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Deterpenation of *citrus* essential oil via extractive distillation using imidazolium-based ionic liquids as entrainers

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ABSTRACT

Background: The deterpenation of *citrus* essential oils (CEO) is crucial in many industries to promote the stability and preserve the organoleptic properties of the final product, improving considerably the oxygenated fraction purity.

Methods: Two imidazolium ionic liquids (ILs), [C_4mim][OAc] and [C_4mim]Cl, were applied as novel separation agents in a deterpenation process constituted by an extractive distillation column and a flash separator unit, aiming to remove hydrocarbon terpenes from the essential oil. The CEO was modeled as a mixture of the commonly found limonene (monoterpene) and linalool (monoterpenoid). To support the process simulation, isobaric vapor-liquid equilibrium measurements were conducted for the binary limonene/linalool and ternary limonene/linalool/IL mixtures at 5 kPa, and the data were successfully correlated with the NRTL model.

Significant findings: The simulation results demonstrate that [C_4mim]Cl improved the purity of linalool in the final product. Moreover, both [C_4mim]Cl and [C_4mim][OAc] reduced the required stages in the distillation column to obtain a terpeneless CEO with a certain purity, [C_4mim]Cl being the most effective option.

1. Introduction

Essential oils (EO) are complex mixtures mostly composed of terpenes and terpenoids that can be extracted from different parts of plants (e.g., flowers, seeds, leaves, peels) generally by steam distillation, hydrodistillation or liquid-liquid extraction [1]. The EO obtained from *citrus* fruits are among the most commercially attractive options, being widely explored as natural fragrances and flavors [2]. Besides their pleasant aromas, *Citrus* essential oils (CEO) show other appealing properties, such as antioxidant, antidiabetic, insecticidal, antifungal, and antibacterial activities [3]. Among their vast range of applications, CEO are used as a flavoring or additive ingredient in perfumes, foods, pharmaceuticals, cosmetics, and personal care products [3,4]. The broad diversity of the *citrus* genus also contributes to the CEO large commercial exploitation [3]. The most abundant hydrocarbon component in CEO profiles is limonene, whose concentration typically varies between 25% and 98% depending on the variety of the *citrus* fruit [3,5]. Besides, smaller quantities of oxygenated terpenes, including linalool, citral, α-terpineol, citronellol, and geraniol, are often detected in the CEO profiles [3–5].

Although hydrocarbon monoterpenes are frequently the major components in CEO profiles [6], these compounds contribute little to the oil aroma and organoleptic properties. Also, hydrocarbons might be easily oxidized, leading to the formation of undesired products [5]. Therefore, separating hydrocarbon from the oxygenated monoterpene fraction, a process known as deterpenation, is an essential step to improve the stability and quality of the final product [7]. In such a process, the obtained CEO can be classified as concentrated oil, when part of the hydrocarbon fraction is removed, or terpeneless oil, when the hydrocarbon fraction in the final product is much lower [5]. These

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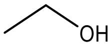
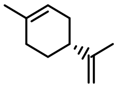
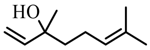
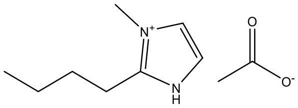
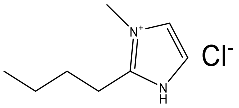
Table 1
Chemical structure, CAS, source, and mass purity, of the terpenes and ionic liquids studied in this work.

Compound	CAS	Structure	Source	Purity (mass fraction)[a]	Water content (% mass fraction)
ethanol	64-17-5		Synth	≥ 0.995	0.10
R-(+)-limonene	5989-27-5		Aldrich	≥ 0.97	0.65
linalool	78-70-6		Aldrich	≥ 0.97	0.11
[C_4mim][OAc]	284049-75-8		Iolitec	≥ 0.99	0.97
[C_4mim]Cl	79917-90-1		Iolitec	≥ 0.99	0.21

[a] Minimum mass purities given by the manufacturer.

concentrated or terpeneless CEO have improved solubility in water, organic solvents, and other solvents used in food technology [5].

At the industrial level, the deterpenation of CEO is frequently carried out by liquid-liquid (or solvent) extraction or vacuum distillation [5]. Despite the simplicity of solvent extraction, this technology usually requires large amounts of solvent, which must be purified before being recycled into the system [8], and often provides CEO with lower purities of oxygenated compounds [7,9] compared to distillation techniques [7,10,11]. Regarding the latter, vacuum operation is preferred since lower operating temperatures are required, preventing possible degradation of CEO constituents [8,12].

A crucial step in liquid-liquid extraction or distillation processes is the selection of a suitable solvent or entrainer to aid in the fractionation of the CEO. In the case of liquid-liquid extraction, traditional solvents such as glycols and aqueous solutions of organic polar solvents (e.g., methanol, ethanol, acetone, ethyl acetate) have been evaluated [5]. In addition, ionic liquids (ILs) [13–15] and, more recently, deep eutectic solvents (DES) [16–18] have also been reported. In contrast, alternative solvents as entrainers in distillation processes remain less explored in studies addressing the fractionation of CEOs, though a few works [7,10] show promising results for imidazolium-based ILs. Nonetheless, ILs and DESs have been recently reported as promising entrainers for other extractive distillation-based processes, such as the removal of contaminants from fuels [19] and the separation of azeotropes [20–22] and refrigerants [23].

Among the solvents currently addressed as green alternatives to traditional organic solvents, ILs are certainly one of the classes that have received more attention in recent years [24–26]. Constituted by organic cations and anions, ILs exhibit appealing properties to be used as solvent media in separation processes, such as excellent chemical and thermal stability, low volatility and flammability, and high selectivity solvation ability [27–29]. Besides, these solvents can be "tailored" by combining different cations and anions to reach specific physicochemical applications, expanding their range of applications [27,30]. In previous works from our group [30–32], imidazolium and phosphonium-based ILs were studied as separation agents to fractionate binary terpene mixtures. Selectivities and capacities, derived from experimental activity coefficient at infinite dilution, suggested that 1-butyl-3-methylimidazolium acetate ([C_4mim][OAc]) and 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) were potential options to separate hydrocarbon/alcohol monoterpene mixtures. Also, Ganem et al. [10] reported that [C_4mim][OAc] improved the fractionation of CEOs via extractive distillation. Thus, in this work, [C_4mim][OAc] and [C_4mim]Cl were studied as separation agents to deterpenate CEO. A model mixture composed of R-(+)-limonene (hydrocarbon) and linalool (oxygenated) was selected to represent the CEO, in line with several works available in the literature [7,10,13–15,33]. Isobaric vapor-liquid equilibrium (VLE) measurements of the binary limonene/linalool mixture and the ternary limonene/linalool/[C_4mim][OAc] and limonene/linalool/[C_4mim]Cl mixtures were carried out at 5 kPa, using a dynamic recirculation ebulliometer. Then, these data were correlated with the NRTL activity coefficient model [34,35], and the fitted parameters were used to simulate an extractive distillation process with the commercial software Aspen Plus V11. For comparison purposes, the separation process was simulated with and without IL.

2. Materials and methods

2.1. Chemicals

The terpenes and ionic liquids used in this work are listed in Table 1, along with their CAS, chemical structure, mass fraction purity, and water content (%). The latter was measured by Karl-Fisher titration (Metrohm, 848 Titrino Plus). All the compounds used in this work were stored at room temperature and used as received from the supplier.

2.2. Isobaric VLE measurements

The isobaric VLE experiments of the binary (limonene + linalool) and ternary (limonene + linalool + IL) mixtures were conducted using a dynamic recirculation ebulliometer (Fischer GmbH, model 0602) coupled to a vacuum pump (Edwards, model RV5), a pressure control unit (Fisher system M101), and a thermostatic bath (Nova Ética, model NT 281). The pressure and temperature ranges of the dynamic recirculation ebulliometer are (0.25-300) kPa and (293.2-523.2) K, respectively. The experiments were performed at 5 kPa to avoid higher operation temperature ranges where the organoleptic properties of the CEOs can be compromised [8,10]. The ebulliometer operates under continuous recirculation of the liquid and vapor phases until reaching the equilibrium, assumed after (30-40) min of continuous and smooth vapor phase circulation at constant temperature and pressure. Two samples with volumes between (0.1-0.5) cm^3 were collected from the liquid and condensed vapor phases with a gas-tight syringe through sampling nozzles covered by silicone seals.

The composition of the mixtures was determined by refractometry (Mettler Toledo, model RE40D, uncertainty of 1×10^{-4} nD) using

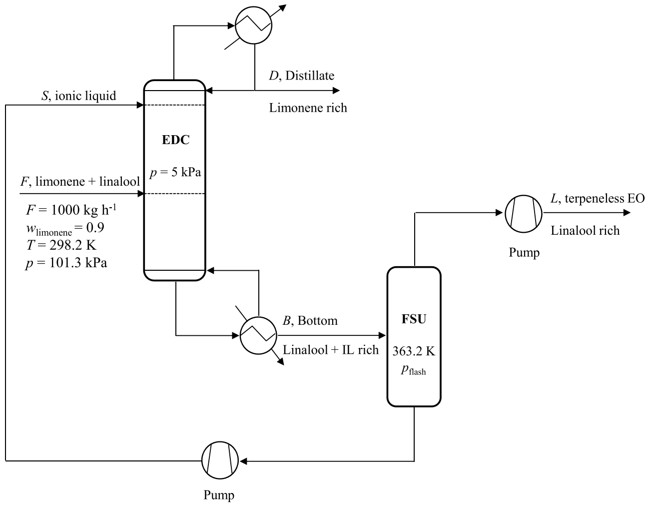


Fig. 1. Schematic flowsheet of the deterpenation processes composed of an extractive distillation column and a flash separator unit.

calibration curves covering the mixture composition range. The calibration curves were built considering at least 17 standard solutions prepared independently using an analytical scale (Shimadzu, model AUY220, ± 0.1 mg). For the limonene + linalool + IL systems, the standard solutions had a constant mass fraction of IL of (0.050 ± 0.001), following the approach proposed by Souza et al. [36]. To validate the experimental procedure, the VLE of the ethanol + water mixture (at 13 kPa), and the vapor pressures of pure ethanol and R-(+)-limonene (range 5-95 kPa) were measured and compared to the literature data.

Table 2
Experimental VLE data of the R-(+)-limonene (1) + linalool (2) binary mixture obtained in this work, at 5.0 ± 0.1 kPa.[a,b]

T/K	x_1	y_1
359.3	0.917	0.961
360.7	0.821	0.910
362.2	0.726	0.857
363.5	0.659	0.817
364.7	0.592	0.773
365.5	0.553	0.748
366.5	0.503	0.713
367.5	0.441	0.677
368.7	0.383	0.631
370.6	0.307	0.563
371.8	0.262	0.513
372.6	0.233	0.477
373.6	0.198	0.430
374.7	0.162	0.378
375.4	0.143	0.345
377.1	0.099	0.268
378.2	0.073	0.210

[a] The estimated uncertainties are u(*T*) = 0.1 K; u(*x*) = 0.005; u(*y*) = 0.005.

[b] Overall quality factor following the methodology proposed by Kang et al [41]: $Q_{VLE} = 0.45$.

Table 3
Experimental VLE data of the R-(+)-limonene (1) + linalool (2) + $[C_4mim][OAc]$ (3) ternary mixture obtained in this work, at 5.0 ± 0.1 kPa.[a,b]

T/K	x_1	x_2	y_1
358.5	0.885	0.080	0.956
359.4	0.824	0.141	0.928
360.3	0.773	0.191	0.904
361.1	0.715	0.249	0.878
362.1	0.659	0.304	0.850
363.0	0.610	0.354	0.821
364.1	0.554	0.410	0.785
365.3	0.495	0.468	0.748
366.3	0.449	0.514	0.713
367.5	0.400	0.562	0.672
368.6	0.353	0.609	0.631
369.6	0.314	0.648	0.597
370.5	0.279	0.683	0.558
371.5	0.241	0.721	0.513
372.7	0.202	0.760	0.462
373.5	0.175	0.786	0.420
374.1	0.156	0.806	0.388
374.6	0.143	0.819	0.367
375.5	0.117	0.845	0.318
376.1	0.103	0.858	0.290
376.9	0.085	0.876	0.251
377.5	0.071	0.890	0.222
379.6	0.030	0.931	0.112

[a] The estimated uncertainties are u(*T*) = 0.1 K; u(*x*) = 0.005; u(*y*) = 0.005.

[b] The mass fraction of $[C_4mim][OAc]$ was 0.05 for all data points.

2.3. Process simulation

A binary mixture of limonene (mass fraction $w_{limonene} = 0.90$) and linalool ($w_{linalool} = 0.10$) was selected to represent the citrus essential oil [7,10,33]. Considering that vacuum distillation is one of the most suitable methods to deterpenate CEO [5,7], an extractive distillation column (EDC) was selected. In this case, a limonene-rich phase is obtained at the top of the distillation column (distillate), and the terpeneless CEO, enriched in linalool, exits at the bottom. Additionally, the use of ILs ($[C_4mim][OAc]$ or $[C_4mim]Cl$) as entrainers to facilitate the deterpenation of the CEO was tested. In this scenario, the IL fed to the EDC is recovered in the bottom stream with the terpeneless CEO, and an additional step is required for its recovery. Hence, a flash separator unit (FSU) was added to separate the linalool-rich phase from the IL, which is then recycled to the distillation column. The process simulation was performed using the Aspen Plus V11 commercial software. A schematic flowsheet of the process is presented in Fig. 1. The IL input parameters are presented in Table S1. The deterpenation process flow proposed in this work is similar to those reported by Ganem and co-authors [7,10], where the authors propose a process containing an extractive distillation unit connected to a flash separator operating under a high vacuum. More details on the simulation of the deterpenation process are presented in Section S1 of the SM. CO_2 produced in the distillation unit was predicted considering the approach proposed by Gadalla et al.[37,38] and described in detail in Section S1 of the SM.

3. Results and discussion

3.1. VLE measurements

The vapor pressures of ethanol and R-(+)-limonene are listed in Table S2 and compared with the literature data in Fig. S1 of the SM. In Table S3, the Antoine constants regressed with the experimental vapor pressures measured in this work are presented. Likewise, the VLE data obtained for the ethanol/water system (shown in Table S4) are discussed and compared with data collected from the literature (Fig. S2) in Section S3 of the SM. The NRTL parameters correlated for the ethanol + water mixtures using the VLE data obtained in this work, and the obtained deviations ($\sigma(T)$, $\sigma(y_1)$,$\sigma(y_{12})$) are given in Table S5. The VLE data obtained in this work is comparable to those available in the literature [39,40], while the dataset was found to be consistent by the method proposed by Kang et al. [41] ($Q_{VLE} = 0.8$).

The isobaric (5 kPa) VLE data measured for the R-(+)-limonene/linalool binary mixture are listed in Table 2. The overall quality factor (Q_{VLE}) [41] obtained for the system was 0.45. Moreover, a comparison between the data obtained in this work and reported by Ganem et al.[7] (Fig. S3) reveals that the datasets present similar trends.

The VLE data of R-(+)-limonene/linalool/$[C_4mim][OAc]$ and R-

Table 4
Experimental VLE data of the R-(+)-limonene (1) + linalool (2) + [C4mim]Cl (3) ternary mixture obtained in this work, at 5.0 ± 0.1 kPa.[a,b]

T/K	x_1	x_2	y_1
359.9	0.691	0.269	0.891
360.6	0.651	0.308	0.875
361.2	0.619	0.340	0.861
362.0	0.575	0.384	0.843
362.5	0.549	0.409	0.828
362.9	0.530	0.428	0.821
364.1	0.474	0.484	0.789
365.0	0.439	0.519	0.765
366.0	0.401	0.556	0.739
366.9	0.369	0.589	0.713
367.9	0.334	0.623	0.686
369.0	0.292	0.665	0.649
370.0	0.256	0.701	0.611
371.1	0.224	0.733	0.573
372.1	0.192	0.764	0.533
372.9	0.168	0.789	0.503
373.7	0.149	0.808	0.472
374.3	0.137	0.819	0.451
374.9	0.126	0.830	0.430
375.4	0.114	0.842	0.409
376.5	0.092	0.864	0.367
377.4	0.072	0.884	0.323
378.2	0.058	0.898	0.279
379.1	0.041	0.914	0.222
380.3	0.025	0.933	0.150

[a] The estimated uncertainties are u(*T*) = 0.1 K; u(*x*) = 0.005; u(*y*) = 0.005.
[b] The mass fraction of [C_4mim]Cl was 0.05 for all datapoints.

(+)-limonene/linalool/[C_4mim]Cl mixtures are presented in Table 3 and Table 4, respectively. In these cases, the mass fraction of the IL was kept at 5%. The modified McDermott−Ellis method by Wisniak and Tamir [42,43] was applied to the ternary mixtures. This method has been successfully used to evaluate multicomponent VLE datasets' consistency [44], including systems with salts or ILs [45,46]. A detailed description of this method is presented in Section S5 of SM, and the consistency test results of the ternary systems are shown in Table S6. All the experimental data points for the ternary systems passed the test.

In Fig. 2, the obtained relative volatilities (α_{12}) of the terpenic mixtures are presented. The α_{12} value calculated from the VLE data reported by Ganem et al. [10] for the limonene/linalool/[C_4mim][OAc mixture (at $w_{[C_4mim][OAc]}$ = 4.5%) was included in Fig. 2 for comparison purposes. The definition of α_{12} is presented in SM.

The results obtained in this work reveal that the introduction of [C_4mim][OAc] (5% in mass fraction) slightly increases the relative volatility of the R-(+)-limonene/linalool mixtures for $x_1^{'} < 0.8$, which is somewhat lower than expected. However, the relative volatility obtained from the data available in the literature [10], for an IL mass fraction of 4.5%, is surprisingly much higher than the values found in this work. Unfortunately, no further comparison is feasible since the other VLE data points reported by Ganem et al. [10] were obtained for higher IL mass fractions (>10%) than the 5% considered in this work. In the case of R-(+)-limonene/linalool/[C_4mim]Cl, results showed a more significant increase in the relative volatilities of the terpenic mixture, particularly when low amounts of limonene are present in the liquid phase. An increase of at least 50% in the α_{12} values is observed compared to the binary terpene mixture. These are promising results for the use of the studied IL in the deterpenation of CEO by extractive distillation.

3.2. *Process simulation*

The simulation of the process illustrated in Fig. 1 was conducted by varying the reflux ratio on the condenser (*R*), the theoretical number of stages of the distillation column (*n*), and the solvent/CEO feed ratio (*S/F*, in mass fraction). The first goal was to evaluate the effect of the ILs on the linalool and limonene recoveries (represented, respectively, by the amounts of linalool in the terpeneless CEO and limonene in the distillate divided by their amounts in the feed CEO). In this step, three values of *R* (0.5, 1.0, 1.5) and *S/F* (0.025, 0.050, 0.075) were tested, and *n* was varied from 5 to 30. The IL was supplied at the second stage of the distillation column, while the CEO was fed at the column's middle stage (*n*/2). The VLE data obtained in this work were correlated with the NRTL model [34,47] using the software Aspen Plus, and the model parameters were considered in the process simulation. The NRTL parameters and σ deviations are presented in Table S7 of the SM.

The results are summarized in Fig. 3 (*R* = 0.5 and *R* = 1.0) and Fig. S4 (*R* = 1.5), where the limonene and linalool recoveries are presented as a function of *n* for the selected reflux ratios. The recoveries improve by increasing the number of stages, more evidently up to *n* = 15. Similarly, an increase in the reflux ratio leads to higher limonene and

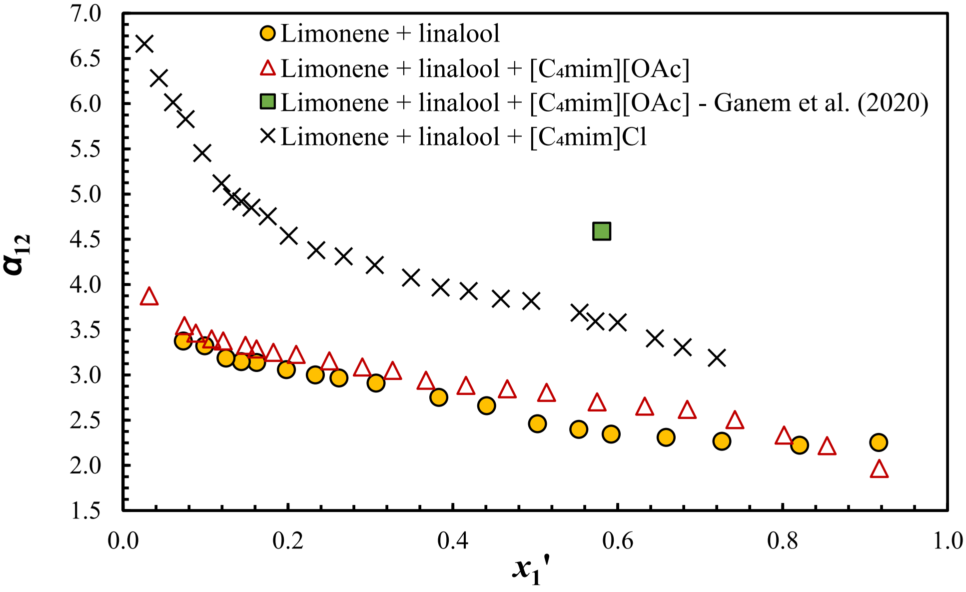


Fig. 2. Experimental relative volatilities of the binary R-(+)-limonene/linalool and ternary R-(+)-limonene/linalool/IL ([C_4mim][OAc] or [C_4mim]Cl) mixtures at 5.0 ± 0.1 kPa. The mass fractions of the ILs in the mixtures studied in this work are kept at 5%. The data point reported by Ganem et al. [10] was obtained at $w_{[C_4mim][OAc]}$ = 4.5%.

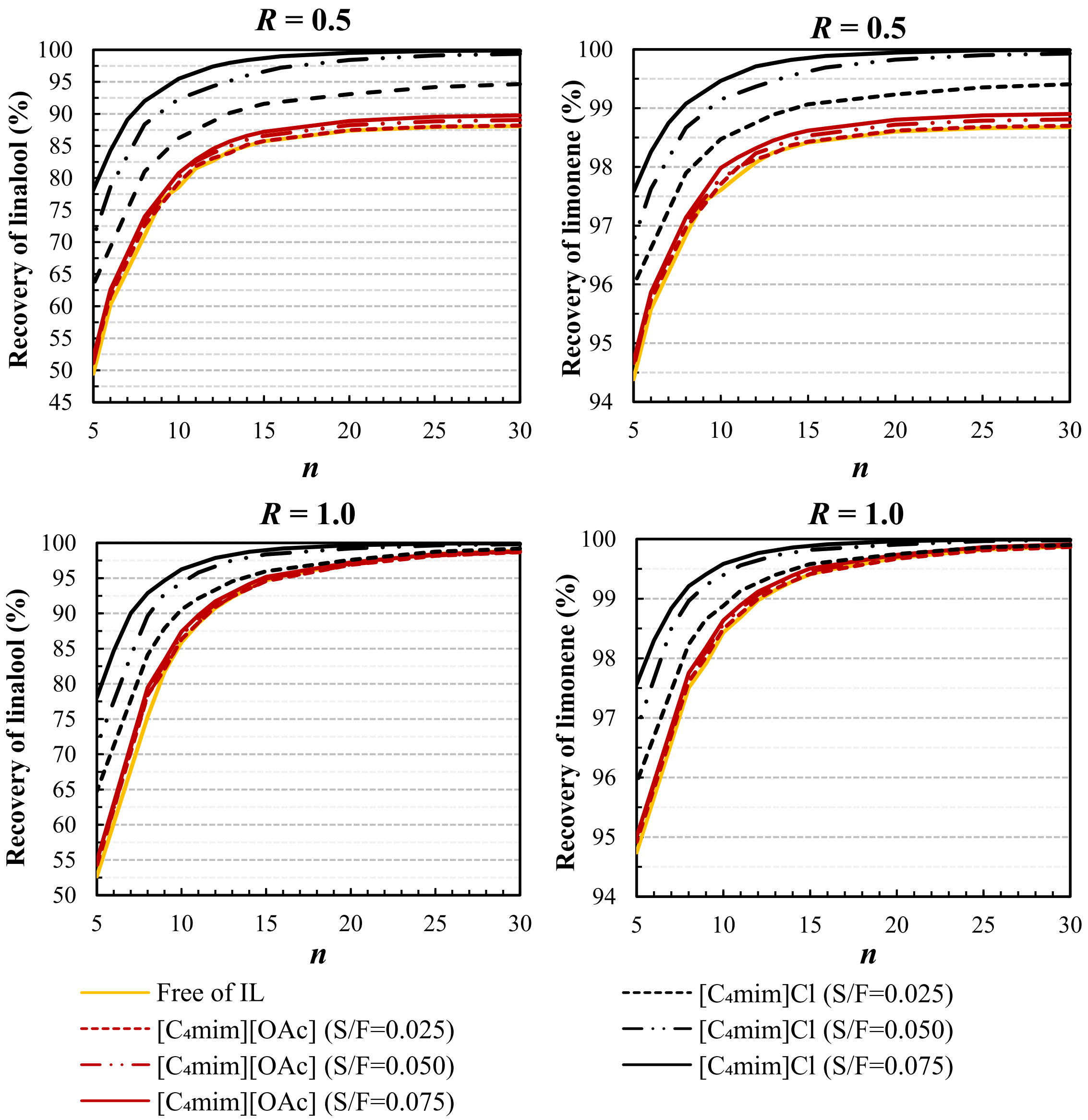


Fig. 3. Comparison of the limonene and linalool recoveries (%) as a function of the number of stages in the distillation column for the three studied reflux ratios (0.5, 1.0, 1.5), and different S/F ratios.

linalool recoveries, with more substantial increments observed by increasing *R* from 0.5 to 1.0 than 1.0 to 1.5. The influence of these parameters is more significant in the recovery of linalool in the terpeneless CEO since the percentage of this monoterpenoid in the fed oil is much lower than limonene. The results show that [C$_4$mim]Cl as entrainer is much superior to [C$_4$mim][OAc], and also the weak impact of changing the mass percentage of [C$_4$mim][OAc] in the mixture, which is very close to the results obtained in the absence of IL. On the opposite, changing the *S/F* ratio of [C$_4$mim]Cl from 0.025 to 0.075 influences significantly the recovery of both components or the number of stages guaranteeing a fixed recovery.

To better assess the effects of the *R* and *S/F* values on the product recovery, the results obtained varying those parameters for a fixed number of stages ($n = 15$ or $n = 30$) are presented in Fig. S5 of the SM. At a reflux ratio of 0.5 and $n = 30$, the linalool and limonene recoveries, without an entrainer, are 88.1% and 98.7%, respectively. The addition of [C$_4$mim][OAc] slightly increases those values. On the other hand, [C$_4$mim]Cl delivers much better performances in all analyzed scenarios, with limonene and linalool recoveries varying from 94.7% and 99.4% ($S/F = 0.025$) to 99.99% and 99.9% ($S/F = 0.075$), respectively. Likewise, similar trends were obtained for $n = 15$, reavaling that [C$_4$mim]Cl is still much more effective in performing the separation than [C$_4$mim][OAc] at columns with fewer stages. In all scenarios, an increment in the *S/F* ratio leads to higher recoveries of the products.

To further explore the effects of *R* on the processes, Fig. 4 was built, where the number of stages of the distillation column is presented as a function of linalool recovery in the terpeneless CEO, for all the studied reflux ratios, in the absence of IL and in the presence of [C$_4$mim]Cl. The addition of [C$_4$mim][OAc] was not considered in this scenario since the product recovery curves are very close to those obtained for the binary limonene/linalool mixture, as discussed above. On the other hand, [C$_4$mim]Cl has a clear impact on the required column stages. For instance, to reach a minimum recovery of 95% of linalool when $R = 1.0$, the presence of [C$_4$mim]Cl reduces *n* from 16 (IL-free) to values varying between 14 ($S/F = 0.025$) and 9 ($S/F = 0.075$). Likewise, distillation columns of 10 and 9 stages ($S/F = 0.025$ and $S/F = 0.075$, respectively) are required to achieve 95% of linalool recovery when $R = 1.5$, while a minimum of 13 stages is necessary in the absence of IL. When comparing the achieved linalool recoveries for columns with equal stages, the effects of [C$_4$mim]Cl are evident: while the IL-free process with a column

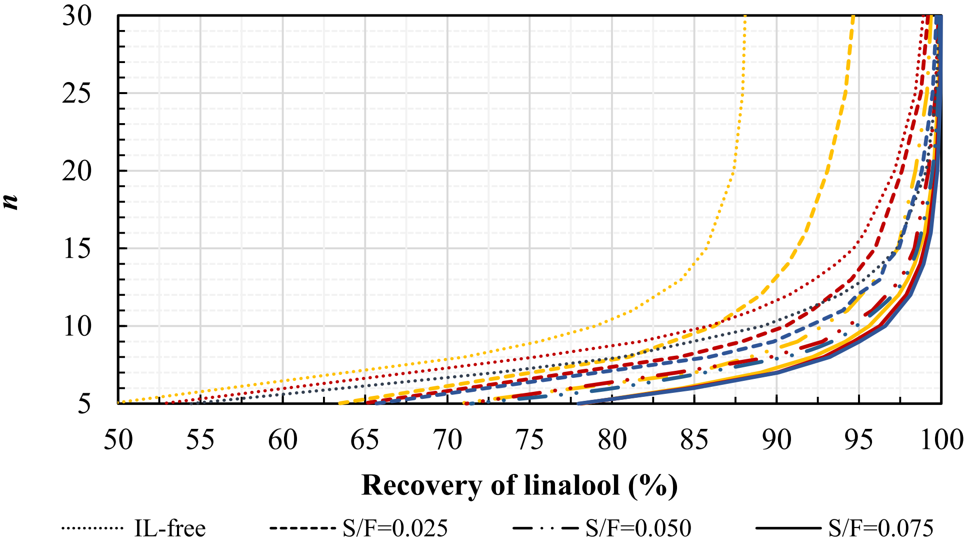


Fig. 4. Comparison of the required number of stages as a function of the linalool recovery for the processes absent of IL and with [C_4mim]Cl. Different reflux ratios were tested: $R = 0.5$ (yellow lines), $R = 1.0$ (red lines), and $R = 1.5$ (blue lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

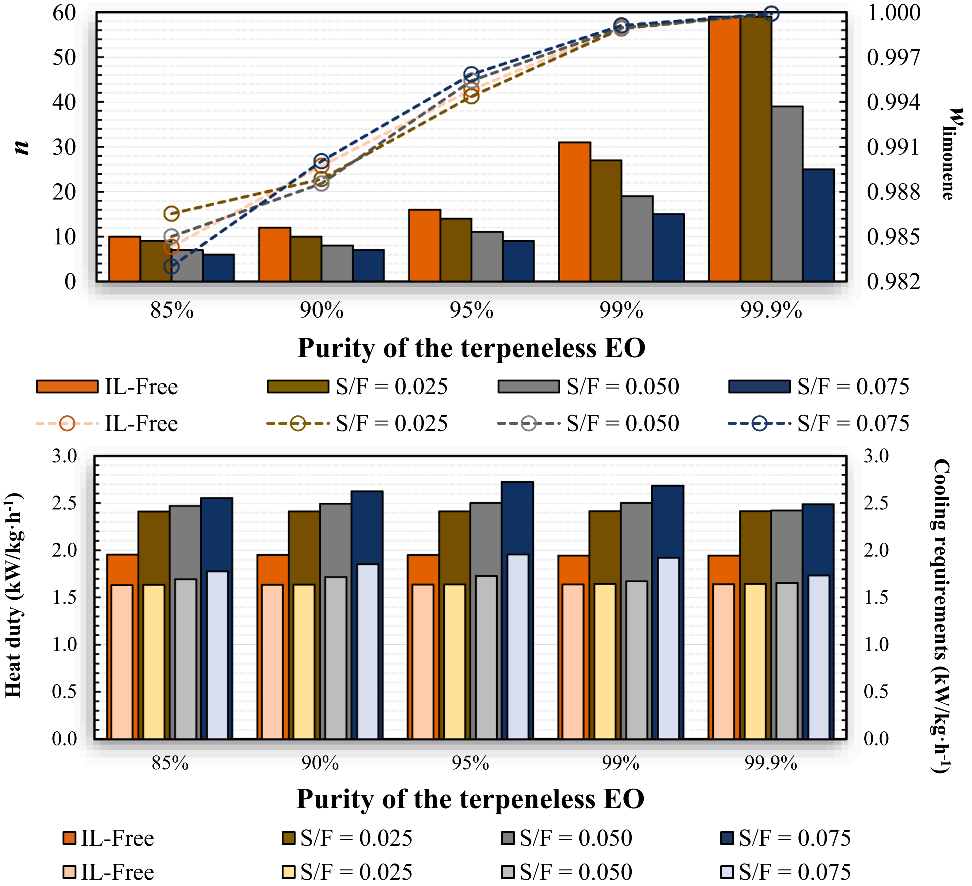


Fig. 5. Overview of the requirements to obtain the target linalool purities in the terpeneless CEO from the process free of IL and with [C_4mim]Cl for $R = 1.0$. The dark bars correspond to *n* or the specific heat duty, the light bars are the specific cooling requirements, and the circles represent the limonene mass fraction obtained in the distillate. The lines connecting the circles are guides for the eyes.

with 15 stages delivers a recovery of linalool of 86% (at $R = 0.5$), the recoveries are improved to 92% and 99% when S/F of 0.025 and 0.075 of [C_4mim]Cl, respectively, are fed to processes.

Due to the positive effects of adding [C_4mim]Cl to the deterpenation process evidenced above, the conditions to achieve a specific minimum linalool purity in the terpeneless CEO were also evaluated. The target linalool purities were fixed at 85%, 90%, 95%, 99%, or 99.9%. In such a scenario, the total specific heat duty (sum of the heat duty of the reboiler and flash separator per kg·h^{-1} of terpeneless CEO), and the specific cooling requirements (on the condenser of the distillation column), were calculated. Avoiding higher operating temperatures in the distillation column, *n* and *R* values varied from 5-60 and 0.5-1.5, respectively. The pump energy requirements are negligible compared to process heat duty and, therefore, neglected. The results obtained for $R = 1.0$ are presented in Fig. 5, while Figs. S6 and S7 show the results for $R = 0.5$ and $R = 1.5$, respectively. Since no significant improvements were observed by adding [C$_4$mim][OAc] to the process, the results with this IL were omitted from Fig. 5 and Figs. S6 and S7.

As expected, more stages in the distillation column are required to obtain higher linalool purity in the final product. Also, the limonene purities in the distillate increase as the target linalool increases, though high limonene purities ($w_{\text{limonene}} > 0.98$) are achieved in all cases. Moreover, an increment in the reflux ratio reduces *n* in most cases, having a positive effect on the process investment cost. Nonetheless, increasing *R* values lead to higher total specific heat duties and cooling requirements, increasing operational costs. Indeed, the reflux ratio has a stronger impact on the specific heat duties, cooling requirements than the number of stages in the distillation column or the *S/F* ratio. Regarding the latter, an increase in the amount of IL tends to reduce the number of stages in the distillation column, particularly when higher linalool purities ($w_{\text{linalool}} > 0.99$) are desired.

Adding [C$_4$mim]Cl to the process considerably reduces the minimum number of stages required to achieve the target linalool purities at certain operating conditions. On the other hand, higher specific heat duties are also observed. Although an increase in the specific heat duties leads to higher operating costs, savings in the total number of stages in the distillation column reduce the investment cost. At $R = 1.0$ and $S/F = 0.050$ (Fig. 5), reductions between 30% (CEO with 85% of linalool) and 39% (99% of linalool) in the minimum *n* value were registered, whereas the corresponding increment in the specific heat duties was always lower than 29%. By keeping $R = 1.0$ and increasing the *S/F* to 0.075, columns containing at least 40% fewer stages are required to achieve the target linalool purities. In these operating conditions, *n* decreases from 59 (IL-free) to 25 when 99.9% is the linalool target purity, with a 28% increment in the specific heat duty. Nevertheless, less expressive reductions of the required column stages (< 17%) are observed at $R = 1.0$ and *S/F* 0.025, while increments of around 24% in the heat duties were observed.

At $R = 0.5$, [C$_4$mim]Cl also significantly benefits the deterpenation process since it improves the maximum purity of the terpeneless CEO (Fig. S6). While the process free of IL delivers a maximum purity of 88%, the utilization of [C$_4$mim]Cl, even at a $S/F = 0.025$, enables the obtention of essential oil with 95% purity ($n \geq 37$); linalool purities of 99% and 99.9% are also achievable at solvent-feed ratios of 0.050 and 0.075. Besides, reductions up to 57% ($S/F = 0.075$) in the number of stages are achieved when [C$_4$mim]Cl is added to the process to attain 85% purity in the terpeneless CEO, at $R = 0.5$, while the corresponding heat duty increment is 35%. At $R = 1.5$, higher contents [C$_4$mim]Cl in the process also leads to less stages in the column, but the reductions are less pronounced than those obtained for lower studied *R* values, 0.5 and 1.0.

It is worth mentioning that, at an equivalent reflux ratio, the deterpenation process with [C$_4$mim]Cl as the entrainer also exhibits higher cooling requirements than other options. The increments, however, are more pronounced when higher solvent-feed ratios are applied. At $S/F = 0.050$, the cooling requirements increased between 1% and 8% compared to the IL-free process, whereas increments between 3 and 20% are observed at $S/F = 0.075$. In contrast, the increases in this parameter were lower than 1% when a $S/F = 0.025$ of [C$_4$mim]Cl is applied to the process. The cooling requirements (energy released on the condenser) could be considered in energy integration studies.

Table 5

Optimized parameters for the deterpenation processes to obtain a terpeneless CEO with 99% of linalool.

Parameters	IL-free	[C$_4$mim][OAc]	[C$_4$mim]Cl
EO feed stage	46	44	29
number of stages (*n*)	58	54	41
reflux ratio (*R*)	0.77	0.74	0.52
S/F	-	0.52	0.27
specific reboiler duty (kW/kg·h^{-1})	1.8	1.7	2.1
specific cooling requirements (kW/kg·h^{-1})	1.4	1.4	1.3
flash separator specific duty (kW/kg·h^{-1})	-	0.09	0.04
distillate mass flow (kg·h^{-1})	900	900	900
limonene mass fraction purity in the distillate	0.999	0.999	0.999
terpeneless CEO mass flow (kg·h^{-1})	100	100	100
linalool mass fraction purity in the terpeneless CEO	0.99	0.99	0.99
CO$_2$ emission (kg·h^{-1})	43	43	52

3.3. Process optimization

The optimum conditions for the proposed deterpenation process were obtained using the Aspen Plus® Model Analysis/Optimization tool with the Sequential Quadratic Programming (SQP) convergence method [48–50]. The objective function was defined as distillation column reboiler specific heat duty (i.e., the ratio of the reboiler heat duty and the mass flow rate of the terpeneless CEO), and the process variables were the reflux ratio, the *S/F* ratio, the number of stages, and the feed position of the essential oil in the distillation column. The process constraints were the linalool mass fraction purity (>0.99±0.01%) and mass flow rate (>99±0.1 kg·h^{-1}) in the terpeneless CEO. The *R* and *S/F*values varied between (0.5-1.5) and (0.25-0.75), respectively, whereas *n* varied between 5 and 60. The essential oil feed conditions, the distillation column pressure, and the flash separator operating pressure and temperature values were the same as those presented in Fig. 1. The IL was fed at the second stage of the distillation column.

The optimum parameters obtained for the processes with [C$_4$mim][OAc] or [C$_4$mim]Cl are compared with the values for the IL-free process in Table 5. The CO$_2$ consumption for optimum conditions is included in Table 5.

The results reveal that the process with [C$_4$mim][OAc] requires a column with 4 stages less than the IL-free process. Similar specific heat duties (1.8 kW/kg·h^{-1}) and colling requirements (1.4 kW/kg·h^{-1}) are obtained in both cases. When [C$_4$mim]Cl is added as entrainer, a reduction of 29% is observed in the column-required stages ($n = 41$) compared to the IL-free processs ($n = 58$), whereas an increase of 19% in the specific heat duty is observed. Consequently, adding [C$_4$mim]Cl to the deterpenation process might lead to lower investment costs and higher operational costs. The estimated CO$_2$ emission in the distillation column reboiler is 43 kg·h^{-1} for both IL-free and the process with [C$_4$mim][OAc], and 52 kg·h^{-1} when [C$_4$mim]Cl is added as entrainer. The optimum specific heat duties listed in Table 5 are at least 10% lower than those presented in Fig. 5 ($R = 1.0$) when a linalool purity of 99% in the CEO is specified.

4. Conclusions

The results of the process simulation reveal that [C$_4$mim]Cl significantly improves the linalool recovery in the deterpenation process, while the effects of [C$_4$mim][OAc] on this parameter are less substantial. Moreover, [C$_4$mim]Cl is often a promising option when targeting specific linalool purities in the terpeneless CEO. The addition of [C$_4$mim]Cl to the process, at $R = 0.5$, improves the maximum attainable linalool purity from 88% (IL-free) to 95% ($S/F = 0.025$) and 99.9% (*S/F* of 0.05 and 0.075). Besides, savings up to 58% ($R = 1.0$, $S/F = 0.075$, $w_{\text{linalool}} = 0.995$) in the minimum required stages are achieved when supplying the chloride-based IL to the distillation column. Adding [C$_4$mim]Cl to the process increases the total specific heat duties, but the required number of stages (n) decreases. By aiming to minimize the process heat duty, a reduction of 29% in n is achieved when [C$_4$mim]Cl is the entrainer, while an increment of 19% in the specific heat duty is observed. Reducing n lowers the investment costs, which compensates for the increase in the operating cost. Moreover, [C$_4$mim]Cl increases the specific cooling requirements of the deterpenation process by up to 20% (at equivalent reflux ratios), which could be considered in energy integration studies.

This work encourages further research in the field, focused on investigating potential neoteric solvents (e.g., ILs, DES, bio-based solvents) and the required technologies to improve the deterpenation of CEOs.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jtice.2024.105367.

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