

IMPROVEMENT OF SOLUBLE COFFEE AROMA USING AN INTEGRATED PROCESS OF SUPERCRITICAL CO₂ EXTRACTION WITH SELECTIVE REMOVAL OF THE PUNGENT VOLATILES BY ADSORPTION ON ACTIVATED CARBON

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Abstract - In this paper a two-step integrated process consisting of CO₂ supercritical extraction of volatile coffee compounds (the most valuable) from roasted and milled coffee, and a subsequent step of selective removal of pungent volatiles by adsorption on activated carbon is presented. Some experiments were carried out with key compounds from roasted coffee aroma in order to study the adsorption step: ethyl acetate as a desirable compound and furfural as a pungent component. Operational parameters such as adsorption pressure and temperature and CO₂ flowrate were optimized. Experiments were conducted at adsorption pressures of 12-17 MPa, adsorption temperatures of 35-50°C and a solvent flow rate of 3-5 kg/h. In all cases, the solute concentration and the activated particle size were kept constant. Results show that low pressures (12 MPa), low temperatures (35°C) and low CO₂ flowrates (3 kg/h) are suitable for removing the undesirable pungent and smell components (e.g. furfural) and retaining the desirable aroma compounds (e.g. ethyl acetate). The later operation with real roasted coffee has corroborated the previous results obtained with the key compounds.

Keywords: Coffee aroma; Supercritical extraction; Supercritical adsorption; Activated carbon; Supercritical CO₂

INTRODUCTION

Roasted coffee contains volatile substances, constituting the characteristic fragrance. These volatile compounds are generally called aroma and almost 700 compounds have been reported in coffee (Ishii, 1987; Shibamoto, 1992). The desirable smell in coffee is produced by a delicate balance in the composition of volatiles. It is important to recover coffee volatiles that are released during production

of soluble coffee and to put them back in to the liquid coffee extracts or dry products of the extract. This enhances the smell of coffee products and satisfies consumer preferences for such products.

The quality of soluble coffee has been improved by adding an aroma-absorbed coffee oil to coffee powder. In recent patents Jimenez and Liou (1998) and Furrer and Gretsche (2002) described several methods including supercritical technology.

Supercritical extraction-adsorption processes

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have been demonstrated to be a powerful tool for aroma recovery studies but efforts have been made in this field (Ramos *et al.*, 1998; Sarrazin *et al.*, 2000). In this paper a method of recovery and put-back of aromas to coffee based on an integrated process consisting of SCE and separation by adsorption is proposed. It is a two-step pilot plant comprising CO₂ supercritical extraction of volatile coffee compounds (the most valuable fraction) from roasted and milled coffee and a subsequent step of selective recovery of these flavor chemicals and removal of pungent volatiles by adsorption on activated carbon. The adsorbent is regenerated by heating and the concentrate stream of volatile coffee compounds is recovered by absorption with 15 cm³ of coffee oil. The enriched coffee oil, analyzed by GC/MS, is sprayed on soluble coffee powders to improve the quality of the soluble coffee aroma before it is packed. More details about the experimental procedure are included in previous work (Lucas *et al.*, 2004a).

In order to study and simplify the overall process several key compounds were selected from coffee aroma. In this paper ethyl acetate and furfural were chosen as key components. Ethyl acetate is a desirable volatile compound responsible for the fruity and brandy component of coffee aroma, and it is the most common ester present in several kinds of fruit (apples, grapes, etc.). On the other hand, furfural is an undesirable volatile compound with a pungent or foul smell. Lucas *et al.* (2004a) reported adsorption equilibrium data for both compounds.

MATERIAL AND METHODS

Adsorbent

The granular activated carbon (CAL-Chemviron) evaluated in this research was obtained from Aguas de Levante S.A. (Barcelona, Spain). It was characterized experimentally and the most relevant properties are BET specific area (963 m²/g), external area (105 m²/g), total pore volume (0.715 cm³/g), bed porosity (0.453), particle porosity (0.588), average particle size (0.9-1.1 mm) and bed density (450 kg/m³).

Analysis of Coffee Aroma

A gas chromatograph (model PERKIN ELMER AUTOSYSTEM XL) with an MS detector (model PERKIN ELMER QMASS 910) was used to measure the composition of the aroma compounds. A

capillary column (SGL-20, 0.25 mm × 60 m) was used for the separation. Oven temperature was raised from 40°C to 180°C at 15°C/min. An aliquot of 0.1 cm³ of aroma gas was sampled with a gas-tight syringe and injected in the gas chromatograph. Each component in the aroma-containing gas was identified by comparison with standards.

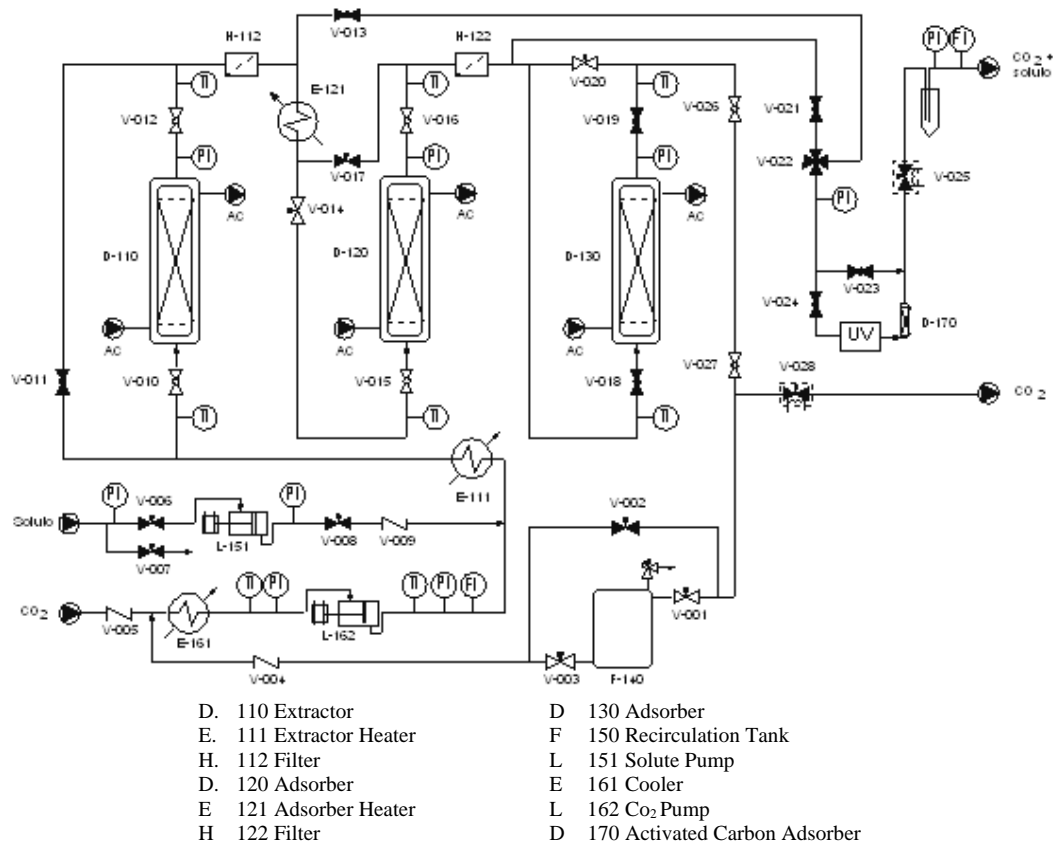
Roasted Coffee Beans and Coffee Oil

Commercial coffee beans and coffee oil were employed in this work.

EXPERIMENTAL SET-UP

A pilot plant for selective aroma recovery was designed and built in the Chemical Engineering Department at Valladolid University (Spain). It is a two-step integrated plant comprising CO₂ supercritical extraction and selective coffee aroma recovery by adsorption on activated carbon. The pilot plant was designed to operate at P < 30 MPa, T < 80°C and a CO₂ mass flowrate of 1-20 kg/h and has a treatment capacity of 0.2 kg_{coffe}/load. It consists of three pressurized vessels of 1L (i.d. = 0.04 m, L = 0.50 m) that can operate as extractors or adsorbers depending on needs; a diaphragm pump to supply solvent and to recirculate CO₂ during operation (LEWA Herbert Leomberg type EH1); and auxiliary equipment such as heat exchangers, pressure, temperature, and flow meters and valves and fittings suitable for high-pressure processes together with the data acquisition system (Cocero *et al.*, 2000).

The pilot plant flow diagram is schematically presented in Figure 1. It was based on two consecutive integrated steps comprising CO₂ supercritical extraction and aroma recovery on the adsorbent. In the extraction, the supercritical CO₂ flows through a fixed bed of milled and roasted coffee beans and dissolves the extractable components of the solid. The added solvent is removed from the extractor and fed into the adsorber where activated carbon has been placed. The clean solvent leaving the adsorber is recirculated to column with the pilot plant under quasi-isobaric conditions (neglecting pressure drop). After 15 minutes, the pump is turned off and the adsorbent is regenerated by heating up to 65°C and the concentrate stream of volatile coffee compounds is recovered by absorption with 15 cm³ of coffee oil. The enriched coffee oil is then analyzed by GC/MS.



FLOW DIAGRAM
Supercritical Extraction/Adsorption Plant
Operating Mode: EXTRACTION/ADSORPTION (Coffee)

Figure 1: Flow diagram of the supercritical extraction-adsorption pilot plant.

RESULTS AND DISCUSSION

(a) Ethyl Acetate and Furfural

The Effect of Pressure

Some supercritical adsorption experiments for ethyl acetate and furfural in the range of 13-17 MPa were performed in order to check the effect of operating pressure. The temperature was fixed at 37°C with a constant CO₂ flowrate of 3.5 kg/h.

The corresponding breakthrough curves were treated mathematically in order to obtain the characteristic adsorption parameters such as breakthrough and saturation time (t_b and t_s), breakthrough and saturation adsorptive capacity (q_b and q_s) and fractional bed utilization (FBU). From the results shown in Table 1 for both solutes it can be deduced that at a low pressure (13 MPa) the adsorption cycle is faster (shorter breakthrough time), the capacity of the adsorbent (amount of solute adsorbed per kg of adsorbent) is higher and utilization of the bed improves. This result suggests that at a low pressure the interaction forces between

solute and activated carbon surface are higher than the corresponding solute-solvent binding forces (Ryu *et al.*, 2000). Moreover at a low pressure all mass transfer resistances decrease and it is possible to get a higher degree of fractional bed utilization (Lucas *et al.*, 2004b).

The Effect of Temperature

The adsorption results for ethyl acetate and furfural obtained at temperatures of 35-50°C at a fixed pressure (14 MPa) and a constant CO₂ flowrate of 3.5 kg/h are shown in Table 2. Operating at lower temperatures (37°C) enables the obtainment of shorter adsorption cycles and higher adsorptive capacities; as can be deduced from analysis of Table 2. The fractional bed utilization decreases slightly with temperature. This affirmation is valid for both solutes and can be attributed to the increase in solvent power with temperature due to the increase in a vapor pressure. This means that at a lower temperature the solute-adsorbent interaction forces versus the corresponding solute-solvent attraction forces prevail.

Table 1: The effect of pressure. A summary of SC adsorption of ethyl acetate and furfural.

P (MPa)	t _b (min)	t _s (min)	q _b (g _{SOL} /g _{CA})	q _s (g _{SOL} /g _{CA})	FBU (%)	*Removal Ratio (%)
ETHYL ACETATE						
12.8	10.9	15.0	0.077	0.084	92.0	78.7
15.2	14.6	19.5	0.072	0.081	88.9	70.0
17.0	15.7	26.5	0.060	0.075	79.7	68.5
FURFURAL						
13.0	12.9	15.9	0.089	0.098	90.8	80.4
15.6	14.8	18.0	0.084	0.094	89.1	77.5
17.2	13.1	18.4	0.081	0.092	87.5	75.0

*Removal ratio is the ratio of the amount of solute adsorbed to that fed into the adsorption column.

Table 2: The effect of temperature. A summary of SC adsorption of ethyl acetate and furfural.

T (°C)	t _b (min)	t _s (min)	q _b (g _{SOL} /g _{CA})	q _s (g _{SOL} /g _{CA})	FBU (%)	*Removal Ratio (%)
ETHYL ACETATE						
36.8	11.0	15.0	0.090	0.102	88.6	75.0
38.7	13.8	19.0	0.087	0.095	92.0	72.3
50.9	14.3	19.5	0.064	0.075	85.4	66.1
FURFURAL						
36.6	10.8	14.3	0.092	0.107	86.4	80.3
38.5	10.8	14.7	0.090	0.103	87.7	79.4
50.9	14.8	18.4	0.087	0.098	88.3	75.2

*Removal ratio is the ratio of the amount of solute adsorbed to that fed into the adsorption column.

The Effect of CO₂ Flowrate

The adsorption results for ethyl acetate and furfural obtained with CO₂ flowrates of 3-5 kg/h at fixed pressure (14 MPa) and temperature (37°C) are shown in Table 3.

Operating at a low CO₂ flowrate produces longer adsorption cycles; although higher adsorptive capacities and higher fractional bed utilization are achieved (Table 4). The amount of solute adsorbed increases with the decrease in solvent flowrate because the solute-adsorbent contact time is shorter.

Table 3: The effect of CO₂ flowrate. A summary of SC adsorption of ethyl acetate and furfural.

F _{CO2} (kg/h)	t _b (min)	t _s (min)	q _b (g _{SOL} /g _{CA})	q _s (g _{SOL} /g _{CA})	FBU (%)	*Removal Ratio (%)
ETHYL ACETATE						
3.0	15.5	23.5	0.085	0.098	86.3	78.7
4.4	13.7	19.0	0.072	0.084	85.6	75.6
5.2	12.1	16.8	0.062	0.073	85.4	69.1
FURFURAL						
2.9	14.8	18.0	0.096	0.107	89.3	83.5
3.7	11.5	13.1	0.087	0.098	89.0	81.5
5.0	10.9	13.3	0.070	0.079	88.8	77.5

*Removal ratio is the ratio of the amount of solute adsorbed to that fed into the adsorption column.

From the adsorption point of view similar adsorption curves with the same values of adsorptive capacities and fractional bed utilization were obtained for both solutes. The compounds have similar molecular weights ($M_{EA} = 88.1$ g/mol and $M_{FF} = 96.1$ g/mol) and molecular dimensions; which makes the selective adsorption of furfural (the undesirable component) is more difficult than that of ethyl acetate. Nevertheless the furfural molecule has greater electronic mobility and reactivity associated with the carbonyl group-aromatic ring linkage. This phenomenon explains the stronger bonding forces between furfural and activated carbon and as a consequence, the higher values of the removal ratio for all the experiment. The higher adsorption heat of furfural (20-32 kJ/mol) than of ethyl acetate adsorption heat (8-9 kJ/mol) corroborates this fact (Lucas *et al.*, 2004a).

(b) Commercial Coffee

Some experiments were carried out in order to determine the optimal conditions for the extraction, adsorption and regeneration steps involved in the overall process.

Extraction-Adsorption Pressure (Experiments 1, 2, 3 and 4)

($P_{\text{ext-ads}} = 6.5, 7.4, 8.5, 11.4$ MPa; $T_{\text{ext}} = 36.5^\circ\text{C}$;

$T_{\text{ads}} = 33^\circ\text{C}$; $F_{\text{CO}_2} = 3.5$ kg/h)

From the results shown in Table 4, it can be seen that at a higher extraction-adsorption pressure (11.4 MPa) the amount of extractable compounds increased significantly in the final coffee oil. This effect of pressure may be due to the increase in

density.

Extraction Temperature (Experiments 5, 6 and 7)

($P_{\text{ext-ads}} = 10.0$ MPa; $T_{\text{ext}} = 44.0, 50.5, 56.5^\circ\text{C}$;

$T_{\text{ads}} = 34^\circ\text{C}$; $F_{\text{CO}_2} = 3.5$ kg/h)

When the extraction temperature was higher (56.5°C) the amount of the compounds extracted increased slightly. This behavior can be attributed to the increase in extraction rate with temperature (Table 4).

Adsorption Temperature (Experiments 3 and 9)

($P_{\text{ext-ads}} = 8.5$ MPa; $T_{\text{ext}} = 37.0^\circ\text{C}$;

$T_{\text{ads}} = 34.0, 46.0^\circ\text{C}$; $F_{\text{CO}_2} = 3.5$ kg/h)

At a lower adsorption temperature (34.0°C) the amount of extractable compounds fixed in the coffee oil increased meaningfully. This effect may be due to the decrease in density with temperature versus the increase in vapor pressure at this operating pressure (Table 4).

CO₂ Flow-Rate (Experiments 1 and 8)

($P_{\text{ext-ads}} = 6.6$ MPa; $T_{\text{ext}} = 32.0^\circ\text{C}$;

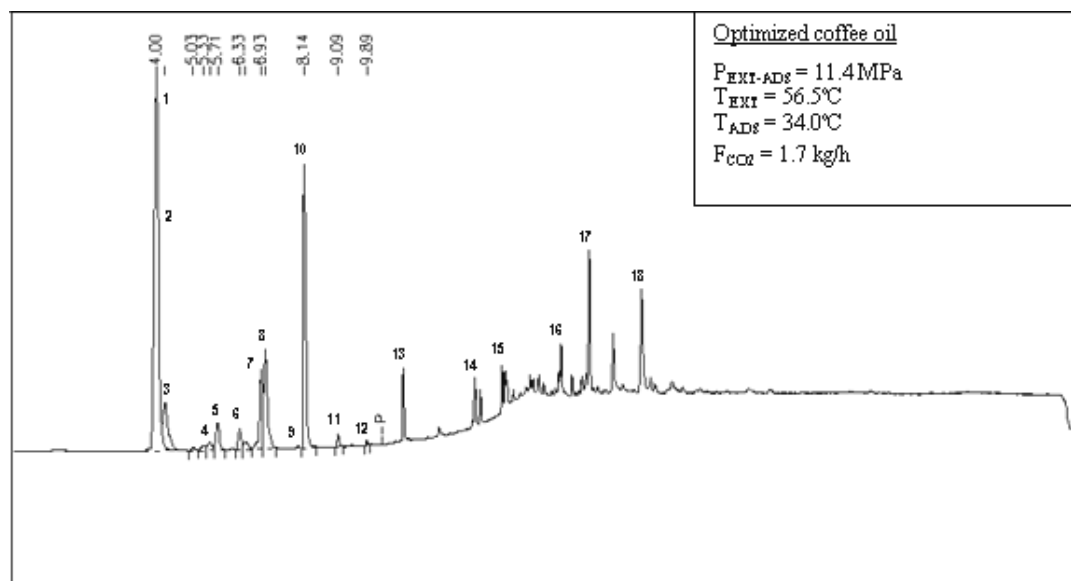
$T_{\text{ads}} = 33.0^\circ\text{C}$; $F_{\text{CO}_2} = 3.5, 1.7$ kg/h)

In the selected range no effect of flowrate can be observed in the final coffee oils (Table 4).

In Figure 2 the chromatogram of the final coffee oil obtained under the optimal operating conditions is shown.

Table 4: GC/MS analysis of original and final coffee oils obtained by the process of SC extraction-adsorption.

Compounds	Experiments / % Area									
	Oil	1	2	3	4	5	6	7	8	9
2,4-Imidazolidindione	85.51	87.47	51.99	64.84	41.97	87.58	54.54	89.21	87.48	99.28
2-Aminopropanol	8.85	8.83	28.10	23.35	24.82	10.74	7.15	4.77	9.65	-
2-Acetoxi-propene	-	1.29	15.27	-	26.82	-	3.29	2.57	1.04	-
Ethyl acetate	-	0.77	2.88	4.12	2.37	0.82	1.12	1.17	0.57	-
Dichloromethane	-	-	-	-	1.82	0.47	11.71	0.47	-	0.37
Octametilcycletetraxyloxane	5.64	2.64	1.77	7.69	2.19	0.39	22.19	1.81	1.06	0.36



- | | | |
|--------------------------|---------------------------------|---------------------------|
| 1. 2,4-Imidazolidindione | 7. 2-Methylbutanal | 13. 2,4-Furandione |
| 2. 2,4-Imidazolidindione | 8. Dichloromethane (solvent) | 14. 2-Methylpyrimidine |
| 3. 2,4-Imidazolidindione | 9. 2,3-Butanedione | 15. 1-Hydroxi-2-propamine |
| 4. 2-Aminopropanol | 10. Octametilcycletetrasiloxane | 16. Acetic anhydride |
| 5. Acetoxipropene | 11. 2,3-pentanedione | 17. Furfural |
| 6. Ethyl acetate | 12. Piridine | 18. 2-Furanmethanol |

Figure 2: Chromatogram of enriched coffee oil obtained under the optimal operating conditions.

CONCLUSIONS

Optimization of the operating conditions of the integrated process proposed comprising CO₂ supercritical extraction and aroma concentration on activated carbon reveals that an extraction-adsorption pressure of 12 MPa (quasi-isobaric process), an extraction temperature of 56°C, an adsorption temperature of 35°C and a CO₂ flowrate of 2 kg/h permit to be obtained a delicate balance in the composition of volatiles in the final coffee oil. This general result corroborates the optimization of the adsorption step carried out with ethyl acetate and furfural as key coffee compounds. This analysis revealed that low adsorption pressures (12 MPa), low adsorption temperatures (35°C) and low CO₂ flowrates were suitable for retaining ethyl acetate (desirable compound) and removing furfural (pungent compound).

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NOMENCLATURE

FBU	Fractional Bed Utilization	(%)
F _{CO₂}	CO ₂ flowrate	(kg/h)
M	Molecular weight	(g/mol)
P	Adsorption pressure	(MPa)
q _b	Adsorption capacity at breakthrough point	(g _{SOLUTE} /g _{CARBON})
q _s	Saturation adsorption capacity	(g _{SOLUTE} /g _{CARBON})
Removal Ratio	Removal ratio efficiency	(%)
T	Adsorption temperature	(°C)
t _b	Breakthrough time	(min)
t _s	Saturation time	(min)

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