

# High-Pressure Phase Equilibrium Measurements Using a Double-Chamber Recirculation Apparatus for the System Carbon Dioxide – Lemon Essential Oil

C. Capparucci, F. Gironi, M. Maschietti\*

Dipartimento Ingegneria Chimica Materiali Ambiente (DICMA),  
Università degli Studi di Roma “La Sapienza”, Via Eudossiana 18 – 00184 Roma  
M. Maschietti: e-mail [maschiet@ingchim.ing.uniroma1.it](mailto:maschiet@ingchim.ing.uniroma1.it); fax +39 06 4827453

## ABSTRACT

Lemon essential oil is a valuable raw material for the perfume, cosmetics, and food industry due to its flavour and fragrance. The removal of monoterpenes from the oil is a common industrial practice which allows to increase the concentration of the oxygenated compounds, which are the most valuable, and the stability of the oil. This process can be successfully performed using supercritical carbon dioxide, which allows to obtain a high-quality deterpenated oil.

In this paper the available phase equilibrium experimental data on the multicomponent system carbon dioxide – lemon essential oil are briefly discussed. In addition, new experimental data on the gas-liquid equilibrium of this system are reported. More specifically, the solubility of the oil in supercritical carbon dioxide, the solubility of carbon dioxide in the oil, and the oil composition in the two phases were measured at 50°C and 70°C in a wide range of pressure, using an apparatus and an experimental procedure which were validated in previous works on binary systems.

The apparatus is composed of two chambers, of 170 cm<sup>3</sup> each. In the first chamber, the 'equilibrium cell', the liquid phase coexists with the supercritical phase, whereas the second chamber, the 'gas cell', contains only the supercritical phase. The supercritical phase is continuously recirculated between the two chambers in order to reduce time for equilibration. Before sampling, the gas cell is separated from the equilibrium cell by closing valves, in order to avoid any disturbances of the equilibrium when reducing pressure during the withdrawal of the supercritical phase. The main advantage of this method is the possibility of sampling a large amount of supercritical phase, thus leading to accurate measurements.

## INTRODUCTION

The essential oil obtained from lemon fruit peel is a valuable raw material for the food, cosmetics and perfume industry because of its flavour and fragrance. It is a complex natural mixture composed of more than 100 compounds, the most relevant of which can be roughly grouped into three main classes: monoterpenes, which typically represent more than 90% of the oil, monoterpene oxygenated derivatives, and sesquiterpenes. Monoterpenes and sesquiterpenes are C<sub>10</sub> and C<sub>15</sub> unsaturated hydrocarbons, respectively; oxygenated compounds include several classes of chemical species, such as aldehydes, ketones, esters, alcohols, and acids [1,2].

The oxygenated compounds provide the most important contribution to the flavour of the oil and are thus the most valuable components due to their aroma qualities. On the other hand, the terpene hydrocarbons tend to decompose giving off-flavour compounds when the oil is heated or in contact with oxygen. For these reasons, the partial removal of monoterpenes from

lemon essential oil, which is the so-called deterpenation process, is a common industrial practice that allows to increase the concentration of the aroma compounds, while increasing the stability of the oil [1]. It was proved that the deterpenation process can be effectively performed fractionating the oil through supercritical carbon dioxide as a solvent. In fact, supercritical carbon dioxide dissolves the monoterpene compounds in the gas phase to a higher extent with respect to the oxygenated compounds, thus generating a refined oil with a higher concentration of the latter [3-5]. The supercritical process allows the essential oil to undergo minimal alteration, due to low operating temperatures and complete removal of the solvent from the product, thus producing a deterpenated oil with excellent aroma qualities [1].

In spite of the relevance of the system carbon dioxide – lemon oil in the context of the supercritical deterpenation process, only a few literature works report thermodynamic data on the high-pressure gas-liquid phase equilibrium of this system. This information is important for improving and validating thermodynamic models used for process simulation and design. Coppella and Barton [6] studied the phase equilibrium of this system in the temperature range 30 – 40°C, for pressures up to 9 MPa. The authors observed a two-phase gas-liquid behaviour up to 7.4 MPa at 30°C, 7.8 MPa at 35°C, and 9 MPa at 40°C. At higher pressures the system under investigation exhibited a single-phase behaviour. No three-phase behaviour was observed. The authors measured the composition of both the gas and the liquid phase, determining both the concentration of carbon dioxide in the two phases and the concentration of the main components of the oil. In the range of the operating parameters which was investigated, the solubility of lemon oil in carbon dioxide was in the range of 1 to 3% by weight. Several years later de la Fuente and Bottini [7] measured bubble point pressures of the system carbon dioxide – lemon oil at 30°C and 40°C. The oil used by the authors had a high content of monoterpenes (97.6% by weight). The overall mass fraction of carbon dioxide in the system, which was treated as pseudo-binary, was varied from 3.5 to 93.5% by weight. In these operating conditions, the measurements provide only information on the solubility of carbon dioxide in the oil. No liquid-liquid immiscibility behaviour was observed by the authors. More recently, Franceschi et al. [8] measured equilibrium pressures of the system carbon dioxide – lemon oil in a broader temperature (40-70°C), pressure (up to 19 MPa), and composition range (overall mass fraction of carbon dioxide from 5 to 98% by weight). Also in this case, the system was treated as pseudo-binary, not determining the concentration of single oil fractions at equilibrium. The oil utilised by the authors had a low content of monoterpenes (91.4% by weight), whereas it exhibited a high content of sesquiterpenes (4.1%). According to the authors, different kinds of phase equilibrium were observed: gas-liquid equilibrium up to a heteroazeotropic pressure (slightly variable with carbon dioxide mass fraction) where a liquid-liquid-gas equilibrium was observed, and a (liquid-liquid)-like behaviour above the heteroazeotropic pressure. In particular, at 50°C and 70°C the gas-liquid behaviour disappeared to give rise to a liquid-liquid-gas system at pressures around 10 MPa and 14 MPa, respectively. The curve representing the solubility of carbon dioxide in the liquid phase as a function of pressure undergoes a sharp change in the slope when pressure crosses the heteroazeotrope, that is to say when the system passes from a gas-liquid to a (liquid-liquid)-like behaviour. It is here noted that all the equilibrium data at pressures below the heteroazeotrope (i.e., in the gas-liquid region) refer to overall carbon dioxide mass fractions corresponding to bubble pressures. Therefore, with reference to the two-phase gas-liquid behaviour only the solubility of carbon dioxide in the liquid phase is provided.

On the whole, no gas-liquid equilibrium experimental data above 50°C reporting the composition of both phases have been found in the literature. Furthermore, no experimental

data above 50°C report the equilibrium composition of the major oil fractions in the phases at equilibrium. Nevertheless, such data are relevant since the deterpenation process can be conveniently performed at temperatures above 50°C [5] and full composition data (i.e., not treating the system as pseudo-binary but including the composition of the major oil fractions) allow the calculation of the selectivity of the solvent with respect to the components to be separated. Therefore, in this work measurements of gas-liquid phase equilibrium for the system carbon dioxide – lemon oil were carried out, focusing on the pressure ranges of major interest in the context of the deterpenation process. Both the composition of the liquid and the gas phase were determined, measuring both the concentration of carbon dioxide and of the major oil fractions.

## **MATERIALS AND ANALYSIS**

The essential oil used in this work is from Sicily and it is obtained by cold-pressing lemon peels. After purchasing it from Simone Gatto (Sicily, Italy), the oil was stored at -25°C and filtered before use in order to remove waxes. The composition of the oil was determined by means of Gas Chromatographic (GC) analysis, according to the procedure reported in detail elsewhere [4]. The same procedure is also applied for measuring the composition of the oil samples obtained in the equilibrium experiments. The GC analysis was repeated 10 times to determine the composition of the feed oil, whereas it was repeated 3 times on each oil sample obtained in the equilibrium experiments. The composition values are reported in terms of the three main classes of compounds: monoterpenes (mt), monoterpene oxygenated derivatives (ox), and sesquiterpenes (st). The composition of the feed oil resulted to be (mass percent, average value and standard deviation): mt 93.75% ± 0.29%, ox 4.27% ± 0.20%, st 1.98% ± 0.11%. Carbon dioxide used in this work had purity higher than 99.9% (Siad, Italy). Ethanol p.a. 99.8% (Fluka Chemica) was used to prepare the samples for GC analysis.

## **APPARATUS AND EXPERIMENTAL PROCEDURE**

The apparatus used in the present work was developed and utilised in previous works [9-11] which focused on high-pressure phase equilibrium measurements of binary systems composed of carbon dioxide and relevant compounds of lemon essential oil (i.e., limonene [9], citral [10], and β-caryophyllene [11]). In particular, the apparatus utilised in this work is identical to that described in the works of Gironi and Maschietti [10] and of Maschietti [11], to which the reader is addressed for further details.

The apparatus is composed of two cylindrical chambers of 170 cm<sup>3</sup> each (i.d. 16 mm), which can be kept at the desired temperature through heating jackets. One of the two chambers is initially loaded with a certain amount of lemon essential oil (approximately 30 g) and then carbon dioxide is fed to both chambers up to the desired pressure. Therefore, in one chamber (the ‘equilibrium chamber’) the contact between the two phases is established, whereas the other chamber (the ‘gas chamber’) contains only the gas phase. In order to hasten the attainment of the equilibrium condition, the gas phase is continuously recirculated (for about 6 hours) between the two chambers. During the recirculation step, both the temperature and the pressure of the two chambers are kept constant at the specified values for the particular run. In order to keep the pressure constant in this step, pure carbon dioxide is sporadically fed to the system to counterbalance the pressure decrease caused by gas dissolution in the liquid phase. When the system is approaching equilibrium the pressure is stable, without the need of feeding further carbon dioxide. Since the specified quantities of each experimental runs are pressure, temperature, volume, and the amount of lemon oil

loaded in the apparatus, the amount of carbon dioxide at equilibrium can not be fixed in advance but it is one of the quantity which is measured in the experiments.

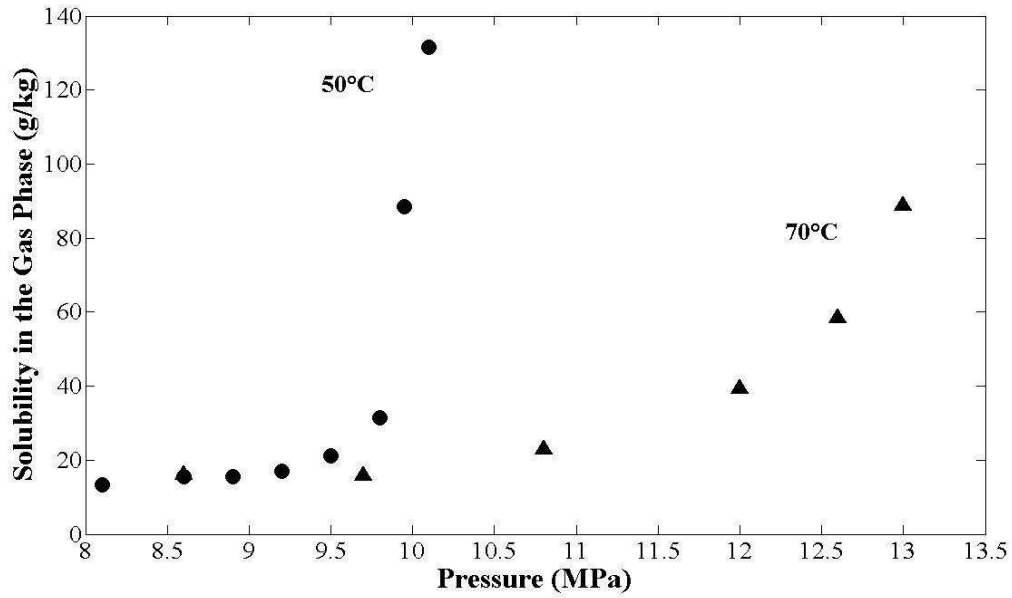
After the recirculation period, the two chambers are separated by closing valves in order to allow the whole content of the gas chamber to be sampled. The possibility of trapping and sampling a large volume (i.e., 170 cm<sup>3</sup>) of saturated gas phase without disturbing the attained gas-liquid equilibrium condition is a remarkable feature of this procedure, especially when dealing with low-solubility systems as those commonly encountered in supercritical processes. The gas phase sampling is carried out in two steps, according to the procedure described in detail elsewhere [9]. Subsequently, two samples of liquid phase are withdrawn from the bottom of the equilibrium chamber, according to the procedure described in a previous work [10]. The size of each sample of liquid phase corresponds to 0.5 litres of sampled carbon dioxide (measured at ambient conditions). The amount of solute collected during the phase sampling is determined gravimetrically, whereas the amount of carbon dioxide is determined by means of the gas meter whose specifications are reported elsewhere [10]. The amount of the lemon oil fraction withdrawn from the gas chamber (i.e., ‘the extract’) resulted to be in the range 0.51 – 12.75 g, corresponding to a sampled volume of carbon dioxide in the range 19 – 55 l (measured at ambient conditions). As far as the liquid phase sampling is concerned, the amount of a single sample of lemon oil fraction withdrawn from the bottom of the equilibrium chamber (i.e., ‘the raffinate’) resulted to be in the range 0.25 – 2.7 g. The composition of the samples of extract and raffinate is determined by means of the GC analysis, according to the procedure described in the previous section.

After the liquid phase sampling, the equilibrium chamber is depressurised. The amount of liquid collected in the depressurisation step, originating from both the liquid and the gas phase which were previously in equilibrium in the chamber, is determined gravimetrically in order to check the mass balances referred to the whole experimental run. The amount of carbon dioxide exiting the chamber in the depressurisation step is also measured, in order to obtain the necessary data for calculating the equilibrium overall composition of the system.

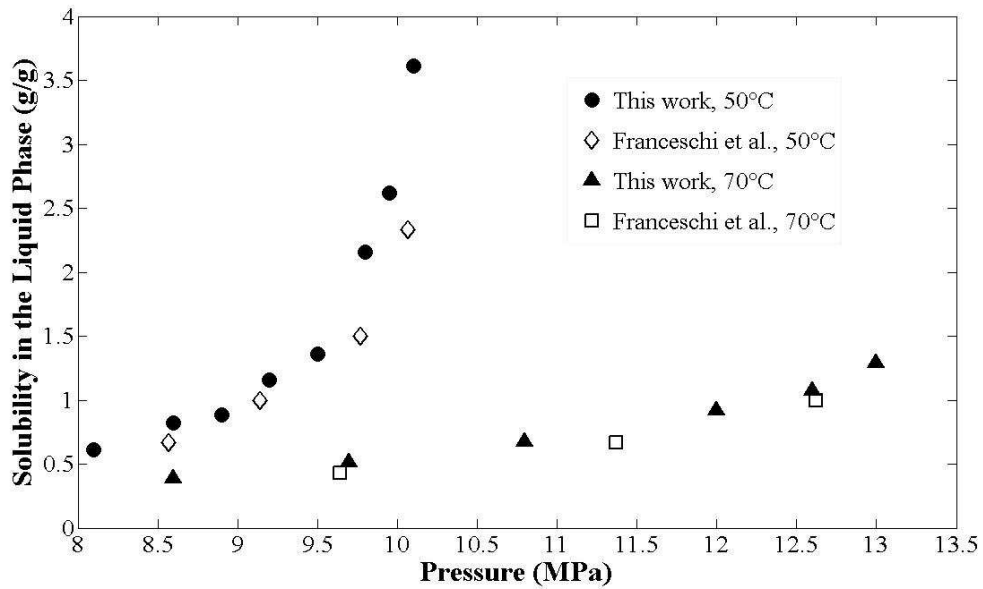
## RESULTS AND DISCUSSION

The phase equilibrium of the system carbon dioxide – lemon essential oil was investigated at 50°C and 70°C, for pressures in the range 8.1 – 10.1 MPa and 8.6 – 13.0 MPa, respectively. These pressure and temperature values are particularly relevant for this system, since they represent potential operating parameters for the efficient application of the supercritical deterpenation process.

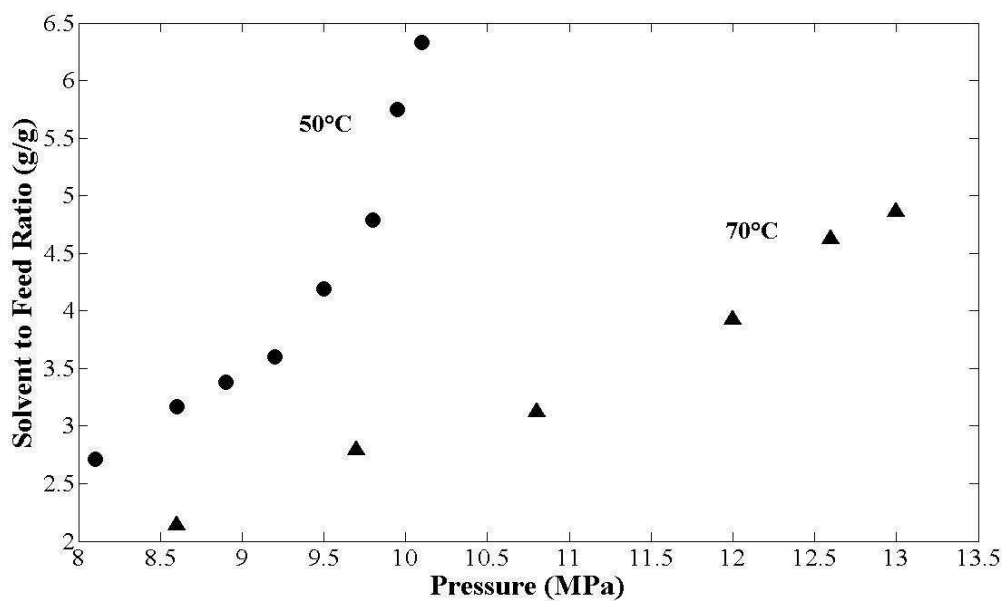
Fig. 1 shows the solubility of the oil in supercritical carbon dioxide as a function of pressure, at the two temperatures under investigation. No literature experimental data on the system carbon dioxide – lemon oil are available for comparison for these pressure and temperature values. The data measured in this work show that at 50°C the solubility of the oil increases from approximately 13 to 130 g/kg, for pressures ranging from 8.1 to 10.1 MPa; at 70°C the solubility increases from approximately 16 to 90 g/kg, for pressures ranging from 8.6 to 13 MPa. As typical for the dissolution of liquids in supercritical carbon dioxide, both the solubility and the derivative of the solubility (with respect to pressure) increase with pressure. As far as the dependence on temperature is concerned, at 8.6 MPa the solubility is approximately the same at the two temperatures under investigation, whereas at higher pressures the solubility decreases with temperature. Therefore, the value 8.6 MPa appears to be a crossover pressure, marking a change in the behaviour of the relationship between gas phase solubility and temperature.



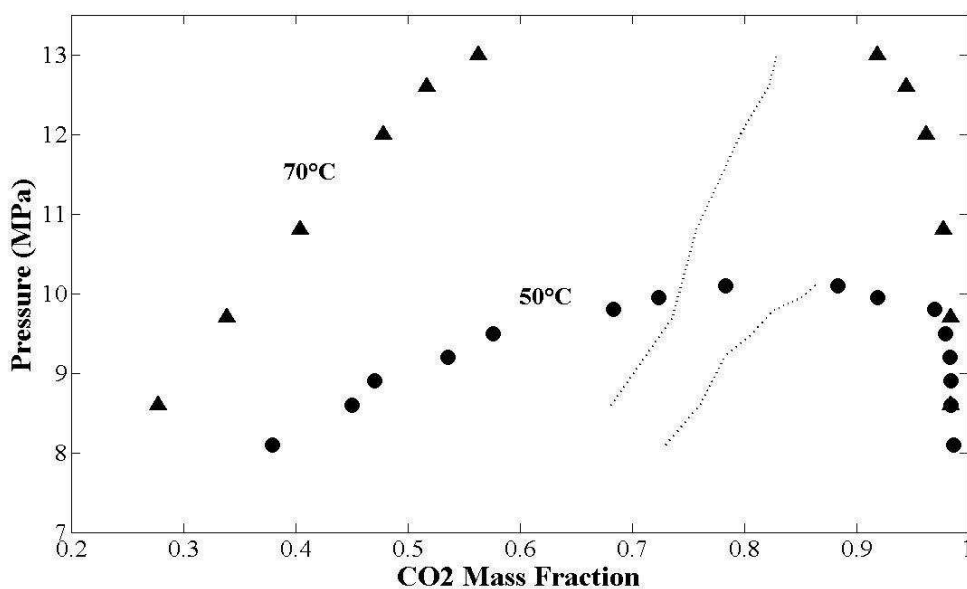
**Figure 1:** solubility of lemon essential oil in supercritical carbon dioxide at 50°C and 70°C, as a function of pressure. The solubility is expressed as gram of oil per kilogram of carbon dioxide.



**Figure 2:** solubility of carbon dioxide in lemon essential oil at 50°C and 70°C, as a function of pressure. The solubility is expressed as grams of carbon dioxide per gram of oil. A comparison with the data of Franceschi et al. [8] is reported.



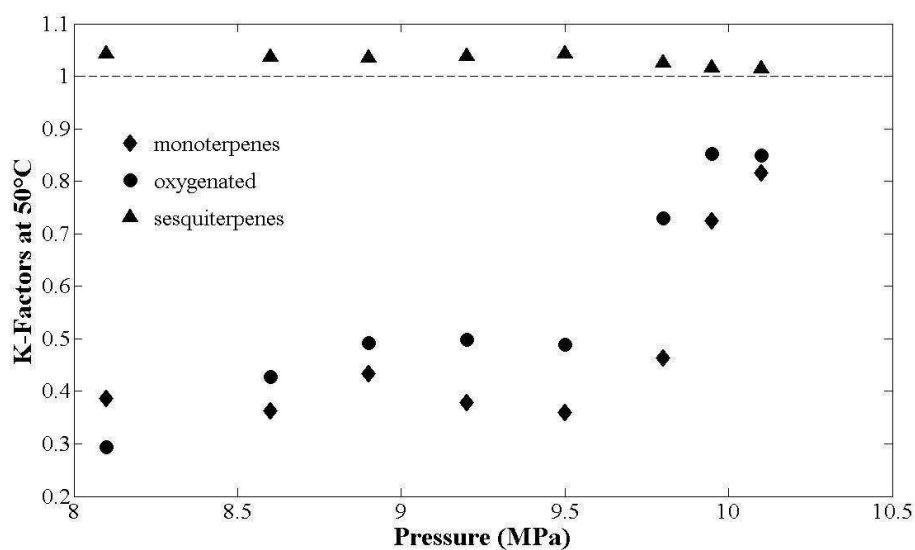
**Figure 3:** carbon dioxide ('the solvent') to lemon oil ('the oil') ratio in the experimental runs. Isothermal data at 50°C and 70°C reported as a function of pressure.



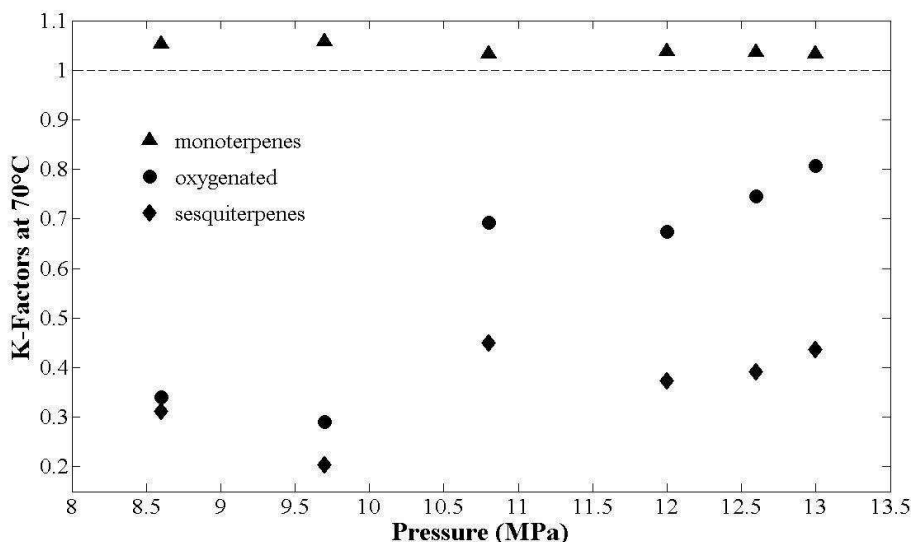
**Figure 4:** P-x-y isothermal diagrams for the system carbon dioxide – lemon oil at 50°C and 70°C. Compositions are on mass basis. Dotted lines indicate the overall composition of the system in the experimental runs which were carried out.

Fig. 2 shows the solubility of carbon dioxide in the liquid phase, as a function of pressure. The solubility of the gas in the liquid phase increases with pressure and decreases with temperature, for the values of pressure and temperature under investigation. At 50°C, an increase from approximately 0.6 to 3.6 g/g is observed, whereas the solubility increases from 0.4 to 1.3 g/g at 70°C. In this case, the bubble pressure data reported by Franceschi et al. [8] allow a comparison with the data of the present work. As it can be seen from Fig. 2, the two data sets are in good agreement. From a quantitative standpoint, the average discrepancy between the two sets of solubility data is approximately 15% (with respect to average values between the two data sets). This value is consistent with the typical discrepancies on solubility data encountered when dealing with high-pressure gas-liquid equilibrium measurements. Furthermore, it should be bear in mind that the lemon oil utilised by Franceschi et al. [8] has a different composition with respect to the one used in this work, exhibiting a higher content of heavy compounds (monoterpenes 91.7%, oxygenated compounds 4.6%, sesquiterpenes 4.1%). In addition, also the carbon dioxide ('the solvent') to lemon oil ('the feed') ratio is not the same in the two data sets. With reference to the experimental points measured by Franceschi et al. [8] which are reported in Fig. 2, the solvent to feed ratio (S/F) increases from 0.67 to 2.33 and from 0.43 to 1, at 50°C and 70°C, respectively. On the other hand, in the present work the equilibrium was established for higher values of S/F, as reported in Fig. 3. Some aspects related to the overall composition of the system (i.e., S/F) are addressed in the next paragraph.

As underlined in the Section 'Apparatus and Experimental Procedure', the experimental runs were conducted maintaining pressure and temperature constant, in a constant-volume system with a fixed amount of loaded oil. It thus should be bear mind that the solubility curves reported in Figs. 1-2 refer to a multicomponent system with variable overall composition. More specifically, the curves are obtained with a variable amount of carbon dioxide, that is to say that each experimental point refers to a different value of S/F. Fig. 3 addresses to this aspect, reporting the values of S/F for each experimental run. At a stated



**Figure 5:** K-factors on mass basis for the three classes of compounds selected for representing lemon oil: monoterpenes, oxygenated compounds, and sesquiterpenes. Equilibrium values at 50°C reported as a function of pressure.



**Figure 6:** K-factors on mass basis for the three classes of compounds selected for representing lemon oil: monoterpenes, oxygenated compounds, and sesquiterpenes. Equilibrium values at 70°C reported as a function of pressure.

temperature, the amount of solvent increases as the equilibrium pressure increases since the amount of loaded oil is approximately constant. Comparing the curves referred to different temperatures, it can be observed that the same pressure is obtained with a lower amount of carbon dioxide at 70°C. The lower amount of solvent which is necessary at the higher temperature in order to attain a specific pressure value is due to the lower solubility of the gas in the liquid phase and to the higher specific volume of the two phases.

The data reported in Figs. 1-3 can also be observed in the isothermal P-x-y diagrams reported in Fig. 4, which provide an overview of the behaviour of the system at the two temperatures. In the area of the diagrams corresponding to the presence of two phases (gas-liquid equilibrium), the overall composition of the system referred to the specific conditions of the experimental runs is reported as a dotted line.

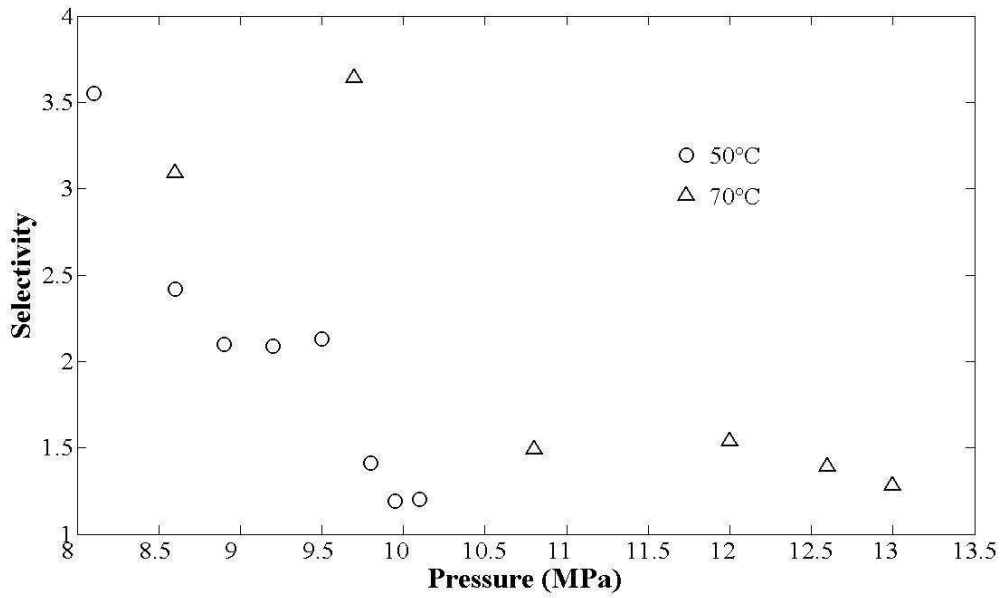
The measurements of the compositions of the extract and the raffinate allowed to calculate the distribution coefficients (i.e., the K-factors) of the three selected classes of compounds representing the oil and the selectivity of carbon dioxide (i.e., the solvent) with respect to the separation between monoterpenes (mt) and oxygenated compounds (ox). In this work, the K-factors and the selectivity of the solvent between monoterpenes and oxygenated compounds are defined as:

$$K_i = \frac{Y_i}{X_i} \quad (1)$$

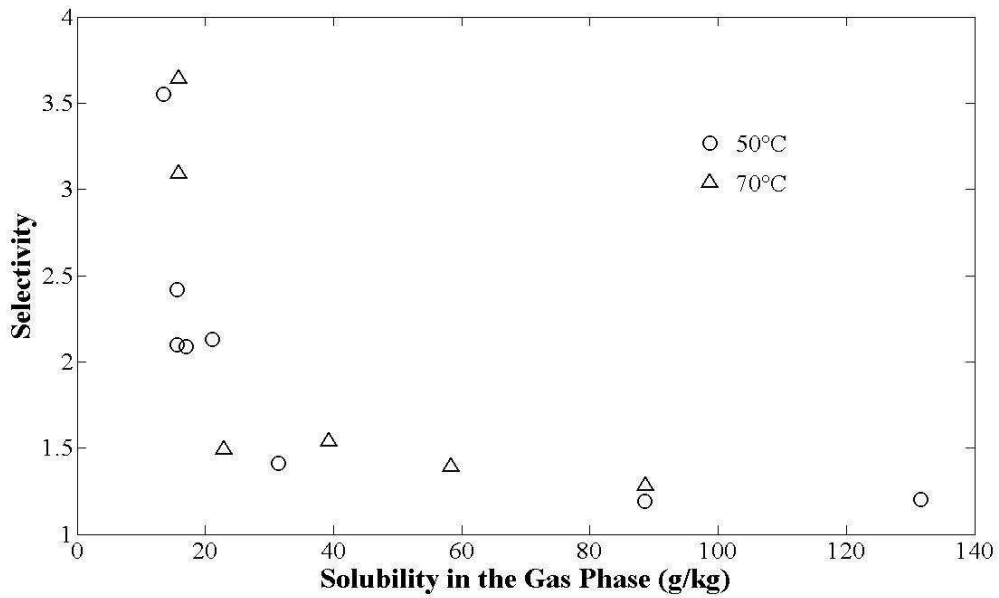
$$S_{mt/ox} = \frac{K_{mt}}{K_{ox}} \quad (2)$$

where  $Y_i$  and  $X_i$  stand for the mass fractions on solvent free basis in the gas and in the liquid phase, respectively. Fig. 5 and Fig. 6 show the trend of the K-factors at 50°C and 70°C, respectively. No literature experimental data are available for comparison. As it can be seen, the monoterpenes are concentrated in the gas phase ( $K > 1$ ), whereas the oxygenated and





**Figure 7:** Selectivity between monoterpenes and oxygenated compounds (mass basis) at 50°C and 70°C as a function of pressure.



**Figure 8:** Selectivity between monoterpenes and oxygenated compounds (mass basis) at 50°C and 70°C. Data are reported as a function of the solubility in the gas phase.

sesquiterpenes compounds concentrate in the liquid phase ( $K < 1$ ), being the  $K$ -factors of the sesquiterpenes only slightly smaller than those of the oxygenated compounds. The  $K$ -factors of the monoterpenes are only slightly greater than 1, mainly because of their high mass fraction in the feed oil (i.e., 94%) and the low values of  $S/F$  in the experimental runs. As pressure increases and the two phases at equilibrium become similar, all  $K$ -factors tend to 1.

The values of the selectivity between monoterpenes and oxygenated compounds are reported as a function of pressure in Fig. 7. At the lower pressures the selectivity of the solvent is higher (maximum values around 3.5) and it decreases as pressure increases, approaching 1 when the two phases become similar. In order to get information on optimal parameters for the efficient application of the deterpenation process, it is necessary to take into account also the solubility of the oil in the solvent. In fact, low-pressure operating conditions typically correspond to high selectivity and low solubility, whereas the opposite occurs at high pressures. Optimal operating conditions typically arise from a compromise between these two aspects. In this regard, Fig. 8 is useful since it reports the selectivity as a function of the solubility, for the two temperatures under investigation. With a single exception, probably due to some inaccuracies in the experiments, at 70°C the selectivity is slightly higher with respect to 50°C, for pressures leading to the same solubility. On the basis of this result, operating conditions at higher temperatures appear to be more favourable.

## CONCLUSIONS

The gas-liquid phase equilibrium of the system carbon dioxide – lemon oil was investigated at 50°C and 70°C, utilising an essential oil with 93.7% of monoterpenes, 4.3% of oxygenated compounds, and 2.0% of sesquiterpenes (mass percent). In the range of pressures under investigation, no evidence of equilibria other than the (two-phase) gas-liquid equilibrium was found. Both the composition of the gas and the liquid phase were determined, treating the essential oil as a three-component system (monoterpenes, oxygenated compounds, sesquiterpenes). The analysis of the solubility of the oil in the gas phase and of the selectivity of the solvent with respect to the two classes of oil components to be separated (i.e., monoterpenes and oxygenated compounds) shows that, for a stated solubility, slightly higher selectivities can be achieved operating at the higher of the two temperatures under investigation.

## REFERENCES

- [1] BRADDOCK, R.J., Handbook of Citrus By-Products and Processing Technologies, Wiley, New York, **1999**, pp. 149-174.
- [2] HUI, Y.H., Encyclopedia of Food Science and Technology, Wiley, New York, 1992.
- [3] REVERCHON, E., J. Supercrit. Fluids, Vol. 10, **1997**, p. 1.
- [4] GIRONI, F., MASCHIETTI, M., J. Supercrit. Fluids, Vol. 35, **2005**, p. 227.
- [5] GIRONI, F., MASCHIETTI, M., Chem. Eng. Sci., Vol. 63, **2008**, p. 651.
- [6] COPPELLA, S.J., BARTON, P., ACS Symposium Series, Vol. 329, Chapter 16, **1987**, p. 202.
- [7] DE LA FUENTE, J.C., BOTTINI, S.B., Fluid Phase Equilib., Vol. 175, **2000**, p. 45.
- [8] FRANCESCHI, E., GRINGS, M.B., FRIZZO, C.D., OLIVEIRA, J.V., DARIVA, C., Fluid Phase Equilib., Vol. 226, **2004**, p. 1.
- [9] GIRONI, F., MASCHIETTI, M., J. Supercrit. Fluids, Vol. 55, **2010**, p. 49.
- [10] GIRONI, F., MASCHIETTI, M., J. Supercrit. Fluids, Vol. 57, **2011**, p. 25.
- [11] M. MASCHIETTI, J. Supercrit. Fluids, in press, **2011**,(doi:10.1016/j.supflu.2011.07.020)