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Distributed Activation Energy Modelling for Thermal Decomposition of Microalgae Residues

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Two microalgae residue samples of *Chlorella sorokiniana CY1* and *Chlamydomonas sp. JSC4* from Taiwan were experimentally studied by means of a thermogravimetric analyzer (TGA), PerkinElmer Diamond TG/DTA, operated non-isothermally in N_2 environments. The obtained TGA data was used for a kinetic analysis, assuming the distributed activation energy model (DAEM). The results of the kinetic analysis were compared with that from our previous study assuming a five pseudo-components model.

1. Introduction

Microalgae are aquatic biomass, which can be cultivated in marine seawater, freshwater, or even wastewater. Microalgae are considered as CO_2 fixer due to its ability to consume CO_2 during the growing process. After harvesting and extracting the lipid and other extractives from microalgae biomass, for pharmaceutical chemicals such as *Omega 3* and/or for biodiesel production, the residue is normally considered as waste. The residue contains hollocellulose (celluloses and hemicelluloses), lignin, remaining lipid and protein. This residue is a valuable resource for bioenergy production via thermochemical conversion and has the potential to be a big resource of biomass materials due to the increasing demand of bio-diesel as well as derived products from microalgae (Kebelmann, Hornung et al. 2013, Bui, Tran et al. 2015). Several studies on kinetics for microalgae pyrolysis have been reported.
Recently, we have reported the results from our kinetic study (Bui, Tran et al. 2015) for the pyrolysis of microalgae residues assuming five pseudo-components model. In this study, the activation energy for each pseudo-component was assumed constant. On the other hand, it is believed that the thermal decomposition of each pseudo-component can be described better by a model of multiple reactions with different activation energies – distributed activation energy model (DAEM). Therefore, the present work is carried out to look at the pyrolysis kinetic of microalgae residues adopting the DAEM, assuming five pseudo-components.

2. Experiment and method

2.1 Material and experimental methods

All samples of microalgae residues used in this study were characterized and obtained from the previous work (Su, Giridhar et al. 2007, Chen, Huang et al. 2014). Two species of microalgae, *Chlamydomonas sp. JSC4* (C.sp.JSC4) and *Chlorella sorokiniana CY1* (C.sorokiniana CY1) were collected from Southern Taiwan. The lipid oils were then extracted by the direct transesterification method (Su, Giridhar et al. 2007). After the step of oil extraction, the samples were dried at 105^{o}C for 24 h, following by grounding and sieving to obtain the particle size less than 0.42 mm. The obtained powder was stored in sealed plastic bags and kept at room temperature. Table 1 presents result from the characterization of the microalgae residues, which includes data from composition analysis, proximate analysis, and elemental analysis. For the composition analysis, the contents of crude protein, crude lipid and carbohydrate were determined by three different methods, being Kjeldehl method, Soxhelt method and phenol-sulfuric acid method, respectively (Peng, Wu et al. 2001). The proximate analysis was performed adopting the US standard method ASTM E870-82. A PerkinElmer 2400

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Series II CHNS/O elemental analyzer was employed to study the elemental analysis; meanwhile the oxygen content was determined by difference. The calorific value was measured by a bomb calorimeter (IKA C5000).

Table 1. Characterization of two microalgae residues

Biomass	*C. sp. JSC4*	*C. sorokiniana CY1*
Composition analysis (wt%)		
Crude protein	12.18	18.81
Crude lipid	6.85	9.90
Carbohydrate	35.70	35.67
Others	42.27	35.62
Proximate analysis (wt%)		
Volatile matter (VM)	75.50	73.20
Fixed carbon (FC)	15.60	15.10
Moisture	3.50	3.80
Ash	5.20	7.90
Elemential analysis (wt%, dry-ash-free)		
C	40.32	45.07
H	7.38	7.64
N	2.61	3.88
O (by difference)	44.50	35.52
Chemical formula	$CH_{2.2}O_{0.83}N_{0.06}$	$CH_{2.03}O_{0.59}N_{0.07}$
HHV (MJ Kg-1, dry basic)	17.41	20.40

A thermogravimetric analyzer (TGA), PerkinElmer Diamond TG/DTA, was employed to investigate the non-isothermal pyrolysis (or decomposition in nitrogen environment) of microalgae residues. Approx. 5 mg of the dried samples, together with the nitrogen flowrate of 100 cc min^{-1}, was used for each TG analysis. The nitrogen flow was employed as purging gas to eliminate any possible air content in the reactor and prevent the loaded samples from oxidation reaction. The TGA analyses were performed while the samples were being heated from room temperature to 1000 K, with the heating rate of 20^{o}C.min^{-1}.

2.2 DAEM

The distributed activation energy model (DAEM) is believed to be proposed first by Pitt (Pitt 1962), which is presented by a series of parallel first-order reactions with different activation energy values but the same pre-exponential factor. The n^{th}-order DEAM was latter developed by Braun et al. (Braun and Burnham 1987). A general equation for DAEM is shown below:

$$1-\frac{V}{V^*}=\int_0^{\infty} exp\left(-A\int_0^{t} e^{\frac{-E_a}{RT}}dt\right)f(E)dE \qquad (1)$$

In Eq. 1, the term *f(E)* is the distribution function of activation energy. Several forms of *f(E)* are reported in the literature including Gaussian, Weibull, and Gamma distribution (de Caprariis, De Filippis et al. 2012). Among these functions, the Gaussian representing a mean activation value (E_0) and its standard deviation σ according Eq. 2 is the most widely used,

$$f(E)=\frac{1}{\sigma\sqrt{2\pi}}exp\left(-\frac{(E-E_0)^2}{2\sigma^2}\right) \qquad (2)$$

The most challenging in applying the DAEM to studying the thermal degradation of biomass is that this model has a double-layer integral and one variable (*E*) going from 0 to infinite, which could not be computed directly. Several simplifications (Miura 1995, Miura and Maki 1998, Please, McGuinness et al. 2003, Cai, He et al. 2007, Cai and Liu 2007) were proposed to reduce the complexity of Eq. 1 in practical calculation.

In our present study, the calculation proposed by Cai et al. (Cai and Liu 2008) was adopted. Eq. 3 was employed to determine the mass fraction of releasing volatiles (*x*).

$$1-x=\int_0^{\infty} exp\left(-\frac{A}{\beta}\int_0^{T} e^{\frac{-E_a}{RT}}dT\right)f(E)dE\,,\ \ i=1,\,3 \qquad (3)$$

Three series of kinetic parameters including E_0, σ, *A*, and *c* were determined for three components of biomass. It should be noticed that the DAEM was first applied for modelling the releasing volatiles, thus it can be easy to model the remaining solids, which is recorded in a thermo-gravimetric experiment. However, when the TGA data are differentiated to obtain DTG data, some serrations will occur and therefore it needs to smooth the TGA data in a separated step after searching for kinetic values.

2.3 Modelling and optimization

The pyrolysis kinetic of biomass materials can be simulated by employing the DAEM, based on the assumption that the overall pyrolysis process is just a single reaction to produce volatile matter and char. However, this assumption cannot characterise precisely the thermal-decomposition behaviour of biomass due to its variable composition. Recently, the parallel-reaction model has been proven as an accurate approach (Tran, Bach et al. 2014). Since the microalgae residues contain the remaining lipid, protein and the cell wall including hemicellulose, cellulose and lignin, it is reasonable to assume a five pseudo-components for the pyrolysis of microalgae residues (Bui, Tran et al. 2015). Following this assumption, the pyrolysis kinetic can be interpreted by Eq. (4), in with c_i is the contribution factor of i component.

$$\frac{d\alpha}{dt} = \sum_{1}^{5} c_i \frac{d\alpha_i}{dt} \qquad i = 1,2,3,4,5 \qquad (4)$$

The non-linear least square is employed for the optimization of kinetic simulation which aim to minimize the objective function as described in Eq. (5)

$$S = \sum_{i=1}^{n} \left[\left(\frac{d\alpha_i}{dt}\right)_{exp} - \left(\frac{d\alpha_i}{dt}\right)_{model} \right]^2 \qquad (5)$$

where $\left(\frac{d\alpha_i}{dt}\right)_{exp}$ and $\left(\frac{d\alpha_i}{dt}\right)_{model}$ are the experiment and modelled conversion rate, n is the number of experimental points. The quality of curve fitting is evaluated by Eq. (6) (Tran, Bach et al. 2014)

$$Fit\ (\%) = \left(1 - \frac{\sqrt{\frac{S}{N}}}{\left[\left(\frac{d\alpha_i}{dt}\right)_{exp}\right]_{max}} \right) .100\% \qquad (6)$$

The five pseudo-components model was simulated for both cases of the reaction order equal one (*n*=1) or different than one (*n*#1)

3. Results and discussion

3.1 Kinetic analysis assuming the DAEM

The simulated five pseudo-components model for C. sp. JSC4 and C. sorokiniana CY1 is graphically demonstrated in Figure 1 and Figure 2 whereas the extracted kinetic parameters from the modelling and simulation are presented in table 1 and table 2, respectively. It can be seen from the figures that hemicellulose is the most reactive among five pseudo-components since it decomposed firstly, followed by cellulose and lignin. Nevertheless, hemicellulose and cellulose decomposed within a relative narrow range of temperature; however, the decomposition process of lignin persisted for wild range temperature until about 850 K. In addition, thermal decomposition of protein took place before lipid and this feature is similar for both C. sp. JSC4 and C. sorokiniana CY1. Overall, the observation trend was in good agreement with literature (Tran, Bach et al. 2014, Bui, Tran et al. 2015).

Table 1. Extracted kinetic data (n=1)

Sample		E_a (KJ/mol)	σ (KJ/mol)	A (min^{-1})	c	Fit (%)
C. sp. JSC4	Hemicellulose	90.61	16.24	1.36E+06	0.17	98.07
	Cellulose	211.57	37.92	3.13E+14	0.37	
	Lignin	71.44	12.81	1.27E+03	0.16	
	Lipid	108.59	19.46	8.72E+05	0.12	
	Protein	90.46	6.21	1.71E+05	0.18	
C. sorokiniana CY1	Hemicellulose	88.14	15.80	4.74E+05	0.12	99.10
	Cellulose	281.08	50.38	2.30E+19	0.35	
	Lignin	42.53	25.45	4.20E+03	0.20	
	Lipid	168.01	30.11	5.46E+09	0.13	
	Protein	119.03	21.33	2.07E+07	0.18	

The calculated kinetic parameters of hemicellulose, cellulose and lignin, shown in Table 1, coincidence with reported data (Grønli, Várhegyi et al. 2002, Hu, Jess et al. 2007). The mean activation energy of *C.*

sorokiniana CY1 was somehow quite high, 281.08 kJ/mol and 295.25 kJ/mol for *n*=1 and *n*#1, in comparison with common activation energy. However, these number were compatible with other reported investigation on cellulose (Zhou, Long et al. 2015) . Remarkably, for both case with *n*=1 and *n*#1, it appeared that the mean activation energy of protein and lipid of *C. sorokiniana CY1* was higher than this of *C. sp. JSC4*. Moreover, the fit quality of the case *n*#1 was better compared to the case *n*=1 for both microalgae residues.

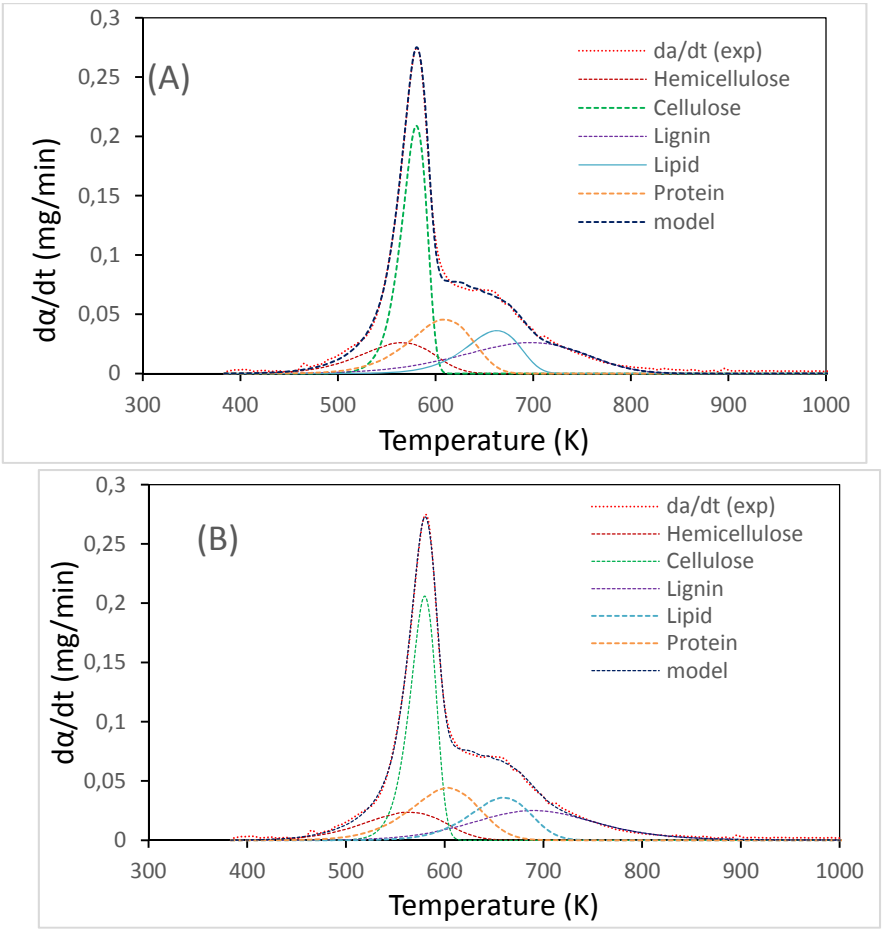

Figure 1 Simulation and curve fitting of C. sorokiniana CY1 (A) n=1; (B) n#1

Table 2. Extracted kinetic data (n#1)

Sample		E_a	σ	A	c	n	Fit
		(KJ/mol)	(KJ/mol)	(min^{-1})			(%)
C. sp. JSC4	Hemicellulose	90.60	16.24	9.21E+05	0.16	1.02	98.45
	Cellulose	224.05	40.16	2.75E+15	0.36	1.18	
	Lignin	61.74	11.07	2.46E+02	0.16	1.36	
	Lipid	101.07	18.12	2.82E+05	0.14	1.12	
	Protein	79.78	14.30	3.30E+04	0.19	1.25	
C. sorokiniana CY1	Hemicellulose	78.90	14.15	9.75E+04	0.12	1.01	99.35
	Cellulose	295.25	52.92	2.41E+20	0.34	1.11	
	Lignin	53.90	32.25	9.08E+04	0.20	1.60	
	Lipid	158.78	28.46	1.57E+09	0.14	1.12	
	Protein	113.92	20.42	1.10E+07	0.19	1.12	

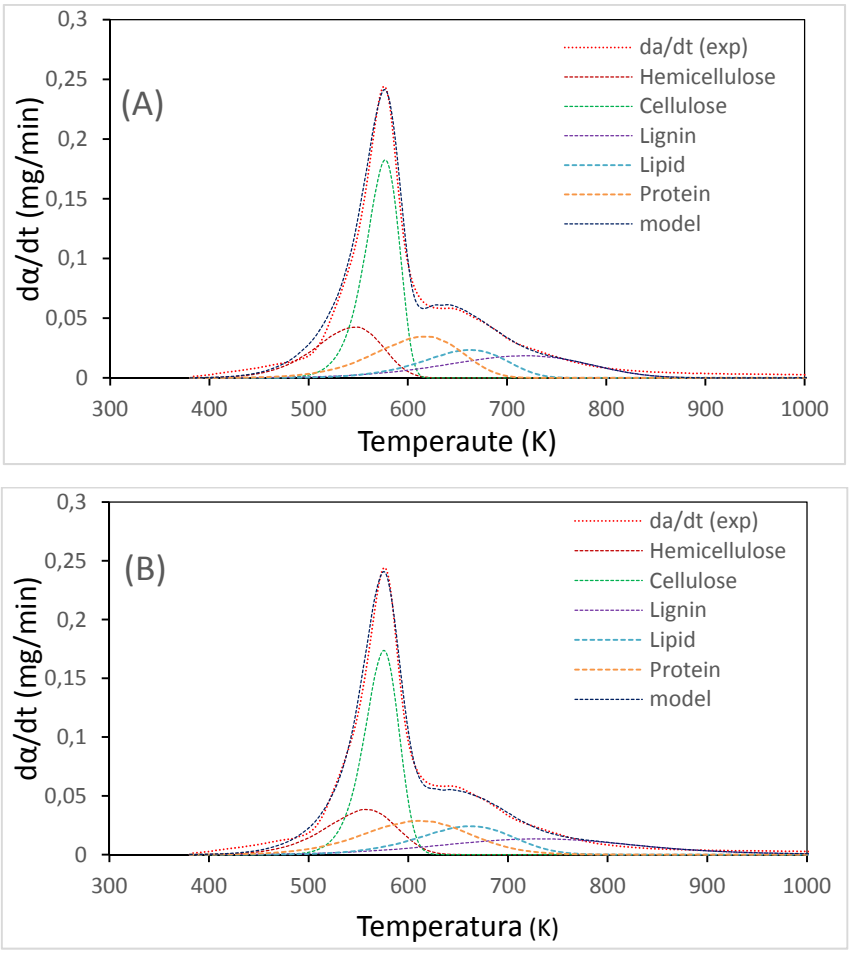

Figure 2 Simulation and curve fitting of C. sp. JSC4 (A) n=1; (B) n#1

3.2 Discussions

Overall, the extracted kinetic parameters of hemicellulose, and lignin are in agreement with the literature (Manyà, Velo et al. 2003, Tran, Bach et al. 2014, Bui, Tran et al. 2015). The mean activation energy of cellulose of *C. sorokiniana CY1* is somehow high compared to the activation energy of cellulose reported in the literature being between 195-213 kJ/mol (Grønli, Várhegyi et al. 2002). However, the activation energy obtained by assuming the DAEM has the mean value that its standard deviation, σ, also need to be taken into consideration. In general, the standard deviationof cellulose is the highest among other pseudo-components, indicating that the actual activation energy varies in a wild range. In addition, the obtained results also conforms to our previous study (Bui, Tran et al. 2015), assuming the five pseudo-components model.
Interestingly, the simulated curves demonstrate that lipid started decomposing after protein for both samples with the temperature range of about 500-700 K for protein and about 560-740 K for lipid. These observations were confirmed by another investigation on pyrolysis of extracted protein and lipid from green microalgae (Kebelmann, Hornung et al. 2013). Furthermore, the protein and lipid simulated curve of *C. sp. JSC4* is more flattened in the case *n*#1 than the case *n*=1 for three different models. Noticeably, the lipid and protein of *C. sorokiniana CY1* owned higher mean activation energy than these of *C. sp. JSC4*.
The results revealed that the reaction order of every pseudo-component varied between one and two, lying within a reliable range. The fit quality of the case n#1 was always slightly higher than that of *n*=1 and its kinetic parameters were more reasonable since pyrolysis process is extremely complicated to assume the first order reaction.

4. Conclusions

Two microalgae residue samples of *Chlorella sorokiniana CY1* and *Chlamydomonas sp. JSC4* from Taiwan were experimentally studied by means of a thermogravimetric analyzer (TGA), PerkinElmer Diamond TG/DTA,

operated non-isothermally in N_2 environments. The obtained TGA data was used for a kinetic analysis, assuming the distributed activation energy model (DAEM). The extracted kinetic parameters were within the acceptable range, compared to literature. Regarding the fit quality, the case of $n \neq 1$ was slightly better than this of $n = 1$. In addition, the obtained results also conforms to our previous study, assuming the five pseudo-components model.

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