Combustion behavior and kinetics of low-lipid microalgae via thermogravimetric analysis

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HIGHLIGHTS

- Combustion of low-lipid microalgae *C. pyrenoidosa* and *S. platensis* were studied.
- Chemical functional groups present in two microalgae were investigated via FTIR.
- Apparent activation energies for combustion of the two microalgae were calculated.
- *C. pyrenoidosa* has a higher reactivity compared to *S. platensis* during combustion.

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ABSTRACT

Thermogravimetric analysis and differential thermal analysis were employed to investigate combustion characteristics of two low-lipid microalgae, *Chlorella pyrenoidosa* (CP) and *Spirulina platensis* (SP) and iso-conversional Starink approach was used to calculate the kinetic parameters in the present study. The results showed that three stages of mass loss, including dehydration, devolatilization and char oxidation, were observed during combustion of both of two low-lipid microalgae. The whole weight loss of combustion of two microalgae was both shifted to higher temperature zones with increased heating rates from 10 to 40 K/min. In the 0.1–0.9 conversion range, the apparent activation energy of CP increased first from 51.96 to 79.53 kJ/mol, then decreased to 55.59 kJ/mol. Finally, it slightly increased to 67.27 kJ/mol. In the case of SP, the apparent activation energy gradually increased from 68.51 to 91.06 kJ/mol.

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1. Introduction

Primary fossil energy sources such as coal, petroleum and natural gas have become gradually exhausted over the past several decades, contributing to the development of clean, renewable energy sources like wind, solar and biomass. Converting biomass to biofuels has become one of the hotspots in the field of renewable energy, in terms of biodiesel and bioethanol production from crop plants. It has made a great contribution to the world energy consumption, but this research drew some criticism because it will encroach on arable land and affect food commodity prices. Alternatively, microalgae grow in freshwater/marine systems and there is no requirement for land, which has been gradually recognized as potential feedstocks for the next generation of biofuels and chemical (Williams and Laurens, 2010; Anastasakis and Ross, 2011;

López-González et al., 2014). Several possible pathways for converting microalgae to bioenergy have been investigated, mainly including biochemical conversion like anaerobic digestion and alcoholic fermentation, thermochemical conversion such as combustion, pyrolysis, gasification and liquefaction (Rizzo et al., 2013; Gai et al., 2014; Stucki et al., 2009).

Combustion of biomass has recently gained much attention due to their fuel flexibility, high heat-transfer and combustion efficiency (Magdziarz and Wilk, 2013). Compared to lignocellulosic biomass, microalgal biomass have lower decomposition temperatures during the combustion process, which means higher reactivity and lower operational costs. One of the reasons is due to the different major components. Proteins, lipids and carbohydrates are the major composition of microalgae, which are less thermal resistant than the main components of lignocellulosic biomass in terms of cellulose, hemicellulose and lignin (López-González et al., 2014). Another reason is that the relatively high ash content of microalgae was observed to have a catalytic effect in the decomposition process. However, the industrial problems in terms of

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slagging and fouling brought by the high ash content during combustion should not be overlooked either. Washing with water has been verified to alleviate such problems. For example, Fahmi et al. (2007) concluded that washing with water could remove up to 70% of the alkali metals during the pyrolysis and combustion of grasses. Teng and Wei (1998) investigated the influence of water treatment on pyrolysis of rice hulls and reported the same conclusion. Centrifugation can also decrease the ash content in microalgae before the energy production. Chen et al. (2014) reported that ash content of wastewater with centrifugation was reduced from 28.6% to 18.6%. Additionally, the relatively high content of nitrogen due to the presence of proteins in microalgae compared to lignocellulosic biomass may render high emissions of NO_x during combustion. The adoption of proper gas cleaning and catalytic treatment systems of the flue gas are required (Rizzo et al., 2013).

To help design and scale-up of the industrial combustor/gasifier, a knowledge of the kinetics of the combustion process is essential, which is usually investigated via thermogravimetric analysis (TGA) and differential thermal analysis (DTA). TGA and DTA are very useful tools for assessing the thermal characteristics of biomass and its components under a controlled environment and is often associated with kinetic modeling (Magdziarz and Wilk, 2013; Branca and Di Blasi, 2015). Numerous papers have concerned with the kinetics of combustion of lignocellulosic biomass, in terms of rice husk (Saldarriaga et al., 2015), corn straw (Fang et al., 2013), miscanthus (Jayaraman and Gökalp, 2015) and date palm wastes (Sait et al., 2012). Despite the literatures regarding lignocellulosic biomass is abundant, only a limited number of studies are concerned about the combustion of microalgae.

High-lipid microalgae have been main feedstocks in the production of biofuels, especially algae-to-biodiesel technology (Williams and Laurens, 2010). High-lipid microalgae mean a lipid accumulation in microalgae under a stressed condition such as nitrogen depletion. It will sacrifice biomass productivity, reduce the net energy yield, and make the process very sensitive to contamination (Yu et al., 2011). According to Williams and Laurens (2010), high lipid containing algae may not necessarily be the most favorable candidate organisms. Compared with high-lipid algae, low-lipid algae typically have a higher biomass yield and can grow in harsher environments. Thus it has a greater potential for biofuel production but less attention has been paid to this kind of microalgae. The aim of this study was to study the combustion characteristics of low-lipid microalgae by TGA–DTA technique. *Chlorella pyrenoidosa* (CP) and *Spirulina platensis* (SP) were selected due to their low-lipid content. Iso-conversional method was adopted to determine the kinetic parameters for the thermal decomposition process.

2. Methods

2.1. Materials and characterization

CP and SP were purchased from a health food store as food-grade material (NOW FOODS, Bloomington, IL). The dry solid content was calculated as the dry residue at 105 °C for 24 h. The ash content was determined as the solid residue after the combustion of feedstock at 575 °C for 3 h. The elemental analyzer (CE-440, Exeter Analytical Inc., North Chelmsford, MA) was employed to determine carbon, hydrogen and nitrogen contents of the feedstock. The contents of crude protein, crude fat, and carbohydrate were measured by the Kjeldahl method, Soxhlet extraction, and phenol–sulfuric acid method, respectively (Yu et al., 2011). The proximate analysis, elemental composition and chemical composition of microalgae samples are shown in Table 1.

The possible functionalities present in the two low-lipid microalgae were investigated via FTIR technique. The FTIR spectra was

collected using a Thermo Nicolet Nexus 670 Fourier Transform Infrared Spectroscopy (FTIR). With a model of Transmission E.S.P., 0.5 cm^{-1} resolution, 128 scans adsorption interferogram were collected in the 4000–750 cm^{-1} wavelength for each spectra.

2.2. Apparatus and procedures

Combustion characteristics of two low-lipid microalgae were analyzed by a thermogravimetric analyzer (TGA-Q50, TA Instruments, New Castle, DE) at air atmosphere. To minimize the effects of mass and heat transfer limitation, very small sample sizes (about 10 mg) were loaded into the ceramic crucible. All combustion experiments were conducted at atmospheric pressure, using temperature ranging from ambient temperature to 1073 K with different heating rate (10, 20, 30 and 40) and air flux of 20 ml/min. Each experiment was repeated twice to guarantee the data repeatability.

3. Results and discussion

3.1. Infrared spectra of CP and SP

Infrared spectra of the two low-lipid microalgae (CP and SP) are available in Supplementary data. The locations of adsorption peaks for the two microalgae are identical, suggesting the types of functionalities of the two microalgae does not make too much differences. The prominent adsorption peaks at 1800–1500 cm^{-1} suggest the presence of proteins (Phukan et al., 2011), consistent with the relative high content of proteins for the two microalgae. The carbonyl stretching $\text{C}=\text{O}$ appeared at 1647 cm^{-1} is related to amide-I bonds while the $\text{C}-\text{N}$ stretching and $\text{N}-\text{H}$ bending at 1533 cm^{-1} are ascribed to amide-II bonds. Both peaks suggest the presence of peptide bond between two amino acid molecules. Small adsorption peaks could be observed at 3100–2800 cm^{-1} , which is ascribed to $-\text{CH}_2$ stretching in lipids. The peaks at 2928 cm^{-1} and 2860 cm^{-1} indicate the asymmetric and symmetric vibration of $-\text{CH}_2$ stretching in lipids. These peaks for lipids are not as prominent as that of proteins, consisting with the analysis of chemical composition in Table 1 that both materials are low-lipid microalgae. In addition, some adsorption peaks are observed at 1200–900 cm^{-1} , which is ascribed to the stretching $\text{C}-\text{O}$, $\text{C}-\text{C}$, $\text{C}-\text{O}-\text{C}$ and $\text{C}-\text{O}-\text{P}$, confirming the presence of certain non-fibrous carbohydrates in the two microalgae.

3.2. Combustion characteristics

The TG–DTG–DTA curves for the combustion of CP and SP at the heating rate of 10 K/min are presented in Fig. 1. Based on the formation of pronounced peaks in TG–DTG–DTA curves, it can be seen that both two low-lipid microalgae exhibited three stages of weight loss during the combustion process. To be specific, the first stage (stage I) was from ambient temperature to around 400 K, which is a dehydration process as described by various literature (Agrawal and Chakraborty, 2013; Rizzo et al., 2013). A slight endothermic peak appeared in this stage from DTA curves of CP and SP, indicating the evaporation of moisture from the microalgae. The second mass loss stage (stage II) started at around 400 K and ended at about 650 K. It is related to the devolatilization of main components of microalgae including protein, lipid and non-fibrous carbohydrates and the formation of chars. This stage has an exothermic peak in DTA curve, suggesting that the devolatilization of volatile components of microalgae releases a large amount of heat. The third stage (stage III) was ranged from approximate 700–1000 K, corresponding to a process of exothermic char oxidation.

Table 1

Characteristics of CP and SP.

	<i>C. pyrenoidosa</i>	<i>S. platensis</i>		<i>C. pyrenoidosa</i>	<i>S. platensis</i>		<i>C. pyrenoidosa</i>	<i>S. platensis</i>
Proximate analysis (wt.% db ^a)			Elemental composition (wt.% da ^b)			Chemical composition (da ^b)		
Dry solid (ar ^c)	93.3	93.8	Carbon	51.2	49.6	Protein	71.5	64.7
Moisture (ar ^c)	6.7	6.2	Hydrogen	6.8	6.2	Lipid	0.2	4.8
Volatile solid	94.4	90.3	Nitrogen	11.3	10.8	Non-fibrous	22.5	19.3
Ash content	5.6	9.7	Oxygen ^d	30.7	33.4	Carbohydrates		

^a Dry basis.^b Dry and ash free basis.^c As received basis.^d By difference. **Fig. 1.** Typical TG–DTG–DTA curve of combustion of CP and SP at the heating rate of 10 K/min.

Some difference could be observed in the TG–DTG–DTA curves between CP and SP. For the major mass loss of stage II, the maximum mass loss rate of CP is higher than that of SP while SP is higher than that of CP for the stage III. These differences are mainly attributed to the different compositions of protein, lipid and non-fibrous carbohydrates in two microalgae illustrated in Table 1. Furthermore, it can be seen in Table 1 that both CP and SP contain high content of proteins, which are composed of different types and quantities of amino acids. According to the differential enthalpie analysis of amino acids carried out by Olafsson and Bryan (1970), the decomposition temperatures of different amino acids are not identical. The last decomposition step (stage III) is mainly attributed to the decomposition of inorganic material (López-González et al., 2014). It can be seen in Table 1 that SP almost has twice as much of ash content than that of CP, which is mainly due to the high alkali metal content in the feedstock (Kay, 1991). Previous studies (Liden et al., 1998; Czernik and Bridgwater, 2004) showed that sodium, potassium, magnesium and silicate in ash significantly affect pyrolysis degradation of biomass material, while potassium, sodium, calcium and magnesium are the main components influencing the combustion process. According to Kay (1991), the content of potassium, sodium, calcium and magnesium of SP is higher than that of CP. The high contents of these metals increase the rate of degradation and as a result, the maximum mass loss rate of SP is higher than that of CP for the stage III. In addition, the stage III of char oxidation is also affected by the char yield. Similarly, Fahmi et al. (2007) investigated the effect of alkali metals on combustion of grass samples and it was observed that the char yield from combustion increased as alkali metals increased.

According to El May et al. (2012), during combustion process the sample burning at lower temperatures and shorter time exhibits higher reactivity. Overall, the combustion characteristics of CP

are higher than that of SP from the difference mentioned above. It should be noted that emissions of NO_x and SO₂ are one of the major problems during the combustion of CP and SP due to the high content of nitrogen from protein in the two microalgae. Addition of organic calcium compounds (OCCs) has been proved to be a feasible method to simultaneously remove such pollutant emissions during the combustion of lignocellulosic biomass (Zhang et al., 2015). It is expected to further improve the combustion behavior of CP and SP using OCCs, which is recommended for further study.

3.3. Effect of heating rate

The TG–DTG curves for the combustion of CP and SP under different heating rates are illustrated in Figs. 2 and 3. To illustrate

Fig. 2. TG curves for the combustion of CP (a) and SP (b) at the heating rate of 10, 20, 30, 40 K/min.

Fig. 3. DTG curves for the combustion of CP (a) and SP (b) at the heating rate of 10, 20, 30, 40 K/min.

the effect of heating rates on the combustion process, characteristic parameters derived from the TG–DTG curves are presented in Table 2. It can be observed in Figs. 2 and 3 that the whole weight losses during the combustion process for CP and SP was both

shifted to higher temperature zones with increasing the heating rates from 10 to 40 K/min. In case of stage I, the temperature of the maximum rate of mass loss (T_p , K) was increased from 338 K to 379 K for CP and 349 K to 381 K for SP, respectively. During stage II, T_p was increased from 556 K to 610 K for CP and 553 K to 588 K for SP. As for stage III, T_p was gradually increased from 813 K to 898 K for CP and 842 K to 933 K for SP, respectively. In addition, the temperature of initial ignition (T_i) and final burnout (T_f) for any stage of CP and SP both increased gradually with the increment of heating rate. It is mainly attributed to the increased temperature gradient throughout the cross-section of the sample at higher heating rates, which affected the heat transfer between the thermogravimetric instrument and sample. Similar results were reported by combustion of microalgal biomass such as *Chlorella vulgaris* (Chen et al., 2013) and *Nannochloropsis oculata* (Ali et al., 2015) and lignocellulosic biomass such as switch grass (Chandrasekaran and Hopke, 2012), and eucalyptus wood (López-González et al., 2013).

In stage I of dehydration, no obvious impact of heating rate was observed on the variation of maximum mass loss rate ($-\text{DTG}_{\text{max}}$, %/K) for CP and SP. As for the stage II of devolatilization, the value of $-\text{DTG}_{\text{max}}$ for CP and SP were both gradually from 0.340%/K and 0.312%/K to 0.359%/K and 0.352%/K, respectively. It showed the same trend with combustion of *C. vulgaris* (Agrawal and Chakraborty, 2013). However, the variation of $-\text{DTG}_{\text{max}}$ for CP and SP is different for the stage III of char oxidation. The value of $-\text{DTG}_{\text{max}}$ of CP was always increased from 0.265%/K to 0.295%/K, while in case of SP, the value of $-\text{DTG}_{\text{max}}$ was decreased from 0.410%/K to 0.247%/K. It may be due to the different catalytic effects of ash for CP and SP at different heating rates and further investigation regarding this issue is needed in future study.

In terms of HTZ (i.e., the full temperature width at half-maximum of the value of $-\text{DTG}_{\text{max}}$ K), it was gradually increased from 78 K for CP and 106 K for SP to 95 K and 137 K, respectively. In stage II and stage III, the heating rate has different effects on the value of HTZ. As for CP, it was gradually decreased from 124 K for stage II and 177 K for stage III to 104 K and 145 K, respectively. The value of HTZ of SP was conversely increased from 120 K for stage II and 78 K for stage III to 131 K and 146 K, respectively. The heating rate was observed to have the same effect on the variation of the total mass loss (ML, %) for CP and SP. In stage I,

Table 2
Characteristic parameters for the combustion process of CP and SP.

Sample CP	Stage I						Sample SP	Stage I					
	T_i (K)	T_f (K)	T_p (K)	$-\text{DTG}_{\text{max}}$ (%/K)	HTZ(K)	ML (%)		T_i (K)	T_f (K)	T_p (K)	$-\text{DTG}_{\text{max}}$ (%/K)	HTZ(K)	ML (%)
10 K/min	298	401	338	0.067	78	5.975	10 K/min	298	402	349	0.056	106	5.346
20 K/min	298	418	350	0.069	82	6.604	20 K/min	298	405	354	0.061	110	5.460
30 K/min	298	431	362	0.069	84	6.918	30 K/min	298	420	365	0.063	132	5.546
40 K/min	298	454	379	0.072	95	7.103	40 K/min	298	429	381	0.054	137	5.672
Sample CP	Stage II						Sample SP	Stage II					
	T_i (K)	T_f (K)	T_p (K)	$-\text{DTG}_{\text{max}}$ (%/K)	HTZ(K)	ML (%)		T_i (K)	T_f (K)	T_p (K)	$-\text{DTG}_{\text{max}}$ (%/K)	HTZ(K)	ML (%)
10 K/min	419	672	556	0.340	124	47.16	10 K/min	421	703	553	0.312	120	45.18
20 K/min	437	709	567	0.347	122	47.39	20 K/min	435	715	565	0.331	125	46.86
30 K/min	449	728	586	0.353	119	47.67	30 K/min	440	724	574	0.343	129	47.79
40 K/min	463	766	610	0.359	104	48.24	40 K/min	457	751	588	0.352	131	49.37
Sample CP	Stage III						Sample SP	Stage III					
	T_i (K)	T_f (K)	T_p (K)	$-\text{DTG}_{\text{max}}$ (%/K)	HTZ(K)	ML (%)		T_i (K)	T_f (K)	T_p (K)	$-\text{DTG}_{\text{max}}$ (%/K)	HTZ(K)	ML (%)
10 K/min	685	1039	813	0.265	177	38.36	10 K/min	714	1020	842	0.410	78	39.31
20 K/min	714	1048	842	0.276	161	37.42	20 K/min	723	1027	855	0.324	108	38.99
30 K/min	743	1051	867	0.284	157	37.11	30 K/min	739	1034	882	0.317	111	37.42
40 K/min	791	1058	898	0.295	145	35.85	40 K/min	774	1048	933	0.247	146	34.28

Note: T_i : initial ignition temperature at any stage, K; T_f : final burnout temperature at any stage, K; T_p : temperature of the maximum rate of mass loss, K; $-\text{DTG}_{\text{max}}$: maximum mass loss rate at any stage, %/K; HTZ: full temperature width at half-maximum of the value of $-\text{DTG}_{\text{max}}$, K; ML: total mass loss at any stage, %.

the value of ML for CP and SP was gradually increased from 5.975% and 5.346% to 7.103% and 5.672%, respectively. In stage II, it was increased from 47.16% for CP and 45.18% for SP to 48.24% and 49.37%, respectively. On the contrary, the value of ML for CP and SP in stage III was gradually decreased from 38.36% and 39.31% to 35.85% and 34.28%, respectively.

3.4. Kinetic analysis

The characteristic parameters derived from the TG–DTG curves were used to determine the kinetic parameters such as apparent activation energy for combustion of CP and SP. Compared to model-fitting method such as Coats–Redfern or Freeman–Carroll, iso-conversional approach can determine the apparent activation energy without assuming the reaction model, thus eliminating the manifestation of “kinetic compensation effect” brought by a false assumption of reaction model via model-fitting methods. Therefore, kinetic analysis in this study was carried out using an iso-conversional method. The combustion process of microalgae is a typical heterogeneous solid-state reaction, and the global combustion reaction kinetics can be described as:

$$\frac{dx}{dt} = k(T)f(\alpha) \quad (1)$$

where T is the reaction temperature, t is the reaction time, $f(\alpha)$ is the differential function of conversion, α is the mass conversion ratio, which can be determined as:

$$\alpha = \frac{w_i - w_t}{w_i - w_f} \quad (2)$$

where w_i , w_f and w_t are the initial mass of the sample, the residual mass at the end of combustion process and the sample mass at reaction time t /reaction temperature T . $k(T)$ is the reaction rate constant, which can be described by the Arrhenius equation:

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

where A is the pre-exponential factor, s^{-1} , E_a is the apparent activation energy, kJ mol^{-1} , R is the gas constant, $8.314 \text{ J (mol K)}^{-1}$.

Eq. (1) can be converted into Eq. (2) expressed as:

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right) \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (4)$$

where β is heating rate ($\beta = dT/dt$).

The integration form of the Eq. (4) is:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = G(\alpha) = \left(\frac{A}{\beta}\right) \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT = \left(\frac{A}{\beta}\right) p(x) \quad (5)$$

where $p(x)$ in Eq.(5) is known as the temperature integral. The temperature integral does not have an exact analytical solution in closed-form. However, it can be approximately calculated via different empirical interpolation formulas such as Luke, Broido, Doyle, MacCallum–Tanner and Krevelen–Heerden–Huntjens approximation.

The Flynn–Wall–Ozawa (FWO) method and Kissinger–Akahira–Sunose (KAS) method are the two most common model-free methods for determining the kinetic parameters, which has been widely used in complex processes in terms of the decomposition of biomass (Tahmasebi et al., 2013). Doyle's approximation (Doyle, 1961) is the empirical approximation used by the FWO method, which is represented as:

$$\int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT = \frac{E}{R} (0.00484e^{-1.0516u}) \quad (6)$$

Combining Eqs. (5) and (6) and then taking the logarithm of both sides lead to the expression for FWO method (Ozawa, 1965):

$$\ln \beta_i = \ln \left[\frac{AE}{RG(\alpha)} \right] - 2.315 - 0.4567 \frac{E}{RT} = C_0 - 0.4567 \frac{E}{RT} \quad (7)$$

In terms of KAS method, the employed empirical approximation is the following expression:

$$\int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT = \frac{E\beta}{RAT} \quad (8)$$

Substituting of Eq. (8) into Eq. (5), and then taking the logarithm of both sides lead to the expression for KAS method (Kissinger, 1957):

$$\ln \left(\frac{\beta_i}{T_{pi}^2} \right) = \ln \left(\frac{A_k R}{E_k} \right) - \frac{E_k}{RT_{pi}} = C_K - \frac{E_k}{RT_{pi}} [i = 1, 2, 3, 4, 5, 6] \quad (9)$$

Based on the Starink method (Starink, 1996), the expression of FWO method (Eq. (7)) and KAS method (Eq. (9)) can both be transformed into the same formula expressed as:

$$\ln \left(\frac{\beta}{T^s} \right) = C_s - \frac{BE}{RT} \quad (10)$$

where for the FWO method (Eq. (7)), $s = 0$, $B = 0.4567$; for the KAS method (Eq. (9)), $s = 2$, $B = 1$. It has been verified by Starink (Starink, 1996) that when the parameters of s and B are adjusted to 1.8 and 1.003, respectively, the precision of this expression (Eq. (10)) is higher than either FWO or KAS method. Consequently, the Starink method can be represented as:

$$\ln \left(\frac{\beta}{T^{1.8}} \right) = C_s - 1.0037 \frac{E}{RT} \quad (11)$$

The apparent activation energy was calculated from the slope and intercepts of the iso-conversional lines for a given conversion fraction from the TG curves of various heating rates. In the plot of $\ln(\beta/T^{1.8})$ versus $1/T$, the slope is $-1.0037E/R$ from which the apparent activation energy can be determined. In this study, at different heating rates ranging from 10 to 40 K/min, nine levels of conversion fraction varying from 10 wt.% to 90 wt.% were used to determine the dependence of apparent activation energy on the conversion fraction during the combustion process. The regression lines of CP and SP are illustrated in Fig. 4. The variations of apparent activation energy at different conversion fractions for CP and SP are shown in Fig. 5.

Fig. 5 illustrated that the apparent activation energy of two low-lipid microalgae both varied greatly with different conversion fractions rather than keeping constant. Specifically, with increasing the conversion fraction from 10 to 90 wt.%, the apparent activation energy of CP increased first from 51.96 kJ/mol at 10 wt.% to 79.53 kJ/mol at 40 wt.%, then decreased to 55.59 kJ/mol at 70 wt.%. Finally, it slightly increased to 67.27 kJ/mol at 90 wt.%. Idris et al. (2012) investigated the combustion characteristics of palm biomass materials using iso-conversional Vyazovkin method. It was reported that the apparent activation energy of palm samples underwent the process a fall after a rise. The same behavior is observed in the literature (Ali et al., 2015), which investigated the variation of apparent activation energy of *N. oculata* at different conversion stages using iso-conversional FWO and KAS approach. Besides, the apparent activation energy of SP increased gradually from 68.51 to 91.06 kJ/mol. These results agree well with literature (Chen et al., 2012) reporting that the variation of apparent activation energy for *C. vulgaris* increased gradually based on FWO and KAS method. The different variation trends of apparent activation energy for CP and SP suggest that the combustion process of CP and SP may proceed with varied reaction mechanisms.

In addition, it can be seen in Fig. 5 that the average values of apparent activation energy for CP, 65.15 kJ/mol, is lower than that of SP, 84.29 kJ/mol. It is consistent with the TG–DTG–DTA curves

Fig. 4. Regression lines to apparent activation energy proposed by Vyazovkin approach for CP (a) and SP (b) at the heating rate of 10, 20, 30, 40 K/min.

Fig. 5. Plot of apparent activation energy at different conversion fractions for CP and SP.

for CP and SP that the entire combustion process of CP is a bit earlier than that of SP. A reaction with lower apparent activation energy requires less energy to break down the chemical bonds between atoms and hence the reaction rate is faster. Thus kinetic analysis in the present study suggests that CP is preferable to SP in terms of thermochemical conversion for biofuel production.

4. Conclusions

Combustion characteristics of two low-lipid microalgae, *C. pyrenoidosa* and *S. platensis* were analyzed by TGA. Results

indicated that three stages of mass loss were observed for two microalgae, and the whole weight loss during the combustion was both shifted to higher temperature zone with increasing the heating rates from 10 to 40 K/min. With the increment of conversion fractions from 10% to 90%, the apparent activation energy of *C. pyrenoidosa* and *S. platensis* presented different trends and the average values of apparent activation energy for *C. pyrenoidosa*, 65.15 kJ/mol, is lower than that of *S. platensis*, 84.29 kJ/mol.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.biortech.2015.01.045>.

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