Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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D. M. Kassim[a]; M. S. Hameed[ab]
[a] PETROLEUM RESEARCH CENTRE COUNCIL OF SCIENTIFIC RESEARCH, BAGHDAD, IRAQ [b] Department of Chemical Engineering, University of Technology, Baghdad, Iraq

To cite this Article Kassim, D. M. and Hameed, M. S.(1989) 'Direct Extraction-Separation of Essential Oils from Citrus Peels by Supercritical Carbon Dioxide', Separation Science and Technology, 24: 15, 1427 — 1435
To link to this Article: DOI: 10.1080/01496398908050661
URL: http://dx.doi.org/10.1080/01496398908050661

SEPARATION SCIENCE AND TECHNOLOGY, 24(15), pp. 1427-1435, 1989/90

Direct Extraction-Separation of Essential Oils from Citrus Peels by Supercritical Carbon Dioxide

D. M. KASSIM AND M. S. HAMEED*

PETROLEUM RESEARCH CENTRE
COUNCIL OF SCIENTIFIC RESEARCH
JADIRIYAH, BAGHDAD, IRAQ

Abstract

Essential oils from citrus peels were extracted and separated with CO_2 under supercritical conditions in a single process. The peels were placed together with ethanol, as an entraining solvent, inside a high pressure cell filled with carbon dioxide at a pressure < 130 bar and a temperature of 35°C. The extract was fractionated in various pressure ranges after achieving equilibrium, and it was analyzed with a gas chromatograph. The initial fraction contained most of the water content of the peels while the following fractions were rich in essential oils. A mechanism for the extraction and separation is also given.

INTRODUCTION

Physical separation techniques usually result in concentration differences. The common methods used for the isolation of volatile organic material from natural products are steam distillation, solvent extraction, heat desorption, vapor collection by cryogenic concentration, and adsorption. Essential oils are the volatile odoriferous principals present in many plant materials and can be isolated by some of these methods. They are normally complex mixtures containing many organic compounds. Steam distillation and solvent extraction methods result in losses of part of the

*On sabbatical leave from the Department of Chemical Engineering, University of Technology, Baghdad, Iraq.

volatile materials; heat desorption and vapor collection are usually not reproducible (*1*). The essential oils may also suffer structural changes during these processes.

Recently, industrial research to develop alternative separation techniques has been intensified to reduce process costs and to produce quality to meet the demand for improved health and safety standards (*2*). Consideration has been given lately for the use of supercritical fluids (SCF) for extraction (*3–9*). Paul and Wise (*7*) reviewed the theory and practice of SCF and also areas of potential applications in important separation processes. Irani and Funk (*10*) described the advances made in the thermodynamic analysis of SCF. Industrial applications of the process have been reviewed by Kohn and Savage (*9*), and several patents related to the extraction of food products were listed by Bott (*11*). The extraction of essential oils using carbon dioxide at supercritical conditions was also carried out by Stahl et al. (*12*); the product showed no quality deterioration such as that normally encountered with steam distillation due to thermal or hydrolytic effects.

The present work studied the potential of supercritical CO_2 (SC-CO_2) for the extraction and separation of essential oils from citrus peels by using an improved system.

EXPERIMENTAL

Apparatus

The basic design of the apparatus used for SC-CO_2 extraction was an improved version of that presented by King et al. (*13*). Two essential improvements were made: 1) extraction recovery could be done from the extraction cell, 2) the liquid content of the cell was continuously removed to glass receivers and different product fractions were obtained. The apparatus is schematically shown in Fig. 1. It consists mainly of an equilibrium cell (E) and an air-driven recirculating pump (C) contained in an air bath maintained at constant pre-set temperatures to $\pm 0.1\,^{\circ}C$ (H) by means of temperature controllers from Parr Instruments Co., a mercury injector pump (D), high pressure gauges (I) and glass receivers (B) with appropriate high pressure valves (Ruska type) and stainless steel tubing (¼″ i.d.).

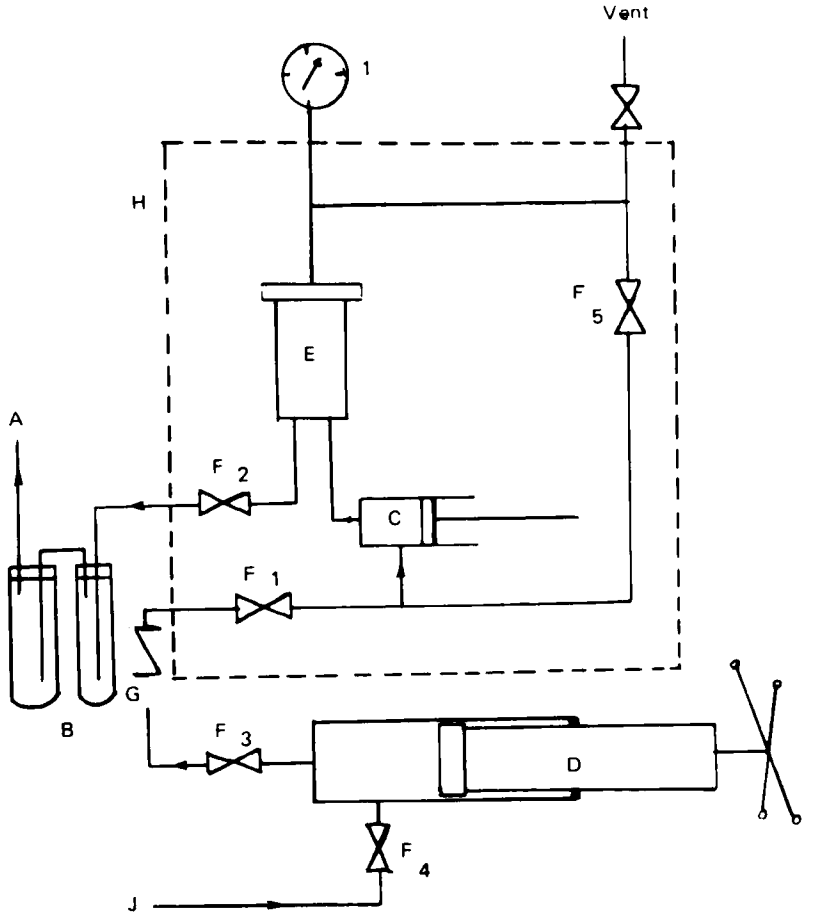

FIG. 1. Schematic diagram of the SCF extraction apparatus: (A) expansion system and manometer; (B) two glass receivers; (C) recirculating pump; (D) injection pump; (E) equilibrium cell; (F) high pressure valves; (G) one-way valve; (H) controlled temperature air bath; (I) Helse pressure gauge; and (J) gas source.

The glass sample container was placed inside a stainless steel equilibrium cell of 1 L capacity (Ruska Co.). In addition to recirculating the fluids, the air-driven pump (Model MC 188, 1000 psi from Haskel Co.) served as a compressor to deliver CO_2 from the source to the system.

Procedure

Preliminary experiments were carried out to establish favorable conditions for the extraction. Peels (75 g) were placed with an equal quanitity of absolute ethyl alcohol in a glass container that fits in the equilibrium cell. The fresh peels used were *Citrus aurantium,* while other citrus peels used were kept frozen. The glass container (as shown in Fig. 4). was placed inside the equilibrium cell (E), and the cell was firmly capped. The system was then filled with CO_2 from a high pressure CO_2 cylinder (J). The pressure of the gas was then increased with the aid of a mercury injection pump (D) and an air-driven pump (C) to 125 bar; meanwhile the air bath was kept at 35°C. With the air-driven pump (C) in operation, continuous feeding of CO_2 was accomplished. Valves F_2 and F_5 were opened and closed alternatively, and samples were collected continuously at different supercritical pressure ranges (decreasing order), resulting in products of different compositions. The samples, which were CO_2 free, were collected in glass receivers (B) and were later analyzed by gas chromatography by using a Pye Unicam GC 204 equipped with a Spectra Physics minigrator and a thermal conductivity detector. Analysis determined the concentrations of water, ethanol, and essential oils. The analyses were made by using a 1.5-m long column of 4 mm o.d. packed with Carbowax 20M, and operated at 80°C.

RESULTS AND DISCUSSION

Figures 2 and 3 show the mode of recovery of the oil, water, and ethanol as a function of pressure (average of pressure range during sample collection) for *Citrus aurantium* and *C. clementine,* while the percentage recovery for sweet lemon is given in Table 1. The yield plotted in the figures represents the percent amount of each component relative to the total amount collected. Chemical analysis (GC) of the extract indicated that the SC method of extraction succeeded not only in the complete extraction of

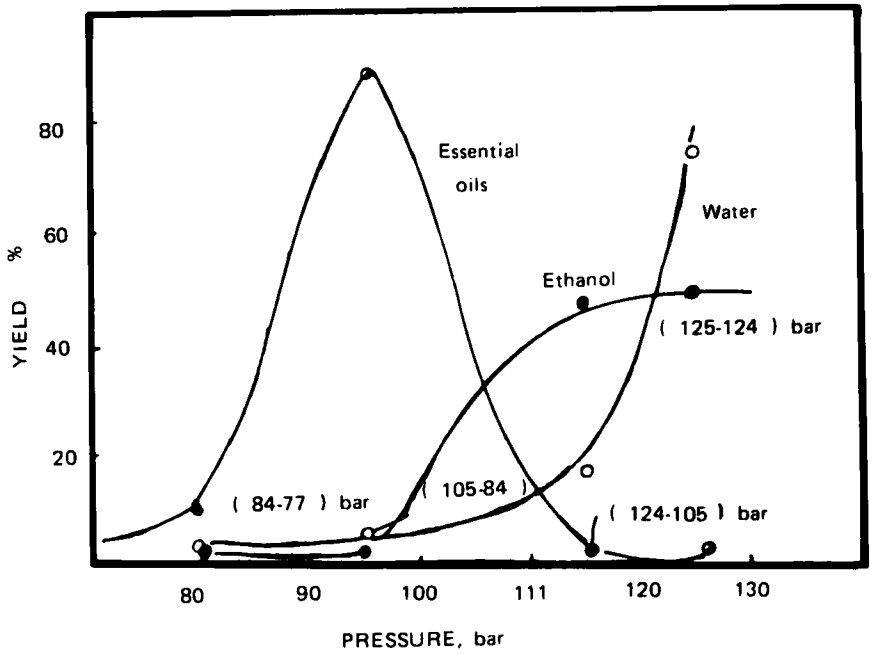

FIG. 2. Recovery of ethanol, water, and essential oils from fresh *Citrus aurantium* peels at various pressures.

essential oils and water from peels but also in the efficient fractionation and separation of the components. Water represents a large percentage of peel extract. In the present case the first few samples (2–4) were rich in water relative to the other components. The remaining samples were relatively rich in the essential oils as shown in Figs. 2 and 3. For *Citrus aurantium* the first two samples contained ~90% of the total water, while the third and fourth samples were rather alcoholic solutions of essential oils with only traces of water. Similarly, in the cases of lemon and *C. clementine* peels, water could be efficiently separated from the rest of the components. It appeared experimentally that as CO_2 gas is introduced to the system, it dissolves in ethanol (*14*) as indicated by the CO_2 pressure decreasing inside the system with time. Water and water-soluble essential oils are extracted by this highly polar liquid, while the hydrocarbon part of the oil is less soluble in this liquid. The presence of water increases the amount of

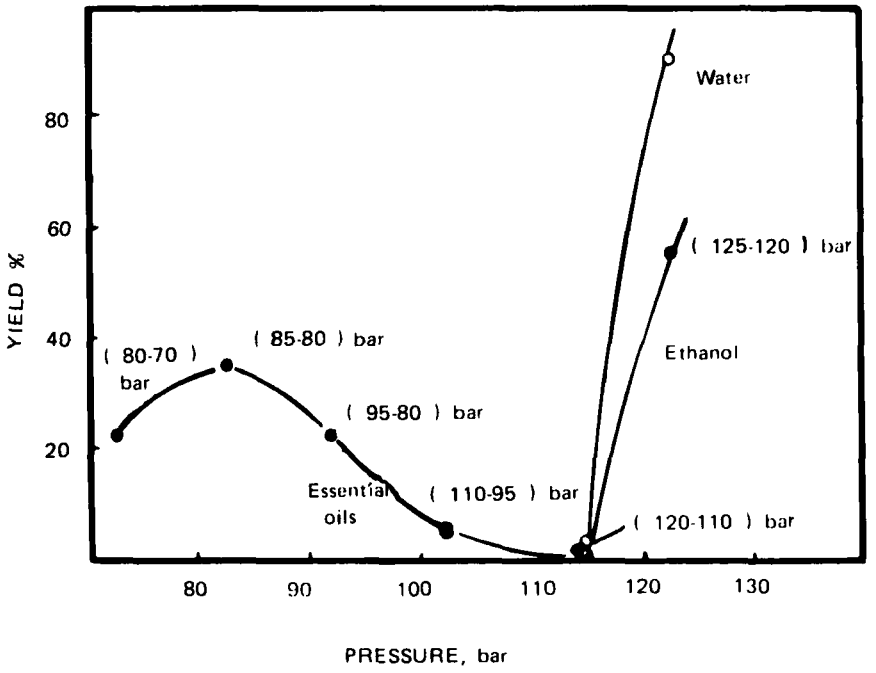

FIG. 3. Recovery of ethanol, water, and essential oils from frozen *Citrus clementine* peels at various pressures.

dissolved CO_2, which leads to the formation of carbonic acid. This acid is stable under the operating conditions used. The ethanol and water are believed to settle to the bottom of the glass container in the cell, while CO_2 is formed in the upper layer, as shown in Fig. 4. Two phases, therefore, are assumed to exist inside the glass container in the cell: water-ethanol at the bottom and liquid CO_2 at the top. The release of pressure through the sampling device pushes the higher density liquid outside the system because the sampling arrangement was made to draw out the bottom layer first. That layer was rich in water and the water-ethanol soluble components and contained little CO_2. The upper liquid phase was withdrawn afterwards, with the release of CO_2 as a gas that contained the liquid CO_2 soluble parts of the oils. The formation of solid carbon dioxide (dry ice accumulation) in the sampling taps gave rise to some experimental

TABLE 1.
Experimental Results for the SCF-CO_2 Extraction of Essential Oils from Sweet Lemon Peels

Sample no.	Collected sample (g)	Average pressure (bar)	% Composition (CO^2-free basis)[a]		
			Ethanol	Essential oils	Water
1	13.63	123.5 (125–122)	44.3	Trace	55.5
2	2.41	118.0 (122–114)	67.2	0.2	32.0
3	0.49	106.0 (114–99)	86.3	0.7	12.2
4	0.47	96.0 (99–93)	79.1	0.2	20.0
5	1.47	88.0 (93–83)	87.0	0.3	12.1
6	0.76	79.5 (83–76)	86.5	0.5	12.3
7	1.87	75.0 (76–74)	90.0	0.4	9.5
8	1.77	74.0 (74–74)	30.0	0.0[b]	70.0
9	2.74	72.0 (74–70)	22.2	0.0[b]	77.6
10	0.16	70.0 (70–70)	15.0	0.0[b]	85.0
11	11.25	—[c]	93.7	0.0[b]	6.1
12	38.8	—[c]	43.3	0.0[b]	56.1

[a]Obtained by GC analysis.

[b]Highly volatile essential oils are excluded.

[c]The system is vented and the pressure drops gradually to atmospheric.

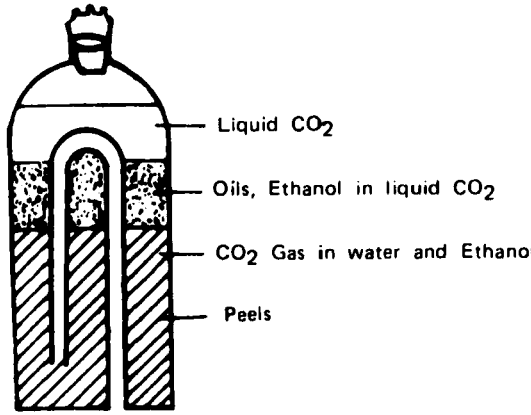

FIG. 4. Glass container composition during extraction.

difficulties after the removal of the bottom layer. This observation supports the mechanism proposed for the extraction process.

It appears that water is easily extracted from deep frozen peels (90% of its weight in the first fraction) as compared to fresh peels (50% of its weight in the first fraction). On the other hand, the ethanol used could be quantitatively recovered in the case of the fresh peels and only semiquantitatively recovered from the deep frozen peels.

Such a phenomenon may be explained as follows: During deep freezing, the water existing inside the pockets and the cells of peels solidifies and expands in volume, bringing about cracks and cuts of the cell walls inside the peels. This facilitates the passage of water outward and the movement of ethanol and liquid CO_2 inward. A portion of the ethanol therefore replaces the water exiting from the peels. Eventually, the peels are soaked in ethanol compared to the dry peels of fresh material.

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Received by editor January 4, 1989