



Tecnología, Ciencia, Educación

ISSN: 0186-6036

imiqac@sercom.com.mx

Instituto Mexicano de Ingenieros Químicos A.C  
México

Castillo-Ruz, María Carolina; Guillermo-Alcocer, Carlos Gerardo; Bojórquez-Gamboa, Rubén Ricardo;  
Rocha-Uribe, José Antonio

Extraction of vanilla oleoresin (*Vanilla planifolia* Andrews) with supercritical CO<sub>2</sub>  
Tecnología, Ciencia, Educación, vol. 26, núm. 2, julio-diciembre, 2011, pp. 80-84  
Instituto Mexicano de Ingenieros Químicos A.C  
Monterrey, México

Disponible en: <http://www.redalyc.org/articulo.oa?id=48221175004>

- Cómo citar el artículo
- Número completo
- Más información del artículo
- Página de la revista en redalyc.org

redalyc.org

Sistema de Información Científica  
Red de Revistas Científicas de América Latina, el Caribe, España y Portugal  
Proyecto académico sin fines de lucro, desarrollado bajo la iniciativa de acceso abierto

# Extraction of vanilla oleoresin (*Vanilla planifolia* Andrews) with supercritical CO<sub>2</sub>

## Extracción de oleoresina de vainilla (*Vanilla planifolia* Andrews) con CO<sub>2</sub> supercrítico

María Carolina Castillo-Ruz, Carlos Gerardo Guillermo-Alcocer, Rubén Ricardo Bojórquez-Gamboa, José Antonio Rocha-Uribe\*

Universidad Autónoma de Yucatán, Facultad de Ingeniería Química, Periférico Nte. Km 33.5 Tablaje Catastral 13615, Col. Chuburná de Hidalgo Inn, 97203 Mérida, Yucatán; México. Tel. (Phone) (+52 999) 946 0981 Ext 1177; Fax 52 (999) 946 0994, correo-e (e-mail): antonio.rocha@uady.mx

### ABSTRACT

Vanilla oleoresin is a widely used natural product, mainly used as flavor. In this work, the extraction of vanilla oleoresin using supercritical CO<sub>2</sub> is evaluated. The main extraction parameters on the oleoresin yield and composition was determined, namely: pressure, temperature, particle size, and contact time. Results indicate that lower particle size favors mass transfer and oleoresin yield. High pressure and temperature also provide higher yields of vanilla oleoresin. Extreme conditions of pressure and temperature decrease the quality of vanillin possibly because of the degradation of some compounds. The maximum concentration of vanillin (97.35% w/w) is found at 408 bars and 40°C, with a mass yield of 5.82% after 40 minutes of dynamic extraction. The extraction of vanilla oleoresin with supercritical CO<sub>2</sub> is possible, and optimizing the operational conditions may provide higher oleoresin yield with good vanillin concentration; an economic analysis would be needed to determine the best extraction time.

### RESUMEN

Actualmente la oleoresina de vainilla es uno de los productos naturales con alto uso. Su principal aplicación es como saborizante. En este trabajo se evalúa la extracción de oleoresina de vainilla usando CO<sub>2</sub> supercrítico. Los principales parámetros variados para ver el efecto sobre el rendimiento

**Palabras clave:** CO<sub>2</sub>, extracción, fluido supercrítico, vainilla, vainillina, *Vanilla planifolia* Andrews

**Keywords:** CO<sub>2</sub>, extraction, supercritical fluid, vanilla, vanillin, *Vanilla planifolia* Andrews

\*Autor a quien debe dirigirse la correspondencia  
(Recibido: Junio 3, 2011,  
Aceptado: Junio 29, 2011)

y la concentración de vainillina fueron: presión, temperatura, tamaño de partícula, y tiempo de contacto. Obviamente los tamaños de partícula menores favorecen la transferencia de masa y el mayor rendimiento de la oleoresina. Los valores mayores de presión y temperatura también dan mejores rendimientos de la oleoresina de vainilla. Las condiciones extremas de presión y temperatura reducen la calidad de la vainillina posiblemente debido a la degradación de algunos compuestos. La concentración más alta de vainillina (97.35% masa) se encuentra a una presión de 408 bar y a una temperatura de 40°C, con un rendimiento en masa de 5.82% con 40 minutos de extracción dinámica. La extracción de la vainilla con CO<sub>2</sub> supercrítico es posible y la optimización de las condiciones de operación puede mejorar el rendimiento de la oleoresina con una buena concentración de vainillina. Para obtener el mejor tiempo de extracción es necesario realizar un análisis económico de factibilidad.

### INTRODUCTION

Vanilla (*Vanilla planifolia* Andrews) is native from southeastern Mexico and is considered the world's main flavor (Brandt, 1996, Havkin-Frenkel y Belanger, 2011). The first component of vanilla aroma is vanillin, which is obtained from a natural fermentation process known as curing. According to Ranadive (1992), since most of the components that provide the flavor are volatile and thermolabile, extraction and purification methods of vanilla extracts determine the overall quality of the final product. Presently, the main extraction method for vanilla oleoresin is multistage lixiviation, or leaching at 80°C employing ethyl alcohol, but if the process does not have a good control of temperature, degradation of vanilla may occur and a loss of extract exists.

Supercritical extraction with CO<sub>2</sub> seems to be a good alternative, because it operates at a lower temperature, mass transfer is improved, and no residual solvent

is present in the final product. These advantages are important and seem promising for the industrial use of this technology in the extraction of thermolabile compounds (Moyler and Heath, 1988).

Moyler (1987) reviews the sub- and supercritical CO<sub>2</sub> extraction of essential oils and compare results with steam distillation for ginger, hop, clove bud, black pepper, juniper berry oil, and vanilla bean. Rice and Singh obtained a patent in 1990 for the continuous extraction of solid material using solvents such as CO<sub>2</sub> by circulating a mixture of the solids in CO<sub>2</sub> at elevated pressure through a closed-loop pipeline. Carbonell (1991) reviews extraction with CO<sub>2</sub> of ginger, black, green, and white pepper, and vanilla. Fu et al. (2002a,b), report the extraction of vanilla with supercritical CO<sub>2</sub> fluid. Kvasenkov and Kvasenkov (2010) patented the preparation of coffee-substitute beverages using supercritical extraction of a mixture of cocoa husk, cinnamon and vanilla spices with liquid nitrogen.

The objective of this research is to evaluate the yield and final concentration of vanilla oleoresin extracted by supercritical CO<sub>2</sub>. A study of the effect of pressure, temperature, particle size, and contact time is also included.

## MATERIALS AND METHODS

### Materials

The raw materials were vanilla beans from Papantla, Veracruz, Mexico (from Casa Larios). The vanilla beans were classified as superior quality based on the parameters accepted in Mexico (Mexican Act NMX-FF-074-1996). The content of vanillin in the vanilla beans was determined according to the same norm. The traditional extraction procedure consists of maceration of vanilla beans cut to about 0.65 cm on ethanol. Total vanillin content was 3.6% w/w after 3 days of maceration time. The extraction yield is defined as grams of oleoresin extracted and recovered divided by the grams of solid material in the extraction recipient. The concentration of vanillin was characterized by HPLC as recommended by Thomson and Hoffmann (1988). Yield and composition obtained in this research are compared against the values reported by Nguyen et al. (1991).

### Solvents

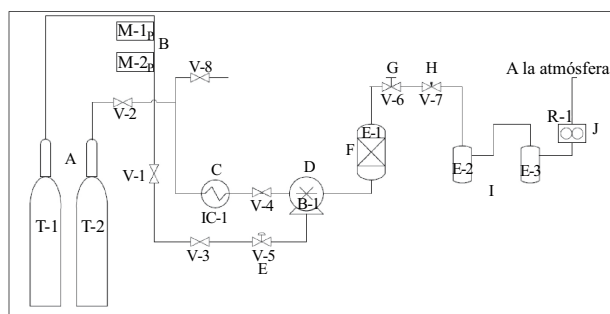
The solvent was industrial-grade CO<sub>2</sub> at 99.98% w/w, supplied by Praxair-Mexico. Other reactants and solvents were purchased from Merck (Mexico). Vanillin

standard with 99% purity was supplied by Sigma-Aldrich (Mexico).

## SUPERCritical EXTRACTION

### Equipment

The supercritical extraction of vanilla oleoresin was performed with lab-scale equipment (model SFT-150 System Extractor from Supercritical Fluid Technologies, Inc. Newark, DE, USA) A typical diagram is shown in Figure 1. The capacity of the extraction cell is 0.1 L and usually was charged with 23 g of vanilla beans. The equipment has an air-driven reciprocating pump to compress the CO<sub>2</sub>. The heating elements are 2000 W resistances and a temperature proportional integral derivative (PID) controller allows fixing the temperature in the range from 0 to 120°C. The flow of CO<sub>2</sub> is between 1 and 330 mL/min (1-250 g/min) of liquid CO<sub>2</sub> under normal operation.



**Figure 1.** Extraction system using supercritical CO<sub>2</sub>: A. Air cylinder (T-1) and CO<sub>2</sub> cylinder (T-2); B. Manometer for air (M-1 y M-2); C. Cooler for liquid CO<sub>2</sub> (IC-1); D. Reciprocant pump (B-1); E. Regulatory valve for air fed to pump (V-5); F. Extractor (E-1); G. Valve on/off (V-6); H. Needle valve (V-7); I. Containers: Extractor (E-2) solvent trap (E-3); J. Flow meter (R-1)

### Operational conditions

Table 1 shows the operational conditions studied in the experimental runs (data obtained by triplicate) and reported by Castillo-Ruz (2007). The temperature and pressure range is wider than that reported by Nguyen et al. (1991). The extractions were performed at 40, 45, and 50°C, and at four different pressures 272,

340, 408, and 476 bar (4000, 5000, 6000, and 7000 psi, respectively). The particle size was between 16 and 30  $\mu\text{m}$  for most of the runs. One of the runs included vanilla beans pieces of 5 mm in length as a reference. Particle size was determined with standard sieves (Newark, US). For most of the runs, contact time was 40 minutes, but for each pair of pressure and temperature contact times of 30 and 60 minutes were also tested to see the effect of these variables.

**Table 1**

*Summary of the operational conditions used in the experimental data to be obtained from the temperature dependent design for vanilla supercritical extraction*

	Temperature, °C		
	40	45	50
Pressure (bar)	272.11	272.11	272.11
	340.14	340.14	340.14
	408.16	408.16	408.16
	476.19	476.19	476.19

For each supercritical extraction run with  $\text{CO}_2$  the yield was calculated as follows:

$$\text{yield} = \frac{\text{grams of vanilla oleoresin extracted}}{\text{grams of vanilla charged to extraction cell}} \quad (1)$$

### Extraction procedure

Referring to Figure 1, at the beginning of the extraction the on/off valve (V-6) is closed and valves V-2 and V-4 for liquid  $\text{CO}_2$  are opened. The extraction cell (E-1) is filled with 23 g of vanilla beans, closed, and fixed. The desired temperature set point is set on the PID controller. The pressure is gradually increased by using the regulatory valve V-5 until the desired pressure is obtained. The soaking time starts once the operational conditions for temperature and pressure are established; this takes 15 minutes, and during this lapse there is no flow of  $\text{CO}_2$  to the extraction cell. After the soaking time,  $\text{CO}_2$  is allowed to flow by opening the on/off valve (V-6); then the supercritical  $\text{CO}_2$  flows upwards through the solid matrix of vanilla beans, extracting the oleoresin both from the pores and the outer part of the bean particles, diffusing out along with the  $\text{CO}_2$ . The extract is collected in the container (E-2), where the  $\text{CO}_2$  de-pressurization occurs down to atmospheric conditions. The continuous extraction process takes 40 minutes. The decompressed gaseous  $\text{CO}_2$  leaves the container (E-2) and enters a second container (E-3)

which is immersed in ice. The purpose of this second container is recovering the extract that may remain dissolved in the gaseous  $\text{CO}_2$ . The flow used for the dynamic extraction period is measured with a flow meter (R-1) before  $\text{CO}_2$  is discarded to the atmosphere. The  $\text{CO}_2$  flow is regulated with a needle valve (V-7). When the dynamic extraction period ends, valves V-1, V-2, V-3, and V-4 are closed, and valve V-6 is opened. Then the extraction cell (E-1) is de-pressurized, the remaining solid matrix and the collected extract are weighed, a mass balance is performed, and the oleoresin yield is calculated with Equation 1.

### HPLC analysis

Identification and quantification of vanilla in the extracts was carried out by liquid chromatography (Perkin Elmer 250) with a binary pump and a UV absorbance detector at 275 nm. For the chromatographic separation, an analytic column Spherisorb ODS2 was used. For identification and quantification of vanillin, a standard with 99% purity was obtained from Sigma-Aldrich (Mexico).

## RESULTS AND DISCUSSION

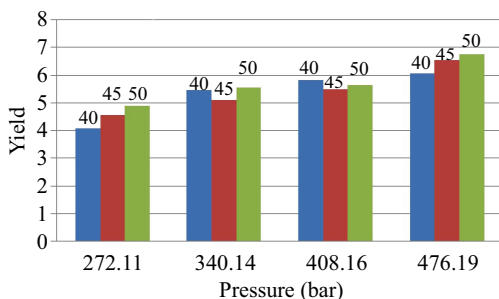
### Effect of particle size on the yield of vanilla oleoresin

Preliminary extractions at 272 bar (4000 psi) and 50°C using the 5 mm and 16-30  $\mu\text{m}$  particle sizes, were performed. As expected, the yield (4.95%) for the smaller matrix (16-30  $\mu\text{m}$ ) is higher than the yield (1.5%) for vanilla beans cut at 5 mm, confirming that smaller size favors mass transfer of solute to the supercritical  $\text{CO}_2$ , because of a larger transfer surface-area, according to Fick's law. Therefore, all the other runs were performed using the smaller particle size (16-30  $\mu\text{m}$ ).

### Effect of temperature and pressure on the oleoresin yield

Figure 2 show the oleoresin yields obtained at different pressure and temperature with a dynamic time of 40 minutes.

A general tendency of higher yields for higher temperature and pressure conditions is observed. It seems that pressure increments provide higher oleoresin yields. A maximum yield of 7.77% is found for 50°C and 476.19 bar for an extraction time of 40 minutes, for grinded vanilla beans (16-30  $\mu\text{m}$ ). Nguyen et al (1991) reported



**Figure 2.** Yield of vanilla oleoresin expressed on mass percentage at 40, 45, 50°C

yields from 0.3 to 8.0%, using a lower temperature range (33-36°C) and lower operational pressure (110 bar), as well as an average particle thickness of 1.8 mm, average width of 4 mm and average length of 19 mm, and higher extraction times (5-1540 h). These authors also report experimental data for 110 bars, 36°C with cryoground vanilla with a yield of 10.6% for a time of 50 hours.

Yields obtained in this research are higher than those reported by Nguyen et al (1991), with a lower extraction time. The reasons in order of importance from low to high are:

- Higher temperature (40-50 vs. 33-36°C)
- Higher pressure (272-476 vs. 110 bar)
- Lower particle size (0.023 vs. 19 mm)

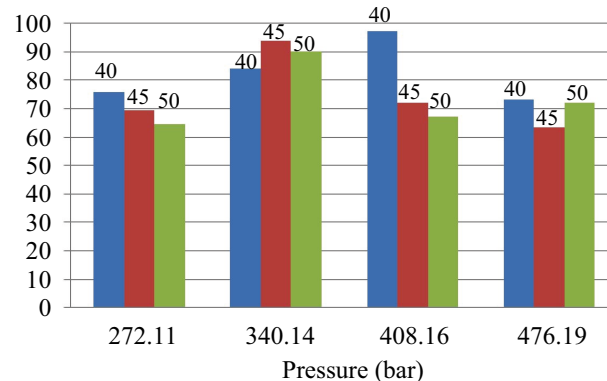
#### Identification of vanillin on oleoresin

Once the yield of oleoresin was measured, the oleoresin was analyzed for vanillin and other compounds by liquid chromatography as recommended by Thompson and Hoffmann (1988). Retention time for vanillin was 7 minutes. Depending upon temperature and pressure conditions used on the extractions, other compounds that contributed for the vanilla oleoresin bouquet were found. For example, on the performed extract chromatograms (272 bars and 50°C) a peak at 2.59 minutes of retention time was observed, which corresponds to p-hydroxybenzoic acid.

#### Effect of temperature and pressure on vanillin concentration

Figure 3 shows the percentages of vanillin, measured on the extracts by using HPLC analyses. Considering the pressure and temperature that provided the maximum percentage of vanillin, it was found that intermediate pressure values between 340 and 408 bar,

and temperatures around 40 and 45°C favor vanillin concentration. The maximum mass concentration of vanillin (97.35%) is found at a pressure of 408 bars and a temperature of 40°C.

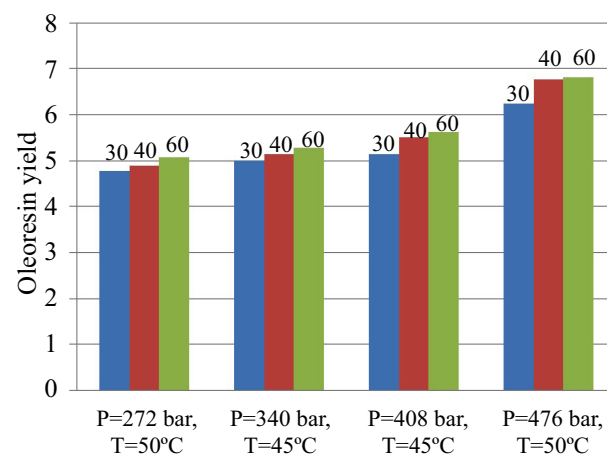


**Figure 3.** Mass percentage of vanillin at different operation conditions (40, 45, 50°C)

#### Effect of contact time

Figure 4 shows the effect of dynamic extraction time. As expected, there is a higher extraction yield for longer times. It is observed that, mainly for higher pressures, from 30 to 40 minutes the increment in the yield is about double than the increment from 40 to 60 minutes.

Using an extraction time of 40 minutes leaves solute in the solid matrix. Working at extraction times of 60 minutes the recovery of solute is a little higher. For industrial extraction, an economical analysis would be needed to determine the optimum extraction time.



**Figure 4.** Effect of extraction time over oleoresin yield (30, 40, 60 min)

## CONCLUSIONS

From this research the following conclusion may be drawn:

Lower particle size favors mass transfer and oleoresin yield, higher pressure and temperature also provide higher yields of vanilla oleoresin.

Extreme conditions of pressure and temperature decrease the quality of vanillin, possibly due to degradation of some compounds. The maximum concentration of vanillin (97.35% w/w) is found at a pressure of 408 bars and a temperature of 40°C, with a mass yield of 5.82% after 40 minutes of dynamic extraction.

The extraction of vanilla with supercritical CO<sub>2</sub> is possible and optimizing the operational conditions may provide higher oleoresin yields with a good vanillin concentration.

An economical analysis is needed to determine the optimum extraction time.

## ACKNOWLEDGMENTS

The authors would like to acknowledge the valuable support of:

- i. Dr. Juan-Daniel Pacho-Carrillo and Dra. Rosa-María Domínguez-Espinoza
- ii. Dr. Julio C. Sacramento Rivero
- iii. PRIORI Program (Program of Impulse and Orientation to Research, Spanish acronym), Autonomous University of Yucatan, Mexico
- iv. Multimarcas y Servicios de México, S.A.
- v. The experimental work was performed at the Faculty of Chemical Engineering, Autonomous University of Yucatan, Mexico. It was reported as the professional thesis of María Carolina Castillo-Ruz (2007).

## NOMENCLATURE

HPLC High performance liquid chromatography  
PID Proportional integral derivative controller

## BIBLIOGRAPHY

- Brandt, L. 1996. The creation and use of vanilla. *Food Product Design Magazine*. March 01. Available from <http://www.foodproductdesign.com>
- Carbonell, E. S. 1991. Extraction of flavors with supercritical carbon dioxide. *Cereal Foods World*. 36(11):935-937.
- Castillo-Ruz, M. C. 2007. Extracción de oleoresina de vainilla (*Vanilla planifolia* Andrews) con CO<sub>2</sub> supercrítico. *Tesis profesional*. Industrial Chemical Engineering, Universidad Autónoma de Yucatán. Mérida, Yucatán, México.
- Fu, S., Huang, M., Zhou, J., Li, S. 2002a. Determination of chemical constituents of vanilla by supercritical CO<sub>2</sub> fluid extraction. *Huaxue Yanjiu Yu Yingyong*. 14:208-210.
- Fu, S., Huang, M., Zhou, J., Li, S. 2002b. Study of components of vanilla extract by different extracting technology. *Shipin Kexue*. 23:109-112.
- Havkin-Frenkel, D., Belanger, F. 2011. *Handbook of Vanilla Science and Technology*. Wiley-Blackwell. Nueva York, NY. EEUU.
- Kvasenkov, O. I., Kvasenkov, I. I. 2010. Method for production of coffee drink "Rossiiskii". *Russian Patent* RU 2402914 C1. Moscú, Rusia.
- Mexican Act NMF-FF-074-1996: Food products not industrialized for human consumption – species and condiments –entire and dry vanilla (*Vanilla fragrant* Salisbury Ames o *Vanilla planifolia* Andrews). Diario Oficial de la Federación. Estados Unidos Mexicanos. Mexico City, Mexico.
- Moyler, D. A. 1987. Liquid carbon dioxide extraction of flavor materials. En *Dev. Food Flavours [Industrial Co-op Symp.]*, pp. 119-29. Conference. General review 1986. Elsevier Appl. Sci. Londres, Reino Unido.
- Moyler, D. A., Heath, B. 1988. Liquid carbon dioxide extraction of essential oils. Flavors and fragrances: A world perspective. En *Proceedings of the 10th International Congress of Essential Oils, Fragrances and Flavors*. Pp. 41-63. Elsevier. Londres, Reino Unido.
- Nguyen, K., Barton, P., Spencer, J. 1991. Supercritical carbon dioxide extraction of vanilla. *The Journal of Supercritical Fluids*. 4(1):40-46.
- Ranadive, A. S. 1992. Vanillin and related flavor compounds in vanilla extracts made from beans of various global origins. *J. Agric. Food Chem.* 40:1922-1924.
- Rice, W.K., Singh, L. 1990. Dynamic supercritical fluid extraction system, *US Patent* No. 4898673 A. Washington, DC. EEUU.
- Thompson, R. D., Hoffmann, T. J. 1988. Determination of coumarin as an adulterant in vanilla flavoring products by high performance liquid chromatography. *Journal of Chromatography*. 438:369-382.