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

Dynamic Extraction of Spearmint Oil Components by Using Supercritical CO_2

Kyoung Heon Kim[a]; Juan Hong[b]
[a] National Renewable Energy Laboratory, Golden, CO, U.S.A. [b] DEPARTMENT OF CHEMICAL AND BIOCHEMICAL ENGINEERING AND MATERIALS SCIENCE, UNIVERSITY OF CALIFORNIA, IRVINE, IRVINE, CALIFORNIA, USA

Online publication date: 17 January 2000

To cite this Article Kim, Kyoung Heon and Hong, Juan(2000) 'Dynamic Extraction of Spearmint Oil Components by Using Supercritical CO_2', Separation Science and Technology, 35: 2, 315 — 322
To link to this Article: DOI: 10.1081/SS-100100159
URL: http://dx.doi.org/10.1081/SS-100100159

SEPARATION SCIENCE AND TECHNOLOGY, **35**(2), pp. 315–322, 2000

TECHNICAL NOTE

Dynamic Extraction of Spearmint Oil Components by Using Supercritical CO_2

KYOUNG HEON KIM* and JUAN HONG†
DEPARTMENT OF CHEMICAL AND BIOCHEMICAL ENGINEERING AND MATERIALS SCIENCE
UNIVERSITY OF CALIFORNIA, IRVINE
IRVINE, CALIFORNIA 92697, USA

ABSTRACT

The effects of various extraction conditions on the dynamic extraction of the essential oil components carvone and limonene from spearmint leaves using SC-CO_2 were investigated. The extraction rate increased with increasing pressure or decreasing temperature. An increase of the CO_2 flow rate increased the extraction rate but decreased the solvent efficiency of CO_2. Ground leaf samples with a smaller particle size showed an enhanced initial extraction rate for carvone as compared to larger particle size leaf samples. The use of an ethanol modifier did not enhance the extraction rate but did cause the coextraction of pigment and waxy substances.

Key Words. Extraction; Supercritical carbon dioxide; Spearmint oil; Carvone; Limonene

INTRODUCTION

Solvent extraction and steam distillation have been conventionally used to isolate essential oils from plant materials for industry. Supercritical CO_2 (SC-CO_2) has been considered as an alternative solvent due to its nontoxicity, nonflammability, relatively moderate critical point, and low cost even at high pu-

* Current address: National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, CO 80401, USA.
† To whom correspondence should be addressed. Telephone: (949) 824-8278. FAX: (949) 824-2541. E-mail: jhong@uci.edu

rity. Compared to phase equilibrium studies using SC-CO_2, relatively fewer studies are available on the extraction of natural products using SC-CO_2 (1). Since extraction from plant matrices is much different from extraction for equilibrium solubility measurements of pure substances, knowledge of the extraction behavior in actual SC-CO_2 extraction from plant matrices would be useful for industrial applications.

Spearmint oil is one of the most popular flavoring materials used in foods, pharmaceuticals, and perfumes. The major components of spearmint oil are *l*-carvone and *l*-limonene, and the unique odor of spearmint is characterized by *l*-carvone (2–5). Spearmint oil extraction using SC-CO_2 was carried out by Barton et al. (6) and Ozer et al. (7). However, no information exists on the time-dependent extraction behavior and mass transfer mechanism for spearmint oil extraction. For this paper the effects of temperature, pressure, exiting CO_2 flow rate, leaf particle size, and ethanol modifier on the SC-CO_2 extraction of essential oil components from spearmint leaves were studied.

EXPERIMENTAL SECTION

Materials

Spearmint leaves obtained from southern California were washed with deionized water and air-dried at room temperature for 1 week. They were then cut into pieces of 0.15 mm average radius. When fine particle-sized leaves were needed, the cut leaves were ground using a mortar and pestle to reduce their average radius to 0.03 mm. CO_2 of 99.6 or 99.9% purity was used. Methanol (99.9% purity) was used as a collection solvent, and ethanol (99.9% purity) was used as a modifier.

Apparatus and Procedure

Extraction experiments were performed with the apparatus schematically shown in Fig. 1. The heart of the supercritical delivery system (CCS, Unionville, NJ) is an ISCO μLC-50 syringe pump with a capacity of 50 mL. This pump was designed to compress CO_2 and to deliver fluids up to 6000 psi.

A spearmint leaf sample (2 g) was placed with about 40 mL of glass beads (2 mm diameter) in the extraction vessel to disperse the leaf particles in the SC-CO_2 phase. The extractor was pressurized and heated, and when the pressure and temperature of the extractor reached the desired points, the heated flow restriction valve was opened. This marked the start of extraction.

The supercritical CO_2 stream laden with essential oil left the extractor and expanded at atmospheric pressure after the restriction valve, passing through the flowmeter before being vented. The flow rate of the exiting CO_2 was recorded to determine the cumulative amount of CO_2 passed during extrac-

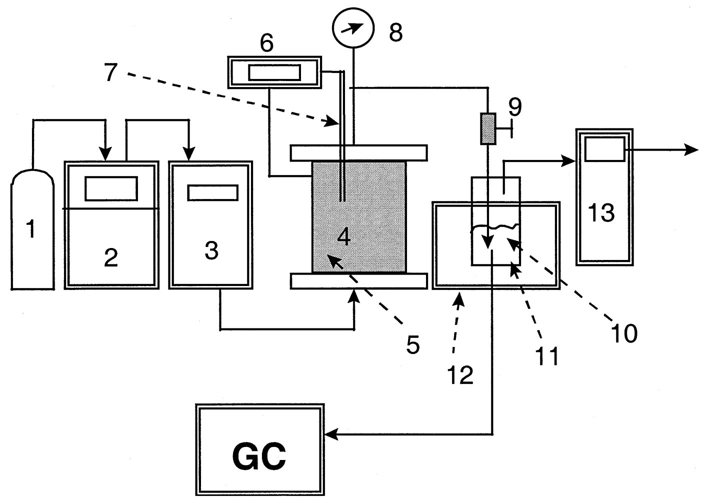

FIG. 1 Schematic diagram of the experimental apparatus: (1) CO_2 cylinder; (2) fluid delivery system; (3) valve oven; (4) extraction vessel; (5) heating tape; (6) temperature controller; (7) thermocouple; (8) pressure gauge; (9) flow restriction valve; (10) collection solvent; (11) collection vessel; (12) ice bath; (13) flowmeter.

tion. The essential oil extract dissolved in methanol was taken at specific time intervals to obtain extraction curves with extraction time.

The analysis of the extract dissolved in methanol was performed by using a Varian 3350 gas chromatograph (3% OV101 on Chromosorb packed column, a thermal conductivity detector, and N_2 as the carrier gas).

RESULTS AND DISCUSSION

Effect of Pressure

Figure 2 shows the effect of pressure on the cumulative amount of carvone and limonene with extraction time at 39°C. It is likely that an increase of the dissolving power of CO_2 which resulted from a density increase of CO_2 at higher pressure increased the extraction at higher pressure.

The extraction rate in the initial period was probably higher in comparison with that in the latter period due to the relatively easy extraction of accessible solute from the leaf matrices in the initial period. In other words, the extraction rate decreased with time since relatively inaccessible solute inside the particles needed to be extracted as extraction time passed.

The extraction at 1500 psi resulted in the coextraction of waxy materials and green pigments along with the essential oil components. Due to the higher dissolving power of SC-CO_2 at a higher extraction pressure, such less soluble substances could be coextracted. Similar results were reported by others (8–10).

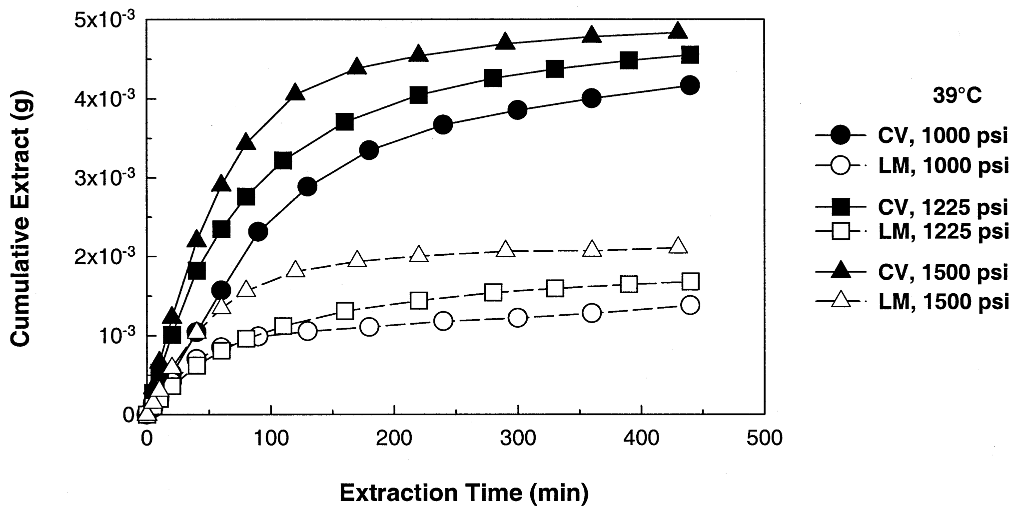

FIG. 2 Effect of pressure on the extraction of carvone (CV) and limonene (LM) from spearmint leaves at 39°C. The CO_2 flow rates were 196, 195, and 192 mL/min at STP for 1000, 1225, and 1500 psi, respectively.

Effect of Temperature

To find the effect of extraction temperature, extraction was carried out at 39 and 49°C. As can be seen in Fig. 3, the total extraction rates of carvone and limonene were higher at 39°C than at 49°C. Due to a higher density of SC-CO_2 at the lower temperature, the rapid extraction at a lower temperature

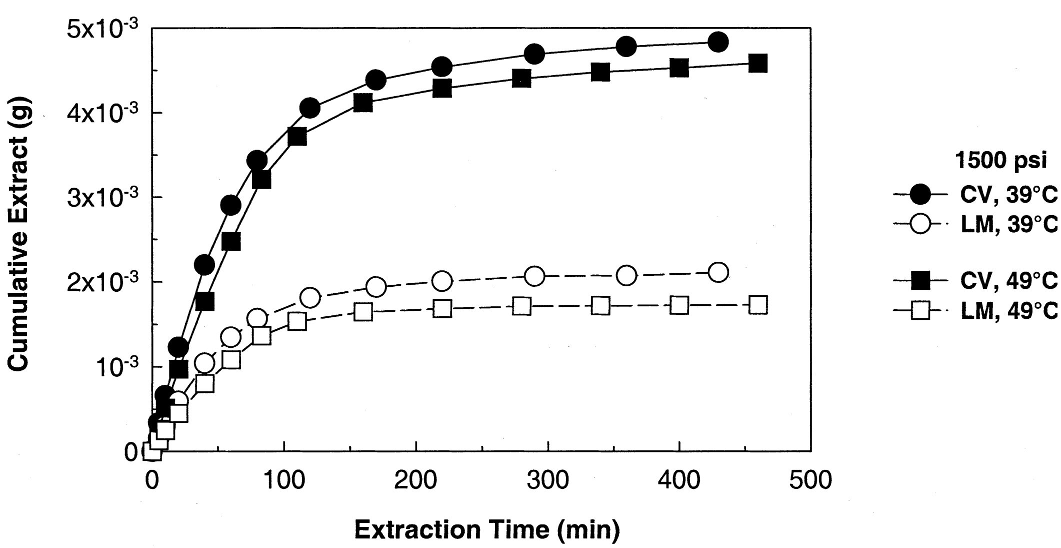

FIG. 3 Effect of temperature on the extraction of carvone (CV) and limonene (LM) from spearmint leaves at 1500 psi. The CO_2 flow rates were 192 and 198 mL/min at STP for 39 and 49°C, respectively.

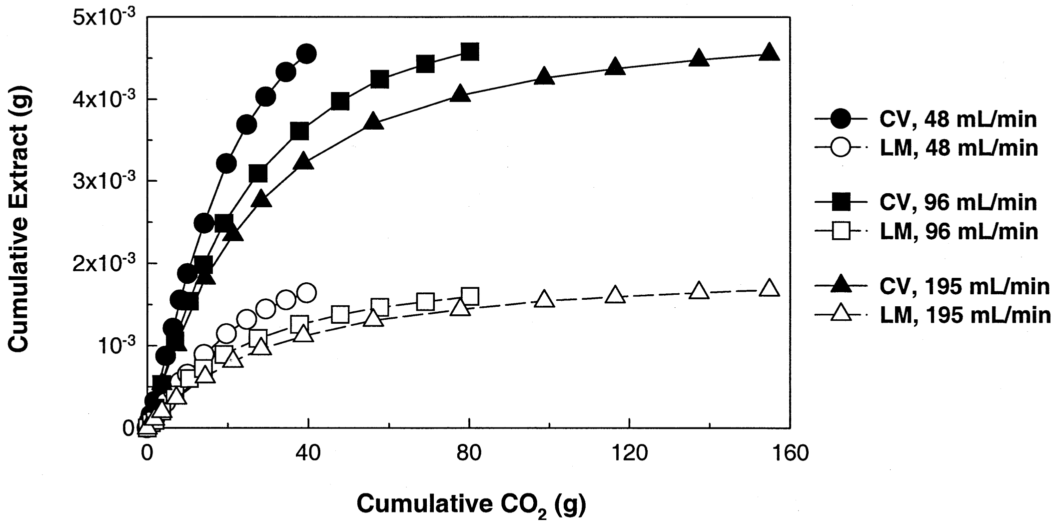

FIG. 4 Effect of CO_2 flow rate on the extraction of carvone (CV) and limonene (LM) from spearmint leaves at 39°C and 1225 psi. The volumetric CO_2 flow rates were measured at STP.

could be caused by a higher solubility of the oil components in SC-CO_2 at a lower temperature.

Effect of CO_2 Flow Rate

Figure 4 shows the effect of performing extraction at different flow rates. The cumulative masses of carvone and limonene were highly dependent on the CO_2 flow rate. The initial extraction rates were higher with faster exiting CO_2 flow rates. It appears that in the initial period the solvent efficiency (defined by the ratio of cumulative mass of extracted oil to cumulative mass of passed CO_2) decreased with an increase in CO_2 flow rate. That is to say, the extended contact time of CO_2 with spearmint leaf particles for the lower flow rate resulted in higher solvent efficiency. This fact indicates that the internal mass transfer resistance was more significant than the external mass transfer resistance in essential oil extraction from spearmint leaves.

Effect of Leaf-Particle Size

As shown in Fig. 5, there exists a significant difference between the initial extraction rates of two different particle-size leaf samples. The initial extraction rate of carvone was higher with ground leaves having an average radius of 0.03 mm than with cut leaves having an average radius of 0.15 mm. It is likely that a shorter traveling path for the smaller particle size caused faster extraction of carvone in the initial period. This explanation supports the results from the effect of the CO_2 flow rate which showed that internal mass transfer is more important than external mass transfer.

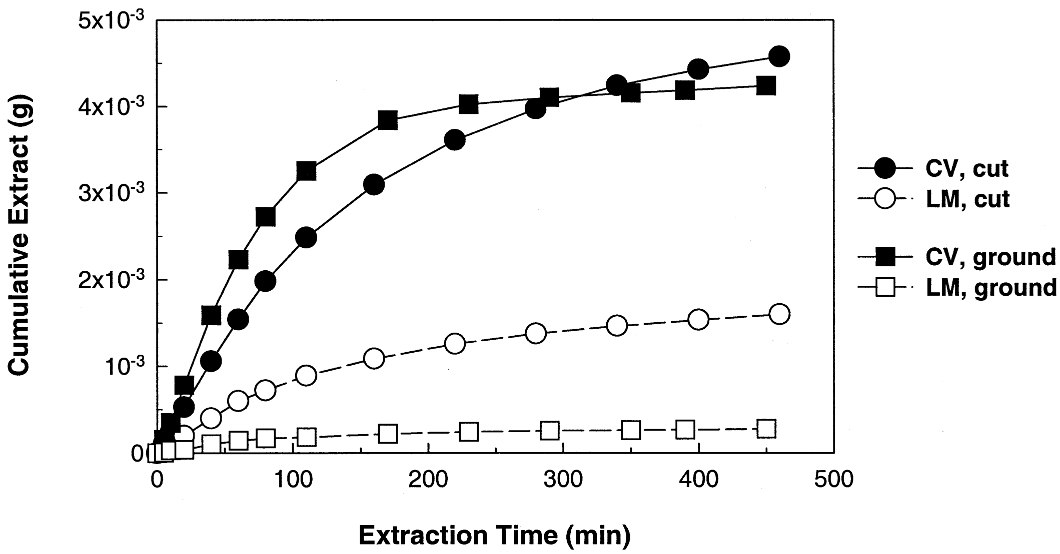

FIG. 5 Effect of leaf-particle size on the extraction of carvone (CV) and limonene (LM) from spearmint leaves at 39°C and 1225 psi. The CO_2 flow rates were 96 and 94 mL/min at STP for the cut and dried leaves, respectively.

Interestingly, the final yield of limonene from the ground leaves was lower than what was achieved from cut leaves. This may have been caused by the loss of limonene during the grinding process as discussed by Goto et al. (9) concerning the grinding of peppermint leaves. The final yield of carvone from

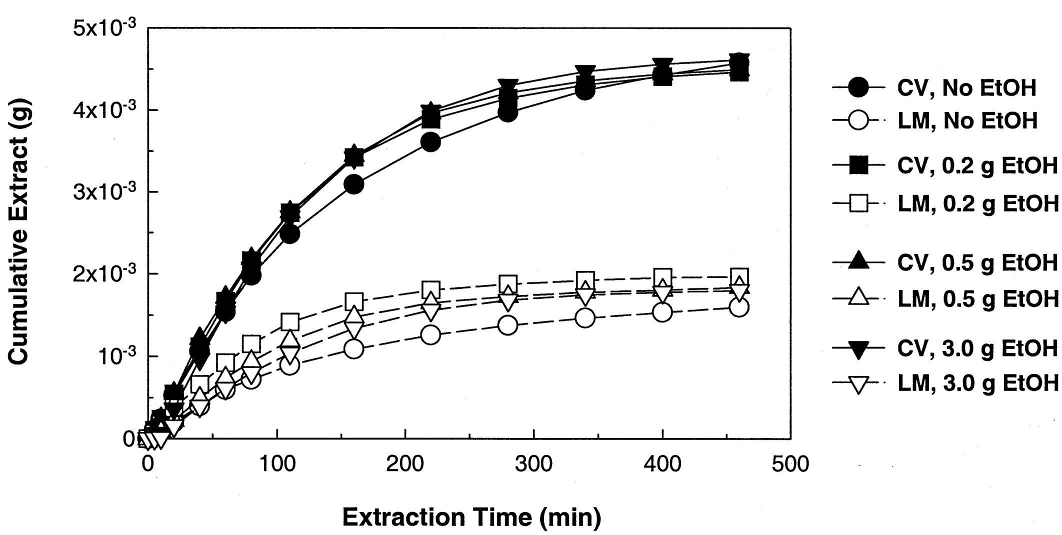

FIG. 6 Effect of ethanol modifier on the extraction of carvone (CV) and limonene (LM) from spearmint leaves at 39°C and 1225 psi. The CO_2 flow rates were 96, 97, 96, and 96 mL/min at STP for 0.0, 0.2, 0.5, and 3.0 g ethanol modifier, respectively.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

the ground samples was slightly lower than that from the cut ones, and this may also be due to loss during the grinding process.

Effect of Ethanol Modifier

Since carvone contains a carbonyl group and limonene does not, ethanol was used as a modifier to enhance the extraction of carvone rather than limonene based on polarity. Figure 6 displays the effect of ethanol modifier added to the spearmint leaves prior to extraction. The ethanol modifier did not significantly affect the extraction rate of carvone. Instead, large amounts of undesirable green pigments and waxy materials were extracted when either 0.5 or 3.0 g of ethanol were added. A similar disadvantage from using a modifier has been reported by Cocero and Calvo (11).

CONCLUSIONS

The essential oil components carvone and limonene were extracted from spearmint leaves by using SC-CO_2. Higher extraction rates were observed at higher pressures and lower temperatures. Higher extraction rates were obtained at higher CO_2 flow rates, but the SC-CO_2 solvent efficiency was lower in the initial period. The initial extraction rate from small particle-size leaves was higher than that from large particle-size leaves. The addition of ethanol did not result in any preferential extraction of carvone to limonene.

ACKNOWLEDGMENTS

The authors acknowledge the grant support of the University of California Energy Institute and the Monsanto Co. K.H.K. acknowledges the scholarship support of the Ministry of Education, South Korea.

REFERENCES

1. J. F. Brennecke and C. A. Eckert, "Phase Equilibria for Supercritical Fluid Process Design," *AIChE J.*, *35*, 1409–1427 (1989).
2. K. Bauer, D. Garbe, and H. Surburg, *Common Fragrance and Flavor Materials*, 2nd ed., VCH, Weinheim, 1990.
3. R. Croteau, F. Karp, K. C. Wagschal, D. M. Satterwhite, D. C. Hyatt, and C. B. Skotland, "Biochemical Characterization of a Spearmint Mutant That Resembles Peppermint in Monoterpene Content," *Plant Physiol.*, *96*, 744–752 (1991).
4. G. Fenaroli, *CRC Fenaroli's of Handbook of Flavor Ingredients*, Chemical Rubber Co., Cleveland, OH, 1970.
5. S. Kokkini, R. Karousou, and T. Lanaras, "Essential Oils of Spearmint (carvone-rich) Plants from the Island of Crete (Greece)," *Biochem. Syst. Ecol.*, *23*, 425–430 (1995).
6. P. Barton, R. E. Hughes Jr., and M. M. Hussein, "Supercritical Carbon Dioxide Extraction of Peppermint and Spearmint," *J. Supercrit. Fluids*, *5*, 157–162 (1992).

7. E. O. Ozer, S. Platin, U. Akman, and O. Hortacsu, "Supercritical Carbon Dioxide Extraction of Spearmint Oil from Mint-Plant Leaves," *Can. J. Chem. Eng.*, *74*, 920–928 (1996).
8. E. Reverchon, "Fractional Separation of SCF Extracts from Marjoram Leaves: Mass Transfer and Optimization," *J. Supercrit. Fluids*, *5*, 256–261 (1992).
9. M. Goto, M. Sato, and T. Hirose, "Extraction of Peppermint Oil by Supercritical Carbon Dioxide," *J. Chem. Eng. Jpn.*, *26*, 401–407 (1993).
10. B. C. Roy, M. Goto, A. Kodama, and T. Hirose, "Supercritical CO_2 Extraction of Essential Oils and Cuticular Waxes from Peppermint Leaves," *J. Chem. Tech. Biotechnol.*, *67*, 21–26 (1996).
11. M. J. Cocero and L. Calvo, "Supercritical Fluid Extraction of Sunflower Seed Oil with CO_2–Ethanol Mixtures," *J. Am. Oil Chem. Soc.*, *73*, 1573–1578 (1996).

Received by editor October 23, 1998
Revision received May 1999