to the linear form of Eq. (6) and Eq. (7) by mean square method. The parameters of the two models are illustrated in table 6.

<table>
<thead>
<tr>
<th>Model</th>
<th>Equation</th>
<th>i</th>
<th>( \eta_i ) (Pa.s)</th>
<th>( b_i )</th>
<th>( E_a ) (Kcal/mol)</th>
<th>( r^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(6)</td>
<td>3</td>
<td>( 8.93 \times 10^{-7} )</td>
<td>5.83 ( \times 10^{-2} ) (Brix(^{-1}))</td>
<td>3.922</td>
<td>0.975</td>
</tr>
<tr>
<td>2</td>
<td>(7)</td>
<td>4</td>
<td>( 2.03 \times 10^{-6} )</td>
<td>-6.34( \times 10^{-4} )(Brix(^{-1}))</td>
<td>3.922</td>
<td>0.992</td>
</tr>
<tr>
<td>2</td>
<td>(7)</td>
<td>5</td>
<td>( - )</td>
<td>( 8.43 \times 10^{-4} ) (Brix(^2))</td>
<td>( - )</td>
<td>( - )</td>
</tr>
</tbody>
</table>

Table 6

Combined effect of temperature and concentration on viscosity parameters of Eqs. (6) and (7).

Figure 5 is a three-dimensional plot of viscosity-temperature-concentration for the samples according to Eq. (7). The measured values of viscosity for each temperature are compared to predicted viscosities (Figure 6).
Statistical correlation curves between the predicted and measured viscosity show a reasonable agreement, with $r^2$-value of 0.967. Therefore, the mathematical models obtained would be very useful for fast determination of prickly pear juice viscosity during evaporation. As a unit operation in food processing, evaporation is usually a vital step for improving the energy efficiency of a subsequent process such as drying.

![Figure 6](image)

Plot of experimental viscosity versus calculated viscosity. Concentration ($\diamondsuit$ 12°Brix, $\bullet$ 25°Brix, $\Delta$ 35°Brix, $\times$ 45°Brix and $\circ$ 58°Brix).

4 – CONCLUSION

A prickly pear juice was for the first time clarified by microfiltration to obtain juice with a reduced content of pulp. The performance traduced by the flux and the clarification was satisfactory. This process offers the advantages of a separation at low temperature and requires low energy input. Then the microfiltrated juice was investigated for chemical and rheological properties.

The sugar acid ratio characterizing sensorial qualities was lower than sensorial criterion of pleasant sweet sour taste, that data might be examined and corrected for deliver a pleasant product to the market.

The parameters of colour were studied for raw and microfiltrated prickly pear juice. The obtained juice has a yellow-orange colour that makes the natural product attractive for the consumers. The parameters $a^*$ and $b^*$ were in good agreement with this visual colour.

The clarified juice was concentrated up to 58°Brix. Rheological behaviour of concentrated juices was tested at temperatures varying from 10 to 70°C. Our study shows that for this range of temperatures with soluble solids content 12-58°Brix, microfiltrated prickly pear juices have a Newtonian flow, probably related to the nature of polysaccharides contents of juice.

The combined effect of temperature and concentration was fitted to mathematical model. Within the range of 12-58°Brix and temperatures between 10-70°C, the relation is applicable as:

$$\eta = 2.03 \times 10^{-6} \exp \left( \frac{1974}{T} - 6.34 \times 10^{-4} C + 8.43 \times 10^{-4} C^2 \right)$$
Further investigations should be carried out on the nature of particle retained by the microfiltration membrane (polysaccharides, pectin...) and the influence of process on yield of juice.

REFERENCES


HOFFMANN W., 1980. The many uses of prickly pear (Opuntia Mill.) in Peru and Mexico. Plant Research and Development, 12, 58-68.


