CO_2-EXTRACTION TEST FACILITY FOR EXTRACTION PRESSURES UP TO 1000 BAR: EXPERIMENTS FOR THE EXTRACTION/DECAFFEINATION OF COCOA

Josef Schulmeyr

NATECO$_2$ GmbH & Co.KG
Auenstraße 18-20
85283 Wolnzach, Germany
e-mail: Josef.Schulmeyr@nateco2.de

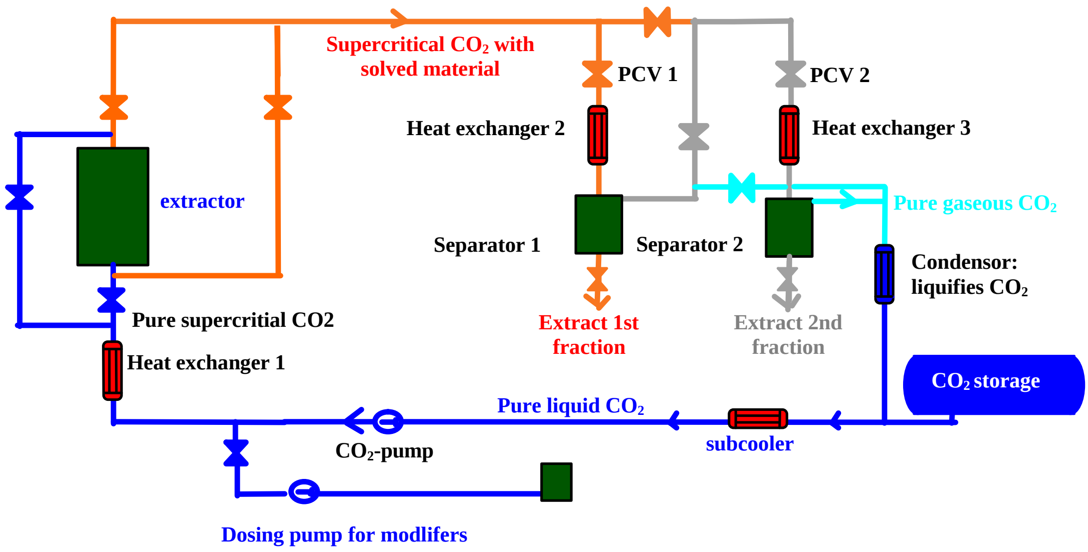
1 INTRODUCTION

From the literature it is known, that the solubility of substances in supercritical carbon-dioxide depends on the pressure and temperature of the solvent. Higher pressure and therefore higher density often improves the solubility of substances. Beyond this changes in interactions allow to extract molecules which are difficult to dissolve at lower pressures.
Most of the larger production facilities work with pressures below 300 bar. The design pressures are limited to approx. 500 bar as the plant costs rise superproportionally with increasing pressure. This paper describes a pilot plant which was built in order to be able to examine new extraction areas, requirements specific to the plant, special chemical engineering features and economic effects.

2 DESCRIPTION OF THE 1000 BARS PILOT PLANT

The plant is arranged according to the flow chart shown in Figure 1.

Figure 1: Flow-sheet of the 1000 bar CO_2 extraction plant



The pump compresses the CO_2 to the desired pressure and the solvent is tempered to extraction conditions in the heat exchanger 1. The carbon-dioxide flows either from the bottom to the top of the extractor or vice versa. The plant can be operated with a 2-step separation or with 2 parallel separators.

The loaded gas is depressurized at the PCV 1 (pressure control valve) to the separation pressure of the first separation step. Heating or cooling follows in heat exchanger 2 to adjust the separation conditions. Parts of the dissolved material fall out and are collected in separator 1.

At the PCV 2 the gas pressure from the separator 1 is reduced to the CO_2 storage pressure and the carbon-dioxide is set to the required temperature of the second separation step by heat changer 3. The substances are separated in separator 2.

The regenerated solvent is then liquefied in a condenser and subcooled and recirculated to the CO_2 pump.

A dosing pump allows addition of modifiers between CO_2-pump and heat exchanger 1.

Table 1: High pressure test facility 1000 bar

Components	design pressure	design temperature	volume
1 Extraction vessel	1025 bar	-10 °C/140 °C	75 l
2 Baskets			52 l
2 Separation vessels	350 bar	-10 °C/140°C	43 l
Heat exchanger 1	2000 bar	150°C	-
Heat exchanger 2/3	400 bar	150°C	-
Condenser	100 bar	120°C	-
Subcooler	100 bar	120°C	-
Storage tank for CO_2	100 bar	-10 °C/150°C	700 l
Circulation pump for CO_2	1000 bar	-	300 kg/hr
Dosing pump for modifiers	3000 bar	-	0-7 l/hr

Performance of the test facility

Extraction

extraction pressure	:	70 bar – 1000 bars
extraction temperature	:	5 °C – 120°C
mass flow of CO_2	:	180 kg/hr – 300 kg/hr
flow direction of the solvent in the extraction vessel	:	upward or vice versa
dosing of modifiers	:	0-7 l/hr (water, ethanol, acetone, etc.)

Separation

separation pressure in Separator 1	:	65 bar – 300 bar
separation pressure in Separator 2	:	60 bar – 65 bar
temperatures in the separators	:	15°C – 120°C
Separation, flow of solvent	:	serial (pressure fractionation) or parallel (time fractionation)

All vessels are equipped with quick closures (see figure 2), minimizing standstill during the individual cycles. The plant design allows quick and efficient cleaning and therefore easy changes in products.

Figure 2: 1000 bar-extractor`s c

The extraction parameters can be varied between 70 bar – 1000 bar and 5 – 140°C.

The separation conditions can be varied between 65 und 300 bar in Separator 1 and 60-65 bar in Separator 2. For both separators the separation temperature can be set between 15-120°C.

The selected extraction volume (approx. 50 l) allows the preparation of extract samples and the calculation of production costs.

3 PRESENT STATE ON THE DEXANTHINISATION OF COCOA WITH COMPRESSED CO_2

- Theobromine and caffeine can be extracted from green unroasted cocoa nibs with CO_2 after swelling of the nibs with water without affecting the concentration of cocoa butter in the nibs. [1]
- Theobromine and caffeine can be extracted from cocoa nibs with CO_2 adding ethanol as cosolvent in much shorter times. Simultaneously cocoa butter is extracted. [2]
- Theobromine and caffeine can be extracted from cocoa shells with CO_2 after swelling the shells with water. Large quantities of solvent have to be cycled. [3]
- Theobromine and caffeine can be extracted from roasted cocoa nibs with CO_2 adding ethanol and water as cosolvent. The best extraction parameters are 280 bar, 80°C and

9,5 weight-% ethanol in CO_2. With these parameters the relative amount of CO_2 needed is 150 kg CO_2/kg nips (m_{rel}). [4]

4 TESTS FOR DEXANTHINISATION OF COCOA WITH CO_2 AT PRESSURES UP TO 1000 bar

Is it possible to remove xanthines from cocoa without entrainers at higher pressures (max. 1000 bar)?

4.1 STARTING MATERIALS

Three different processed cocoa products were used for the tests:

- defatted cocoa cake: fat content < 1 weight-%, defatted with supercritical carbon-dioxide (p ∠ 300 bar)
- cocoa cake 10/12: cocoa cake, pressed to a fat content between 10 and 12 weight-%
- roasted cocoa nibs: broken and roasted cocoa beans without shells

4.2 TESTING METHOD

The various cocoa products were filled into the extraktor´s basket of the 1000 bar pilot plant. Carbon-dioxide flowed through extraction material from the bottom to the top.
Entrainers have been injected when needed.

4.3 RESULT AND DISCUSSION

- **Tests without entrainers**

- defatted cocoa cake

Ex-press.	Ex-temp.	m_{rel}	Theobromine	Theophylline	Caffeine	Fat
Starting material			2.20 %	n.n.	0.15 %	0.10 %
800 bar	80°C	500	1.69 %	n.n.	0.13 %	0.02 %

- Cocoa cake 10/12

Ex-press.	Ex-temp.	m_{rel}	Theobromine	Theophylline	Caffeine	Fat
Starting material			2.04 %	0.01 %	0.18 %	10.1 %
800 bar	50°C	100	1.72 %	0.01 %	0.16 %	0.03 %
800 bar	80°C	100	1.63 %	0.01 %	0.13 %	n.n.
800 bar	80°C	500	1.35 %	n.n.	0.16 %	0.03 %

- Cocoa nibs

Ex-press.	Ex-temp	m_{rel}	Theobromine	Theophylline	Caffeine	Fat
Starting material			2.20 %	0.06 %	0.20 %	50.1 %
800 bar	80°C	360	1.87 %	0.04 %	0.19 %	30.8 %

Theobromine, theophylline and caffeine contents calculated on water and fat-free cocoa.

Dry carbon-dioxide at 800 bar and 80°C is in a position to extract theobromine from the cocoa products tested. However, considerable amounts of CO_2 have to be circulated to attain a reduction of approx. 30 %.

When reducing the extraction temperature from 80°C to 50°C the reduction is only approx. 15 %.

Cocoa butter was extracted in the case of all three cocoa products. With defatted cocoa cake and cocoa cake 10/12 the fat was almost totally extracted. Also in the case of cocoa nibs the fat content dropped from 50.1 weight-% to 30.8 weight-%.

Cocoa dexanthinisation cannot be carried out economically with dry CO_2 as regards any of the three tested cocoa products.

- **Tests with water as entrainer**

- defatted cocoa cake, cocoa cake 10/12
An extraction with water-saturated carbon-dioxide is impossible, because cocoa adsorbs the water, swells and finally blocks CO_2-flow.
- cocoa nibs

Ex-press.	Ex-temp.	m_{rel}	Theobromine	Theophylline	Caffeine	Fat
Starting material			2.20 %	0.06 %	0.20 %	50.1 %
800 bar	80°C	500	0.07 %	n.n.	n.n.	7.8 %

Theobromine, theophylline and caffeine contents calculated on water and fat-free cocoa. Cocoa nibs can be almost completely dexanthinised with wet carbon-dioxide. The cocoa nibs were not moistened before the extraction. During the extraction the water-content of the nibs raised from 3.1 weight-% to 35.4 weight-%, so that afterwards they had to be dried.

5 CONCLUSION

Dexanthinisation of cocoa with dry carbon-dioxide is not possible in an economically feasable time even with pressures of 800 bar. The xanthines can be almost totally extracted by adding water as an entrainer. This means that due to higher extraction pressures the ethanol fed as a second entrainer can be omitted.

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