

## Desorption of Food Related Phenolic Acids from Charcoal in Single Solute Model System

Won-Young Lee and Yong-Hee Choi<sup>\*</sup>

*Institute on Agricultural Science and Technology, Kyungpook National University, Taegu 702-701, Korea*  
*\*Dept. of Food Science and Technology, Kyungpook National University, Taegu 702-701, Korea*

### Abstract

Phenolic acids are regarded as harmful materials in food and environment science but recently, as useful materials, and thus adsorption is recommended as an effective separation technique to recover or remove phenolic acids from diluted solution. If the adsorbed phenolic compounds were useful materials, the materials should be recovered through desorption. Desorption using supercritical carbon dioxide(SC-CO<sub>2</sub>) was tried to separate food-borne phenolic acids from charcoal in single solute system. In the comparisons of desorption amounts, gallic acid had the lowest solubility to SC-CO<sub>2</sub>. Gallic acid has more hydroxy functional groups than the other phenolic acids, which was immiscible with nonpolar SC-CO<sub>2</sub>. Ferulic acid was yielded more than *p*-coumaric acid, because ferulic acid had much bigger molecular weight, which was affected more by van der Waals force. It was found that the most affecting factor on desorption amounts was the solubility of phenolic acids to SC-CO<sub>2</sub>. The second affecting factor was van der Waals force. Response surface methodology(RSM) was conducted to read the trend of desorption. Increasing density of SC-CO<sub>2</sub> raised solubility of phenolic acids.

**Key words:** phenolic acid, desorption, supercritical carbon dioxide

### INTRODUCTION

The term of phenolic compounds embraces a wide range of compounds that possess an aromatic ring bearing a hydroxy substituent, including their functional derivatives. Phenolic compounds present in many plants are directly related to the characteristics of foods such as taste, palatability, nutritional value, pharmacological and toxic effects, and microbial decomposition(1-4). Moreover, many researchers have been interested in these compounds because of their abilities recovering or removing ionic ions and their properties of anti-cancer, anti-mutant and inhibitors of bindings between HIV and CD4 proteins(5-10). No matter what phenolic compounds are recognized as harmful or useful materials as mentioned above, they need to be removed or recovered. In order to separate the compounds from aqueous matrix, adsorption using charcoal has been widely employed. After adsorption, desorption is carried out for regeneration of adsorbent and recovering of adsorbate. Desorption of phenolic acid using SC-CO<sub>2</sub>(supercritical carbon dioxide) was employed in this study.

The critical temperature and pressure of CO<sub>2</sub> are 31°C

and 7.3MPa, respectively. Supercritical zone over critical point is called a supercritical fluid having characteristics of both gases and liquids. It has the similar density of a liquid and functions like a liquid solvent, but it diffuses easily like gas. The high density of a supercritical fluid allows it to dissolve large quantities of organic compounds that normally have low solubility in the ordinary liquid or gaseous states of the same fluid(11-13).

The purpose of this study was to find out the possibility of removing or recovering adsorbate by SC-CO<sub>2</sub> and figure out desorption dynamics. Model system was composed of *p*-coumaric acid, gallic acid and ferulic acid, which were widely distributed in food or plant materials. Desorbed amounts depending on consumed CO<sub>2</sub>, desorption isotherms, response surfaces for desorption according to changes of temperature and pressure were investigated.

### MATERIALS AND METHODS

#### Preparation of desorbent

According to the method described by Lee et al.(14), charcoal was screened to 0.84~1.00mm mesh, washed again

<sup>†</sup>Corresponding author

5 times with deionized water and dried for 48 hours at 105°C. Then 4g charcoal was soaked in 500ppm phenolic acid solutions(1L) and shaken under condition of 200rpm, 25°C for 24hr. The charcoal containing phenolic acids was dried for 24hr at 40~50°C, 660~760mmHg. The dried charcoal was used for desorption inspection.

Charcoal as desorbent has physical properties of 26.227 m<sup>2</sup>/g total pore area, 26.02% porosity and 0.8093g/ml bulk density. BET specific surface area was 1,040m<sup>2</sup>/g cat.

## Reagents

Phenolic acids used for desorption were *p*-coumaric acid, gallic acid and ferulic acid, which had over 99% purity. To analyze phenolic acids, bis-trimethylsilyl acetamide and acetonitrile were used for TMS and *p*-hydroxy benzoic acid was used as internal standard. All reagents for this study were purchased from Sigma Co. (St. Louis, MO 63178, USA).

## Desorption using SC-CO<sub>2</sub>

SC-CO<sub>2</sub> extraction apparatus(ISCO Model SFX2-10, Lincoln, NE, USA) was shown in Fig. 1. Carbon dioxide was compressed to desired pressure and supplied to extraction column by a syringe pump. The system was designed to maintain the constant extraction pressure at any temperature and flow rate. The volume of extraction column was 10ml. Carbon dioxide was flowing downward in the column because the materials were solid and channelling could be prevented. The phenolic acids laden carbon dioxide tended to flow to the bottom of the ex-

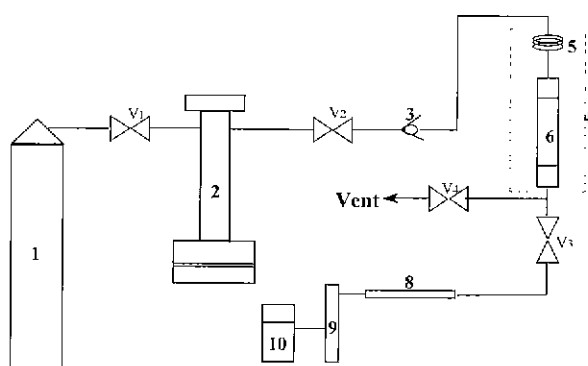


Fig. 1. Schematic diagram of supercritical CO<sub>2</sub> desorption system.

1. Liquid CO<sub>2</sub> cylinder 2. Syringe Pump and Controller 3. Check valve 4. Constant temperature bath 5. Preheater 6. Extraction column 7. Filter 8. Capillary restrictor 9. Heating chamber 10. Solvent trap V1-V4. Valves

traction(15). The restrictor was stainless steel capillary restrictor(OD 300µm).

The system was vented with gaseous CO<sub>2</sub> at low pressure for 5min to remove air from the extraction system. After the extractor reached to the desired temperature, the system was pressurized to the desired pressure. After sample was allowed to stand for 10min for the equilibrium of temperature and pressure, the extraction was performed as the CO<sub>2</sub> flowed through the column, and the extracted phenolic acids were separated by pressure reduction and then collected in the test tube containing distilled water. Desorption was carried out at different pressures of 20.67, 34.46 and 48.24 MPa and temperatures of 40, 60 and 80°C. The CO<sub>2</sub> flow rate was 1.1~2.0 g/min. The desorbed phenolic acids was collected at 30 min intervals. Charcoal, which was equilibrated with 500 ppm phenolic acid through adsorption, was used to investigate the relationship of desorbed amount changes depending on consumed CO<sub>2</sub> under 41.35MPa, 70°C. Desorption isotherms was predicted by Freundlich equation, which were come from relations between desorbed amount and equilibrium concentration under the same condition.

## Desorption experimental design for RSM

Response surface methodology(RSM) of SAS program was employed to investigate the trend of desorption and optimum condition. Experiments were designed according to central composite design which has three levels as summarized in Table 1. It was assumed that one mathematical function is present for the response variable(desorption yield of phenolic acids) in terms of two independent processing factors.

To approximate the function, second degree polynomial equation was used;

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \sum_{j=1}^k \beta_{ij} X_i X_j + \epsilon$$

where  $\beta_0$ ,  $\beta_i$ ,  $\beta_{ii}$ , and  $\beta_{ij}$  are constant coefficient and  $X_i$

Table 1. The central composite design by RSM computer program during supercritical carbon dioxide desorption

Coded	Uncoded	
	Temperature(°C)	Pressure(MPa)
-1	40	20.67
0	60	34.46
1	80	48.24

is the coded independent variable. Statistical Analysis System was used to fit the second order polynomial equation to the experimental data. Significances were considered as  $p < 0.05$ .

### Analysis of phenolic acids

Phenolic acids were analyzed by Hobert and Senter's method(16). Phenolic acids in 10ml effluent solution were re-extracted by ethyl acetate and 5ml re-extracts were dried under vacuum. The dried phenolic acids were dissolved with 100 $\mu$ l acetonitrile and added 50 $\mu$ l BSA (N.O-bis-trimethylsilyl acetamide) reagent and 25 $\mu$ l *p*-hydroxy benzoic acid as internal standard. After TMS for 5 minutes at 90°C the preparing sample was analyzed by gas chromatography(Pye Unicam Series 304, Philips, England) equipped with a flame ionization detector. Packing material was SE-30 60~80mesh(Shimadzu Co. Japan) and glass column was used, which was 4mm I.D. and 1.5m length. The oven temperature was programmed from 180°C to 240°C increasing 2°C/min. The injector and detector temperatures were 260°C and 270°C, respectively. Nitrogen flow rate as carrier gas was 30ml/min.

## RESULTS AND DISCUSSION

### Desorbed amounts in single solute system

Desorbed amounts of phenolic acid depending on con-

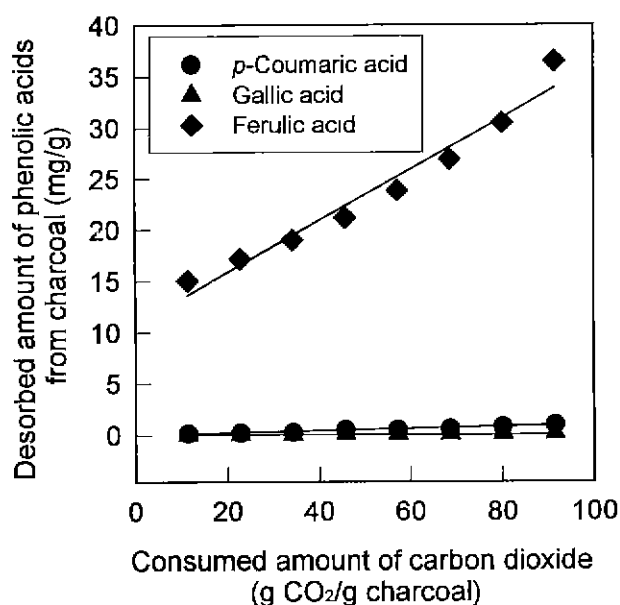


Fig. 2. Desorption of phenolic acids depending on consumed carbon dioxide from charcoal at 70°C, 41.35MPa.

sumed carbon dioxide which were showed in Fig. 2. Linear increments of desorbed phenolic acid were thought that charcoal has a little ink bottle on surface area and adsorbate concentration was too higher than desorbed concentration. The slopes of ferulic acid, *p*-coumaric acid and gallic acid in single solute system were steep, moderate steep, almost constant, respectively. Ferulic acid had most steep slope, *p*-coumaric acid was next and gallic acid was low. Ferulic acid slope had 40 folds steeper than *p*-coumaric acid and 300 folds than gallic acid (Table 2.)

### Desorption isotherms in single solute system

Freundlich model equation was commonly adapted to predict desorption isotherms(17-20). Desorbed amounts depending on concentration increment of phenolic acids were showed in Fig. 3. Gallic acids had a little increment while *p*-coumaric acid and ferulic acid increased exponentially. Maximum desorbed amounts of *p*-coumaric acid, gallic acid and ferulic acid in single solute system were 5.27, 0.24, 23.32% respectively.

Table 2. Desorption rate constant of phenolic acid in single solute system

Mixture type	Phenolic acid	Slope
Single solute	<i>p</i> -Coumaric acid	3.88E-3
	Gallic acid	5.50E-4
	Ferulic acid	1.59E-1

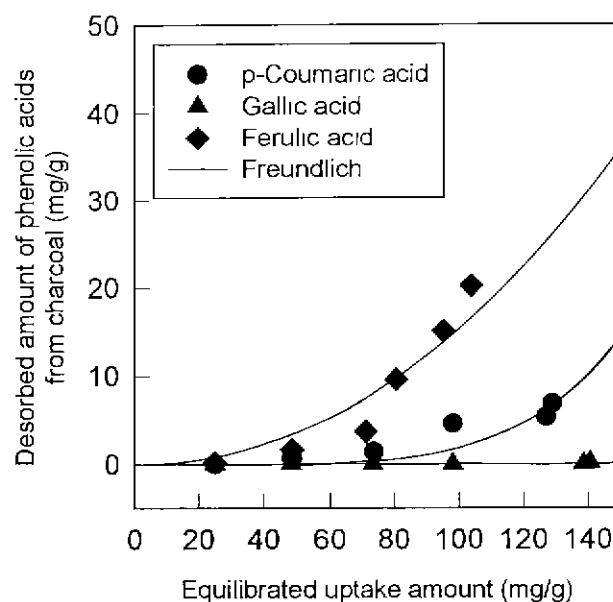
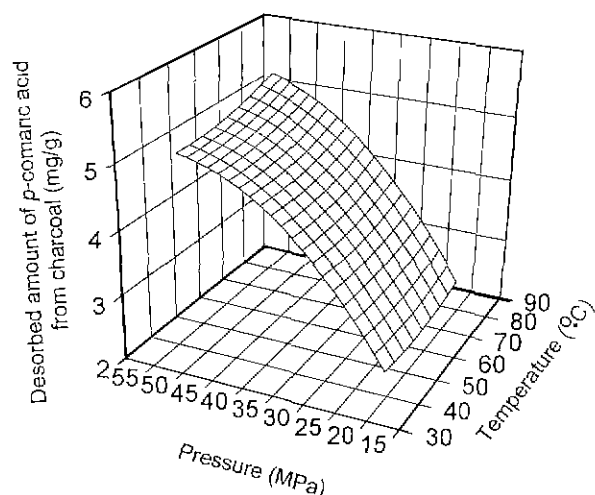


Fig. 3. Desorption isotherm of phenolic acids from charcoal in single solute system 70°C, 41.35MPa.

**Table 3. Freundlich parameters and correlation coefficient of each phenolic acids**

Mixture system	Phenolic acid	$K_f$	$n_f$	Correlation coefficient
Single solute	<i>p</i> -Coumaric acid	1.23E-10	1.96E-1	0.8322
	Gallic acid	2.04E-42	0.53E-1	0.9545
	Ferulic acid	9.93E-4	4.77E-1	0.9663

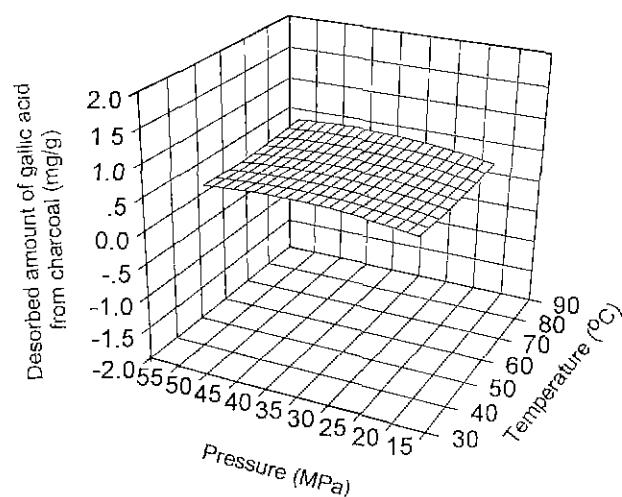
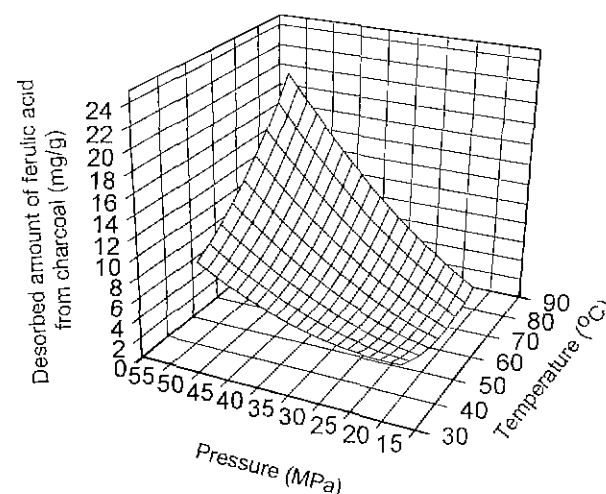
**Fig. 4. Desorption response surface of *p*-coumaric acid from charcoal.**

The correlation coefficients and parameters of prediction model were presented in Table 3. Correlation coefficients of gallic acid and ferulic acid were over 0.95, suggesting Freundlich equation was the acceptable model to predict food-borne phenolic acid desorption isotherms.

### Desorption trends using RSM

Response surfaces were composed by the central composite design which had 3 levels of temperature and pressure. RSM was conducted to determine maximum desorption conditions and to find overall desorption trend according to process variables. Density increment of SC-CO<sub>2</sub> with increment of pressure raised solubility of phenolic acids.

*p*-Coumaric acid was affected more by pressure than

**Fig. 5. Desorption response surface of gallic acid from charcoal.****Fig. 6. Desorption response surface of ferulic acid from charcoal.**

by temperature and the desorbed amount was almost linearly increased with pressure (Fig. 4). Gallic acid was desorbed constantly with changes of temperature and pressure in Fig. 5. Gallic acid having more hydroxy functional groups than the other phenolic acids has higher polarity. The polarity made it difficult to desorb gallic acid from charcoal, because a polar gallic acid was

**Table 4. Polynomial equations calculated by RSM program for phenolic acid desorption**

Response	Polynomial equation	R-square
<i>p</i> -Coumaric acid	$Y = -0.409523 - 0.0029905x_1 + 0.001409x_2 + 0.000239x_1^2 - 0.000001163x_1x_2 - 8.474537E-8 x_2^2$	0.9969
Gallic acid	$Y = 0.381733 - 0.014784x_1 + 0.000184x_2 + 0.000119x_1^2 + 0.000000285x_1x_2 - 1.584479E-8 x_2^2$	0.9402
Ferulic acid	$Y = 26.568682 - 0.677991x_1 - 0.004243x_2 + 0.003898x_1^2 + 0.0000648222x_1x_2 + 0.249E-6 x_2^2$	0.9339

immiscible with nonpolar SC-CO<sub>2</sub>. Ferulic acid was recovered more than *p*-coumaric acid as shown in Fig. 4 and 6. Because ferulic acid has a bigger molecular weight than *p*-coumaric acid, ferulic acid was more affected than *p*-coumaric acid by van der Waals effect. It could be said from the results that the most effective factors affecting desorbed amount were the first solubility of phenolic acids to SC-CO<sub>2</sub> and van der Waals force.

Response surface equation was expressed in Table 4. Correlation coefficient was over 0.93 and the equation was acceptable to explain overall desorption trends. The more increment of pressure resulted in the more desorbed amounts, which means high density of SC-CO<sub>2</sub> rise solubility of phenolic acids up. The similar results were reported for rice bran and soybean oil extractions using SC-CO<sub>2</sub>.

## REFERENCES

- Hui, Y. H. : Phenolic compounds. In "Encyclopedia of food science and technology" Wiley Interscience, Vol.3, p.2055 (1991)
- Lee, J. and Lee, S. R. : Analysis of phenolic substances content in Korean plant foods. *Korean J. Food Sci. Technol.* **26**, 310(1994)
- Amiot, M. J., Aubert, S. and Nicolas, J. : Phenolic composition and browning susceptibility of various apple cultivars at maturity. *J. Food Sci.*, **57**, 958(1992)
- Kang, S. T. : Treatment of wastewater containing phenol by *Pseudomonas* sp. B3. *Ph.D. Thesis*, Kyungsan university(1996)
- Sakagami, H., Nakashima, H., Murakami, T., Yamamoto, N., Hatano, T., Yoshida, T. and Okuda, T. : Structures and activities of tannins in crude drugs(4). Proceedings of the 8th symposium on the studies and application of naturally curing drugs. July 25, Tokyo(1991)
- Wright, C. W. : Natural products in the fight against aids. *The Pharmaceutical J.*, **254**, 583(1995)
- Nakajima, A. and Sakaguchi, T. : Recovery of uranium by tannin immobilized on agarose. *J. Chem. Tech Biotechnol.*, **87**, 223(1987)
- Chibata, R., Tosa, T., Mori, T., Watanabe, T. and Sakata, N. : Immobilized tannin—a novel adsorbent for protein and metal ion *Enzyme Microb. Technol.*, **8**, 130(1986)
- Randall, J. M., Reuter, W. and Waiss, A. C. : Removal of cupric ion from solution by contact with peanut skins. *J. App. Polymer Sci.*, **19**, 1563(1975)
- Kumar, P. and Dara, S. S. : Binding heavy metal ions with polymerized onion. *J. App. Polymer Sci.*, **19**, 397(1981)
- Sovova, H., Komers, R., Kucers, J. and Jez, J. : Supercritical carbon dioxide extraction of caraway essential phenolic acids *Chemical Eng. Sci.*, **49**, 2499(1994)
- Rizvi, S. S. H., Benado, A. L., Zollweg, J. A. and Daniels, J. A. : Supercritical fluid extraction fundamental principles and modeling methods. *Food Technol.*, **40**, 6, 55(1986)
- Rizvi, S. S. H., Daniels, J. A., Benado, A. L. and Zollweg, J. A. : Supercritical fluid extraction : Operating principles and food applications. *Food Technol.*, **40**, 7, 57(1986)
- Lee, J. J., Chang, Y. H. and Cho, B. R. : Adsorption characteristics of Cd-chelate compounds on activated carbon. *Hwahak Konghak*, **23**, 313(1985)
- Lee, A. K., Bulley, N. R., Fattori, M. and Meisen, A. : Modeling of supercritical carbon dioxide extraction of canola oilseed in fixed bed. *J. Am. Oil Chem. Soc.*, **53**, 921 (1986)
- Hobert, R. J. and Senter, S. D. : A gas-liquid chromatographic method for analysis of phenolic acids in plants. *J. Agric. Food Chem.*, **28**, 1292(1980)
- Roop, R. K., Hess, R. K. and Akgerman, A. : Supercritical extraction of pollutants from water and phenolic acids. In "Supercritical fluid science and technology" Johnston, p.468(1989)
- Ballesta, P. P., Feerradas, E. G. and Aznar, A. M. : Desorption isotherms of volatile organic compounds adsorbed on activated charcoal. *American Industrial Hygiene Association J.*, **56**, 171(1995)
- Locke, M. A. : Sorption-desorption kinetics of a chlor in surface phenolic acids from two soybean tillage systems. *J. Environ. Qual.*, **21**, 558(1992)
- Moyler, D. A. : Carbon dioxide extracted ingredients or fragrances. *Perfumer and flavorist*, **9**, 109(1984)

(Received October 30, 1997)