



**HAL**  
open science

## Separation of lipids from wet microalgae: implementation of a coupled supercritical carbon dioxide extraction/fractionation device

Laure Wetterwald, Antoine Leybros, Audrey Hertz, Jean-Francois Sassi,  
Florian Delrue, Gatien Fleury, Paul Chambonniere, Claire Sahut, Damien  
Sorigué, Bertrand Légeret

### ► To cite this version:

Laure Wetterwald, Antoine Leybros, Audrey Hertz, Jean-Francois Sassi, Florian Delrue, et al.. Separation of lipids from wet microalgae: implementation of a coupled supercritical carbon dioxide extraction/fractionation device. CHISA - 26th International Congress of Chemical and Process Engineering, Oct 2022, Prague, Czech Republic. cea-04728746

**HAL Id: cea-04728746**

**<https://cea.hal.science/cea-04728746v1>**

Submitted on 18 Oct 2024

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## Separation of lipids from wet microalgae: implementation of a coupled supercritical carbon dioxide extraction/fractionation device

L. WETTERWALD, A. LEYBROS, A. HERTZ

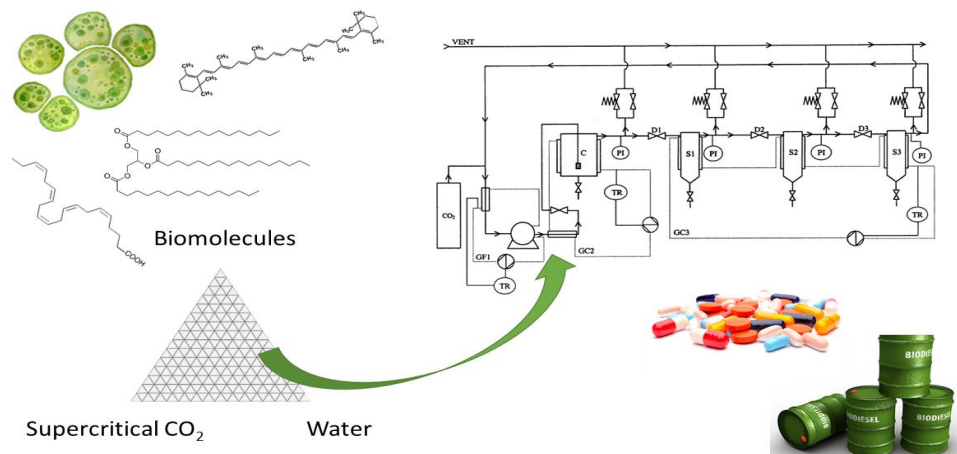
*CEA, DES, ISEC, DMRC, Univ Montpellier, Marcoule, France*

J-F. SASSI, F. DELRUE, G. FLEURY, P. CHAMBONNIERE

*CEA, DRT, CTREG, DSUD MicroAlgae Processes platform (MAP), Cadarache, France*

C. SAHUT, D. SORIGUE, B. LEGERET

*CEA, DRF, BIAM, Cadarache, France*



Fossil fuel depletion, one of the biggest challenge of this century, drives the development of alternative energies. Microalgae stand for a potential green and sustainable source of biofuels, as they may produce high levels of lipids that can stand as substitute to petroleum fuels. Moreover, algal biomass contains valuable biomolecules such as polyunsaturated fatty acid or carotenoids with nutraceutical, pharmaceutical or cosmetic industrial applications.

Extraction processes using conventional (hexane, chloroform, methanol) or green solvents (ethyl acetate, cyclopentyl methyl ether, isoamyl alcohol) have been widely carried out to extract lipids and carotenoids from algal biomass [2][4][5]. Supercritical CO<sub>2</sub> may be an attractive alternative to solvents, allowing a solvent power modulation in an easy way, while avoiding thermal degradation of valuable extracts and residual solvent traces. Moreover, solvent extractions are generally combined with pre-treatments (ex. grinding) and dehydration (ex. lyophilisation) steps. Depending on its residual concentration, water content enhances or inhibits extraction. On one hand, water is expected to hinder extraction by acting as a barrier to CO<sub>2</sub> penetration. On the other hand, water may act as a co-solvent, allowing to increase solute solubility. The project aims to support the scale-up of the biorefinery concept applied to microalgae, which strives to be more profitable by recovering both biofuel substrate and high-added value biomolecules, while minimizing the whole process energy consumption. Thus a coupling between extraction and continuous countercurrent fractionation processes in supercritical CO<sub>2</sub> medium for wet material with minimal pre-treatment has been considered in this study.

A lipid-rich strain of *Chlorella vulgaris* (lipid content: 31% MS) has been selected as a representative microalgae. Based on its composition, three target molecules have been considered. Oleic acid can represent up to 66% of neutral lipids and can be found either as a free fatty acid or as a part of a triglyceride molecule. According to the prediction method developed by Filho and al. [1], triolein is the most likely triglyceride conformation.  $\beta$ -carotene has been chosen as representative molecule for the carotenoids.

Solubility measurements of oleic acid, triolein and  $\beta$ -carotene in supercritical CO<sub>2</sub> are carried out within suitable pressure (80-300 bar) and temperature (40-100°C) ranges. Other binaries systems are characterized as well, using Karl-Fischer/Total Organic Carbon analysis for aqueous-organic systems, UV-vis spectroscopy for systems containing  $\beta$ -carotene, or DSC when dealing with liquid-solid systems. Such experimental data are required to determine binary interaction coefficients, allowing ternary and quaternary systems description through thermodynamic modelling. Cubic equation of state and cubic plus association (CPA) are assessed and compared in terms of accuracy for calculation of phase equilibria in operating conditions. Otherwise, supercritical CO<sub>2</sub> extractions on selected *Chlorella vulgaris* biomass have been carried out considering CO<sub>2</sub> density ranging between 780 kg/m<sup>3</sup> (150 bar, 40°C) and 879 kg/m<sup>3</sup> (250 bar, 40°C) in conditions similar to Kwan et al. [3]. The best extraction yield (160 mg/g microalgae) was obtained for a density equal to 787 kg/m<sup>3</sup> (250 bar, 60°C). Not only the yield, but also the selectivity of the process considering total lipid and carotenoids was assessed by GC-FID chromatography and UV spectroscopy.

Such preliminary results are promising in a view to design and scale-up a SC-CO<sub>2</sub> extraction/fractionation process. In this way, flow-balance models considering binary/ternary systems thermodynamics study and experimental results will be implemented to size the diameter/ height equivalent to theoretical plate of a fractionation column device. Such tool will be beneficial for the building of pilot or industrial scale supercritical CO<sub>2</sub> extraction/fractionation process of lipids/carotenoids from microalgae.

- [1] Filho, N. R. Antoniosi, O. L. Mendes, et F. M. Lanças. « Computer Prediction of Triacylglycerol Composition of Vegetable Oils by HRGC ». *Chromatographia* 40, n° 9 (1 mai 1995): 557-62. <https://doi.org/10.1007/BF02290268>.
- [2] Jesus, Sérgio S. de, Gabriela F. Ferreira, Larissa S. Moreira, Maria Regina Wolf Maciel, et Rubens Maciel Filho. « Comparison of Several Methods for Effective Lipid Extraction from Wet Microalgae Using Green Solvents ». *Renewable Energy* 143 (1 décembre 2019): 130-41. <https://doi.org/10.1016/j.renene.2019.04.168>.
- [3] Kwan, Thomas A., Qingshi Tu, et Julie B. Zimmerman. « Simultaneous Extraction, Fractionation, and Enrichment of Microalgal Triacylglycerides by Exploiting the Tunability of Neat Supercritical Carbon Dioxide ». *ACS Sustainable Chemistry & Engineering* 4, n° 11 (7 novembre 2016): 6222-30. <https://doi.org/10.1021/acssuschemeng.6b02214>.
- [4] Pagels, Fernando, Ricardo N. Pereira, António A. Vicente, et A. Catarina Guedes. « Extraction of Pigments from Microalgae and Cyanobacteria—A Review on Current Methodologies ». *Applied Sciences* 11, n° 11 (janvier 2021): 5187. <https://doi.org/10.3390/app11115187>.
- [5] Soares, Aline Terra, Dayane Cristine da Costa, Bruna Ferreira Silva, Rafael Garcia Lopes, Roberto Bianchini Derner, et Nelson Roberto Antoniosi Filho. « Comparative Analysis of the Fatty Acid Composition of Microalgae Obtained by Different Oil Extraction Methods and Direct Biomass Transesterification ». *BioEnergy Research* 7, n° 3 (septembre 2014): 1035-44. <https://doi.org/10.1007/s12155-014-9446-4>.