Journal of Membrane Science 326 (2009) 64–75

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Vacuum membrane distillation of the main pear aroma compound: Experimental study and mass transfer modeling

Nazely Diban, Oana Cristina Voinea, Ane Urtiaga, Inmaculada Ortiz*

Department of Chemical Engineering, University of Cantabria, Avda. de los Castros s/n. 39005 Santander, Spain

ARTICLE INFO

Article history:
Received 6 February 2008
Received in revised form 11 July 2008
Accepted 15 September 2008
Available online 24 September 2008

Keywords:
Aroma recovery
Kinetic modeling
Vacuum membrane distillation
Hollow fiber module
Surface diffusion

ABSTRACT

In this work, the recovery of the main pear aroma compound, ethyl 2,4-decadienoate, by means of vacuum membrane distillation is studied. A commercial hollow fiber module of polypropylene (PP) microporous membranes and a model solution of ethyl 2,4-decadienoate in ethanol–water mixtures were used in the experimental study. The effect of the operating variables, aroma feed concentration, feed flow rate, temperature and downstream pressure onto the process performance was analysed. Aroma enrichment factors up to 15 were experimentally obtained. A strong and reversible sorption of the aroma compound onto the PP material was observed. This phenomena was characterized by a linear adsorption isotherm, $q_a = K_{ads} C_a^e$, where $K_{ads}(295.96\,K) = 0.27\,kg\,kg^{-1}\,m^3\,kg^{-1}$.

A mathematical model able to predict the kinetics of the components separation and the partial component fluxes and enrichment factors was developed. In this model the classical gas transport mechanisms through the membrane pores, i.e. Knudsen and molecular diffusion, together with the sorption-diffusion phenomenon through the non-porous membrane portion, expressed by means of the surface diffusivity, were considered. The surface diffusivity of ethyl 2,4-decadienoate on the polypropylene was estimated to be $D_a^s = 1.01 \times 10^{-11}\,m^2\,s^{-1}$ at 296 K.

1. Introduction

Flavours are key components for the fruit juice industry. They give the proper quality to the final product and determine the customer's acceptance. In the thermal treatments used to concentrate the juices, the volatile aroma compounds are removed in the vapour phase, thus leading to the loss of the organoleptical properties of the product [1]. After condensation, the aroma compounds are recovered from the aqueous condensate by high temperature distillation, a technology that implies important energy consumption and does not prevent flavour spoilage. Membrane and solid-phase based alternative processes to this conventional aroma recovery technique have been considered lately, such as pervaporation [2–4], membrane air-stripping [5,6], membrane-based L–L extraction [7,8], adsorption [9–11], and vacuum membrane distillation [12].

Membrane processes, in general, are very attractive because of their simplicity and flexibility. Their basic properties make them ideal for application in the production of high quality fruit juices. They generally use gentle temperatures during the operation and do not involve phase changes or chemical additives. They are characterised by low energy consumption and ease scaling-up [13]. Another important advantage over the conventional separation processes is that the interfacial area is known and independent of the operating conditions, and thus, this value remains constant, facilitating the prediction of the process performance [14].

Vacuum membrane distillation (VMD) employs a porous hydrophobic membrane that acts as a physical barrier to prevent the aqueous feed phase passing through and creates a liquid–vapour interface at the membrane pores. The most suitable material for VMD membranes include polymers such as polytetrafluoroethylene (PTFE), poly(vinylidene fluoride) (PVDF) and polypropylene (PP) [15]. These membrane materials are widely used in the food industry and they are commercially available [16]. Some of the benefits of VMD, compared to other separation processes, already introduced by Lawson & Lloyd [17], worthy of mention are that it uses lower operating temperatures and reduced vapour spaces (compactness) than conventional distillation and lower pressures than conventional pressure-driven membrane separation processes and has, therefore, less demanding mechanical requirements.

Vacuum membrane distillation has been evaluated recently for its application to the concentration of sucrose solutions during beverage production [13,18]. Regarding the applicability of

* Corresponding author. Tel.: +34 942201585; fax: +34 942 201591.
E-mail address: ortizi@unican.es (I. Ortiz).

0376-7388/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2008.09.024

Table 1
General properties of the compounds in the feed solution.

Compound	CAS number	Molecular formula	M ($\times 10^{-3}$ kg mol^{-1})	BP (°C)	ρ_i at 25 °C (kg m^{-3})	Water solubility at 25 °C	p_i^{sat} at 22 °C (Pa)	[a] γ_i at 22 °C	$V_{b,i}$ (cm^3 mol^{-1})
Ethyl 2,4-decadienoate	3025-30-7	$C_{12}H_{20}O_2$	196.29	260	905	[b] 8.6 mg L^{-1}	1.51	8.5×10^5	[c] 237.5
Ethanol	64-17-5	C_2H_6O	46.07	78	789	Totally miscible	6654	6.6	51.5[c]
Water	7732-18-5	H_2O	18.02	100	1027	–	2670	1.0	17.5

[a] Estimated using the UNIFAC Calculator software [19].
[b] Estimated value using the EPI SuiteTM estimation program developed by the Syracuse Research Corporation (SRC) and the U.S. Environmental Protection Agency (copyright 2000).
[c] The liquid molar volume, V_b, was estimated by the Tyn and Calus method [20] and Vetere's relationship [21].

this technique to the recovery of aroma compounds, scarce literature was found. Bagger-Jørgensen et al. [12] evaluated the potential of VMD to recover blackcurrant juice aroma, concluding that this technology was very promising and deserved further investigation.

In this work, the analysis of the separation and concentration of the main pear aroma compound, ethyl 2,4-decadienoate, from aqueous model solutions, by means of vacuum membrane distillation was made. A polypropylene membrane in hollow fiber configuration and inserted into a module, commercially available, was used to perform the experiments at laboratory scale. The effects of the main operational variables, such as aroma concentration, flow rate and temperature of the feed phase and downstream pressure, on the process performance were studied, and the feasibility of the application of VMD to the recovery and concentration of the main pear aroma compound from aqueous feeds was determined. Finally, a kinetic model was developed considering, on one hand, the classical membrane distillation mechanism, which is based on liquid–vapour distribution and gas diffusion within the membrane pores for the major components of the feed phase, i.e.: water and ethanol. On the other hand, the transport of the aroma compound was described by considering a mechanism of adsorption onto the membrane material and surface diffusion through the non-porous portion of the membrane. This model, together with the estimated parameter surface diffusion coefficient, D_a^s, allowed an adequate simulation of the kinetics of the components separation and their partial fluxes and enrichment factors.

2. Experimental methods and materials

In this work, the separation of a tricomponent mixture containing water/ethanol/ethyl 2,4-decadienoate was studied applying vacuum membrane distillation. According to the literature and CG-MS characterization carried out in a previous work [10], the ethyl 2,4-decadienoate has been identified as one of the impact aroma compounds present in pear juice and thus it was selected as the aroma compound to be recovered and concentrated from the aqueous solution. The feed phase consists of a model solution of ethyl 2,4-decadienoate (Sigma–Aldrich) diluted into a mixture of approximately 3% (v/v) ethanol absolute (Panreac Química) and Milli-Q water (Millipore Corporation). The physico-chemical properties of the components are given in Table 1. The range of the aroma concentration was selected according to the values found in the Barlett pear brandy [22].

A diagram of the experimental set-up is shown in Fig. 1. The membrane module, purchased from Enka-Mycrodyn (unit MD 020 TP 2N) was also employed in a previous work [23] dealing with the VMD of chloroform from wastewaters. The membrane characteristics are compiled in Table 2. The feed phase was contained in a 1 L capacity tank continuously stirred. The feed tank was introduced into a thermostatizing bath to keep the feed temperature constant. The feed solution was circulated through the lumen side of the hollow fibers in a closed circuit while the permeate vapours were removed from the shell side using a vacuum pump (Telstar TE124000) and condensed in cold traps refrigerated by liquid nitrogen. The feed temperature was monitored by means of two thermoresistance probes (Pt-100), with an accuracy of ±0.2 °C, located at the inlet and outlet ports of the membrane module. A vacuum meter (Afora, model 8100) connected to the shell side of the module permitted the measurement of the vacuum pressure applied on the permeate side.

According to the results obtained in preliminary experiments, a strong affinity between the aroma compound and the membrane material had been observed. This led to the need to study the adsorption equilibrium of ethyl 2,4-decadienoate onto the polypropylene membrane. Adsorption experiments were conducted for 6 h, working as previously explained, without applying vacuum to the permeate side. These tests showed that sorption reached equilibrium within 2 h. Next, the VMD experiments were performed as follows: an initial time period (2 h) allowing for the sorption phenomenon to reach equilibrium, followed by a period of time (2–4 h) where permeation was enhanced due to the low pressure applied to the permeate side. The detailed experimental conditions are shown in Table 3.

Samples of 2 mL were taken periodically from the feed tank using a syringe and introduced into chromatography vials that were kept refrigerated (4 °C) until analysis. At the end of the experiment, the condensed permeate was collected, the volume was measured and a sample was taken for component analysis. Both ethanol and ethyl 2,4-decadienoate concentrations in aqueous samples were measured by means of GC (Shimadzu, model GC2010) with a flame ionization detector (FID) and equipped with a DB-Wax chromatographic column (10 m × 0.10 mm I.D. × 0.20 μm film thickness).

The partial mass fluxes of the component i that crosses the membrane toward the permeate side, j_i, and the enrichment factors, β_i, were calculated as follows,

$$J_i = \frac{m_i^P}{A_m t_f} \quad (1)$$

Table 2
Characteristics of the hollow fiber membrane module MD020 TP 2N as supplied by Enka-Mycrodyn.

Membrane material	Polypropylene
Housing material	Polypropylene
Inner diameter of the shell (m)	0.02
Inner diameter of the hollow fibers (m)	5.5×10^{-3}
Wall thickness (m)	1.55×10^{-3}
Nominal pore diameter (m)	0.2×10^{-6}
Porosity (%)	75
Number of hollow fibers	3
Module length (m)	0.75
Effective membrane area (m^2)	0.0389
Mass of polypropylene membrane (kg)	0.016