Algal Research 8 (2015) 168–173

Contents lists available at ScienceDirect

Algal Research

journal homepage: www.elsevier.com/locate/algal

Forward osmosis with waste glycerol for concentrating microalgae slurries

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ARTICLE INFO

Article history:
Received 18 November 2014
Received in revised form 10 February 2015
Accepted 11 February 2015
Available online xxxx

Keywords:
Microalgae
Glycerol
Forward osmosis
Osmotic dehydration

ABSTRACT

Forward osmosis of microalgal suspensions was performed by using a dialysis membrane submerged in pure glycerol or a simulated crude glycerol of a biodiesel production process. Freshwater, marine and hypersaline microalgae were concentrated from around 1 to 2.5 $g \cdot L^{-1}$ within an hour of treatment with crude glycerol. Cultures of marine microalgae could be osmotically dehydrated using crude glycerol as the draw solution at fluxes of around 2.75 $L \cdot m^{-2} \cdot h^{-1}$. This dewatering method was shown to be reliable and may be used in conjunction with other dewatering methods to improve the overall energy efficiency of a biomass recovery process.

1. Introduction

Fuels produced from microalgae oils may potentially displace some of the fossil fuels as sources of energy [1–4]. Triglycerides-rich algal oil is readily converted to biodiesel, or fatty acid methyl esters (or ethyl esters), via transesterification with methanol (or ethanol) [5,6]. Recovered algal crude oil, the oil-rich biomass paste and the dried biomass may be used directly in making biodiesel.

Algae are grown in large volumes of water. Typically, the dry biomass concentration in an algal broth tends to be in the range of 0.5 to 4 g L^{-1}. For further processing of the biomass, the water must be removed to obtain a biomass paste with a moisture content of roughly 90%. Dewatering is usually achieved by centrifugation, a method with a high recovery efficiency, but a high consumption of energy [7–11]. An alternative to centrifugation is the use of flocculating agents to aggregate the microalgal cells for subsequent concentration by gravity sedimentation [10,12–14]. Flocculation–sedimentation requires less energy, but needs high doses of flocculants that cannot be recovered and may also affect the quality of the biomass [14,15]. Lack of a low-cost and low-energy alternative to the currently used biomass recovery methods is one factor limiting the large scale production of microalgal fuels [3,4,16].

Glycerol is a by-product of all biodiesel production processes. The production of a metric ton of biodiesel generates between 0.1 and 0.2 tons of glycerol as a byproduct of the transesterification of triacylglycerol oils [17,18]. Pure glycerol is a non-toxic, biodegradable and recyclable liquid that may be processed into many valuable products [18]. Unfortunately, the crude glycerol from the manufacture of biodiesel contains impurities such as water, methanol, other organic substances and salts that make its purification expensive. With continuing growth of biodiesel production from various sources, the global production of glycerol has been increasing [17,19,20] and, therefore, new uses for glycerol are sought.

This work investigated the potential of crude glycerol as a draw solution for dewatering microalgae suspensions in a forward osmosis process. The efficacy of the method for freshwater, marine and hypersaline microalgae was examined. The objectives were to develop a low-energy process for concentration of microalgal biomass and make use of the increasingly cheap crude glycerol being produced by the oil transesterification processes. In forward osmosis, water is drawn out of an aqueous feed solution (the slurry of microalgal cells) through a semipermeable membrane and into a draw solution. The driving force for this process is the difference in water activities of the feed and the draw solutions. The feed must have a higher water activity than the draw solution. Activity of pure water is 1 whereas a water-miscible draw fluid containing no water at all has a water activity of zero. Forward osmosis is reviewed in detail elsewhere [21,22].

2. Materials and methods

2.1. Microalgae culture

The freshwater microalgae *Neochloris* sp., *Choricystis minor* and *Scenedesmus* sp. were grown separately in BG11 medium [23]. The

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http://dx.doi.org/10.1016/j.algal.2015.02.008
2211-9264/

Nomenclature

A	membrane area available for mass transfer, cm^2 or m^2
A_0	membrane area available for mass transfer at $t = 0$, cm^2 or m^2
c	concentration, $mol \cdot L^{-1}$
DR	dewatering rate, g of water·per g of sample per·min
J_w	water flux, $L \cdot m^{-2} \cdot h^{-1}$ or $L \cdot m^{-2} \cdot min^{-1}$
K	specific conductance of the medium, $mS \cdot cm^{-1}$
k_1	Peleg rate constant, min
k_2	dimensionless Peleg capacity constant
M	mass of sample and tube, g
M_0	initial mass of sample and tube, g
MWCO	molecular weight cut-off of membrane, kDa
R	volumetric ratio between draw and feed solutions, $L \cdot L^{-1}$
rpm	revolutions per minute, min^{-1}
t	time (min)
t_0	start time (min)
V	volume of the sample, m^3
WR	weight reduction, $g \cdot g^{-1}$
WR_0	weight reduction at $t = 0$, $g \cdot g^{-1}$

Greek symbols

π_g	osmotic pressure of glycerol solution, MPa
ρ_w	density of water, $g \cdot cm^{-3}$

first two species had been purchased from Landcare Research, Lincoln, New Zealand, and the other mentioned species had been isolated at Massey University, Palmerston North, New Zealand. *Neochloris* sp. was also grown heterotrophically by supplementing the BG11 medium with a freshly autoclaved concentrated stock of D-glucose to achieve a final glucose concentration of 0.1 M. Cells were grown for 10 days in a 4 L (3.5 L working volume) stirred bioreactor. The autotrophic cultures were grown in 1 L culture vessels bubbled with air enriched with 5% (by volume) of CO_2. The incident irradiance at the surface of the vessels was 330 μE m^{-2} s^{-1}. All cultures were grown at 25 °C.

The marine microalgae *Nannochloropsis salina* (CCAP 849/3), *Piccochlorum* sp. (BEA0400; Banco Español de Algas, Spain), *Porphyridium cruentum* (from Instituto de Ciencias Marinas, Puerto Real, Spain) and the hypersaline microalga *Dunaliella salina* (BEA0303B; Banco Español de Algas, Spain) were grown for 10 days in a 2.5 L (2 L working volume) sparged bioreactor incubated at 25 °C. The incident irradiance at the surface of the bioreactor was 330 μE m^{-2} s^{-1}. The bioreactor was aerated at 1 L min^{-1} with a mixture of air containing carbon dioxide to the level of 4.7% by volume. BG11 medium made with natural sea water was used for *N. salina* and *P. cruentum* [23]. The ASP12 medium [24] was used for *Picochlorum* and *D. salina*. For the latter alga, the concentration of NaCl in the medium was twice the normal concentration of the standard ASP12 medium.

In all cases, the culture media and vessels were sterilized by autoclaving at 120 °C for 15 min. The aeration gas was sterilized by passing through a 0.2 μm Teflon membrane filter cartridge (Midisart® 2000; Sartorius, AG, Goettingen, Germany). Irradiance was measured using a QSL-100 quantum scalar irradiance sensor (Biospherical Instruments, San Diego, CA, USA). All measurements were in duplicate.

2.2. Osmotic dehydration

2.2.1. Preparation of crude glycerol

The crude glycerol was prepared by mixing the following to achieve the specified mass fraction: 80.5% (w/w) of glycerol (GPR Rectapur®, 98% of purity), 10.1% (w/w) of distilled$\pi_g = 2.23c + 0.33c^2$ water, 5.2% (w/w) of sodium chloride (Sigma Aldrich, AGS Grade, 99% of purity), 0.4% (w/w) potassium chloride (Sigma Aldrich, AGS Grade, 99% of purity), 2% (w/w) methanol (Sigma Aldrich, 99.8% of purity), 2% (w/w) oleic acid (Fluka) [25].

2.2.2. Typical procedure for osmotic dehydration

For 60 mL of an algal broth sample, a 40 cm dialysis tubing (molecular weight cut-off (MWCO): 12–14 kDa, standard regenerated cellulose, flat width 25 mm, 2 mL/cm, 16 mm diameter; Spectrum Labs, USA). Prior to use the tube was soaked for 30 min in deionized water to remove the preservatives. One end of the tube was then closed using a weighted closure (Spectra/Por®). The sample of the algal culture broth was pipetted into the dialysis tube and the other end of the tube was sealed with a standard closure (Spectra/Por®). Unless stated otherwise, the tube containing the culture was held in a 2 L reservoir (wide mouthed flask) containing 1000 mL of the osmotic draw solution. The 2 L reservoir containing the tube was placed on an orbital shaker (150 rpm) at 25 °C. Every 5 min during the first hour of operation and afterwards at longer intervals, the tube containing the sample was removed from the osmotic solution, carefully blotted with absorbent towels to remove the osmotic solution adhering to the external surface, and weighed. The tube was removed and weighed periodically until a constant weight was achieved. The final weight measurements were made in triplicate for estimating the error in blot-drying and weighing. The final volume of the broth in the tube was measured by transferring the contents to a graduated cylinder.

2.2.3. Calculations

The osmotic pressure (π_g, MPa) of an aqueous glycerol solution with a glycerol concentration c ($mol \cdot L^{-1}$) was estimated by the following equation [26]:

$$\pi_g = 2.23c + 0.33c^2. \quad (1)$$

The initial weight (M_0) of the tube, the closures and the broth, and the weight (M) after a certain period of forward osmosis were used to calculate the weight reduction (WR), as follows:

$$WR = \left(\frac{M_0 - M}{M_0}\right). \quad (2)$$

The weight loss profile during the osmotic dehydration was interpreted using experimentally validated Peleg model [27]; thus,

$$WR = WR_0 \pm \frac{t}{k_1 + k_2 t} \quad (3)$$

where WR is the weight loss at time t, WR_0 (i.e., WR at $t = 0$) is zero, and k_1 and k_2 are Peleg constants. The constants k_1 and k_2 could be estimated from the measured WR values using the linearized form of Eq. (3); thus

$$k_1 + k_2 t = \frac{t}{WR}. \quad (4)$$

If the weight loss of the algal broth, or the feed, is mainly due to water loss, the volume reduction of the feed solution is readily estimated as $(M_0 - M)/\rho_w$ where ρ_w is the density of water. The water flux, J_w, through the tubing can then be calculated using the total membrane area (A_0) of the tubing and the duration of the osmotic dehydration process; thus,

$$J_w = \frac{(M_0 - M)}{(t - t_0) A_0 \rho_w}. \quad (5)$$