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Preliminary Study on the Supercritical Carbon Dioxide Extraction of Nicotine from Tobacco Wastes

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ABSTRACT

This study examines the supercritical extraction of dry tobacco powder using supercritical carbon dioxide (SC-CO_2) as solvent. The experiments were conducted between 15–30 MPa and 50–70°C. The extract obtained was a waxy-like material rich in aroma that contained a low percentage of nicotine. The nicotine content in the solid matrix decreased slightly from 1.00 to 0.57% at the best conditions. Further experiments of nicotine extraction from aqueous solutions using SC-CO_2 as solvent were performed. The recovery of the alkaloid was also low at the operating conditions analyzed.

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Key Words. Supercritical extraction; Tobacco wastes; Nicotine; Carbon dioxide extraction

INTRODUCTION

In the industrial processing of tobacco leaves for cigar and cigarette manufacturing, a mixture of powder and leaf bits results during drying of the tobacco leaves (*Nicotina tabacum*). In countries like Brazil, Cuba, United States, Greece, etc., where tobacco production is important and many tons of tobacco wastes are available each year, these wastes offer a potentially sizable source of alkaloids (1), aromatic substances (2), and protein fractions (3).

Nicotine, the alkaloid present in tobacco, has been used in the form of nicotine sulfate as an aphicide on fruits, vegetables, and ornamentals because of its insecticide properties (4), but with the advent of synthetic insecticides its use diminished. However, there is a renewed interest in nicotine because of its low persistence (5).

A number of workers have analyzed the extinction and separation of nicotine from tobacco leaves by extraction with liquid solvents (5–7) and with supercritical fluids (1, 8–10). These studies have indicated that supercritical extraction is more appropriate because this separation method is more selective for nicotine than extraction with commonly used liquid solvents (e.g., alcohol, acetone, hexane), which usually extract unwanted components as well.

With this in mind, the present study is aimed at evaluating the feasibility of obtaining nicotine by supercritical carbon dioxide (SC-CO_2) extraction of tobacco wastes (leaf bits and powder). Two important features distinguish this work from the studies reported above. First, the primary aim of those pioneer works was not nicotine production but, following a trend toward manufacturing mild cigarettes with light taste (i.e., with low nicotine and low tar), to reduce the nicotine content of tobacco to the desired levels without affecting its smoking properties. Second, the starting material was not tobacco waste but tobacco leaf and, as it is well known, matrices with different characteristics usually behave differently.

Finally, taking into account that dilute nicotine solutions can be easily obtained by aqueous extraction of tobacco wastes (5), this work also analyzes the feasibility of a nicotine production process that involve two stages, aqueous extraction of waste and subsequent concentration of the nicotine solution using SC-CO_2.

MATERIALS AND EXPERIMENTAL PROCEDURE

Black tobacco wastes (powder + leaf bits) from the Cigar Company of Havana Clavel No. 4 were used in the extraction experiments. Tobacco leaf from the San Luis tobacco harvest (1996) was the original raw material from which the wastes were recovered. The bulk density of the waste was 450 kg/m^3, and its particle size ranged between 0.2 and 1 mm. The original water content was about 10% w/w, and the average nicotine content was 1% w/w on a dry basis.

In tobacco, nicotine is partly in the free state and partly combined with the tobacco constituents. The latter type of nicotine must be liberated if extraction is to be completed. A treatment that helps in the liberation of combined nicotine is moistening with water (11). Therefore, in this work, the tobacco wastes were moistened until the water content was 20% w/w, the highest moisture level that did not cause operating problems during SC-CO_2 extraction. (When the water content exceeded this value, the extractor pressure built up to unsafe levels due to blockage of the metering valve. Attempts were made to avoid this obstruction by using a 2-μm in-line filter after the extractor, but in such cases blockage of the filter occurred.)

Tap water was used to make up the aqueous solutions containing nicotine together with other tobacco waste matter. According to Ref. 5, the solution was produced by leaching tobacco waste for 24 hours using a liquid/solid mass ratio such that the nicotine concentration of the solution was 1 g/L. Then the extract was pooled and filtered through glass wool.

The supercritical extraction experiments were performed in an extraction system designed and assembled at the Chemical Engineering Division of Castilla-La Mancha University. The flow schematic of this supercritical extraction unit is shown in Fig. 1, and its detailed description is given in a previous work (12). Operation of the system is as follows: Liquid carbon dioxide is pumped and heated to the extractor operating conditions. Next, the fluid is passed through the extractor. At the beginning of each run the system is maintained under static conditions for a period of approximately 15 minutes. This allows the system to compensate for the decrease in the amount of nicotine extracted during an initial "equilibration time" of about 5 minutes (time necessary to reach, again, the desired operating temperature and pressure in the extractor after they changed when all valves were opened to pressurize the various sections of the apparatus) with respect to the nicotine that would have been extracted during this same period at the desired operating conditions. A heated metering valve is then opened, which commences the flow of saturated supercritical fluid

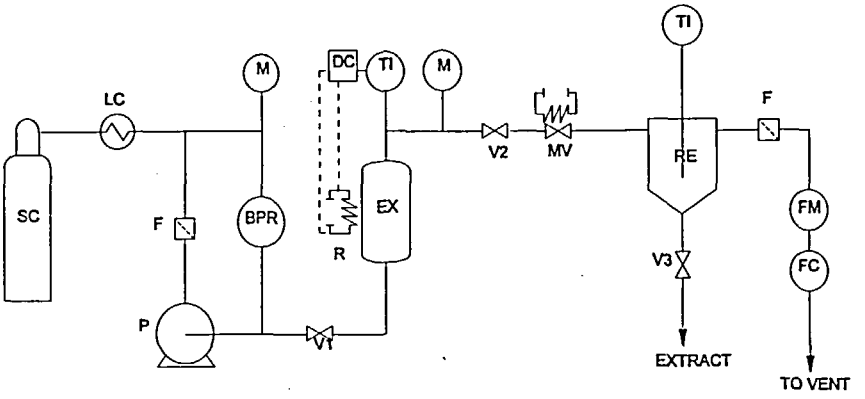

FIG. 1 Supercritical extraction system (SC, CO_2 steel cylinder; LC, liquid cooler; F, filter; P, pump; BPR, backpressure-regulating valve; M, manometer; V1, V2, and V3, shut-off valves; DC, temperature digital controller; R, resistor; EX, extractor; MV, metering valve; FM, turbine flowmeter; FC, flow computer; RE, receiver; TI, temperature indicator).

and the precipitation of the solute. Then the extracted products are collected in the separation vessel and the carbon dioxide, now in the gas phase, leaves the system through a turbine flowmeter.

The extractor used for the supercritical extraction of the solid tobacco wastes was a stainless steel tube of 17.48 mm inside diameter and 30.48 cm height. Nicotine extraction from the nicotine aqueous solutions was made in a 300-mL stirred autoclave (Autoclave Engineers Inc., Erie, PA). The separation vessel was a glass absorber filled with a 0.05 N H_2SO_4 solution.

The nicotine content of both the supercritical extracts and the nicotine aqueous solutions was determined by ultraviolet spectrophotometry following a method first proposed by Willits et al. (13) and later modified as indicated in Ref. 6. The modification allowed the omission of a time-consuming steam distillation and its replacement with an activated carbon cleanup stage to remove impurities that interfered with the analysis.

The absorbance was measured using a Perkin-Elmer UV/VIS spectrophotometer, model Lambda 3B, at three wavelengths: at λ_{max} (259 nm) and at 23 nm on either side of the maximum, i.e., 236 and 282 nm. The relationship between the absortion values was given by Willits et al. (13) as:

$$A'_{259} = 1.059[A_{259} - 0.5(A_{236} + A_{282})]$$

where A' is the corrected absorbance contributed by the nicotine in solu-

tion. A calibration line of absorbance versus nicotine concentration was produced and used to read off the concentration of nicotine in the samples.

RESULTS AND DISCUSSION

Supercritical Extraction of Solid Tobacco Wastes

This section reports the first results of the supercritical extraction experiments conducted on tobacco wastes (leaf bits and powder). Samples of about 100 g were used in each run. The extraction temperature, extraction pressure, and time of extraction were identified as the most significant variables of the process, and therefore their effect on nicotine recovery was studied in detail. With this end in view, a series of experiments was planned whose operational variables are given in Table 1.

The accuracy of the experimental data was determined by comparing the results obtained from four independent runs carried out under identical conditions (P = 25 MPa, T = 60°C, Q = 0.5 L/min). In these experiments the amount of nicotine recovered after 3 hours of extraction was very similar (3.9, 3.8, 3.8, and 3.7 mg/g dry waste), indicating that reproducibil-

TABLE 1
Extraction of Solid Tobacco Wastes: Operating Variables

Experiment	Pressure (MPa)	Temperature (°C)	Flow (L/min)	Extraction time (hours)
E-1	15	60	0.5	5
E-2	25	60	0.5	5
E-3	30	60	0.5	5
E-4	30	40	0.5	3
E-5	30	50	0.5	3
E-6	30	60	0.5	3
E-7	30	70	0.5	3
E-8	25	40	0.5	3
E-9	25	50	0.5	3
E-10	25	60	0.5	3
E-11	25	70	0.5	3
E-12	15	40	0.5	3
E-13	15	50	0.5	3
E-14	15	60	0.5	3
E-15	15	70	0.5	3
E-16	30	60	0.1	3
E-17	30	60	0.3	3
E-18	30	60	0.5	3
E-19	30	60	1	3

ity of the experimental data was good and, therefore, that replication of the experiments was not necessary. However, in order to minimize the experimental error, duplicate experiments were performed at all experimental conditions.

The nicotine extracted from tobacco wastes ranged from 2.4 to 4.3 mg/g dry waste, i.e., only 24–43% of the nicotine present in the waste was extracted. Compared with the data reported in the literature for the SC-CO_2 extraction of tobacco leaf, this yield is rather low. For example, Roselius, Vitzthum, and Hubert (1, 14, 15) studied extensively the separation of nicotine from tobacco using SC-CO_2 and reported extraction yields higher than 90% when the moisture content of tobacco was 25% and the extraction temperature and pressure were very similar to those used in this work.

This large difference between the yields obtained in the extraction of nicotine from two different starting materials (tobacco *waste* and tobacco *leaf*) should not be surprising. For example, in the extraction of vegetable products, not only the solubility of the substances to be extracted, but also the structure of the matrix and the way in which such substances are bound to the vegetable matrix have considerable influence. Thus, the results obtained in this work do not necessarily have to parallel those obtained in the SC-CO_2 extraction of tobacco leaves. Furthermore, taking this into account and considering that the bound state of the extract should be essentially the same in both matrices, the differences could be due to the external characteristics of the matrix constituents (i.e., a mixture of tobacco powder and leaf bits versus only tobacco leaf). This result is similar to that found by Eggers et al. (16) in the extraction of oil from rapeseed. In their studies they showed that the oil extraction efficiency differed depending on mechanical preconditioning of the seed (only peeling, peeling + cell cracking, peeling + shaping into thin platelets, etc.).

Figure 2 shows the evolution with time of the nicotine content in tobacco waste during extraction (Experiments E-1 to E-3 of Table 1). It can be observed that no significant decrease in nicotine occurs after 3 hours from the beginning of the experiment. Therefore, as a good compromise between the length of the experiment and the amount of solute extracted, in subsequent experiments an extraction time of 3 hours was chosen.

Figure 3 shows that the amount of nicotine extracted from tobacco waste at a given temperature increases with increasing pressure (Experiments E-4 to E-15), the increase being less significant at the smallest temperature. This result conforms with the general principles of supercritical fluid extraction (11) and other studies on the extraction of nicotine from tobacco leaf (1, 14, 15) which state that, in general, the solubility of a substance in a supercritical fluid increases with pressure at constant

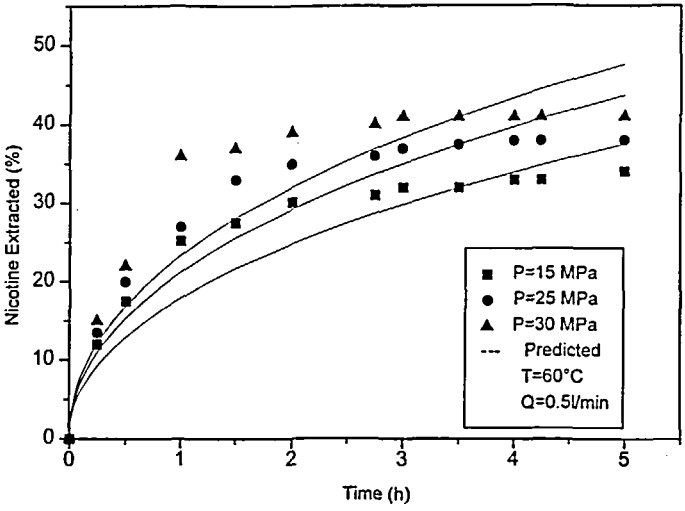

FIG. 2 Evolution with time of nicotine extracted from tobacco wastes.

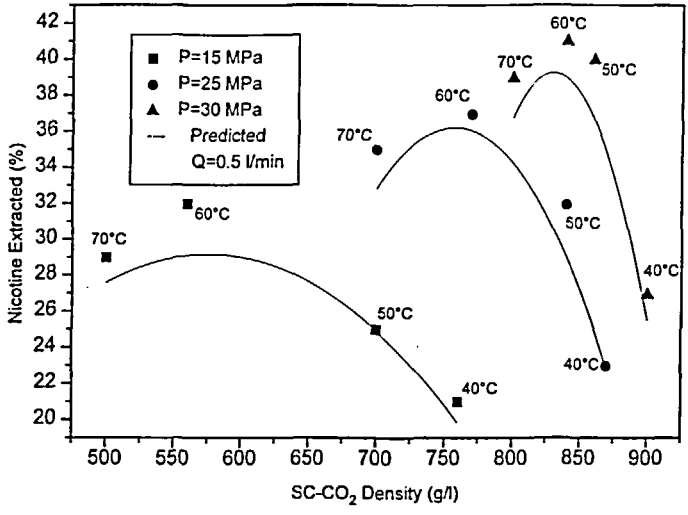

FIG. 3 Effect of pressure and temperature on the extraction efficiency of nicotine from tobacco wastes.

temperature. The fact that at 40°C the increase of nicotine extracted with increasing pressure is less pronounced than at higher temperatures might be due to the solute–matrix linkage, which should be much more difficult to break at low temperatures.

The effect of temperature is also shown in Fig. 3. It is observed that at all pressure levels the extraction yield increases with temperature from 40 to 60°C, probably because in this temperature range the breaking of the linkage between the solute and the solid matrix is favored as the temperature rises. In the 60–70°C temperature range, it can be observed that solvent density is the factor that enhances the extractor capability of SC-CO_2.

Finally, supercritical extraction Experiments E-16 to E-19 were performed to check the effect of fluid flow on the extraction yield. No significant influence of the variable was found, which indicates that external diffusion did not control the extraction process in the experimental range analyzed.

Modeling the SC-CO_2 Extraction of Nicotine

The yield of nicotine has been modeled using a mathematical model proposed in the literature for the extraction of natural products with SC-CO_2 (17). The model is based on a heat transfer analogy and neglects the external mass transfer resistance, the concentration profile along the bed, and the accumulation in the fluid phase. According to these hypotheses, the extraction yield (Y) is expressed as

$$Y = 100\left[1 - 6\sum_{n=1}^{\infty}\left(\frac{\left(\frac{hr}{a_n}\right)}{(hr(hr-1)+a_n^2)\exp\left(-\frac{a_n^2 Dt}{r^2}\right)}\right)\right] \quad (1)$$

with h defined as

$$h = \left(\frac{k_v W r}{3\rho D(1-\epsilon)V}\right)$$

where a_n is the root of the equation $a_n \cot(a_n) = 1 - hr$; r is the radius of the spherical particle (m); D is the internal diffusion coefficient (m^2/s); t is the extraction time (seconds); k_v is the volumetric partition coefficient of nicotine between the solid and fluid phases at equilibrium; W is the CO_2 mass flow rate (kg/s); ρ is the solvent density (kg/m^3); ϵ is the bed porosity; and V is the extraction volume (m^3).

The resulting model curves are shown in Figs. 2 and 3. It can be observed (Fig. 2) that the model tends to underestimate the nicotine extracted at short extraction times and overestimates it at long times. This may be attributed to the fact that, in tobacco, nicotine is partly in the free state and partly combined with tobacco constituents such as chlorogenic acid, citric acid, etc. (1). Thus, whereas some of it can be removed very easily, the rest is more difficult to extract. In spite of this, the model can be used to give a first estimation of the diffusion and partition coefficients, D and k_v, respectively.

Values obtained for the diffusion coefficient, D, range between 3.1×10^{-14} and 1.4×10^{-13} m^2/s. These values have the same order of magnitude as those observed for other chemical compounds (terpenes, sesquiterpenes, oxygenated terpenes, . . .) extracted from natural substrates at temperature and pressure ranges similar to the ones adopted in this work (18, 19). On the other hand, values obtained for the volumetric partition coefficient (k_v) range between 0.18 and 0.24 for solvent densities between 0.5 and 0.9 g/cm^3. Experimental information on the partition factor was given by Spiro and Kandiah (20) who evaluated the partition factors during extraction of ginger oleoresins from ginger rhizomes. They obtained mass partition factors (k_m) ranging from 0.21 to 0.38 for SC-CO_2 at densities of 0.415 and 0.775 g/cm^3.

Supercritical Extraction of Dilute Nicotine Solutions

The low efficiency of SC-CO_2 in the extraction of nicotine from tobacco wastes led us to consider the possibility of concentrating dilute nicotine aqueous solutions using SC-CO_2. The solutions were prepared from the tobacco wastes by extracting its nicotine content with water as indicated in the Materials and Experimental Procedure Section. In other words, the second part of the present study is aimed at evaluating the possibility of a nicotine recovery process that involves nicotine aqueous extraction from tobacco wastes and a subsequent concentration of the solution with SC-CO_2. More specifically, the objective of this section is to analyze the effect of the most significant variables of the SC-CO_2 extraction process, pressure and temperature, on nicotine recovery from aqueous solutions.

In this series of experiments the fluid flow rate was 0.3 L/min and the stirring speed was 250 rpm since preliminary runs showed that extraction efficiency was similar at lower flow rates (0.1 L/min) and higher stirring speeds (300 rpm) but decreased at 0.5 L/min (higher flow rate) and 200 rpm (lower stirring speed). As in SC-CO_2 extraction from solid wastes, the accuracy of the experimental data was good. However, to minimize

experimental error, duplicate experiments were performed at all experimental conditions.

Figure 4 shows the evolution with time of the percentage of nicotine extracted from the aqueous solution. As can be seen, only 24% of the nicotine was recovered after 10 hours of extraction, the fractional yield in the last 2 hours being less than 1%. For subsequent runnings, an extraction time of 10 hours was used.

Figure 5 shows that the extraction yield increases linearly with increasing pressure, according to the well-known fact that the solubility of a substance in a supercritical fluid increases with fluid density at a given temperature and, therefore, with pressure.

The effect of temperature is presented in Fig. 6. As can be seen, the nicotine extraction yield was not affected by this variable in the experimental range analyzed. This result may be explained by considering that nicotine, unlike most other molecules that are soluble in supercritical gases, does not exhibit larger solubility as the temperature rises (21). Although the extractability of a compound is not determined by its solubility alone, in this particular system the linkage of nicotine to water should not be strong enough to affect extraction.

These yields are rather low (20–28% w/w) compared to the yields obtained in the SC-CO_2 extraction of solid wastes (24–43% w/w). Therefore,

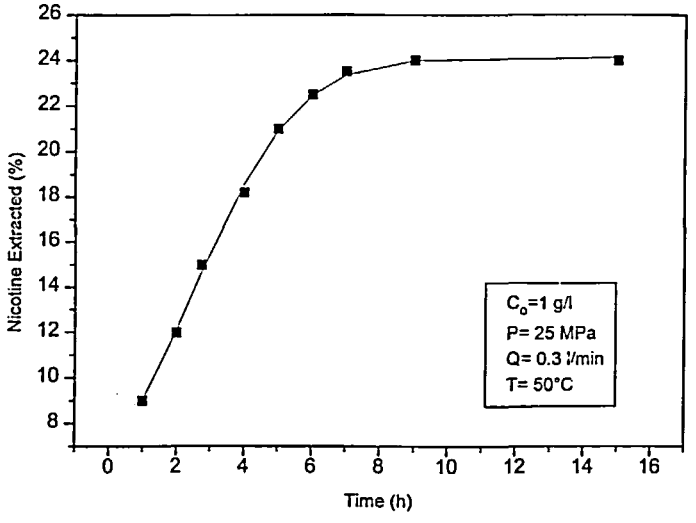

FIG. 4 Kinetics of nicotine recovery from aqueous solutions.

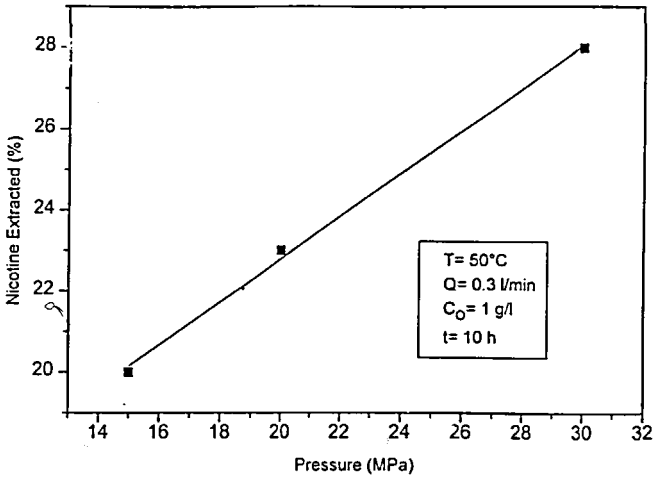

FIG. 5 Effect of pressure on the extraction of nicotine from aqueous solutions.

the two-stage process involving nicotine aqueous extraction of the waste and subsequent concentration of the dilute aqueous solution with SC-CO_2 does not seem to offer any advantage versus direct extraction of the waste with SC-CO_2.

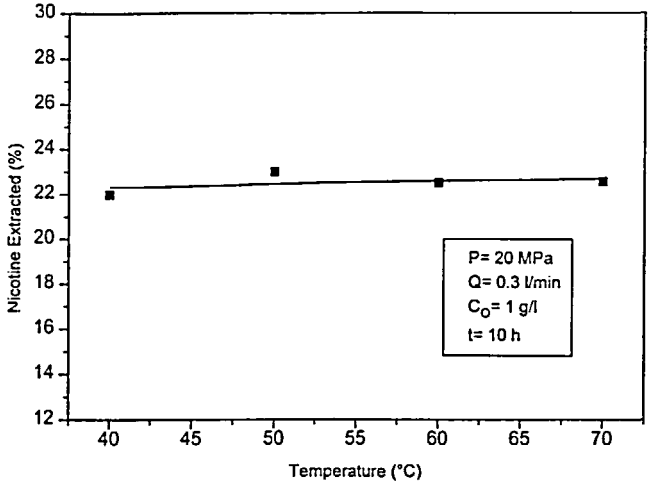

FIG. 6 Effect of temperature on the extraction of nicotine from aqueous solutions.

CONCLUSIONS

The recovery by SC-CO_2 extraction of nicotine from wastes of the tobacco processing industry has been studied experimentally. It has been found that the extraction yield increases with pressure, which was attributed to the increasing solubility power of the fluid with increasing pressure. The influence of temperature differed depending on the temperature range analyzed. Thus, at lower temperatures (40–60°C) the increasing yield with temperature was imputed to a solute-matrix linkage that is easier to break as temperature rises. At higher temperatures (60–70°C) the decrease in yield with temperature can be explained in terms of solvent density. Finally, the constant extraction yield value at different fluid flows allows us to argue that the extraction process is not controlled by external diffusion, at least in the experimental range analyzed.

Modeling of the SC-CO_2 extraction of nicotine was attempted using a model proposed in the literature for studying the supercritical extraction of natural products (17). Although fitting of the data was not very satisfactory, it allowed us to obtain first estimates of both the internal diffusion and the volumetric partition coefficients.

The relatively poor results obtained in the first part of the work (the extraction yields ranged between 24–43% w/w) led us to consider the possibility of recovering the nicotine content of tobacco wastes by a two-stage process involving aqueous extraction of nicotine from tobacco wastes and subsequent nicotine concentration of the liquid solutions using SC-CO_2.

Aqueous solutions containing 1 g/L of nicotine were obtained by leaching tobacco wastes with water for 24 hours. The SC-CO_2 extraction of nicotine from these solutions was investigated at different pressures and temperatures. It was found that the extraction yield increased with pressure, but no temperature effect was observed. The first result was easy to explain since fluid density, and therefore its solubility power, increases with pressure. The second finding could be imputed to the fact that nicotine does not tend to exhibit larger solubilities as the temperature rises.

REFERENCES

1. P. Hubert and O. G. Vitzthum, *Angew. Chem. Int. Ed. Engl.*, *17*, 710–715 (1978).
2. R. M. Browning, British Patent 2,173,985 (1986).
3. B. Dumery, French Patent 2,340,349 (1983).
4. J. B. Claffey, *Ind. Eng. Chem.*, *44*, 729 (1952).
5. C.V. Narasimha and M. K. Chakraborty, *Res. Ind.*, *37*, 115–117 (1992).

6. D. L. C. Millen and W. R. Murphy, *Ind. Eng. Chem. Res.*, *32*, 3056–3060 (1993).
7. J. B. Claffey, C. O. Badgett, J. J. Skalamera, and G. W. Philips, *Ind. Eng. Chem.*, *42*, 166–171 (1950).
8. D. F. Williams, *Chem. Eng. Sci.*, *36*, 1769–1788 (1981).
9. G. Donsi, E. Reverchon, P. Salatino, and V. Tufano, *Chem. Biochem. Eng. Q.*, *4*, 21–24 (1990).
10. H. Uematsu, J. Itoh, M. Takeuchi, and Y. Yonei, in *Proceedings of the 3rd International Symposium on Supercritical Fluids, Strasbourg*, Institut National Polytechnique de Lorraine, Vandoeuvre-les-Nancy, 1994, pp. 335–340.
11. E. Stahl, K. W. Quirin, and D. Gerard, "Application of Dense Gases to Extraction and Refining," in *Dense Gases for Extraction and Refining*, Springer-Verlag, Berlin, 1987.
12. A. García, A. de Lucas, J. Rincón, A. Alvarez, I. Gracia, and M. A. García, *J. Am. Oil Chem. Soc.*, *73*, 1127–1131 (1996).
13. C. O. Willits, M. L. Swain, J. A. Connely, and B. A. Brice, *Anal. Chem.*, *22*, 430–433 (1950).
14. W. Roselius, O. Vitzthum, and P. Hubert, German Patent 2,043,537 (1972).
15. W. Roselius, O. Vitzthum, and P. Hubert, US Patent 4,153,063 (1979).
16. R. Eggers, U. Sievers, and W. Stein, *J. Am Oil Chem. Soc.*, *62*, 122–130 (1985).
17. K. D. Bartle, A. A. Clifford, S. B. Hawthorne, J. J. Langenfeld, D. J. Miller, and R. A. Robinson, *J. Supercrit. Fluids*, *3*, 143 (1990).
18. E. Reverchon and L. Sesti Ossèo, in *Proceedings of the 3rd International Symposium on Supercritical Fluids, Strasbourg*, Institut National Polytechnique de Lorraine, Vandoeuvre-les-Nancy, 1994, pp. 189–193.
19. A. de Lucas, J. Rincón, and I. Gracia, in *Proceedings of the 26 Reunión Bienal de la Real Sociedad Española de Química, Cádiz*, Universidad de Cádiz, Cádiz, 1997, pp. 513–515.
20. M. Spiro and M. Kandiah, *Int. J. Food Sci. Technol.*, *25*, 566 (1990).
21. K. Schulz, E. E. Martinelli, and G. A. Mansoori, "Supercritical Fluid Extraction an Retrograde Condensation (SFE/RC). Applications in Biotechnology," in *Supercritical Fluid Technology. Reviews in Modern Theory and Applications* (T. J. Bruno and J. F. Ely, Eds.), CRC Press, Boca Raton, FL, 1991.

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