

Supercritical Carbon Dioxide Extraction of Turmeric (*Curcuma longa*)

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Turmeric oil was extracted from turmeric (*Curcuma longa*) with supercritical carbon dioxide in a semicontinuous-flow extractor. Extraction rate was measured as a function of pressure, temperature, flow rate, and particle size. The extraction rate increased with an increase in CO₂ flow rate and with a reduction of particle size. The effect of pressure and temperature on turmeric extraction suggested the use of higher pressure and lower temperature at which solvent density is greater and thus the solubility of the oil in the solvent is greater in the range of 313–333 K and 20–40 MPa. The major components (~60%) of the extracted oil were identified as turmerone and *ar*-turmerone by GC-MS.

Keywords: *Supercritical fluid extraction; carbon dioxide; turmeric; GC-MS; turmerone; ar-turmerone*

INTRODUCTION

The rhizomes of the plant *Curcuma longa* (turmeric), a tropical herb of the Zingiberaceae family native to southern Asia, have a traditionally important role as a coloring component and are widely used a spice and a common food and beverage additive (Govindarajan, 1980; Salzer et al., 1975). Turmeric and its oleoresin are commercial products produced in large quantities of ~166000 tons per year (Govindarajan, 1980; Furia and Bellanca, 1975). The dried rhizomes of *C. longa* have been reported to contain 3–5% essential oil and 0.02–2.0% aromatic yellow curcuminoids. Many of its components have reputed medicinal properties that have been substantiated. For example, pharmacological studies have demonstrated that the extracts and fractions from turmeric used in traditional medicine possess anti-inflammatory, antifungal, and antitumor activities (Yamamoto et al., 1997; Apisariyakul et al., 1995; Ruby et al., 1995). *ar*-Turmerone [(*S*)-2-methyl-6-(4-methylphenyl)-2-hepten-4-one] is the major sesquiterpene found in turmeric volatile oil and has potential as an antivenom agent. It has been shown that *ar*-turmerone neutralizes both the hemorrhagic activity present in *Bothrops jararaca* venom and the lethal effect of *Crotalus durissus terrificus* venom in mice (Ferreira et al., 1992). Considering the potential of isolating specific bioactive compounds from *C. longa*, we have conducted a preliminary study on the extraction of active components from its rhizome.

Extraction of turmeric is usually accomplished by using organic solvents such as ethanol (Taylor and McDowell, 1989; International Standard ISO 5566, 1982), acetone, or methanol (Smith and Witoska, 1984) and gives turmeric oleoresin components, which consist of both flavor and color principles. The essential oil when extracted with liquid solvents lacks a strong aroma due to the loss of volatile compounds during the

evaporation process of the solvents. Furthermore, the alcohol extraction of the flavors was found to produce artifacts by esterification, etherification, and/or acetal formation. Complete removal of the residual solvent is one of the main criteria used to assess alternative methods of extraction.

Supercritical fluid extraction (SFE) is an attractive alternative to conventional liquid extraction due to its use of environmentally compatible fluids, reduced solvent consumption, oxygen-free extraction environment, and shorter extraction times. SFE performed in multiple steps by increasing the SCF density and a multistage separation technique gives superior quality products compared with those obtained by the use of the traditional techniques. Carbon dioxide has several advantages, such as its nontoxicity, nonflammability, lack of chemical residue problem, and low critical temperature (31.2 °C), over other solvents used for SFE. Thus, CO₂ is the most widely used solvent in SFE. Various applications have been implemented on an industrial scale, for example, coffee and tea decaffeination, recovery of aromas from fruits, meat, fish, etc., extraction of hop resins, extraction of spices, and reduction of nicotine in tobacco.

A process for the extraction and separation of curcumin from turmeric using SFE and supercritical fluid chromatography has been reported (Sangi et al., 1993). The literature lacks precise information on the extraction of essential oil from turmeric by supercritical carbon dioxide. Therefore, the aim of the present work was to examine the effect of extraction conditions (flow rate, pressure, and temperature) and particle size on the yield and composition of the turmeric oil and to evaluate the possibility of the SC-CO₂ extraction of sesquiterpenes. The composition of the oil extracted by this means was compared with that of a steam-distilled oil.

MATERIALS AND METHODS

Materials. The turmeric was obtained from a commercial source. It was ground before extraction by a coffee grinder, in 20 s time. This sample was packaged in a polyethylene bag and stored at room temperature.

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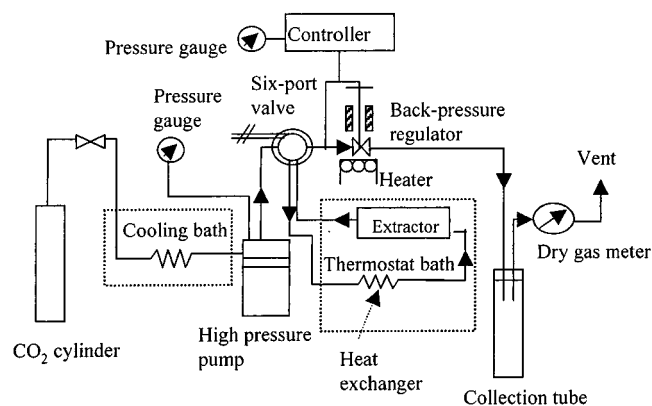


Figure 1. Schematic representation of the SFE apparatus.

Experimental Apparatus and Procedure. A schematic flow diagram of the extraction apparatus is shown in Figure 1. Turmeric oil was extracted with supercritical carbon dioxide in a semicontinuous-flow extractor. Liquid carbon dioxide from a cylinder with a siphon attachment was passed through a cooling bath (~ 273 K) and was then compressed to the operating pressure by an HPLC pump (Jasco, PU-980). Compressed carbon dioxide flowed into the extraction vessel of 50 mm length and 20 mm i.d. containing turmeric samples of 9 g. The extraction column containing the raw material to be extracted was in a thermostatically controlled water bath, the temperature inside the extractor being controlled by a digital controller within an accuracy of ± 0.1 K. After the pressure and fluid flow rate reached the desired values, the six-port valve was turned on so that carbon dioxide was passed through the extractor to start the extraction. At the beginning of a run, the highest flow rate of CO_2 ($10 \text{ cm}^3 \text{ min}^{-1}$ at the pump) was maintained until the operating pressure was reached and then immediately changed to the operating flow rate. The exit fluid from the extractor was expanded to ambient pressure by a back-pressure regulator.

The extract was fractionated into six or seven fractions for each run at definite time intervals and weighed gravimetrically to obtain the extraction curves. The effect of flow rate was studied at 40°C and 40 MPa . The flow rates of CO_2 employed were $(3.5\text{--}8.6) \times 10^{-5} \text{ kg s}^{-1}$. The volume of CO_2 consumed was measured using a wet gas meter. The three different pressures employed at 313 K were 20, 30, and 40 MPa . The solubilities of oil were calculated as the initial slope of the weight of collected samples versus the eluted volume of carbon dioxide.

Gas Chromatography—Mass Spectrometry (GC-MS)

Analysis. Extracts were analyzed using a GC-MS (Hewlett-Packard 5890 series) coupled with a mass selective detector (HP 5972). The sample extracts were injected (injection temperature = 270°C) onto a high-resolution HP-5 gas chromatographic column (dimensions: 30 m, 0.25 mm i.d., film thickness = $0.25 \mu\text{m}$), which was perfused with helium and operated with a split ratio of 10. The GC conditions were as follows: oven temperature, 70°C for 5 min, then programmed from 70 to 230°C at $2^\circ \text{C min}^{-1}$, and subsequently isothermal at 230°C for 5 min. The weight compositions of the oil were computed from the GC peak areas without using any correction factors.

RESULTS AND DISCUSSION

Panels a and b of Figure 2 show the extraction curves of oil plotted as total yield versus extraction time and total yield versus amount of CO_2 used at different flow rates, respectively, for particles of 0.208 mm average diameter. The yield was defined as the weight extracted divided by the weight of the original. The extraction rate was increased with an increase in flow rate of CO_2 as shown in Figure 2a. The extraction curves for different flow rates almost coincide in the plot against the amount

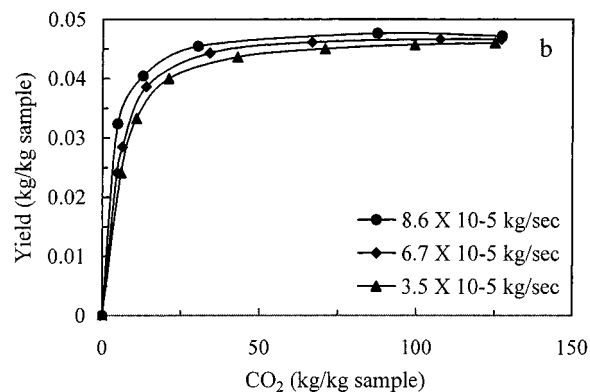
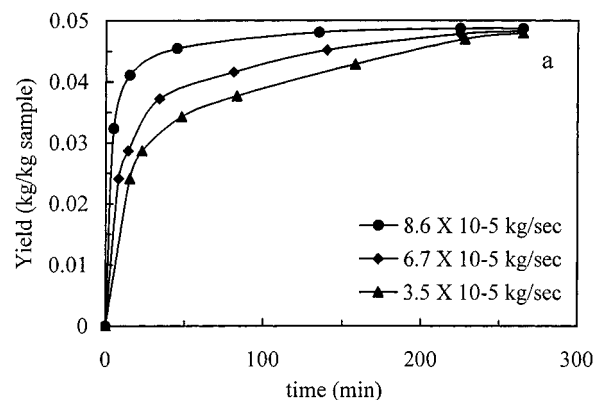


Figure 2. Effects of flow rate on the extraction yield of turmeric oil at 313 K and 30 MPa : (a) yield versus time; (b) yield versus CO_2 flow rate on extraction curves.

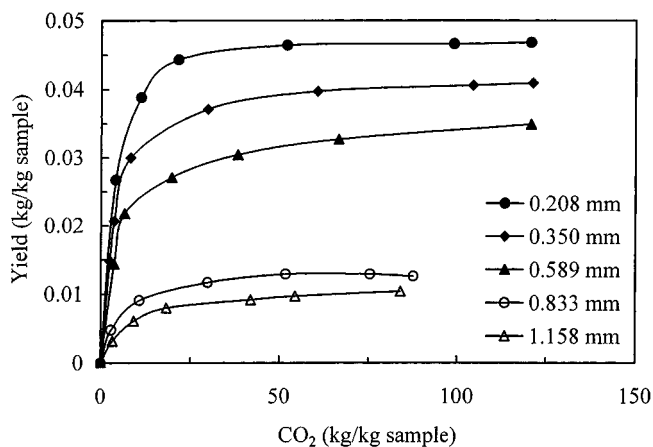


Figure 3. Effect of particle size on the extraction yield at 313 K and 30 MPa .

of carbon dioxide as shown in Figure 2b, which indicates the extraction curves should agree for different flow rates if equilibrium was established or dissolved solute in CO_2 phase was saturated without any mass transfer resistance.

The influences of particle size were analyzed for the essential oil extraction curves. Figure 3 shows essential oil extraction curves obtained for five different particle sizes at a constant solvent flow rate of 3 mL/min . In this figure, one can see that the extracting rate decreased when particle size increased because the intra-particle diffusion resistance is smaller for smaller particle size due to the shorter diffusion path. The grinding process increases the surface area and may disrupt the cell walls, reducing mass transfer resistance and leaving the essential oil more accessible to the

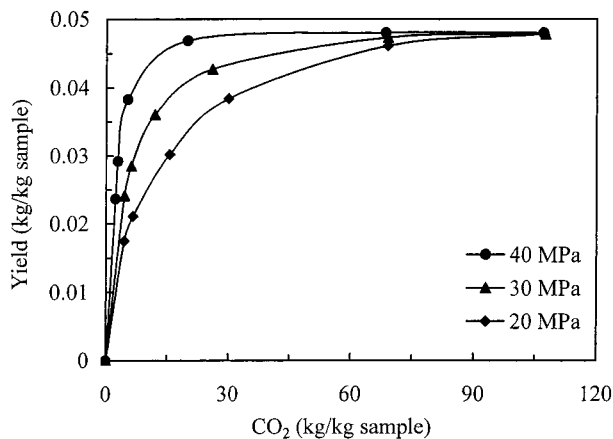


Figure 4. Effect of pressure on the yield of turmeric oil at 313 K.

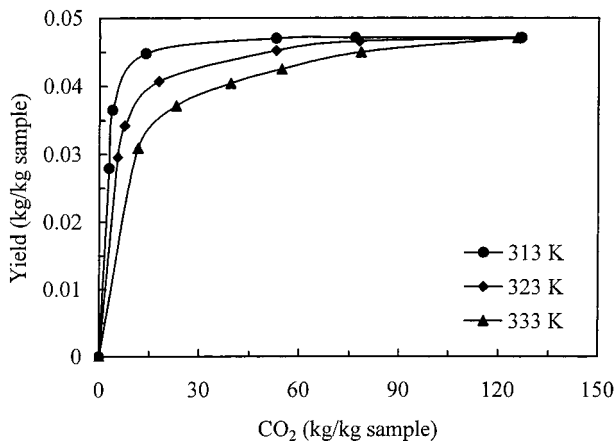


Figure 5. Effect of temperatures on the yield of turmeric oil at 30 MPa.

solvent and, consequently, increasing the extraction rate. An increasing amount versus particle size has already been noticed by Goto et al. (1996), who concluded that cellular structures should be broken to get a complete extraction of substances. The observed reduction in extraction yield with increasing particle size indicates that supercritical carbon dioxide is not able to reach all of the oil inside the cells, extracting only the exposed oil.

A series of exhaustive extractions was carried out at different pressures to determine the extent of extraction achieved and the amount of CO_2 required. Figure 4 shows the effect of pressure on extraction efficiency at 313 K, measured as the total amount of oil extracted. From these curves, it was apparent that the extraction rate and the yield increased markedly with pressure. As the pressure increases at constant temperature, the extraction rate was increased due to the change in solubility. It has long been known that higher pressure results in an increase in the solvent power and in the solubility of essential oil. To determine the influence of the temperature in the efficiency of extraction for turmeric oil, a study was carried out in which the temperature was varied from 313 to 333 K in 10 K intervals. Temperature had an adverse effect on the extraction rate of oil as shown in Figure 5. Experiments showed that the extraction rate decreased with an increase in temperature at 30 MPa, reflecting the reduction in density of the solvent. The extraction rate increase at higher pressure and lower temperature

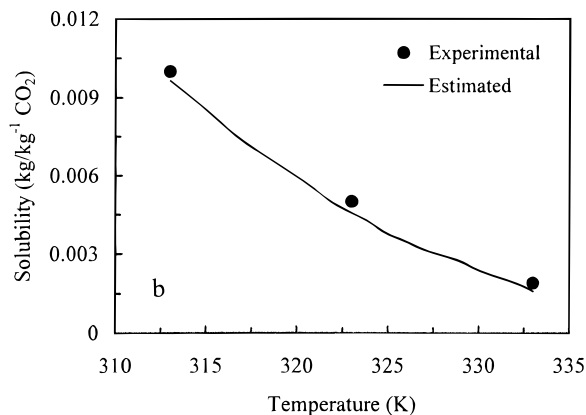
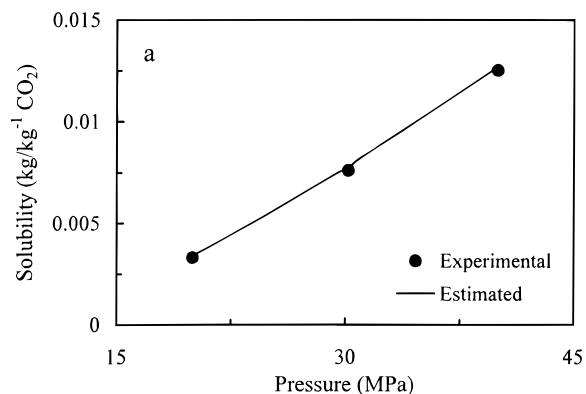


Figure 6. Solubility of turmeric oil as a function of pressure at 313 K (a) and temperature at 30 MPa (b).

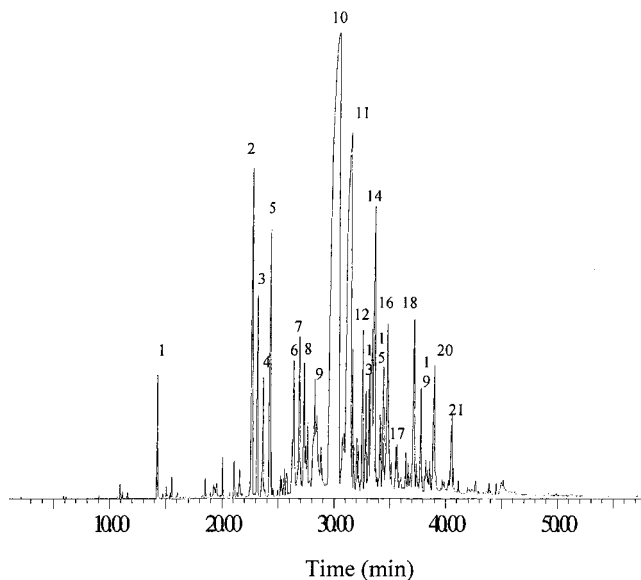


Figure 7. GC-MS profile of SCF extracted oil at 30 MPa and 313 K.

suggests the use of increased solvent density results in increased solubility of the oil in the solvent.

The initial part of the extraction curves increased linearly with a slope corresponding to the solubility of oil (kilograms per kilogram of CO_2). The solubilities of the oil, obtained from the slopes in Figures 4 and 5, are plotted as a function of pressure and temperature as shown in panels a and b of Figure 6, respectively. The solubility of oil increases significantly with pressure at 313 K but decreases as temperature increases at 30 MPa due to the increase in the density of carbon dioxide.

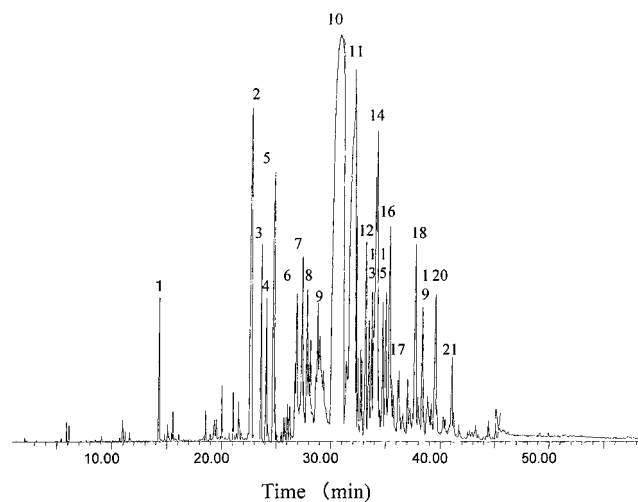


Figure 8. GC-MS profile of steam-distilled oil.

Table 1. Compositions of Oil Extracted from Turmeric at 313 K and 30 MPa and Steam-Distilled Oil

peak	component	peak area (%)	
		SFE extracted oil	steam-distilled oil
1	α -pinene	1.25	1.23
2	camphene	5.50	5.12
3	cubebene	2.16	2.43
4	<i>p</i> -cymene	1.15	0.85
5	citronellal	4.05	4.13
6	menthofuran	1.99	1.92
7	caryophyllane	1.63	1.53
8	α -bergamotene	1.40	1.45
9	borneol	1.08	1.10
10	<i>ar</i> -turmerone	42.00	41.05
11	turmerone	16.12	16.43
12	α -terpineol	0.96	1.05
13	carvone	2.12	1.96
14	linalool	1.01	1.12
15	germacrene D	1.02	0.96
16	β -sesquiphellandrene	3.17	2.96
17	α -curcumene	4.23	4.10
18	nerol	1.53	1.32
19	phellandrol	1.84	1.75
20	citronellyl pentanoate	2.94	2.94
21	xanthorrhizol	1.14	0.85

This initial turmeric oil solubility was observed to follow a pattern similar to that found for the solubility of soybean oil in supercritical carbon dioxide (Stahl and Quirin, 1983). The following equation has been proposed (Del Valle and Aguilera, 1988) to predict the solubility of vegetable oil in supercritical carbon dioxide:

$$Cr = [\exp(40.361 - 18708/T + 2186840/T^2) \times (0.001\rho)^{10.724} \pm 2.7]/\rho \quad (1)$$

Cr is the solubility (kg/kg of CO₂), *T* is the temperature (K), and ρ is the density (kg·m⁻³) of CO₂. The solid lines in Figure 6a,b indicate the solubility of oil estimated from eq 1. The experimental solubilities obtained from the slope of the extraction curves are in good agreement with the estimated solubilities.

The carbon dioxide extracted turmeric oil at 30 MPa/313 K and steam-distilled oil were analyzed using GC-MS. The GC traces are shown in Figures 7 and 8, respectively, with compound identifications reported in Table 1. Sesquiterpene hydrocarbons, *ar*-turmerone and turmerone (Figure 9), represented 60% of the turmeric

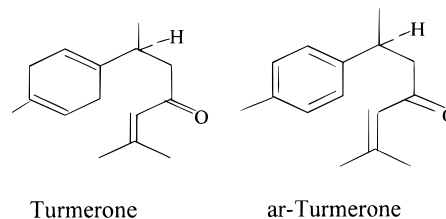


Figure 9. Structures of turmerone and *ar*-turmerone.

oil composition, which is reported to be a potent anti-venom against snakebite (Ferreira et al., 1992). No significant differences in the relative composition of the resulting turmeric extracts could be observed with extraction time as a factor. The total yield of turmeric oil obtained by steam distillation was 5.5%. The composition of steam-distilled oil was similar to that of SC-CO₂ extracted oil, as compared in Table 1.

In conclusion, the experimental results indicated that the oil fraction of turmeric could be efficiently extracted by SFE.

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