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Regeneration Methods for Caffeine-Loaded CO_2

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ABSTRACT

Supercritical gas extraction for the decaffeination of green coffee beans has become an established method in the last decade. However, because of the commercial aspects in this field, few research results on applications have been published. In this publication, three different methods for the regeneration of caffeine-loaded CO_2 are presented: depressurization, adsorption with activated carbon, and absorption with water. For all these methods, phase equilibrium experiments with pure caffeine were done. Furthermore, pilot-plant experiments were performed to decaffeinate green coffee beans.

1. INTRODUCTION

The decaffeination of coffee has become a multibillion dollar business. The annual consumption of decaf-coffee in the United States has reached the level of 220 kt (1). The beginning of research for the removal of caffeine from coffee was in the early twentieth century by Roselius and Wimmer (2). Many researchers have published on gas extraction of caffeine by supercritical solvents (3–8). Most of these publications concentrate on the solubility of caffeine or mass transport problems of decaffeination. Only a few papers exist that are related to the regeneration of the CO_2. Unfortunately, there are no data contained in most of the publications. In this paper, phase equilibrium data for the regeneration methods of depressurization, adsorption with activated carbon, and absorption with water are given. Other ways of regeneration that are discussed in the literature include the admixing of nitrogen to lower the solubility (7) or a method called de-entrainment (9).

2. PHASE EQUILIBRIUM MEASUREMENTS

2.1. Phase Equilibrium Caffeine–CO_2 for Low Pressures

The solubility of caffeine in supercritical carbon dioxide was measured with a static analytical apparatus that is described elsewhere (10). The experimental pressures ranged from 8.3 to 19.9 MPa, the density from 324 to 839 kg/m^3, and the temperatures of 313, 318 and 333 K. For the isotherms of 318 K, only the pressure range from 9.1 to 10.1 MPa was measured. The solubilities ranged from 39.9 mg/kg at 8.3 MPa and 333 K up to 1.34 g/kg at 19.9 MPa and 333 K. The measured data are listed in Table 1 and also displayed in Fig. 1 as the solubility in mg/kg versus the

TABLE 1
Solubilities of Caffeine in Supercritical Carbon Dioxide

Temperature (K)	Pressure (MPa)	Density (kg/m^3)	Solubility (mg/kg)	Mole fraction (10^{-6})
313	8.3	324.43	39.9	9.0
	8.8	435.60	47.5	10.8
	9.2	525.28	53.0	12.0
	9.3	542.70	100.5	22.8
	9.8	605.24	191.5	43.4
	11.2	688.75	355.0	80.5
	13.2	746.64	586.0	132.9
	15.2	783.19	708.0	150.6
	15.3	784.73	752.0	170.6
	17.3	811.66	924.0	209.6
	19.3	833.43	1121.0	254.2
	19.9	839.25	1300.0	295.0
318	9.1	357.88	48.6	11.0
	9.6	436.64	68.3	15.5
	10.1	510.00	119.4	27.1
333	10.7	339.17	74.5	16.9
	11.2	376.51	83.0	18.9
	11.7	414.79	98.0	22.2
	13.1	511.69	387.0	87.8
	15.1	606.22	606.0	137.4
	19.9	721.57	1340.0	304.0

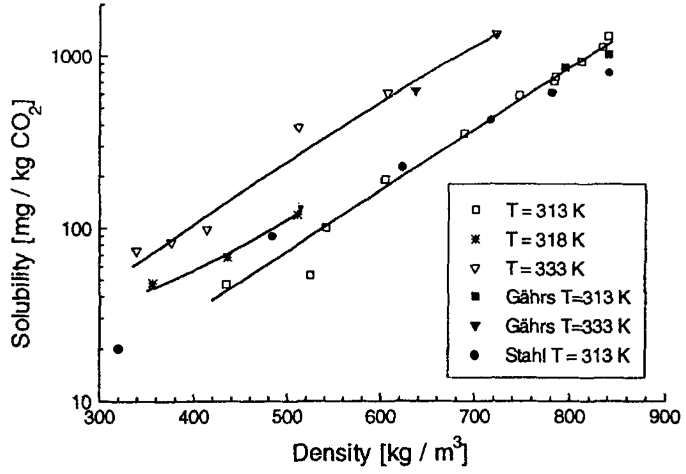

FIG. 1 Solubility of caffeine in supercritical CO_2 versus density.

density kg/m^3. Data from Gährs (7) and Stahl and Schilz (8) are compared to our data and show nearly the same solubilities as the new data presented.

The isotherms for 313 and 333 K are presented as solubility versus the density of CO_2 in Fig. 2. Data from Johannsen (10) in the pressure range between 20 and 35 MPa are added (hollow curve symbols).

A correlation of the binary equilibrium caffeine–CO_2 was done with the data regression system of ASPEN+. The best fit was done with the Redlich–Kwong–Aspen equation of state that is a Soave–Redlich–Kwong EOS modified by Mathias (11).

$$P = \frac{RT}{v - \sum_i \sum_j x_i x_j b_{ij}} - \frac{\sum_i \sum_j x_i x_j a_{ij}}{v(v + \sum_i \sum_j x_i x_j b_{ij})} \tag{1}$$

where

$$a_{ij} = \sqrt{a_i a_j}\left(1 - k^0_{aij} - k^1_{aij}\frac{T}{1000}\right) \tag{2}$$

$$b_{ij} = \frac{b_i + b_j}{2}\left(1 - k^0_{bij} - k^1_{bij}\frac{T}{1000}\right) \tag{3}$$

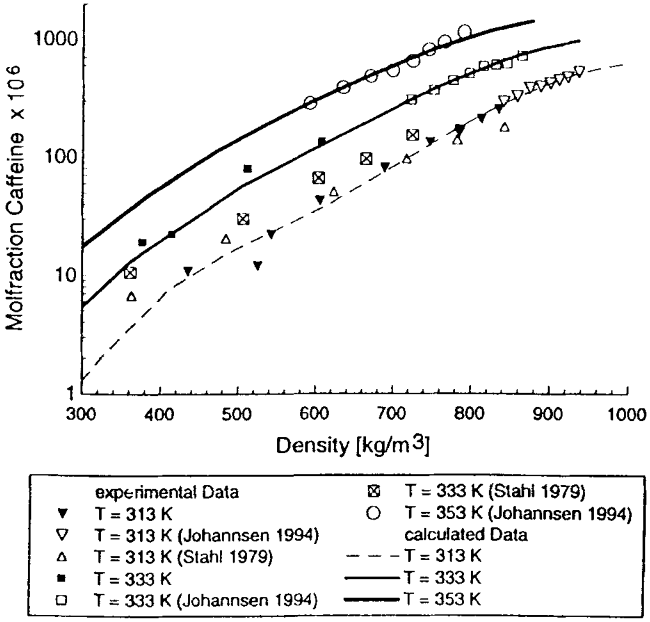

FIG. 2 Solubility of caffeine in supercritical CO_2 versus density correlated with Redlich–Kwong–Aspen EOS.

with the pure components constants:

$$a_i(T) = 0.42747\,\frac{R^2T^2_{\mathrm{cr},i}}{P_{\mathrm{cr},i}} \times \left(1 + m_i\left[1 - \left(\frac{T}{T_{\mathrm{cr},i}}\right)^{0.5}\right] - \eta_i\left[\left(\frac{T}{T_{\mathrm{cr},i}}\right)^2 - \frac{1.7T}{T_{\mathrm{cr},i}} + 0.7\right]\right)^2 \tag{4}$$

$$b_i(T) = 0.08664\,\frac{RT_{\mathrm{cr},i}}{P_{\mathrm{cr},i}} \tag{5}$$

$$m_i = 0.48508 + 1.55191\omega_i - 0.15613\omega_i^2 \tag{6}$$

in the supercritical region, Boston and Mathias (12) changed $a_i(T)$ to

$$a_i(T) = 0.42747\,\frac{R^2T^2_{\mathrm{cr},i}}{P_{\mathrm{cr},i}}\left(\exp\left[c_i - c_i\left(\frac{T}{T_{\mathrm{cr},i}}\right)^{(c_i-1)/c_i}\right]\right)^2 \tag{7}$$

$$c_i = 1 + 0.5m_i + 0.3\eta_i \tag{8}$$

The coefficients derived for the experimental data of the CO_2–caffeine system for the above equation of state are:

$\eta_{CO_2} = -0.5407$ $\quad k^1_{aCO_2,Caffeine} = -0.23831$

$\eta_{Caffeine} = 0.3705$ $\quad k^0_{bCO_2,Caffeine} = 0.11711$

$k^0_{aCO_2,Caffeine} = 0.15235$ $\quad k^1_{bCO_2,Caffeine} = -0.74074$

The vapor pressure of caffeine (15), which is compulsory for the calculation with ASPEN+, was fitted as

$$\ln P_{VP} = 33.63 - \frac{12970}{T} \tag{9}$$

The data are fitted with an average error of 6% for all points above 12 MPa. The calculated isotherms show larger deviations below 12 MPa.

2.2. Phase Equilibrium of Caffeine–CO_2–Activated Carbon

To measure the adsorption of caffeine on the surface of activated carbon, a swinging vessel (Andreas Hofer, Mühlheim, FRG, $V = 0.5$ L) was used. This is shown in Fig. 3. A weighed amount of caffeine and activated carbon were placed inside the vessel. The vessel temperature was controlled by a PID-controller with electric heating.

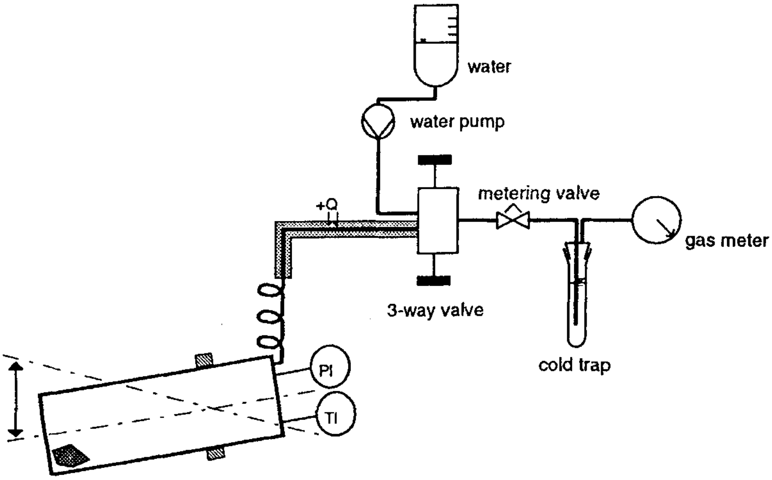

FIG. 3 Set-up of the swinging vessel for the adsorption experiments.

After pumping compressed CO_2 (Kohlensärewerke Deutschland, Bad Mönningen, FRG, purity 99.8%) into the vessel, the system was shaken for at least 1 day to equilibrate the system; then gas samples were taken from the fluid phase. The required equilibrium time was determined by pre-experiments. The result was that for $P = 20$ and 30 MPa and lower loadings, the system was equilibrated within a day. For $P = 13$ MPa and higher loadings, the time was extended to 3 days. This is because of the low caffeine solubility in the fluid phase for $P = 13$ MPa and mass transport resistance in the activated carbon pores.

The vessel was connected with flexible tubing to a sampling unit that consists of a 3-way valve (Autoclave Engineers, Erie, USA, Type: 10V2075), a metering valve (Autoclave Engineers 10VRMM2812), and a cold trap followed by a gas meter. The cold trap is not cooled but half-filled with water to absorb the remaining caffeine in the depressurized gas leaving the metering valve. After a liter of expanded CO_2 has flowed through the gas meter, the valve connection to the vessel is closed, and the connection to the water pump is opened. Water is pumped through the tubings and valves to wash out the precipitated caffeine in the tubings and beyond the metering valve. The flashing ends when the cold trap is filled completely. The water is analyzed with a UV-photospectrometer at a wavelength of 273 nm.

Experiments were done with the ternary system caffeine–CO_2–activated carbon and the quaternary system water–caffeine–CO_2–activated carbon. Variations of parameters were done on the amount of caffeine in the vessel (0.5–5 g), the pressure (13, 20, and 30 MPa) and the amount of water in the vessel (0, 1, 2, 4, and 10 g). The amount of dry activated carbon (Chemviron Carbon, Neu-Isenburg, FRG, Type: WS 4 Supra) was kept constant at 10 g. The mass of CO_2 in the vessel was measured by a Rheonik mass flowmeter that integrated the mass flow rate over the time for filling the vessel. Knowing the mass of the components in the vessel and the sampled caffeine loading in the supercritical phase, it was possible by a simple mass balance to determine the loading of the activated carbon. The loading of the caffeine is the amount of caffeine in the vessel that is not dissolved in the supercritical fluid:

$$X\left[\frac{\mathrm{kg}_{\mathrm{caff.}}}{\mathrm{kg}_{\mathrm{AC}}}\right] = \frac{M_{\mathrm{caff.},\alpha} - (M_{\mathrm{CO_2}} Y_{\mathrm{caff.}})}{M_{\mathrm{AC}}} \tag{10}$$

The data for all 3 different pressures are presented in Table 2 and displayed in Fig. 4. Langmuir-type isotherms for $P = 13$, 20, and 30 MPa are included in the diagram. The pressure of 13 MPa shows the best adsorption while the curve for $P = 30$ MPa shows the worst adsorption with the

TABLE 2
Experimental Adsorption Isotherms for Caffeine on Activated Carbon from Supercritical Carbon Dioxide

Pressure (MPa)	*Y* (mg/kg)	*X* (kg/kg)
30	14.5	0.050
	31	0.195
	57	0.246
	106	0.290
	152	0.300
	251	0.391
	770	0.480
20	5	0.050
	20	0.190
	21	0.200
	91	0.300
	172	0.398
	520	0.480
13	1.6	0.0530
	4.4	0.140
	9	0.204
	19	0.309
	21.3	0.310
	53.7	0.400
19	2.4	0.101
T = 343 K	13.4	0.205

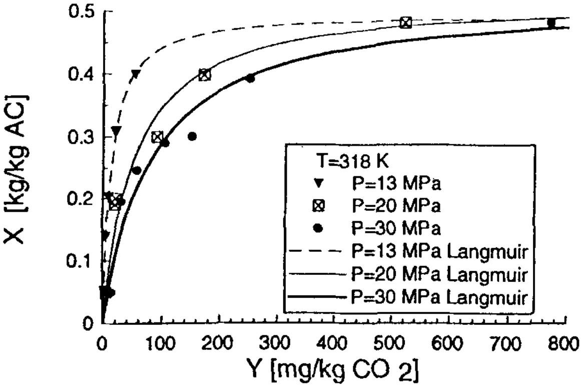

FIG. 4 Caffeine loading on the activated carbon versus the caffeine loading in the supercritical fluid (SCF) phase.

curve for $P = 20$ MPa in between. This is mainly because of two effects: 1) the solubility of caffeine for $T = 318$ K is strongly sensitive to the pressure, and 2) the competition between the supercritical carbon dioxide and the caffeine for the active spots on the surface of the activated carbon. This latter effect is described by King (13). Both effects lead to the displayed behavior of the system. The Langmuir model equation can represent the measured data well.

$$X\left[\frac{\mathrm{kg_{caff.}}}{\mathrm{kg_{AC}}}\right] = X_{\mathrm{max}}\,\frac{Kc_{\mathrm{caff.}}}{1 + Kc_{\mathrm{caff.}}} \qquad (11)$$

In Table 3 the coefficients k and X_{max} for the three different pressures are given.

In a second series of experiments water was added to the vessel. Most experiments were done at $P = 20$ MPa and 4 g caffeine. The tendency is as follows: Water enhances the adsorption in all cases. There is a maximum adsorption for the amount of 2 g water per 10 g activated carbon and 404 g carbon dioxide. This can be seen in detail of Fig. 5. The experiment with 10 g water in the vessel was done by soaking the activated carbon in water and determining the difference in weight. The explanation for this behavior is that the water is either dissolved in the fluid phase or forms a monomolecular layer on the surface of the activated carbon. This enhances the adsorption process. If there is too much water in the vessel, the water forms drops in the pores of the activated carbon and reduces the active surface. This behavior can also be observed for smaller loadings but not as significantly as for the loading of 0.4. The data point for $P = 19$ MPa, $T = 343$ K, and 2 g water shows no significant deviation from the curve for $P = 20$ MPa and $T = 318$ K.

2.3. Phase Equilibrium Caffeine–Water–CO_2

For the calculation of absorption processes, the equilibrium of caffeine between the water and the supercritical fluid (SCF) phase must be known. This was measured with a static cell apparatus that is described elsewhere

TABLE 3
Langmuir Adsorption Equilibrium Constants of Caffeine on Activated Carbon

$T = 318$ K	k	X_{max}
$P = 13$ MPa	0.0839	0.49
$P = 20$ MPa	0.0201	0.52
$P = 30$ MPa	0.0127	0.52

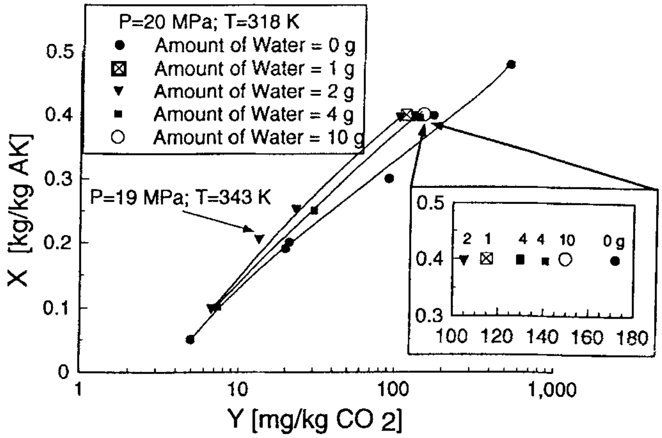

FIG. 5 Caffeine loading on the activated carbon versus the caffeine loading in the supercritical fluid phase for the pressures $P = 20$ MPa, $T = 318$, and different amounts of water in the vessel. Inset: the data point for $P = 19$ MPa and $T = 343$ K with 2 g water.

(14). Experiments were done by varying the initial caffeine loading in the water, pressure, and temperature. Caffeine was dissolved in warm water and sucked into a vessel that was evacuated with a vacuum pump. The water phase filled about half of the vessel volume (1 L). Then CO_2 was pumped into the vessel until the desired pressure was reached. The system was thermostated by an oil bath at system temperature (Fig. 6). The sys-

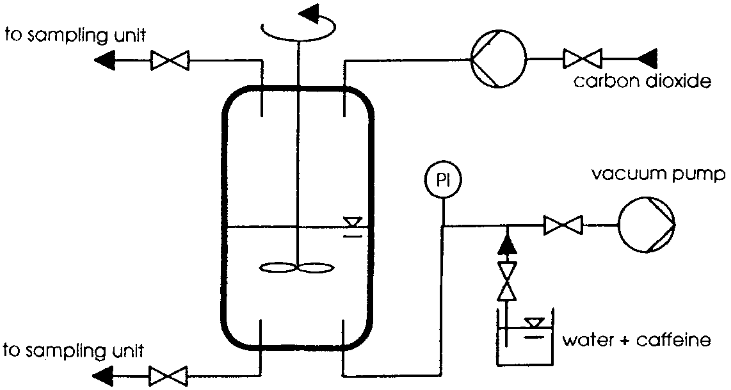

FIG. 6 Set-up for the absorption experiments.

tem was stirred for half an hour, and then the same time was allowed for phase separation. Samples were taken from the liquid and the SCF phase. The sampling unit for the SCF phase was the same as for the adsorption experiments. The liquid samples from the water phase were collected in a small beaker and then analyzed. Figure 7 shows the data for T = 343.1 K with pressures of 19 and 28 MPa and for T = 323.1 K with a pressure of 19 MPa. The curve for P = 28 MPa and T = 343.1 K is significantly above the curve for P = 19 MPa. The multiple data points are repeated measurements and show the reliability of the system. The reason for the higher loadings for P = 28 MPa is the higher density of the SCF phase. At constant pressure the curve for T = 323.1 K is above the curve for T = 343.1 K. In the Fig. 7 inset the data for low loadings are displayed in a linear graph. It can be seen that both curves do not form a line through zero. Because the zero point is an inherent point of the equilibrium curve, the curve has to form a rise toward the first data where the curve slope becomes smaller. The reason that the curve for the lower temperature is above the curve for the higher temperature is again the higher density. As a second effect, the higher solubility of caffeine in warmer water (15) influences the system behavior.

See also Table 4.

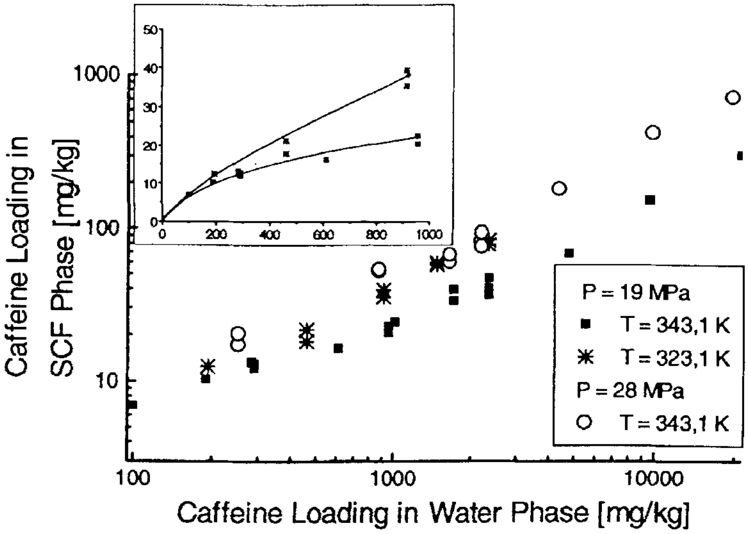

FIG. 7 Caffeine loading in the SCF versus caffeine loading in the water phase.

TABLE 4
Experimental Adsorption Isotherms for Caffeine in Water from Supercritical Carbon Dioxide

Temperature (K)	P = 19 MPa		P = 28 MPa	
	Y (mg/kg)	X (mg/kg)	Y (mg/kg)	X (mg/kg)
323	193	12.5	170	19.7
	193	12.5	170	20.9
	460	21.5	405	30.8
	460	18.1	405	33.8
	913	39.3	837	53
	913	35.4	837	51.5
	1,479	59.5	1,319	90.6
	1,479	57.4	1,319	98
	2,346	83.2	2,161	148.3
	2,346	77.9	2,161	130.4
333	368	19.6	330	34.6
	368	23.9	330	30.3
	854	46.9	820	93.1
	854	55.2	820	91.6
	4,808	140.92	3,989	314.9
	4,808	161.3	3,989	334.36
343	100	6.9	251	17.1
	190	10.3	251	20.3
	290	12.9	875	52.1
	290	12.1	875	53.4
	284	13.2	1,655	59.9
	284	13.3	1,655	66.9
	611	16.3	2,186	82.3
	956	22.7	2,200	76.4
	956	20.6	2,200	93.9
	1,015	24.1	43,585	180.2
	1,716	33.1	9,800	423
	1,716	39.3	19,535	722.4
	2,358	38.0		
	2,358	40.1		
	2,368	43		
	4,793	67.8		
	9,587	150.9		
	21,255	304.4		
353	248	13.6	231	18.9
	480	16.5	231	18.4
	480	15.4	454	27.7
	953	29.7	454	26.7
	953	25.1	887	41.1
	2,375	34.3	887	44.6
	2,375	39	2,187	97
	4,413	52.7	2,187	96.2
	4,413	65	4,150	181.2
			4,150	186.1

3. PILOT-PLANT EXPERIMENTS WITH DECAFFEINATION OF GREEN COFFEE BEANS

The extraction of coffee beans with carbon dioxide has been described by many authors (6, 16). In the experiments presented here, the main emphasis was directed toward regeneration. The pilot plant consists of extractor, metering valve, separator, saturator, and recycling compressor as shown in Fig. 8.

For three different sorts of experiments, alterations on the set-up were made. Malaysian coffee beans with an initial caffeine content of 2.0 wt% were chosen for the experiments. The coffee beans were presoaked with water, resulting in a water content of 50 wt%. The experiments with the green coffee beans are not fully equivalent to the pure caffeine experiments described before because the CO_2 was saturated with water and other solutes like lipids were dissolved in the SCF and influenced the phase equilibrium. Still, the phase equilibrium of pure caffeine gives a good approximation of the behavior.

3.1. Regeneration of CO_2 with Absorption

Experiments were done with a 25-L extractor and a 8-L absorber. A small pressure difference (1 MPa) between extractor and absorber was maintained by the metering valve. The solvent ratio (SR), defined as the mass flow of water relative to the mass flow of SCF, was varied. The solvent-to-feed ratio (S/F) was kept constant at 75 (1 kg coffee in the extractor was extracted with a solvent flow of 75 kg/h). The preheated water mass flow was varied while the water temperature was kept constant

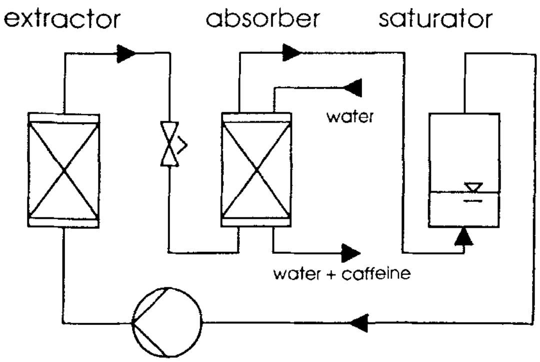

FIG. 8 Set-up of the closed cycle pilot plant.

at 343 K and pressure in the absorber at 19 MPa. In Fig. 9 inlet and outlet loading of caffeine in the SCF are displayed for two different SR values (SR = 0.02 and 0.1) in dependence of extraction time *t*. It can be seen that at the beginning of the experiment the inlet caffeine loading is not equal to zero in both cases. This is because the extractor was filled with carbon dioxide before circulation was started so that the fluid leaving the extractor was already loaded. The outlet curve of SR = 0.02 is nearly parallel to the inlet curve, and the difference between the inlet and outlet curves is small. Because of the small SR, only a small amount of caffeine was absorbed in the water, resulting in poor regeneration. The recycled solvent contains a high loading of caffeine so that only a reduced amount of caffeine can be extracted in the extractor due to a small concentration gradient from inside of the coffee beans to the SCF. The total extraction time to reach a certain residual caffeine concentration in the beans would be very long. In contrary to SR = 0.02, SR = 0.1 produces small outlet loadings and a large difference between the inlet and outlet loadings. The amount of absorbed caffeine is larger, so the time of total extraction is reduced. The extraction can be divided into two phases: an unsteady-state at the beginning followed by a quasi-steady-state part. For the extraction displayed in Fig. 8, the first part ends after approximate 1 hour. In Fig. 10 the inlet and outlet loading pairs for measurements in the quasi-steady-state part are displayed as outlet loading versus inlet loading. It can be seen that for SR = 0.1 and 0.07, the outlet loadings are between 10 and 20 mg/kg. The dependence of the inlet loading is detectable but small.

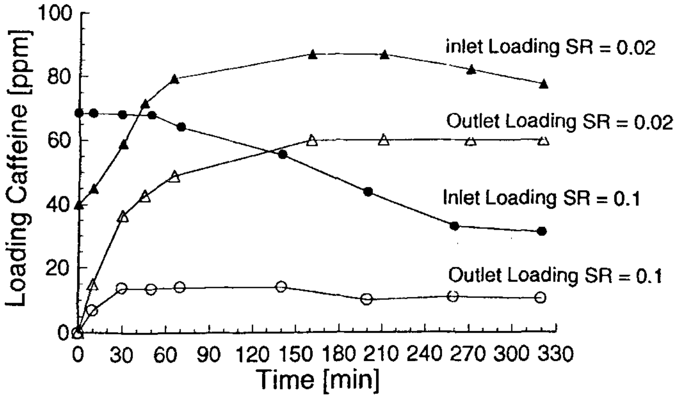

FIG. 9 Inlet and outlet caffeine loading versus time for experiment with absorption as a regeneration method (P = 19 MPa, S/F = 75).

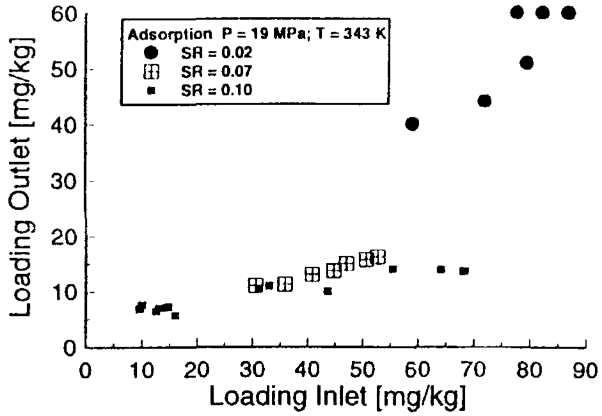

FIG. 10 Outlet caffeine loading versus inlet loading for three different experiments with adsorption as a regeneration method.

The data for SR = 0.02 show a different behavior: here the loadings are dependent on the inlet loadings, and the outlet loadings are much higher than for the other SR.

3.2. Regeneration of CO_2 with Adsorption

For the experiments with adsorption as a regeneration method, the regenerator was filled with activated carbon (same type as for phase equilibrium experiments). Four experiments were performed: a) 1.0 kg coffee beans in the extractor extracted with a solvent mass flow of 75 kg/h at P_{ex} = 20 MPa (S/F = 75); b) 2.1 kg coffee beans with a solvent mass flow of 315 kg/h at P_{ex} = 20 MPa (S/F = 150); c) 3.0 kg coffee beans in the extractor with a solvent mass flow of 450 kg/h at P_{ex} = 30 MPa (S/F = 150), and d) 1.0 kg coffee beans with a solvent mass flow of 300 kg/h at P_{ex} = 20 MPa (S/F = 300). A pressure difference of 1 MPa between extractor and adsorber was maintained by the metering valve. In Fig. 11 the inlet and outlet loading of caffeine is displayed versus extraction time for Case a) and the curves are marked Adsorption Inlet and Adsorption Outlet. The outlet caffeine loading is close to 8 mg/kg for the complete extraction except for the starting phase. This is not because of a breakthrough directly after the beginning of extraction but because of a behavior that is not explained by the usual adsorption theories. According to the adsorption isotherm equations of Langmuir, Freundlich, or BET, the loading of solute in the SCF should be reduced to zero as long as no breakthrough has occurred. Even though activated carbon is a very good adsorbent for caffeine, the loading in the SCF was not zero. It is possible that

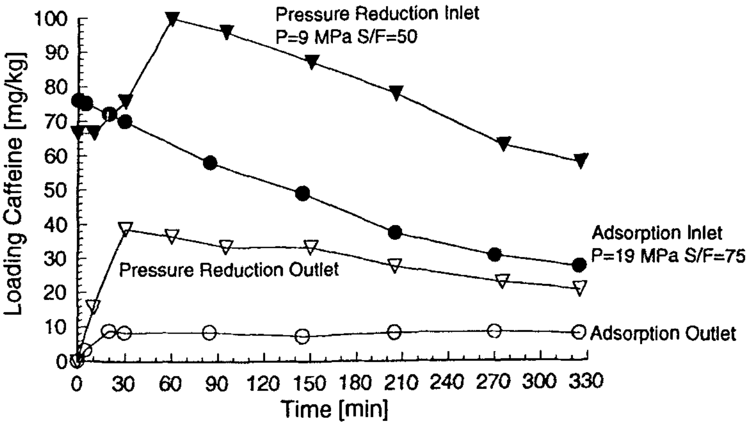

FIG. 11 Inlet and outlet caffeine loading versus time for experiment with adsorption and pressure reduction as a regeneration method.

below a certain limit the concentration gradient is not large enough to transport caffeine into the pores of the activated carbon. Because the adsorber has a length-to-diameter ratio of 5, it is unlikely to have a strong influence of channeling. This effect made it impossible to calculate the adsorption process with the usual methods. In Fig. 12 the inlet and outlet loading pairs for measurements in the quasi-stationary part are displayed as outlet loading versus inlet loading. The outlet loading is less than 15

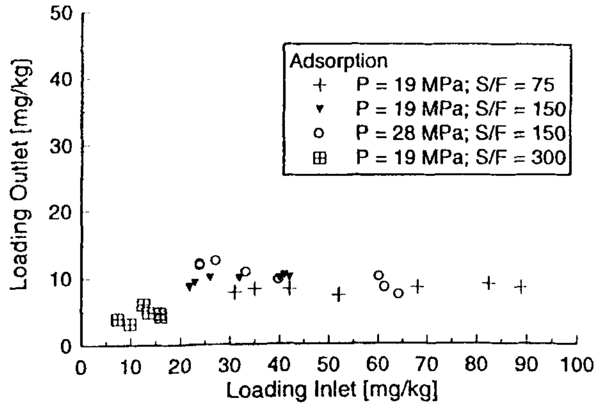

FIG. 12 Outlet caffeine loading versus inlet loading for four different experiments with absorption as a regeneration method.

mg/kg for all experiments, and is the smallest for experiments with S/F = 300. Here the average outlet loading is 5 mg/kg. Compared to the adsorption data presented in Fig. 5, the outlet loadings are in equilibrium with a loading on the activated carbon of 0.15. With negligible error the isotherm that was measured at a pressure of 20 MPa can be compared with the experiment that was performed with a regeneration pressure of 19 MPa. The loading on the activated carbon was measured after the experiment by determining the mass difference of the activated carbon. The loadings were determined at three different layers of the adsorber bed and are shown in Fig. 13 for $P = 19$ and 28 MPa. For the lower pressure the loading of the activated carbon is 0.14 in the entry section of the bed and declines from there. In the later part the loading was still zero for the pressure of 19 MPa but it was 0.08 for the higher pressure. This is in good agreement with the adsorption isotherm.

3.3 Regeneration of CO_2 with Pressure Reduction

For the experiments with pressure reduction as the regeneration method, the separator was empty and the extractor was exchanged with a 4-L extractor. This was done to maintain the same S/F ratios as in the previous experiments. Because the solvent mass flow was drastically reduced due to the low suction pressure of the compressor, the amount of coffee beans was only 0.4 kg and therefore a smaller extractor was more efficient. Solvent mass flow was varied from 30 to 90 kg/h. The pressure was lowered by the metering valve to 10, 9, and 7.2 MPa. Because of gas expansion, different residence times were obtained. In Fig. 11 the inlet and outlet loadings are compared to the curves for the adsorption

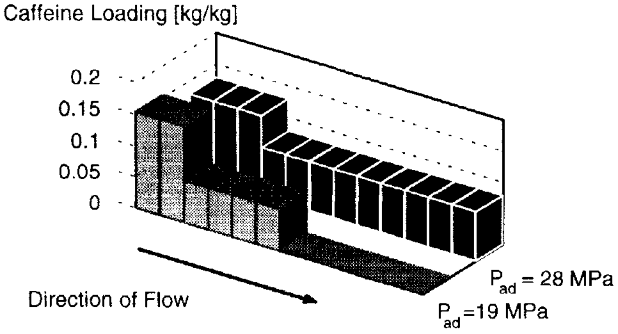

FIG. 13 Caffeine loading of the activated carbon bed for two different pressures.

method. The curves for the pressure reduction method are significantly higher. This is due to incomplete regeneration. For both methods the inlet loading starts at a level of approximately 70 ppm. While the inlet curve for the adsorption method declines, the curve for the pressure reduction method rises toward a high level.

Even though the solubility of caffeine is defined by pressure and volume and is the same for the complete extraction time, the outlet loading is dependent on the inlet loading. This shows that both mass transport and residence time play a role. In Fig. 14 the outlet loading is displayed versus the inlet loading for $P = 9$ MPa and $T = 313$ K in the regenerator. The longest residence time (24.7 minutes) in the regenerator yields the lowest outlet loadings, while the shortest residence time (8.2 minutes) produces the highest outlet loadings. The high inlet loadings for the residence time of 24.7 minutes are due to the small solvent-to-feed ratio for this particular experiment. As a consequence of this, the solvent was given enough time to extract caffeine, which results in high caffeine loadings. The data for the shorter residence time show a correlation between the inlet and outlet loadings. This is most obvious for the shortest residence time (8.2 minutes). The horizontal line shows the equilibrium solubility of caffeine in dry CO_2 without water. The solubility of caffeine in humid CO_2 (CO_2 saturated with water) can be higher (17) by the factor of 3.7 to 5.8. Still, the outlet loadings are significantly below the equilibrium line for the dry

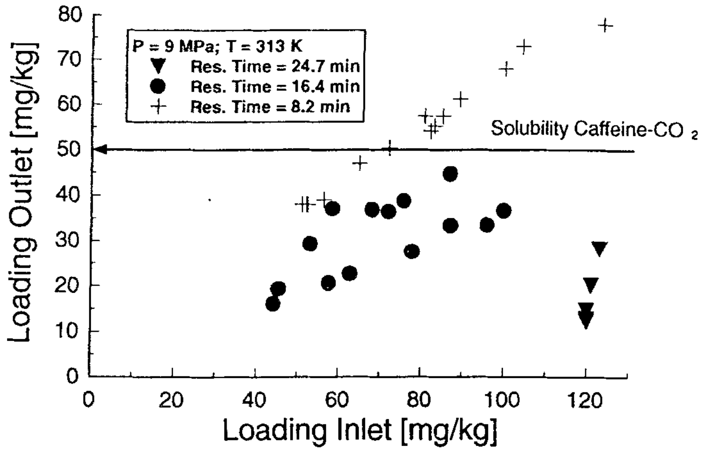

FIG. 14 Outlet caffeine loading versus inlet loading for three different experiments with depressurization as a regeneration method ($P = 9$ MPa).

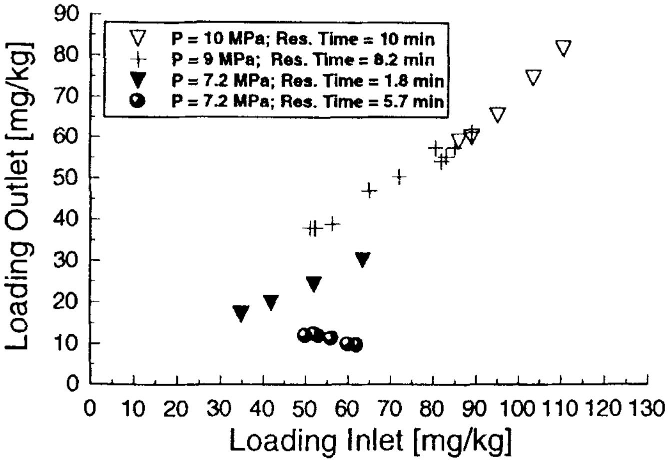

FIG. 15 Outlet caffeine loading versus inlet loading for four different experiments with depressurization as a regeneration method.

system. This effect can only be caused by a absorption effect of the precipitated water in the separator. Caffeine in dissolved in the drops and therefore the outlet loading is below the solubility.

In Fig. 15 the outlet loading is displayed versus the inlet loading for different pressures in the regenerator (P_{sep} = 10.0, 9.0, 7.2 MPa). Depressurization to a subcritical pressure (P = 7.2 MPa) gives the best results but causes the highest loss of energy in the cycle. Here again the curve for a residence time of 5.7 minutes shows better results than for 1.8 minutes.

The influence of the residence time can be drastically reduced when a cyclone regenerator (18) is used instead of a pressure vessel that does not use centrifugal forces for separation of the precipitated solids and the fluid phase.

4. MODELING OF THE ABSORPTION

When using the isotherms presented in Section 2.3, the number of theoretical stages can be calculated by knowing the mass flows and the equilibrium curve. Because the mass of caffeine is negligible compared to the mass flow of water and SCF, one can assume the operating curve to be linear with a slope of m.

$$A = SR/m \tag{12}$$

If unloaded water is used to absorb the caffeine, the number of theoretical stages can be determined by

$$N_{th} = \frac{\ln\left(\frac{Y_\alpha}{Y_\omega}\left[1 - \frac{1}{A}\right] + \frac{1}{A}\right)}{\ln A} \tag{13}$$

The number of theoretical stages was equal to 1.0 for cases of SR = 0.1 and 0.07. For the case of SR = 0.02, the number of theoretical stages was equal to 0.4.

5. CONCLUSIONS AND DISCUSSION

Data for the phase equilibrium CO_2–caffeine, CO_2–caffeine–water, and CO_2–caffeine–activated carbon have been presented. The data were compared to the results from closed cycle experiments done with three different regeneration methods: adsorption, absorption, and pressure reduction. The results of pilot-plant experiments show that the general behavior can be described by the phase equilibrium data. For all pilot-plant experiments the presence of water and other components contained in green coffee beans must be considered when comparing the outlet loading data with the phase equilibrium data. The outlet loadings of the depressurization experiments are below the equilibrium solubility limit, which is impossible as long as no third component is involved. The formation of water drops is a possible explanation of the effect.

Because of the high energy consumption of the depressurization method, this method is not the best method for large-scale plants. A second problem with the depressurization method is the fact that caffeine is solid. This creates the possibility of blockage in the tubings. When enough water is precipitated, the caffeine and the water form a sludge that can be transported by the pressure, but the method is unreliable.

The adsorption of caffeine on activated carbon has the advantage of low outlet concentrations of the caffeine, but a drawback is that adsorption is always an unsteady-state process. Regeneration of the loaded activated carbon can only be done at high temperatures and with the loss of adsorber material. Caffeine cannot be produced using this method. The adsorber is also not selective enough for caffeine, so that valuable ingredients of the coffee beans are also extracted and then adsorbed.

The best method is the absorption method because of its high selectivity for caffeine and because it is a stationary process. No water must be added in addition to the absorption. The addition of water is needed for the two other processes because water is precipitated in the depressurization process and adsorbed on the activated carbon. The only problem is regeneration of the caffeine–water mixture. This can be done with membrane separation, as described in the patent of Katz (4).

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NOMENCLATURE

A	absorption factor
a	attraction parameter
b	hard core volume
c	constant, Eq. (8)
k	binary parameter
K	constant in Langmuir isotherm equation
m	characteristic constant
M	mass (kg)
P	pressure (MPa)
R	gas constant
S/F	solvent-to-feed ratio
SR	mass flow of water relative to mass flow of SCF
t	extraction time (min)
T	temperature (K)
v	molar volume
x	mole fraction
X	loading of caffeine in liquid or solid phase
Y	loading of caffeine in SCF phase

Subscripts

cr	critical property
i, j	component identifications
α	start

ω	end
S	solvent
max	maximum loading

Greek Letters

α	adimensional factor
η	polar parameter, Eq. (4)
ω	acentric factor

Superscripts

0, 1	constant identification, Eqs. (2) and (3)

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