Deterpenation of Origanum Oil *(Origanum Munituflorum)* via Adsorption/Desorption Following Dense-CO_2 Extraction

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Abstract – A continuous adsorption/desorption process coupled with dense-CO_2 extraction is developed to improve the quality of origanum oil through selectively removing its monoterpene hydrocarbons (deterpenation). Enhanced fractionation of the oil is obtained via adsorption at 40°C/7.5MPa and desorption at 40°C with step-wise pressure increase method: first at 8.0MPa to recover the monoterpene (MT) components, then at 14.5MPa to collect the non-monoterpene (NMT) constituents. The results suggest that activated carbon is a promising adsorbent in deterpenating origanum oil by supercritical-CO_2.

Introduction

Origanum oil, like many other essential oils, contain MT hydrocarbons which do not contribute much to the flavor and fragrance of the oil and are also very unstable to heat and light. Thus, the quality of essential-oil products decreases with increasing fraction of the MTs [1]. The most commonly used processes to concentrate the NMTs, mostly oxygenated fraction of essential oils, have the drawbacks of low yields, formation of thermal degradation products, and contamination with organic solvents. These deficiencies of the conventional methods fostered research in application of the SuperCritical-Fluid (SCF) technology as an alternative process for the deterpenation and purification of higher-value essential oil fractions [1,2].

SC-CO_2 is a prominent candidate for fractionation of essential oils, since CO_2 does not leave any residue in the product and the separation can be performed at low temperatures. However, it is known that in a simple SC-CO_2 extraction process, it is often difficult to reconcile conditions that lead to high recovery (yield) with those that result in high selectivity [3]. An alternative approach is the coupling of SCF extraction to an adsorption process [4]. Based on this idea, a continuous adsorption/desorption process coupled with dense-gas extraction is developed in the aim of obtaining an origanum-oil product possibly almost free of MT hydrocarbons.

Materials and Methods

The origanum oil (*Origanum Munituflorum*), supplied by Altes Ltd. Co., Ýstanbul, was used as the feed material. CO_2 (99.7% pure) was supplied by Hergaz Inc., Ýstanbul. Activated carbon (35 mesh size and total surface area of 1300 m^2/g) was used as the adsorbent.

The plan of attack consisted of a number of experiments that were conducted in order to remove the MTs and leave the NMTs behind i.e., on the activated carbon; hence a minimum amount of NMT components in the origanum-oil product was desired. In each case, the evolution of the process performance was obtained by taking samples at fixed time intervals (30 min) from the

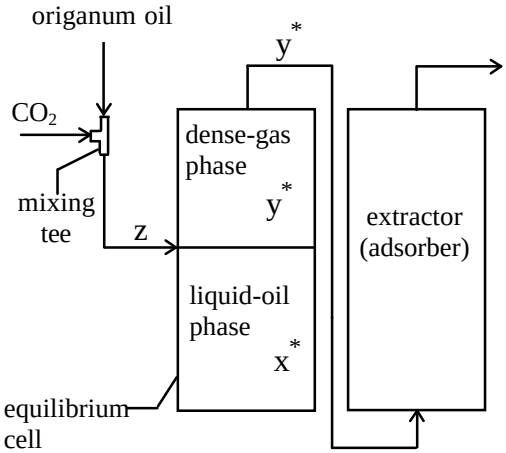


Figure 1: SC-CO_2 extraction at 40°C/7.5MPa.

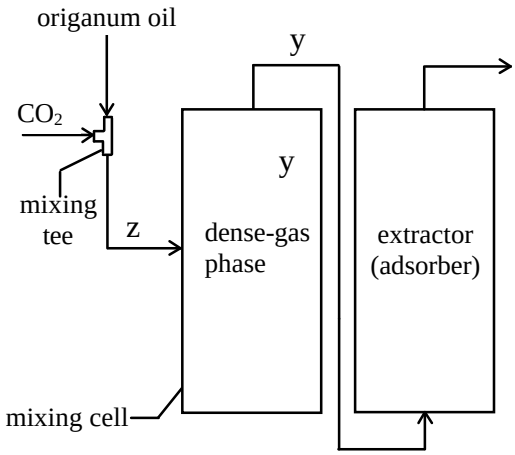


Figure 2: SC-CO_2 extraction at 40°C/10.0MPa.

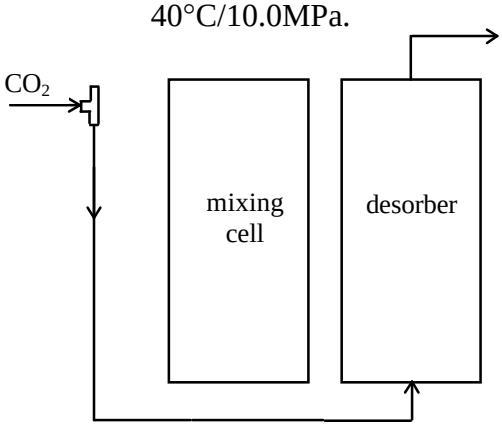


Figure 3: Desorption with pure SC-CO_2.

cold trap. This sample was further diluted in ethanol (Riedel de Haen, 99.9% pure), and the resulting mixture was analyzed by GC/MS (HP 5890/5971). The detailed description of the experimental apparatus, procedure and analyses of sample are given elsewhere [5]. Here, the different forms of operations adopted are presented by simple diagrams, Figs.1-3.

First, simple SC-CO_2 extraction process was executed in the aim of fractionating origanum oil and isolating its MT constituents. Two types of extraction experiments were performed, as shown schematically in Figs. 1 and 2. The mixing cell (packed with glass beads) situated prior to the extractor, was used in preparing the feed solution through mixing the SC-CO_2 and the origanum-oil streams; this feed was then allowed to enter the extractor. In Figs. 1 and 2, the overall composition of the feed stream entering the mixing cell is labeled as z.

As can be seen in Fig.1, if at 40°C/7.5MPa, the origanum-oil/CO_2 system falls in the two-phase region, then a liquid-oil and a dense-gas phase in which CO_2 and the dissolved oil components appear are present. In this case, equilibrium conditions are attained, thus the feed mixture entering the extractor (leaving the mixing cell) has the equilibrium composition of origanum oil in the dense-gas phase, y*, and $y^* << z$. This fact offers the advantage that the feed mixture entering the extractor is already separated into groups of components of differing properties (volatility and/or polarity) in the mixing cell. So, at this operating conditions, the mixing cell acts as a flash chamber adding an extra degree of flexibility to the system. The validity of this argument was established experimentally, and the SC-CO_2 extraction experiment performed at 40°C/7.5MPa conditions confirmed the presence of a liquid-oil phase (residual oil) accumulated in the bottom of the mixing cell (CO_2 continuously bubbled through it). The distinctively different compositions [5] of the original origanum oil and residual oil further strengthened the validity of the hypothesis that indeed two phases existed.

On the other hand, at 40°C/10.0MPa conditions (Fig.2), the origanum-oil/CO_2 system is expected to be in the single phase region. In this case, equilibrium conditions are not attained, thus the composition of the feed to the extractor is equal to the composition of the feed to the mixing cell, i.e., z is equal to y, and x is equal to zero (no liquid phase). The validity of the single-phase

occurrence was also established, and the SC-CO_2 extraction experiment performed at 40°C/10.0MPa conditions confirmed that all the oil pumped (by the HPLC pump) was completely miscible in CO_2 (since no residual oil was collected from the bottom of the mixing cell at the end of the experiment).

Next, SC-CO_2 adsorption following the dense-gas extraction (from now on, will be called as SC-CO_2 adsorption) was carried out in the aim of enhancing the separation between the MT and NMT components of origanum oil. Two different forms of adsorption experiments were performed, as schematically presented in Figs. 1 and 2. In the extraction runs, the extractor was packed with 3 mm glass beads, whereas in the adsorption runs the same vessel was packed with the sorbent. The adsorption process was performed on a fixed bed filled with activated carbon with a continuous feed of origanum-oil/CO_2 mixture. The adsorption process was expected to enhance the selectivity according to the different affinities of the origanum-oil components for the sorbent.

Last, SC-CO_2 desorption following the origanum-oil/CO_2 adsorption coupled with dense-gas extraction (from now on, will be called as SC-CO_2 desorption) was executed in order to recover adsorbed compounds (Fig.3). The desorption with pure SC-CO_2 was performed at 40°C using step-wise pressure increase method: first at 8.0 MPa for 240 minutes, then at 14.5 MPa for the subsequent 450 minutes of desorption.

Results and Discussion

Total MT and NMT hydrocarbon content in the original origanum oil is 40.43% and 59.57%, respectively. The classification, and normalized weight percentages (normalized area counts) of the 12 key components of the origanum oil and information on boiling points, vapor pressures, can be found in [5].

The normalized area percents for MT (or, NMT) component groups in the original oil, $C^{o}_{i,MT}$, and in samples, $C_{i,MT}$, were used to calculate the dense-gas phase CO_2-free relative-distribution ratios of the MT cut, R_{MT}, with respect to the original oil [$R_{MT} = \Sigma C_{i,MT} / \Sigma C^{o}_{i,MT}$ $i = 1,...,n$ ($i \neq CO_2$)]. The R values greater than one means that the MT-cut (or, the NMT cut) concentration is more in the recovered oil (in the sample collector) than in the original oil fed to the system. The R values equal to one means that the MT-cut concentration is the same in the recovered oil and in the original oil fed to the system. The R values less than one means that the MT-cut concentration is less in the recovered oil and in the original oil fed to the system.

The relative-distribution ratios of the MT and NMT cuts, R_{MT} and R_{NMT}, were used to calculate the separation factor, α, [$\alpha = R_{MT}/R_{NMT}$]. The value of the separation factor is important in determining the degree of the fractionation. It is impossible to separate MT hydrocarbons in the origanum oil from the oxygenated flavor compounds when α equals to one, because in that case, both MT and NMT hydrocarbons will be equally soluble in dense CO_2. The condition for desirable deterpenation is at α values greater than one, where the MT constituents of the origanum oil are preferentially removed by CO_2.

The experimental results obtained will be discussed in terms of the separation factor and MT and NMT fractions of the oils collected during sampling. It should be understood that the samples collected in all the experiments (Figs.1-3), are not instantaneous but integral samples. Therefore, and since the MTs are expected to appear in the effluent earlier than the NMTs due to their low

molecular mass, high vapor pressure and low polarity [1] (CO_2 is a non-polar solvent), the fraction of the MTs in the samples collected decreases as their amount in the original origanum oil (in the stream going to the collector) decreases with time. Consequently, the concentration of the NMTs in the integral samples increases with time.

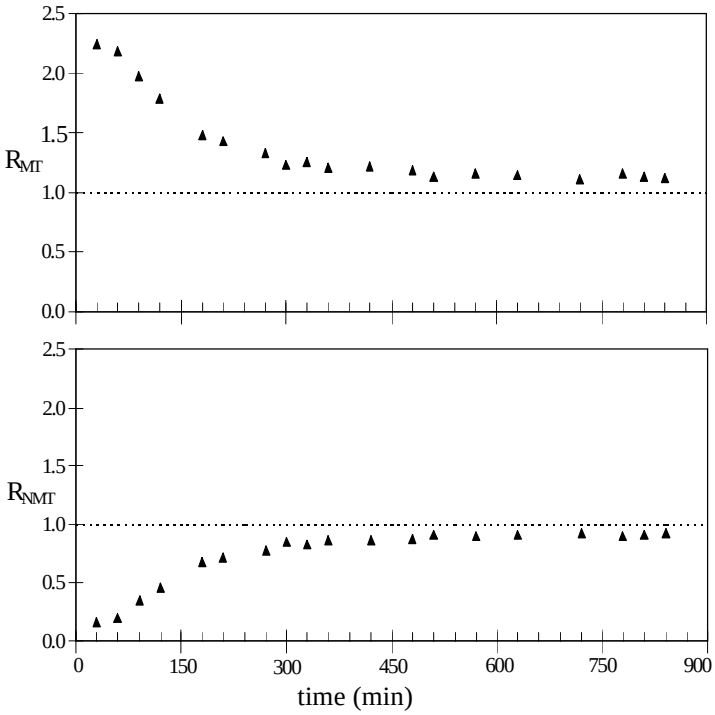


Figure 4: Relative-distribution ratios of MT and NMT cuts in the extraction run at 40°C/7.5 MPa.

Fig.4 shows the R-values of the MT and NMT cuts of the extracts obtained via SC-CO_2 extraction at 40°C/7.5 MPa. Clearly, the MTs were extracted (R>1) by dense CO_2 to a greater extent and the NMT hydrocarbons (R<1) were left in the liquid-oil phase remaining at the bottom of the extractor (Fig.1), almost independent of the extraction time. The optimum extraction time for the fractionation of origanum-oil components can be estimated as 480 min since after that period, the composition of the extracts do not change significantly. Fig.4 also gives the evidence that the R values of both MT and NMT cuts approach to one, as time proceeds.

Fig.5 shows the change in the separation factor as a function of the extraction time. The GC/MS analysis of the extracts revealed that under this operating condition, CO_2 had some selectivity towards the MT hydrocarbons since α-values were greater than one during the entire run. There is a decrease in selectivity as extraction proceeded, but above 480 min, a remained nearly constant at 1.25. Hence, deterpenation of origanum oil with dense CO_2 is possible at 40°C/7.5 MPa through the selective extraction of MTs from NMTs. Next, adsorption and desorption steps were included to the simple SC-CO_2 extraction system. The introduction of the adsorbent was expected to increase the selectivity of the fractionation process.

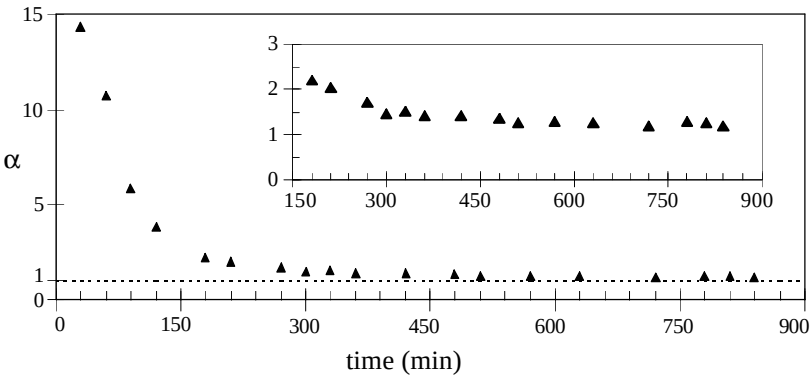


Figure 5: Separation factor, a, in the extraction run at 40°C/7.5 MPa.

Fig.6 shows the R values of the MT and NMT fractions of the oil collected during the SC-CO_2 adsorption runs performed at 40°C/7.5MPa (Fig.1) and 40°C/10.0MPa (Fig.2). The breakthrough behavior of the MT and NMT cuts can be explained regarding the relative strength of interactions occurring during adsorption between the solute, the sorbent, and the fluid phase. Dealing with a supercritical medium, vapor pressure, polarity and molecular mass are properties

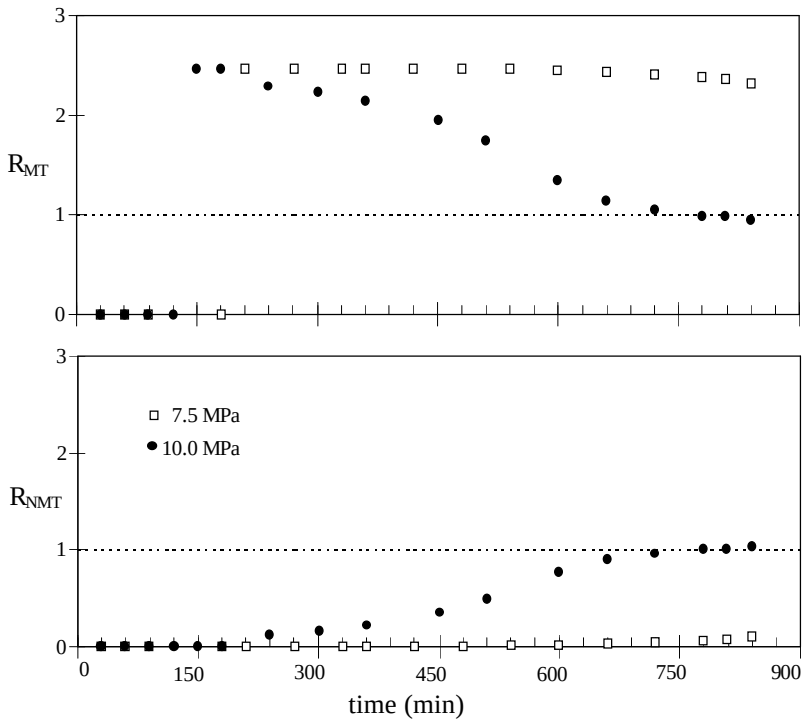


Figure 6: Pressure-dependence of the relative-distribution ratios of MT and NMT cuts in the adsorption run at 40°C using 8 g activated carbon.

which have special influences on solubility. On the other hand, the surface of activated carbon is nonpolar (or slightly polar) [6]. In that case, MT hydrocarbons would have an affinity for the nonpolar surface, but the oxygenated compounds (NMTs) could also compete with the MTs for the same apolar sites due to the nonpolar part of their molecule [7]. In the earlier stages of adsorption at 7.5MPa, both compound families were strongly adsorbed on the carbon. Later, components with stronger affinity for the sorbent replaced the ones with weaker affinity. As a result, MTs exhibited a low affinity for the carbon in conjunction with a high affinity for the fluid phase, whereas NMTs showed the opposite behavior. In this case, the R values of the MT cut were greater than unity indicating that MTs tended to concentrate in the dense-gas phase, whereas NMTs were preferentially adsorbed on the sorbent with R<<1. This observation also supports the argument that the more soluble the components are in SC-CO_2 the less strongly they will be adsorbed on the activated carbon.

The most striking characteristic in Fig.6 is that at 10.0MPa, the R-values of MT and NMT cuts asymptotically approach to one. This is because with increasing pressure (from 7.5 to 10.0 MPa), the effect of solvating power of the solvent increases, and the MT and NMT constituents of origanum oil become equally soluble in CO_2. However, at the beginning of adsorption at 10.0MPa, both MTs and NMTs were strongly adsorbed on the carbon. Then, MTs with weak affinity for the sorbent (and high to CO_2) emerged in the effluent. As NMTs with stronger affinity for the carbon (and lower to CO_2) appeared in the effluent, the R values of the MT cut sharply decreased and that of the NMT cut sharply increased. As also seen in Fig.6, adsorption with origanum-oil/CO_2 feed mixture of composition of y* (Fig.1) gave more diversified fractions, whereas during adsorption with the same feed mixture in the single phase region, the process selectivity with respect to the effluent composition was rapidly lost.

Fig.7 shows the pressure-dependence of the separation factor against the adsorption time. As clearly seen, compared to adsorption at 10.0 MPa, deterpenation of origanum oil via SC-adsorption at 7.5MPa is more favorable since enhanced separation between MT and NMT components is obtained. Therefore, the presence of the flash chamber before the adsorber maintains an enrichment in MTs over the NMT hydrocarbons. Then, the origanum-oil/CO_2 feed mixture comprised of a high content of MT components can be further fractionated according to the different affinity of origanum-oil components with activated carbon. However, as adsorption proceeded the degree of fractionation decreased sharply due to the appearance of the NMTs in

the sample collector. Samples collected after 540 min of SC-CO_2 treatment of origanum oil at 40°C/7.5MPa showed that the separation between MT and NMT groups was around 1.2 and 244.3 in the case of extraction (Fig.5) and adsorption (Fig.7), respectively. Hence, activated carbon adsorbent enhanced the deterpenation of origanum oil. However, the amount of carbon introduced into the column is very important since the breakthrough-time of NMTs increase as the amount of carbon increases [5]. Therefore, in the aim of improving origanum oil quality, the trade-off between adsorption duration and elimination of MT hydrocarbons should be taken into consideration in optimizing the operating conditions.

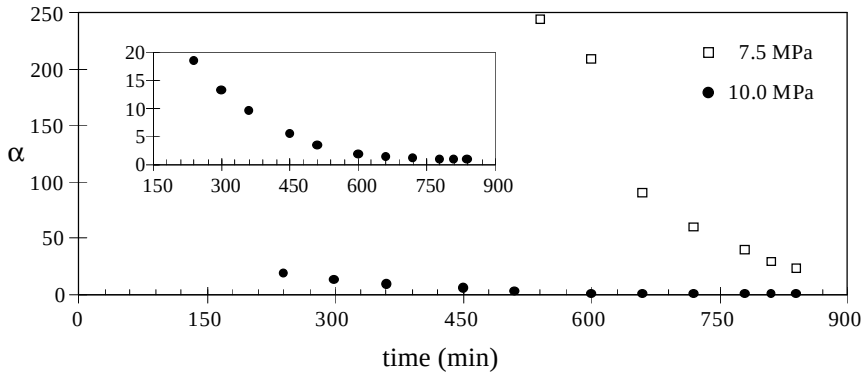


Figure 7: Pressure-dependence of the separation factor, a, in the adsorption run at 40°C using 8 g activated carbon.

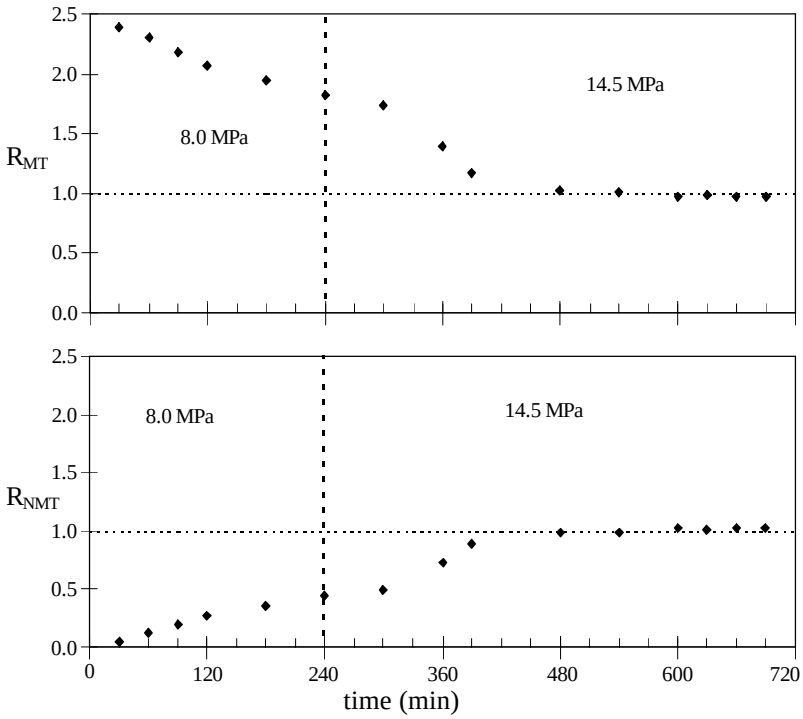


Figure 8: Relative-distribution ratios of MT and NMT cuts in the desorption run at 40°C with step-wise pressure increase from 8.0 to 14.5 MPa.

Last, desorption with pure SC-CO_2 was performed in order to recover the valuable constituents (NMTs) of origanum oil. Fig.8 shows the R values of the MT and NMT cuts during desorption with step-wise pressure increase method. At 8.0MPa, fast desorption of MTs was observed, whereas NMTs were desorbed slowly. However, significant change in the R values of both compound families was obtained by increasing the pressure to 14.5MPa (Fig.8). The transition between these steps was encountered by the change in the slope of the relative-distribution curves, but after a limited time (480 min), the curves flattened indicating that no further appreciable gain was accomplished by increasing the desorption pressure. This observation suggests that adsorption-equilibrium limitations were dominating the desorption process and that the solubilities of MT and NMT hydrocarbons in CO_2 were not controlling the transport mechanism.

As seen in Fig.9, desorption at 40°C/8.0MPa via SC-CO_2 proved to be effective in fractionating origanum oil since at the end of this step, the separation between MT and NMT cuts in the

desorbed fraction was 4.2 indicating that MTs, being the most volatile substances of origanum oil, were selectively desorbed by CO_2. However, increasing the pressure to 14.5MPa, a large decrease in desorption selectivity was observed. This is because solubilities of essential-oil components grow dramatically due to strong increase of solvent density [1]. Hence, a greater quantity of NMTs was co-desorbed. A decrease in selectivity was expected since the amount of MT hydrocarbons on the activated carbon decreased with time. Consequently, the concentration of the harder-to-desorb substances (NMTs, due to high molecular mass coupled with their strong affinity for the sorbent) increased with time. Therefore, in fractionating origanum oil via SC-CO_2 desorption and in optimizing the operating policies, the trade-off between complete recovery of NMT hydrocarbons and selectivity of the process should be prudently taken into consideration.

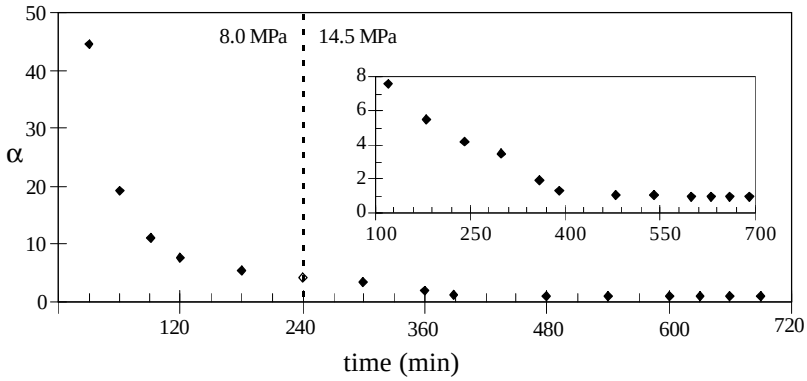


Figure 9: Separation factor, a, in the desorption run at 40°C with step-wise pressure increase from 8.0 to 14.5 MPa.

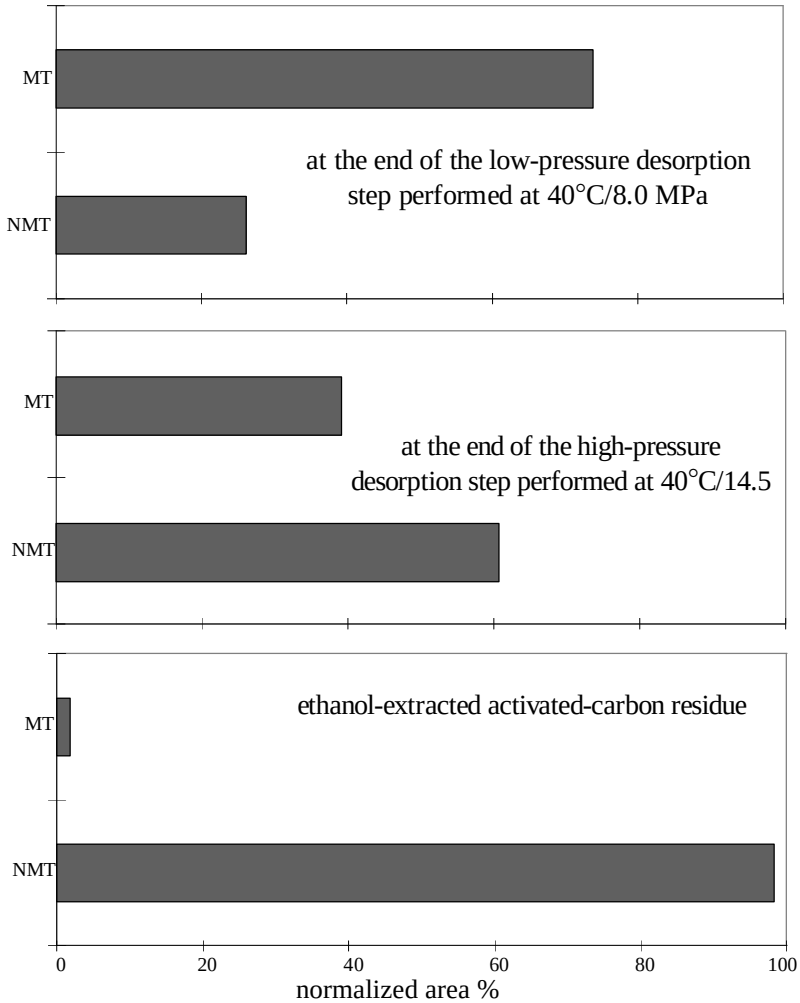


Figure 10: Normalized area % in the desorption run at the end of 40°C/8.0 MPa step, 40°C/14.5 MPa step and in the ethanol-extracted activated-carbon residue.

The SC-CO_2 desorption of origanum oil performed by the step-wise pressure increase procedure was terminated after 690 min, then the activated carbon sample was removed and washed with ethanol to remove the strongly-adsorbed fraction of the oil. Fig.10 shows the normalized area percent of the MT and NMT cuts in the fraction collected at the end of the low-pressure desorption step, at the end of the high-pressure desorption step, and the ethanol-extracted activated carbon residue. At the end of the first step, the percent content of MT/NMT cuts (73.80/26.20) was different from the one in the original origanum oil (40.43/59.57) due to the fact that MT components were desorbed faster than NMTs as a consequence of higher vapor pressure, lower

polarity and lower molecular weight. These properties, coupled with the weak bonding forces between the activated carbon and MT compounds, makes them easily desorbable by SC-CO_2. At the end of the second step (Fig.10), the solubility of NMT hydrocarbons increased due to the increased solvating power of the solvent; hence large quantities of NMT constituents (60.7%) were co-desorbed with small quantities of MT components (39.2%). This evidence could demonstrate that the first step performed at 8.0MPa produced the selective desorption of the MT hydrocarbons and the second one performed at 14.5MPa assured the fast desorption of the NMT components.

Furthermore, the low MT hydrocarbon content (1.8%) of the ethanol-extracted activated-carbon residue indicates that MT components were almost successfully eliminated from the carbon, but a small quantity still remained on the sorbent. Hence, the minor content of MT constituents in the residue indicates that perhaps longer processing times are necessary to obtain a thorough desorption of these highly volatile compounds. However, an optimum should exist between the recovered quantities and the processing time. On the contrary, the residue, which contained a high-percentage of NMT compounds (98.2%), will have the essential odor and properties of the origanum oil. Therefore, these two steps allowed a fast and quasi-complete recovery of all NMT constituents contained in this origanum oil. The proposed fractionation scheme (by SC-CO_2 desorption) is not the only procedure that it is possible to apply. For example, a larger pressure increase after 240 min of desorption could produce faster processing.

Conclusions

Fractionation and successful deterpenation of origanum oil was achieved through the continuous adsorption/desorption process coupled with dense-gas extraction. The activated carbon column proved to be very effective in enhancing the selectivity of the process (maximum separation between MT and NMT cuts was obtained at 40°C/7.5 MPa with 8 grams activated carbon). In light of these experimental results, it can be concluded that the process utilizing the mixing cell as a flash chamber was better in obtaining an origanum-oil product possibly free of its MT hydrocarbons.

Acknowledgments

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