

Contents lists available at [ScienceDirect](http://www.sciencedirect.com)

Journal of Food Engineering

journal homepage: www.elsevier.com/locate/jfoodeng

Concentration of aroma compounds from an industrial solution of soluble coffee by pervaporation process



Thiago André Weschenfelder^{a,*}, Pedro Lantin^a, Marcelo Caldeira Viegas^c,
Fernanda de Castilhos^b, Agnes de Paula Scheer^a

^a Department of Chemical Engineering, Federal University of Paraná, Centro Politécnico, Jardim das Américas, Curitiba, Paraná 81531-980, Brazil

^b Department of Chemical Engineering, Federal University of Santa Maria, Av. Roraima, 1000, Santa Maria, Rio Grande do Sul 97105-900, Brazil

^c Companhia Iguaçú de Café Solúvel S.A., Research and Development Department, BR-369, Km 88, Cornélio Procópio, Paraná, Brazil

ARTICLE INFO

Article history:

Received 26 December 2014
Received in revised form 9 March 2015
Accepted 18 March 2015
Available online 27 March 2015

Keywords:

Soluble coffee
Aroma compounds
Pervaporation
Industrial solution
PDMS membrane

ABSTRACT

Pervaporation experiments with PDMS membrane have been performed in a plate and frame module to investigate its ability to concentrate volatile compounds identified in an industrial soluble coffee solution. Eight compounds were chosen to depict key aroma of soluble coffee. The effect of feed flow rate, temperature and permeate pressure on the pervaporation performance has been analyzed. Concentration polarization phenomena was not identified in the feed flow rate studied. The temperature effect showed a good agreement with the nonlinear Arrhenius equation. The permeate pressure followed the solution–diffusion model behavior. Results showed that pervaporation is a promising alternative to concentrate aroma compounds from soluble coffee.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Coffee is a major commodity in the world economy, behind only to petroleum, involving twenty-five million farmers and coffee workers in over fifty countries around the world ([Global Exchange, 2014](#)). Coffee beverage aroma is very enjoyable and consumer attractive, with more than 800 volatile compounds ([Maarse and Visscher, 1996](#)) in a wide range of functional groups ([Sarrazin et al., 2000](#); [Fisk et al., 2012](#)). Nevertheless, a delicate balance in the composition of volatiles is necessary to produce the desirable smell in coffee ([Borrelli et al., 2002](#)).

Nowadays, coffee is industrially produced in roasted, ground and instant ways. The soluble coffee processing requires more technology and, consequently, greater investment than the production of roasted and ground coffee. Its industrial process consists of cleaning the beans, roasting and grinding to proceed to the extraction step. The following steps are the concentration, typically by thermal evaporation, freeze drying and spray drying. After the atomization, the coffee passes through the sintering process to be packaged ([Clarke and Vitzthum, 2001](#)). During the processing of soluble coffee, transformations and aromatic losses occur, which quantitatively and qualitatively changes the fraction of volatile

compounds. Some of these transformations exert negative impact on flavor and aroma of soluble coffee when compared to conventionally roasted coffee ([Flament, 2002](#)).

An alternative that could be adopted to increase the aromatic perception of instant coffee would be add natural volatile compounds recovered in some stage of its processing. It is known that processes used to recover coffee aromas in industries ([Herrera et al., 1970](#); [Nestec and Liu, 1986](#)), boil down to wetting roast and ground coffee, but present the drawbacks of high-energy spending and the possibility of degradation of the compounds involved. Other alternatives for the recovery of coffee aroma have been investigated as adsorption ([Canteli et al., 2014](#); [Carpiné et al., 2013](#); [Sacano et al., 1996, 1999](#); [Zuim et al., 2011](#)), supercritical extraction ([Lucas and Cocero, 2006](#); [Lucas et al., 2004](#)), wet grinding ([Baggenstoss et al., 2010](#)), nanofiltration ([Vincze and Vatai, 2004](#); [Pan et al., 2013](#)) and other membrane processes ([Brazinha et al., 2015](#)).

Although pervaporation has been successfully used in aroma recovery from fruits and juices, alcoholic drinks, dairy flavors and seafood, most researchers have utilized synthetic solutions to represent real systems ([Rafia et al., 2011](#); [Peng and Liu, 2003](#); [Isci et al., 2006](#); [She and Hwang, 2006a,b](#); [Pereira et al., 2006](#); [García et al., 2008](#); [Diban et al., 2008](#); [Olsson and Tragardh, 1999](#); [Borjesson et al., 1996](#); [Rajagopalan and Cheryan, 1995](#); [Karlsson et al., 1995](#); [Overington et al., 2008, 2011](#); [Martínez](#)

* Corresponding author. Tel.: +55 41 3361 3232; fax: +55 41 3361 3424.
E-mail address: thiago.weschenfelder@gmail.com (T.A. Weschenfelder).

et al., 2011, 2013; Bourseau et al., 2014). Only a few researchers have already worked with real matrices such as Zhang and Matsuura (1991), Alvarez et al. (2000), Cassano et al. (2006), Aroujalian and Raisi (2007), Raisi et al. (2008), Catarino et al. (2009), Olmo et al. (2014).

Pervaporation has become quite attractive for the food industry due to no need of chemical compounds addition and its low temperature operation, which prevents the degradation of thermosensitive compounds and reduces energy costs. Despite these advantages, few works in the literature were found on the use of this process in the recovery of coffee aromas (Oliveira et al., 2014; Bizzo et al., 2008). However, no systematic investigation of the pervaporation process performance was carried out by these authors.

In this context, the aim of this study was to investigate the feasibility of pervaporation process in the recovery of aromatic compounds of soluble coffee from a real solution obtained after the industrial extraction step. The influence of feed flow rate, temperature and pressure was evaluated in order to assess pervaporation performance.

2. Theory

In a pervaporation process, the solution–diffusion model can be used to describe the transport of permeating components through the membrane. The flux of component i through the polymeric membrane is proportional to the difference in partial vapor pressure at both sides of the membrane and can be described by Eq. (1) (Blume et al., 1990):

$$J_i = Q_{OV,i}(x_i\gamma_i^\infty p_i^{sat} - y_i p_p) \quad (1)$$

where J_i is the partial flux of each component i in the model solution ($\text{mol}/\text{m}^2 \text{ s}$); γ_i^∞ is the activity coefficient at infinite dilution of component i ; $Q_{OV,i}$ is the pressure-normalized permeation flux (permeance) ($\text{mol}/\text{m}^2 \text{ s Pa}$); x_i is the mole fraction of component i in the feed side; y_i is the mole fraction of component i in the permeate side, p_p is the permeate pressure (Pa) and p_i^{sat} is the saturation vapor pressure of component i (Pa).

According to the resistance-in-series model (Liu et al., 1996), assuming that the resistance at permeate side is negligible, the mass transfer through the membrane can be described by:

$$\frac{1}{Q_{OV,i}} = \frac{1}{Q_{M,i}} + \frac{1}{Q_{L,i}} \quad (2)$$

where $Q_{L,i}$ is the mass transfer coefficient of component i with driving force of partial vapor pressure at feed side ($\text{mol}/\text{m}^2 \text{ Pa s}$) and $Q_{M,i}$ is the mass transfer coefficient of component i with driving force of partial vapor pressure in membrane ($\text{mol}/\text{m}^2 \text{ Pa s}$). The parameter $Q_{L,i}$ is related to the feed hydrodynamic conditions and can be more conveniently expressed as follow:

$$Q_{L,i} = \frac{\rho k_{bl,i}}{\gamma_i p_i^{sat}} \quad (3)$$

where $k_{bl,i}$ is the liquid boundary layer mass transfer coefficient (m/s) and ρ is the total mass volume concentration of feed (g/m^3). The $k_{bl,i}$ value can be quantified for laminar flow regime, Reynolds number (Re) lower than 2300, by L ev eque correlation for a plate-and-frame module (Lipnizki et al., 2002; Trifunovi c et al., 2006; Garc a et al., 2008):

$$Sh = \frac{d_h k_{bl,i}}{D_i} = 1.62 \left(\text{Re Sc} \frac{d_h}{L} \right)^{1/3} \quad (4)$$

where Sh and Sc are the Sherwood and Schmidt numbers, respectively, d_h is the hydraulic diameter (m), L is the membrane length

(m) and D_i is the diffusivity coefficient of the component i in the liquid phase (m^2/s). The value of D_i can be estimated using the Wilke–Chang correlation (Poling et al., 2001).

To describe the separation performance of a pervaporation membrane in dilute aqueous solutions, the enrichment factor is commonly used. It is defined as the ratio between the concentration in the permeate and in the feed for a determined component i (Mart nez et al., 2013):

$$\beta_i = w_{i,p}/w_{i,f} \quad (5)$$

where β_i is the enrichment factor of component i , $w_{i,p}$ is its concentration in the permeate side and $w_{i,f}$ is its concentration in the feed side of membrane.

The effect of feed temperature can normally be described by an Arrhenius type equation, as shown in Eq. (6):

$$J_i = J_{i,0} \exp \left(-\frac{E_{a,i}}{RT} \right) \quad (6)$$

where $E_{a,i}$ is the apparent activation energy of permeation (kJ/mol); $J_{i,0}$ is the pre-exponential factor ($\text{mol}/\text{m}^2 \text{ s}$), R is the gas constant and T is the absolute temperature. The apparent activation energy parameter describes the overall temperature dependence of the permeation flux and thus includes the temperature dependence of the driving force (Olsson and Tragardh, 1999). In the literature, $E_{a,i}$ has been evaluated through the linear slope in the $\ln J$ vs $1/T$ plot (Feng and Huang, 1996). However, as shown by Schwaab and Pinto (2007), the use of the so-called linear form of the Arrhenius equation is very controversial and should be avoided. According to these authors, the intrinsic mathematical structure of this equation introduces a very strong dependence between the pre-exponential and activation energy parameters, turning the estimation of the correct values of these parameters very hard. In order to overcome this difficulty, the reparameterization of the Arrhenius equation was suggested by introducing a reference temperature in the form (Schwaab et al., 2008):

$$J_i = J_{i,\text{ref}} \exp \left(-\frac{E_{a,i}}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right) \quad (7)$$

where $J_{i,\text{ref}}$ is the specific permeation flux at the reference temperature T_{ref} . The reference temperature is usually defined as a suitable average temperature of the analyzed experimental data. For instance, Veglio et al. (2001) suggested the use of the inverse average:

$$\frac{1}{T_{\text{ref}}} = \frac{1}{\text{NE}} \sum_{i=1}^{\text{NE}} \frac{1}{T_i} \quad (8)$$

where NE is the number of experimental temperature values and T_i is the temperature for individual experiments. According to Schwaab and Pinto (2007), proper definition of reference temperature allows the elimination of parameter correlation improving parameter estimates precision. Taking these considerations into account, in the present work, the parameter estimation of the Arrhenius equation was carried out without any linearization, minimizing the least square function in the Statistica software (StatSoft):

$$F = \sum_{i=1}^{\text{NE}} (J_{i,\text{exp}} - J_{i,\text{pred}})^2 \quad (9)$$

where $J_{i,\text{exp}}$ and $J_{i,\text{pred}}$ are the experimental and predicted partial fluxes of a volatile compound.

3. Experimental

3.1. Feed solution

Real feed solution was provided by a soluble coffee industry (Cia. Café Iguazú). Coffee aromatic solution was obtained in the concentration step in the soluble coffee production. It is important emphasize that soluble coffee feed solution was a very dilute solution with no particles in suspension, presenting physical chemical characteristics similar to pure water. Feed solution was cooled and kept at $-18\text{ }^{\circ}\text{C}$ until the pervaporation experiments, in order to retain the aromatic compounds in the coffee solution. More than 88 aromatic compounds could be identified using a headspace-solid phase dynamic extraction–gas chromatography/mass spectrometry (HS-SPDE–GC/MS). Among them, eight compounds were selected to describe the industrial aqueous solution of soluble coffee: two ketones (2,3-butanedione (CAS 431-03-8) and 2,3-pentanedione (CAS 600-14-6)), three aldehydes (3-methylbutanal (CAS 590-86-3), benzaldehyde (CAS 100-52-7) and acetaldehyde (CAS 75-07-0)), two furans (furfural (CAS 98-01-1) and 5-methyl furfural (CAS 620-02-0)) and one pyrazine (2,5-dimethyl pyrazine (CAS 123-32-0)). The aromatic compounds furfural and acetaldehyde confer negative characteristics in the coffee and the other six aroma afford positive characteristics (Flament, 2002).

Table 1 shows the concentration in feed solution, organoleptic characteristic and odor threshold values (OTV) in water of the selected volatile aroma compounds. The odor threshold value is the lowest concentration of an odor compound that is perceivable by the human sense of smell. Although some compounds presented their initial concentration, lower than their OTV values, the eight chosen compounds were the volatile aromas with the highest concentration identified in the feed solution. As it can be seen in this Table, concentration of the key flavor compounds in feed solution is lower than 3 ppm (mass of organic in mass of water), corresponding to a dilute aqueous solution. Also, it can be verified in Table 1, that chosen compounds present different organoleptic characteristic.

Physical properties of selected compounds are listed in Table 2. The liquid molar volume for all aromatic compounds was estimated by Tyn and Calus method and Vetere relationship (Poling

et al., 2001). Vapor pressure was obtained or predicted by using the software Chemcad 6 (2008) except for 2,3-pentanedione that was obtained from Martínez et al. (2013) and 5-methyl furfural that was obtained from Lomba et al. (2014). Activity coefficients at infinite dilution in water were estimated using the predictive method UNIFAC–Dortmund, except for 2,3-pentanedione, 3-methyl butanal and benzaldehyde which were obtained from the literature (Martínez et al., 2012). Henry law constants were obtained from Yaws (1999) and by the multiplication of activity coefficient at infinite dilution and the vapor pressure, according to Martínez et al. (2012).

3.2. Membrane

A commercial flat-sheet polymer hydrophobic membrane provided by Pervatech BV (The Netherlands) was used in the experiments. The membrane has a polydimethylsiloxane (PDMS) functional layer and a polyethylene terephthalate (PET) support layer material and was cut into a round shape with a diameter of 8 cm to reach the effective membrane area of 50 cm^2 in the pervaporation module.

3.3. Pervaporation experiments

Fig. 1 shows the stainless steel pervaporation unit used in all experiments. The feed was recirculated through the membrane and back into the jacketed feed tank of 4 L using a diaphragm pump (Bomax, Brazil). Temperature was controlled by recirculating water from a temperature-controlled water bath (Quimis, Brazil). The permeate pressure was measured just downstream of the membrane, using a digital vacuum pressure gauge (model VDR-920, Instrutherm, Brazil) and was controlled by adjusting the needle valves upstream of the cold traps. A circular plate and frame membrane module, built in stainless steel with 50 and 350 mm of height in permeate and feed sides, respectively, housed the circular membrane. Vacuum on permeate side of the system was maintained with a vacuum pump (model RV12, Edwards, West Sussex, UK).

New membranes were conditioned before the pervaporation experiments, by recirculating approximately 500 mL of distilled

Table 1
Selected aroma compounds in the industrial soluble coffee solution (Flament, 2002).

Aromatic compound	Initial concentration (ppb)	Organoleptic characteristic	OTV (ppb)
2,3-Butanedione	52.54	Sweet, buttery, creamy and milky	15
2,3-Pentanedione	102.32	Sweet buttery, creamy, slightly toasted dairy	30
3-Methylbutanal	327.90	Cheesy, sweaty and fruity	1000
Benzaldehyde	278.33	Sweet, oily, almond and cherry	160
Acetaldehyde	1148.93	Purgent	15
Furfural	2552.69	Vegetable, burnt astringent nuance	175,000
2,5-Dimethylpirazine	219.14	Nutty-like	1000
5-Methyl furfural	1398.30	Sweet, spicy, warm odor with a sweet, caramel-like	0.4

Table 2
Physical properties of soluble coffee aroma compounds studied in this work.

Compound	MW	BP ($^{\circ}\text{C}$)	$p_{20^{\circ}\text{C}}^{\text{s}}$ (Pa)	$\gamma_{20^{\circ}\text{C}}^{\infty}$	VM^{BP} (cm^3/mol)	$\text{H}_{20^{\circ}\text{C}} \times 10^{-4}$ (Pa)
2,3-Butanedione	86.09	88.0	8303.81	13.0	88.8	10.0
2,3-Pentanedione	100.11	108.0	2918.54	282.0	121.0	38.8
3-Methylbutanal	86.13	92.5	6574.13	164.0	118.9	89.3
Benzaldehyde	106.12	178.8	181.00	273.0	122.6	13.8
Acetaldehyde	44.05	20.2	128522.76	4.0	58.8	47.1
Furfural	96.08	161.0	297.3	60.6	83.9	1.8
2,5-Dimethylpirazine	108.14	154.0	530.62	35.8	108.4	1.9
5-Methyl furfural	110.11	187.0	255.97	324.0	99.4	8.3

*MW: molecular weight, BP: boiling point, $p_{20^{\circ}\text{C}}^{\text{s}}$: vapor pressure at $20\text{ }^{\circ}\text{C}$; $\gamma_{20^{\circ}\text{C}}^{\infty}$: activity coefficient at infinite dilution; VM^{BP} : liquid molar volume at boiling point; $\text{H}_{20^{\circ}\text{C}}$: Henry law constant at $20\text{ }^{\circ}\text{C}$.

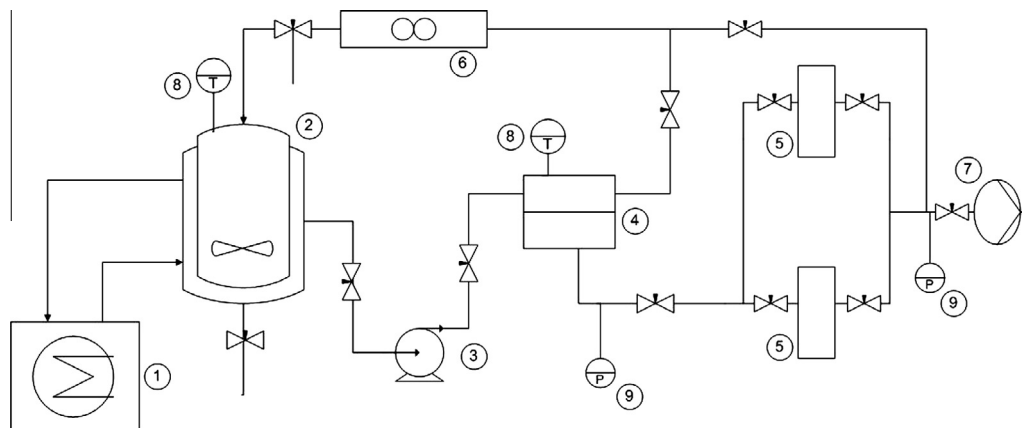


Fig. 1. Schematic diagram of experimental pervaporation apparatus. 1 – temperature control bath; 2 – feed tank; 3 – diaphragm pump; 4 – membrane module; 5 – liquid N₂ cold traps; 6 – flowmeter; 7 – vacuum pump; 8 – temperature indicator; 9 – digital pressure indicator.

water at 30 °C through the pervaporation apparatus for 12 h, and under high vacuum (300 Pa) in the permeate side. It was assumed that 12 h was sufficient to pre-swell the membrane to allow steady state operation. Original condition of the membrane was evaluated between the experiments, through a verification procedure that consisted in measuring total flux using water as feed solution under standard conditions (300 Pa and 20 °C).

The feed tank was fully empty; this way, due to small amount of permeate product, volatile compounds concentration in the feed tank was kept approximately constant along operation. Each pervaporation run was carried out over six hours. Retentate samples were collected at the beginning and the end of the experiment. Permeate samples were collected every 2 h, after thawing and weighting of the whole permeate. Permeate samples were collected in glass cold traps cooled with liquid nitrogen. Only one of the two parallel cold traps was used at a time, and the active cold trap was changed every hour to enable permeate samples to be removed during each pervaporation run. Samples were kept at –18 °C prior to analysis.

Temperature, permeate pressure and feed flow rate effects were investigated in the range of 10–40 °C, 300–2200 Pa and 1 L/min to 3 L/min, respectively. PDMS membrane behavior was also investigated through pure water experiments in the same temperature and permeate pressure condition used with real solution experiments.

3.4. Sample analysis

Quantitative analysis of aroma compounds for all samples was carried out in triplicate using the method described in Viegas and Bassoli (2007). Coffee volatile compounds were sampled with solid phase microextraction (SPME) at 70 °C during 30 min using a PDMS (Supelco, Switzerland) fiber. GC-MS analysis of aroma compounds was carried out on an Agilent 6890 N gas chromatograph (GMI, United States) coupled to a quadrupole mass spectrometer. The SPME fiber was desorbed in the split/splitless injector at 250 °C. Aroma compounds were then separated on a 60 m × 320 μm × 0.25 μm polar HP-Innowax capillarity column (Agilent, United States) with the following temperature program: 40 °C (5 min); 40–60 °C, 4 °C/min (5 min); 60–250 °C, 8 °C/min (3 min). Helium was used as a carrier gas at a feed flow rate of 1.2 mL/min. The mass spectrometer was operated in the following conditions: ionization potential of 70 eV; interface temperature of 280 °C; quadrupole temperature of 150 °C and ion source temperature of 230 °C. The generated data was interpreted by MSD Chemstation software coupled with the NIST/2002 mass spectrum library.

4. Results and discussion

4.1. Pure water as feed solution

In order to verify the behavior of the PDMS membrane, the effect of temperature and pressure was studied using pure water as feed solution. Temperature and permeate pressure were changed in the same range for the volatile aroma compounds. Fig. 2 shows the influence of temperature in water and organic fluxes. It is possible to observe that water and organic fluxes increase exponentially with temperature. This behavior allows to express the water flux dependence with temperature with an Arrhenius-type relationship. An apparent activation energy for water of 40.92 kJ/mol was estimated by nonlinear regression with a correlation coefficient equal to 0.996. The organic flux presented in this figure was added only in order to compare both water and organic fluxes.

Fig. 3 presents the effect of permeate pressure on water permeation and industrial solution fluxes. It can be seen in this figure that water permeation flux follows the trend of solution–diffusion model of pervaporation (Eq. (1)). In other words, by increasing the permeate pressure, water permeation flux decreases as a consequence of partial pressure gradient decreasing. This behavior affirms that the both water and industrial solution are governed by the solution–diffusion model. A similar behavior was obtained

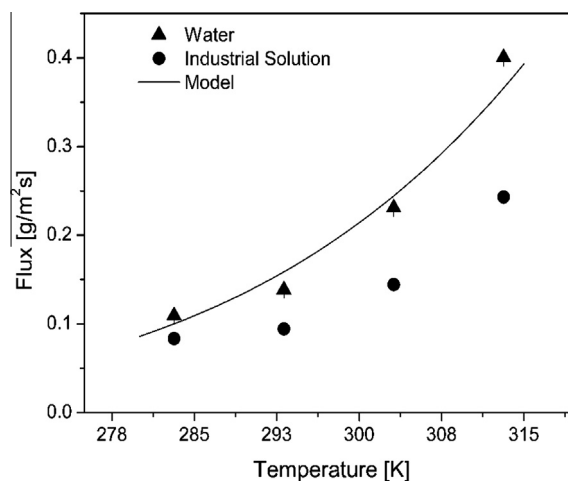


Fig. 2. Effect of temperature on water and industrial solution permeation fluxes and fitted model to water flux ($p_p = 300$ Pa, feed flow rate = 1.5 L/min).

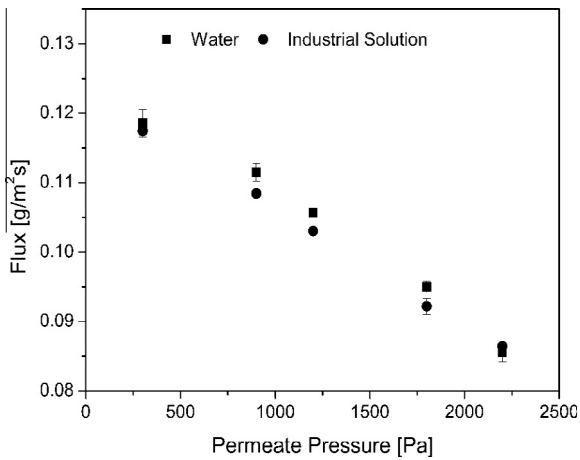


Fig. 3. Effect of permeate pressure on water and industrial solution permeation fluxes ($T = 20\text{ }^{\circ}\text{C}$, feed flow rate = 1.5 L/min).

by Martínez et al. (2011) for a polyoctylmethylsiloxane (POMS) membrane, by She and Hwang (2004) for a PDMS composite membrane and by García et al. (2008) for a PDMS membrane. In the present work, water permeance for PDMS membrane was calculated from the flux data and driving force and was constant for the range of both temperature and pressure investigated ($4.2 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$).

4.2. Influence of feed flow rate

The influence of feed flow rate on the permeation flux of soluble coffee aroma compounds through the membrane is shown in Fig. 4. The boundary layer effect was studied in the multicomponent pervaporation system in a feed flow rate range between 1 L/min and 3 L/min, corresponding to a Reynolds number of 2400 and 7150 respectively, for the apparatus and module configuration used in this work. Usually hydrophobic membranes, as PDMS, are significantly more permeable to dissolved organic compounds than to water, causing a depletion of the former compounds in a liquid boundary layer. Therefore, the concentration polarization phenomenon occurs. According to resistance-in-series model, when the boundary layer resistance is dominant, mass transfer across the membrane increases with feed flow rate due to a reduction in the boundary layer thickness. However, if hydrodynamics conditions are optimized, membrane resistance could be the rate-

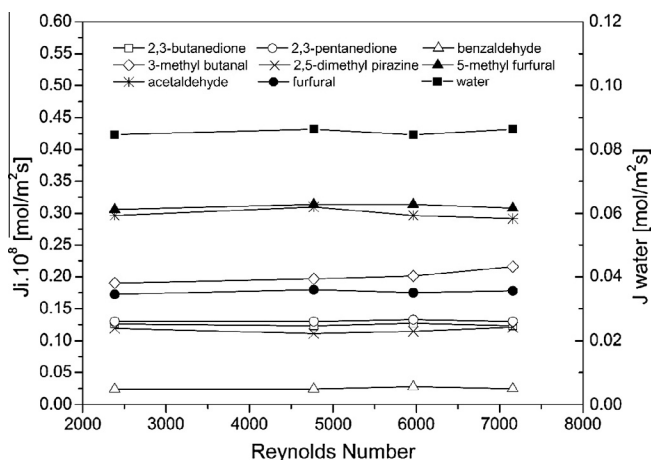


Fig. 4. Water and individual organic compounds permeation fluxes at different Reynolds number ($p_p = 300 \text{ Pa}$; $T = 20\text{ }^{\circ}\text{C}$).

limiting step in the pervaporation separation process (García et al., 2008).

As shown in Fig. 4, water and individual organic fluxes were not affected by the feed flow rate increase. This fact implies that the mass transfer resistance of these aroma compounds is governed by the resistance exerted by the membrane. In order to confirm this hypothesis, the apparent dominant influence of the membrane resistance was investigated calculating the boundary layer mass transfer coefficient k_{bl} according to Sherwood correlation. No relative significance of the boundary layer mass transfer resistance was observed, since k_{bl} values lower than 1% of the total resistance were computed. According to Lipnizki et al. (2002), a Reynolds number higher than 2300 for plate and frame modules characterizes a turbulent behavior, where the concentration polarization phenomenon can be negligenced. Besides, Martínez et al. (2011) affirm that the mass transfer coefficient of the liquid boundary layer obtained through the Sherwood correlation could be overestimated, and a necessary attention is recommended. This statement also confirms that membrane resistance is dominant in the pervaporation process of this work. For all other experiments, involving the effect of temperature and pressure, an intermediate feed flow rate of 1.5 L/min was fixed.

4.3. Influence of temperature

Temperature is an important operating variable since it affects the feed/membrane characteristics and the driving force of the process. The compounds properties, both in the feed solution (diffusivity and viscosity) and in the membrane (permeability) are affected by the temperature increase. In addition, in pervaporation, the permeating molecules diffuse through the free volumes of the membrane, produced randomly by the thermal motion of the polymer chain in the amorphous regions. As the temperature increases, frequency and amplitude of the polymer chain jumping increase. As a result, the free volume in the membrane raises. Thus, the diffusion rate of individual permeating molecules increases, leading to a high permeation flux as the temperature increases (Isci et al., 2006). Fig. 5(a) and (b) shows the effect of temperature on volatile compounds permeation flux and the Arrhenius equation fit. The experiments were carried out at a fixed permeate pressure (300 Pa). For all organic compounds, permeation flux increases with temperature. It can also be seen in this figure, the good adjustment of the Arrhenius equation to experimental data.

Fig. 6 shows the predicted and observed values for the nonlinear estimation of apparent activity energies. The result in this figure corroborates the good adjustment of the Arrhenius equation in its non linear form, to describe the individual flux dependence with the temperature.

Table 3 reports the estimated apparent activation energies for permeation of coffee aroma compounds and water with their respective correlation coefficient values. A higher value of apparent activation energy indicates a more sensitive behavior toward temperature changes (Martínez et al., 2013). It can be observed from Table 3 that for the most of the organic compounds, $E_{a,i}$ is higher than water $E_{a,i}$, except for 2,3-butanedione, benzaldehyde and furfural. However, in these cases, these differences are not so high. Similar results were found in Martínez et al. (2013) for 2,3-pentanedione (66.3), 3-methyl butanal (54.4) and benzaldehyde (37.5), however, these authors used a synthetic aroma compounds in the multicomponent model solution.

According to Olsson and Tragardh (1999), the permeation activation energy $E_{p,i}$ describes the effect of temperature on the membrane permeability, and can be estimated by subtracting the vaporization enthalpy ΔH_v from the calculated apparent activation energy. Also, $E_{p,i}$ can be expressed as the activation energy

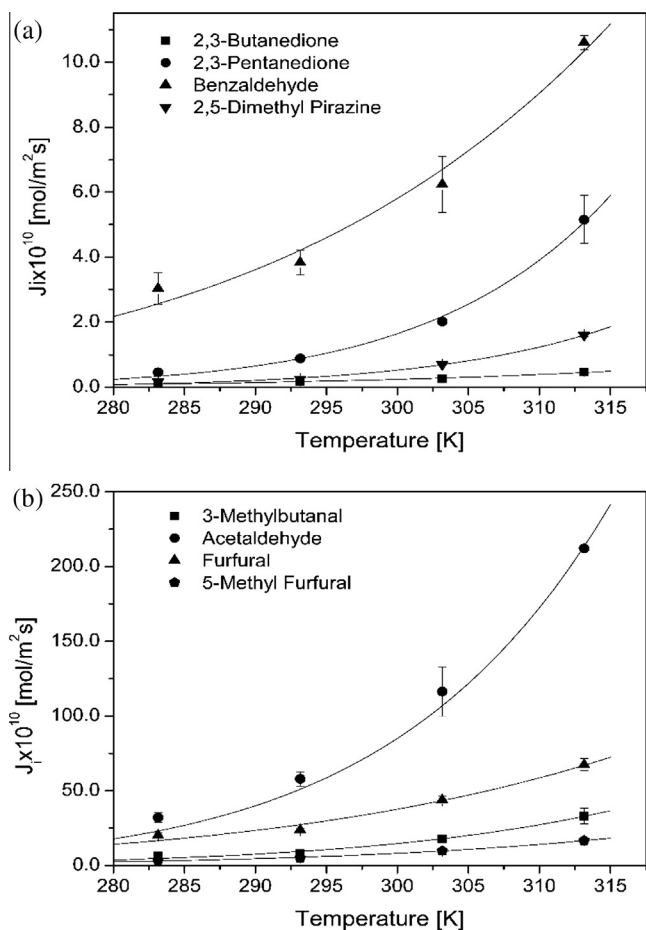


Fig. 5. Effect of temperature on volatile compound permeation flux ($p_p = 300$ Pa, feed flow rate = 1.5 L/min): (a) 2,3-Butanedione, 2,3-Pentanedione, Benzaldehyde and 2,5-Dimethyl Pirazine, (b) 3-Methylbutanal, Acetaldehyde, 5-Methyl Furfural and Furfural.

of permeating compounds to diffuse through the membrane, E_D , plus the enthalpy of dissolution, ΔH_s (Feng and Huang, 1997). For the organic compounds of this work, activation energy was calculated subtracting ΔH_p and followed the order: $E_{p,benzaldehyde} (-10.71 \text{ kJ/mol}) < E_{p,5\text{-methyl furfural}} (-7.29 \text{ kJ/mol}) < E_{p,furfural} (-5.55 \text{ kJ/mol}) < E_{p,2,3\text{-butanedione}} (4.51 \text{ kJ/mol}) < E_{p,3\text{-methyl butanal}} (14.75 \text{ kJ/mol}) < E_{p,2,5\text{-dimethyl pirazine}} (18.78 \text{ kJ/mol}) < E_{p,acetaldehyde} (28.92 \text{ kJ/mol}) < E_{p,2,3\text{-pentanedione}} (32.19 \text{ kJ/mol})$. Negative values of $E_{p,i}$ indicate that membrane's permeability decreases with temperature. The level of contribution from the enthalpy of dissolution and diffusion coefficient can lead positive or negative values of $E_{p,i}$. This behavior, for benzaldehyde, 5-methyl furfural and furfural, where the value of $E_{p,i}$ is negative, indicates that for these aroma compounds the temperature has greater effects on sorption in membrane permeability. However, for the other coffee aroma compounds, the effect of temperature, in the PDMS membrane permeability studied, has greater influence on diffusion than on sorption. These results disagreed with the behavior observed by Martínez et al. (2013) and She and Hwang (2004) for PDMS membranes. However, different chemical class compounds were studied in these reports, which can change the general behavior of the pervaporative membrane. In addition, a real solution involving other aromatic compounds, even if in low concentration, can promote changes in the thermodynamic behavior of the feed solution with the pervaporative membrane studied.

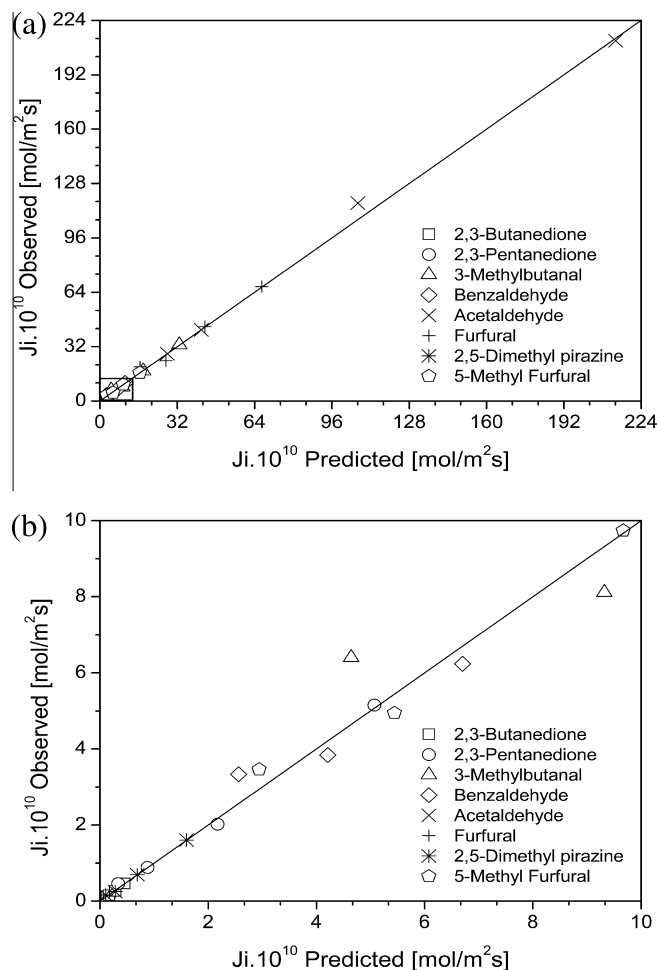


Fig. 6. Observed vs predicted individual aroma compounds permeation fluxes in complete scale (a) and in an amplified scale (b) for better visualization.

Table 3

Apparent activation energy estimated of aroma compounds for PDMS membrane and correlation coefficient (R) values.

Compound	E_a (kJ/mol)	R
2,3-Butanedione	37.32	0.997
2,3-Pentanedione	66.87	0.998
3-Methylbutanal	48.07	0.995
Benzaldehyde	34.31	0.985
Acetaldehyde	54.66	0.998
Furfural	34.28	0.991
2,5-Dimethylpirazine	66.34	0.998
5-Methyl furfural	42.45	0.997
Water	40.92	0.996

Fig. 7 shows the enrichment factor at four temperatures studied in this work for volatile compounds. According to this Figure, it cannot be generalized for PDMS hydrophobic membrane that enrichment factors of volatile coffee compounds increase with temperature. For almost all aroma compounds, the temperature of 10 °C presented the lowest enrichment factor. The 2,3-butanedione and 2,5-dimethyl pirazine presented the highest enrichment factor in a temperature of 20 °C. Furfural and 5-methyl furfural compounds, from furfural chemical group, did not show perceptible changes in the temperature range studied. The effect of temperature on selectivity depends on sorption changes of organic compound, their diffusion through the membrane and chemical

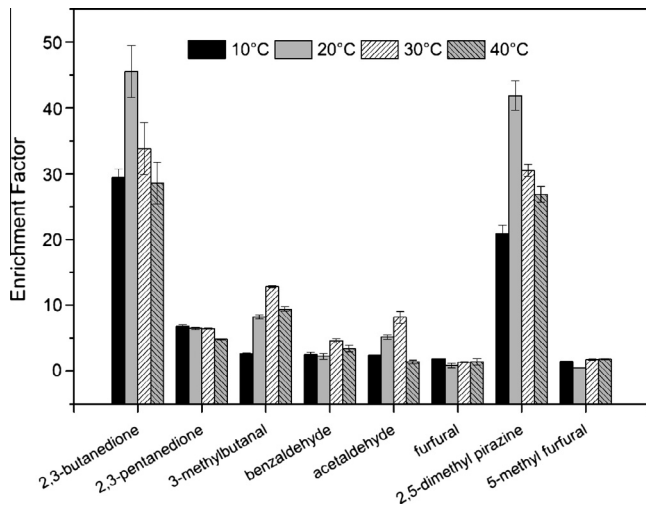


Fig. 7. Effect of temperature on the enrichment factor of the volatile compounds ($p_p = 300$ Pa, feed flow rate = 1.5 L/min) for PDMS membrane.

affinity with the membrane polymer. Therefore, differences, as shown in Fig. 7, are common and reported in the literature (Aroujalian and Raisi, 2007; Trifunović et al., 2006; Lipnizki et al., 2002) when several different compounds compose the solution.

4.4. Influence of permeate pressure

Permeate pressure is one of the most important process parameters which, with the operating temperature, determines the driving force of the whole process (Rafia et al., 2011). It was varied in the range of 300–2200 Pa at fixed feed temperature (20 °C). Changes in pressure directly affect the chemical potential gradient through the membrane, thus the flux is influenced by the downstream pressure (Isci et al., 2006). According to Eq. (1), as the permeate pressure increases, driving force for the permeation through the membrane decrease, resulting in a reduction in the permeation flux. Fig. 8 illustrates this fact where organic permeation fluxes have been plotted as a function of partial pressure. The pressure-normalized permeation flux (permeance) $Q_{ov,i}$ was calculated from the plot of the organic flux J_i versus the partial pressure by linear regression and it is shown in Table 4.

As shown in Fig. 8, the effect of permeate pressure on the 5-methyl furfural flux was almost negligible in comparison to the other aromatic compounds. She and Hwang (2004) observed a similar behavior for ethyl butyrate. This result allows affirming that there would be an optimum permeate pressure based on the balance of organic flux and operating cost, since a relatively low vacuum for industrial application is preferred to a high vacuum system that is more expensive. It can be seen in Fig. 8 that a good adjustment was obtained for all volatile compounds, which is corroborated by the correlation coefficient values shown in Table 4.

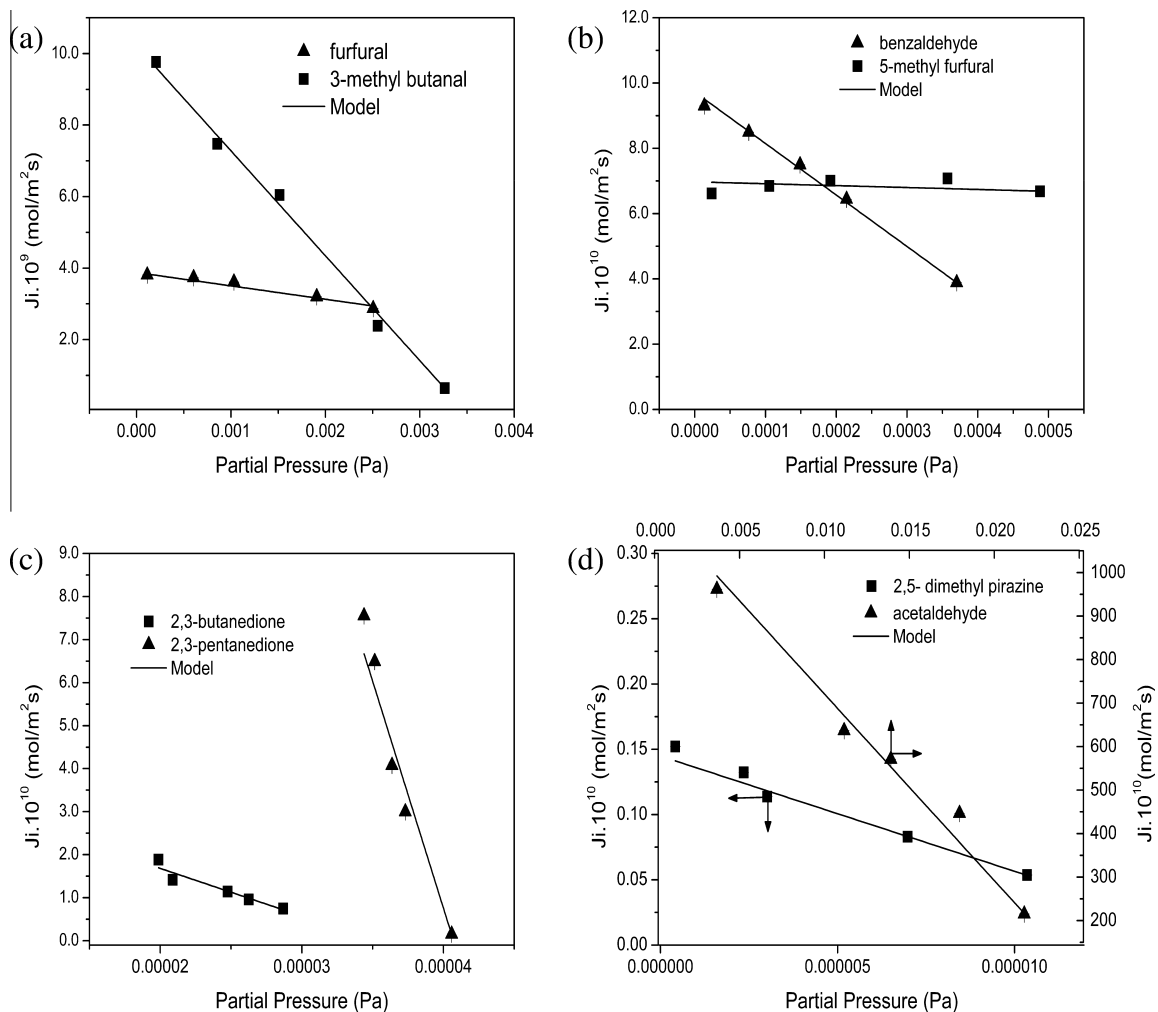


Fig. 8. Effect of permeate pressure on partial permeation flux of (a) furfural and 3-methyl butanal, (b) benzaldehyde and 5-methyl furfural, (c) 2,3-butanedione and 2,3-pentanedione and (d) 2,5-dimethyl pyrazine (left y axis) and acetaldehyde (right y axis) for PDMS membrane ($T_{feed} = 20$ °C; feed flow rate = 1.5 L/min).

Table 4

Estimated permeances for the coffee aroma compounds and correlation coefficient ($T_{\text{feed}} = 20\text{ }^{\circ}\text{C}$).

Compound	$Q_{\text{Ov},i} \cdot 10^7$ (mol/m ² s Pa)	R^2
2,3-Butanedione	11.10	0.93
2,3-Pentanedione	1.05	0.97
3-Methylbutanal	3.73	0.97
Benzaldehyde	15.70	0.99
Acetaldehyde	42.80	0.98
Furfural	29.30	0.99
2,5-Dimethylpirazine	8.82	0.99
5-Methyl furfural	0.58	0.96

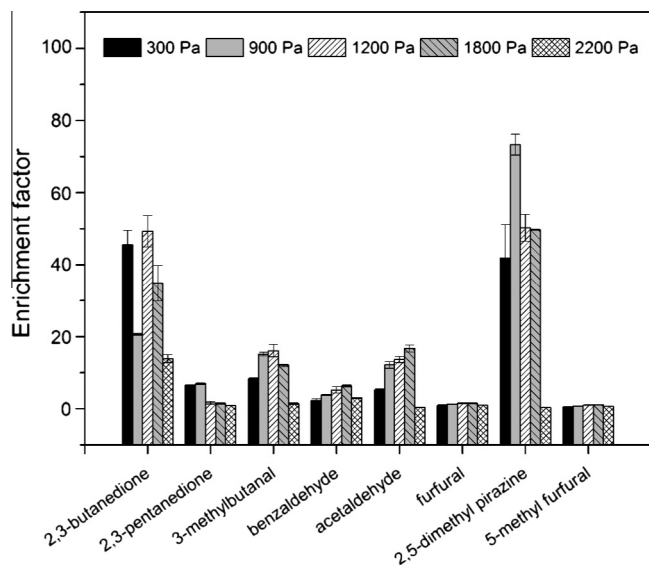


Fig. 9. Effect of permeate pressure on the enrichment factors of volatile compounds for PDMS membrane ($T_{\text{feed}} = 20\text{ }^{\circ}\text{C}$, feed flow rate = 1.5 L/min).

Fig. 9 presents the effect of permeate pressure on the enrichment factor for volatile compounds. For furfural and 5-methyl furfural, with low values of Henry's law constant, the enrichment factors have been found to remain constant with permeate pressure. On the other hand, for 2,3-butanedione and 2,5-dimethyl pirazine, an increase on enrichment factors with permeate pressure is remarkable. In addition, the highest enrichment factor for these compounds was obtained in an intermediate permeate pressure. This fact was appointed by Wijimans et al. (1996) that shows a unique characteristic for pervaporation, since separation can be improved by decreasing the driving force of the process. For the compounds acetaldehyde and 3-methyl butanal, with high values of Henry's law constant, the enrichment factor also increases with permeate pressure, but in a smother manner and except for the 2200 Pa pressure. Benzaldehyde and 2,3-pentanedione compounds present enrichment factors without great changes with permeate pressure. Benzaldehyde behavior differs from the literature (She and Hwang, 2004; Martínez et al., 2013, 2011), however it must be pointed out that this result refers to an industrial solution and that the presence of other aroma compounds even in low concentration can change the thermodynamic properties of the feed solution.

5. Conclusions

In this work, recovery of volatile compounds from an industrial solution of soluble coffee was performed by pervaporation process

with a polymeric PDMS membrane. Membrane has been found to be effective to recover some key aroma compounds studied. Results showed that liquid boundary layer resistance was negligible in the feed flow rate range investigated.

The effect of pervaporation temperature and permeate pressure on pervaporation performance has been analyzed. For all organic compounds, permeation flux increased with temperature and could be well described by Arrhenius type relationship, through a non linear regression. As a general trend, results also indicated that aroma compound fluxes decreased with partial pressure, except for 5-methyl furfural. Regarding enrichment factors obtained in different pressure values, a distinct behavior among aroma compounds studied was observed. Among volatile compounds investigated, 2,3-butanedione and 2,5-dimethyl pirazine presented the highest enrichment factors in the experimental conditions evaluated in this work. For industrial purposes, an optimization should be recommended in order to concentrate aroma compounds according to desired aroma profile for soluble coffee.

Acknowledgments

The authors are grateful to CAPES and Cia Iguacú de Café Solúvel for research grant and to Fundação Araucária throughout the project 22926/2012 for the financial support.

References

- Alvarez, S., Riera, F.A., Alvarez, R., Coca, J., Cuperus, F.P., Bouver, S., Boswinkel, G., van Gemert, R.W., Veldsink, J.W., Giorno, L., Donato, L., Todisco, S., Drioli, E., Olsson, J., Tragardh, G., Gaeta, S.N., Panyor, L., 2000. A new integrated membrane process for producing clarified apple juice and apple juice aroma concentrate. *J. Food Eng.* 46, 109–125.
- Aroujalian, A., Raisi, A., 2007. Recovery of volatile aroma components from orange juice by pervaporation. *J. Membr. Sci.* 303, 154–161.
- Baggenstoss, J., Thomann, D., Perren, R., Escher, F., 2010. Aroma recovery from roasted coffee by wet grinding. *J. Food Sci.* 75 (9), 697–702.
- Bizzo, H.R., Oliveira, A., Cabral, L.M.C., Freitas, S.P., 2008. Volatile composition of concentrated aroma extracts of soluble coffee beverage obtained by pervaporation. In: *International Conference on Coffee Science*, p. 154.
- Blume, I., Wijimans, J.G., Baker, R.W., 1990. The separation of dissolved organics from water by pervaporation. *J. Membr. Sci.* 49, 253–286.
- Borjesson, J., Karlsson, H.O.E., Tragardh, G., 1996. Pervaporation of a model apple juice aroma solution: comparison of membrane performance. *J. Membr. Sci.* 119, 229–239.
- Borrelli, R.C., Visconti, A., Mennella, C., Anese, M., Fogliano, V., 2002. Chemical characterization and antioxidant properties of coffee melanoidins. *J. Agric. Food Chem.* 50, 6527–6533.
- Bourseau, P., Massé, A., Cros, S., Vandanjon, L., Jaouen, P., 2014. Recovery of aroma compounds from seafood cooking juices by membrane process. *J. Food Eng.* 128, 157–166.
- Brazinha, C., Cadima, M., Crespo, J.G., 2015. Valorisation of spent coffee through membrane processing. *J. Food Eng.* 149, 123–130.
- Canteli, A.M.D., Carpiné, D., Scheer, A.P., Mafra, M.R., Mafra, L.I., 2014. Fixed-bed column adsorption of the coffee aroma compound benzaldehyde from aqueous solution onto granular activated carbon from coconut husk. *LTW Food Sci. Technol.* 59, 1025–1032.
- Carpiné, D., Dagostin, J.L.A., da Silva, V.R., Mafra, L.I., Mafra, M.R., 2013. Adsorption of volatile aroma compound 2-phenylethanol from synthetic solution onto granular activated carbon in batch and continuous modes. *J. Food Eng.* 117, 370–377.
- Cassano, A., Figoli, A., Tagarelli, A., Sindona, G., Drioli, E., 2006. Integrated membrane process for the production of highly nutritional kiwifruit juice. *Desalination* 189, 21–30.
- Catarino, M., Ferreira, A., Mendes, A., 2009. Study and optimization of aroma recovery from beer by pervaporation. *J. Membr. Sci.* 341, 51–59.
- Clarke, R.J., Vitzthum, O.G., 2001. *Coffee: recent developments*. Blackwell Science, Oxford, UK, pp. 140–164.
- Diban, N., Urtiaga, A., Ortiz, I., 2008. Recovery of key components of bilberry aroma using a commercial pervaporation membrane. *Desalination* 224, 34–39.
- Feng, X., Huang, R.Y.M., 1996. Estimation of activation energy for permeation in pervaporation process. *J. Membr. Sci.* 118, 127–131.
- Feng, X., Huang, R.Y.M., 1997. Liquid separation by membrane pervaporation: a review. *Ind. Eng. Chem. Res.* 36, 1048–1066.
- Fisk, I.D., Kettle, A., Hofmeister, S., Virdie, A., Kenny, J.S., 2012. Discrimination of roast and ground coffee aroma. *Flavour*, 1–14.
- Flament, I., 2002. *Coffee flavor chemistry*. Wiley, London, UK.

- García, V., Diban, N., Gorri, D., Keiski, R., Urriaga, A., Ortiz, I., 2008. Separation and concentration of bilberry impact aroma compound from dilute model solution by pervaporation. *J. Chem. Technol. Biotechnol.* 83, 973–982.
- Global Exchange <<http://www.globalexchange.org/fairtrade/coffee/faq>> (accessed in 08.12.14).
- Herrera, W.R., Klein, P., Raben, I.A., 1970. Method of making aromatized oil. US Patent No. 3535118 A from 20.10.1970. Priority from 31.12.1964.
- Isci, A., Sahin, S., Sumnu, G., 2006. Recovery of strawberry aroma compounds by pervaporation. *J. Food Eng.* 75, 36–42.
- Karlsson, H.O.E., Loureiro, S., Tragardh, G., 1995. Aroma compound recovery with pervaporation – temperature effects during pervaporation of a muscat wine. *J. Food Eng.* 26 (2), 177–191.
- Lipnizki, F., Olsson, J., Tragardh, G., 2002. Scale-up of pervaporation for the recovery of natural aroma compounds in the food industry. Part 1: simulation and performance. *J. Food Eng.* 54, 183–195.
- Liu, M.G., Dickson, J.M., Côté, P., 1996. Simulation of a pervaporation system on the industrial scale for water treatment. Part I: Extended resistance-in-series model. *J. Membr. Sci.* 111, 227–241.
- Lomba, L., Giner, B., López, M.C., Aldea, L., Lafuente, C., 2014. Thermophysical properties of furfural compounds. *J. Chem. Eng. Data* 59 (2), 329–338.
- Lucas, S., Cocero, M.J., 2006. Improvement of soluble coffee aroma using an integrated process of supercritical CO₂ extraction with selective removal of the pungent volatiles by adsorption on activated carbon. *Brazilian J. Chem. Eng.* 23 (2), 197–203.
- Lucas, S., Cocero, M.J., Zetzl, C., Brunner, G., 2004. Adsorption isotherms for ethylacetate and furfural on activated carbon from supercritical carbon dioxide. *Fluid Phase Equilib.* 219, 171–179.
- Maarse, H., Visscher, C.A., 1996. Volatile compounds in foods. Quantitative and qualitative data. TNO Food Analysis Institute. The Netherlands, 7th Zeist.
- Martínez, R., Sanz, M.T., Beltrán, S., 2011. Concentration by pervaporation of representative brown crab volatile compounds from dilute model solution. *J. Food Eng.* 105, 98–104.
- Martínez, R., Sanz, M.T., Beltrán, S., Corcuera, E., 2012. Activity coefficients at infinite dilution of volatile compounds in water: effect of temperature and salt concentration. *J. Chem. Eng. Data* 57, 1480–1485.
- Martínez, R., Sanz, M.T., Beltrán, S., 2013. Concentration by pervaporation of brown crab volatile compounds from dilute model solutions: evaluation of PDMS membrane. *J. Membr. Sci.* 428, 371–379.
- Nestec, S.A., Liu, R.T., 1986. Process for improving the flavor and aroma of instant coffee. US Patent No. 4606921 A from 19.08.1986. Priority from 03.06.1980.
- Oliveira, A., Cabral, L.M.C., Bizzo, H.R., Arruda, N.P., Freitas, S.P., 2014. Identification and recovery of volatile organic compounds (VOCs) in the coffee-producing wastewater. *J. Water Res. Prot.* 6, 375–380.
- Olmo, A., Blanco, C.A., Palacio, L., Pradanos, P., Hernández, A., 2014. Pervaporation methodology for improving alcohol-free beer quality through aroma recovery. *J. Food Eng.* 133, 1–8.
- Olsson, J., Tragardh, G., 1999. Influence of temperature on membrane permeability during pervaporative aroma recovery. *Sep. Sci. Technol.* 34 (8), 1643–1659.
- Overington, A., Wong, M., Harrison, J., Ferreira, L., 2008. Concentration of dairy flavor compounds using pervaporation. *Int. Dairy J.* 18, 835–848.
- Overington, A., Wong, M., Harrison, J., 2011. Effect of feed pH and non-volatile dairy components on flavor concentration by pervaporation. *J. Food Eng.* 107, 60–70.
- Pan, B., Yan, P., Zhu, L., Li, X., 2013. Concentration of coffee extract using nanofiltration membranes. *Desalination* 317, 127–131.
- Peng, M., Liu, S.X., 2003. Recovery of aroma compounds from dilute model blueberry solution by pervaporation. *J. Food Sci.* 68 (9), 2706–2710.
- Pereira, C.C., Ribeiro, C.P., Nobrega, R., Borges, C.P., 2006. Pervaporative recovery of volatile aroma compounds from fruit juices. *J. Membr. Sci.* 274, 1–23.
- Poling, B.E., Prausnitz, J.M., O'Connell, J.P., 2001. *The Properties of Gases and Liquids*. McGraw-Hill, New York.
- Rafia, N., Aroujalian, A., Raisi, A., 2011. Pervaporative aroma compounds recovery from lemon juice using poly(octyl methyl siloxane) membrane. *J. Chem. Technol. Biotechnol.* 86, 534–540.
- Raisi, A., Aroujalian, A., Kaghazchi, T., 2008. Multicomponent pervaporation process for volatile aroma compounds recovery from pomegranate juice. *J. Membr. Sci.* 339–348.
- Rajagopalan, N., Cheryan, M., 1995. Pervaporation of grape juice aroma. *J. Membr. Sci.* 104, 243–250.
- Sacano, T., Yamamura, K., Tamon, H., Miyahara, M., Okazaki, M., 1996. Improvement of coffee aroma by removal of pungent volatiles using A-type zeolite. *J. Food Sci.* 61 (2), 473–476.
- Sacano, T., Tamon, H., Okazaki, M., 1999. Selective removal of methyl mercaptan in coffee aroma using oxidized microporous carbon. *J. Chem. Eng. Jpn.* 32 (5), 701–704.
- Sarrazin, C., Le Quéré, J.L., Gretsche, C., Liardon, R., 2000. Representativeness of coffee aroma extracts: a comparison of different extraction methods. *Food Chem.* 70, 99–106.
- Schwaab, M., Pinto, J.C., 2007. Optimum reference temperature for reparameterization of the Arrhenius equation. Part 1: Problems involving one kinetic constant. *Chem. Eng. Sci.* 62, 2750–2764.
- Schwaab, M., Lemos, L.P., Pinto, J.C., 2008. Optimum reference temperature for reparameterization of the Arrhenius equation. Part 2: Problems involving multiple reparameterizations. *Chem. Eng. Sci.* 63, 2895–2906.
- She, M., Hwang, S.T., 2004. Concentration of dilute flavor compounds by pervaporation: permeate pressure effect and boundary layer resistance modeling. *J. Membr. Sci.* 236, 193–202.
- She, M., Hwang, S.T., 2006a. Recovery of key components from real flavor concentrates by pervaporation. *J. Membr. Sci.* 279 (1–2), 86–93.
- She, M., Hwang, S.T., 2006b. Effects of concentration, temperature, and coupling on pervaporation of dilute flavor organics. *J. Membr. Sci.* 271, 16–28.
- Trifunović, O., Lipnizki, F., Tragardh, G., 2006. The influence of process parameters on aroma recovery by hydrophobic pervaporation. *Desalination* 189, 1–12.
- Veglio, F., Trifoni, M., Pagnanelli, F., Toro, L., 2001. Shrinking core model with variable activation energy: a kinetic model of manganiferous ore leaching with sulphuric acid and lactose. *Hydrometallurgy* 60, 167–179.
- Viegas, M.C., Bassoli, D.G., 2007. Utilização do índice de retenção linear para caracterização de compostos voláteis em café solúvel utilizando GC-MS e coluna HP-Inowax. *Química Nova* 30, 2031–2034.
- Vincze, I., Vatai, G., 2004. Application of nanofiltration for coffee extract concentration. *Desalination* 162, 287–294.
- Wijmans, J.G., Athayde, A.L., Daniel, R., Ly, J.H., Kamaruddin, H.D., Pinnau, L., 1996. The role of boundary layers in the removal of volatile organic compounds from water by pervaporation. *J. Membr. Sci.* 109, 135–146.
- Yaws, C.L., 1999. *Chemical Properties Handbook*. McGraw-Hill, New York.
- Zhang, S.Q., Matsuura, T., 1991. Recovery and concentration of flavor in apple essence by pervaporation. *J. Food Proc. Eng.* 14, 291–296.
- Zuim, D.R., Carpiné, D., Distler, G.A.R., Scheer, A.P., Mafra, L.L., Mafra, M.R., 2011. Adsorption of two coffee aromas from synthetic aqueous solution onto granular activate carbon derived from coconut husks. *J. Food Eng.* 104, 284–292.