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Extraction of Lycopene from Tomato Skin with Supercritical Carbon Dioxide: Effect of Operating Conditions and Solubility Analysis

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Supercritical carbon dioxide ($SCCO_2$) extraction of lycopene from waste tomato skins was investigated. The experiments were carried out at pressures and temperatures ranging from 20 to 50 MPa and 313 to 373 K, respectively, without any modifiers. The flow rate of CO_2 was maintained at 2.5 mL/min for 330 min extraction time. Solvent flow rate effect was examined for CO_2 flow rates from 1.5 to 4.5 mL/min. The extracts were analyzed by high-performance liquid chromatography and UV−visible spectroscopy. The results showed that with optimized operating conditions, the maximum yield of lycopene (1.18 mg of lycopene/g of sample) was obtained at 40 MPa, 373 K, and 2.5 mL of CO_2/min. Chromatographic analysis indicated that lycopene was extracted from tomato skin with negligible degradation at the optimum conditions and the amount extracted represented more than 94% of the total carotenoid content of the sample. The solubility of lycopene was modeled by use of the Chrastil equation.

KEYWORDS: Lycopene; supercritical CO_2 extraction; solubility; tomato skin; HPLC

INTRODUCTION

Lycopene ($C_{40}H_{56}$), an open-chain hydrocarbon with 11 conjugated double bonds, has the highest degree of unsaturation among carotenoids and is the pigment principally responsible for the characteristic deep-red color of ripe tomato fruits and tomato products (**Figure 1**). It has attracted attention due to its biological and physicochemical properties, particularly in relation to its effects as a natural antioxidant. Although it has no provitamin A activity, lycopene does exhibit a physical quenching rate constant for singlet oxygen almost twice as high as that of β-carotene. This makes its presence in the diet of considerable interest. Increasing clinical evidence supports the role of lycopene as a micronutrient with important health benefits, because it appears to provide protection against a broad range of epithelial cancers (*1*, *2*). However, the human body cannot produce this module and needs to obtain it from foods such as apricots, pink grapefruit, guava, watermelon, and, mainly, tomatoes and tomato products (*3*). Lycopene in fresh tomato fruits occurs essentially in the all-trans configuration. However, undesirable degradation is unavoidable owing to isomerization of *trans*-lycopene to the cis form induced by thermal processing and oxidation during processing (*1*). This results in some loss of color and biological activities. Oxidative degradation, the principal cause of extensive losses of carotenoids, depends on the availability of oxygen and is stimulated by light, enzymes, some metal ions, and co-oxidation with lipid hydroperoxides. Conditions necessary for isomerization and oxidation of carotenoids exist during preparation, processing, and storage of food. Carotenoids are also subject to isomerization and oxidation during analysis, and preventative measures must be taken to guarantee the reliability of analytical results (*4*).

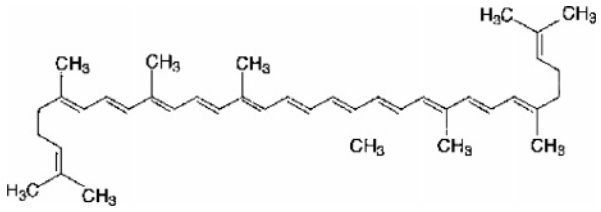

Figure 1. Structure of lycopene.

Tomatoes are an integral part of diets worldwide, and millions of tons of tomatoes are processed annually to manufacture products such as ketchup and sauces (*5*). During tomato processing (fresh tomatoes), almost 40% of the raw material is removed as waste, including the skin, pulp, and seeds. The concentration of lycopene in tomato varies from 30 to 200 mg/kg in the fresh fruit and from 430 to 2950 mg/kg on a dry basis and represents more than 85% of the total carotenoid content (*6*). The skin can contain about 5 times more lycopene than

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tomato pulp (*7*). Hence, utilizing waste tomato skins would not only save money in transport and waste disposal but increase product range and quality. Since lycopene is highly soluble in organic solvents, it is extracted with organic solvents, which are usually toxic, expensive, and hazardous to handle and may remain in the product. Consumer concern about health and environment has resulted in increasing interest in clean technologies and alternative and reliable extraction methods for lycopene and other carotenoids (*8*, *9*).

Supercritical fluid extraction (SFE) with carbon dioxide as a solvent has provided an excellent alternative to the use of chemical solvents. During the extraction processes, CO_2 behaves similarly to a liquid, penetrating the tomato skin to dissolve lycopene. As a gas, carbon dioxide can penetrate the skin of a tomato but is too light to adhere to lycopene and carry it away; as a supercritical fluid, it is denser and has the ability to successfully relocate lycopene. This process also reduces the time needed for the extraction and concentration of organic compounds. Supercritical fluids have solvent strengths approaching those of liquid solvents. The solvent strength of a supercritical fluid, which is directly related to its density, can be tuned by changing the extraction pressure and temperature. The utilization of supercritical carbon dioxide ($SCCO_2$) for extraction of various carotenoids from a number of matrices, including tomatoes, has been studied by several authors (*6*, *8*, *10*−*18*). However, $SCCO_2$ technology has been applied only for the recovery of carotenoids from tomato wastes at lower operating conditions: temperature and pressure and use of organic solvents as modifier, leaving out the purity of lycopene. Most lycopene extracted for nutritional supplements was not pure enough for scientists. Recently, Rozzi et al. (*11*) have examined the effects of temperature, pressure, flow rate, and CO_2 volume on SFE of lycopene from a byproduct of tomato processing, which includes tomato skins and seeds. It was shown that both temperature and pressure had an effect on the extraction of lycopene and that an optimum temperature and pressure combination, 359 K and 34.47 MPa, resulted in extraction of 61.0% of the lycopene. Gomez-Prieto et al. (*12*) investigated the possibility of using SFE to obtain the most stable isomer (all-trans form) of lycopene by maintaining the temperature at 313 K, which should preclude the risk of oxidative degradation. They observed that the amount of the trans form extracted rises (and the cis form content decreases) if the extraction pressure becomes greater due to the consequent increase of the $SCCO_2$ density. Sabio et al. (*8*) studied $SCCO_2$ extraction of lycopene and β-carotene from tomato skins and mixtures of skin and seeds at lower pressures of 25 and 30 MPa and temperatures of 333 and 353 K. The results indicated that, at the lower flow rate studied and extraction conditions of up to 30 MPa and 353 K, it was possible to extract only 80% of the total lycopene content and 88% of β-carotene from tomato skin. Other than this, the scientific literature offers a lack of information about the solubility of lycopene. Gomez-Prieto et al. (*19*) determined the solubility in $SCCO_2$ of *cis*-lycopene and *all-trans*-lycopene of tomato skin for CO_2 densities between 400 and 800 g/L with extraction vessel temperatures of 313, 323, and 333 K and corroborated this using the Chrastil model.

So far, much research have been done on lycopene extraction from tomato products but the feasibility of a few of them was compared to actually performed processes. Industrially, the separation of components from, for example, solid materials by means of a supercritical fluid as a solvent under high pressure is troublesome and requires high capital costs for high-pressure extraction equipment. Nevertheless, operating costs can be minimized by optimization of operating conditions of lycopene extraction. Nowadays, commercial plants prefer high-pressure $SCCO_2$ extractions for natural materials to achieve their desired products considering the economical aspects. With respect to this, we report here our first results on the recovery of lycopene from tomato skin by optimization of the SFE process and a solubility study of lycopene in $SCCO_2$. The purpose of this work was to obtain the best extraction conditions by assessing the influence of pressure and temperature at higher levels and CO_2 volume on SFE of lycopene from waste tomato skins without any modifier. The results of SFE extraction were also compared with results obtained by traditional solid−liquid extraction. The Chrastil model was used to state a solubility equation for lycopene, and the parameters were compared with those reported in the literature.

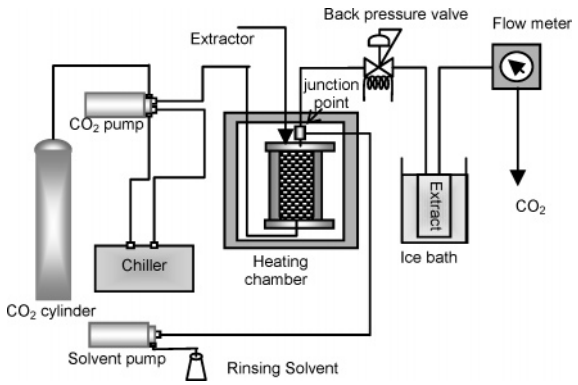

Figure 2. Diagram of the supercritical fluid extraction apparatus.

MATERIALS AND METHODS

Materials. Dried tomato skins used in this study were supplied by Kagome Co., Ltd. (Japan). They were stored at 253 K until used and did not undergo any further pretreatment. CO_2 was acquired from Uchimura Sanso with a purity of 99.9%. HPLC-grade solvents, including methanol and tetrahydrofuran (THF), were purchased from Wako Chemicals (Japan).

Extraction. Extraction with $SCCO_2$ was performed with the apparatus shown in **Figure 2**. Liquid CO_2 flowing from the cylinder into the extraction vessel (10 mL vessel, Thar Designs, Inc.) was compressed and controlled with a HPLC pump [PU-2080-100 MPa, 5 mL/min, SSQD (slow suction, and quick delivery) pumping system is ideal to ensure the most reliable and pulse free solvent flow, Jasco Co., Japan] which was cooled with a chiller (Sibata Co., Japan) to keep CO_2 in a liquid state. After reaching the extractor, CO_2 was transformed into a supercritical state by a heating chamber (Tabai Espec Co., Japan) that envelops the extractor. Operating pressure was controlled by a back-pressure regulator (max 60 MPa, Akico Co., Ltd., Japan). The supercritical CO_2 flowing through the fixed bed in the extraction vessel was expanded into a collection tube immersed in an ice bath, where the extracted lycopene and the CO_2 solvent were easily separated. The amount of CO_2 consumed during the extraction period was determined by use of a wet gas meter (Sinagawa Co., Tokyo, Japan).

Supercritical CO_2 extraction was conducted on samples of different volumes. Tomato skins were ground immediately prior to extraction and the total volume of the vessel was well filled with tomato skins and glass beads as the fixed bed formation. It was found that smaller particles of tomato skin resulted in improved recovery of lycopene. Filters were placed at the top and bottom of the vessel to provide a continuous flow of CO_2. To minimize the decomposition and oxidation of extracted compounds, all samples were protected from the actions of light and oxygen in the air by use of aluminum foil. THF was used for washing the system after extraction at the connection point illustrated in **Figure 2** in order to square with the solvent injected into the HPLC column and mobile phase used in the analysis.

Analysis. The total amount of extractable *trans*-lycopene and β-carotene was determined after three 12-h extractions with chloroform

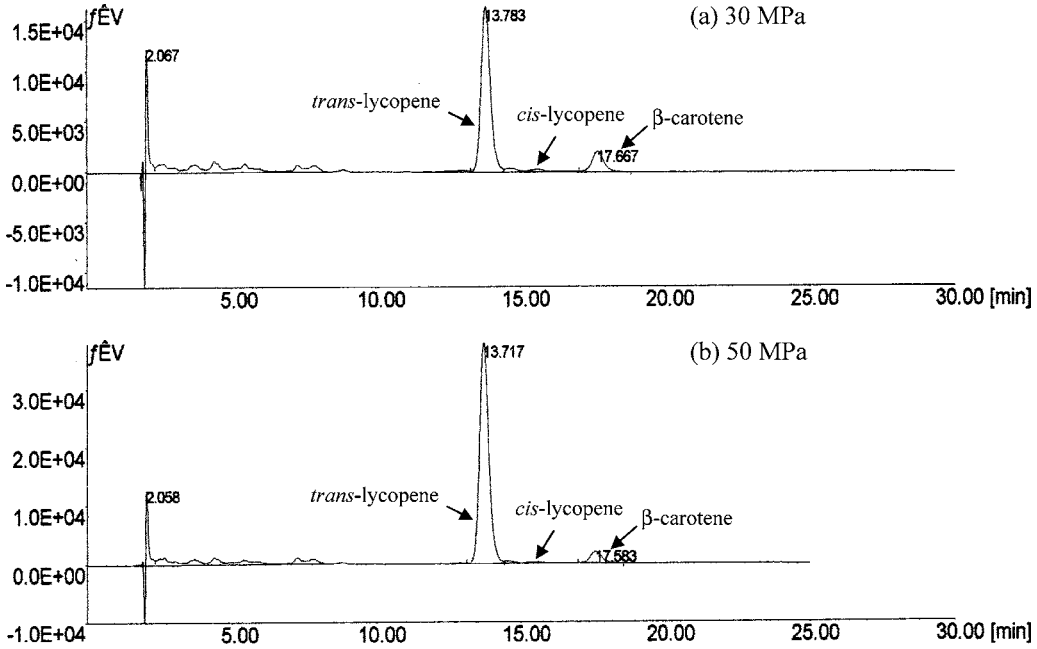

Figure 3. HPLC analyses of the extracts at (**a**) 30 and (**b**) 50 MPa, constant temperature of 353 K and CO_2 flow of 2.5 mL/min after 30 min extraction time.

in a Soxhlet extractor. Similar to $SCCO_2$ extraction, the Soxhlet extractor was covered with aluminum foil to prevent oxidation and degradation of the valuable carotenoids. The amount of lycopene was determined in an HPLC apparatus equipped with a UV−visible detector (UV-970, Jasco, Japan) and a column (STR ODS-II 10 L × 4.6 (S), 250 mm, Shinwa Chemical Ind., Ltd.). A mixture of methanol and THF in a 90:10 ratio was used as the mobile phase, with a flow rate of 1.5 mL/min (6 μL injection volume) and a column temperature of 303 K, supplied by a column heater (Sugai U-620, Japan) in 25 min detection time; detection was set at 470 nm for lycopene and 450 nm for β-carotene, which are previously known absorbance values (*21*). The peaks of *trans*-lycopene and β-carotene were identified by comparing the retention times (13.85 and 17.9 min, respectively) with those of standard compounds. To calculate the concentrations of lycopene and β-carotene in the extract, a calibration curve was drawn for each from five solutions of known concentration in THF.

In this study, scanning electron microscopy (SEM) was also employed to characterize any changes in the surface morphology of the tomato skins as a result of the $SCCO_2$ extraction applied such as the appearance of cracking or crazing of the cells.

RESULTS AND DISCUSSION

The initial lycopene content of tomato skins was found to be 1.13 mg of lycopene/g of raw material, as determined by Soxhlet extraction. β-Carotene was also detected in trace amounts: 0.046 mg of β-carotene/g of sample, which corresponds to almost 4% of the total carotenoid content. Extraction of lycopene was carried out by supplying the tomato skins with a continuous flow of $SCCO_2$. During the extraction process, the solubility of lycopene sharply decreased after expansion of $SCCO_2$ by use of the back pressure regulator so that CO_2 was no longer in the supercritical state but in the gaseous state. Therefore, rinsing solvent was used to remove all extracted lycopene from the system. To prevent a cosolvent effect, the rinsing solvent was prevented from flowing during the extraction and was used after the extraction was completed. The pipeline of solvent flow was connected to the system at the junction point as shown in **Figure 2**.

To investigate the effects of temperature, pressure (1), and CO_2 volume (2) and thus optimize the operating conditions, $SCCO_2$ extraction was carried out under the following sets of conditions: (1) temperature ranging from 343 to 373 K and pressure from 20 to 50 MPa, at a constant CO_2 flow rate of 2.5 mL/min for 330 min extraction time; (2) a CO_2 flow rate ranging from 1.5 to 4.5 mL/min at a constant temperature and pressure of 360 K and 40 MPa, respectively at the same extraction period of 330 min. **Figure 3** represents two examples of HPLC analysis of the extracts obtained at pressures of 30 MPa (**a**) and 50 MPa (**b**) at constant temperature of 353 K after 30 min extraction time. Before lycopene was detected, some small peaks corresponding to other carotenoids such as lutein (a xanthophyll), α-tocopherol, phytoene, or phytofluene appeared (*19*) where we neglected to identify each of them and focused on *trans*-lycopene under the scope of this study. In addition, although tentative assignments of *cis*-lycopene (pointed out in **Figure 3**) could not be made, isomerizations of *trans*-lycopene into cis form were hardly visible in the HPLC chromatograms obtained at higher operating conditions. Percent ratio of the relative peak areas of *cis*-lycopene to that of trans form calculated was only 1.77% at 30 MPa and 0.78% at 50 MPa where increasing the pressure decreased the amount of *cis*-lycopene and enhanced the purity of *trans*-lycopene (*12*). Larger amounts of β-carotene were detected at lower temperatures and pressures due to its solubility in $SCCO_2$ (*20*). Under all operating conditions where the details were given above, β-carotene was not observed in chromatographic analysis after a certain extraction period. SEM photos of the tomato skins were taken in order to investigate the effect of supercritical carbon dioxide on the tomato skin matrix as it penetrates the skin to extract lycopene present in crystalline form in cell chromoplasts. Representative SEM micrographs, taken at magnifications of 500× and 750× are shown in **Figure 4** (**a**) before extraction and (**b**) after extraction, respectively. The destruction of the tomato skin cells by penetration of CO_2 at supercritical conditions was clearly observed where the data might be useful elsewhere such as in modeling of the extraction.

Figures 5, **6**, and **7** illustrate the effects of pressure on extraction yields at constant temperatures of 343, 353, and 363

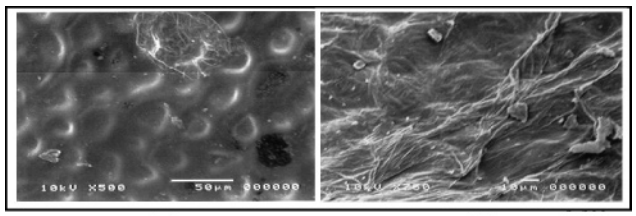

Figure 4. SEM photographs of tomato skins (**a**) before and (**b**) after extraction.

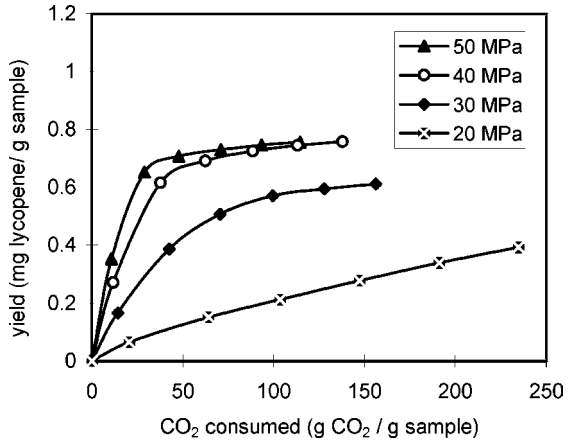

Figure 5. Yield vs CO_2 consumed at constant *T* (343 K) and a flow rate of 2.5 mL/min.

K, respectively. It can be seen that increasing the operating pressure from 20 to 40 MPa at 10 MPa intervals resulted in a gradual increase in the yield of extraction as well as in the recovery of lycopene. It is known that an increase in pressure at constant temperature enhances solvent density, and at higher densities, molecular interactions between the solvent and the solute are boosted, resulting in greater dissolution of the solute. In contrast, at a constant temperature of 343 K, an increase in pressure from 40 to 50 MPa did not improve the total amount of lycopene extracted, even though initial solubility (initial slope of the extraction curve) of 2.97×10^{-2} g/L at 50 MPa was higher than that of the solubility of 1.99×10^{-2} at 40 MPa. The reason for this may be that the increased pressure caused compacting of the sample and channeling of the CO_2 flow, resulting in the restriction of CO_2 movement in to and out of the tomato skin. Compacting or squeezing was observed in residue removed from the extraction column. Similar behavior was seen for $SCCO_2$ extraction at a constant temperature of 353 K with varying pressure, as shown in **Figure 6**.

Figure 7 illustrates the yield (milligrams of lycopene/gram of sample) versus CO_2 consumed (grams of CO_2/gram of sample) at a constant temperature of 363 K. Increasing the pressure from 40 to 50 MPa did not improve the extraction yield of lycopene, for the reason explained above. The maximum yield of 1.17 mg of lycopene/g of sample seemed to be obtained at 40 MPa and 363 K at a CO_2 flow rate of 2.5 mL/min for 5.5 h extraction time. Further, while the pressure was held constant at 40 MPa, the extraction temperature was increased up to 373 K. **Figure 8** shows the effect of temperature on the extraction yield ranging from 343 to 363 K. Usually, an isobaric increase in temperature decreases the density of the supercritical solvent and hence decreases solubility due to the density effect. However, the same increase in temperature increases the volatility of the solute, resulting in an increase in solubility due to the volatility effect. A further increase in temperature from

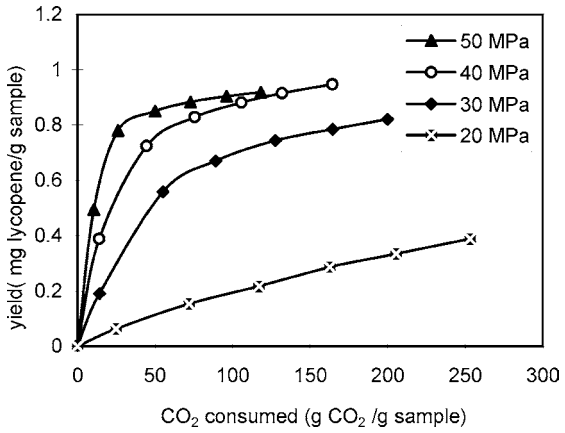

Figure 6. Yield vs CO_2 consumed at constant *T* (353 K) and a flow rate of 2.5 mL/min.

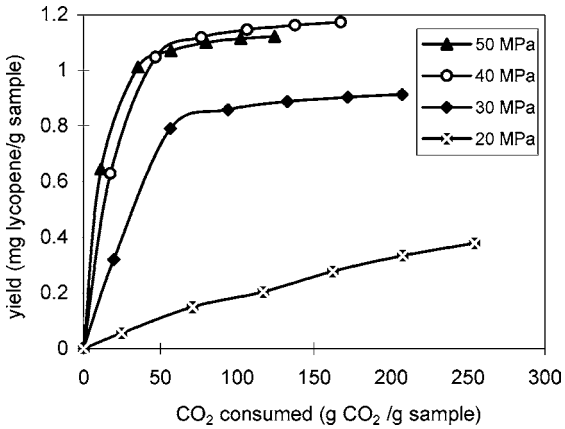

Figure 7. Yield vs CO_2 consumed at constant *T* (363 K) and a flow rate of 2.5 mL/min.

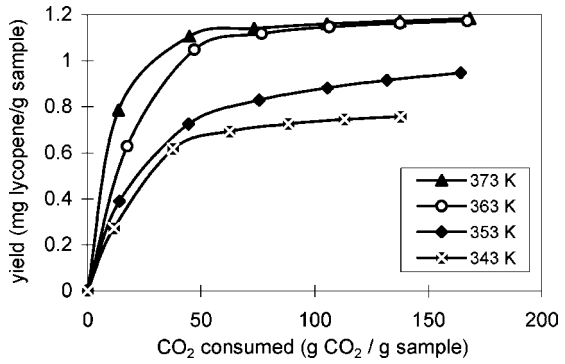

Figure 8. Yield vs CO_2 consumed time at constant *P* (40 MPa) and different temperatures at a flow rate of 2.5 mL/min.

363 to 373 K at a constant pressure of 40 MPa provided almost the same amount of lycopene (1.17 and 1.18 mg of lycopene/g of sample, respectively), as there was some degradation of lycopene at the elevated temperature. Moreover, the continuing increase in the yield of extraction that was lying on a straight line in the extraction curves (first part, solubility effective) diminished after 2 h of extraction time. It was implied that the second part of the extraction process (the curvature of the yield data, which do not lie on a straight line) can be correlated to the presence of a mass transfer resistance. A similar amount was reached in 12 h by Soxhlet extraction. By the way, calculations of $SCCO_2$ extraction efficiencies are usually based upon the solvent extraction that provides the total extractable amount. Eventually, the extracted lycopene amount (1.13 mg

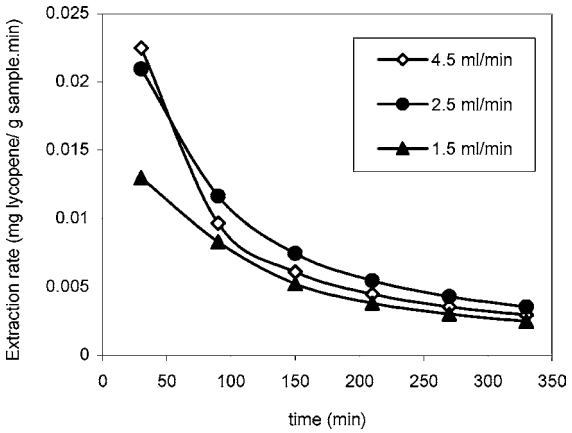

Figure 9. Extraction rate curve at $P = 40$ MPa, $T = 363$ K.

of lycopene/g of sample) in Soxhlet extraction was lower than in $SCCO_2$ extraction (1.18 mg of lycopene/g of sample obtained at 40 MPa and 373 K) where the degradation of present lycopene and other carotenoids were unavoidable.

Figure 9 shows the typical extraction rates for a low initial concentration of extract in the solid substrate, referring to the extracted lycopene amount per unit time for different flow rates ranging from 1.5 to 4.5 mL/min. Although the initial rate of extraction is higher at a greater flow rate of 4.5 mL/min, it decreased rapidly soon after the initial extraction time, compared with extraction at a flow rate of 2.5 mL/min. Such a high extraction rate is due to the solubility of the extracted material in supercritical solvent. In other words, this amount of solvent is enough to remove lycopene molecules from the tomato skin cells through the extraction vessel. Increasing the flow rate of CO_2 from 2.5 to 4.5 mL/min resulted in a decrease in the amount of lycopene extracted at later stages of extraction. One of the reasons for this may be the channeling effect, whereby the solvent is forced through the sample at such a high flow rate that it passes around the solid matrix and does not diffuse through the pores within the sample (*23*). For a CO_2 flow rate of 1.5 mL/min, although it seemed that the time of contact between solvent and sample was greater, insufficient amounts of CO_2 led to a reduction in the extraction yield. For each flow rate, a decline in the extraction rate and in the concentration of extract in the outflowing solvent was observed. This is because the amount of lycopene in the solid substrate near the solid/gas interface is depleted soon after extraction begins, and transport of lycopene to the interface from within the solid adds additional resistance. Moreover, the length of the fixed bed containing the extract is not large enough to enable maximum loading of the solvent (*22*). After a certain time, no more lycopene was recovered from the tomato skin cells even at higher flow rates.

The effect of temperature and pressure on the extraction of phytochemical compounds can be related to changes in the density of CO_2 and the vapor pressure of these compounds. At lower densities, the polarity of supercritical CO_2 is more like that of hexane, while at higher densities, it is more like that of chloroform (*22*); carotenoids display much higher solubility in chloroform compared to hexane (*11*), and it was observed that high temperatures and pressures resulted in an increase in solubility and hence the amount of lycopene extracted. As shown in **Figure 10**, the optimum extraction conditions were obtained at 40 MPa and 373 K with a CO_2 flow rate of 2.5 mL/min, providing an extraction yield of 1.18 mg of lycopene/g of sample.

Figure 11 shows the relationship between the concentration of lycopene and CO_2 density at temperatures from 343 to 363

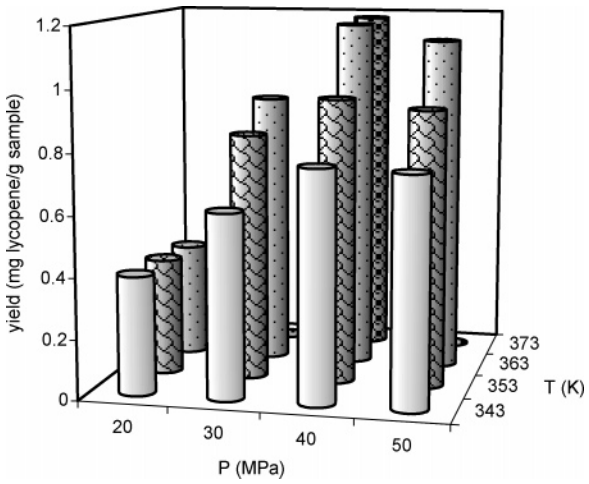

Figure 10. Yield vs pressure at constant temperatures: $T = 343$, 353, 363 K.

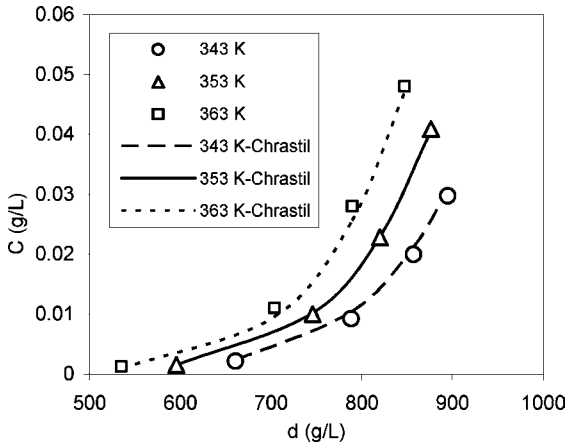

Figure 11. Comparison of experimental and correlated Chrastil solubility curves at temperatures of 343, 353, and 363 K and at a constant CO_2 flow rate of 2.5 mL/min.

K and pressures of 20−50 MPa. The concentration of lycopene in CO_2 was calculated by taking the initial slope of the extraction curve after 30 min extraction time for each set of conditions. The increase in lycopene solubility in $SCCO_2$ with increasing density showed an exponential curve and was enhanced by increases in both temperature and pressure. The Chrastil model, which relates the solubility of a solute to the density of the solvent and the working temperature, was used to state a solubility equation (*24*):

$$C = d^k \exp\left(\frac{a}{T} + b\right) \quad (1)$$

$$\ln(C) = k \ln d + \left(\frac{a}{T} + b\right) \quad (2)$$

Equation 1 assumes that a solvato complex is formed between the solute and the gas molecules. C (grams/liter) is the solute concentration in the gas, d (grams/liter) is the gas density, and T (kelvin) is the working temperature; k represents the average number of gas molecules that form the solvato complex, a is a constant that depends on the heat of solvation, and b depends on the molecular weights and melting points of the solute and the gas. Equation 1 can be converted into a linear function by taking the logarithmic mean of both sides (eq 2), and constant parameters can be obtained by use of different temperature values; here we use 343, 353, and 363 K. Upon plotting ln C

versus ln d at these three different temperatures, the slope of the straight line gives us the k value. Other constants a, b can be found in a similar way by plotting ($a/T + b$) versus $1/T$. The correlated parameters and calculated solubility values agreed well with the experimental results (**Figure 11**), giving the following Chrastil equation:

$$C = d^{8.59} \exp - \left(\frac{5565}{T} + 45.65\right) \quad (3)$$

To estimate the data correlation between experimental and calculated values, the percentage of the average absolute deviation (AAD %) was calculated by consideration of all the concentration values (eq 4). The results showed that Chrastil equation fairly represented the solubility behavior of *trans*-lycopene in $SCCO_2$ with AAD % of 5.7, almost high probity.

$$\text{AAD (\%)} = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{C^{\text{exp}} - C^{\text{calc}}}{C^{\text{exp}}}\right|_i \times 100 \quad (4)$$

On the other hand, some discrepancies were observed when these results were compared with previously conducted solubility studies on lycopene (*6*, *19*). Vasapollo et al. (*6*) have calculated the constants k, a, and b at 34 MPa for different temperature values to be 4.643, −5157, and −21.17, respectively. Gomez-Prieto et al. (*19*) also reported the calculated parameters of solubility of *trans*-lycopene in supercritical carbon dioxide, obtaining the Chrastil equation points by combining CO_2 densities between 400 and 800 g/L with extraction vessel temperatures of 313, 323, and 333 K. For *all-trans*-lycopene, constant k, a, and b values were calculated as 8.06, −4336.06, and −47.63, respectively. Here, at higher temperatures and pressures, use of the previously calculated solubility constants giving an AAD % of 86.5 in the Gomez-Prieto study (*19*) and 53.9% in the Vasapollo study (*6*) resulted in huge divergence from our experimental results.

The results of this study indicate that operating conditions (temperature, pressure, flow, time, etc.) are crucial points in the supercritical carbon dioxide extraction of lycopene from waste dried tomato skins. A total of 1.18 mg of lycopene/g of sample, 94% of the total carotenoid content, was recovered from dried tomato skins ground to a small size at optimum operating conditions, which are as follows: pressure 40 MPa, temperature 373 K, and CO_2 flow rate 2.5 mL/min. Pure high-quality lycopene can easily be extracted and recovered from tomato skin without the use of modifiers by using supercritical fluid technology at the optimum operating conditions. Degradation of lycopene can be minimized by protecting the system from light and oxygen. At the same time, operating the extraction process at elevated pressures and temperatures prevents cis formation of *trans*-lycopene, and increasing the solubility of it in $SCCO_2$. This is probably the most challenging point in industrial applications. To make use of the highly functional substance lycopene, which is a natural antioxidant that protects people from a broad range of epithelial cancers, modeling of $SCCO_2$ extraction of lycopene from tomato skin and other tomato processing waste products should be the subject of further study. Moreover, the solubility behavior of lycopene in $SCCO_2$ is still compelling, and its measurement is tedious due to its instability.

LITERATURE CITED

(1) Shi, J.; Le Maguer, M. Lycopene in Tomatoes: chemical and physical properties affected by food processing. *Crit. Rev. Food Sci. Nutr.* **2002**, *40*, 1−42.

(2) Pyke, K. A.; Howells, C. A. Plastid and Stromule Morphogenesis in Tomato. *Ann. Bot.* **2002**, *90*, 559−566.

(3) Bohm, V.; Bitsch, R. Intestinal absorption of lycopene from different matrices and interactions to other carotenoids, the lipid status, and the antioxidant capacity of human plasma. *Eur. J. Nutr.* **1999**, *38* (3), 118−25.

(4) Lee, M. T.; Chen, B. H. Stability of lycopene during heating and illumination in a model system. *Food Chem.* **2002**, *78*, 425−432.

(5) Rao, A. V.; Waseem, Z.; Agarwal, S. Lycopene content of tomatoes and tomato products and their contribution to dietary lycopene. *Food Res. Int.* **1998**, *31* (10), 737−741.

(6) Vasapollo, G.; Longo, L.; Rescio, L.; Ciurlia, L. Innovative supercritical CO_2 extraction of lycopene from tomato in the presence of vegetable oil as co-solvent. *J. Supercrit. Fluids* **2004**, *29*, 87−96.

(7) Sharma, S. K.; Le Maguer, M. Lycopene in tomatoes and tomato pulp fractions. *Ital. J. Food Sci.* **1996**, *8* (2), 107−113.

(8) Sabio, E.; Lozano, M.; Montero de Espinosa, V.; Mendes, R. L.; Pereira, A. P.; Palavra, A. F.; Coelho, J. A. Lycopene and β-Carotene Extraction from Tomato Processing Waste Using Supercritical CO_2. *Ind. Eng. Chem. Res.* **2003**, *42*, 6641−6646.

(9) Phelps, C. L.; Smart, N. G.; Wai, C. M. Past, present, and possible future applications of supercritical fluid extraction technology. *J. Chem. Educ.* **1996**, *73* (12), 1163.

(10) Cadoni, E.; De Giorgi, M. R.; Medda, E.; Poma, G. Supercritical CO_2 extraction of lycopene and β-carotene from ripe tomatoes. *Dyes Pigments* **1999**, *44* (1), 27−32

(11) Rozzi, N. L.; Singh, R. K.; Vierling, R. A.; Watkins, B. A. Supercritical Fluid Extraction of Lycopene from Tomato Processing Byproducts. *J. Agric. Food Chem.* **2002**, *50*, 2638−2643.

(12) Gomez-Prieto, M. S.; Caja, M. M.; Herraiz, M.; Santa-Maria, G. Supercritical Fluid Extraction of *all-trans*-Lycopene from Tomato. *J. Agric. Food Chem.* **2003**, *51* (1), 3−7.

(13) Suoqi, Z.; Yunxiang, H.; Guonpeng, Q.; Renan, W.; Kuifang, L.; Yumei, L.; Dejun, C.; Yuyin, L. Extracting Lycopene from Tomato Powders by Supercritical Propane and Carbon dioxide with Industrial Scale Pilot. Proceedings of the 6th Annual Meeting of the International Society for the Advancement of Supercritical Fluids, Versailles, France, 2003; Vol. 1, N13, p 83.

(14) Nobre, B. P.; Palavra, A. F.; Mendes, R. L. Supercritical Fluid Extraction of Carotenoids from Tomato Industrial Wastes. 7th Italian Conference on Supercritical Fluids and Their Applications, Trieste, Italy, 2004; N22.

(15) Pol, J.; Hyoetylaeinen, T.; Ranta-Aho, O.; Riekkola, Marja-L. Determination of lycopene in food by on-line SFE coupled to HPLC using a single monolithic column for trapping and separation. *J. Chromatogr. A* **2004**, *1052* (1−2), 25−31.

(16) Ollanketo, M.; Hartonen, K.; Riekkola, Marja-L.; Holm, Y.; Hiltunen, R. Supercritical carbon dioxide extraction of lycopene in tomato skins. *Eur. Food Res. Technol.* **2001**, *212* (5), 561−565.

(17) Paolo, A.; Ireneo, K.; Angelo, C.; Alessia, F.; Marisa, T.; Crucil, I. Lycopene Extraction from Processed Tomatoes Using Supercritical CO_2. Second Central European Meeting of the 5th Croatian Congress of Food Technologists, Biotechnologists and Nutritionists; Croatia, 2004; P7.

(18) Favati, F.; Pietrafesa, A.; Galgano, F. Extraction of natural antioxidants (Carotenoids and tocopherols) from byproducts of the tomato processing industry. Proceedings of the 6th Annual Meeting of the International Society for the Advancement of Supercritical Fluids, Versailles, France, 2003; Vol. 1, PN46, p 321.

(19) Gomez-Prieto, M. S.; Caja, M. M.; Santa-Maria, G. Solubility in supercritical carbon dioxide of the predominant carotenes of tomato skin. *J. Am. Oil Chem. Soc.* **2002**, *79* (9), 897−902.

(20) Pascale, S.; Sandrine, C.; Hatem, K.; Yves, G. Contribution to the determination of the solubility of β-carotene in supercritical carbon dioxide and nitrous oxide: experimental data and modeling. *Fluid Phase Equilibria* **1997**, *131*, 269−286.

(21) Epler, K. S.; Sander, L. C.; Ziegler, R. G.; Wise, S. A.; Craft, N. E. Evaluation of reversed-phase liquid chromatographic columns for recovery and selectivity of selected carotenoids. *J. Chromatogr.* **1992**, *595*, 89−101.

(22) Brunner G. *Gas Extraction—An Introduction to Fundamentals of Supercritical Fluids and the Application to Separation Processes*; Springer: New York, 1994; pp 59−73 and 179−199.

(23) Tonthubthimthong, P.; Chuaprasent, S.; Douglas, P.; Luewisutthichat, W. Supercritical CO_2 extraction of nimbin from neem seeds—an experimental study. *J. Food Eng.* **2001**, *47*, 289−293.

(24) Chrastil, J. Solubility of Solids and Liquids in Supercritical Gases. *J. Phys. Chem.* **1982**, *86*, 3016−3021.

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