Selective extraction of natural products with benign solvents and recovery by organophilic pervaporation: fractionation of D-limonene from orange peels†

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There has been a growing awareness of the need to replace volatile organic compounds (VOCs) by benign solvents aiming to implement more sustainable processes. Accordingly, this work aims at evaluating a new and more friendly process based on the use of benign solvents with different hydrophobicities, namely common alimentary oil, polypropylene glycol and polyethylene glycol, for the selective recovery of natural products, followed by pervaporation. Particularly, the extraction and fractionation of limonene from orange peels was studied and optimised, where a high value product is obtained from a highly abundant material that is mostly disposed. Firstly, the best benign solvents were selected, in order to obtain high yields of extraction, and then pervaporation and vacuum distillation were compared after the extraction process, in order to obtain high yields of global recovery of limonene with the least contaminants possible. The integrated process selected was the extraction of limonene from orange peels using polypropylene glycol 240 (PPG), followed by organophilic pervaporation, providing the selective recovery of limonene free of solvent.

Introduction

The development of nonhazardous alternatives (one of the goals of green chemistry and engineering) is vitally important for the continued and sustainable growth of the chemical enterprise, as regulatory pressure is increasingly focusing on the use, manufacture, and disposal of organic solvents. There are many potential advantages to replacing volatile organic compounds (VOCs) with water or various types of benign solvents. The most obvious are reduced flammability, reduced toxicity, and reduced environmental risk. Water and aqueous-based solvent systems may represent an increasingly significant choice for the replacement of traditional solvents in the chemical industry. Other leading VOC solvent alternatives include supercritical carbon dioxide[1] and ethane[2] fluids, ionic liquids in microwave-assisted extractions,[3,4] immobilized solvents, solventless conditions, and the use of fluorous solvents. Alimentary oil (cooking oil), PPGs (polypropylene glycols) and PEGs (polyethylene glycols) can be considered as benign solvents due to their low-toxicity, low volatility, thermal stability, and biodegradability. They are also attractive due to their relatively low ecotoxicity and cost, unlike most ionic liquids, and can be considered as a bulk commodity chemical.

Pervaporation is a membrane separation technique, whose separation principle is based on the preferential partitioning of a solute from a liquid feed phase into a dense, non-porous membrane through which it diffuses according to its chemical potential gradient.[5] This gradient is the driving force for the solute transport across the membrane. It is in general established by maintaining a low vacuum on the membrane downstream side, while keeping the membrane upstream side, which is in contact with the liquid feed, under mild conditions, at ambient pressure. According to the solution–diffusion model, the partial flux J_i of a solute i across the membrane is given by:

$$J_i = \frac{S_i \cdot D_i}{Z_m} \cdot \Delta\mu_i = \frac{S_i \cdot D_i}{Z_m} \cdot (\mu_i^f - \mu_i^p) \quad (1)$$

with S_i the sorption coefficient of solute i between the feed liquid phase and the membrane; D_i the diffusion coefficient of i in the membrane; z_m the membrane thickness; $\Delta\mu_i$ the chemical potential gradient of i over the membrane; $\Delta\mu_i^f$ and $\Delta\mu_i^p$ are the chemical potential of i in the liquid feed phase and the permeate, respectively. By selecting the right type of membrane, it is possible to control which compound will preferentially remain in the feed and which will preferentially permeate through. The effectiveness of pervaporation integrated with the use of benign solvents for chemical processing was already successfully demonstrated by a few authors.[6]

The potential advantages of the use of benign solvents with extremely low vapour pressure for recovery of target solutes by pervaporation can be summarized as follows: i) benign solvents can solubilise a large range of organic molecules and transition metal complexes, that may present reduced solubility in conventional solvents; ii) due to their non-measurable vapour pressure, benign solvents with extremely low vapour pressure, unlike water and aqueous-based solvent systems, do not desorb to the vapour phase at the downstream surface of non-porous, dense membranes, whether they are organophilic or hydrophilic, which allows for solute recovery free of solvent, under the operating

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conditions used; recovered solutes do not get contaminated by the solvent and therefore do not need further purification for solvent removal; iii) there are no solvent losses from the original feed neither to the permeate nor to the environment, which reflects on the process economy and environmental benignity; and hence the solvent can be reused; iv) due to selective solute–polymer interactions, it is possible to remove/recover target solutes from the reaction media, while keeping other products; solute recovery may be governed by these interactions.[7,8]

This work is focused on assessing the potential of using benign solvents for the extraction of target compounds and further recovery by pervaporation, in a sustainable process. Particularly, benign solvents are studied as extracting agents for solubilising target compounds from natural matrices, followed by a fractionation of these compounds by organophilic pervaporation.

Our case-study is the valorisation of residues of the orange juice industry produced in high quantities, the orange peels, which can be used in obtaining citrus oils[9] although a significant part of it is disposed or used as biofuel.[10] It was reported that the orange peels contain more than 40 compounds, with high amounts of different important monoterpenes, mainly D-limonene,[11,12] and also α- and β-pinene and β-myrcene in lower concentrations.

The recovery of D-limonene from natural matrices is commonly performed through supercritical CO_2 extractions.[9,13–15] Compared with this method, the integrated system proposed in this work is simpler, also efficient and operates under mild conditions.

Due to its high solvency, attractive citrus odour and versatility, D-limonene is used in wide range of products and applications, such as a flavouring or fragrance in the food and cosmetic industry, or as a solvent in household and industrial cleaners.

Additionally, the monoterpenes present in orange peels are important sources of intermediates for the pharmaceutical, flavour and fragrance industries.[16] Particularly, valuable products have been synthesised through the hydrogenation of myrcene[17] and of limonene[18–20] using supercritical CO_2. Moreover, the use of ionic liquids combined with supercritical CO_2 was reported in the literature[21] in order to enhance the selectivity of the hydrogenation of limonene into one of its important derivatives.

Our work aims at optimising the recovery and fractionation of limonene from orange peels in a process which comprises the following steps: 1 – optimisation of the extraction of limonene from orange peels with benign solvents, with different hydrophobicities; 2 – optimisation of the fractionation of limonene by pervaporation, and comparison with vacuum distillation,[22] under operating conditions as equivalent as possible. For each set of operating conditions studied, the overall efficiency of the operation was quantified by calculating fluxes and enrichment factors of the permeates, captured by condensation.

Experimental

Materials

The solvents PPG 240 and PEG 300 were gift samples from Clariant Ltd. and alimentary oil Pingo Doce brand was purchased at a Portuguese supermarket. The reagent (Hydranal–Coulomat Oil) used for Karl–Fischer titration was supplied by Riedal de Haen Ltd. The model organic compounds such as α-pinene, β-pinene, myrcene, octanal, 3-carene, limonene, octanol, nerol, linalool and α-terpineol used for the GC calibration were procured from Aldrich and Fluka Ltd and used as received. The pervaporation membrane used was a polyoctylmethylsiloxane on polyetherimide (POMS-PEI) membrane, kindly given by GKSS, Germany.

Experimental set-up and operating conditions

Extraction of limonene. Different extracts of orange peels were produced using different solvents with different hydrophobicities such as alimentary oil (cooking oil: AO), polypropylene glycol 240 (PPG), and polyethylene glycol 300 (PEG). Table 1 shows the physicochemical properties of the solvents used for the extraction of orange peels. The efficiency of extraction of these solvents was compared with the extraction using hexane, a typical hydrophobic solvent. Initially the peels were chopped finely with the help of a mixer and dissolved into the solvents in a 1 : 1 ratio (w/w). The content was stirred and heated in a closed vessel at 100 °C for 24 h for the effective extraction of natural compounds into the solvents. Later it was cooled, filtered using cotton plug and weighed. Each extract obtained was used as feed solution in the pervaporation and in the vacuum distillation processes.

Pervaporation process (PV)

The PV set-up consists of a permeation unit in which the feed was circulated and kept at constant temperature (20 °C). The membrane was supported on a perforated stainless steel disk. Two pairs of O-rings between flanges provided the vacuum seal. The volume of the feed cell was 20 cm^3 and the effective membrane area exposed to the feed solution (upstream) and vacuum (downstream), was 7.065 cm^2. The feed was stirred continuously with the help of an agitator at 200 rpm, measured with a digital tachometer. The permeate was condensed with liquid nitrogen for 10 h. The downstream pressure was controlled at 2.0 ± 0.1 mbar. Fig. 1 shows the schematics of the pervaporation experimental rig. The pervaporation membrane performance

Table 1 Physicochemical properties of the solvents used for the extraction of the orange peels

Solvent	Molecular weight/g ml^{-1}	Density/g ml^{-1} 20 °C	Vapour Pressure/mbar 20 °C	Viscosity at 20 °C	Solubility in water
Alimentary oil	—	0.924[a]	<0.07	92[a]	Insoluble
PPG	240	0.998	<0.01	256	Insoluble
PEG	300	1.12	<0.1	61	Soluble

[a] Measured in this work.

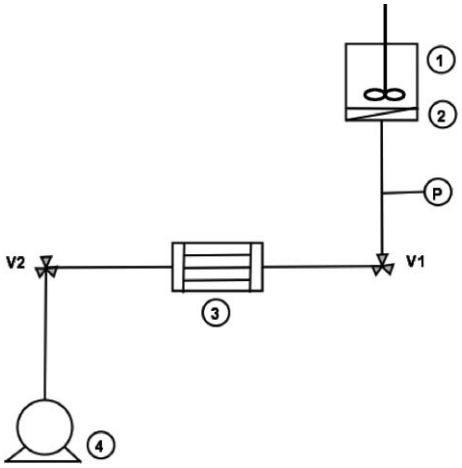

Fig. 1 Schematic representation of a pervaporation lab unit: (1) feed vessel; (2) membrane; (3) condenser; (4) vacuum pump; (P) pressure transducer; V1 is an on-off valve; V2 is a needle valve.

was tested under different operational process conditions. The efficiency of the operation was quantified by calculating the total flux (J) and the enrichment factor (β) of each permeate.

Vacuum distillation process (VD)

For the vacuum distillation experiments the same rig was used (20 cm^3 capacity). However, during these experiments the feed cell was closed from one side using a metallic foil and the other side was kept open for the vacuum outlet. The feed was stirred continuously with the help of a magnetic stirrer at 200 rpm, measured with a digital tachometer. The evaporate was condensed with liquid nitrogen for 10 h. The downstream pressure was kept constant at 2 ± 0.1 mbar. Fig. 2 shows the schematics of the vacuum distillation experiment. The performance of the vacuum distillation experiment was tested under different operational process conditions and the efficiency of the operation was quantified by calculating the total flux (J) and the enrichment factor (β) of the condensates and compared with the correspondent values of the pervaporation experiments.

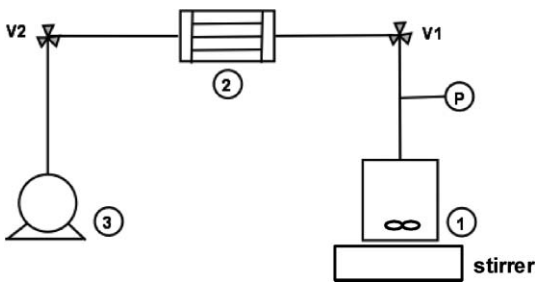

Fig. 2 Schematic representation of a vacuum distillation lab unit: (1) feed vessel; (2) condenser; (3) vacuum pump; (P) pressure transducer; V1 is an on-off valve; V2 is a needle valve.

Analytical

The viscosity of the alimentary oil was measured by a digital viscometer (model DV-II, Brookfield Engineering Laboratories Inc., USA) and the density was determined by using a density bottle.

The water content in the initial solvents, in each feed solution (at initial time of the pervaporation and vacuum distillation experiments) and in each condensate (from the pervaporation and from the vacuum distillation experiments) were determined using an automated Karl–Fischer. The organic compounds, namely aroma compounds, present in each initial feed solution and in each condensate were initially qualitatively analyzed by GC-MS (Shimadzu Corporation, RTX column) and identified by Mass Spectrometry, through comparison with a commercial library (data not shown). Later, these compounds were quantified by GC using an internal standard. The Gas Chromatograph used (GC-2014, Shimadzu Corporation, Japan) was controlled by GC Solution software, using a packed Carbowax-10 column with 22 m × 0.32 mm and 0.25 μm film thickness. The oven temperature was initially set at 70 °C and then increased from 70–250 °C at 2 °C min^{-1} and held isothermal for 60 min. The injectors were set at 250 °C, with a split ratio of 1/50 for FID. The FID detector was maintained at 270 °C. The sample volume injected was 50 μl. The carrier gas was hydrogen, at a constant flow rate of 0.95 ml min^{-1}. There were made 3 injections per sample, with the addition of the internal standard dodecane. The initial feed samples of AO and PPG were diluted in dichloromethane (DCM) to reduce their viscosity before being analysed by GC. On the other hand, the samples of PEG and the condensates were extracted with dichloromethane, due to their hydrophilic character, and then each organic phase was analysed by GC. The results were obtained by using calibration curves, prepared *a priori*, for each individual aroma compound.

Results and discussion

Study of the effect of the benign solvent used in the extraction of limonene

In order to study the effect of the solvent used in the extraction of limonene, benign solvents with different hydrophobicities were tested, namely the water insoluble PPG and alimentary oil, and the hydrophilic PEG. The water and aroma compounds concentrations of each extract are shown in Table 2.

For obtaining high yields of extraction of limonene, the solvent to be selected should have a high affinity for this compound, which exhibits an hydrophobic character, a low solubility in water,[12] a low air/water partition to water and a high air/oil partition to oil.[23] As expected, the highest concentration in limonene was observed in the extract with the highly hydrophobic

Table 2 Feed composition of the different extracts in hexane, alimentary oil (AO), polypropylene glycol 240 (PPG) and polyethylene glycol 300 (PEG). Aroma concentrations were measured by gas chromatography. Water concentrations were measured by Karl–Fisher titration

Feed concentration/mg L^{-1}				
Compound	Hexane	AO	PPG420	PEG300
α-Pinene	203.4	474.3	403.4	230.8
β-Pinene	83.1	134.4	134.6	—
Myrcene	446.2	206.5	146.9	9.1
Octanal	497.2	371.6	371.6	37.5
3-Carene	239.8	459.2	456.4	—
Limonene	19 877	12 703.8	10 414.8	484.8
Octanol	177.4	162.5	141.0	—
Nerol	122.5	209.7	209.2	—
Linalool	332.4	—	515.0	85.1
Terpineol	60.0	—	—	—
Water	49.1	1383.3	10 672.2	315 613.0

Table 3 Partial fluxes (J_i) and enrichment factors (β_i) of each compound present in the pervaporation and vacuum distillation processes using as feed solutions the extracts in alimentary oil (A), the extracts in polypropylene glycol 240 (B) and the extracts in polyethylene glycol 300 (C)

A. Extracts in alimentary oil as feed solutions

	Pervaporation system		Vacuum distillation system	
Compound	J_i(mol/m2/h)	β_i(–)	J_i(mol/m2/h)	β_i(–)
α-Pinene	0.001	2.5	0.001	2.1
β-Pinene			0.000(2)	2.9
Myrcene			0.001	4.8
Octanal	0.001	2.7	0.000(4)	1.9
3-Carene			0.001	2.3
Limonene	0.073	11.4	0.047	7.0
Octanol	0.000	2.2	0.000(1)	1.5
Nerol	0.000	2.8		
Linalool				
Terpineol				
Water	2.886		3.362	
SUM	2.960		3.411	

B. Extracts in polypropylene glycol 240 as feed solutions

	Pervaporation system		Vacuum distillation system	
Compound	J_i(mol/m2/h)	β_i(–)	J_i(mol/m2/h)	β_i(–)
α-Pinene			0.000(4)	1.8
β-Pinene				
Myrcene			0.00(4)	4.7
Octanal	0.001	2.8	0.001	2.4
3-Carene			0.001	3.0
Limonene	0.065	12.9	0.032	6.0
Octanol			0.000(2)	2.4
Nerol			0.000(4)	4.2
Linalool	0.001	4.7	0.001	3.8
Terpineol				
Water	3.085		3.618	
SUM	3.151		3.653	

C. Extracts in polyethylene glycol 300 as feed solutions

	Pervaporation system		Vacuum distillation system	
Compound	J_i(mol/m2/h)	β_i(–)	J_i(mol/m2/h)	β_i(–)
α-Pinene	0.000(3)	3.3	0.004	2.4
β-Pinene				
Myrcene	0.000(2)	38.4	0.000(4)	6.7
Octanal	0.000(4)	24.8	0.004	14.1
3-Carene				
Limonene	0.051	237.8	0.474	146.3
Octanol				
Nerol				
Linalool	0.001	24.9	0.010	19.6
Terpineol				
Water	3.238		53.546	
SUM	3.291		54.038	

hexane (with a *n*-octanol/water partition coefficient of 10^4 at 25 °C[24]), widely used in industry. Nevertheless, hexane shall not be used because it is a hazardous, rather volatile solvent. The hydrophilic PEG shall also not be used since its extract shows the lowest concentration in limonene. The best candidates as extracting solvents for the integrated extraction/fractionation process seems to be the alimentary oil and PPG, because the concentrations of limonene in their extracts were within the same order of magnitude of the extract obtained with hexane, with the advantage of being benign solvents.

Optimisation of the fractionation of limonene in the integrated process – comparing the separation processes pervaporation and vacuum distillation after solute recovery by extraction

Aiming at fractioning limonene using the extracts produced with benign solvents as feed solutions, pervaporation and vacuum distillation processes were compared under operating conditions as equivalent as possible: same experimental rig, equal stirring speeds although different stirrers have to be used, and same vacuum pressure. As the selected solvents are essentially

non-volatile both methods may be used for the recovery of limonene, assuring that the recovered solutes will be collected solvent-free. The reason why organophilic pervaporation may represent an interesting alternative derives from the fact that this recovery process is not governed by liquid–vapour equilibrium. As discussed in the introduction section, pervaporation is ruled by solvent and solute interactions with the polymer matrix of the membrane. When using a hydrophobic POMS-PEI membrane, it is expected that the solute of interest will be recovered with a high selectivity against water (present in the extracts produced) and also against other minor solutes which establish less favourable interactions with the membrane polymer. A fair comparison between vacuum destillation and organophilic pervaporation as to be established under the same stirring (external mass transfer) and vacuum conditions.

Table 3 shows the partial fluxes (J_i) and the enrichment factors (β_i) for each compound i present in the pervaporation and vacuum distillation processes.

When comparing pervaporation and vacuum distillation it may be concluded, for each extract produced, that: 1 – the total and water fluxes are lower in pervaporation than in vacuum distillation, which is expected because the membrane acts as a selective barrier; 2 – the aroma enrichments factors (mass of aroma in the condensate/mass of aroma in the feeding extract) are always higher in pervaporation than in vacuum distillation, due to the favourable selective interaction of the aroma compounds with the pervaporation organophilic membrane; 3 – the enrichment factors obtained for limonene by pervaporation are always higher that the corresponding enrichment factors for other aroma compounds present in the feed extracts (by a factor of 4 to 5); this result is extremely positive because it results in an effective limonene enrichment against other "contaminating" compounds; 4 – the enrichment effect described in 3 for limonene is higher when organophilic pervaporation is used, in comparison with vacuum distillation; 5 – pervaporation represents a more economical and rational use of energy: from a thermodynamic point of view only the permeating compounds involve an expense of energy (in vacuum distillation more energy is wasted on the evaporation of water).

Taking into account all these remarks, pervaporation is clearly selected for the recovery and fractionation of limonene. In general terms, it can be concluded that the optimised integrated process shall consist of an extraction with PPG followed by organophilic pervaporation.

Conclusions

In this work, an integrated and sustainable process is proposed consisting of using benign solvents for the extraction of target aroma compounds, followed by organophilic pervaporation for their recovery and fractionation. The case-study of this work, the valorisation of the residues of orange juice industry, is a process relevant from an economical and environmental point of view. Indeed, limonene is a high value product obtained from a source that is mostly disposed. The effect of different benign solvents in this sustainable process is studied, and organophilic pervaporation is compared with the traditional vacuum distillation in terms of global efficiency of the process. Another important advantage of this process is the observed by ^{1}H NMR absence of contamination of the permeate by the benign solvent due to its low volatility.

The integration of the process was succeeded. Alimentary oil and polypropylene glycol 240 efficiently solubilised limonene, the target compound in this work. Furthermore, organophilic pervaporation enabled an efficient concentration of limonene, with fewer contaminants, and it also enabled a lower water content when compared with the traditional vacuum distillation, which favours the stabilisation of the target solute.

The combined extraction-pervaporation process may be applied to the efficient recovery of other fragrancies from natural sources without contamination of the target compounds by the extracting solvents, allowing for their complete reuse. Finally, the simplicity of this process turns it into a better candidate for its scaling-up at industrial scale.

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