Essential-Oil Fractionation by Dense CO_2: Process Flowsheet Development and Optimization in HYSYS Environment

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Abstract – A multi-purpose process flowsheet for supercritical-CO_2 fractionation of the Essential Oils (EOs) of *origanum*, *tea-tree*, and *lemon* is developed, simulated, and optimized using the process flowsheet simulator HYSYS. Components constituting about 91% by weight of the EOs are selected and classified as *monoterpenes* (MTs) and *non-monoterpenes* (NMTs). The objective of the processes is set as the separation of the undesired MTs from the more valuable NMTs without employing temperatures higher than 55 ^oC to prevent degradation of heat-labile EO components. The proposed multi-purpose process flowsheet that is effective for all three EOs achieves 95% purity and, depending on the EO composition, 79-91% recovery for the desired NMT compounds.

Keywords: Supercritical CO_2, essential-oil, fractionation, flowsheet development, HYSYS

INTRODUCTION

Essential Oils (EOs), also known as volatile or ethereal oils, are the concentrated aromatic essences of plants. Over thirty families of plants, with some ninety species, represent the main oil producing group. These odorous products of complex composition are obtained from the plant material conventionally by expression, water or steam distillation, solvent extraction, and recently by SuperCritical-Fluid (SCF) extraction. EOs may be found and extracted from various parts of plants such as the petals (rose oil), wood (sandalwood oil), fruit (bergamot oil), leaves (eucalyptus oil), seed (caraway oil), roots (sassafras oil), and resin (pine oil). EOs and their derivatives are important ingredients utilized by food, cosmetics, pharmaceutical and other related industries. As most natural extracts, EOs upon proper fractionation may yield more specialized products of higher economic values. The components of EOs are heat-sensitive. Because of the high temperatures involved, conventional distillation may cause product degradation. On the other hand, in conventional solvent-extraction methods, possible use of toxic liquid solvents and their removal from the final EO product introduce problems.

These deficiencies of the conventional methods and ever increasing demand for high-quality EOs have resulted in considerable interest and fostered research in application of the SCF technology to extraction and fractionation of EOs. What render the dense-gas (sub-/super-critical fluid) fractionation process as valuable in application to natural extracts are: *a)* the flexibility it provides (due to sensitivities of the solvent power of SCFs to variations in temperature, pressure, density, and modifier concentration) in adjusting operating conditions to preserve desired product qualities under varying feedstock properties, *b)* its cost-effectiveness especially for high-value-added products, and *c)* its favorable environmental impact. Thus, SCF-aided fractionation, capitalizing on temperature and/or pressure effects at mild operating conditions, is considered to be the most advantageous method for the rectification and purification of higher-value EO fractions.

In this work, a multi-purpose process flowsheet for fractionation of three types of EOs (*origanum*, *tea-tree*, and *lemon* oils) by supercritical CO_2 is developed, simulated, and optimized using the process flowsheet simulator HYSYS (Hyprotech Ltd., Canada). 9 to 14 components constituting the bulk (about 91% by weight) of the EOs are selected and classified as *monoterpene* (MT) hydrocarbons and *non-monoterpene* (NMT) hydrocarbons. The objective of the processes is set as the separation of the undesired MTs that lower the value of the EO by undergoing oxidation reactions from the more valuable NMTs; thus

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producing more valuable monoterpeneless oils from the feed oils at mild operating conditions by capitalizing on high solvent power yet relatively low critical temperature and pressure of CO_2 (T_c=304.2 K, P_c=72.8 atm).

ESSENTIAL-OIL COMPONENTS AND PROPERTIES

The three types of EOs, that will be used as feedstock for the multi-purpose process flowsheet, were selected to be the **OO**: *Origanum Oil* (*Origanum Syriacum* of Turkish origin), **TO**: *Tea-Tree Oil* (Australian origin), and **LO**: *Lemon Oil* (Indian origin); because of their different MT and NMT contents. The composition of the oils were taken from the *ESO-97: The Complete Database of Essential Oils* (BACIS, 1997), and only the major components (9 for OO, 10 for TO, and 14 for LO) constituting the bulk (by weight: 91.3% for OO, 91.0% for TO, 90.7% for LO) of the EOs were selected and classified as MTs and NMTs. The total number of components in all three EOs is 25. Table.1 lists the components and some of their properties which are essential for flowsheet simulations. Table.2 shows the normalized compositions (weight %) of the three EOs.

Table 1. List of essential-oil components and their critical properties.

ID	Component	Formula	Mol. Weight	Class.	T_b (^oC)	T_c (^oC)	P_c (atm)	ω
1	1-octenol-3	$C_8H_{16}O$	128	NMT	190	353	29.0	0.803
2	α-pinene	$C_{10}H_{16}$	136	MT	156	358	28.5	0.323
3	aromadendrene	$C_{15}H_{24}$	204	NMT	262	469	19.4	0.434
4	α-terpinene	$C_{10}H_{16}$	136	MT	175	378	27.6	0.359
5	α-terpineol	$C_{10}H_{18}O$	154	NMT	217	403	31.0	0.700
6	α-thujene	$C_{10}H_{16}$	136	MT	151	347	29.0	0.350
7	β-caryophlene	$C_{15}H_{24}$	204	NMT	263	483	19.9	0.360
8	β-elemene	$C_{15}H_{24}$	204	NMT	241	441	18.1	0.389
9	β-pinene	$C_{10}H_{16}$	136	MT	166	383	28.2	0.250
10	carvacrol	$C_{10}H_{14}O$	150	NMT	238	450	33.9	0.581
11	δ-cadinene	$C_{15}H_{24}$	204	NMT	247	439	19.3	0.501
12	decanal	$C_{10}H_{20}O$	156	NMT	208	379	22.3	0.653
13	geranial	$C_{10}H_{16}O$	152	NMT	229	444	25.2	0.403
14	geraniol	$C_{10}H_{18}O$	154	NMT	230	399	25.4	0.827
15	geranyl acetate	$C_{12}H_{20}O_2$	196	NMT	242	417	20.2	0.669
16	γ-terpinene	$C_{10}H_{16}$	136	MT	183	392	27.6	0.359
17	ledene	$C_{15}H_{24}$	204	NMT	269	475	19.8	0.466
18	limonene	$C_{10}H_{16}$	136	MT	176	381	27.1	0.343
19	linalool	$C_{10}H_{18}O$	154	NMT	197	360	25.5	0.761
20	myrcene	$C_{10}H_{16}$	136	MT	167	357	23.9	0.364
21	nerol	$C_{10}H_{17}O$	153	NMT	225	392	25.4	0.827
22	para-cymene	$C_{10}H_{14}$	134	NMT	177	384	28.7	0.357
23	terpinen-4-ol	$C_{10}H_{18}O$	154	NMT	209	416	32.8	0.508
24	terpinolene	$C_{10}H_{16}$	136	MT	186	396	27.8	0.347
25	trans-sabinene hydrate	$C_{10}H_{18}O$	154	NMT	205	428	38.1	0.447

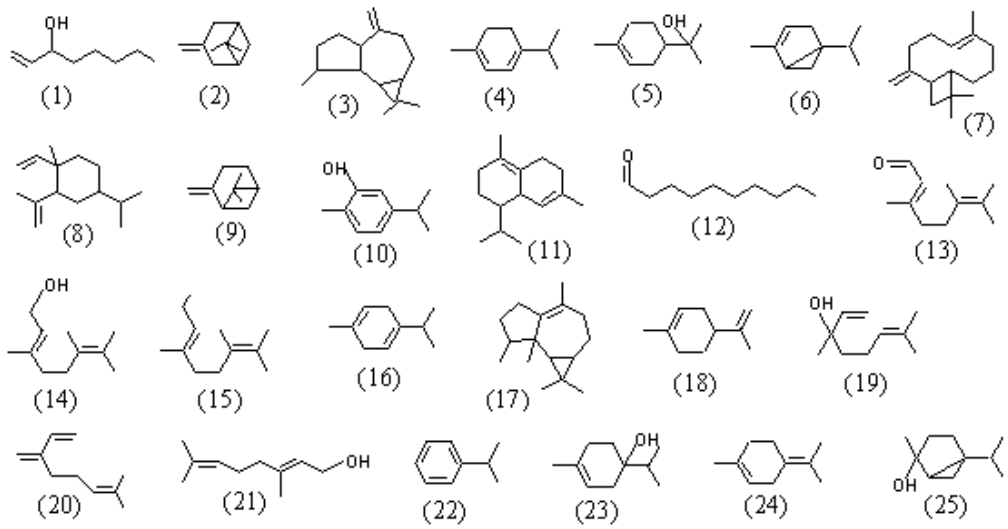


Figure 1. The chemical structures of the components.

The chemical structures of the components, shown in Fig.1, were obtained from Adams (1995). The critical temperatures and pressures were estimated from the Joback group-contribution method (Reid et al., 1987) that requires accurate normal-boiling-point data. The experimental values for the normal boiling points of most of the compounds were obtained from the CRC Handbook of Chemistry and Physics (Lide,

1994), however, for four components (ID: 1, 8, 11, and 25), for which the experimental data were not available, the normal boiling points were estimated from the group-contribution method of Constantinou and Gani (Constantinou and Gani, 1994) which can account for isomer structures. The acentric factors were obtained from the Lee-Kesler correlation (Reid et al., 1987). All thermophysical properties, including normal boiling points, of the EO components can also be estimated on the basis of their molecular (UNIFAC) structures using the property-estimation package of HYSYS, however, in this work, all the properties listed in Table.1 along with the UNIFAC structures of the EO components were supplied to HYSYS.

Table 2. Compositions of essential oils.

OO		TO		LO	
ID	weight %	ID	weight %	ID	weight %
6	2.41	2	2.42	9	4.41
2	1.20	4	8.79	20	0.99
20	1.75	16	18.68	18	55.13
4	1.64	24	3.85	22	3.31
16	6.13	22	6.59	13	2.76
1	1.86	23	43.95	21	1.65
22	13.47	5	4.39	19	1.65
10	70.21	11	4.17	23	2.21
25	1.31	3	3.52	5	16.54
		17	3.65	14	4.41
				12	0.88
				15	2.21
				8	1.10
				7	2.76
Σ MT	13.14		33.73		60.53
Σ NMT	86.86		66.27		39.47

In the simulations, the Peng-Robinson equation-of-state option of HYSYS was used for both the liquid and gas phases, and for enthalpies. However, for the vacuum-distillation simulations, in which no CO_2 was present, the UNIQUAC option was used for the liquid phase. Since the binary VLE data for the individual EO components and CO_2 systems are not present in the literature (except for few components), all the binary-interaction coefficients, in the mixing rule for the Peng-Robinson equation of state, were set to zero.

FLOWSHEET DEVELOPMENT AND SIMULATIONS

Various process flowsheets composed of equilibrium-flash separators, liquid-liquid, and gas-liquid extractors were conceived and tested for the purpose of separating the MT and NMT fractions of the three EOs equally well; i.e., with high *purity* and *recovery*, and without employing temperatures higher than 55 ^{o}C to prevent degradation of heat-labile EO components. The proposed flowsheet that is effective for all three EOs is shown in Fig.2. The EO feed, labeled as F-OIL, and the solvent feed, labeled as F-CO2, are the inputs to process, and the streams labeled as P-MT, and P-NMT are the MT-rich and NMT-rich (monoterpenless oil) product streams. Units labeled as V1, V3, and V4 are equilibrium-flash separators, whereas V2 and V5 can be considered as expansion valves. Unit labeled as T-100 is the countercurrent dense-CO_2 absorber (with 20 equilibrium stages), and due to inverse temperature effects encountered around the critical point of the gas solvent, the absorber has an inverse temperature profile (bottom temperature is slightly lower than the top temperature).

For the OO, which contains the least amount of the undesired MTs among the three EOs, an alternative flowsheet may be used. In this flowsheet that requires less energy consumption, the flash unit, V1, before the absorber, T-100, is removed and the EO is fed directly to the top of the absorber, and the fresh CO_2 feed is mixed with S14 and then fed to the bottom of the column. In this way, the solvent-recycle loop, RCY3 (S19, S23, S22, S12), is completely removed from the base flowsheet.

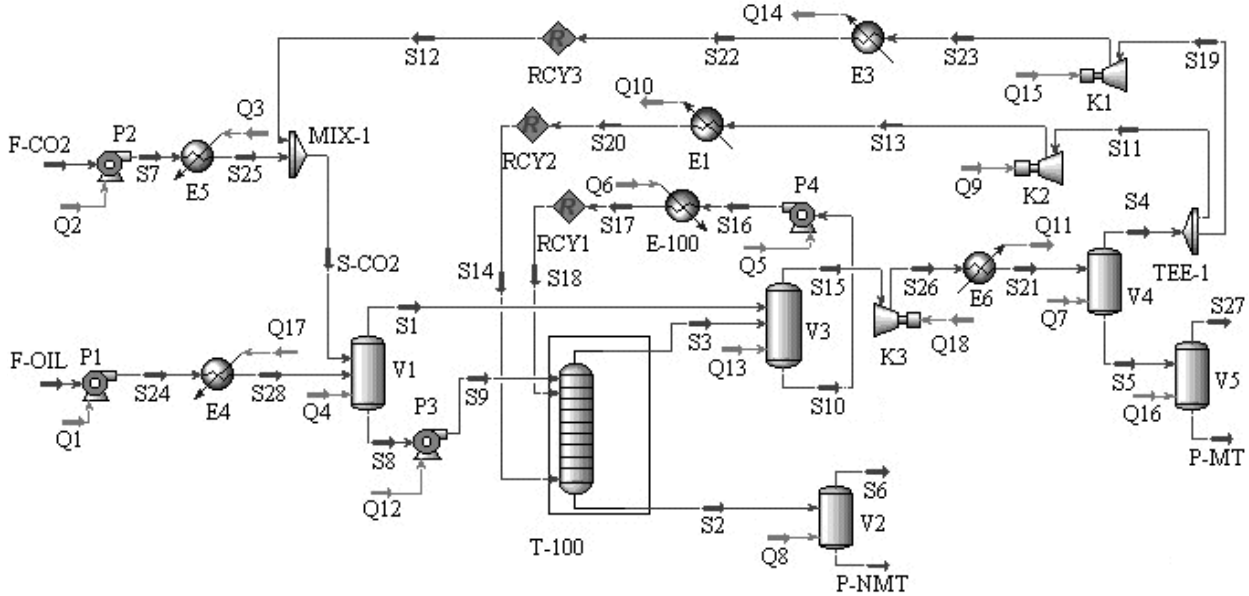


Figure 2. The proposed multi-purpose process flowsheet.

The operating conditions (temperature, pressure, solvent-to-feed ratio, solvent-recycle rate) that were optimized partly by HYSYS and partly by trial-and-error, are listed in Table.3 for each stream of the multipurpose flowsheet, for the basis of 100 kg/h of EO feed. The compositions of the streams are reported in Table.3 as MT and NMT weight %'s which are not normalized, hence the remaining part is CO_2.

Table 3. Optimized operating conditions and stream compositions for the multipurpose process flowsheet.

Oil →	OO					TO					LO				
Stream Label ↓	T °C	P atm	Flow kg/h	MT wt %	NMT wt %	T °C	P atm	Flow kg/h	MT wt %	NMT wt %	T °C	P atm	Flow kg/h	MT wt %	NMT wt %
F-OIL	20	1	100	13.13	86.85	20	1	100	33.72	66.27	20	1	100	60.52	39.48
F-CO2	20	60	146	0.00	0.00	20	60	279	0.00	0.00	20	60	138	0.00	0.00
S-CO2	50	95	3500	0.02	0.01	40	97	3900	0.03	0.01	40	90	4250	0.05	0.01
S-1	–	–	–	–	–	50	97	3807	0.63	0.90	43	85	3929	0.61	0.20
S-2	49	92	198	2.00	40.29	52	105	261	1.03	20.98	48	95	116	1.49	26.90
S-3	50	92	3409	0.31	0.40	54	105	4479	1.21	1.66	49	95	5386	1.23	0.54
S-4	15	40	3353	0.02	0.01	20	40	8052	0.04	0.01	20	35	9139	0.05	0.01
S-5	15	40	48	18.87	14.69	20	40	92	33.57	12.49	20	35	121	48.65	6.75
S-6	35	1	114	0.17	0.20	35	1	204	0.08	0.18	35	1	83	0.11	0.09
S-7	24	95	100	13.13	86.85	27	97	279	0.00	0.00	26	90	138	0.00	0.00
S-8	–	–	–	–	–	50	97	193	5.78	16.97	43	85	421	9.13	7.58
S-9	–	–	–	–	–	51	105	193	5.78	16.97	45	100	421	9.13	7.58
S-10	30	1	7	11.15	88.28	30	1	142	31.44	67.94	31	1	56	48.42	50.95
S-11	–	–	–	–	–	20	40	4428	0.04	0.01	20	35	5026	0.05	0.01
S-12	–	–	–	–	–	40	97	3621	0.04	0.01	40	90	4112	0.05	0.01
S-13	95	95	3353	0.02	0.01	111	105	4428	0.04	0.01	120	100	5026	0.05	0.01
S-14	50	95	3353	0.02	0.01	50	105	4405	0.04	0.01	50	100	5026	0.05	0.01
S-15	30	1	3402	0.29	0.21	30	1	8144	0.42	0.14	31	1	9260	0.68	0.10
S-16	34	95	7	11.15	88.28	34	105	142	31.44	67.94	34	100	56	48.42	50.95
S-17	40	95	7	11.15	88.28	50	105	142	31.44	67.94	45	100	56	48.42	50.95
S-18	40	95	7	11.16	88.27	50	105	142	31.44	67.96	45	100	56	48.42	50.95
S-19	–	–	–	–	–	20	40	3623	0.04	0.01	20	35	4113	0.05	0.01
S-20	50	95	3353	0.02	0.01	50	105	4428	0.04	0.01	50	100	5026	0.05	0.01
S-21	60	40	3402	0.29	0.21	70	40	8144	0.42	0.14	60	35	9260	0.68	0.10
S-22	–	–	–	–	–	40	97	3623	0.04	0.01	40	90	4113	0.05	0.01
S-23	–	–	–	–	–	103	97	3623	0.04	0.01	110	90	4113	0.05	0.01
S-24	27	95	146	0.00	0.00	24	97	100	33.72	66.27	24	90	100	60.52	39.48
S-25	40	95	100	13.13	86.85	40	97	279	0.00	0.00	40	90	138	0.00	0.00
S-26	445	40	3402	0.29	0.21	444	40	8144	0.42	0.14	425	35	9260	0.68	0.10
S-27	25	1	33	0.76	0.30	20	1	50	0.49	0.09	25	1	54	0.83	0.21
S-28	50	95	146	0.00	0.00	40	97	100	33.72	66.27	40	90	100	60.52	39.48
P-MT	25	1	16	55.45	43.77	20	1	43	72.20	26.99	25	1	67	87.19	12.04
P-NMT	35	1	84	4.48	95.03	35	1	57	4.40	95.09	35	1	33	4.98	94.50

The *purity* is defined as the ratio of the total mass of the NMT components to the total solvent(CO_2)-free mass in stream P-NMT. The *recovery* is defined as the ratio of the total mass of the NMTs in stream P-NMT to the total mass of the NMTs in the EO feed stream, F-OIL. The MTs are preferentially solubilized by the dense CO_2 due to their low molecular weights and high vapor pressures compared to NMTs (Stahl and Quirin, 1987; Platin et al., 1994; Köse et al., 1998), and thus, in the flowsheet, the gas streams are rich in MTs, and the NMTs concentrate in the liquid streams. Table.4 shows the purity and recovery of the NMT components for all three EOs in the desired-product stream, P-NMT.

Table 4. Purity and recovery of the NMT components in P-NMT.

Oil	% Purity in P-NMT	% Recovery in P-NMT
OO	95.5	91.3
TO	95.4	81.5
LO	95.2	79.1

The proposed process operates with relatively low fresh-solvent to oil-feed ratio, however, relatively high solvent-to-oil ratios are present in the recycle loops. The trade-off between purity and recovery of the desired NMT components as a function of the flowrate of the recycle stream S-CO2 (or, in the case of the modified flowsheet for the OO, recycle stream S14) is shown in Fig.3 for the temperatures and pressures reported in Table.3. It is clear that for all EOs, considering % purity, the use of solvent-recycle rates greater than about 5000 kg/h is unneeded. When the operating temperatures of the flash units V1 and V3 are increased, the purity in product stream P-NMT increases but recovery of the NMTs decreases. A decrease

in the operating pressure of V1 causes the same effect in stream P-NMT. Similarly, the purity in product stream P-NMT increases and recovery of the NMTs decreases with increasing pressure of the absorber T-100.

As can be seen from Table.3, the temperatures of streams S13, S23, and S26 in the flowsheet is noticeably higher than others due to heavy-duty compressor K1, K2, and K3. However, such high temperatures do not affect the product quality since streams S13 and S23 contain trace amounts of EO components, and stream S26 carries mostly undesired MT components and CO_2. The highest temperature encountered in the flowsheet is due to compressor K3 which takes stream S15 with a high flowrate from 1 atm to 40 atm. However, this is unavoidable since the pressure of the flash unit V3 must be lowered to 1 atm, otherwise the recycle stream RCY1 will not contain enough amount of the NMTs, and thus, the overall recovery is adversely affected.

The heating, cooling, and mechanical (pump and compressor) energy requirements for all three EOs are shown in Fig.4. The energy use of the process increases with increasing content of the undesired MT components of the oils (see Table.2). The reason for significantly lower energy need for processing of the OO compared to those of the TO and LO is partly due to removal of the recycle loop, RCY3, from the base flowsheet.

Conventionally, EOs are fractionated in atmospheric- or vacuum-distillation columns, the latter is preferred to avoid the exposure of the heat-sensitive EOs to high temperatures (see Table.1 for the normal boiling points of the components). Table.5 shows the purity and recovery of the NMT compounds when the EOs are distilled under 0.015 atm vacuum conditions in a single distillation column with 20 equilibrium stages (no CO_2 is involved, UNIQUAC option was used for the liquid phase). Compared to the proposed supercritical-CO_2-fractionation process, comparable purities and recoveries of the NMT compounds can be achieved, however, at the expense of exposing the EOs to significantly higher temperatures at the bottom section of the column.

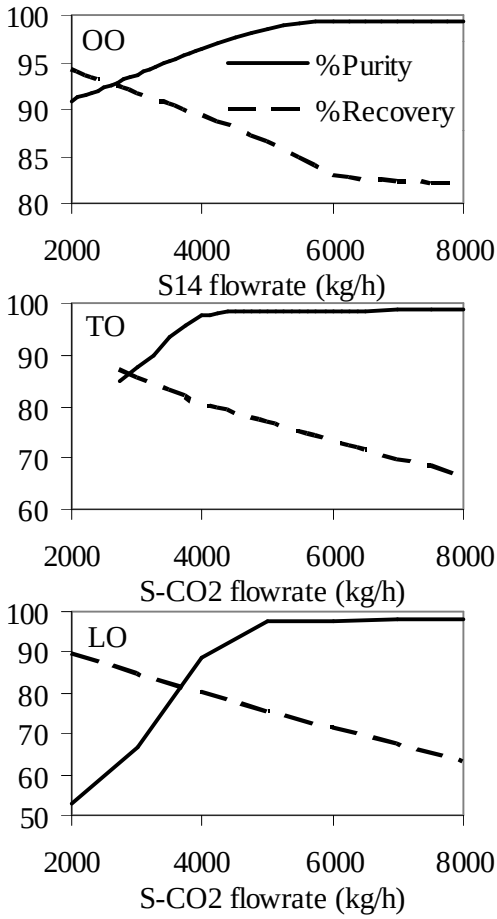


Figure 3. Trade-off between purity and recovery of the NMT components as a function of the solvent-recycle flowrate.

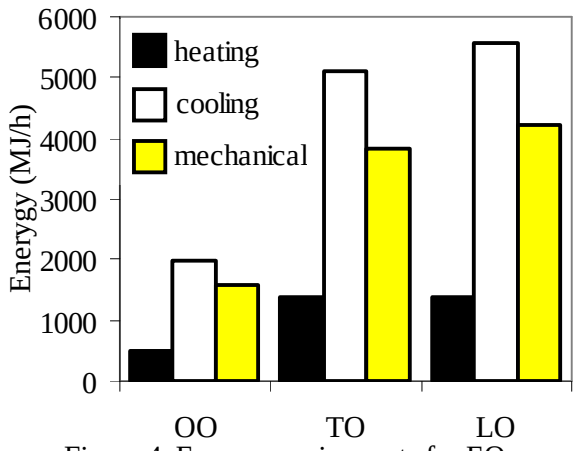


Figure 4. Energy requirements for EOs.

Carbon dioxide is a non-polar solvent and dissolves non-polar components preferentially. Small amount (2-5% by weight) of a polar co-solvent (entrainer) such as ethanol can be mixed with CO_2 to increase the polarity of the dense-gas solvent in order to dissolve polar components as well. To test the effect of the use of supercritical CO_2 doped with polar co-solvent, the fresh solvent (F-CO2) was mixed with ethanol such that the concentration of ethanol reached about 5% (by weight) in stream S-CO2. However, the simulations showed that the use of polar co-solvent adversely affected both the recovery and purity of the NMTs in the product stream P-NMT; since the presence of ethanol caused the polar MT components to appear in significant amounts in the liquid phases of all flash units.

Table 5. Purity and recovery of the NMT components for vacuum distillation at 0.015 atm.

Oil	Top T (^oC)	Bottoms T (^oC)	% Purity in bottoms	% Recovery in bottoms
OO	46.2	87.8	95.0	94.1
TO	52.6	85.4	95.1	90.4
LO	50.5	91.4	95.1	92.2

Simulations with model EOs (with two or three oil-characterizing components) instead of the real EOs (with full set of oil components) is the customary way of treatment for essential oils in the literature. For all three EOs, simulations of model EOs with 3 pseudo components yielded results close to those of the simulations with full set of oil components.

Appropriate selection of oil-characterizing components had a crucial effect on the results. The comparative simulations for the LO with 2 and 3 characterizing components illustrated this effect. The simulation with only limonene and α-terpineol, representing the MTs and NMTs, respectively, yielded 97.4% recovery of the NMT components as product with 95% purity, whereas the addition of p-cymene as the third component decreased the recovery value to 83.8%. This difference was due to the fact that the volatility of the NMT component p-cymene was similar to MTs and its presence changed the results significantly. With regard to energy consumptions, the results with the real and model essential oils did not differ significantly.

The sensitivity of the results to binary-interaction parameters in the mixing rule for the Peng-Robinson equation of state was tested by repeating the simulations with the parameters estimated by the HYSYS; the % purity values for all three EOs did not change more than 2-3%.

CONCLUSIONS

A multi-purpose process flowsheet that had the flexibility for fractionation of three types of essential oils (EOs) (*origanum*, *tea-tree*, and *lemon* oils) by supercritical CO_2 was developed, simulated, and optimized using the process flowsheet simulator HYSYS. Components constituting about 91% by weight of each of the EOs were classified as *monoterpenes* (MTs) and *non-monoterpenes* (NMTs). The objective of the processes was the separation of the undesired MTs that lower the value of the EOs from the more valuable NMTs, equally well for all three oils, and thus, the production of more valuable monoterpeneless oils from the feed oils at mild operating conditions by capitalizing on the high solvent power yet relatively low critical temperature and pressure of the supercritical-fluid solvent CO_2.

The process did not employ temperatures higher than 55 ^oC to prevent degradation of heat-labile EO components, and was effective for all three EOs. With the proposed process, 95% purity for all three EOs and 91, 82, and 79% recovery for the desired NMT compounds of the origanum, tea-tree, and lemon oils, respectively, were achieved. At the optimized operating conditions, the process employed an oil-to-solvent ratio of about 1/40 in the recycle loop, however, the same ratio for the feed oil and fresh solvent was about 1/2.

It was observed that the heating, cooling, and mechanical energy consumptions increased with increasing undesired MT content of the oils. The trade-off analyses between purity and recovery of the desired NMT components showed that, for all three EOs, the use of solvent-recycle rates greater than about 5000 kg/h did not have a noticeable effect on purity, however, the recovery was continued to decrease with increasing recycle rate.

Comparable recoveries and purities of the NMT components were also obtained in a 20-stage distillation column operating under 0.015 atm vacuum conditions, however, at the expense of reaching temperatures as high as 91 ^oC at the bottoms end, leading to the possibility of degrading the heat-labile NMT fraction of the oils.

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