



Extraction of oxygenated compounds from crude *citrus latifolia* peel oil using ethanol/water mixtures as solvents: Phase equilibrium and continuous equipment operation

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ABSTRACT

Citrus latifolia (acid lime) essential oil, an important commodity in the international market, was fractionated by solvent extraction. New liquid–liquid equilibrium (LLE) data for systems composed of crude acid lime essential oil (CALEO), ethanol, and water at $T = (298.2 \pm 0.1)$ K were acquired for different water contents in the solvent and mass ratios between the solvent and CALEO (S/EO). The performance of the NRTL parameters available in the literature was evaluated by comparing the predicted LLE phases compositions with the experimental data. Higher water content in the solvent led to lower migration of the components from the raffinate to the extract phase but increased the solvent selectivity for oxygenated compounds. Low S/EO also decreased the migration of the components. The predicted composition exhibited satisfactory results, with global deviations in mass fraction up to 0.02. The CALEO was also fractionated in a perforated rotating disc contactor, using ethanol/water mixtures as solvents. The process performance was evaluated by experimental and simulated extraction indices. As in the LLE, additional water in the solvent and lower solvent to feed mass flow ratio (S/F) led to less extraction of the components, but higher experimental *Folds* were achieved (6-fold using ethanol 40 and 8-fold using 50% w/w water). Finally, greater water content in the solvent was also related to higher experimental values of density, viscosity and surface tension, especially for the extract phases, contributing for better operational conditions.

1. Introduction

Essential oils (EOs) and terpenic by-products are important commodities in the international market. In 2016, Brazil was ranked as one of the main exporters of these raw materials, with approximately 52.6 thousand tons exported [1], which corresponds to approximately 7.6% of the world's exports [2]. *Citrus latifolia* Tanaka, or Tahiti lime [3], is recognized as “common lemon” in Brazil, since it is the typical lemon cultivated in this country, being the 5th most-common fruit exported [4]. The EO extracted from the acid lime fruit peels, predominantly by cold pressing, is a key ingredient for soft drink formulations, especially for “cola” flavor [5,6], and is also reported as a constituent in ice creams, candies and baked goods, being also used to cover up disagreeable odors in drugs and cosmetic products [7].

As a typical citrus EO, the crude acid lime essential oil (CALEO) is a complex mixture of volatile components (85–99% w/w), mainly terpene hydrocarbons and their oxygenated derivatives, and non-volatile compounds (1–15% w/w), such as waxes, pigments, fatty acids, and

carotenoids [8,9]. The volatile portion is mostly composed of limonene (40–60%), γ -terpinene (10–20%), β -pinene (10–16%), α -pinene (1–3%), neral (1–5%), and geranial (1–6%) (w/w) [5,9–13]. Its composition depends on several factors, such as weather, soil conditions, fruit variety, procedure used for the EO extraction, and others [14]. The terpene fraction is reported to be less stable and more susceptible to degradation reactions when exposed to the air, light or heat, which may generate off-flavor compounds [7,10,14–17], besides to present low contribution to the EO aroma [9,14,15,18]. Otherwise, the oxygenated derivatives, mainly the isomers neral and geranial (citral), are related to the typical lemon aroma, higher stability and acceptability [5,15,19–21]. Thus, the concentration of oxygenated compounds by their separation from terpenes is a common industrial process [14,22], known as deterpenation or folding [10,23].

In the literature, some studies about the deterpenation of lemon EOs by supercritical CO₂ extraction [10,22,24] can be found, and products with a good quality were obtained. On the other hand, several studies have shown that the separation between terpenes and oxygenated

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Nomenclature		σ	surface tension ($\text{mN}\cdot\text{m}^{-1}$)
w	mass fraction	$\Delta\sigma$	difference between the surface tensions of extract and raffinate streams ($\text{mN}\cdot\text{m}^{-1}$)
F	feed mass flow ($\text{kg}\cdot\text{s}^{-1}$)	Abbreviations	
S	solvent mass flow ($\text{kg}\cdot\text{s}^{-1}$)	LLE	liquid–liquid equilibrium
R	raffinate mass flow ($\text{kg}\cdot\text{s}^{-1}$)	EO	essential oil
E	extract mass flow ($\text{kg}\cdot\text{s}^{-1}$)	CALEO	crude acid lime essential oil
E_{OMB}	overall mass balance error (%)	COEO	crude orange essential oil
E_{MBi}	specific component relative error in the mass balance (%)	PRDC	perforated rotating disc contactor
$K_{E'a}$	overall volumetric mass transfer coefficient of oxygenated compounds based on the composition of the extract stream ($\text{kg}_{\text{oxygen}}\cdot\text{s}^{-1}\cdot\text{m}^{-3}\cdot(\text{kg}_{\text{oxygen}}\cdot\text{kg}_{\text{extract}}^{-1})^{-1}$)	OC	overall composition
%EXT _{OXYG}	percentage of oxygenated compounds extracted from the feed (%)	S/EO	solvent to CALEO mass ratio (for LLE)
%EXT _{TERP}	percentage of terpenes extracted from the feed (%)	S/F	solvent to feed mass flow ratio (for continuous extraction)
%OE	percentage of oxygenated compounds in the extract phase on a solvent-free basis (%)	Subscripts	
%M _{SOLV,R}	percentage of solvent migrated to the raffinate stream (%)	F	feed stream (acid lime crude essential oil)
O/T	oxygenated to terpenes mass ratio in relation to the initial EO composition	S	solvent stream (ethanol/water mixture)
ρ	density ($\text{kg}\cdot\text{m}^{-3}$)	R	raffinate stream (terpene-rich phase)
$\Delta\rho$	difference between the densities of extract and raffinate streams ($\text{kg}\cdot\text{m}^{-3}$)	E	extract stream (solvent-rich phase)
η	dynamic viscosity (mPa·s)	1	terpene group
$\Delta\eta$	difference between the dynamic viscosities of extract and raffinate streams (mPa·s)	2	oxygenated compounds group
		3	ethanol
		4	water

compounds in citrus EOs is technically possible using ethanol/water mixtures as solvents [7,9,14,17,18,23,25–28]. Moreover, recent studies have proved that the original EO aroma is maintained when this deterpenation procedure is adopted [9,18]. Koshima et al. [7] reported liquid–liquid equilibrium data for lemon model systems, composed of limonene, β -pinene, γ -terpinene, citral, ethanol, and water, at $T = (298.2 \pm 0.1)$ K, and adjusted interaction parameters of the NRTL and UNIQUAC thermodynamic models. Gonçalves et al. [9] determined LLE data of systems composed of CALEO, ethanol and water, at $T = (298.2 \pm 0.1)$ K, for different ethanol/water mixtures. In both studies, the fractionation process was evaluated by thermodynamic approaches, dealing with parameters such as the partition coefficients

(k) of terpenic and oxygenated compounds, as well as the solvent selectivity for the oxygenated compounds (S). Dupuy et al. [29] conducted the fractionation of limonene/citral mixture by liquid–liquid extraction in a polypropylene membrane contactor, using ethanol/water mixtures as solvents. The authors evaluated the equipment performance in terms of operational parameters and calculation of k and S values.

Although the LLE of system composed of CALEO, ethanol and water, at $T = (298.2 \pm 0.1)$ K, was already described in previous study [9], a deepening on the deterpenation of CALEO using ethanol/water mixtures as solvent is still important. Furthermore, experimental data concerning the deterpenation of CALEO by solvent extraction using

Table 1

CAS numbers, supplier and experimental purities, sources and experimental physical properties at $T = 298.2$ K^a.

Material	CAS registry number	Supplier Purity (%)	Experimental Purity (%) ^b	Source	ρ ($\text{kg}\cdot\text{m}^{-3}$) ^c	η (mPa·s) ^d	σ ($\text{mN}\cdot\text{m}^{-1}$) ^e
Standards							
(-)- β -Pinene	18172-67-3	99.00	99.87	Sigma-Aldrich, USA	866.95	1.53	27.4
(R)-(+)-Limonene	5989-27-5	98.80	98.81	Sigma-Aldrich, USA	841.35*	0.92*	27.6*
γ -Terpinene	99-85-4	97.00	97.69	Sigma-Aldrich, USA	845.16	0.85	27.3
Citral	5392-40-5	95.00	99.05	Sigma-Aldrich, USA	884.84*	1.93	31.9
Ethanol	64-17-5	99.80	99.99	Merck, Germany	785.18*	1.06*	21.6*
Water	7732-18-5				997.04*	0.87*	71.1*
Solvents (%w/w water in the solvent)							
20 \pm 1					841.91	1.68	24.8
24.4 \pm 0.3					852.24	1.73	25.1
31.4 \pm 0.7					865.50*	1.80*	25.6*
42.6 \pm 0.5					890.10*	2.18*	26.7*
51 \pm 1					909.35	2.24	28.2
Crude Acid Lime Essential Oil (CALEO)				Louis Dreyfus Company, Brazil	864.57	1.23	25.3

^a Standard uncertainties u are $u(T) = 0.1$ K, $u(\rho) = 0.01$ $\text{kg}\cdot\text{m}^{-3}$, $u(\eta) \leq 0.03$ mPa·s, and $u(\sigma) \leq 0.1$ $\text{mN}\cdot\text{m}^{-1}$.

^b Experimentally determined by GC-FID, given as mass percentage, without further purification.

^c Density.

^d Dynamic viscosity.

^e Surface tension.

* Experimental data in agreement with values previously reported in the literature [17,23,28,29].

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