CHEMICAL ENGINEERING TRANSACTIONS

VOL. 45, 2015

A publication of
AIDIC
The Italian Association
of Chemical Engineering
www.aidic.it/cet

Guest Editors: Petar Sabev Varbanov, Jiří Jaromír Klemeš, Sharifah Rafidah Wan Alwi, Jun Yow Yong, Xia Liu

ISBN 978-88-95608-36-5; **ISSN** 2283-9216

DOI: 10.3303/CET1545095

Effects of Pretreatment on Microalgae Drying

Keat Ping Yeoh, Tsz Ching Kimmy Cheung, Ergys Pahija, Chi Wai Hui*

Department of Chemical and Biomolecular Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong
kehui@ust.hk

The use of microalgae for biodiesel or solid fuel production is a promising alternative for reducing the dependence on fossil fuel. When converting microalgae into fuels, a large amount of energy is consumed for dewatering and/or drying the microalgae. Pretreatment methods such as thermal treatment, acid or alkali treatment are proven to have positive effects on microalgae drying, e.g. increasing the drying rate, reducing the amount of energy usage, etc. However, there are not too many discussions in literature regarding material losses during the pretreatment processes. Material losses not only reduce the productivity of fuels but also generate impacts to the environment as more waste is produced.

In this paper, experimental and modelling studies documenting the effects of different pretreatment processes on the drying rate and material losses are presented. Samples of microalgae (i.e. chlorella vulgaris) are first centrifuged and filtered before undergoing an alkali (i.e. sodium hydroxide), acid (i.e. sulphuric acid) or hydrothermal treatment. The moisture content, dry weight and compositions (i.e. ultimate analysis) of the samples are measured before and after the treatments. The untreated and pretreated samples are then subjected to thermogravimetric analysis (TGA) to determine their drying rate during the drying process. The drying kinetic is derived from the TGA results.

Findings show that the Page model can be used to represent the drying process with an R^2 of 0.99, material losses can be significant for certain cases (as high as 18 %) and changes in elemental analyses after pretreatment e.g. in sulphur, hydrogen and oxygen content occur after pretreatment.

1. Introduction

As fossil fuel reserves continue to be depleted, biofuels derived from microalgae may be a feasible solution if an energy crisis occurs. The advantages of using microalgae as a feedstock to produce biofuels include its high photosynthetic efficiency and short growth cycle as compared to terrestrial plants (Rashid et al., 2014). Furthermore, the biomass productivity of microalgae is high (15 – 25 t/ha/y), while the biomass productivity of other biofuel feedstocks such as soybean and jatropha range from only 0.4 to 4.14 t/ha/y (Rashid et al., 2014). Also microalgae can be grown in different environments and can be used to purify wastewaters containing useful nutrients (Mata et al., 2013). In general, the procedure to produce biofuels from microalgae involves culturing microalgae followed by harvesting, drying, lipid extraction, transesterification and purification of the resulting biofuel. Various methods of pretreatment are today used to enhance the output of bioproducts (de Azevedo Rocha et al., 2014).

During the process of converting microalgae into biofuels, a significant amount of energy is expended to remove moisture from the microalgae. Dewatering increases the calorific value of microalgae and is an essential step before gasification of microalgal biomass (Aziz et al., 2014). Furthermore, dewatering increases the viability and efficiency of lipid extraction (Guldhe et al., 2014). Also, they can be used for direct combustion (Amin, 2009). Drying microalgae involves separating excess water from the microalgae bulk after the harvesting process as well as extracting water from microalgal cells. Pretreatment methods may be used to disrupt the microalgal cell walls before the drying process to facilitate removal of intracellular water. Certain methods of pretreatment such as thermal pretreatment are proven to have positive effects such as increasing the drying rate (Viswanathan et al., 2012). However, there appears to be a lack of discussion regarding material losses during the pretreatment process as discussions in literature tend to emphasise the energy savings or increase in effective diffusivity arising from

Please cite this article as: Yeoh K.P., Cheung T.C.K., Pahija E., Hui C.W., 2015, Effects of pretreatment on microalgae drying, Chemical Engineering Transactions, 45, 565-570 DOI:10.3303/CET1545095

pretreatment. Material losses will reduce the productivity of the biofuel production process and generate environmental impacts if the waste is not appropriately handled.

In this paper, experimental and modelling studies documenting the effects of three pretreatment processes on the drying rate and the material losses are presented. Samples of microalgae (i.e. chlorella vulgaris) were first centrifuged and filtered before being undergoing an alkali, acid or thermal treatment. The moisture content, weight and ultimate analysis of the samples were measured before and after the treatments. The untreated and pretreated samples were then subjected to TGA to determine their drying rate during the drying process. The TGA results were then used to derive the drying kinetics.

2. Materials and methods

2.1 **Microalgae culturing and harvesting**

Microalgae was cultivated in a fish tank irradiated with a fluorescent lamp to simulate an open pond photobioreactor system. The culture medium used was prepared from laboratory grade chemicals and deionised water according to the composition of the Bristol Medium (UTEX, 2014). The composition of the culture medium used is as follows: $NaNO_3$ (2.94 mmol/dm^3), $CaCl_2$•$2H_2O$ (0.17 mmol/dm^3), $MgSO_4$•$7H_2O$ (0.30 mmol/dm^3), K_2HPO_4 (0.43 mmol/dm^3), KH_2PO_4 (1.29 mmol/dm^3) and NaCl (0.43 mmol/dm^3).

The growth of microalgae was monitored daily. After around two weeks of cultivation, the harvesting process took place. During the harvesting process, around half the contents of the tank was removed and replaced by fresh culture medium of equivalent volume. The microalgal suspension was then centrifuged using the Centurion Scientific K2015 and the supernatant poured away to obtain microalgae cake. Distilled water was then added to the microalgae cake and the mixture was shaken before being centrifuged again in order to eliminate ions. The supernatant was again poured away and the remaining microalgae cake was used in the subsequent experiments.

2.2 Initial moisture content of microalgae cake

About 1 g of the microalgae cake obtained from the harvesting process was placed in a clean, dry crucible. The crucible containing the microalgae cake was then stored in an oven at 100 °C and left to dry. The mass of the crucible with the microalgae was weighed every two hours until no more change in mass was observed between subsequent weightings. The mass of the empty crucible (M_C), the mass of the empty crucible with microalgae cake before drying (M_B) and the mass of the crucible with microalgae cake after drying (M_A) were weighed respectively using an electronic balance and the mass values were recorded. The initial moisture content of the microalgae cake was calculated as follows:

$$Initial\ Moisture = \frac{M_B - M_A}{M_B - M_C} \times 100\ \% \qquad \bullet \quad (1)$$

Note that the mass loss represents the moisture content of the sample. The above procedure was also performed on microalgae cake obtained after each pretreatment method to determine the moisture content before the TGA process. This initial moisture content was then used in the drying models.

2.3 Acid pretreatment

The acid pretreatment utilised 3 % v/v sulphuric acid, H_2SO_4 solution. Approximately 1 g of microalgae cake was scooped into a tube. 3 % v/v sulphuric acid, H_2SO_4 solution was then added to obtain a microalgae suspension of 15 g/dm^3 with regard to dry mass of the microalgae cake. The tube was shaken vigorously to homogenize the microalgae suspension before undergoing centrifugation. After centrifugation, the supernatant was poured away.

The mass of the empty tube, the mass of the tube with the microalgae cake and the mass of the tube after centrifugation without the supernatant were all weighed using an electronic balance and the values recorded in order to calculate the material loss after centrifugation.

2.4 Alkali pretreatment

3 mol/dm^3 sodium hydroxide, NaOH solution was used in the alkali pretreatment. The experiment for alkali pretreatment was the same as the acid pretreatment except that sulphuric acid, H_2SO_4 solution was replaced by sodium hydroxide, NaOH solution.

2.5 Hydrothermal pretreatment

Similar to the acid and alkali pretreatment, distilled water was added to microalgae cake to produce a microalgae suspension of 15 g/dm^3 with regard to dry algal mass. The tube containing the microalgae suspension was then shaken and placed in a water bath heated by a plate heater at 100 °C for 30 min. The tube was then removed from the water bath and cooled down to ambient temperature. Afterwards, the same procedure described for acid and alkali pretreatment was performed.

2.6 Analytical methods

Thermogravimetric analysis (TGA) was carried out on the resulting samples of each pretreatment method using a thermogravimetric analyser (TGA, Q5000, TA Instruments, New Castle, USA). TGA records the decrease in mass % of the microalgae samples over time and was carried out at temperatures ranging from 60 – 100 °C as this is a range commonly used in literature for the biomass drying process (e.g., Chen et al., 2012). The thermogravimetric analyser was operated using nitrogen in the sample chamber. The procedure method consisted of two steps: jump from ambient temperature to the desired one followed by maintaining a constant temperature for 30 min (jump + isothermal).

Other than that, the material losses after pretreatment and centrifugation were calculated and compared between the different pretreatment methods. Elemental analysis (C, H, N, S) was also performed on the samples before and after pretreatment.

2.7 Modelling of the drying kinetics

As mentioned also by other authors (Viswanathan et al., 2012), the Newton and Page models can be used to fit the drying curves of microalgae obtained from TGA. Only two models were considered as previous research has reported that these models are able to model the drying curves of microalgae to a satisfactory extent (Viswanathan et al., 2011). Further information and derivation of the models may be found from Jayas et al. (1991). The model equations and parameters are shown below.

Newton Model: $$MR = \frac{M(t)-M_{eq}}{M_0-M_{eq}} = \exp(-k_1 t) \qquad (2)$$

Page Model: $$MR = \frac{M(t)-M_{eq}}{M_0-M_{eq}} = \exp(-k_2 t^n) \qquad (3)$$

where MR is the dimensionless moisture ratio and is defined as the ratio of free water still to be removed at any time t to the total free water initially available, M(t) is the instantaneous moisture content on a dry basis, Mo is the initial moisture content on a dry basis, M_{eq} is the equilibrium moisture content on a dry basis and k_1 (min^{-1}) as well as k_2 (min^{-n}) are the drying constants (Viswanathan et al., 2012).

3. Results and discussion

3.1 Change in moisture content after pretreatment

The change in moisture content after each pretreatment was calculated to investigate whether the moisture content of microalgal cells changed as a result of the pretreatment. Results on the changes in moisture content are presented in Table 1 below. The alkali and hydrothermal pretreatments resulted in an increase of the moisture content. However, the increase is negligible and could simply be due to some residual moisture from when the supernatant was poured away (after centrifugation). The significant decrease in moisture content after acid pretreatment is noteworthy as this could mean that less heating is required to dry the microalgae, thus resulting in energy savings. It is also possible that the mass loss after acid pretreatment was partially due to loss of volatile compounds and not just moisture, which is possible if microalgal cells were ruptured during the pretreatment process.

Table 1: Change in moisture content after pretreatment

Pretreatment Method	Moisture content before pretreatment / %	Moisture content after pretreatment / %	Change in moisture content / %
Alkali	92	93	+1
Acid	92	74	-18
Hydrothermal	92	94	+2

3.2 Thermogravimetric Analysis (TGA) results and model fitting

The Newton and Page models were fitted to the experimentally-obtained TGA curves using the GRG Nonlinear method of the Solver Add-in available in Microsoft Excel. In order to statistically verify the suitability of the models, the coefficient of determination, R^2 and sum of absolute errors, SAE was calculated. Table 2 below provides a summary of the model parameters, R^2 values and SAEs obtained, while Figure 1 provides a graphical representation of one of the results (hydrothermal at 90 °C) that displayed the highest R^2 of 0.9998. This result has been displayed graphically because it shows that the Page model can be used to accurately represent the drying curve with pretreatment given that the equilibrium moisture content at the drying temperature is known. Furthermore, the correlation between a high R^2 value and the accuracy of the curve fitting of the two models can be observed in Figure 1. Other than that, the drying curves for other pretreatment methods and the untreated sample showed a similar curve trend. While both models appeared to be good fits with the lowest R^2 being 0.92, the Page model displayed a consistent R^2 value of 0.98 and above for all pretreatment methods and temperatures and the SAEs are low considering the fact that they were aggregated over 3,600 data points. The Page model would therefore be a suitable model in the modelling of microalgae drying after the pretreatment methods investigated. Although no other models were investigated, the Page model already provides an excellent fit to the experimental data.

Table 2: Model parameters, R^2 values and Sum of Absolute Errors after curve fitting

Pretreatment Type	Temperature / °C	Newton Model			Page Model			
		k_1	R^2	SAE	k_2	n	R^2	SAE
Untreated	60	0.3113	0.9823	63.96	0.1899	1.367	0.9995	14.31
	70	0.4034	0.9803	56.06	0.2588	1.404	0.9995	11.99
	80	0.8032	0.9220	66.68	0.4195	1.363	0.9994	11.27
	90	0.5493	0.9764	46.12	0.3802	1.480	0.9994	12.16
	100	0.7701	0.9904	22.11	0.7167	1.179	0.9949	22.61
Alkali	60	0.2648	0.9923	56.70	0.2904	0.9383	0.9933	47.60
	70	0.3626	0.9783	83.49	0.4450	0.8243	0.9875	55.93
	80	0.3770	0.9860	63.75	0.4430	0.8588	0.9917	41.68
	90	0.4966	0.9940	34.82	0.5195	0.9483	0.9946	30.00
	100	0.6110	0.9923	32.31	0.6312	0.9500	0.9928	29.20
Acid	60	0.2648	0.9930	54.10	0.2906	0.9380	0.9941	44.35
	70	0.3874	0.9915	46.93	0.3464	1.103	0.9933	47.37
	80	0.3911	0.9929	39.34	0.3407	1.127	0.9956	38.18
	90	0.6729	0.9870	45.44	0.6557	1.051	0.9874	46.79
	100	0.4500	0.9934	40.90	0.4755	0.9428	0.9941	35.32
Hydrothermal	60	0.3351	0.9712	80.93	0.1725	1.518	0.9994	11.79
	70	0.4428	0.9735	60.30	0.2670	1.507	0.9998	6.708
	80	0.5694	0.9762	44.90	0.3985	1.482	0.9997	6.517
	90	0.6543	0.9769	39.07	0.4920	1.471	0.9998	4.202
	100	0.9107	0.9723	30.95	0.7884	1.547	0.9997	3.766

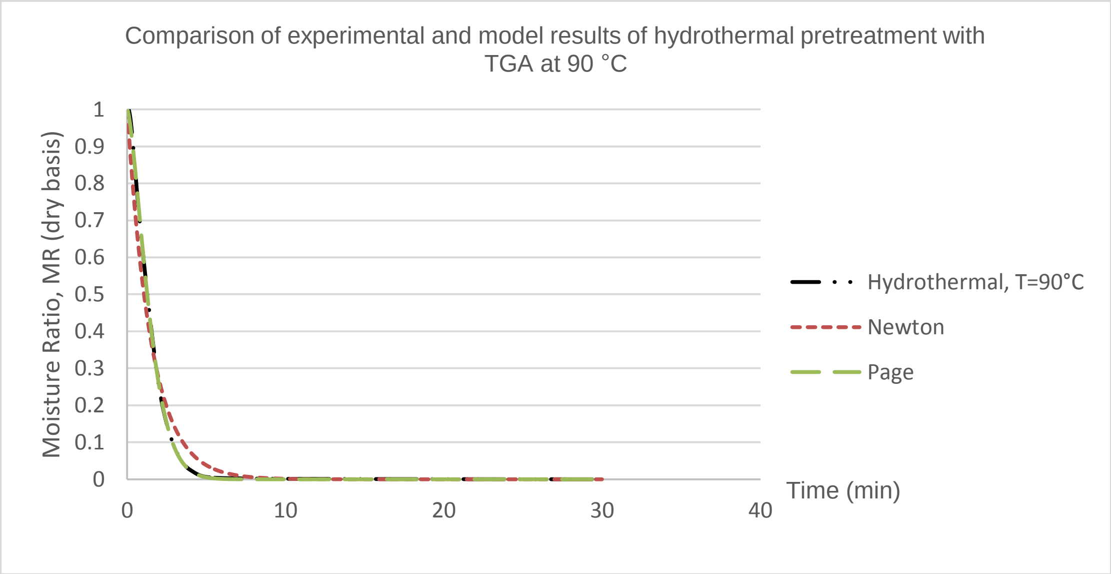

Figure 1: Experimental and model drying curves for hydrothermal pretreatment with TGA at 90 °C

3.3 Elemental analysis of microalgae after pretreatment

Elemental analysis was carried out on microalgae samples after pretreatment to determine the change in composition that arose due to the chemical pretreatment methods. As expected, the sulphur content increases after pretreatment with sulphuric acid, H_2SO_4. The observed increase in the sulphur content shows that some sulphuric acid is still present in the microalgae which could be a concern if the microalgae biomass after transesterification were to be used as animal feed. Furthermore, the elevated levels of sulphur decreases the calorific value of the microalgae as the formation of SO_2 is endothermic and SO_x will cause the formation of acid rain (Linstrom and Mallard, 2015). Another value of interest is the mass percentage of oxygen in the NaOH pretreated sample. The oxygen content in the NaOH pretreated sample appears to have increased significantly. This may be due to the mass of sodium being considered as oxygen because the oxygen content is calculated by difference i.e. by subtracting mass of all the other elements from the original sample mass. Other than that, while the hydrogen content increased after hydrothermal pretreatment, the oxygen content decreased. This could be because some water is retained by the microalgae but some dissolved oxygen originally present in the microalgae was released during the heating process. Another reason to explain this phenomenon could be that the observed increase in percentage of hydrogen present is because there is loss of organic compounds containing carbon, nitrogen and oxygen. Table 3 shows the elemental analysis results averaged over 3 trials.

Table 3: Elemental analysis results

Pretreatment type	Elements / mass %				
	C	H	N	S	O
Untreated	8.27	1.54	1.47	0.197	88.5
Alkali	4.19	1.43	0.327	0.103	93.9
Acid	6.48	1.15	0.917	5.23	86.2
Hydrothermal	5.68	6.58	0.750	0.477	86.5

3.4 Material losses after pretreatment

It was hypothesised that some material loss may occur after the pretreatment when pouring the supernatant away. After obtaining the material loss data, it was found that both material loss and material gain occurred. Material gain was only observed for the acid pretreated microalgae samples and this may be explained by the elemental analysis as sulphur has a high atomic mass of 32.065 (NIST, 2015). The material gain by the acid pretreated samples further supports the theory that some sulphuric acid, H_2SO_4 is retained after pretreatment. Table 4 shows the average change in mass of the microalgae samples after each pretreatment method.

As can be seen from Table 4, the loss of mass after hydrothermal treatment is profound at 18 %. This may also be explained by the earlier theory that organic compounds were poured away with the supernatant after centrifugation. Further investigation is required to more accurately determine the real loss in the acid and alkali pretreatments.

On the other hand, it is not easy to determine the real loss in the acid and alkaline pretreatments. One method that could yield more information would be repeating the experiment from dried microalgae samples instead of moist ones, adding the pretreating solution before centrifugation, eliminating the supernatant followed by drying the microalgae once again. In this way it would be possible to calculate the loss of material in the absence of moisture.

Table 4: Change in mass after pretreatment

Pretreatment Method	Alkali	Acid	Hydrothermal
Mass of empty tube / g	6.69	6.635	6.6275
Mass of empty tube + microalgae / g	7.71	7.37	7.57
Microalgae added / g	1.02	0.735	0.9425
Mass of tube + algae suspension (after adding the chemical) / g	16.05	12.835	14.64
Mass of tube + microalgae (after pouring the supernatant) / g	7.62	7.405	7.4
Change in mass of microalgae sample / g	-0.09	0.035	-0.17
Percentage change in mass of microalgae sample / %	-8.82	4.76	-18.04

4. Conclusion

Drying models, mass loss and change in elemental composition of microalgae samples after pretreatment were investigated. Based on curve fitting using the TGA results, the Page model can be used to represent the drying process of both untreated and pretreated microalgae biomass at temperatures from 60 – 100 °C with high R^2 values of 0.98 and above, a finding that agrees with other publications such as Viswanathan et al. (2012). Other than that, it was discovered that material loss after pretreatment and centrifugation can be significant in some cases, with losses as high as 18 % mass resulting from hydrothermal pretreatment. However, further investigation is required to determine the nature of compounds lost. Comparisons between the elemental analyses of untreated and pretreated microalgal samples showed that H_2SO_4 pretreated samples displayed an increase in sulphur content as expected, while NaOH pretreated samples appeared to have elevated oxygen content compared to the untreated sample and hydrothermal pretreated samples exhibited a decrease in hydrogen content. It is theorised that the elevated oxygen content of the NaOH pretreated sample is actually due to mass of Na being considered as oxygen since oxygen content was calculated by the difference in mass of the sample and other elements. The profound mass loss and higher hydrogen content in hydrothermal pretreated samples could be due to the loss of material after pretreatment, since the biomass itself contains C, N and S.

Further investigation on the phenomena reported is required. Future work could include repeating the experiments at different concentrations of acid and alkali and by measuring whether there is mass loss after hydrothermal pretreatment.

References

Amin S., 2009, Review on biofuel oil and gas production processes from microalgae. Energy conversion and management, 50(7), 1834-1840.

Aziz M., Oda T., Kashiwagi T., 2014, Integration of energy-efficient drying in microalgae utilization based on enhanced process integration. Energy, 70, 307-316.

Chen D., Zheng Y, Zhu X., 2012, Determination of effective moisture diffusivity and drying kinetics for poplar sawdust by thermogravimetric analysis under isothermal condition. BioresourceTechnology, 107, 451-455.

de Azevedo Rocha E.G., da Costa A.C., Aznar M, 2014, Use of Protic Ionic Liquids as Biomass Pretreatment for Lignocellulosic Ethanol Production, Chemical Engineering Transactions, 37, 397-402.

Guldhe A., Singh B., Rawat I., Ramluckan, K., Bux F., 2014, Efficacy of drying and cell disruption techniques on lipid recovery from microalgae for biodiesel production. Fuel, 128, 46-52.

Jayas D., Cenkowski S., Pabis S., Muir W., 1991, Review of thin-layer drying and wetting equations; Drying Technology, 9(3), 551-588.

Mata T.M., Meloa A.C., Meirelesb S., Mendesa A.M., Martinsc A.A., Caetanoa N.S., 2013, Potential of microalgae Scenedesmus obliquus grown in brewery wastewater for biodiesel production, Chemical Engineering Transactions, 32,901-906.

Linstrom P.J., Mallard W.G., Eds. NIST Chemistry WebBook, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg MD, 20899, <webbook.nist.gov> accessed 07.05.2015.

Rashid N., Rehman M.S.U., Sadiq M., Mahmood T., Han J., 2014, Current Status, issues and developments in microalgae derived biodiesel production. Renewable and Sustainable Energy Reviews, 40, 760–778.

UTEX (The Culture Collection of Algae at the University of Texas at Austin), 1953, Bristol Medium <www.utex.org> accessed 20.09.2014.

Viswanathan T., Mani S., Das K.C., Chinnasamy S., Bhatnagar A., Singh R.K., Singh M., 2012, Effect of cell rupturing methods on the drying characteristics and lipid compositions of microalgae, Bioresource Technology, 126, 131-136.

Viswanathan T., Mani S., Das K.C., Chinnasamy S., Bhatnagar A, 2011, Thin layer drying kinetics and chemical composition of microalgae consortium. Bioresource Technology, 126, 131-136.