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Supercritical Extraction of Essential Oil from Aniseed (*Pimpinella anisum* L) Using CO_2: Solubility, Kinetics, and Composition Data

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Supercritical fluid extraction (SFE) from aniseed using carbon dioxide was performed at 30 °C and pressures of 80−180 bar. The chemical composition of the SFE extract was determined by GC-MS; the quantitative analysis was done by GC-FID and TLC. The total amount of extractable substances or global yield (mass of extract/mass of feed) for the SFE process varied from 3.13 to 10.67% (mass). The solubilities of the anise essential oil in CO_2 were 0.0110, 0.0277, 0.0143, and 0.0182 kg of solute/kg of CO_2 at 80, 100, 140, and 180 bar, respectively. The major compounds identified and quantified in the extracts were anethole (∼90%), γ-himachalene (2−4%), *p*-anisaldehyde (<1%), methylchavicol (0.9−1.5%), *cis*-pseudoisoeugenyl 2-methylbutyrate (∼3%), and *trans*-pseudoisoeugenyl 2-methylbutyrate (∼1.3%). The Sovová model described quite well the experimental overall extraction curves.

KEYWORDS: Aniseed; chemical composition; *Pimpinella anisum*; mass transfer rate; solubility; supercritical extraction

INTRODUCTION

Supercritical fluid extraction (SFE) has been extensively investigated as an alternative process to produce extracts from vegetable matrices such as essential oils, oleoresins, and pigments. For thermally sensitive compounds, SFE can replace steam distillation advantageously due to the use of moderate temperatures. In addition, it is often found that with steam distillation, yields are considerably lower than that of the SFE process. Even so, conventional solvent extraction can produce higher yields compared to both SFE and steam distillation. In any case, the composition of extracts obtained by steam distillation, conventional solvent extraction, and SFE can differ appreciably as demonstrated by Monteiro et al. (*1*). Therefore, the choice of a suitable process will be determined by the intended use of the vegetable extract.

Anise belongs to the Umbelliferae family and originates from Asian countries, Egypt, and Greece. It is cultivated in Turkey, Russia, South Africa, Latin America, and Brazil. In general, the essential oil is extracted from the fruits, but the roots may also be used (*2*). According to Sousa et al. (*3*) aniseed contains 1.5−6.0% (mass) of a volatile oil consisting primarily of anethole, but it may also contain as much as 8−11% (mass) of lipids rich in fatty acids, such as palmitic and oleic acids, and approximately 4% (mass) of carbohydrates and 18% (mass) of protein. The phytotherapeutic applications of the plant include digestive, carminative, diuretic, and expectorating actions. Anise infusions are largely used for problems in the intestinal tract. Aniseed oil is used in food processing to impart flavor to cakes, alcoholic beverages such as liquors, sweet snacks, and so on. Anethole, the aniseed oil major compound, is largely used as a substrate for the synthesis of various substances of pharmaceutical interest such as chloral, an anticonvulsion agent, and pentobarbital (*3*). Pourgholami et al. (*4*) investigated the anticonvulsant effects of *Pimpinella anisum* essential oil. Boskabady and Ramazani-Assari (*5*) reported the bronchodilatory effects of the essential oil, the aqueous extract, and the ethanolic extract of *P. anisum*; the authors concluded that the relaxant effect of the plant is not due to an inhibitory effect of histamine but instead due to inhibitory effects on muscarinic receptors. Tunc et al. (*6*) studied the fumigant activity of the essential oils of *Pimpinella anisum*, *Cuminum cyminum*, *Eucalyptus camaldulensis*, *Origanum syriacum* var. *bevanii*, and *Rosmarinus officinalis* against eggs of two stored-product insects; the exposure to vapors of essential oils from anise and cumin resulted in 100% mortality of the eggs, whereas the others achieved mortalities ranging from 45 to 89%. Ondarza and Sanchez (*7*) compared the yield and the quality of the oil and oleoresin obtained by both SFE and steam distillation. These authors suggested that the SFE extract obtained at 167 bar and 55 °C had a better quality than the steam-distilled oil. Calame and Steiner, cited by Moyler (*8*), obtained an SFE anise extract

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at 300 bar and 40 °C and subsequently fractionated it at 75 bar and 40 °C. The yields were 9.7% for the SFE process and 2.1% for the steam distillation process.

Tuan and Ilangantileke (*9*) and Della Porta et al. (*10*) applied SFE to star anise (*Illicium verum* Hook), another source of anethole. Tuan and Ilangantileke (*9*) compared the yields of both processes: steam distillation and SFE; they reported yields of 10.2 and 11.2% and anethole contents of 92.2 and 89%, respectively.

Despite the available information related to obtaining anise essential oil by SFE, kinetic data required for process design and development are still lacking. Therefore, the objective of this work was to study SFE applied to the system aniseed/CO_2 using a process design approach. Thus, the solubility of the pseudoternary system aniseed (cellulosic structure + solute)/CO_2 was measured. The effects of pressure on kinetics were assessed through the composition of the extract, the global yield, and the overall extraction curves (OEC); the overall extractions curves, mass of extract, and yield as a function of extraction time or CO_2 amount were modeled using the pseudo-steady-state model of Sovová (*11*).

MATERIALS AND METHODS

Raw Material Characterization and Preparation. The aniseeds were bought from Rainha da Matta Ltda (São Paulo, Brazil; 2000 crop, harvested in February, lot 224 from Turkey). The seeds were stored in plastic bags, sealed under vacuum (Barbi Ind Mecânica Ltda, São Paulo, Brazil), and kept in a domestic freezer (Brastemp, model 7501, São Paulo, Brazil) at −5 °C. Before the SFE assays, the seeds were triturated in a mill (Brabender OHG, model 981400, series 968052, Duisburg, Germany). The triturated aniseeds were separated according to their sizes (standard testing sieve, series Tyler). Mesh sizes −24 and +48 were selected for the assays. The particles' true density was determined by helium pycnometry (Micrometrics, model Multivolume pycnometer 1305) in the Analytical Chemistry Facilities of the Institute of Chemistry, IQ/Unicamp. The total porosity (bed + particles) was evaluated using the particles' true density and the bed apparent density. The humidity of the seeds was determined by the xylol (P. A. Ecibra, lot 12540, São Paulo, Brazil) distillation method (*12*).

The content of volatile oil was determined by steam distillation using 0.172 kg of whole seeds; the process took 1 h and 30 min, and the assay was replicated. The oil was collected using a graduated pipet and weighed in an analytical scale (Satorius, model A 200S, Goettingen, Germany). The yield was calculated as the mass of oil divided by the mass of feed.

Extraction Procedure for Total Amount of Soluble Material. The total amount of extractable material or global yield (X_0) at a given temperature and pressure was determined using a Speed SFE system (Applied Separations, Allentown, PA) equipped with a 3 or 5 mL extraction cell (Thar Designs, Pittsburgh, PA). The bed density was kept at 760 kg of *P. anisum*/m^3 of bed. Carbon dioxide was admitted into the system at a flow rate of 7.08×10^{-5} kg/s, up to the point where no solute was observed at the exit of the column. The amount of CO_2-soluble material was calculated as the ratio of the total mass of extract and the total initial mass of *P. anisum*. The experiments were run at pressures of 80, 100, 140, and 180 bar, at 30 °C.

Experimental Setup and Procedure: Solubility and Overall Extraction Curves (OEC). The solubility and the OEC assays were done in an SFE unit containing a fixed bed extractor (or equilibrium cell, maximum allowed pressure of 200 bar) of 0.385×10^{-3} m^3 (Berghof model HB-500, series 57050209, Eningen, Germany), operating semicontinuously as described by Rodrigues et al. (*13*). The temperature control was done with thermostatic baths (PolyScience, model 9510, Niles, IL), and the system pressure was maintained with an HPLC-type pump (ThermoSeparation Products, model ConstaMetric 3200 P/F, series 104322, Riviera Beach, FL).

The assays were performed using 0.191 kg (±0.001 kg) of the triturated aniseeds (−24 and +48 mesh, half of each); thus, the hydrodynamic characteristics of the fixed bed were held constant. The temperature control system was turned on ∼2 h before the start of the experimental run to allow the system to reach thermal equilibrium. Afterward, the system was pressurized to the preselected value and the extraction started. Samples of extracts were collected every 10 min in a replaceable separation tank (10 mL glass flasks). The solvent (CO_2, 99.9% purity, White Martins Gases Industriais, São Paulo, Brazil) flow rate was continuously monitored using a digital flow meter (±0.01 mL/min, Sierra Instruments, Inc., model 821-S1-L-1-V4, Monterey, CA) and a flow totalizer (±0.02 L, Laos, model G-1, São Paulo, Brazil). The solute/solvent separation system consisted of a micrometering valve, a separation tank (10 mL glass flasks), and an adsorption column (a glass column packed with Porapak Q, 80/100 mesh, Waters, Milford, MA); the adsorption or capture column was used to prevent losses of extract in the solvent stream. The experimental runs took 3 h, the temperature was held constant at 30 °C, and pressures of 80, 100, 140, and 180 bar were used; assays were not replicated.

The solubility of the solute in carbon dioxide was measured by the dynamic methods using the procedure described by Rodrigues et al. (*13*), and the assays were replicated. The search for the saturation condition was done using solvent flow rates in the range of $(1.23-6.12) \times 10^{-5}$ kg/s.

Characterization of the Anise Extracts. *Chromatographic Analysis Coupled to Mass Spectrometry.* The chemical composition of the anise extracts was determined using a GC-MS (Shimadzu, model QP 5000, Kyoto, Japan) equipped with a capillary column DB-5 (30 m × 0.25 mm × 0.25 μm, J&W Scientific, Folsom, CA). The carrier gas was helium (1.7 mL/min, 99.99% purity, White Martins Gases Industriais, Campinas, Brazil). The column was heated at 50 °C for 5 min, programmed at 5 °C/min to 280 °C, and kept at 280 °C for 5 min. The sample split ratio was 1/30. One microliter of the extract (0.005 g of extract diluted in 1.0 mL of ethyl acetate, P.A., chromatographic grade, EM Science, lot 3903991) was injected. The identification of the substances was based on (i) comparison of the substance's mass spectrum with GC-MS system data bank (Nist 62 Library), (ii) comparison of the mass spectrum with data in the literature (*14*), and (iii) retention index (*15*). Quantification of the extracts' composition was done using a gas chromatograph (GC-FID Shimadzu, model GC 17A, Kyoto, Japan) under the same conditions described for the GC-MS.

Thin-Layer Chromatography (TLC). The SFE extracts were fractionated into heavy and light fractions by TLC by comparing the displacement of SFE extracts with that of steam distillation extracts. TLC was performed using silica plates (PF254, Merck 20 × 20 cm, 1 mm height) and a mixture 80:20 of hexane (EM Science, chromatographic degree, lot 38211, Gibbstown, NJ) and ethyl acetate (EM Science, chromatographic degree, lot 39039911) as the mobile phase. The plates were revealed by UV radiation (254 and 260 nm), and the substances were extracted from the silica gel with ethyl acetate and dichloromethane (EM Science, chromatographic degree, lot 36289). The solvents were evaporated with the aid of a rotary evaporator (Buchi RE, model 215404, Flawil, Germany). The fractions were gravimetrically quantified using the mass of the extract applied in the plate and the mass of the fractions recovered at the end of extraction from the TLC plate. The substances of the recovered fractions were identified by the GC-MS system and quantified as indicated previously.

Quantification of Anethole in the SFE Extract. The anethole in the SFE extracts was quantified using the external standard method (*16*). The anethole (99% purity, Aldrich, lot 06605HR, Milwaukee, WI) was diluted in ethyl acetate (EM Science, chromatographic degree, lot 39039911), and 1.0 μL of sample was injected in the GC-FID system using the conditions given previously.

Calculation Procedures. Using the experimental data, the overall extraction curves were fitted to a spline using two or three straight lines. The spline fitting and the statistical analysis were done using the procedures PROC REG and PROC NLIN of SAS 6.12 (*17*). The first line was identified with the constant extraction rate period (CER). From the spline the extraction rate for the CER period (M_{CER}), the time corresponding to the interception of the first two lines or the duration of the CER period (t_{CER}), and the mass ratio of solute in the supercritical

Table 1. Global Yield (X_0), Solubility (Y^*), Saturation Solvent Flow Rate ($Q^*_{CO_2}$) as a Function of Pressure at 30 °C

P, bar	$X_0 \times 10^2$, kg of solute/kg of CO_2	$Y^* \times 10^3$, kg of solute/kg of CO_2	$Q^*_{CO_2} \times 10^5$, kg/s	t^*_{CER}/60, s
80	3.13	11.0	3.35	85
100	7.94	27.7	3.47	65
140	10.48	14.3	3.27	80
180	10.67	18.2	3.45	85

phase (Y_{CER}) were evaluated; using these parameters the fluid-phase mass transfer coefficients were calculated (*18*).

RESULTS AND DISCUSSION

The mean humidity of the aniseeds was 8.5%. The triturated aniseed particles had a true density of 1321 kg/m^3, the bed apparent density was 496 kg/m^3, and the porosity of the bed plus particles was 0.63.

Table 1 shows the total amount of extractable material or global yield (X_0) and the solubility measure for the system aniseed + CO_2, as a function of pressure for the 30 °C isothermal. The global yield increased with pressure; the increase from 140 to 180 bar was marginal. On the other hand, the solubility (Y^*) showed a maximum at 100 bar. This behavior can be associated with the composition of the extracted mixture: In the SFE process as the pressure increases for a given temperature, the carbon dioxide solvent power increases; thus, larger and more polar substances can be co-extracted. This was indeed observed by TLC: The SFE extracts were fractionated into three fractions, F1, F2, and F3. For all experimental conditions the following was observed: the heaviest fraction (F1) represented ~2.9% of the total extract and was found to be constituted of a mixture of fatty acids and hydrocarbons. Fraction F2 was made up of a mixture of substances usually found in aniseed essential oil, among them *p*-anisaldehyde and other heavier compounds (higher molecular weight), and represented ~5.8% of the total extract. The lightest fraction, fraction F3, contained exclusively essential oil compounds and accounted for 91.3% of the total extract.

Table 2 shows the evolution of the extracts' composition with respect to the extraction time, for the assays performed at the saturation solvent flow rate ($Q^*_{CO_2}$); the effect of pressure on the anise extracts' composition is also shown. The composition of the steam-distilled oil is shown in **Table 3**; **Table 4** shows the effect of solvent flow rate on the composition of the extract retained in the adsorption column inserted downstream with respect to the separation vessel.

From **Tables 2** and **3** it can be observed that the anise essential oil and the SFE anise extracts have similar chemical compositions. The extract retained in the adsorbent column had the same chemical composition (**Table 4**) as the extract in the separation vessel (**Table 2**), which indicates that no further fractionation of the extract occurred in the separation vessel. The major compound in all of the extracts (essential oil and SFE) is anethole; the highest anethole content (90%) is in the extract from the steam distillation process. Similar results were obtained by Ondarza and Sanchez (*7*) and Santos et al. (*2*). Data in **Table 2** show that the relative proportion of methylchavicol is quite low (average of 1.1%) compared to that of *cis*- and *trans*-pseudoisoeugenyl 2-methylbutyrate (average of 5.5%). On the other hand, for the steam distillation oil there was no difference between the relative proportions of the above substances. The presence of *cis*- and *trans*-pseudoisoeugenyl 2-methylbutyrate has been reported in the literature (*19*−*21*).

Table 2. Composition of the SFE Anise Extract as a Function of the Extraction Time[a]

	relative proportion, area %, for extraction time intervals/60, s					
compound	0–20	20–40	40–60	60–80	80–100	100–120
	80 bar and 3.33×10^{-5} kg/s					
methylchavicol	1.56	1.33	1.33	1.19	0.85	0.79
p-anisaldehyde	0.92	0.84	0.83	0.82	0.72	0.72
anethole	89.16	89.14	89.37	89.18	89.23	88.30
γ-himachalene	2.05	2.11	2.12	2.22	2.64	3.11
cis-pseudoiso-eugenyl 2-methyl-butyrate	3.59	3.74	3.65	3.81	4.16	4.15
trans-pseudoiso-eugenyl 2-methyl-butyrate	2.19	2.11	1.97	1.95	1.52	1.24
not identified	0.53	0.73	0.73	0.83	0.88	1.69
	100 bar and 3.47×10^{-5} kg/s					
methylchavicol	1.22	1.45	0.98	0.91	0.86	0.79
p-anisaldehyde	n.d.	0.68	0.64	0.62	0.62	nd
anethole	90.29	89.59	88.97	86.87	85.35	84.52
γ-himachalene	2.36	2.29	2.79	3.14	3.12	3.14
cis-pseudoiso-eugenyl 2-methyl-butyrate	3.42	3.32	3.78	3.48	3.41	3.20
trans-pseudoiso-eugenyl 2-methyl-butyrate	1.76	1.79	1.49	1.25	1.21	1.11
not identified	0.95	0.88	1.35	3.75	5.43	7.24
	140 bar and 3.27×10^{-5} kg/s					
methylchavicol	1.38	1.35	1.16	1.08	0.92	0.93
p-anisaldehyde	0.80	0.79	0.70	0.70	nd	nd
anethole	88.17	88.19	87.54	87.42	87.62	86.30
γ-himachalene	2.15	2.23	2.52	2.67	2.99	3.53
cis-pseudoiso-eugenyl 2-methyl-butyrate	3.88	3.69	3.90	3.82	3.65	3.49
trans-pseudoiso-eugenyl 2-methyl-butyrate	2.22	1.77	1.74	1.67	1.39	1.30
not identified	1.40	1.98	2.44	2.64	3.43	4.45
	180 bar and 3.45×10^{-5} kg/s					
methylchavicol	1.26	1.25	1.22	1.16	1.08	0.99
p-anisaldehyde	0.80	0.77	0.76	0.72	nd	nd
anethole	87.82	88.18	86.66	86.48	86.55	85.73
γ-himachalene	2.26	2.40	2.60	2.71	2.92	2.98
cis-pseudoiso-eugenyl 2-methyl-butyrate	4.07	3.99	3.97	3.90	3.80	3.74
trans-pseudoiso-eugenyl 2-methyl-butyrate	2.11	1.90	1.85	1.76	1.62	1.55
not identified	1.68	1.51	2.94	3.72	4.03	5.01

[a] Data from GC-FID analysis. nd, not detected.

Table 2 shows, for every pressure, that the amount of anethole remained approximately constant for all extraction time intervals; nonetheless, at 100 bar, it decreased by ~6% from the first extraction time interval (0−20 min) to that collected over the last extraction time interval (100−120 min). It was found that the content of methylchavicol decreased during the extractions for all conditions studied. On the other hand, the content of *p*-anisaldehyde recorded an appreciable decrease at both pressures of 140 and 180 bar, and it was not detected in the last two time intervals (80−100 and 100−120 min). The amount of γ-himachalene increased by ~1% over the range of experimental conditions used. The content of the substance identified as *cis*-pseudoisoeugenyl 2-methylbutyrate steadily increased during the extraction at 80 bar and remained approximately

Table 3. Composition of the Aniseed Oil Obtained by Steam Distillation[a]

compound	relative proportion, area %
methylchavicol	2.82
p-anisaldehyde	1.90
anethole	90.88
γ-himachalene	0.75
cis-pseudoisoeugenyl 2-methylbutyrate	2.25
trans-pseudoisoeugenyl 2-methylbutyrate	0.40
not identified	3.65

[a] Data from the GC-MS analysis; yield was 0.72% (mass of oil/mass of feed).

Table 4. Composition of the SFE Anise Extract Retained in Capture Column for Different Solvent Flow Rates at 100 bar and 30 °C; Extraction Time of 140 min

	relative proportion, area %, for solvent flow rate $\times 10^5$, kg/s				
compound	1.87	2.38	3.47	3.55	5.83
methylchavicol	1.31	1.21	0.56	1.50	1.03
anisaldehyde	0.99	1.09	1.11	1.02	1.09
anethole	88.07	88.27	83.27	88.56	88.87
γ-himachalene	2.56	2.66	3.04	2.98	3.08
cis-pseudoisoeugenyl 2-methylbutyrate	3.57	3.51	7.00	3.06	3.11
trans-pseudoisoeugenyl 2-methylbutyrate	1.20	1.14	2.18	0.92	0.94
not identified	2.30	2.12	2.84	1.96	1.88

constant for the other pressures, whereas the content of the *trans* isomer decreased for all conditions. To verify the significance of these differences, a statistical analysis was performed.

The analysis of variance (ANOVA) was done for data in **Table 2**, having the substances relative proportions (area percent) as the response variables and time intervals and pressure as factors. On the basis of the *F*-ANOVA, the effect of pressure was significant ($p < 0.07$) for every substance except methylchavicol ($p = 0.18$). The effect of the extraction time intervals was significant ($p < 0.05$) for all substances except *cis*-pseudoisoeugenyl 2-methylbutyrate ($p = 0.86$).

The quality of the experimental data of solubility measured by the dynamic method requires the composition of the extract to remain constant during the measuring time interval or the duration of the constant extraction rate period (t^*_{CER} of **Table 1**) as discussed by Rodrigues et al. (*13*). A significant *F*-ANOVA tells us that at least one pair of means is different. To identify which pairs are significantly different, a Ryan−Einot−Gabriel−Welsch multiple-test range (*22*) was applied for all response variables where *F*-ANOVA was significant. For all substances, the differences were not significant among the first three time intervals (0−20, 20−40, and 40−60 min); for anethole the effect was not significant up to the fifth time interval (80−100 min). Thus, as required by the dynamic method for the measuring of the solubility of a solute in a supercritical solvent, the composition of the multicomponent mixture remained constant ($t_{CER} < 85$ min, **Table 1**).

Pressure affects the solubility of pure components in carbon dioxide; therefore, the effect of pressure on the composition of the SFE extracts is expected to be significant. The effect of pressure was evaluated using the interaction plots (*23*): The relative proportions of methylchavicol, γ-himachalene, and *trans*-pseudoisoeugenyl 2-methylbutyrate were not affected. At 80 bar, the relative proportions of *cis*-pseudoisoeugenyl 2-methylbutyrate increased at the last extraction time interval (100−120 min.); it decreased for the other pressures. The relative proportions of *p*-anisaldehyde remained approximately constant at 80 bar; at the other pressures this substance was not detected in some samples (**Table 2**). For anethole the relative proportion decreased smoothly for all extraction time intervals; nonetheless, at 80 bar it remained approximately constant, whereas at 100 bar it decreased more rapidly, as can be observed in **Figure 1**.

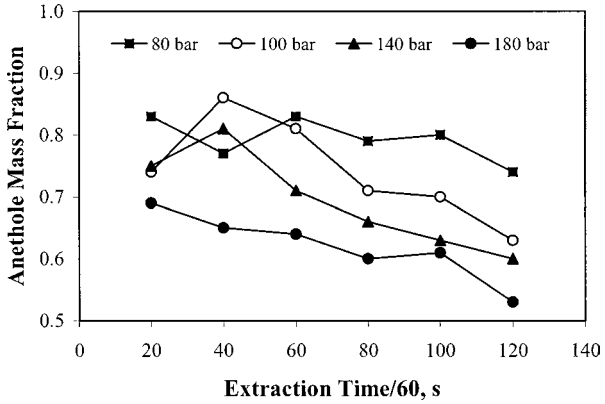

Figure 1. Mass fraction of anethole in extracts from runs performed at 30 °C and the saturation solvent flow rate ($Q^*_{CO_2}$, **Table 1**).

Overall Extraction Curves. Knowledge of the effects of the operating variables particle size distribution, bed and particle porosity, pressure, temperature, and solvent flow rate on the yield and extract composition is needed for process design. To estimate manufacturing costs, overall extraction curve data are required. In addition, the availability of a model to predict OEC is highly desirable. Several models have been proposed to describe SFE from solid materials (*11*, *24*−*28*). Nevertheless, the model of Sovová (*11*) has the advantage of providing a reasonably simple analytical solution to the mass balance equations and a good physical description of the process; it was chosen to describe the OEC. The Sovová model assumes pseudo-steady-state plug flow; temperature, pressure, and solvent velocity are kept constant throughout the extraction. The bed is homogeneous with respect to the solute and particle size distributions.

The procedure employed to calculate the model's parameters was as described by Povh et al. (*18*) except that a search for the best values of t_{CER} and k_{Xa} was allowed in order to minimize the objective function:

$$OF = \frac{1}{n}\sum_i (m_{ext} - m^{calcd}_{ext})_i^2 \qquad (1)$$

The estimated parameters are shown in **Table 5** along with the values of the extracting parameter $k = k_{Xa}\rho_{CS}X_k/k_{Ya}\rho_{CO_2}Y^*$. The modeling was performed for runs carried out at a solvent flow rate at least 1.2 larger than the saturation solvent flow ($Q^*_{CO_2}$). **Figures 2** and **3** compare the experimental and calculated OECs. In these figures, the percent of total extraction is represented by the ratio between the extract mass and the global yield (X_0). In **Figure 2**, in addition to the best-fit curve, curves calculated for other values of the extracting parameter, *k*, are also shown; all other parameters were kept constant. The most significant variable of the Sovová model is the ratio of ruptured to unruptured cells, X_p/X_0. A poor estimate of this parameter is responsible for a poor estimate of the OEC, as can be seen in **Figure 2**. The ratio X_p/X_0 or the parameter *k* is a direct measure of the efficiency of the pretreatment as well as an indirect measure of the solvent power. The more severe the pretreatment,

Table 5. Estimated Parameters for the Sovová Model

$Q_{CO_2} \times 10^5$, kg/s	P, bar	$Y^* \times 10^3$, kg/kg	Z	k	X_p/X_0, kg/kg	$k_{Ya} \times 10^4$, s^{-1}	$k_{Xa} \times 10^5$, s^{-1}	t_{CER}/60 s	t_{FER}/60 s
				0.1614	25.0			21.4	73
				0.1537	28.6[a]			24.5	83
5.17	80	11.0	2.0477	0.1075	50.0	3.2705	1.1364	42.8	140
				0.0538	75.0			64.2	202
6.12	100	27.7	1.9311	0.1706	32.2[a]	3.1373	1.4723	24.9	81
3.65	140	14.3	2.0687	0.1954	14.9	1.9035	3.3591	45.9	162
4.45	140	14.3	2.0051	0.2352	14.9[a]	2.2493	4.7795	38.9	138
4.60	180	18.2	2.2676	0.2037	17.2[a]	2.5074	6.2172	30.7	119

[a] Best fit value; Q_{CO_2} = solvent flow rate; Y^* = solubility of the solute in the solvent phase, Z = parameter of the Sovová model for the CER period; $k = k_{Xa}\rho_{CS}X_k/k_{Ya}\rho_{CO_2}Y^*$ is a model parameter used to introduce the solid-phase mass transfer coefficient (*11*); X_p = mass ratio of solute in ruptured cells (easily accessible solute); X_0 = initial solute mass ratio of solute in the solid phase; k_{Ya} = fluid-phase mass transfer coefficient; k_{Xa} = solid-phase mass transfer coefficient; t_{CER} = end of the CER period; t_{FER} = end of the falling rate period.

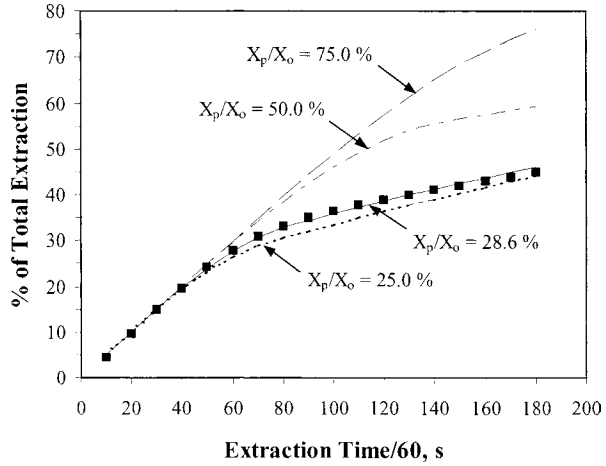

Figure 2. Comparison between experimental and calculated overall extraction curve: 30 °C, 5.17 × 10^{-5} kg/s, 80 bar; the effect of the extraction parameter (k) is shown using the fraction of ruptured cells (X_p/X_0); symbols represent experimental data.

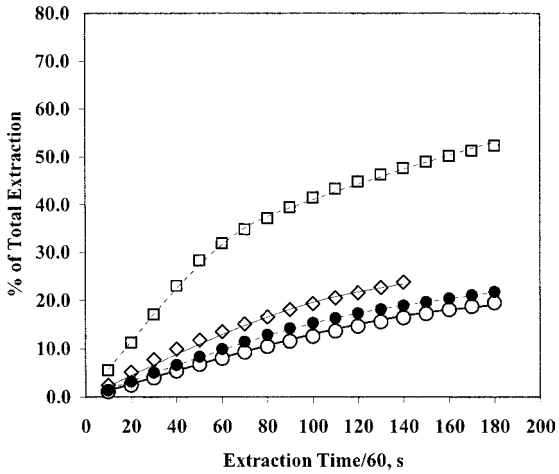

Figure 3. Comparison of experimental and calculated overall extraction curves; symbols represent experimental data and lines the calculated curves, both at the indicated operating conditions: □, 100 bar and 6.12 × 10^{-5} kg/s; ○, 140 bar and 3.65 × 10^{-5} kg/s; ●, 140 bar and 4.45 ×10^{-5} kg/s; ◇, 180 bar and 4.60 × 10^{-5} kg/s.

the larger should be the value of X_p/X_0. The data of **Figures 2** and **3** were all taken under the same pretreatment condition; nonetheless, **Table 5** shows that X_p/X_0 has varied. Two phenomena have contributed to this: the variation of the pressure and the variation of solvent flow rate. The pressure influences the value of X_0, and the solvent flow rate influences the fluid-phase mass transfer coefficient. In any case, the pseudo-steady-state Sovová model quantitatively described the OECs. The experimental conditions that gave the best extraction rates and percent of total extraction were 100 bar and 30 °C.

NOMENCLATURE

CER = constant extraction rate period
k = extraction parameter (dimensionless)
k_{Xa} = solid-phase mass transfer coefficient (s)
k_{Ya} = fluid-phase mass transfer coefficient (s)
m_{ext} = experimental mass of extract (kg)
m_{ext}^{cald} = calculated mass of extract (kg)
M_{CER} = extraction rate for the CER period (kg of extract/s)
OEC = overall extraction curve
P = pressure (bar)
Q_{CO_2} = CO_2 flow rate (kg/s)
t = extracting time (s)
t_{CER} = end of the CER period (s)
t_{FER} = end of the falling extraction rate (FER) period (s)
T = temperature (°C)
X_k = mass ratio of solute inside unruptured cells (kg of solute/kg of cellulosic structure)
X_0 = initial solute mass ratio in the solid phase (kg of solute/kg of cellulosic structure)
X_p = mass ratio of solute in ruptured cells (easily accessible solute) (kg of solute/kg of cellulosic structure)
Y^* = solubility of the solute in the solvent phase (kg of solute/kg of CO_2)
Y_{CER} = solvent-phase solute mass ratio at bed outlet (kg of solute/kg of CO_2)
Z = parameter of the Sovová model for the CER period (dimensionless)
ρ_{CO_2} = carbon dioxide density (kg/m^3)
ρ_{CS} = density of the cellulosic structure (kg/m^3)

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