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DENSIFICATION PROCESSES OF MICROALGAE BRED FOR BIODIESEL PRODUCTION

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An alga technology system has been developed, built and operated for the absorption of carbon dioxide and the production of biodiesel raw material. The main critical point in the technology is the separation of micro algae from the breeding medium (densification of the alga suspension). This is the most cost- and time-intensive part of the technology. The success of options in the literature, as well as further applicable phenomena and operations have also been studied. Along with flocculation, clarification and autoflocculation phenomena, special attention has been paid to membrane separation operations. Our aim is to devise a densification and separation process that has a low energy need and an advantageous operation time. The ultrafilter membrane splits the original mass flow (which consists of homogenized suspensions of different density) into two parts. One part passes the membrane, this is the permeate (deposited feed medium), the other is the concentrate, also called 'retentate' (in this case the concentrated alga suspension). This retentate can be easily and quickly cleaned of the accumulated metabolic products and remaining salt which can later cause a significant disturbance (at processing or in the following examinations). According to the assessment of the experimental results, the optimal solution seems to be membrane separation, on different grounds. It has a low energy need and an advantageous operation time and results in an appropriately clean suspension (i.e. void of metabolic products and salt). A PLC-controlled device equipped with a ZW-10 module was used for the densification experiments. The latter is the property of the Department of Chemical Engineering at the University of Pannonia.

Keywords: micro algae, biodiesel, ultrafiltering, membrane separation, densification

Introduction

Algae are considered to be one of the most efficient organisms on Earth because of their outstandingly high reproductivity, and generally high lipid content. As for their reproduction, they can double their biomass in 24 hours [1, 2, 3, 4]. Their lipid content is 20% on average (60–80% for certain species) [1, 5, 6, 7]. Research for oil production from algae is primarily focused on micro algae. These are photosynthesizing organisms, the size of which does not exceed 0.5 mm. They can be, with a good chance, the solution to carbon dioxide and nitrogen oxide absorption, because they convert them with photosynthetic energy conversion [8]. The end product of the process contains a significant amount of solar energy stored as chemical energy. As a result, "high amounts" of biodiesel can be obtained [4, 9, 10, 11, 12]. Besides the above mentioned advantages, algae can not only be used for fume gas cleaning, but they also use certain components of wastewaters as nutrient substrates, thus cleaning the wastewaters. The contamination provides an excess of nutrient for the algae which start to grow in an exponential rate.

In contrast to the above mentioned advantages, their major disadvantage is the high cost need of production. Harvesting of the algae (harvest, dewatering, drying), the extraction of lipids and their conversion are the most critical steps in the production of alga-based biofuels because of the high investment and operation costs. Thus the biggest challenge to the technology is cost minimization, which can be done first at the separation step.

Harvesting can be done by microfiltration, centrifuging, flocculation, sonochemical processes or by other technologies currently under development [13, 14]. In addition to chemical flocculation, clarification and autoflocculation phenomena, special attention has been paid to membrane separation procedures.

Our aim is to devise a densification and separation process which has a low energy need and an advantageous operation time.

Experimental

Ultrafiltration

Although the operation has "filtration" in its name, there is significant difference between traditional filtration and ultrafiltration. In the former, the liquid medium pressed through the filter moves perpendicular to its surface and

at least one of its components is accumulated inside or on the surface of the filtering medium. As opposed to this, the ultrafiltering membrane splits the original mass flow (alga suspension) into two. One of the two parts passes the membrane, this is the permeate (the separated nutrient substrate), the other is the concentrate (in our case: the concentrated alga suspension). The momentary performance of the filter depends on – besides the applied pressure differences – the viscosity of the medium to be filtered, the size distribution of the solid grains, the thickness of the filter cake, its imporosity and rheology. In the case of the membrane module, no filter cake is formed. Thus the properties of the filter cake do not have an effect on the actual performance of the filtering; however, the applied driving force and the flow of the medium parallel to the membrane do.

The permeability of the membrane is significantly affected by the applied pressure difference, while osmotic pressure in general has only little effect. Thus the permeate flow can be described with the following equation:

$$J = -\left(\frac{k}{\mu}\right) \cdot grad(p) \Rightarrow J = -\frac{k\Delta p}{\mu L} \Rightarrow J_V = P_L \cdot \Delta p \quad (1)$$

Where J_V is the rate of filtration, k is the hydraulic permeability factor that is dependent on the material, L is the thickness of the filtrating layer, *and* μ is the viscosity. This representation is analogue to the D'Arcy law. The gradient is the quotient of the pressure difference between the two sides of the membrane and its thickness. The parameters before this function can be summarized as the liquid permeability constant P_L, which is the water rate of the membrane. The water rate gives the maximal filtering performance of the membrane measured with pure water.

Operational characterization of ultrafiltration

When characterizing the operations, it is advisable to use units that supply the most information of the state of the process from the combination of the most easily measurable parameters. The concentration factor (*CF*) is a generally used descriptor which is defined as follows:

$$CF = \frac{\text{input volume}}{\text{retained volume}} = \frac{V_0}{V_r} \quad (2)$$

The capacity (*REC*) is indicative of the amount of the purified solution.

$$REC = \frac{\text{volume of permeate}}{\text{input volume}} = \frac{V_p}{V_0} \quad (3)$$

With the volume balance equation $V_0 = V_r + V_p$, the two measures can be expressed as follows:

$$CF = \frac{1}{1 - REC} \quad (4)$$

The device used for ultrafiltration

A PLC controlled device, equipped with a ZW-10 module was used for the densification and purification experiments *(Fig. 1)*. The device is the property of the Department of Chemical Engineering of the University of Pannonia.

Figure 1: The device used for the measurements

As regards the permeate flow, the device carries out an outside-in operation. The measurements were done with a ZW-10 immersion module supplied by the company Zenon. According to its specifications, the membrane is capable of retaining particles as small is 1 μm [15, 16, 17]. The module is of hollow fiber type, its outer diameter is 4.5 mm, and it consists of strings of 0.4 μm pore diameter *(Fig. 2)*.

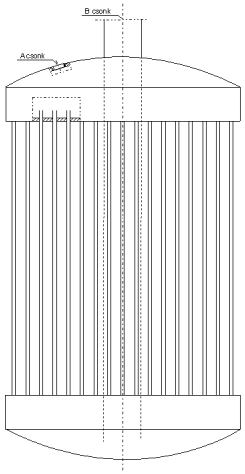

Figure 2: Configuration of the ZW-10 membrane module. A: permeate outtake, B: air injection

The total surface area of the membrane is 0.9 m^2, from which the membrane venting density is 289 m^2/m^3.

According to the manufacturer's specifications, the pressure difference between the two sides of the membrane (Δp_m) cannot be outside the ±0.5 interval for a prolonged period. If the value of $|\Delta p_m|$ is constantly above 0.6 bar, an irreversible decrease in membrane permeability can be expected. This decrease is due to structural changes and pore collapse.

The module functions as part of a PLC controlled device. The construction of the device is illustrated in *Fig. 3*.

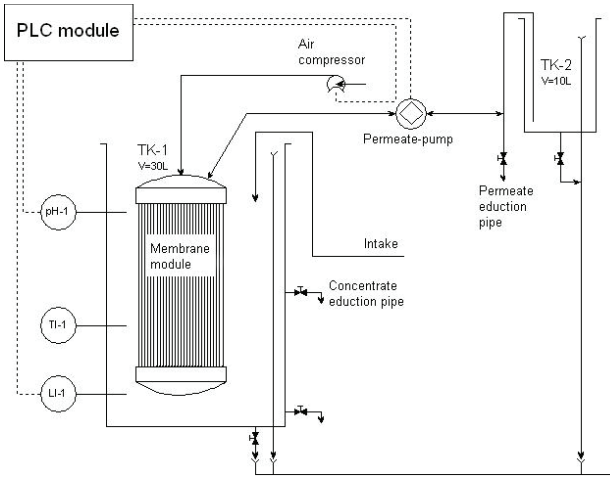

Figure 3: The construction of the ultrafiltrator device

Air is blown into the device immediately next to the membrane fibers which enhances the cleanliness of the surface while also ensuring a steady sludge content due to the mixing effect of the air bubbles.

One of the key units in ultra filtration is the permeate pump. This pump is responsible for permeate eduction in UF (ultra filtering) mode, while in BP (back pulse, backwash) it is responsible for the backpumping of the permeate. The frequency switch in the control module ensures the two-way operation of the pump as well as the stepless regulation of the motor speed.

A manometer (Dp) is installed at the permeate eduction side which gives information about the overpressure on the permeate side of the membrane.

The micro alga suspension is introduced to the technical vessel (TK-1). This is a rectangular prism with a volume of 30 dm^3, equipped with a level indicator (LI), a pH-meter probe (pH-1) and a thermometer (TI).

The permeate (separated nutrient substrate) is introduced to the 10 dm^3 TK-2 permeate vessel. The permeate need of the backwash is also supported from here. Periodic eduction of the permeate is possible through the eduction pipe end, while continuous eduction is possible via the overflow valve.

After overall cleaning, a ZW-10 membrane module was installed in the device. The previous record of the module is known, experiments were done with it on living sludge wastewater. The required conservation procedures were carried out before storage.

Before it was put in practice, the regeneration procedures required by the distributor were carried out on the membrane.

Testing of the used module was done with tap water. This test is informative of the success of conservation and that the membrane is ready for measurement.

Densification experiments

The measurement was done covering the whole operational range with the minimally necessary step interval. The main device parameters are given in *Table 1*.

Table 1: Device parameters

	Ultrafiltration	Backpulse
Volume flow [l/h]	20	25
Time [sec]	600	60

The suspension in the densifying vessel was pneumatically mixed with an injector fed by the air compressor. Sample supply was carried out in the followings with the use of a 1 dm^3 graduated cylinder in order to avoid fluctuation in the liquid level. In order to gain the most data possible from the given sample volume, the measurement was divided into several phases. The alga suspension was removed from the photobioreactors in portions of 40 dm^3 for filtering.

After densifying 40 dm^3 to 20 dm^3, cleansing with distilled water was used. Washing was done until the complete removal of remaining salts, organic material and metabolic products in the suspension.

The extent of cleansing was monitored by measuring the extract content and the electrical conductivity of the permeate.

The following 40 dm^3 of alga suspension was concentrated according to the method described earlier; after this 20 dm^3 cleansed concentrate from the previous densification was given to it. This concentrate was then washed with distilled water again.

The densification experiments were carried out repetitively until reaching the highest possible concentration factor with the device.

Cleansing (washing the concentrate with distilled water) was done until reaching the lowest electric conductivity possible as well as reaching an extract content lower than three decimals *(Fig. 4)*.

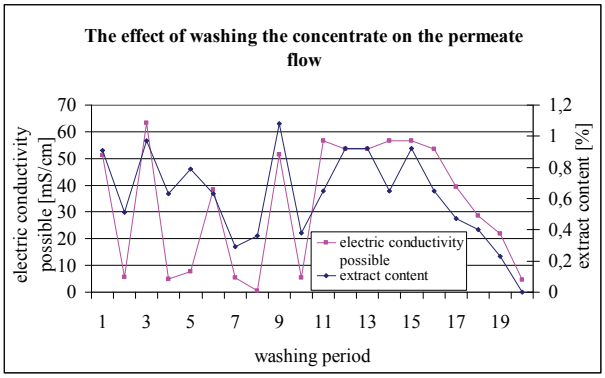

Figure 4: The effect of washing the concentrate on the permeate flow

Results

By using the ZW-10 membrane module in 7 densification phases, 280 dm^3 of alga suspension feed was concentrated to 20 dm^3, the final concentration factor being $CF_{final} = 14$.

The change in extract content of the concentrate is summarized in *Fig. 5*.

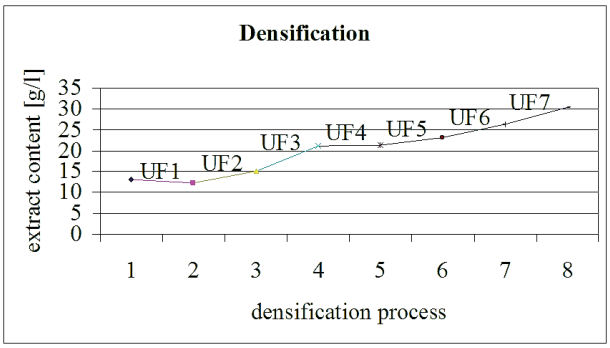

Figure 5: Change in extract content of the concentrate

The decrease in extract content in the first phase is due to the washing. As it can be seen, approx. 50% of the alga suspension consist of residual salts and other organic materials. The initial alga suspension (40 dm^3) was concentrated for a concentration of 13 g/l to 12.2 g/l (20 dm^3). The final alga concentrate has a concentration of 30.4 g/l with respect to algae in a volume of 20 dm^3.

Thus, the extract content was raised from 1.22% to 3.04% during the processes.

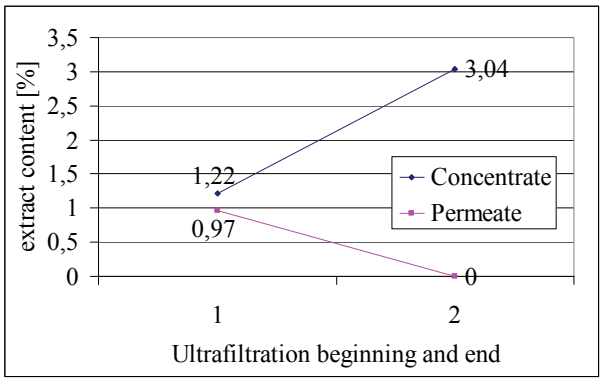

Figure 6: The extract content of the concentrate and the permeate at the beginning and end of the experiment

Summary

According to the evaluation of the experimental results, the membrane separation process seems to be the best solution by the following reasons. It has a low energy need, an advantageous operation time and results in a suspension that is appropriately clean (void of metabolites and salts) and is appropriately concentrated.

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