Packing and Entrainer Effects on Supercritical Carbon Dioxide Fractionation of Origanum Oil

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Abstract – The effects of system pressure, column temperature, packing (1.5 mm Dixon packing), and entrainer (ethanol) on SuperCritical-CO_2 (SC-CO_2) fractionation of origanum oil *(Origanum Munituflorum)* are investigated in a semi-batch fractionation column. Experimental results at various combinations of 70-85 atm pressure and 38-55^oC temperature levels for the top and the bottom of the column are reported and discussed in terms of 14 major components, and monoterpene (MT) and non-monoterpene (NMT) fractions of the oil obtained at four different extraction time-cuts. The use of packing enhances separation of MTs and NMTs by providing greater mass transfer area. The addition of 2.5 wt% ethanol as entrainer to feed oil provides a more effective separation by increasing the polarity of the SC-CO_2 solvent.

Introduction

Origanum oil and its valuable fractions find use mostly in pharmaceutical and food industries. Terpene hydrocarbons make up the major part of the origanum oil. However, they contribute little to the characteristic properties and the aroma of the oil. Terpenes are unstable under heat and thus their presence in essential-oil products is not desired. Therefore a process called deterpenation is applied to essential oils. Conventional methods like hydro- or steam-distillation may cause product degradation because of the high temperatures they employ. Supercritical Fluid Fractionation (SFF), capitalizing on temperature and/or pressure effects at mild operating conditions, is considered to be the most advantageous method of deterpenation.

In a previous study [1] done on the same fractionation apparatus, the packing effect was investigated by using glass beads as the packing material, and it was concluded that packing had no significant effect on the separation efficiency. However, improved performance of packing on separation efficiency of MTs and NMTs must be expected since packing increases the mass-transfer area and the overall mass-transfer rate during fractionation. The reason for obtaining such a result in the previous study might have been due to the fact that glass beads offer a relatively low mass-transfer area as a packing material. Dixon packing is a more efficient packing material than glass beads and thus the effect of packing on separation efficiency could be more pronounced when Dixon packing is used.

The entrainer effect is important in SFF, since the application of SFF with pure nonpolar CO_2 is limited as its selectivity for polar compounds is low. Even though costlier higher-pressure systems may be used to improve the CO_2 properties as a solvent, the separation costs can be substantially lowered using a proper entrainer which improves the solvent power and selectivity of CO_2 for some desired components, without the need for an excessive pressure increase.

In this study, the effects of column temperature, system pressure, packing, and entrainer on SC-CO_2 fractionation of origanum oil are investigated in a semi-batch fractionation column. The extractor, as well as the column`s bottom section, and the top section of the column are operated at two different temperature levels (38-55^{o}C). The fractionation samples are obtained in four collectors at four extraction time-cuts at two different pressure levels (70-85 atm). The samples obtained are analyzed in terms of 14 major components and MT/NMT fractions. The favorable operating conditions for such SC-CO_2 fractionation are suggested.

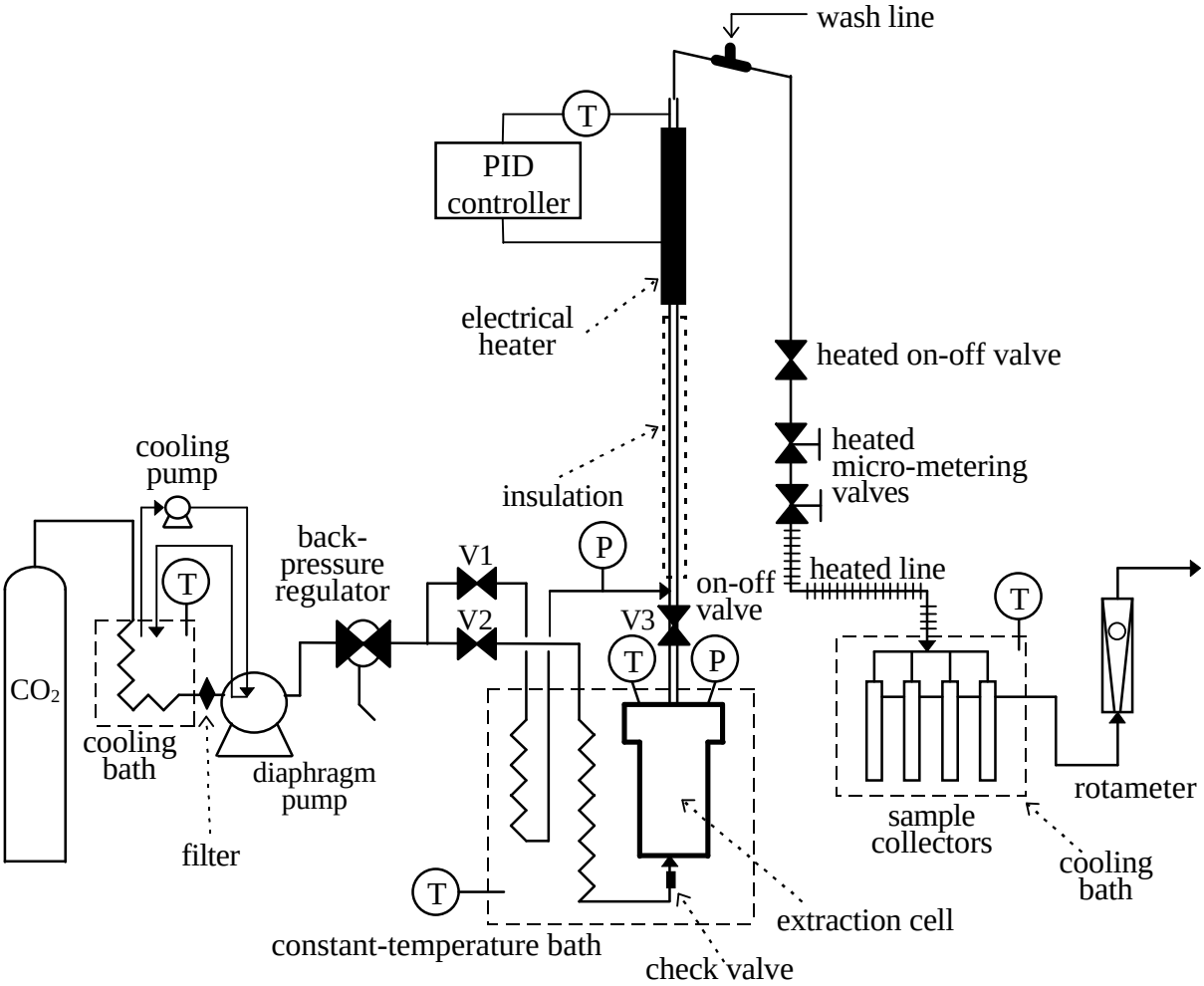


Figure 1: The experimental setup.

Materials and Methods

The origanum oil (*Origanum Munituflorum*) was used as the feed material. The origanum oil, that was obtained from a processing plant in Antalya region of Turkey, was supplied by Altes Ltd. Co., Ýstanbul. 1.5 mm Dixon packing with 80% bed voidage was used as the packing material. Ethanol used was 99.9% pure (Riedel de Haen). Hexane (commercial grade) was used as the cleaning solvent. CO_2 (99.7% pure), in cylinders equipped with dip tubes, was supplied by Habaþ Inc., Ýstanbul. The samples were analyzed using HP5890/5971 GC/MS.

As shown in Fig.1, the setup basically consists of an extraction unit (335 cm^3 volume, 4.5 cm ID), a fractionation column (145 cm height, 0.95 cm ID) which is packed with 1.5 mm Dixon packing, and a four-cell product collector (each 20 cm height, 3 cm ID).

In each experiment, first the constant-temperature water bath, the electrical heater at the top of the column, and the cooling baths were turned on, and the desired temperatures were reached. The on-off valve, V3, at the outlet of the extractor vessel was closed and 15 cm^3 of oil was charged into the extractor chamber. The valve of the CO_2 cylinder was opened, and the extractor and column were filled with CO_2 by opening the valves V1 and V2. Then, the valve V2 was closed and the diaphragm pump was turned on, and the desired pressure and flowrate were achieved by manipulating the flow adjuster of the pump, back-pressure regulator, and the on-off and the micro-metering valves preceding the collectors. After obtaining stable pressure and temperatures throughout the system, the valve V1 was closed and the valve V2 was opened to start the continuous contact of the oil and CO_2. The solvent and extract were allowed to separate at atmospheric pressure only in the collector assigned to the desired extraction-time interval by closing the valves on the remaining three collectors. Thus, extracts obtained in four different time-cuts were trapped in four different collectors. At the end of the last time-cut, the solvent pump was turned off and the battery of collectors was removed from the system. The 14 key components constituting the bulk (93% of total GC area count) of the original oil charged to the extractor and of the oil extracts accumulated in four collectors were identified by GC/MS analyses (HP 5890/5971, Carbowax 20M capillary column). In all experiments, the flowrate of CO_2 was kept constant at about 1 g/min. To observe the packing effect, the fraction column is packed with 1.5 mm Dixon packing with 80% voidage. To observe the entrainer effect, 2.5 wt% ethanol is added to the extractor chamber in the related runs.

Results and Discussion

Table.1 shows the names, classification, and normalized weight percentages (normalized area counts) of the 14 key components in the original oil (information on boiling points, vapor pressures, can be found in [2,3,4]). Fig.2 summarizes the pressure levels studied and the temperature zones imposed on the column in the six experimental conditions reported here.

Component	Class.	Area %
α-thujene	MT	5.24
camphene	MT	1.25
β-pinene	MT	0.45
β-myrcene	MT	3.21
phellandrene	MT	0.52
α-terpinene	MT	2.88
limonene	MT	0.61
cineole	OX	1.32
γ-terpinene	MT	10.96
p-cymene	MT	11.50
linalool	AL	8.82
caryophyllene	ST	4.16
endo-borneol	AL	4.90
carvacrol	PH	44.19
Total MTs %:		36.62
Total NMTs %:		63.38

Table 1: The key components of the origanum oil. AL: alcohol, MT: monoterpene, NMT: non-monoterpene, OX: oxygenated, PH: phenolic, ST: sesquiterpene

The normalized area percentages for each component (or, MT/NMT component groups) in the original feed, C_i^o (Tab.1), and in samples, C_i, were used to calculate the dense-gas phase CO_2-free relative-distribution ratios, R_i, with respect to the original oil [$R_i = C_i / C_i^o$ $i = 1,...,n$ ($i \neq CO_2$)]. The R values greater than one means that the component (or, MT/NMT group) concentration is more in the extracted oil than in the oil fed to the extractor. The R values equal to one means that the component concentration is the same in the extracted oil and in the oil fed to the extractor. The R values less than one means that the component concentration is less in the extracted oil than in the oil feed to extractor.

Fig.3 shows the R values of the MT and NMT cuts of the extracts obtained at the conditions indicated on Fig.2.(a-f); for two cases, with or without packing. In general, Fig.3 shows that, at 70 atm, with low molecular weights and high vapor pressures, the MT components ($R>2$) are preferentially extracted by CO_2 and effectively separated from the NMTs ($R<0.5$), with or without packing. At

the first time-cut, a better separation with packing is observed in Fig.3.b compared to Fig.3.a and Fig.3.c, however, if all time-cuts are taken into consideration, the best separation with packing is observed in Fig.3.c. It is also seen that, at the third and fourth time-cuts, packed-column fractionation does not give results better than the fractionation without packing. Even the unpacked case is better at the third time-cut, as can be seen in Fig.3.a. The explanation for this result can be that, in the packed-fractionation case, the MT components are carried more to the first two collectors than the unpacked case, so that at the third and fourth time-cuts there are less of the MT components in the extractor to be carried to the collectors in the packed cases compared to the unpacked cases. At 85 atm, similarly to that at 70 atm, a better separation of the MT components from the NMT components is observed with packing at the first two time-cuts compared to the third and fourth time-cuts, due to the reason given above. The best separation with packing is observed in Fig,3.c, where the difference between the R values of the MTs and NMTs are more significant.

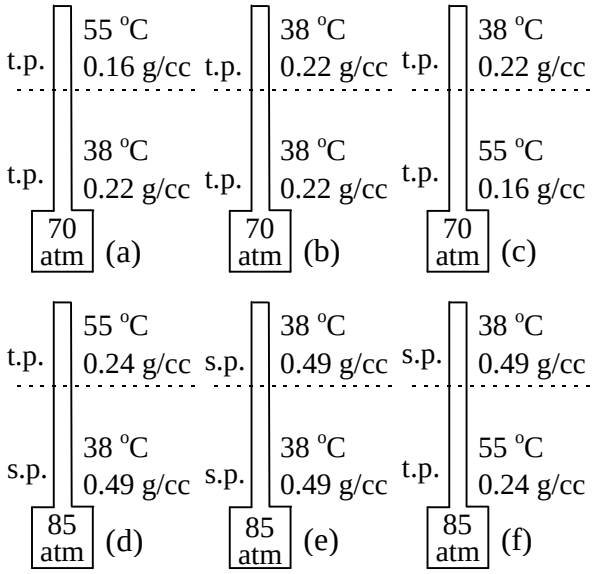


Figure 2: Pressures and temperature zones imposed on the column in the experiments (s.p.: single-phase region, t.p.: two-phase region).

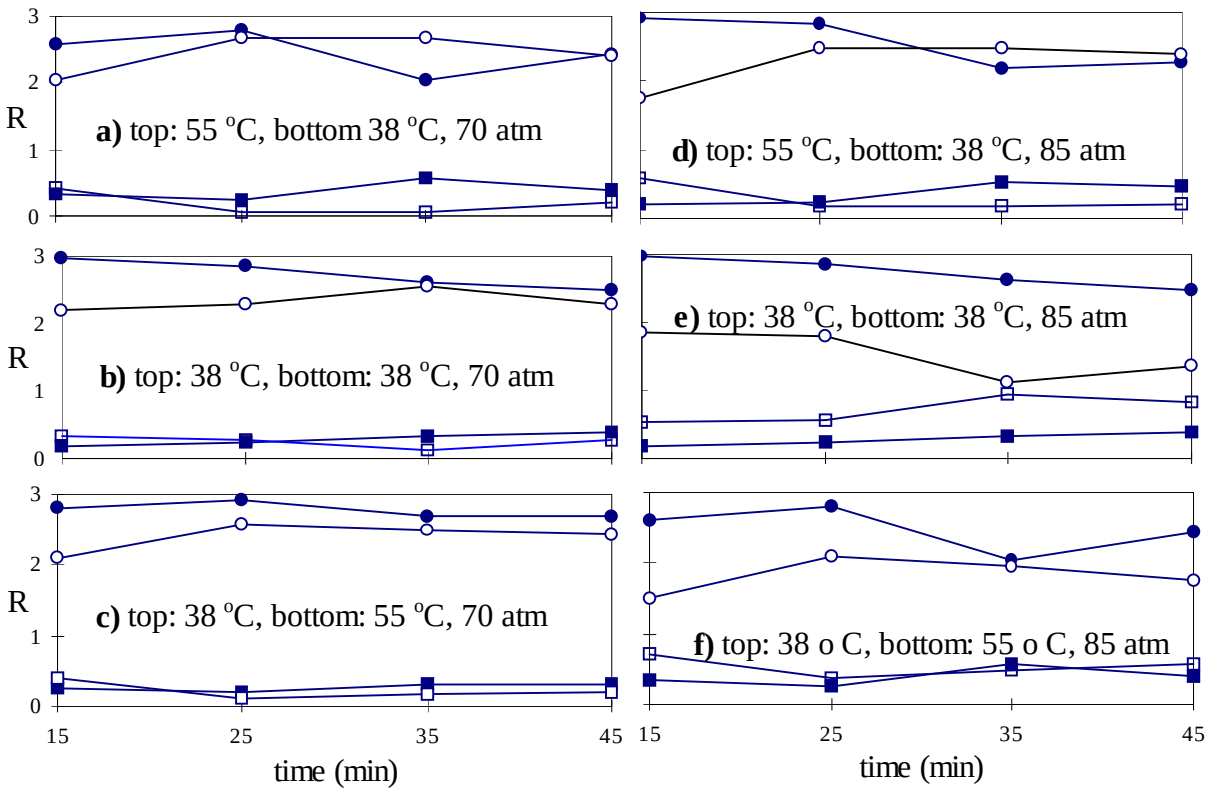


Figure 3: The effects of packing on the relative distributions of MT and NMT components, MT: ϒ-unpacked, λ-packed; NMT: ο-unpacked, ν-packed.

In Fig.4, the R values of the MT and NMT components are shown for the cases with and without packing and 2.5 wt% ethanol in the charge, at 70 atm and at the temperature levels indicated in Fig.2.(a-c). The addition of ethanol to the extractor charge increases the solvent power of CO_2 for the more polar components and thus the separation of the MT (less polar) and NMT (more polar) components is enhanced. This effect is clearly seen in Fig.4.a with 2.5 wt% ethanol. In Fig.4.(b-c), no significant effect is seen. The results obtained with packing and with 5.0 wt% ethanol in feed are also shown in Fig.4.a. It is seen that there is no significant difference between using 2.5 or 5.0 wt% ethanol. The fact that a higher concentration of ethanol does not improve the separation efficiency may be due to the fact that an excessive amount of ethanol affects all components at both phases, and thus the cosolvent effect is minimized. Therefore, it can be concluded that there is no need for using ethanol more than 2.5 wt%.

In Fig.5, the R values of the individual components are depicted for comparison of the packed and unpacked operations, at 70 atm and at the temperature levels indicated in Fig.2.c. The behavior of the individual components are as expected; the R values of the MT compounds in the packed operation are greater than those in the unpacked operation. However, the R values of the MT components γ-*terpinene* and *p-cymene*, and also for the first two-time cuts that of α-*thujene*, are the same in both the packed and unpacked operations. The oxygenated compound *cineole* shows a behavior similar to MTs, but with lower R values [3]. The alcohols *linalool* and *endo-borneol*, and phenolic *carvacrol*, because of their relatively high polarities and low vapor pressures, and the sesquiterpene *caryophyllene* because of its high molecular weight and low vapor pressure are not preferentially in the top product in both the packed and unpacked operations [5].

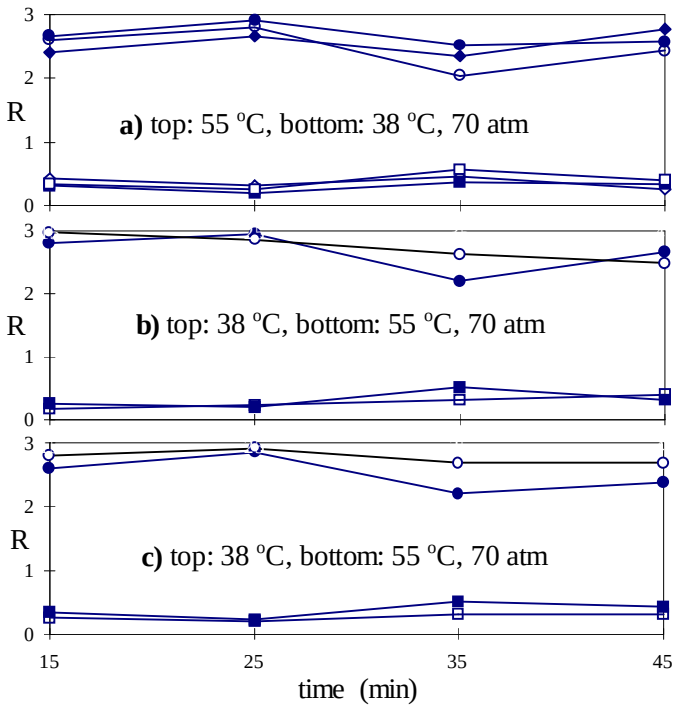


Figure 4: The effect of ethanol entrainer on the relative distributions of MT and NMT components, MT: ϒ-no ethanol, λ-with 2.5 wt% ethanol, ♦-with 5 wt% ethanol, and NMT: -no ethanol, ν with 2.5 wt % ethanol, ◊ with 5 wt % ethanol.

Conclusions

The occurrence of a single-phase region in the column does not improve the separation efficiency. Thus experimental conditions, i.e., temperature and pressure, prevailing in the column should preferably be chosen such that a single-phase region does not occur in the column. In general, the use of Dixon packing enhances the separation of the individual components at all time-cuts. However, the effect of packing on the separation of MTs and NMTs is clearly seen for the first two time-cut samples. The addition of 2.5 wt% ethanol to the oil charge as an entrainer improved the effectiveness of separation as compared to the pure CO_2 experiments. Whereas, a 5.0 wt% ethanol addition gave separation effectivenesses comparable to those of pure CO_2 runs.

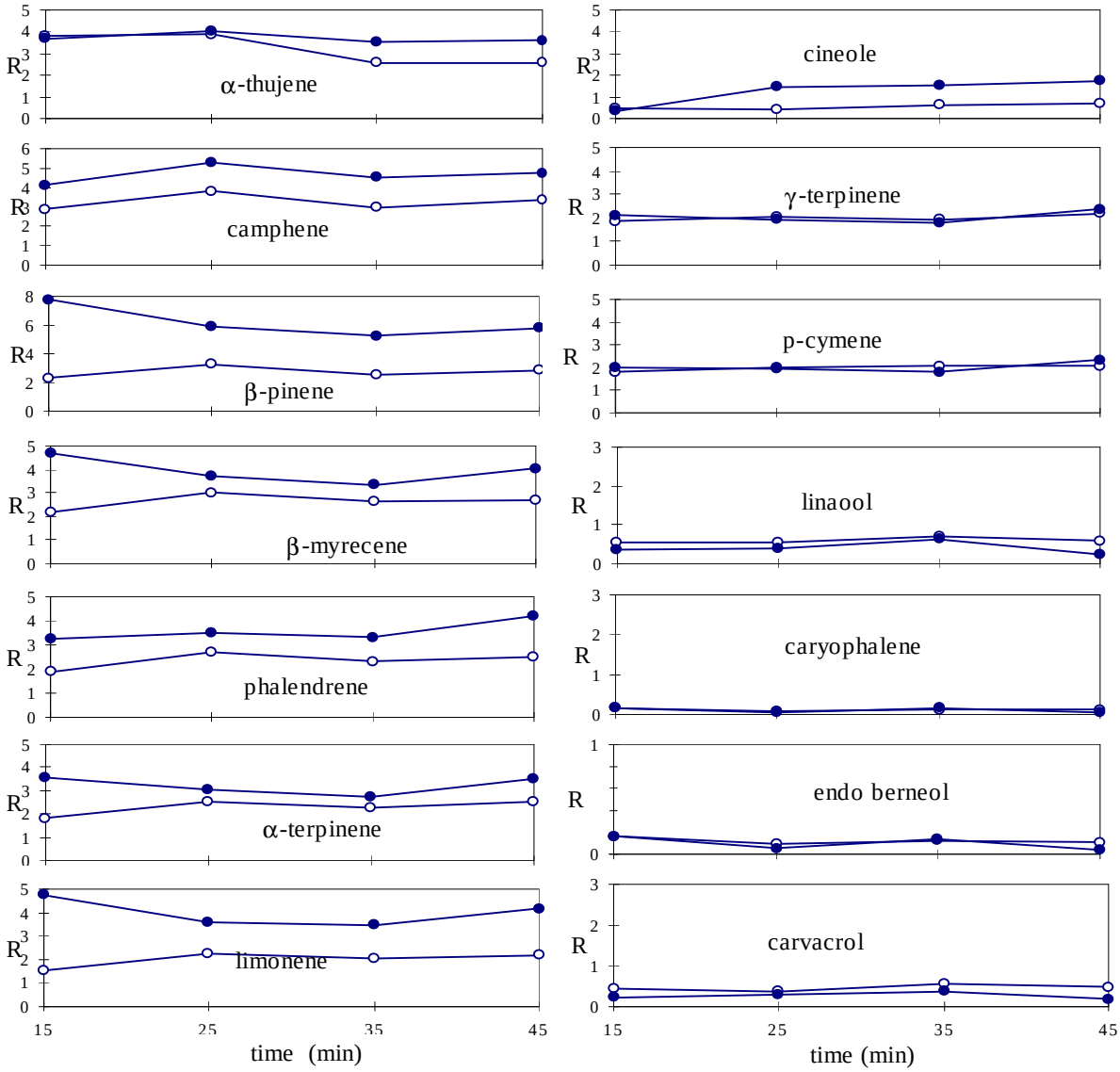


Figure 5: The effects of packing on the relative distributions of the key components (top: 38 °C, bottom: 55 °C, at 70 atm, ϒ: without packing, λ: with packing)

Acknowledgments

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