

## CO<sub>2</sub>-Cryospraying Technology to convert extracts from bioindustrial waste into high value micronized products

TRL (5-6)

Jesús Caramés Bueno<sup>1</sup>, Hana Danan<sup>1</sup>, Pierandrea Esposito<sup>1</sup>, Alfonso Botto<sup>2</sup>

<sup>1</sup>SITEC PharmaBio, Baldiri Reixac 4-8, Barcelona, Spain; <sup>2</sup>Exenia Srl, Via C.Borra 35, Pinerolo, (TO), Italia

[h.danan@sitec-pharmabio.com](mailto:h.danan@sitec-pharmabio.com)

### Introduction

The recovery of bioindustrial waste obtained from processing crops, plants or marine sources, and the extraction and valorization of biomaterials from such residuals, can have a major impact on sustainability of renewable but limited natural resources. Bioindustrial waste valorization still suffers from lack of standardized methods for extraction and separation of valuable components, and from the necessity to process biomaterials with large volumes of organic solvents, which themselves represent a serious waste management issue. Consequently, the introduction of innovative, industrially viable and solvent-free technologies, capable to transform biowaste into value-added products, can contribute to drastically reduce the amount of residuals discarded, while creating markets for important nutrients or biologically active molecules.

For example, residuals from crustaceans processing industry represent 50% of the whole biomaterial, and are the main source of chitosan, a polysaccharide used in pharmaceutical and cosmetic industry. However, only 35% of the carapax components (chitin) is being used for chitosan production, while the rest (>60%) is discarded or used in low value feed applications [1]. Such waste contains valuable biomolecules (carotenoids, anti-oxidants,  $\Omega$  3-PUFAs) which could be instead recovered and valorized.

Similarly, 150 million tons of tomato are produced each year for fresh consumption, and 40 million are processed into products (peeled tomato, paste, etc.). [2] Both fresh and processed tomato have high nutritional value, since they contain micronutrients like carotenoids, vitamins, folates, and polyphenols. However, tomato processing generates about 5-7% w/w of waste fractions (peels and pomace), especially rich in important biomolecules such as lycopene [3], a potent natural antioxidant with potential for nutra- and pharmaceutical applications [4].

In this perspective, the implementation of CO<sub>2</sub>-based processing technologies to obtain purified extracts and semi-finished or finished products for nutraceutical, cosmetic or pharmaceutical markets, can represent a big step forward in the valorization of such biowaste. The objective of this study is to evaluate how an innovative cryospraying technology, based on dense CO<sub>2</sub> expansion (Variosol®), can be used to convert liquid or pasty natural fractions, previously obtained by supercritical CO<sub>2</sub> extraction, into micronized powders with favorable physico-chemical and biopharmaceutical properties. Results on the impact of key formulation and process parameters on microparticles formation and on size and morphology will be presented.

### Results and Discussion

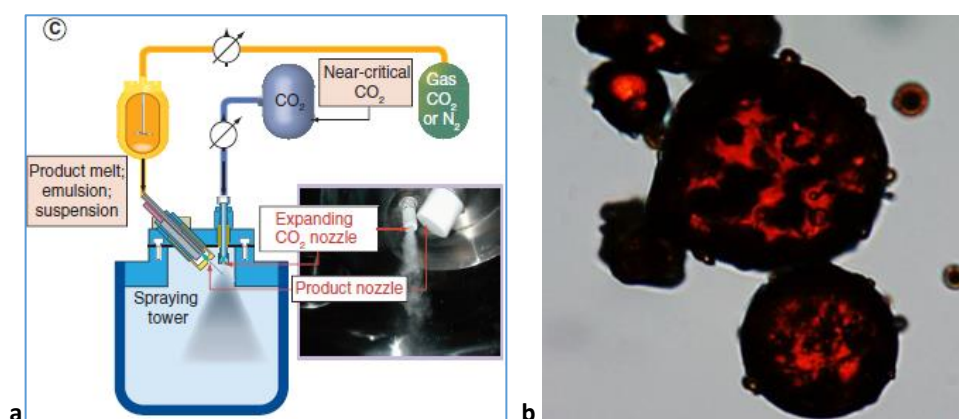
Variosol® cryospraying technology is based on the capability of rapidly expanding liquid-dense CO<sub>2</sub> to adsorb heat (Joule-Thomson effect) while generating a pressure gradient, thus simultaneously inducing rapid cooling, controlled solidification and atomization of fluid materials during spraying. Liquid products are sprayed through a nozzle, under controlled pressure and temperature, into a spraying tower, to obtain microparticles of the desired size. (Figure 1a). The technology can be applied to transform biomolecules-rich, liquid or pasty extracts into micronized, solid powders (Figure 1b) : the combination with lipidic structuring excipients and dissolution enhancers, and the

selection of adequate cryoprocessing conditions (pressure, temperatures, mass flow) allows to obtain dry, flowable, micronized powders with high content in natural extracts (up to 70 % w/w). Notably, microspheres as dry powders could be produced irrespectively of the amount of water initially contained in the natural extract: within certain limits, the process can remove water from the product during low T<sup>o</sup>, CO<sub>2</sub>-expansion spraying [5]. For instance, turmeric SCF extracts, containing more than 30% w/w of water, can be sprayed into solid microspheres, with < 1% residual moisture, and a loading of 65% w/w of curcuminoids-rich extract. Similar results were also obtained from tomato peel fluid extracts, rich in lycopene antioxidant, loaded at >50% w/w. Pasty lipidic extracts obtained from crustacean processing waste, with a high concentration of carotenoids and of fatty acids (85% w/w; of which 65% are most valuable PUFAs Ω-3 EPA and DHA), were also successfully sprayed into solid microparticles .

Microspheres contain amphiphilic excipients combinations, selected to facilitate solubilization or emulsification of highly lipophilic carotenoids and PUFAs, and to improve their absorption from the GI tract. Microspheres products generally present matrix-type morphology (observed by optical microscopy and SEM), an average particles size between 20 μm and 100 μm, with quite narrow distributions, and good flowability properties. The resulting dry powders are being characterized for specific biomolecules content (assay) and bioactivity.

## Conclusions

The establishment of an integrated, industrial line, wholly based on use of CO<sub>2</sub> technologies for the extraction, separation and formulation of biomolecules from natural sources , can represent a big step forward in the valorization of bioindustrial waste, facilitating the recovery of biomolecules and eliminating the need for organic solvents, with a favourable impact on environmental and economical sustainability. As an integral part of the CO<sub>2</sub>-based value chain, Variosol<sup>®</sup> cryospraying technology can be applied to convert extracts from bioindustrial residuals into formulated, micronized dry products, with high concentration of biomolecules or natural extracts, for possible applications in pharmaceutical, nutraceutical and cosmetics industry.



**Figure 1** a) Scheme of Variosol CO<sub>2</sub>-cryospraying process . b) Microscopic image (200x) of 70% -loaded spheres

## References

- [1] H.L. Lauzon, *Primex personal communication to Authors*, 2016
- [2] V.Bugatti, P.Brachi, G.Viscusi, G.Gorrası, *Frontiers in Materials* , 2019, (6), Article 34, 1-10
- [3] R.Driouich, O.Bousseimi ; A.Cherif , *Mediterranean Journal of Chemistry*, 2016, (6) 686-691
- [4] E.Story,R.Kopec,S.J.Schwartz,G.K.Harris,,2010, 1. Annu rev. Food Sci. Tech. doi:10.1146 / annurev. food. 102308.
- [5] L. Galli, H.Danan, P.Esposito, F.Pattarino, L.Segale (2009) *Process for dewatering of product powders and pharmaceutical compositions produced according to this process*. Eur. Pat. EP 2298286 B1.