SUPERCRITICAL CARBON DIOXIDE EXTRACTION OF LIPIDS FROM MICROALGAE FOR BIODIESEL PRODUCTION

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Supercritical carbon dioxide extractions of microalgal lipids were performed, in view to product biofuel. The influence of experimental parameters on extraction yields was studied. The operating conditions tested were: pressure from 28 to 46 MPa, extraction temperature from 318 to 338 K, and CO_2 flow rate from 0.32 to 0.81 kg/h. A comparison of processes based on supercritical CO_2 extraction and other classical processes to obtain biodiesel is also proposed.

INTRODUCTION

Microalgae are ubiquitous in many environments and are able to adapt in really hard conditions. This adaptability and their biological diversity let predict the presence of a multitude of molecules of interest useful in many fields such as human health or energy production [1-7]. Microalgae are particularly able to accumulate fatty acids up to 50 % of their dry weight when submitted to nitrogen defaults. They are then expected to be a new potential renewable source of biodiesel. Algal bio-oil is traditionally obtained using thermal liquefaction [8,9] or pyrolysis [10]. They also may be obtained after an extraction using organic solvents as n-hexane [11,12]. The obtained products should be treated to eliminate phospholipids, and trans-esterified with methanol to be transformed in methylic esters of vegetable oil so called biodiesel. Such methods have the main drawbacks of being energy consuming and/or pollutant. Supercritical CO_2 extraction may be an interesting alternative to these processes. Indeed, this technology is well-known today and is considered as a green process. There are numerous advantages in using supercritical CO_2. This solvent is known to be safe, non flammable, selective and consequently the separation step to recover the target product is avoided. The extract yields, which depend on supercritical extraction conditions, can be high for quite short extraction duration. Supercritical CO_2 is particularly efficient to solubilise non polar compounds; when the molecule of interest is not soluble, the solvent power can be increased using a safe and polar modifier as ethanol.
The aim of this work is to carry out extraction experiments on dried microalgae using supercritical CO_2 and to study the influence of operating parameters on extraction yields.

MATERIALS AND METHODS

A classical extraction device (SEPAREX, France) was used to perform supercritical CO_2 extraction of lipids from a microalgae (ALPHA BIOTECH, France) which content in neutral

lipids is about 16%. The experimental set-up is shown on figure 1. Experiments were performed in an extraction cell of 10 cm^3 corresponding to 7 grams of dried microalgae.

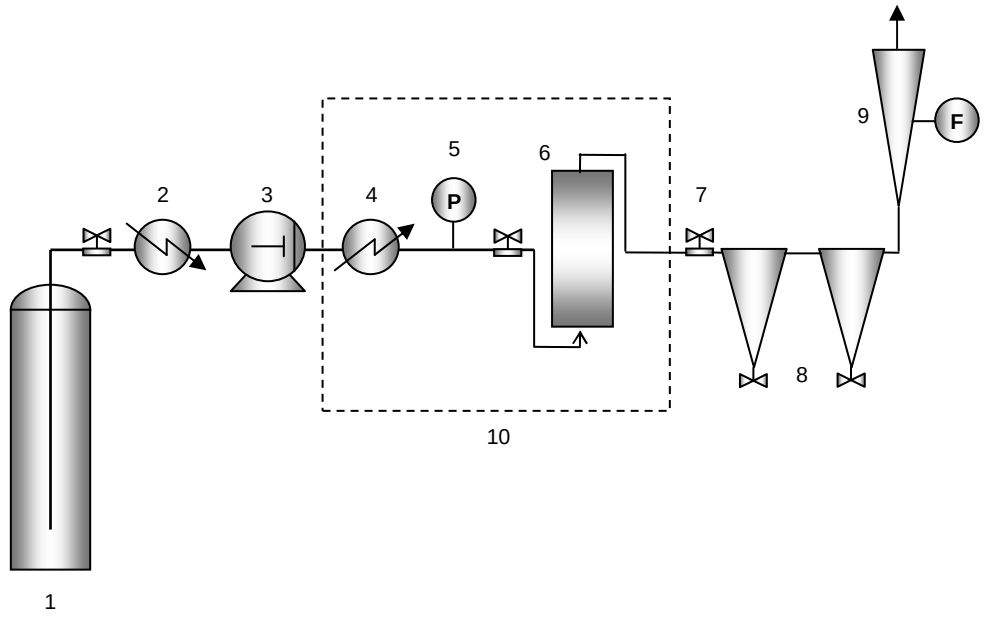

Figure 1: Experimental set-up. 1 – CO_2 cylinder; 2 – Cryogenic bath; 3 – high pressure volumetric pump ; 4 - Heat exchanger; 5 – Manometer ; 6 – Extraction cell; 7 – Expansion valve; 8 – Collectors; 9 – Flow meter ; 10 – Thermoregulated area

RESULTS

a) Preliminary experiments:

First of all, the reproducibility of extraction experiments was tested at three different operating conditions. Each experiment was reproduced 2 or 3 times during an extraction duration of 180 minutes. Regarding the low mass of raw materials, the extraction yields were obtained through the weight loss of the vessel.

Table 1 gives the reproducibility results. It shows that whatever the operating conditions, experiments were reproducible. The reproducibility on the weight loss of the vessel was less than 0.3 %.

The optimum extraction duration was also determined. This parameter was obtained from experiments with extraction duration from 15 to 180 min. Figure 2 shows the evolution of extraction yields versus extraction duration at T = 318 K, at three pressures 15, 28 and 46 MPa, with a CO_2 flow rate Q_{CO2}=15 cm^3/min, i.e. 0.67, 0.79 and 0.87 kg/h respectively. It clearly appears that an experimental duration of 90 minutes brings to yields on the average of 82, 97 and 94 % of the maximum yields. This extraction duration of 90 minutes was finally chosen as optimal duration for the following experimental study.

The different curves of extraction yields (Figure 2) as a function of extraction duration show that the mass transfer is the limiting factor from the beginning of the extraction.

Table 1: Reproducibility of extraction experiments.

Experiment	Extracted weight (g)	Weight loss (%)	Average (%)
T = 328 K - P = 37 MPar - Q_{CO2} = 0.56 kg/h			
1	0.61	8.8	
2	0.63	8.8	8.9 ± 0.1
3	0.63	9.0	
T = 318 K - P = 46 MPa - Q_{CO2} = 0.87 kg/h			
1	0.81	11.7	
2	0.80	11.3	11.6 ± 0.3
3	0.84	11.9	
T = 318 K - P = 28 MPa - Q_{CO2} = 0.79 kg/h			
1	0.44	6,1	6.2 ± 0.1
2	0.43	6,3	

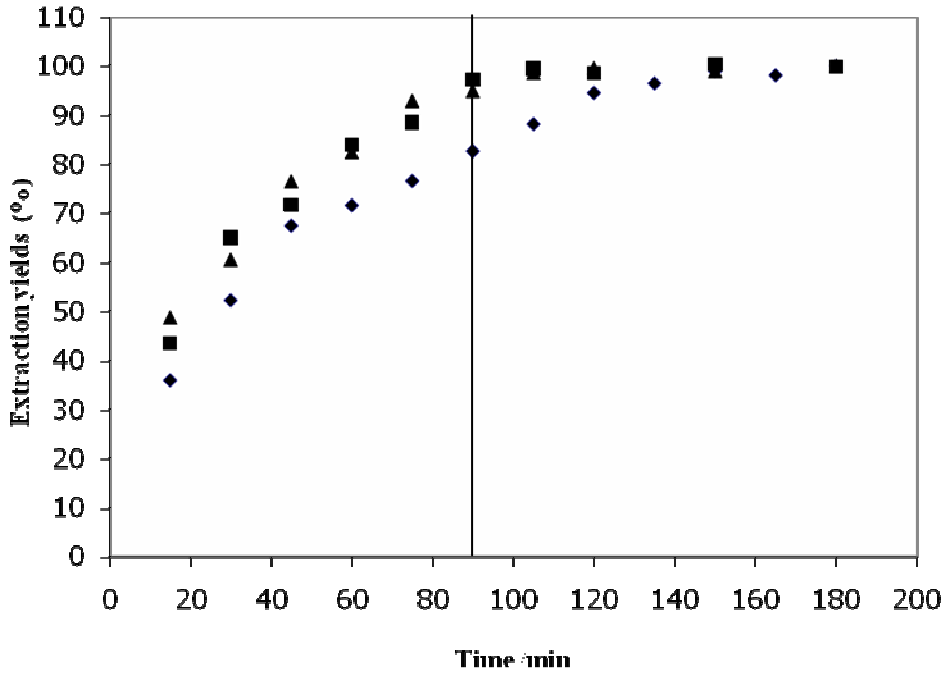

Figure 2: Extraction yields versus time at T = 318 K, at three pressures ◆ 15, ▪ 28 and ▲ 46 MPa with respectively Q_{CO2} = 0.67, 0.79, 0.87 kg/h

b) Influence of operating parameters on extraction yields:

The extraction experiments were carried out with modifying the following parameters: temperature from 318 to 338 K, pressure from 28 to 46 MPa and CO_2 flow rate from 0.32 to 0.81 kg/h. Each experiment was performed during 90 minutes. Table 2 gives the extraction yields for each experiment.

The extraction yields obtained cover a large range of values. The highest ones were reached at 46 MPa, 338 K, as expected. The most influent parameter on extraction yields is the pressure while the less influent is the CO_2 flow rate. The evolution of extracted yields with each parameter is as described in literature [13-23]: the solubility of lipids in CO_2 increased with

pressure, decreased with temperature under low pressures and increased with temperature under high pressures (retro solubility). The transition pressure is about 20 MPa.
Figure 3 shows that supercritical CO_2 also solubilised red and green pigments, probably carotenes and chlorophylls, respectively. Their solubility unfortunately increased with pressure as for lipids.

Table 2: Weight loss versus operating parameters

Experiment	T (K)	P (MPa)	Q (kg/h)	Weight loss (%)
1	318	28	0,32	4,3
2	338	28	0,29	5,5
3	318	28	0,79	6,1
4	318	28	0,79	6,3
5	338	28	0,71	8,2
6	328	37	0,56	8,8
7	328	37	0,56	8,9
8	328	37	0,56	9,0
9	318	46	0,34	9,9
10	318	46	0,84	11,3
11	318	46	0,84	11,7
12	318	46	0,71	11,9
13	338	46	0,32	12,6
14	338	46	0,81	16,3

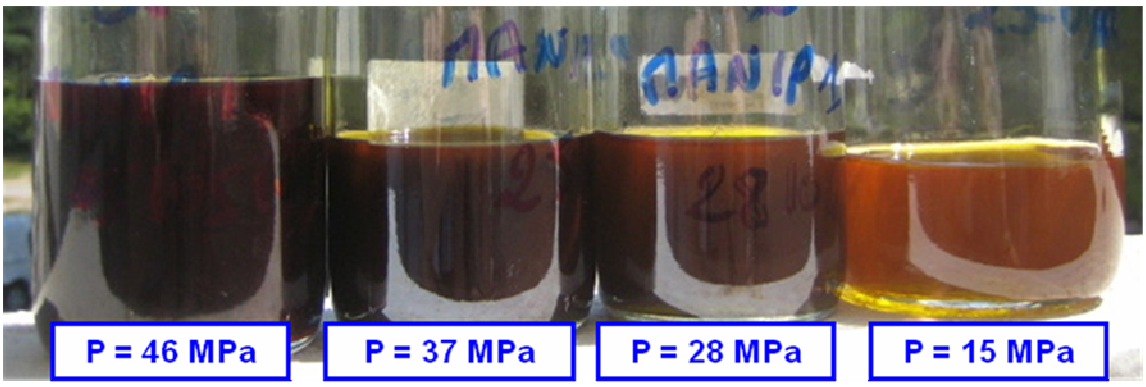

Figure 3: Pigment recovery versus pressure.

Based on the results obtained at lab-scale and taking into account extraction yields and economical considerations, the optimum operating conditions are: a pressure between 30 – 40 MPa, a temperature of 323 K, and a CO_2 flow rate between 0.4 and 0.6 kg/h.

c) Comparison with classical processes to obtain biodiesel from microalgae:

Figure 4 compares n-hexane extraction, thermo chemical liquefaction, pyrolysis and supercritical CO_2 extraction for biodiesel production in terms of operation units and energy consumption. Energy consuming units appear under-lined.
n-hexane extraction needs six operation units from pretreatment to trans-esterification. Among them, three units are particularly energy consuming: pretreatment (drying up to 1%

moisture), heating (up to 323 K) and solvent recovery and treatment. One of the main drawbacks of this process is the use of a toxic solvent.
Thermo chemical liquefaction is interesting because it only needs five operation units since it does not need any pretreatment. The microalgae suspension can be used as harvested. However, this method involves the use of dichloromethane. More, the heating operation up to 623 K and under 3 MPa is particularly energy consuming.
Finally, pyrolysis needs six operation units. The main advantage comparing to the former methods is the non use of toxic solvents. However, it involves two energy consuming units with a drying and a heating up to 873 K.

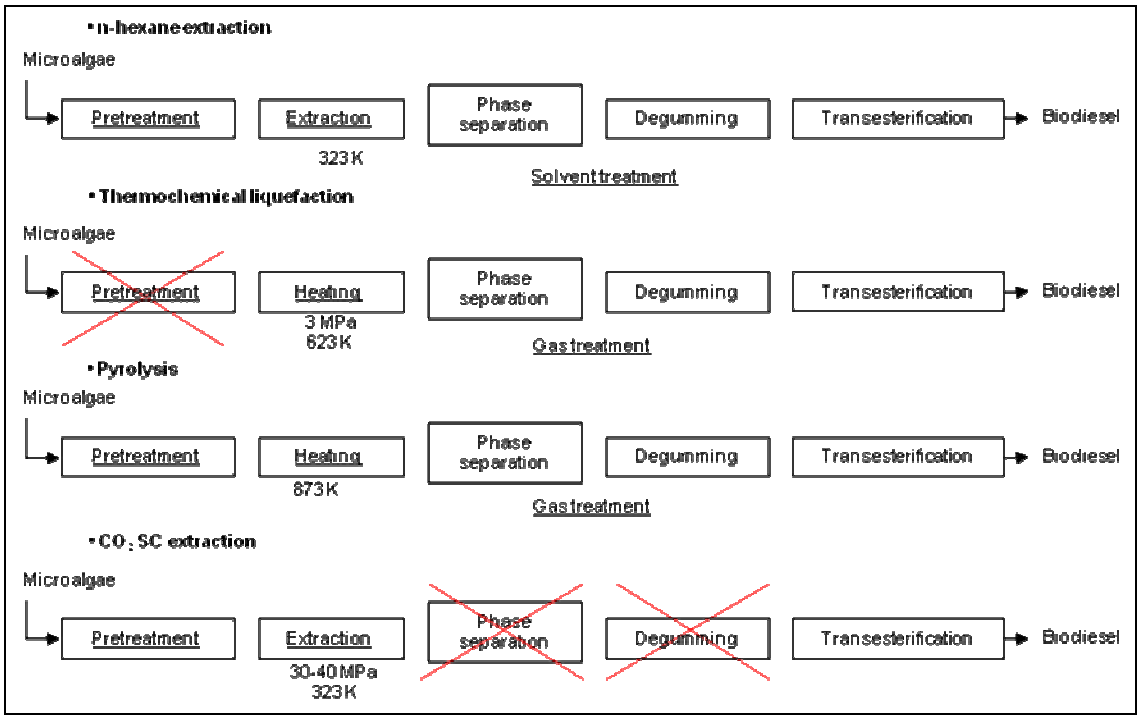

Figure 4: Comparison between n-hexane extraction, thermochemical liquefaction, pyrolysis and supercritical CO_2 extraction for biodiesel production in terms of operation unit and energy consumption.

Comparing these three processes to supercritical CO_2 extraction shows that the latter is competitive since it is a "green" process and a compact one. It needs only three operation units: CO_2 is gaseous at room pressure and temperature so the separation with the extracts is spontaneous during depressurization. More, the clean residue can be used for other purposes. The degumming unit is also unnecessary as phospholipids are not soluble in supercritical CO_2. Among the three units two are energy consuming. Indeed, it needs a drying up to 5 % moisture and the compression up to 30-40 MPa is energy consuming. Nevertheless, for the last three decades, a large number of industrial extraction plants using supercritical fluids have been constructed attesting that this technology is economically viable for a number of applications. Today, there are more than 200 extraction units in the world. Autoclave volumes go up to 10 m^3, the extraction pressures and temperatures go up to 55 MPa and 353 K, respectively, and the extraction production for one unit goes up to 10,000 tons per year. Nevertheless, the economic viability of an industrial plant of supercritical CO_2 extraction dedicated to biodiesel production which means a capacity of at least 100,000 tons per year has still to be demonstrated.

CONCLUSION

From the conducted experiments carried out at lab-scale, it was shown that pressure is the most influent parameter on extraction yields. The optimum operating conditions for an extraction are: a pressure between 30–40 MPa, a temperature of 323 K, and a CO_2 flow rate between 0.4 and 0.6 kg/h. Lastly, all the results obtained have shown that the extraction conditions should be optimized in order to avoid the extraction of pigments as chlorophylls and carotenes, undesirable for a biodiesel application. This last point, along with technico economical considerations, could lead to the optimization of experimental parameters.

Acknowledgments

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