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DEODORIZATION AND DISCOLORATION OF LIPIDIC AND AQUEOUS LIQUIDS BY SUPERCRITICAL CO_2

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ABSTRACT

Meanwhile the natural character of many ingredients incorporated in food, cosmetics, nutraceuticals or phyto-pharmaceuticals is demanded by an increasing number of consumers, a great attention is also paid to their organoleptic properties, especially, taste and odor for edible products, and at least odor and often color for cosmetics.

Supercritical technology is a "green" solution for eliminating off-odors without altering the natural character and possible "organic" label of such materials. We demonstrated deodorization and discoloration of several liquids on the commercial scale by contacting such liquids in a counter-current packed column with supercritical CO_2 that is further depressurized for collection of the liquid extract (often in very limited amounts) and then percolated onto an adsorbent bed (in most cases, active charcoal) prior to recycle. Both lipidic and aqueous streams have been successfully processed.

In the case of lipids, the extremely unpleasant rancid odor resulting from oxidation of unsaturated fatty acids was eliminated from
- Fish oils and polyunsaturated fatty acid ethyl esters,
- Animal greases and fats,
- Free fatty acids.

Aqueous streams can also be processed. However, water being slightly soluble in CO_2, water dissolved in the fluid must be trapped as much as possible upward the carbon bed that might be otherwise completely saturated with water.

INTRODUCTION

The natural character of many products (food, perfumes and cosmetics, and nutraceuticals) is underlined by manufacturers to meet the increasing demands of consumers. But these consumers also demand a *reliable* quality meanwhile the agricultural sources are obviously variable from one location to the other, from one year to another. Moreover, climatic events and accidental contamination increases the need for a strict quality control and production means to reach the desired properties and compositions of such *natural* products.

Among other things, color and odor are obviously the very first properties that are observed by the consumer. And for most products, especially for incorporation in cosmetics and nutraceuticals, the ingredients must be *odorless* and *colorless*. This is a major challenge for industry that must simultaneously preserve the intrinsic quality of the source and reach an "acceptable" presentation of the ingredient: Most known processes for odor and/or color removal cannot be used as they may irreversibly damage the product and ruin its natural character! It is why supercritical CO_2 processes present a keen interest to meet such contradictory demands.

SUPERCRITICAL CO_2 PROCESSES

As it is widely admitted, contacting a natural material with CO_2 does not alter its natural character and possibly its *organic* label. Moreover, supercritical CO_2 is known to be a good solvent of most odorous molecules present in natural materials while most colorants are only very weakly soluble in CO_2.

Extracting odorous compounds from *solid* sources is widely operated in order to produce aromatic and perfume ingredients [1]. Few applications were also developed to eliminate off-flavors from seeds; other ones permit to obtain both an aromatic oil and a valuable odorless wax (i.e. rosemary antioxidant). Similarly, colorants are extracted from natural feeds (astaxanthin from micro-algae; lycopene from tomato wastes, carotenes from tagetes, etc.) or separated from the spice as for chilly (capsaicin and colorant).
We focus our attention on processing liquids on counter-current columns that can be operated on a continuous mode and permit to treat large amounts at relatively low price.

LIPIDIC LIQUIDS PROCESSING

Edible oils generally exhibit strong odors and colors that are eliminated by the classical treatments including neutralization, degumming and vacuum distillation. The main issue is rancidity that is caused by peroxidation of unsaturated bonds in fatty acids, leading to formation of fatty aldehydes of rather short chain that exhibits a significant volatility and an extremely strong characteristic odor that is very unpleasant must be removed for incorporation in food or cosmetics or nutraceuticals.

This is especially the case of polyunsaturated fatty acid-rich (PUFAs) that are of great biological value: ω3-PUFAs present in fish, krill and algae oils, but also in some vegetable oils (*α-linolenic acid* i.e. in black-current seed oil), ω6-PUFAs present in animal fats and some vegetable oils (*γ-linolenic acid* i.e. borage and evening primrose seed oil and *linoleic acid* i.e. grape seed and peanut oil). Moreover, in presence of light

and/or heat, these PUFAs have a tendency to polymerize and oxidize, leading to colored "heavies" that must also be removed to present a clear, pale yellow and odorless oil.
For completing these two operations of deodorization and discoloration, we developed a process especially targeted on marine oils that are of recognized biological interest as food complements [2].

More recently, as this previous process was shown to be too complex, we successfully developed a process using two columns in series (Figure 1), but using only CO_2 and no co-solvent:

- Elimination of heavies by extracting the glycerides (or derivatives in form of fatty acid ethyl esters) at high-pressure, in the range of 180-200 bar and 60°C,
- Elimination of light fractions (especially aldehydes and free fatty acids) and odorous compounds at lower pressure, in the range of 110-125 bar and 60°C.

In both phases, CO_2-to-oil ratio is rather high (30 to 60 kg/kg). CO_2 is recycled after percolation of a carbon bed.

In fact, it is important to follow the peroxides and aldehydes that are quantified by Peroxide and Anisidine Indexes, to be sure to stabilize such oils. Among other advantages, these processed oils remain saturated in CO_2 and are rid of oxygen that is so deleterious to their conservation. However, we emphasize the need for care storage of such oils, with addition of antioxidant (i.e. tocopherols, ascorbyl-palmitate, rosemary wax, etc.) and packaging under inert gas at low temperature and out of any source of light and heat.

As very large amounts of cooking oils are to be disposed of in our countries, we demonstrated that supercritical CO_2 is a very efficient and selective solvent, leading to roughly one third of black and ill-smelling oil (to be incorporated in fuel) and two-thirds of a pale yellow clear oil, looking like the original oil that could be incorporated in poultry alimentation [3,4]. In this case, a rather high pressure (250-300 bar) is preferred to limit the solvent-to-feed ratio for very large amounts of oil to be processed. However, for various regulatory reasons, this process could not be industrialized.

Beyond these rather special cases, we processed several types of vegetable oils for rancid odor elimination, including argan oil, woad (*Isatis tinctoria)* oil, linseed oil and, more importantly, large amounts of linoleic acid that was incorporated in a dermatologic product. Pressure is generally maintained in the range of 150-250 bar and temperature between 40 to 60°C to limit losses. Solvent ratio is in the range of 10 kg CO_2 per kg oil.

We recently operated a complete purification of a cosmetic animal grease: originally black and strongly odorous, the refined oil is a yellow-orange clear and odorless oil, after a first step of deceleration on bentonite and a second step of counter-current contact with CO_2 at a pressure of 250 bar and temperature of 50°C with a solvent ratio of 10 kg CO_2 per kg oil.

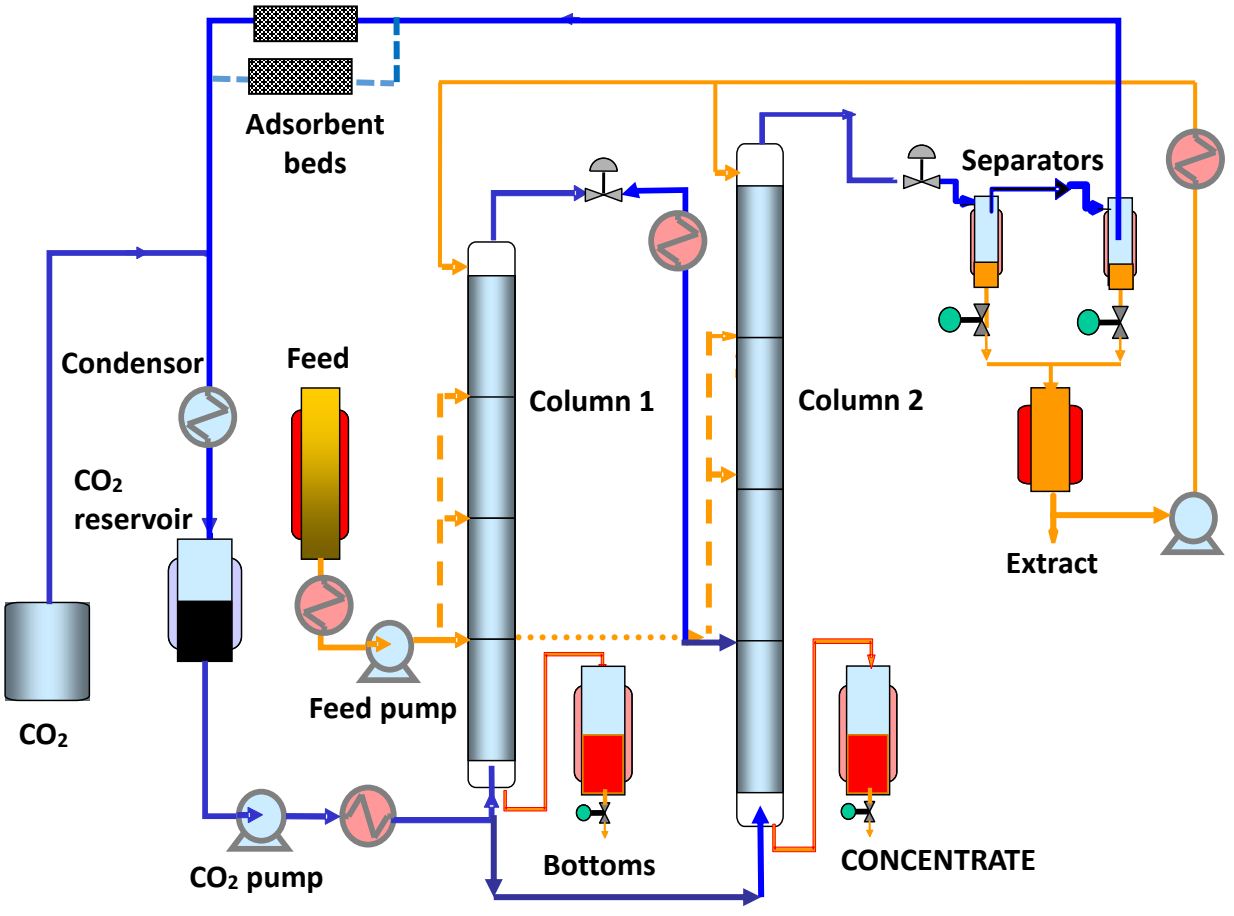

Figure 1 Flow-sheet of discoloration and deodorization of oils or derivatives

AQUEOUS LIQUIDS PROCESSING

More and more active ingredients are now synthesized by bio-processes, essentially by enzymatic reactions or fermentation using specific micro-organisms, both leading to aqueous streams and concentrates thereof. But, it is often observed that such active concentrates exhibit a characteristic unpleasant odor of fermentation, like the one emitted by yeasts, consisting in various volatile aldehydes and more complex compounds including sulfur and nitrogen containing molecules.

Supercritical carbon dioxide appears as a good candidate to remove these compounds, especially when the concentrate cannot be heated or when the active ingredient is too volatile to support vacuum distillation. As for lipid processing, aqueous streams are advantageously treated in a counter-current packed column to ensure an excellent contact between the two phases and odorous compounds are trapped both in the extract separators, but mainly in the adsorbent beds on the CO_2 recycle loop.

The difficulty lies in controlling the liquid-fluid interface due to liquid *foaming* when such liquid is contacted with the fluid. This difficult-to control foaming is caused by proteins that play a role of surfactant in fermentation broth or enzymatic reaction phase. Unfortunately, there is not *universal* system to detect a foaming interface and most level

gauges fail to operate with an acceptable reliability. So, especially on the industrial-scale where large volumes are handled, the periodic withdrawal of the liquid phase at bottom exit of the column must be carefully regulated, under a very limited pressure drop towards the raffinate vessel, with a fine control of the column pressure evolution during such withdrawal.

Sometimes, another issue appears with entrainment of a significant amount of liquid phase by the fluid leading to unacceptable losses. The solution consists in injecting the liquid phase at least one meter below the top of the packing and using the top section of the fractionation column as a demister. In the most difficult cases, a water injection on top of the column increases the efficiency of demisting the fluid along this section. Fluid pressure is not an important parameter while temperature is to be limited as water solubility in CO_2 increases sharply beyond 35°C.

We recently completed a production-scale demonstration on a fermentation broth containing a cosmetic ingredient, presenting a strong fermentation odor that was finally completely removed with minimum losses of product (<8%), using a solvent ratio of 16 kg CO_2/kg.
We met one particularly difficult case consisting in elimination of sulfurous compounds from red cabbage juice, due to a drastic foaming inside the column.
Similarly with the lipid processing, the adsorbent beds are to be changed before the odorous compounds saturate the adsorbent and may be released in the recycled gas. Regeneration is a valuable option for large productions only.

FUTURE TRENDS

No doubt that consumers' demands will continue to increase in the future, concerning not only the most evident properties of ingredients (color, odor), but also *trace compounds* that are potentially harmful:

- *Pesticides* more and more present in most natural products, even in certain cases in organic-labelled ones, especially those having a very long life in environment (organo-chlorinated as DDT, HCH, etc.),
- Many compounds that are widely present in environment although suspected to be *endocrine disruptors*, i.e. *phthalates, nonylphenol and derivatives, some ether, etc.*,
- *Poly-Aromatic-Hydrocarbons* presenting a carcinogenic risk.

Practically no process is available for reducing these trace compounds in mots natural products. As a significant percentage of these pollutants are relatively well soluble in supercritical CO_2, this opens a large variety of applications to manufacture *safe* and *reliable ingredients*, either for solid materials or liquids as discussed in this paper.

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