HYPERFILTRATION OF RIBES NIGRUM JUICE

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ABSTRACT

Blackcurrant juice is very popular among consumers due to its high content of mineral salts, C-vitamin, P-, B1-, B2– vitamin and provitamin A also. The scope of this study was to examine the applicability of a pilot scale reverse osmosis system for the concentration of different enzyme pretreated blackcurrant juice by AFC - 80 polyamide tubular membrane. With two pectinase enzyme preparation (Panzym Super E and Trenolin Rot DF) of the fresh juice for enzymatic depectinization was investigated.
For description of the concentration process and the osmotic pressure model has been used. Van't Hoff model can be applied for the calculation of osmotic pressure differences dependence on the difference of concentrate and permeate concentration. Rautenbach model can be also used, which determines the osmotic pressure in the knowledge of the concentration.

1. INTRODUCTION

Blackcurrant juice is very popular among consumers due to its pleasant taste, as well as its numerous beneficial health effects. It contains mineral salts and vitamins in a great amount. Its C-vitamin concentration is 4–5 times higher than that of the lemon. It is also rich in P -, B1 -,B2 - vitamin, in provitamin A in pigment and anthocyanins [Bánvölgyi et al, 2006]. After harvesting the berries, blackcurrants are usually processed into juices. One of the basic unit operations of fruit juice technology is the concentration process to reduce liquid volume and, therefore, storage and transportation costs. Concentration is expected to increase the total solids content (TSS) of the juice from 10 % up to 75 % by weight [Gunnar Jonsson et al, 2003].
To provide consumers with all beneficial properties of the fresh berry in the products, it is necessary to apply gentle processing method that promotes the preservation of the original characteristics of berries. In recent years, membrane processes such as nanofiltration (NF), reverse osmosis (RO) and alternative membrane based separation: membrane distillation (MD) and pervaporation have been evaluated as concentration processes in fruit juice [Fukumoto and Girard, 2000]. RO has achieved some commercial success in the fruit juice concentration: it presents the advantages of a lower thermal damage to the product, reduction in energy consumption and lower capital equipment costs. However the final concentration of juices is limited to about 25–30 °Brix due to the high osmotic pressure of the feed at those levels [Cassano et at, 2007]. Leaving out prefiltration by microfiltration (MF) or ultrafiltration (UF), and the possibility to avoid enzyme treatment is significant from economical point of view [Heinonen et al, 2001, Keiski et al, 2006].

The aim of the research was to concentrate blackcurrant juice at a pilot scale by reverse osmosis (RO). The effect of clarification by centrifugation, and an enzymatic depectinization was compared to the juice without any pre-treatment by the means of achieved final TSS content, and permeate flux during concentration. To evaluate the possibility of fouling during juice concentration, the osmotic pressure model was used, and the total resistance was calculated taking into account the membrane resistance and fouling resistance.

2. MATERIALS AND METHODS

Extraction and pretreatment of juices

The blackcurrant berries were provided by Fitomark 94 Ltd Hungary farm. Berries were treated with enzymes (pre-press pectinases by Trenolin enzyme) to ease the pressing and increase the yield. They were pressed using a Pera PN BUCHER compressor. The juice was afterwards pasteurized, clarified conventionally by centrifuging. The blackcurrant juices were depectinized by pectolitic enzyme preparations (Panzym Super E and Trenolin Rot DF). The Panzym Super E liquid preparation (pectolitic activity of 2000 FDU 55 °C/mL) is obtained from selected strains of *Aspergillus niger*. A small amount of emzymes (8 ml / 20 l) were used and the treatment time was 12 hours in the case of Panzym Super E at 25 °C, and for 24 hours and 96 hours in case of Trenolin at 25 °C and in refrigerator 6 °C, respectively.

RO unit and experimental procedures

The RO tubular B1 module, which comprises 18 perforated stainless steel tubes from Paterson Candy International (PCI) was used. Each tube is lined with a membrane element of 12.5 mm of diameter and 1.2 m length (0.9 m^2 of total area). The tubes are connected in series. The module contained AFC 80 polyamide tubular membrane. This compact tubular method has been developed to ease the concentration of highly viscous fluids. Temperature is controlled by means of a heat exchanger. After passing through the heat exchanger, the feed temperature was set to 25 °C. Then they were fed through the membrane module and recirculated back to their reservoir. The trans-membrane pressure was fixed at 60 bar, and 60 L of the juices were concentrated in each batches. Cleaning of the membranes was carried out after every test run as follows. The membrane was first rinsed by tap water at a recirculation rate of 25 L/h and trans-membrane pressure of 60 bar for 30 min. This was followed by circulating 0.1 w/w% NaOH solution at same conditions for 30 min and rinsed by tap water. Finally a 0.5 % citric acid solution has been used and circulated for 30 min, followed by rinsing with tap water. Before and after each cleaning procedure, the pure water flux was measured and used later on for the calculation of the total resistance based on resistance-in-series model.

Analytical and calculation methods

Total soluble solid (TSS) content was measured using an Atago PR-101 α digital refractometer. Measurements were made at ambient temperature. TSS was expressed as °Brix. Prior to each set of measurements, the instrument was calibrated at 0 °Brix using deionised water.

3. RESULTS AND DISCUSSION

Permeate flux during RO

The initial total soluble solid content of the feed varied between 16.1-18.9 and has been at the end of the concentration 28.2, 25.7, 25.4 and 22.4 for Panzym Super E, Trenolin Rot at 6°C, Trenolin Rot at 25°C, and Control juice respectively. Add some values, e.g. the maximum TSS of 28.2 °Brix was achieved in case of PSE enzyme pretreatment. At the same time the concentrate volume has been reduced by about one half compared to the feed volume. As it was shown in the Fig. 1, the fluctuation of TSS concentration is rather various at different pretreatment samples. During the first 100 min. the concentration was 26.6, 24.7, 24.2 and 21.7 °Brix PSE, Trenolin at 6°C, Trenolin at 25°C and the Control respectively.

In this figure also could see there is no significant difference between Trenolin samples. However the TSS of Trenolin treated juices was higher till the first 50 minutes than the PSE treated after a while this tendency changed. It seems to be the juice treated with PSE enzyme less attaches in the pores of the RO membrane therefore the fouling will occur later.

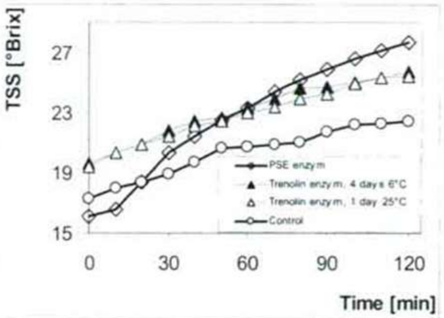

Fig. 1. Comparison of TSS values at different pretreatments.

The permeate fluxes during the concentration procedure varied depending on the feed and applied pretreatment. Permeate flux decreased with rise of TSS in the Fig. 2. When the running progressed the °Brix increased and the most abatement of flux was in the case of PSE enzyme. It was also proven that the highest decreasing rate was observed in PSE. The data are illustrated in Fig. 2 for the depectinized juices (Panzym Super E and Trenolin Rot), and the Control juice. The greatest permeate flux was achieved in the concentration of juice that has been previously depectinized by Panzym Super E treated. The achievable maximum TSS was the lowest in Control case only 22.4 °Brix contrary to depectinized samples. Therefore it is advisable that the depectinization process is carried out at room temperature as it does not require the use of extra energy opposite to refrigeration.

Shown the dynamic of the flux decline which is measured by J/J_0. The normalized fluxes (J/J_0, where J_0 is the measured initial permeate flux value $[L/(m^2h)]$) are plotted on the function of the TSS as shown in the Fig. 3. The normalized fluxes of the different pretreated juices decreased as the TSS rose which was correspond with the literature data of V. Piironen et al measuring in 2003 [Borquez et al, 2002, Piironen et al, 2003]. Since the decreasing rate of the control and Trenolin treated samples were much higher than the PSE treated sample, the application of the pretreatment with PSE is the most economically.

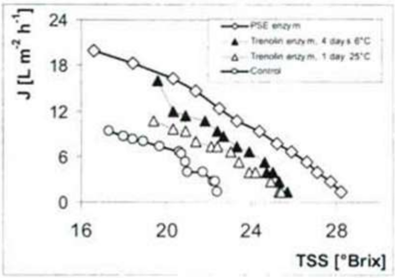

Fig. 2. The effect of TSS on the fluxes.

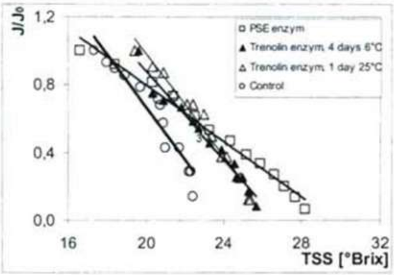

Fig. 3. The normalized flux values.

a. Mathematical modeling

The resistance model of the membrane separation defines the pure water flux as the quotient of the trans-membrane pressure – driving force (Δp_{TM}, Pa) – and the resistance (R_M, 1/m, calculated by water dynamic viscosity: η_W, Pas) arising from the pore size of the membrane – material feature.

$$J_W = \frac{\Delta p_{TM}}{\eta_W \cdot R_M} \qquad (1)$$

The fouling resistance of the applied membranes can be determined from the water flux (J_F, m/s) – measured on a fixed temperature – after flushing the membrane with tap water after concentration test using the following formula:

$$R_F = \frac{\Delta p}{J_F * \eta_W} - R_M \qquad [1/m] \qquad (2)$$

As it known the total resistance is composed of two resistances as:

$$R_T = R_M + R_F \qquad [1/m] \qquad (3)$$

At membrane filtration of liquid mixtures the osmotic pressure model is valid which determines the flux (J, m/s) as the quotient of difference of the trans-membrane pressure (Δp_{TM}, Pa), the osmotic pressure difference ($\Delta\pi$, Pa), and the total membrane resistance (R_T, 1/m). The effect of temperature integrated is into the equation in the knowledge of the permeate (practically water) viscosity (η_w, Pas).

$$J = \frac{\Delta p_{TM} - \Delta\pi}{\eta_W \cdot (R_M + R_F)} \qquad [L/(m^2h)] \qquad (4)$$

Using eqs. (1) – (3) the resistances could be calculated. The results are illustrated in Table 1. The membrane resistance was the same in all cases after effective cleaning, as it has mentioned in experimental procedure. It should be noted that the fouling resistance (R_F) was found to be an order of magnitude lower than the membrane resistance.

The highest fouling resistance was measured with Control and with Trenolin enzyme after 1 day treatment.

Table 1. Calculated resistances of different pretreated juice types.

Pretreatment	R_M	R_F	R_{Total}
Control	$2.92 \cdot 10^{14}$	$1.985 \cdot 10^{13}$	$3.119 \cdot 10^{14}$
PSE enzyme	$2.92 \cdot 10^{14}$	$1.141 \cdot 10^{13}$	$3.034 \cdot 10^{14}$
Trenolin enzyme, 4 days 6°C	$2.92 \cdot 10^{14}$	$1.578 \cdot 10^{13}$	$3.078 \cdot 10^{14}$
Trenolin enzyme, 1 day 25°C	$2.92 \cdot 10^{14}$	$1.962 \cdot 10^{13}$	$3.116 \cdot 10^{14}$

The biggest effect on fouling resistance was shown by PSE enzyme. 41.9% lower R_F value was measured in PSE treated samples than in the case of Control. On the other hand, the fouling resistance seemed not to be determining in the matter of permeate flux, because it is an order of magnitude lower than the membrane resistance, since there was hardly any difference between the total resistances. On the basis of previous statement, the permeate flux can be expressed by using the simplified form of eq. (4):

$$J = \frac{\Delta p_{TM} - \Delta \pi}{\eta \cdot R_M} \qquad [L/(m^2h)] \qquad (5)$$

It is possible that the glucose molecules in the boundary layer near the membrane play a role in the creation of the osmotic pressure. The van't Hoff model can be applied for this phenomenon which determines the osmotic pressure dependence on the difference of concentrate (c_R, $kmol/m^3$) and permeate (c_P, $kmol/m^3$) concentration. R=8314.472 J/kmolK universal gas constant, T=298.15 K temperature of experiment.

$$\Delta \pi = (c_R - c_P) \cdot R \cdot T \qquad [Pa] \qquad (6)$$

Next to the van't Hoff model, the two variables (a, Pa; n, -) Rautenbach model can be used, which determines the osmotic pressure in the knowledge of the concentration (c, Brix°).

$$\pi = a \cdot c^n \qquad [Pa] \qquad (7)$$

By introducing the modified exponential equation of Rautenbach model, where the concentration of the permeate side (c_P) was not taken into consideration, the following formula is obtained:

$$\Delta \pi = a \cdot c_R^n \qquad [Pa] \qquad (8)$$

By the combination of the equations above, the following one is obtained. Taking its logarithm and introducing the pure water flux (J_W, m/s), the two variables can be determined plotting log (J-J_W) versus log c_R (*Table 2*).

$$J = J_W - \frac{a}{\eta_w \cdot R_M} \cdot c_R^n \qquad [L/(m^2h)] \qquad (9)$$

Table 2. The coefficients of Rautenbach-model

Pretreatment	a [10^5 Pa]	n [-]
Control	0,3331	-5,0579
PSE enzyme	0,4161	-5,1885
Trenolin enzyme, 4 days 6°C	0,5637	-5,4005
Trenolin enzyme, 1 day 25°C	0,4161	-5,1885

In the case of the mathematical modeling of the experimental process the Rautenbach model with the exponential relation was better than the van't Hoff one in both processes. The parameters of the experimental relation include the features of the membrane and the raw material.

The reason for under estimation of the osmotic pressure in case of the van't Hoff model could be the fact that it was calculated only on the basis of sugar concentration; even it is well known that the other components of the juice also influence the osmotic pressure of the juice. For these calculations a detailed analysis of the concentration of juice components is necessary which makes the mathematical modeling complicated. The Rautenbach equation is more simple, even empirical but suitable for description of the results of laboratory experiments and useful for designing the pilot and small industrial equipments.

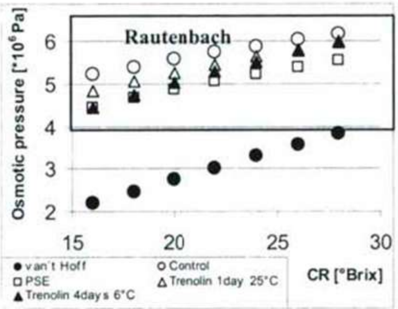

Fig.4. Calculated osmotic pressures by Rautenbach and van't Hoff model.

Higher calculated osmotic pressures were shown by empiric Rautenbach model than van't Hoff (Fig. 4), but lower in case of depectinized samples. This allegation is just more or less true, because in fact the membrane and fouling resistances were determined but the macro and micro solids resistances were not examined during the concentration. Inasmuch the content of TSS was not known exactly, the normative model is the Rautenbach and the measured fluxes of the Rautenbach are the relevant (Fig. 5-6).

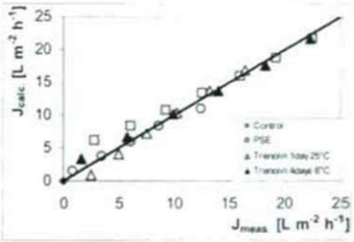

Fig.5. Deviation of calculated and measured fluxes by Rautenbach model. The line is the calculated flux.

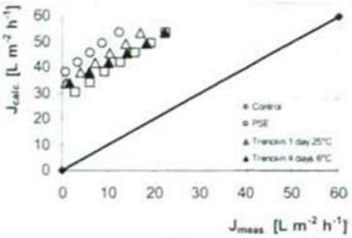

Fig.6. Deviation of calculated and measured fluxes by van't Hoff model. The line is the calculated flux.

4. CONCLUSIONS

The different enzyme pretreatment, with two commercially available pectinase enzymes preparation (Panzym Super E and Trenolin Rot DF) of the fresh juice for enzymatic depectinization was investigated in the interest of different pectinase effects. The highest concentration ratio was observed in case of PSE pretreatment. The total soluble solid content of the concentration was risen 28.2, 25.7, 25.4 and 22.4 for Panzym Super E, Trenolin Rot at 6 °C, Trenolin Rot at 25 °C and Control juice respectively. The highest permeate flux of 20 L/(m^{2}h) and TSS of 28.2 °Brix was achieved in the concentration of juice that has been previously depectinized by Panzym Super E. There has not been significant differences of the two Trenolin treatments in the terms of permeate flux, therefore it is advisable that the depectinization process is carried out at room temperature as it does not require the use of extra energy opposite to refrigeration.
It has been concluded that reverse osmosis was viable method for concentration of blackcurrant juices with the applied membrane at 60 bar trans-membrane pressure and 30 °C operating temperature.
The depectinization effects of PSE and Trenolin enzymes were obvious, which decreased the different resistances and increased the flux. PSE mighty decreased the fouling, while the reduction was lower in presence of Trenolıns.

Since the glucose molecules in the boundary layer near the membrane play a role in the creation of the osmotic pressure, van't Hoff model can be applied for this phenomenon which determines the osmotic pressure dependence on the difference of concentrate and permeate concentration. Next to the van't Hoff model, Rautenbach model can be used, which determines the osmotic pressure in the knowledge of the concentration.
Higher calculated osmotic pressures were calculated by empiric Rautenbach model than van't Hoff and the relevant model was the Rautenbach.
The measured flux values and the calculated fluxes using van't Hoff model were significantly difference which all goes to show this model should not apply for Ribes nigrum juices using Rautenbach model is recommended for this kind of process modeling.

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