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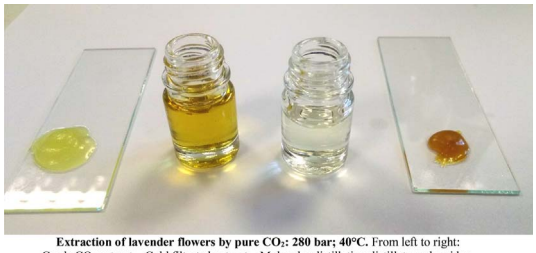
Towards ingredients by combining Supercritical Fluids with other processes

Michel Perrut*, Vincent Perrut

Atelier Fluides Supercritiques, Nyons, France

GRAPHICAL ABSTRACT

Extraction of lavender flowers by pure CO_2: 280 bar; 40 °C. From left to right: Crude CO_2 extract – Cold filtrated extract – Molecular distillation distillate and residue.



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ABSTRACT

"*Crude extracts*" obtained from most natural sources cannot be used as is from a supercritical fluid (SCF) plant and have to be reprocessed to eliminate water, pigments and waxes so as to become "clean extracts" that are concentrated in active compounds for direct use as ingredients in food, cosmetics or nutraceuticals/pharmaceuticals.

On the other hand, the solid or liquid *raw material* can be processed as the ingredient itself from which unwanted compounds are eliminated and/or in which a valuable solute is infused.

Several *on-line* or *off-line* processes are proposed so as to obtain such "ready-for-use" ingredients by combination of supercritical fluid processes (extraction, fractionation, impregnation) and other techniques including vacuum and molecular distillation, centrifugation and dehydration, adsorption on specific adsorbents, cold filtration and winterisation.

1. The challenge

Supercritical extracts from seeds are generally obtained in the form of oil that is usable as it exits from the extraction process; similarly, hop extracts can be directly incorporated into final ingredients. However, most supercritical CO_2 extracts of natural products appear as a viscous paste, like a dark brown or green "mayonnaise" emulsion consisting of a mixture of lipids, water, pigments (carotenoids, chlorophylls) and waxes (Fig. 1).

So it is not surprising that potential clients ready to incorporate SCF-processed extracts into their products are discouraged seeing such extracts that are so far from their specifications. Consequently, they have often abandoned this technological route or delayed its adaptation for long (or for ever!). This may explain the rather limited development of this technology in spite of its numerous advantages in comparison with classical extraction processes.

On the other hand, operators are also facing an economic dilemma:

- Either extraction is operated at rather low pressure, so that waxes and pigments are not present in extracts, but the required solvent ratio is very high and jeopardizes extraction profitability, or
- Extraction is complete with a much smaller solvent ratio in harsher

* Corresponding author.
E-mail address: michel.perrut@atelier-fsc.com (M. Perrut).

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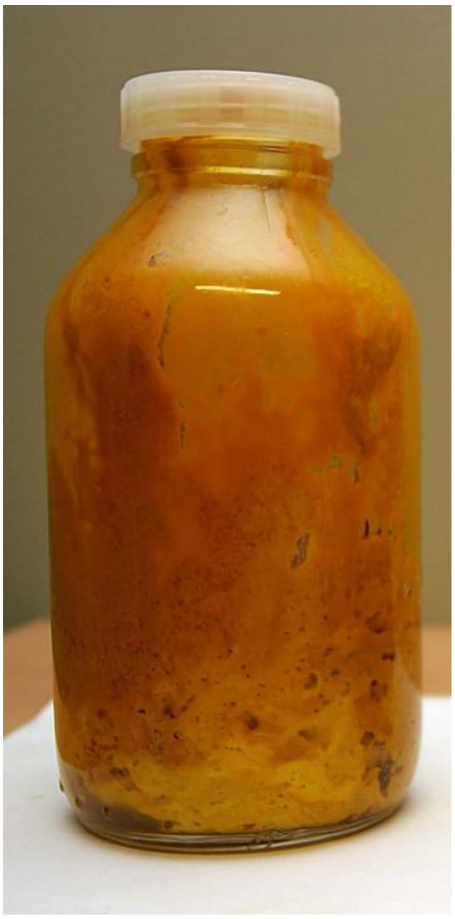

Fig. 1. Total extract of *Thymus vulgaris* L. *linaloliferum*.
Pure CO_2 @ 280 bar; 45 °C; 12 kg CO_2/kg feed; Yield (mass basis): 4%.

conditions leading to an extract that consists of a complex mixture that must be reprocessed to purify the targeted compounds.

Extraction advancement of a flower versus solvent-to-feed ratio at 100 bar and 280 bar, is presented in Fig. 2. At 100 bar, a clear pale yellow oil of great fragrance value is obtained while, at 280 bar, a brown viscous oil with a rather unpleasant odour is collected, but with a higher yield and much lower solvent ratio than with the preceding condition.

In fact, it is necessary to address the following challenge: How should a process be designed to reach a readily usable ingredient at an acceptable cost? This concerns both

– Ingredient quality: consistency (clear liquid, solid or paste), composition, colour, odour, trace compounds and pollutants, stability, possibly organic label,
– Process operation and cost: ingredient yield, process flexibility, process acceptability referring to standards (organic when required), safety and global cost?

Even if most of the techniques leading to “clean extracts” that could be directly incorporated as ingredients into food products, cosmetics or nutraceuticals/pharmaceuticals, have been known for long, such as some of those described in the pioneering books of Stahl et al. [1] and Brunner [2], and many more recent ones (see also all Proceedings of ISASF symposia available on their web site [3]), it is still necessary to support the development of SCF technology. This is a call of utmost importance to all those working in the field.

2. Directions for addressing this challenge

2.1. Water removal

All vegetal stuffs, even dried, do contain some moisture. As water is slightly soluble in CO_2, extracts are often in form of an emulsion that is difficult to break. But it is also a valuable opportunity: in fact, water plays a major role as co-solvent for medium polarity compounds present in plants (i.e. extraction of caffeine from coffee beans and tea leaves by supercritical CO_2 is only possible after humidification of the vegetal material), forms carbonic acid that also improves extractability of some natural compounds and facilitates access to the valuable compounds by influencing cell membrane permeability.

Water removal from crude extracts is sometimes easy by simple *decantation,* but, in most cases, *centrifugation* is required (Fig. 3). When the emulsion is very stable, filtration on a *dehydration salt* (i.e. sodium sulfate or even food-grade sodium chloride) is required to perfectly clarify the oily phase. Moreover, when “dry” raw material (low-moisture content) is processed, *on-line water adsorption* on a 3A-molecular sieve is often sufficient.

Another typical example involves the extraction of vanilla beans by SCF CO_2. After collection, the waxy dark brown extract is heated to 65 °C to obtain a completely liquid product and then decanted to separate the different phases (Fig. 4). This permits to collect two valuable products: A high-value upper lipid phase (with 10% vanillin content) that finds attractive applications in cosmetics, and a solid phase highly concentrated in vanillin (60–90%) obtained by evaporation of the bottom oil phase and the aqueous phase, to be incorporated in food products.

2.2. Waxes and “Ballast” elimination

2.2.1. Precipitation in liquid CO_2

The “best” *on-line* method to eliminate waxes consists of using a first separation-step where CO_2 is in the liquid phase, to cause wax

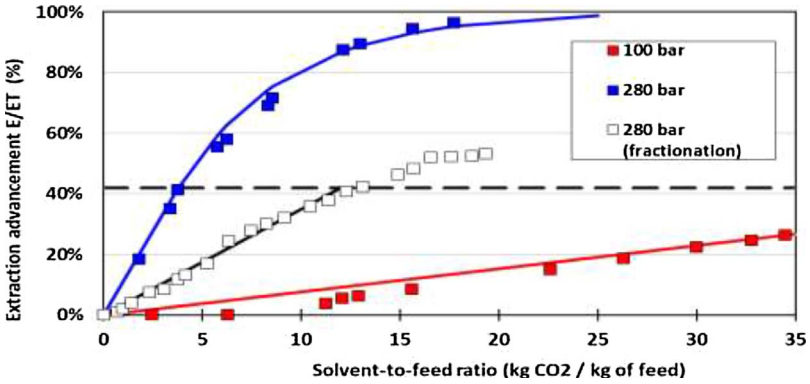

Fig. 2. Extraction kinetics of a flower by pure CO_2 @ 100 and 280 bar; 40 °C.
Ratio of the current extract mass E to the total extract mass E_T versus solvent-to-feed ratio.