

INDUSTRIAL CO₂ PROCESSING OF FOODSTUFFS

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1 Introduction

1.1 THERMAL SEPARATION PROCESSES

"We live in a world of mixtures - the air we breathe, the food we eat, the gasoline in our automobiles ..."[1]
Therefore raw materials as well as synthetic products have to be separated into desired and undesired components for further use.

Normally, the various types of separation processes are defined by the kind of energy used, e.g. mechanical or thermal ones. The separation of solid or liquid substance mixtures by means of extraction which is of interest in the following belongs to the group of thermal separation procedures. In the case of extraction, the separation is effected by an auxiliary agent, the solvent. The different solubilities of the individual components in the phases involved, i.e. the selectivity of the phase transition determines the success of separation. After the separation step, the solvent is removed from the miscella, e.g. by evaporation in order to obtain the dissolved components.

Everyone is familiar with the separation of solid substance mixtures by means of liquid solvents when making coffee or tea.

Solvents are usually inorganic or organic liquids which are volatile under standard conditions. They are able to extract (= remove) other gaseous, liquid or solid substances from a mixture and can be separated afterwards. During this dissolution process no chemical reactions should take place. According to the kind of application, e.g. in the case of obtaining extracts for pharmaceutical purposes or for foodstuffs, different requirements may result.

The request that solvents have to be suitable for their application sounds nearly trivial:

On the one hand, solvents should be able to dissolve the desired components as well as possible so that with a low use of solvents an economic method can be achieved. On the other hand, undesired components shall not be extracted. Mostly, both requirements cannot be met at the same time adequately. The selection is furthermore limited due to environmental standards and security regulations (emission into the atmosphere and waste water) [2].

1.2 PHASE EQUILIBRIA AND SOLUBILITY

Separation procedures which use an auxiliary agent for the separation of substances can be distinguished according to the thermodynamic state of this auxiliary agent. The vapor pressure curve ends in the so-called critical point where the vaporous and liquid phases are identical. That means that one phase can no longer be distinguished from the other. (According to the language of the persons doing research in this field in the 19th century: There is no more "criticism" possible between the two phases). At temperatures and pressures above the critical point it is not possible to reach the two-phase-field (gaseous-liquid) again, neither by reducing the temperature nor the pressure. In this homogeneous field the density and thus the dissolving power may be altered continuously by variation of pressure and temperature. Under ambient conditions gases have no dissolving power, apart from using them as transportation agents during the drying of solid substances and liquids. This is

not surprising since the average molecular distances between gases are in a portion of the hundredfold molecular diameter, while there is a dense packing in the case of liquids. Consequently the particle density of gases is too low, i.e. there are not sufficient molecules available which could solvate and transport the molecules to be dissolved. With the simple methods of the kinetic theory of gases it can be illustrated that at atmospheric pressure CO₂ molecules fill only to a quarter per mil the space available. At a density of 900 kgs/m³ (300 bar and 40°C) only about 13 % of the space are claimed by the molecules. (For the calculation the cross-section of a molecule was assumed with about 4 Angström = 4x10⁻⁸ cm as obtained from the measurement of transportation characteristics).

Gases develop a dissolving power only if a particle density similar to liquids is created. Whereas this dissolving power is achieved with liquids already due to the attraction by intermolecular interactions, it has to be forced by applying pressure from outside in the case of gases.

Therefore, equipment for the extraction with liquefied respectively compressed gases will be remarkable at least by a stronger wall thickness due to the higher pressure of the system. If liquefied gases are being used as means of extraction, the saturation pressure has to be regulated with the respective temperature in order to prevent an evaporation of the gases. Liquefied gases as extraction means have been known for a comparatively long time - a patent of the year 1904 [3] (made up in a pleasant short form) for example suggests the use of liquefied carbon dioxide as solvent for the extraction of fats.

2 Application in the field of natural products

2.1 LIQUID CARBON DIOXIDE: DEVELOPMENT AND APPLICATION

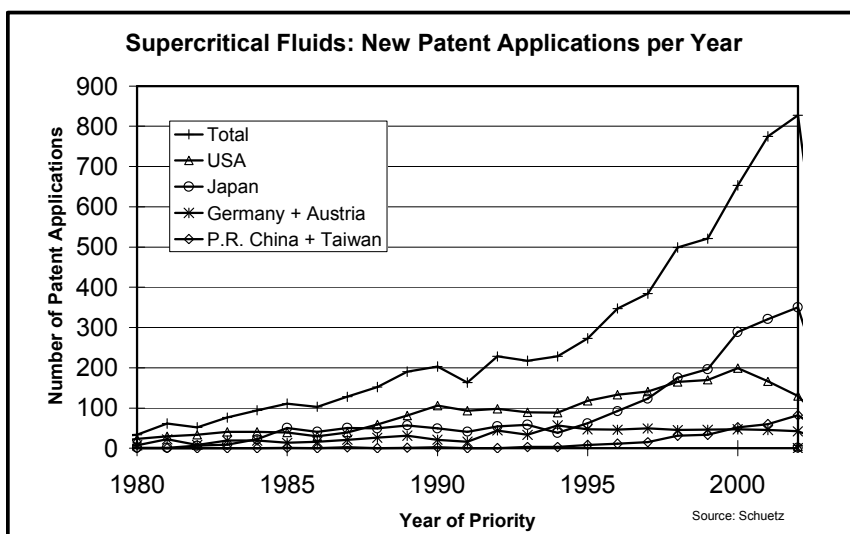
Up to now, liquefied carbon dioxide has only been successfully used for the extraction of hops. Compared to the extraction with supercritical carbon dioxide, however, the percentage is rather low, since the liquid state of the carbon dioxide limits in general the application of higher temperatures during the extraction. Therefore, the diffusion capacity of the components which have to be dissolved from the cellular matrix into the solvent is reduced. Consequently, the extraction time becomes longer and the throughput at a given extraction volume is reduced. Another disadvantage is that part of the polar components which are soluble in supercritical carbon dioxide cannot be dissolved in liquid carbon dioxide. Inevitably, part of the components is not present in the extract.

2.2 PATENTS AS AN INDICATION FOR DEVELOPMENT

The starting point for the application of the extraction with supercritical fluids in the field of natural substances was a research program in the Max-Planck-Institute for Coal Research in Mülheim at the beginning of the 1970ies.

With a basic and very expansive application, it was tried to have the extraction by means of supercritical gases patented [4]. A large number of individual patents for procedures and equipment for the extraction of natural substances as e.g. cacao, spices, hops, coffee, tea, tobacco has subsequently joined the basic patent. Even if partly other solvents are listed besides carbon dioxide, up to now only carbon dioxide has been used in the industrial scale.

Whereas the number of (scientific) publications can be regarded as a measure for the importance of a special range of research the number of patent applications betrays the economic considerations and interests of the industry. In Figure 1 the increasing quantity of applications in the field of high pressure extraction is presented. In the early years of the century mainly applications for gas recovery and refinery are covered. As explained above since the seventies the applications focus to high pressure extraction as we deal with nowadays.



2.3 PATENTGROUPS (SUGGESTIONS FOR APPLICATION)

2.3.1 Extractive - Non extractive applications

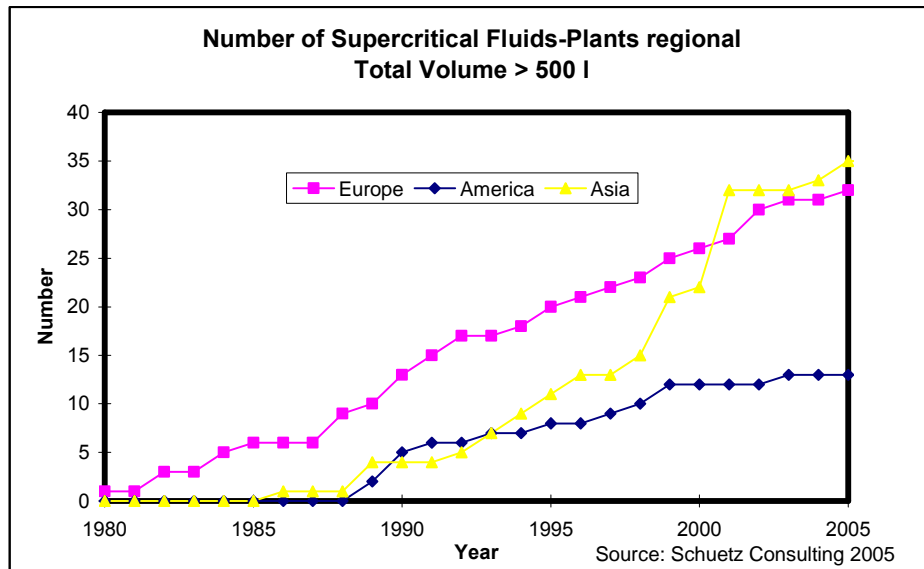
An analysis of the group of patents directly manifests the applications regarded as useful (Table 1). On the other side the number of patents should be considered with care. Up to now there is a considerable difference (perhaps like in all technical applications) between patents and real applications.

Table 1: Patents Supercritical applications

Group 1	SFE	Group 2	Impregnation
	food		textiles
	lipids	Group 3	Chemistry/Reactions
	(chemical) cleaning		supercritical water oxidation
	pharmaceuticals		reactions
	chemistry		polymers
	aromas		biotechnology
	decaffeination	Group 4	Particle generation
	defatting		crystallisation, particles,
			precipitation, micronisation
	oils and fuel		surfaces, coatings
	fractionation		
	environmental protection		
	coal		
	tobacco		
	cleaning of textures		
	drying		
	alcohol		
	cosmetics		
Miscellaneous			
	reduction of mould, yeast, germs, pests		
	chromatography		

2.3.2 Plants and capacities

Existing plants demonstrate the present status of high pressure extraction. In Figure 2 the installed vessels are plotted.



2.4 SUGGESTIONS - REALITY AND PLANTS

2.4.1 Decaffeination

Caffeine has been discovered in 1820 by Friedlieb Ferdinand Runge when he analysed Coffeebeans sent to him by Goethe (Chemische Rundschau 46, 14. November 1986).

Recognition of the physiological effects of caffeine in coffee prompted the development of processes for removing the caffeine ideally without changing flavour and aroma.

In the early 1900's a process was invented by Roselius and Wimmer in Germany for removing caffeine from coffee with an organic solvent. In the USA Roselius decaffeinated and sold coffee under the label of Kaffee HAG since 1912. This company was expropriated in World War I and purchased by Kellogs. In the late 1920 Roselius established a co-operation with General Foods and sold decaf under the label of SANKA. In 1937 General Foods bought the HAG label from Kellogs to become the sole producer of decaf till the mid 50's.

After about 15 years of development in 1978 HAG in Bremen started up its decaffeination process using supercritical CO₂, thus becoming the first large scale processor.

For historical reasons solvents suggested for decaffeination in U.S. patents are listed.

Chlorinated Hydrocarbons	Dichloromethane (Methylene Chloride) Chloroform Carbontetrachlorid Dichloroethylene Trichloroethylene Tetrachloroethylene
Various Fluorinated Hydrocarbons and Aliphatic Hydrocarbons	
Aromatic Hydrocarbons	Benzene Dichlorobenzene Toluene
Esters	Ethylacetate
Aldehydes, Ketones, Alcohols	multitude of examples
Fats and Oils	Coffee Oil, Vegetable oils, Paraffin oils
Inorganic agents	Lime-Soda Solutions Mineral Acids Ammonia Sulfur Hexachloride SF ₆ Carbon Dioxide

Benzene was one of the first commercial solvents used. But as chlorinated hydrocarbons became available at reasonable prices it was dropped in favor of Trichloroethylene and later by Methylene Chloride. Nowadays only

- CO₂
- Water
- Ethylacetate

are used as solvents. To some extent Methylene Chloride is still in use as solvent for the decaffeination of tea.

Most coffee decaffeination is performed on the green beans prior to the roasting process where flavors and aromas are developed. However, (patent) literature discloses a variety of procedures for the decaffeination from already roasted beans as well as roasted coffee extract incorporating procedures for aroma removal prior to decaffeination with addback after the decaffeination step.

Tea can be decaffeinated as green or black tea. Contrary to coffee green tea cannot be converted to black tea after decaffeination.

2.4.2 Hops

Since centuries hops is added to beer as preserver. Only nowadays after practicing sterile production conditions hops is used predominately to give the well known bittering aroma impact.

After the harvest of the hops end of August the strobiles are separated from the plant and are immediately dried and can be stored. Temperature and Oxygen cause the valuable components to deteriorate thus it is recommended to store the product under reduced temperature and in the absence of Oxygen.

Because of the low bulk density of the dried raw hops it is preferred to reduce volume and mass by concentration. Two methods are feasible and practiced:

- The raw hops is milled, optionally concentrated by wind sieving under low temperature (- 30 °C) and then pelleted. The pellets are packed into foils and evacuated or preferably inertised.
- The raw hops is milled and extracted with solvents. Compared to the solvents suggested for decaffeination the list is quite short:

Alcohols	Methanol Ethanol Isopropanol
Hydrocarbons	Pentane Hexane
Chlorinated Hydrocarbons	Dichloromethane Chloroform Trichloroethylene

Today hops is processed to liquid extract with Carbon Dioxide and Ethanol. Plants, solvents and capacities are monitored in the following Table 3.

country	owner	solvent	capacity t/d	other products
Germany	NATECO ₂ GmbH & Co.KG	CO ₂ , supercritical	50-60	tea, cacao defatting, oil seeds, spices, misc.
	Degussa (SKW)	CO ₂ , supercritical	20	tea, cacao defatting
	HHV Hallertauer Hopfenveredelungs- gesellschaft	Ethanol	40	
USA	John I Haas Inc. (Barth-Haas-Group)	supercritical CO ₂ ,	20-25 30	
	S. S. Steiner Inc.	CO ₂ , supercritical	15	
	Cultor (Pfizer) now also Haas	CO ₂ - liquid	20	
Australia	Carlton United Breweries	CO ₂ - liquid	3,6	for own purposes only
UK	Steiner	CO ₂ - liquid	6	
	Botanix (Barth-Haas-Group)	CO ₂ - liquid	12	

Table 3: Extraction plants and capacities for Hops

Processing to liquid extract is performed only successfully since the beginning of the 60ies, although early suggestions date back to the beginning of the 19th century.

2.4.3 Spices

Compared to the large quantities of decaffeinated coffee and tea, as well as extracted hops the throughput of spices is comparatively small. Dominating is the extraction of pepper. Other spices are minor. Pepper extract can be easily separated into the sharp principle - Piperine - and the pepper oils by fractionating separation. One example for the elegant performance of SFE.

2.4.4 Oil recovery

An example for application is the recovery of highly unsaturated fatty acids, rich in gamma linolenic acids, from the seeds of Evening Primrose and Borage (*Borago officinalis*). Fractionating separation is used to split the extracted oil into Fraction 1 containing mainly the fats (fatty acids esters) and Fraction 2 containing concentrated the free fatty acids and water.

Recently the extraction of Saw Palmetto Berries (*Sabal* or *Serenoa Repens*) gets some importance. Some (sitosterols) are comparatively concentrated in the berries and are believed to stop growth of prostate cancer.

2.4.5 Defatting

Cocoa butter is recovered from beans by mechanical pressing. Standard butter content is then about 20 % (weakly deoiled) and 10 % (strongly deoiled). Higher defatting can not be effected by pressing but by solvent

extraction. Hexane as solvent has been replaced partially by SFE using CO₂. After some years of augmentation now the market seems to be stable at reasonable level.

For defatting of e. g. cocoa and egg yolk the use of propane and mixtures of propane and CO₂ has been suggested in the patent literature. Compared to CO₂ propane exhibits a considerably higher solubility thus shortening tremendously the extraction time. An other advantage can be seen by the more than 10 times lower extraction pressure. Nevertheless no larger plants are known.

2.4.6 Others

Some other fats and oils as well as waxes are produced on a small scale for the cosmetic market. Nothing is known with respect to the pharmaceutical market. The manufactures seem not be willing up to now to start the long lasting and expensive procedure at the health authorities for new products or components manufactured with e. g. CO₂ as solvent.

Food ingredients (natural colors, antioxidants) present up to now only a small niche. Consumer expectations will augment this market in the future.

2.5 LIMITS FOR THE APPLICATION OF SFE

Why are supercritical fluids applied so rarely, even though much is said and written about their use?

A possible answer should consider the following two aspects:

- For the mainly processed products as for example coffee, tea, hops, spices, oilseeds, alternative products and/or possibilities of processing to the kinds of application hitherto known, are available: Table 4.

product	raw material	prepared raw material	(cold) pressing	solvent water	solvent Ethyl-acetate	solvent Di-chloro-methane	solvent Ethanol	solvent Hexane
coffee green				yes	yes	yes		
tea (fermented)					yes	yes		
hops	yes	yes					yes	yes
spices	yes					yes	yes	yes
oilseed			yes					yes

Table 4: CO₂ - applications and competing processes

- As to the applications practiced so far, for which in most cases substance mixtures were extracted from a solid substance mixture, only the solvent was replaced. Solvent-free extracts are not yet sufficiently known as alternatives. As regards complicated processes with liquid-fluid phase equilibria or chemical reactions for example there has been a lack of knowledge in spite of many publications. Therefore it has not been possible to optimize processes and energetics. Especially the separation of the dissolved constituents not only into fractions, but also, if possible, into individual components makes it necessary to have an exact knowledge of the phase equilibria.

3 Outlook for the future

It is remarkable that up to now the main impulse for the application of Carbon Dioxide as solvent was the mere replacement of conventional solvents that have become suspicious because of several reasons. Applications where dense gases can exhibit their real advantages like in fractionating extraction or separation or in continuous fluid/liquid countercurrent extraction are somewhat rare up to now. Economics together with legal (environmental) injunctions will determine the future of the applications of dense gases in foodstuff and similar industries. Most often one has to compete with alternative products or processes. Up to now, liquefied carbon dioxide has only been successfully used for the extraction of hops although already in 1904 a patent has been granted for the extraction of fats. Because of higher efficiency (better diffusion at higher temperatures effecting

shorter extraction times and higher throughput at given plant size) extraction with supercritical Carbon Dioxide is dominating in:

Decaffeination of coffee and tea, extraction of hops and spices, extraction of (high quality) seed oils and defatting of cocoa.

Recovery of extracts: Recently the Chinese and Indian market has been developed with SFE plants for spices, aromas and other food ingredients like antioxidants. This might be a step into the processing of raw materials directly in the producing countries.

Cleaning of raw material: This procedure is already practiced with respect of Ginseng, where the pesticides that still in the soil can be removed with CO₂. Formally the decaffeination of coffee and tea can be classified in this scheme. Now it turns out that in Far East a plant will be installed for cleaning of rice (removing of plant protectives) with CO₂.

Generally the large plants (volume of one vessel >2 m³, several extraction vessels) built in the past for

- decaffeination of coffee and tea
- recovery of extract from hops and other spices
- recovery of fats and oils

will continue to produce but will not be multiplied for new applications. The need for the extraction of commodities is decreasing and/or the revenues for these products are getting worse and worse. Unambiguously there is a downtrend for such 'elephant' plants. The future will be open for small, multipurpose and easy to operate plants designed for higher pressures. With these plants high prized, small quantity products will be processed.

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 super-proportionally with increasing pressure. Nevertheless NATECO₂ as a specialist for the extraction with CO₂ designed a **process unit up to 1000 bars** in order to be able to examine new extraction areas, requirements specific to the plant, special chemical engineering features and economic effects. Because of the rather big volume of the extraction vessel (50 l) sizeable quantities can be treated and even with small yields a considerable amount of extract can be recovered for e. g. product evaluation. Extended test series have been conducted to recover Polyphenols (Xanthohumol) from hops, antioxidants like Carotinoids from different sources and to remove Xanthines (Caffeine, Theobromine) from cocoa [8].

Other applications may arise in non food that are already discussed in literature and conferences but have been stressed in this article only shortly (dyeing, particle generation). Also there seems to be a market in 'waste' recovery.

4 References

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