CHEMICAL ENGINEERING TRANSACTIONS
VOL. 65, 2018
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Eliseo Ranzi, Mario Costa

ISBN 978-88-95608- 62-4; **ISSN** 2283-9216
DOI: 10.3303/CET1865072

Experimental Analysis and Diffusion Modelling of Solar Drying of Macroalgae - *Oedogonium sp*.

Lauren Hammond[a], Lisa Bai[b], Madoc Sheehan[a*], Craig Walker[a]

[a]College of Science & Engineering, James Cook University, Townsville, QLD 4811, Australia
[b]MBD energy, James Cook University, Townsville, QLD 4811, Australia
madoc.sheehan@jcu.edu.au

Macroalgae is emerging as an important resource in food, fertiliser and fuel applications. The algae *Oedogonium Sp*. is used in the remediation of nutrient laden wastewaters from tropical aquaculture industries such as prawn farming in Northern Australia. One of the major challenges to the successful commercialisation of macroalgal based processes is reducing the costs of dewatering and drying of the high moisture content material, whilst maintaining product quality. Drying and dryer design are complicated by the shape, density and functional form of the algae, because these variables are considered to influence the drying rate. In this paper, we describe solar drying experiments performed in Tropical Northern Australia (Townsville) using freshly sourced samples of *Oedogonium Sp*. Different algae preparation methods (cut, torn and sheeted) and different algae bed thicknesses or bed densities were examined in order to quantify their influence on the algae drying rate. Profiles of moisture versus time were modelled using Fick's Second Law of Diffusion, which characterises drying in terms of a materials effective diffusivity and thickness, and provides a mechanistic description well-suited to predicting the influence of external variables. The choice of preparation method was found to have an insignificant effect on the effective diffusivity, but increasing algae bed density led to lower effective diffusivities and longer drying times. Significant shrinkage of the algae during the initial period of drying (when moisture ratios are greater than 0.50) was observed and the limitations of Fick's Law approximations are discussed.

1. Introduction

Recently, research into renewable fuels, biodegradable materials and remediation of waste has been at the forefront of scientific advances. One of the major areas of interest is algae, which is emerging to be a promising long-term sustainable source of biomass for applications in bioremediation, biofuel production, fertiliser, animal feed and even human feed (Algal Biomass Organization, 2010). Macroalgae in particular have been found to have a number of advantages, including the potential for rapid growth (Heesch et al., 2009) and a global distribution of species living in a wide range of habitats and environments (Heesch et al., 2009; Kong et al., 2011).

Macroalgae has a high initial moisture content which is bound internally in the material. Reducing the moisture content is important as it improves the biofuel conversion process and helps to decrease costs associated with processing and transport. However, due to the internally bound moisture, the process of drying algae is one of the most energy intensive steps in the production process (Show, Lee, & Chang, 2013). Current drying methods for biomass are not optimised and therefore lead to higher operational costs than necessary, decreasing the viability of the algal products and processes. Optimisation of drying processes and drying equipment requires the use of kinetic modelling which can lead to increased efficiency and improved viability of algae based products. More generally, many different drying methods have been used to dry agricultural products including convective drying, oven drying and solar drying. Solar drying is a commonly used, well-established method of drying agricultural products, where wet biomass is laid out in the sun to dry. Solar drying is a complex process involving surface heating via solar radiation, heat conduction through the material, moisture convection from the material surface, and internal diffusion of moisture induced by a concentration gradient. Despite its complexity, this type of drying is simple to implement and can be low cost, offering

Please cite this article as: Hammond L., Bai L., Sheehan M., Walker C., 2018, Experimental analysis and diffusion modelling of solar drying of macro algae - oedogonium sp, Chemical Engineering Transactions, 65, 427-432 DOI: 10.3303/CET1865072

considerable savings in terms of reduced carbon pollution when compared to more traditional convection systems. However, in practice the lack of predictive tools to describe the drying leads to difficulty controlling the drying rate and final product moisture.

To date there has been little work done to characterise the drying kinetics of macroalgae, although there has been considerable investigation of the drying kinetics of various agricultural materials including aromatic leaves, fruits and vegetables. In a study conducted by Lemus et al (2008) using a convection oven, the effect of various drying temperatures (40-70℃) on the drying time for red alga *Gracilaria* was evaluated. This study observed that algae moisture decreased exponentially with time, indicating drying occurred in the falling rate period and that diffusion modelling may be a suitable theoretical framework for modelling the rate data. In another drying study, Walker et al (2016) investigated the drying kinetics of macroalgae *Ulva ohnoi* and *Oedogonium sp*. using both radiative and convective drying over a range of temperatures (40-60℃). The moisture versus time profiles under both scenarios were fit to Fick's Second Law of Diffusion, shown in Eq(1), with a high degree of correlation. In Eq(1) *D* is the effective diffusivity and *M* is the moisture content.

$$\frac{\partial \mathrm{M}}{\partial \mathrm{t}} = D\nabla^2 M \tag{1}$$

In this paper, we describe lab-scale solar drying experiments performed in Tropical Northern Australia (Townsville) on a locally commercially important species of macroalgae: *Oedogonium Sp*. Using ANOVA statistical techniques, algal preparation method and algal bed thickness or bed density and their influence on drying rate were examined. Drying rates were modelled in a pragmatic way, by assuming diffusion to be the dominant mechanism and using Fick's Second Law of Diffusion to characterise drying in terms of a materials effective diffusivity and thickness. Parameter estimations were used to determine effective diffusivities under the various scenarios considered. Simplifying the mechanistic description by lumping effects into an effective diffusivity makes the resulting data more easily utilised by industry when drying under similar conditions.

2. Material and Methods

Oedogonium sp. is a green freshwater algae, consisting of a long strand which is one cell wide. While it grows as a single strand, it has a tendency to clump together when harvested, forming tangled balls of algae. *Oedogonium sp.* has a high growth rate (Lawton, de Nys, & Paul, 2013) producing 15-20 kg DW/m^2/day at a commercial scale facility at a water depth of 0.5 m. MBD Energy Ltd use this species of macroalgae to develop low cost processes to clean nutrient laden wastewater from a range of industries, including prawn aquaculture. *Oedogonium sp*. is used specifically for its high growth rate (Lawton et al., 2013; Neveux et al., 2014). Samples of *Oedogonium sp*. were collected from local cultures grown at the Marine and Aquaculture Research Facility Unit (MARFU) at James Cook University in Townsville North Queensland, Australia, between June and August 2017.

The algae was collected directly from large open-air growth tanks using mesh bags, which were then centrifuged to dewater the algae as much as possible using a KOH-I-NOOR A-652 spin dryer manufactured by Yaco Eskenazi (maximum speed: 2800 rpm). A Sartorius Moisture Analyser (SMA: MA-45) was used to determine the moisture content of a sub-sample of the algae at the start and end of the solar drying process. Drying trays with dimensions of 29 x 15 x 2 cm were used to contain the algae samples during the two separate sets of test protocols: variation in preparation method; and variation in algae sheet thickness. The trays were made of white plastic to minimise heat conduction from the tray to the algae and to minimise heat adsorption from the sun. The tray and samples were weighed using an ML4002T Precision Balance manufactured by Mettler Toledo. A LP02 Portable Solar Radiation Sensor and LI19 Datalogger manufactured by Hukseflux were used to measure and record global and diffuse solar radiation during the drying period. The LP02 measures in a spectral range of 285 to 3000$\times 10^{-9}$ m with a calibration uncertainty of <1.8% and operates within a temperature range of -40 to 80℃ with the uncertainty of the temperature response being $< \pm$3%. Solar radiation readings in W/m^2 were collected every 60 Seconds and the device was set up next to the trays at a distance of no more than 30 cm away. The LI19 was connected to the LP02 via a 5 m long cable and was used to collect and display the measured radiation data. This device can store the minimum, maximum and average solar radiation in intervals of 2 to 65535 Seconds with a maximum storage capacity of 3518 measurements. A HHF81 Anemometer manufactured by Omega was used to measure the wind speed, temperature and relative humidity at the testing location.

2.1 Experimental methods

The composition of algae can vary significantly depending on external factors such as environmental conditions, growth and nutrition. To ensure each tray is a 'true' representation of the macroalgae species, the cone and quartering method was used.Triplicate tests to determine initial moisture content were conducted using the SMA. In these preliminary tests 1 g samples were obtained via cone and quartering of each tray sample.

In an industrial water remediation process using this species of algae, the dewatered algae is typically processed in two ways. The first is to run the dewatered algae through a cutter that cuts the algae into squares roughly 2 x 2 cm (cut). The second method is to tear apart the dewatered algae sheets by hand into rectangular pieces roughly 3 x 5 cm (torn). A third method was used to prepare the dewatered algae in which large sheets of algae were carefully spread out, without tearing, to cover the entire tray area (sheet). The algae forms resulting from the use of these three preparation methods are shown in Figure 1.

Figure 1: Dewatered and prepared triplicate algae samples prior to solar drying. From L to R: 3x5cm torn samples, 2x2cm cut samples, sheet samples.

The second test protocol examined the effect of sheet thickness on the drying rate. Three different weights of algae (25 g, 50 g and 75 g) were carefully spread across the entire surface area of the tray. Crude measures of the material thickness were estimated by assuming the thickness to be in proportion to the algae sample mass, with the heaviest sample (75g) being as thick as the height of the tray (2 cm).

For each test, undertaken on as stable and sunny day as possible, a period of 6-10 hours was required for each dewatered sample to reach a final moisture content at or below 10wt%. As the solar radiation varied between testing times (typically between 600 and 900 w/m^2), each test hypothesis (i.e. that preparation method or sheet thickness significantly influences the drying rate) was conducted in triplicate on a single day. After the initial sample mass had been measured, the mass of the samples were recorded in 5-minute intervals until the moisture removal fell rate below 1 g per interval. The interval was then extended to 10-minutes, 15-minutes and finally 30-minutes until less than 0.2 g of moisture removal was experienced over a 30-minute period.

2.2 Experimental design

The two experimental designs consisted of two independent variables: preparation method (cut, torn, sheet); and algae thickness (corresponding to 25g, 50g, 75g samples). An ANOVA procedure was used to separately determine the significance of each independent variable on the dependent variable – in this case the parameter estimated value of the effective diffusivity. Each of the tests were conducted in triplicate (indicated by the number of x's in each box in Table 1) and a total of 27 tests were conducted. Referring to Table 1, three experiments were conducted to examine the effect of preparation method (vertical sets of conditions) and three experiments were conducted to examine the effect of initial thickness (horizontal sets of conditions).

Table 1: Summary of experimental test conditions

		Initial Thickness (cm)		
		0.67	**1.37**	**2.00**
Clump Size (cm)	**2 x 2 (cut up)**	XXX	XXX	XXX
	3 x 5 (torn)	XXX	XXX	XXX
	29 x 19 (sheet)	XXX	XXX	XXX

2.3 Data and statistical analysis

Raw data for moisture content was manipulated to obtain moisture ratio (*MR*) versus time profiles using Eq(2), where M_0 is the initial moisture content, *M* is the moisture content at time (*t*) and M_e is the equilibrium moisture content, all on a dry basis. The equilibrium moisture content of the macroalgae was obtained using a Guggenheim- Anderson- de Boer (GAB) model (Anderson, 1946) developed and valid in the range 25-60℃ and 2-60% relative humidity (Walker C., 2017, personal communication, 10 June). The temperature and relative humidity measured across the day was averaged and rounded to the nearest whole number for use in the GAB equation.

MR versus time data were then used to parameter estimate for the optimum effective diffusivity (D_e) in Fick's Second Law of Diffusion (Eq(1)). An analytical series solution to this equation, developed by Sherwood (1932), was utilised to best fit to the data (Eq(2) with n = 10). In Eq(2) *t* is time and *L* is the (infinite slab) thickness. The optimal D_e value which best-fit the experimental data was found by minimising the sum of squared error (SSE) between the model predicted moisture ratio and the experimental data. These calculations were performed using Excel's inbuilt solver function, and ANOVA statistical analysis was performed using Excel's inbuilt statistics functions.

$$MR = \frac{M - M_e}{M_o - M_e} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(-(2n+1)^2\frac{\pi^2 D_e t}{4L^2}\right) \quad (2)$$

3. Results and Discussion

Here we report a selection of results to illustrate the major observations with respect to the influence of preparation method and initial sample thickness on the drying rate of *Oedogonium sp*.

Figure 2 shows drying rate curves obtained for 25g samples prepared using the three different preparation methods (cut up, torn, sheet). Based on parameter estimated effective diffusivities for each time profile, ANOVA analysis confirmed the qualitative observation that the preparation method led to no significant differences in the observed drying rate. The lack of significance of preparation method on drying rate was confirmed across all test conditions (i.e. 50g and 75g samples).

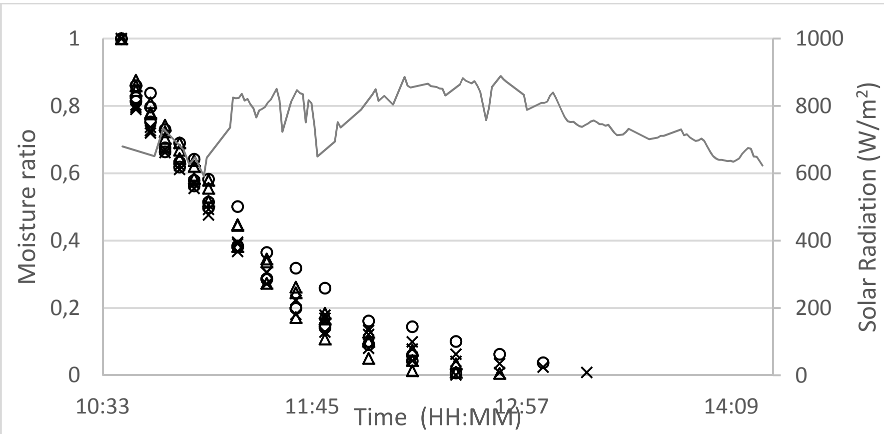

Figure 2: Moisture ratio versus time profiles comparing 25 g samples prepared using three different preparation methods (cut up – triangles, torn – circles, sheet – crosses). Solar radiation is on the right-hand y-axis.

Figure 3 shows a selection of drying rate curves which compare three different thickness samples (25g, 50g and 75g) for each preparation method: Figure 3 (a) for cut samples; Figure 3 (b) for torn samples; Figure 3 (c) for sheet samples. Based on parameter estimated effective diffusivities that best fit each test's moisture ratio versus time profile, ANOVA analysis confirmed that sample thickness has a significant impact of the drying rate.

Figure 4 shows a set of experimental moisture ratio versus time data for 25g samples prepared using the three different preparation methods (corresponding to Figure 2) overlaid with the Fick's Second Law model prediction. Given the lack of significant difference between preparation methods for a fixed sample thickness, the effective diffusivity which best fit this entire set of data (*L*=2cm) was used to generate the model-based drying rate curve (R^2=0.968). The value of the optimised effective diffusivity for this set of data was 5.67x10^{-9} m^2/s. . Based on the regression coefficient, the fit to the data was excellent. Differences between the experimental results and model prediction are due to the many influencing factors neglected in the pragmatic approach. This includes neglect of solar heating and conduction, influenced by the natural fluctuations in solar radiance, as well as fundamental errors in Sherwood's model formulation, particularly the effect of material shrinkage. The analytical solution to Fick's Second Law, as expressed in Eq(2), assumes a constant layer thickness (*L*) throughout the drying time. In reality, macroalgae such as *Oedogonium sp*. shrinks considerably in size as moisture evaporates from the sample. This effect (i.e. non-constant *L*) cannot be accounted for using Eq(2) and a first principles numerical solution to Eq(1), including varying boundary conditions would be necessary to better describe the physics of solar drying macroalgae. Despite these factors, the diffusivity value is in good agreement with effective diffusivity values obtained for *Oedogonium sp*. in radiative drying (Walker et al., 2016). The effective diffusion for the macroalgae is of a similar magnitude to those obtained for drying of other biomaterials under similar conditions e.g. banana slices (2x10^{-10} m^2/s at 40°C) (Nguyen and Price 2007) and powdered peanut shell (9.6x10^{-9} m^2/s at 50°C)(Chen et al 2012).

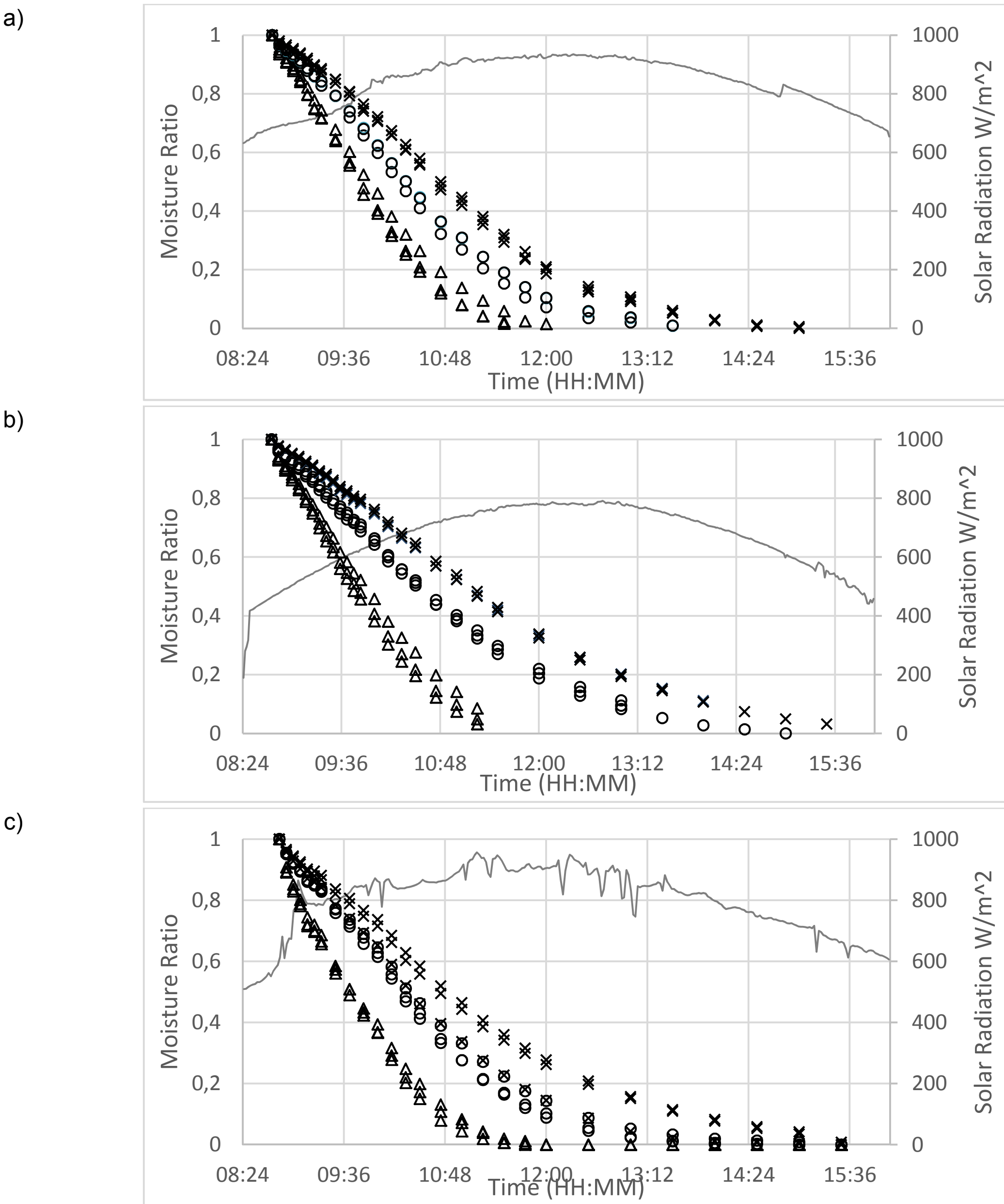

Figure 3: Moisture ratio versus time profiles comparing (a) cut up samples (b) torn samples (c) sheet samples. Three different thicknesses are shown: 2.0cm – triangles; 1.37cm – circles; 0.67cm – crosses.

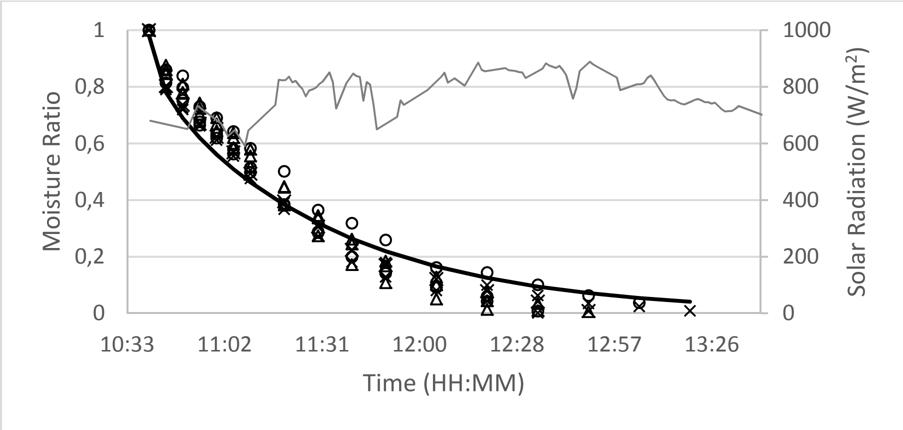

Figure 4: Experimental data for moisture ratio versus time overlaid with model predicted profiles for 25 g samples prepared using the three different preparation methods.

4. Conclusions

This paper detailed experiments undertaken to determine the effects of preparation methods and sample layer thicknesses on the solar drying kinetics of *Oedogonium sp.* The three preparation methods were not significantly different, while increasing the layer thickness was shown to decrease the drying rate. The experimental data were modelled using an analytical series solution of Fick's second Law, with the effective diffusivity of approximately $5x10^{-9}$ m^2/s. While the model showed good correlation, its shape tended to over-predict drying at early stages and under-predict at late stages. Including the solar intensity (and therefore the driving force of drying) and material shrinkage would improve model performance.

Acknowledgements

The financial support of MBD Energy Ltd is gratefully acknowledged.

References

Algal Biomass Organization., 2010, Algae Basics. Retrieved from http://allaboutalgae.com/benefits/ accessed 04.03.17.

Anderson R. B., 1946, Modifications of the brunauer, emmett and teller equation, Journal of the American Chemical Society 68(4): 686-691.

Chen D., Li K., Zhu X., 2012, Determination of effective moisture diffusivity and activation energy for drying of powdered peanut shell under isothermal conditions, Bioresources 7(3), 3670-3678.

Heesch S., Broom J. E. S., Neill K. F., Farr T. J., Dalen J. L., Nelson W. A., 2009, Ulva, Umbraulva and Gemina: genetic survey of New Zealand taxa reveals diversity and introduced species, European Journal of Phycology 44(2), 143-154.

Kong F., Mao Y., Cui F., Zhang X., Gao Z., 2011, Morphology and molecular identification of Ulva forming green tides in Qingdao, China, Journal of Ocean University of China 10(1), 73-79.

Lawton R. J., de Nys R., Paul N. A., 2013, Selecting Reliable and Robust Freshwater Macroalgae for Biomass Applications, PLoS ONE 8(5): e64168.

Lemus R. A., Pérez M., Andrés A., Roco T., Tello C.M., Vega A., 2008, Kinetic study of dehydration and desorption isotherms of red alga Gracilaria, LWT - Food Science and Technology 41(9): 1592-1599.

Neveux N., Yuen A.K., Jazrawi C., Magnusson M., Haynes B.S., Masters A.F., Montoya A., Paul M.A., Maschmeyer T., de Nys R., 2014, Biocrude yield and productivity from the hydrothermal liquefaction of marine and freshwater green macroalgae, Bioresource Technology 155: 334-341.

Nguyen M., Price W. E., 2007, Air-drying of banana: Influence of experimental parameters, slab thickness, banana maturity and harvesting season, Journal of Food Engineering 79(1), 200-207.

Sherwood, T.K., 1932, The Drying of Solids—IV Application of Diffusion Equations, Industrial & Engineering Chemistry 24(3): 307-310.

Show, K. Y., Lee, D. J. ,Chang, J. S. 2013, Algal biomass dehydration, Bioresource Technology 135(0): 720-729.

Walker C., Cole A., Sheehan M., 2015, Modelling of thin layer drying of macroalgae, in Asia Pacific Confederation of Chemical Engineering Congress 2015, Barton, A.C.T. Engineers Australia, 2015.