Combustion Behavior of Algal Biochars Obtained at Different Pyrolysis Heating Rates

Vikul Vasudev, Xiaoke Ku,* and Jianzhong Lin

ABSTRACT: In this work, the combustion performance of Chlorella vulgaris (CV), Dunaliella salina (DS), and Haematococcus pluvialis (HP) algal biochars was analyzed based on the multicomponent method. The biochars were obtained via nonisothermal pyrolysis of raw algal biomasses at three different heating rates (i.e., 30, 40, and 50 °C/min), and biochar combustion was performed from 200 to 700 °C at a heating rate of 5 °C/min. The complex oxidative reaction of algal biochar was resolved into combined reactions of multiple pseudo-components based on the peak deconvolution method using a bi-Gaussian model. The activation energies ($E_a$) for each pseudo-component (PC) of all biochar samples were calculated by the Coats–Redfern isoconversional method and four kinetic models (i.e., diffusion, nucleation, order-based, and shrinking core models). The results showed that the highest $E_a$ values were predicted by the diffusion model. Except that the $E_a$ for the first PC of CV biochar decreased by 16.45%, the $E_a$ values for all other biochar samples generally increased with increasing the pyrolysis heating rate. Moreover, when the diffusion model was used, the $E_a$ for the second PC of CV biochar increased by 50.87%, that for the first PC of DS biochar increased by 16.85%, and those for the first and third PCs of HP biochar increased by 4.66 and 11.66%, respectively. In addition, the combustibility index ($S_\alpha$) was evaluated based on the ignition and burnout temperatures as well as the mean and maximum weight loss rates. Generally, the combustion performance of all biochar samples was good at a low temperature but deteriorated toward a high temperature. As the pyrolysis heating rate increases, an overall increase in the combustion quality was also seen for the second PC of CV biochar and the first PCs of DS and HP biochars because their $S_\alpha$ increased from $2.70 \times 10^{-15}$ to $3.07 \times 10^{-15}$ °C$^{-5}$, $2.53 \times 10^{-15}$ to $3.88 \times 10^{-13}$ °C$^{-5}$, and $3.00 \times 10^{-15}$ to $3.26 \times 10^{-13}$ °C$^{-5}$, respectively.

1. INTRODUCTION

Due to its abundance and carbon-neutral properties, biomass has been considered a renewable energy source with great potential.1,2 The common lignocellulosic biomass (e.g., soybean, cottonseed, and agricultural and forest residues) is generally made up of three major biopolymers, i.e., hemicellulose, cellulose, and lignin.3 Different from lignocellulosic biomass, algal biomass basically consists of carbohydrates, proteins, and lipids and has many intrinsic advantages, for example, short growth cycles, high yield per hectare, and the ability to grow in wastewater and saltwater.4–8 All these factors make algal biomass more attractive than other types of biomass, although the technology that enables us to harness it efficiently is still in the early stage.9,10

Through thermochemical conversion, raw biomass can be transformed to high-quality energy products (e.g., bio-oil, syngas, and biochar) or just burned to release stored energy.1 Among various conversion technologies, pyrolysis is a promising one during which biomass decomposition occurs under an inert environment, and multiple products, such as bio-oil and biochar, can be obtained. Bio-oil could be used in fuel-related areas such as the jet fuel and automobile sectors.11,12 Biochar has the ability to treat wastewater and is also used as a fertilizer for agricultural purposes or barbeque charcoal.13,14 Koçer et al.15 performed a parametric study on algal biochar yield obtained after pyrolysis. Elnour et al.16 studied the effect of pyrolysis temperature on date palm biochar and the morphology of biochar/polypropylene composites. Pyrolysis is also the first process that occurs in many other thermochemical conversion routes (e.g., gasification and combustion).15,17 Therefore, to optimize the reactor efficiency, it is necessary to fully understand the effect of pyrolysis operating conditions on the product yield.

Received: May 12, 2021
Accepted: July 2, 2021
Published: July 14, 2021
Knowledge of reaction kinetics helps in understanding biomass conversion behavior.\textsuperscript{8,10} The most commonly used experimental apparatus for achieving this purpose is a thermogravimetric analyzer (TGA). Generally, a small quantity (5–20 mg) of a biomass sample is placed in a TGA and heated to a high temperature under different gas environments, and meanwhile, the weight loss is recorded.\textsuperscript{8,20} To perform the kinetic analysis, three kinetic parameters, i.e., the activation energy, the pre-exponential factor, and the kinetic model equation, need to be evaluated. Two kinds of methods (i.e., differential and integral isoconversional methods) are normally used to determine these parameters, among which the Coats–Redfern method can use the data of a single nonisothermal study to determine these parameters.\textsuperscript{8} To perform the kinetic analysis, three kinetic parameters, i.e., the activation energy, the pre-exponential factor, and the kinetic model equation, need to be evaluated. Two kinds of methods (i.e., differential and integral isoconversional methods) are normally used to determine these parameters, among which the Coats–Redfern method can use the data of a single nonisothermal experiment to evaluate the kinetic parameters and is suitable for a number of biomass samples.\textsuperscript{21–24}

Biocchar is an important product after pyrolysis, and its combustion is a complex process. If the reaction is considered a single-step process, it might be difficult to estimate the kinetic parameters precisely. Therefore, a multicomponent method is more suitable, and various functions (e.g., Frazer–Suzuki, Weibull, Lorentz, and bi-Gaussian) can be used to identify the components.\textsuperscript{25–28} Hu et al.\textsuperscript{29} performed a pyrolysis kinetic analysis of lignocellulosic biomasses using the deconvolution method and Frazer–Suzuki’s model. They treated the biomass as a mixture of subcomponents, and separate kinetic parameters were evaluated for each subcomponent. Sharma et al.\textsuperscript{30} investigated the nonisothermal pyrolysis kinetics of biomass by resolving raw biomass into pseudo-components using the bi-Gaussian function that incorporates the skewness of the pseudo-components that decomposed at different reaction stages. Thus, the peak deconvolution method was used to divide the whole combustion process into various stages using the bi-Gaussian function that incorporates the skewness of the peaks. To evaluate the activation energy of each pseudo-component (PC), the integral isoconversional method of Coats–Redfern was employed, which is frequently adopted in the literature, and a unique value of “apparent” activation energy can be obtained using only a single heating rate.\textsuperscript{31} Since this method requires prior knowledge of the kinetic model equation, we adopted four different kinetic models, i.e., diffusion, order-based, nucleation, and shrinking core models, to calculate the activation energy individually. Furthermore, to assess the combustion performance, the combustibility index was calculated based on the estimated ignition and burnout temperatures as well as the mean and maximum weight loss rates. A systematic comparison between the results of different pseudo-components of all biochar samples was also made.

### 2. MATERIALS AND METHODS

#### 2.1. Sample Details

Biomass samples from three algal species, *Chlorella vulgaris* (CV), *Dunaliella salina* (DS), and *Haematococcus pluvialis* (HP), were used. These intensively researched algal biomass species have unique properties. For example, CV has a remarkable carbon-capturing property and can be blended with coal for combustion.\textsuperscript{32,33} DS is an industrially important biomass species because of its large-scale growth in high-salinity waters, and HP has a high astaxanthin content.\textsuperscript{34,35} All these raw samples were purchased from WUDILVQI Bioengineering Co., Ltd. (China) in a powdered form, and Table 1 provides their properties. Note that the ultimate analysis was conducted based on the ASTM standard test method (i.e., ASTM E870-82), and the proximate analysis was carried out using the method proposed by Qin and Thunman.\textsuperscript{36} The heating values (HHVs) were obtained by the following empirical correlation.\textsuperscript{37}

\[
\text{HHV} = 0.3443C + 1.192H - 0.113O - 0.024N + 0.093S
\]

#### 2.2. Experimental Methods

All thermogravimetric experiments were performed in a thermogravimetric analyzer (TGA), i.e., a TGA-55 (TA instruments, USA), with a sample size of approximately 12 mg. Initially, the raw samples inside the TGA furnace were dried by increasing the temperature up to 150 °C under nitrogen purging. After that, the pyrolysis process was carried out by increasing the temperature from 150 to 850 °C at three different heating rates (i.e., 30, 40, and 50 °C/min) under nitrogen environment, and the holding time at 850 °C was 5 min. Note that these heating rates are...
typical choices for obtaining biochar and are also frequently used in the literature.\textsuperscript{30,39} After pyrolysis, the temperature was reduced to 200 °C, and the residual material was biochar. Then, the temperature was increased to 700 °C at a heating rate of 5 °C/min under an oxygen environment for biochar combustion.\textsuperscript{30} The heating rate for the biochar combustion process was relatively low, resulting in a long residence time, which allowed a more complete reaction for the biochar samples. In addition, each experimental case was performed at least three times to ensure reproducibility.

2.3. Kinetic Modeling and Deconvolution of Data. Solid-state reactions are generally studied using the fractional conversion parameter \( \alpha \), which is defined as the normalized weight loss.

\[
\alpha = \frac{m_0 - m}{m_0 - m_f}
\]  

where \( m_0, m \), and \( m_f \) are the initial, instantaneous, and final indecomposable masses of the sample during the reaction, respectively. Using \( \alpha \), the reaction rate is generally calculated by the following equation:\textsuperscript{21}

\[
d\alpha/dt = k(T)f(\alpha) = A\exp\left(\frac{-E_a}{RT}\right)f(\alpha)
\]  

where \( k(T) \) is the temperature-dependent Arrhenius function containing the activation energy \( E_a \) and the pre-exponential factor \( A \). \( R \) is the universal gas constant, and \( f(\alpha) \) is the kinetic model. Equation 3 can be written in integral form as

\[
g(\alpha) = \int_0^\alpha \frac{dx}{f(x)} = \frac{AE_a}{\beta R} \int_{T_a}^{T} \frac{\exp(-y)}{y^2} dy
\]  

where \( y = E_a/RT \) and \( y_a = E_a/RT_a \) in which \( T_a \) is the temperature at a fixed \( \alpha \), and \( \beta \) is the constant heating rate. The Arrhenius integral on the right-hand side of eq 4 can be solved by integration by parts. The asymptotic expansion of this integral \( p(y) \) can be written as\textsuperscript{23}

\[
p(y) = \frac{\exp(-y)}{y^2} \times \left(1 + \frac{2^1}{-y} + \frac{3^1}{(-y)^2} + \frac{4^1}{(-y)^3} + \ldots \right)
\]  

Coats and Redfern\textsuperscript{22} made the approximation by adopting the first two terms of this series.

\[
p(y) \cong \frac{\exp(-y)}{y^2} \left(1 - \frac{2}{y}\right)
\]  

Using this approximation, a linear equation can be written from eq 4 as

\[
\ln\left[\frac{g(\alpha)}{T^4}\right] = \ln\left[\frac{AR}{\beta E_a}\right] + \frac{E_a}{RT} - \frac{E_a}{RT}
\]  

By plotting \( \ln[\alpha(T)/T^4] \) against \( 1/T \), the activation energy \( E_a \) can be evaluated from the slope of the linear plot. Note that \( g(\alpha) \) needs to be known beforehand for employing this method. For some samples, the biochar combustion process shows multiple peaks, indicating that different pseudo-components decompose at different temperatures. Such a complex combustion process cannot be described by a single model-fitting method.\textsuperscript{20} The whole process can be treated as multiple independent parallel reactions such that the combustion of each pseudo-component behaves like an individual reaction with its individual kinetic parameters. Therefore, the peak deconvolution of the whole data was performed based on the multiple peak fitting method. \( d\alpha/dT \) of the \( i \)th pseudo-component can be defined using the bi-Gaussian function.\textsuperscript{25,26,28}

\[
\frac{d\alpha}{dT} = \chi_{\alpha,1} + H \exp\left(-0.5 \left[\frac{T - T_{p,i}}{w_{j,i}}\right]^2\right)
\]  

where \( \chi_{\alpha,1} \), \( T_{p,i} \), and \( w_{j,i} \) are the baseline, peak height, peak temperature, and half peak width, respectively. Therefore, the overall decomposition rate \( d\alpha/dT \) containing \( n \) pseudo-components is

\[
\frac{d\alpha}{dT} = \sum_{i=1}^{n} \chi_{\alpha,i} + H \exp\left(-0.5 \left[\frac{T - T_{p,i}}{w_{j,i}}\right]^2\right)
\]  

The unknown parameters in eq 9 were estimated by performing nonlinear regression using the Levenberg–Marquardt algorithm and minimization of the chi-square function.

\[
\chi^2 = \frac{1}{n_{\text{eff}}} \sum_{i=1}^{n_{\text{eff}}} \left(\frac{d\alpha}{dT}\right)_{\text{EXP}} - \left(\frac{d\alpha}{dT}\right)_{\text{CALC}}
\]  

where \( n_{\text{eff}} \) is the total number of data points used in the fitting and \( p \) is the number of adjustable parameters. Note that this is a nonweighted approach; thus, \( w \) is treated as unity. A summary of the overall process, including deconvolution and kinetic modeling, is given in Figure 1.

![Figure 1. Flow chart of the kinetic analysis of algal biochar combustion.](http://pubs.acs.org/journal/acsodf)

3. RESULTS AND DISCUSSION

3.1. Biochar Yield and Combustion Characteristics. The pyrolysis heating rate plays an important role when determining the biochar yield. Table 2 lists the biochar yields obtained after pyrolysis of algal biomass samples at three different heating rates (i.e., 30, 40, and 50 °C/min).
Apparently, for CV and DS, the biochar yield increases with increasing the pyrolysis heating rate, probably because a quicker heating process means less residence time, which leads to an incomplete degradation at the end of the pyrolysis process. Koc et al. studied the biochar yield during pyrolysis and revealed that the biochar yield of CV increased with increasing the pyrolysis heating rate. However, for HP, a very slight decrease in the biochar yield is observed when increasing the heating rate. Angin also found that at 600 °C, the biochar yield of safflower seeds dropped by 1.76% when increasing the pyrolysis heating rate from 10 to 50 °C/min.

The evolution curves of α and dα/dT with temperature T for the biochar combustion process. From the α curves, it is easily seen that the pyrolysis heating rate affects biochar combustion in different ways. For CV biochar, as the pyrolysis heating rate increases from 30 to 40 °C/min, the α evolution curve slightly shifts toward lower temperatures. However, when it further increases from 40 to 50 °C/min, no significant changes appear in the curves. For DS biochar, within the whole range tested, the α evolution curves continuously shift toward lower temperatures with an increase in the pyrolysis heating rate. For HP biochar, there seems to be no observable differences among the three pyrolysis heating rates investigated.

The dα/dT evolution curves presented in Figure 2 shed more light on the combustion behavior of these algal biochars, as multiple components can be observed decomposing at different stages. For the CV and DS biochars, the whole combustion process could be divided into two different stages, as two distinct peaks are observed in the curves. For HP biochar, the reaction seems to be more complex due to the existence of three peaks at different temperatures. These peaks represent the reaction of pseudo-compounds that are probably formed during pyrolysis of raw biomass samples. Since these peaks are quite distinct, it is not good to treat the whole process as a single reaction. Therefore, each pseudo-compound can be treated as a separate reaction.

Table 2. Biochar Yields Obtained at Different Pyrolysis Heating Rates

| sample | heating rate (°C/min) | biochar yield (wt %) |
|--------|------------------------|----------------------|
| CV     | 30                     | 18.36 ± 2.09         |
|        | 40                     | 20.47 ± 4.11         |
|        | 50                     | 21.83 ± 1.89         |
| DS     | 30                     | 14.17 ± 3.44         |
|        | 40                     | 21.91 ± 5.56         |
|        | 50                     | 21.48 ± 2.52         |
| HP     | 30                     | 14.35 ± 1.33         |
|        | 40                     | 14.24 ± 2.54         |
|        | 50                     | 13.94 ± 2.02         |

Figure 2 shows the evolution curves of α and dα/dT with temperature T for the biochar combustion process. From the α curves, it is easily seen that the pyrolysis heating rate affects biochar combustion in different ways. For CV biochar, as the pyrolysis heating rate increases from 30 to 40 °C/min, the α evolution curve slightly shifts toward lower temperatures. However, when it further increases from 40 to 50 °C/min, no significant changes appear in the curves. For DS biochar, within the whole range tested, the α evolution curves continuously shift toward lower temperatures with an increase in the pyrolysis heating rate. For HP biochar, there seems to be no observable differences among the three pyrolysis heating rates investigated.

The dα/dT evolution curves presented in Figure 2 shed more light on the combustion behavior of these algal biochars, as multiple components can be observed decomposing at different stages. For the CV and DS biochars, the whole combustion process could be divided into two different stages, as two distinct peaks are observed in the curves. For HP biochar, the reaction seems to be more complex due to the existence of three peaks at different temperatures. These peaks represent the reaction of pseudo-compounds that are probably formed during pyrolysis of raw biomass samples. Since these peaks are quite distinct, it is not good to treat the whole process as a single reaction. Therefore, each pseudo-compound can be treated as a separate reaction.
component is treated individually for the kinetic analysis in this work.

3.2. Deconvolution. The complex combustion of algal biochar is further analyzed by using the peak deconvolution

Figure 3. Deconvolution analysis of $\frac{dx}{dT}$ evolution curves for the biochar combustion process. (a) CV-30, (b) CV-40, (c) CV-50, (d) DS-30, (e) DS-40, (f) DS-50, (g) HP-30, (h) HP-40, and (i) HP-50.

Table 3. Ignition and Burnout Temperatures ($T_i$ and $T_o$) as well as the Simulation Results of the Bi-Gaussian Model

| sample | pseudo-component | $T_i$ (°C) | $T_o$ (°C) | $y_0$ (°C$^{-1}$) | $H$ (°C$^{-1}$) | $T_p$ (°C) | $w_1$ (°C) | $w_2$ (°C) | $\chi^2$ | $R^2$ |
|--------|------------------|------------|------------|-------------------|----------------|------------|-------------|-------------|---------|-------|
| CV-30  | PC-1             | 423.82     | 490.85     | $9.39 \times 10^{-5}$ | 0.01258       | 465.95     | 33.174      | 19.519      | 7.8829 $\times 10^{-8}$ | 0.99316 |
|        | PC-2             | 570.65     | 644.07     | $9.39 \times 10^{-5}$ | 0.00169       | 622.84     | 41.411      | 17.135      | 1.0402 $\times 10^{-7}$ | 0.98769 |
| CV-40  | PC-1             | 407.06     | 488.78     | $2.96 \times 10^{-5}$ | 0.00106       | 456.38     | 38.999      | 26.008      | 8.5221 $\times 10^{-8}$ | 0.99017 |
|        | PC-2             | 577.99     | 653.48     | $2.96 \times 10^{-5}$ | 0.00203       | 632.42     | 42.627      | 16.199      | 6.5042 $\times 10^{-8}$ | 0.99466 |
| CV-50  | PC-1             | 412.01     | 491.81     | $2.48 \times 10^{-5}$ | 0.0013       | 463.08     | 40.378      | 22.724      | 7.8829 $\times 10^{-8}$ | 0.99316 |
|        | PC-2             | 582.14     | 654.60     | $2.48 \times 10^{-5}$ | 0.00219       | 634.33     | 40.978      | 16.165      | 6.5042 $\times 10^{-8}$ | 0.99466 |
| DS-30  | PC-1             | 335.72     | 442.65     | $7.24 \times 10^{-5}$ | 0.00725       | 373.99     | 29.851      | 54.869      | 9.1235 $\times 10^{-8}$ | 0.98921 |
|        | PC-2             | 438.5      | 466.75     | $7.24 \times 10^{-5}$ | 0.00749       | 453.11     | 10.836      | 10.460      | 5.1772 $\times 10^{-8}$ | 0.99390 |
| DS-40  | PC-1             | 331.09     | 439.62     | $1.60 \times 10^{-5}$ | 0.00858       | 373.92     | 33.880      | 52.461      | 6.2395 $\times 10^{-8}$ | 0.99294 |
|        | PC-2             | 459.89     | 470.58     | $1.60 \times 10^{-5}$ | 0.00627       | 465.57     | 4.959       | 3.496       | 5.1772 $\times 10^{-8}$ | 0.99390 |
| DS-50  | PC-1             | 321.52     | 409.94     | $1.17 \times 10^{-4}$ | 0.00951       | 345.65     | 19.108      | 50.787      | 2.8449 $\times 10^{-7}$ | 0.99624 |
|        | PC-2             | 447.12     | 465.16     | $1.17 \times 10^{-4}$ | 0.00616       | 456.81     | 6.844       | 6.227       | 6.2395 $\times 10^{-8}$ | 0.99646 |
| HP-30  | PC-1             | 440.58     | 495.16     | $1.80 \times 10^{-4}$ | 0.01156       | 479.31     | 30.779      | 12.069      | 6.2395 $\times 10^{-8}$ | 0.99466 |
|        | PC-2             | 401.8      | 538.09     | $1.80 \times 10^{-4}$ | 0.00166       | 479.31     | 62.109      | 46.957      | 6.0165 $\times 10^{-8}$ | 0.99507 |
| HP-40  | PC-1             | 575.92     | 619.81     | $1.80 \times 10^{-4}$ | 0.00229       | 606.85     | 24.666      | 10.421      | 6.0165 $\times 10^{-8}$ | 0.99507 |
|        | PC-2             | 401.79     | 562.74     | $1.76 \times 10^{-4}$ | 0.00143       | 481.25     | 67.504      | 41.663      | 6.0165 $\times 10^{-8}$ | 0.99507 |
| HP-50  | PC-1             | 440.74     | 493.88     | $1.54 \times 10^{-4}$ | 0.00122       | 479.61     | 30.763      | 10.912      | 6.0165 $\times 10^{-8}$ | 0.99507 |
|        | PC-2             | 401.32     | 551.34     | $1.54 \times 10^{-4}$ | 0.0015       | 479.61     | 62.505      | 57.393      | 6.0165 $\times 10^{-8}$ | 0.99507 |
|        | PC-3             | 578.95     | 619.49     | $1.54 \times 10^{-4}$ | 0.00224       | 607.32     | 22.074      | 9.511       | 6.0165 $\times 10^{-8}$ | 0.99507 |
Table 4. Kinetic Models Used in This Work

| model                     | nomenclature | \( f(\alpha) \)                  | \( g(\alpha) \)                  |
|---------------------------|--------------|----------------------------------|----------------------------------|
| Mampel's first order      | F1           | \( 1 - \alpha \)                 | \( -\ln(1 - \alpha) \)          |
| Avrami–Erofeev's nucleation | A3          | \( 3(1 - \alpha)[-\ln(1 - \alpha)]^{1/3} \) | \( [-\ln(1 - \alpha)]^{1/3} \) |
| 3-D diffusion             | D3           | \( 3/(1 - \alpha)^{2/3}[1 - (1 - \alpha)^{1/3}]^{-1} \) | \( [1 - (1 - \alpha)]^{1/3} \) |
| shrinking core            | R3           | \( 3(1 - \alpha)^{2/3} \)         | \( 1 - (1 - \alpha)^{1/3} \)    |

3.3. Activation Energy Analysis. Using the Coats–Redfern method (eq 7), the activation energies were calculated for all the pseudo-components of each biochar sample. As shown in Table 4, four common solid-state reaction kinetic models, i.e., Mampel’s first-order model, Avrami–Erofeev’s nucleation model, 3-D diffusion model, and shrinking core model, are used to obtain the values of activation energies. These \( E_a \) values are estimated between the ignition and burnout temperatures. As sketched in Figure 4, the ignition temperature \( T_i \) is determined by intersecting the tangent passing through the \( T_p \) point on the TG curve with the initial baseline. Similarly, the burnout temperature \( T_b \) is found by intersecting the same tangent with the final baseline.\textsuperscript{28,30} Note that the ignition and burnout temperatures for all the pseudo-components of each biochar sample are also listed in Table 3.

Figure 5 presents the activation energies for all pseudo-components of each biochar sample using four different kinetic models. (a) CV biochar, (b) DS biochar, and (c) HP biochar.

Figure 5. Activation energy distribution for the pseudo-components of each biochar sample using four different kinetic models. (a) CV biochar, (b) DS biochar, and (c) HP biochar.
The $E_a$ of PC-1 decreases from 287.43 to 240.15 kJ/mol for the D3 model, indicating that less heat is required for the combustion of PC-1 when biochar is generated at higher heating rates. Conversely, the $E_a$ of PC-2 increases from 194.05 to 292.77 kJ/mol for the D3 model. For DS biochar, the $E_a$ of PC-1 increases with the pyrolysis heating rate, meaning that more energy is needed for the reaction. However, the increase is moderate as it increases from 163.73 to 191.32 kJ/mol for the D3 model, 82.64 to 98.43 kJ/mol for the F1 model, and 20.23 to 25.74 kJ/mol for the A3 model. In addition, the $E_a$ of its PC-2 increases sharply from 20.23 to 25.74 kJ/mol for the D3 model. In addition, the overall increase in the activation energy as the pyrolysis heating rate increases from 30 to 50 °C/min, indicating that more energy is required for biochar combustion if it is formed at higher heating rates.

### 3.4. Combustibility Index

There are many characteristic parameters that can define the performance of a combustion process. Table 6 lists the maximum and mean mass loss rates, i.e., $(da/dT)_{\text{max}}$ and $(da/dT)_{\text{mean}}$ for each pseudo-component. Note that the ignition and burnout temperatures for all the pseudo-components of each biochar are already summarized in Table 3. High ignition and burnout temperatures indicate that the reaction starts at a high temperature, thus requiring more energy for combustion. Meanwhile, large maximum and mean mass loss rates denote good combustion quality. Therefore, these parameters can be combined into a single parameter called the combustibility index ($S_a$), which defines the combustion quality:

$$S_a = \frac{(da/dT)_{\text{max}} \times (da/dT)_{\text{mean}}}{T_i^2 \times T_o}$$

Table 6. The Maximum and Mean Weight Loss Rates

| sample | pseudo-component | $(da/dT)_{\text{max}}$ | $(da/dT)_{\text{mean}}$ |
|--------|------------------|------------------------|------------------------|
| CV-30  | PC-1             | 0.01267                | 0.00285                |
| PC-2   |                  | 0.00178                | 3.18123 $\times 10^{-4}$|
| CV-40  | PC-1             | 0.01009                | 0.00252                |
| PC-2   |                  | 0.00206                | 3.00694 $\times 10^{-4}$|
| CV-50  | PC-1             | 0.01032                | 0.00253                |
| PC-2   |                  | 0.00221                | 3.08333 $\times 10^{-4}$|
| DS-30  | PC-1             | 0.00733                | 0.00172                |
| PC-2   |                  | 0.00756                | 0.00118                |
| DS-40  | PC-1             | 0.0086                 | 0.00188                |
| PC-2   |                  | 0.00629                | 7.57749 $\times 10^{-4}$|
| DS-50  | PC-1             | 0.00962                | 0.00171                |
| PC-2   |                  | 0.00627                | 9.13184 $\times 10^{-4}$|
| HP-30  | PC-1             | 0.01174                | 0.00246                |
| PC-2   |                  | 0.00184                | 7.56516 $\times 10^{-4}$|
| PC-3   |                  | 0.00246                | 3.62341 $\times 10^{-4}$|
| HP-40  | PC-1             | 0.01204                | 0.00253                |
| PC-2   |                  | 0.00161                | 6.72179 $\times 10^{-4}$|
| PC-3   |                  | 0.00258                | 3.61434 $\times 10^{-4}$|
| HP-50  | PC-1             | 0.01235                | 0.00253                |
| PC-2   |                  | 0.00167                | 7.19271 $\times 10^{-4}$|
| PC-3   |                  | 0.00239                | 3.1502 $\times 10^{-4}$|

Figure 6. Combustibility index $S_a$ for the pseudo-components of all algal biochar samples. (a) PC-1, (b) PC-2, and (c) PC-3.

The lower $S_a$ values for PC-1, PC-2 and PC-3 signify the fact that the combustion performance is low at a high temperature, probably due to ash formation. In addition, as seen from Figure 6a, as the pyrolysis heating rate increases, the $S_a$ for the PC-1 of CV biochar reduces from $4.10 \times 10^{-13}$ to $3.13 \times 10^{-13}$ °C$^{-5}$, whereas the $S_a$ for the PC-1 of DS and HP biochars monotonically increase from $2.53 \times 10^{-13}$ to $3.88 \times 10^{-13}$ °C$^{-5}$ and $3.00 \times 10^{-13}$ to $3.26 \times 10^{-13}$ °C$^{-5}$, respectively. This implies that the combustion performance of the PC-1 of CV biochar is reduced, but those of DS and HP biochars are improved with increasing the pyrolysis heating rate. From Figure 6b, the $S_a$ for the PC-2 of CV biochar increases from $2.70 \times 10^{-15}$ to $3.07 \times 10^{-15}$ °C$^{-5}$, suggesting that the
combustion performance is improved. In contrast, the $S_n$ for the PC-2 of DS biochar decreases from $9.94 \times 10^{-14}$ to $6.16 \times 10^{-14}$ °C$^{-5}$, and for the PC-2 of HP biochar, it reduces from $1.60 \times 10^{-14}$ to $1.35 \times 10^{-14}$ °C$^{-5}$, indicating an overall decrease in the combustion quality of these pseudo-components. Regarding the $S_n$ for the PC-3 of HP biochar, with increasing the pyrolysis heating rate, a small initial enhancement and then a reduction are observed, although the variation is not too significant (Figure 6c).

4. CONCLUSIONS

This work examined the nonisothermal combustion of three algal biochar samples using the multiple component method. Raw algal biomasses were first pyrolyzed at three different heating rates (i.e., 30, 40, and 50 °C/min) to obtain the biochars. Biochar combustion was performed in the temperature range of 200 to 700 °C at a heating rate of 5 °C/min. The results indicated the presence of multiple reactions that appeared to be decomposing as independent parallel processes. Therefore, the bi-Gaussian model was adopted to resolve the global reaction into multiple pseudo-components using the peak deconvolution method. CV and DS contain two pseudo-components (PC-1 and PC-2), and HP contains three pseudo-components (PC-1, PC-2, and PC-3). As the pyrolysis heating rate increases, CV biochar requires more heat at higher temperatures since the peak temperature of CV’s PC-2 increases from 622.84 to 634.33 °C. In contrast, the initial combustion of DS biochar requires less heat as the peak temperature of DS’s PC-1 declines from 373.99 to 345.65 °C. In addition, no considerable change is observed in the peak temperatures of HP’s pseudo-components.

Activation energies ($E_a$) were evaluated for all pseudo-components of each biochar sample by using the Coats–Redfern method as well as four different reaction models. The highest $E_a$ values are seen for the diffusion model followed by the order-based, shrinking core, and nucleation models. Although the $E_a$ values for different kinetic models are different, their evolving trend with the pyrolysis heating rate seems to be consistent. By using the diffusion model, the $E_a$ of CV’s PC-1 decreases from 287.43 to 240.15 kJ/mol, that of CV’s PC-2 increases from 194.05 to 292.77 kJ/mol, and that of DS’s PC-1 increases from 163.73 to 191.32 kJ/mol with increasing the pyrolysis heating rate.

In addition, the combustibility index also reveals that the combustion performance of algal biochar deteriorates toward a high temperature. Apart from the PC-1 of DS and HP and the PC-2 of CV, all other pseudo-components broadly show a significant reduction in the combustibility index, suggesting a decrease in the combustion quality of algal biochars as the pyrolysis heating rate increases.

AUTHOR INFORMATION

Corresponding Author
Xiaoke Ku – Department of Engineering Mechanics and State Key Laboratory of Clean Energy Utilization, Zhejiang University, 310027 Hangzhou, China; orcid.org/0000-0002-2182-3933; Phone: +8657187952221; Email: xiaokeku@zju.edu.cn

Authors
Vikul Vasudev – Department of Engineering Mechanics, Zhejiang University, 310027 Hangzhou, China

Jianzhong Lin – Department of Engineering Mechanics, Zhejiang University, 310027 Hangzhou, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c02493

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is financially supported by the National Natural Science Foundation of China (project numbers 51876191 and 11632016) and the Fundamental Research Funds for the Central Universities (project number 2021FZZX001-11).

REFERENCES

(1) Morgan, T. J.; Youkhana, A.; Turn, S. Q.; Ogoshi, R.; Garcia-Pérez, M. Review of Biomass Resources and Conversion Technologies for Alternative Jet Fuel Production in Hawai‘i and Tropical Regions. Energy Fuels 2016, 30, 2699–2762.
(2) Potters, G.; Van Goethem, B.; Schutte, F. Promising Biofuel Resources: Lignocellulose and Algae Early Thinking on Biofuels Vegetable Oils: The First Generation Biofuels, The Downsidess of Biofuels. Nat. Educ. 2010, 3, 14.
(3) Vasudev, V.; Ku, X.; Lin, J. Kinetic Study and Pyrolysis Characteristics of Algal and Lignocellulosic Biomasses. Bioresour. Technol. 2019, 288, 121496.
(4) Yuan, T.; Tahmasebi, A.; Yu, J. Comparative Study on Pyrolysis of Lignocellulosic and Algal Biomass Using a Thermogravimetric and a Fixed-Bed Reactor. Bioresour. Technol. 2015, 175, 334–341.
(5) Cerriello, F.; Apicella, B.; Russo, C.; Cortese, L.; Seneca, O. Effects of Pressure on Lignocellulosic Biomass Fast Pyrolysis in Nitrogen and Carbon Dioxide. Fuel 2021, 287, 119604.
(6) Brindhadevi, K.; Anto, S.; Rene, E. R.; Sekar, M.; Mathimani, T.; Thuy Lan Chi, N.; Pugazhendhi, A. Effect of Reaction Temperature on the Conversion of Algal Biomass to Bio-Oil and Biochar through Pyrolysis and Hydrothermal Liquefaction. Fuel 2021, 285, 119106.
(7) Gautam, R.; Vinu, R. Reaction Engineering and Kinetics of Algae Conversion to Biofuels and Chemicals: Via Pyrolysis and Hydrothermal Liquefaction. React. Chem. Eng. 2020, 5, 1320–1373.
(8) Li, J.; Qiao, Y.; Zong, P.; Wang, C.; Tian, Y.; Qin, S. Thermogravimetric Analysis and Isoconversional Kinetic Study of Biomass Pyrolysis Derived from Land, Coastal Zone, and Marine. Energy Fuels 2019, 33, 3299–3310.
(9) Kadam, K. L. Environmental Implications of Power Generation via Coal-Microalgae Co-firing. Energy 2002, 27, 905–922.
(10) Bach, Q. V.; Chen, W. H. Pyrolysis Characteristics and Kinetics of Microalgae via Thermogravimetric Analysis (TGA): A State-of-the-Art Review. Bioresour. Technol. 2017, 246, 88–100.
(11) Kim, D. W.; Koriakin, A.; Jeong, S. Y.; Lee, C. H. Co-Processing of Heavy Oil with Wood Biomass Using Supercritical m-Xylene and n-Dodecan Solvents. Korean J. Chem. Eng. 2017, 34, 1961–1969.
(12) Vasudev, V.; Kumar, A.; Saini, V.; Dondapati, B. S. Analytical Estimation for Temperature Dependent Transport Properties of Supercritical Jet Fuel Surrogate. Int. J. Mech. Eng. Technol. 2017, 8, 1292–1298.
(13) Michalak, I.; Bašladyňška, S.; Mokrzycki, J.; Rutkowksi, P. Biochar from a Freshwater Macroalgae as a Potential Biosorbent for Wastewater Treatment. Water 2019, 11, 4–6.
(14) Yu, K. L.; Lau, B. F.; Show, P. L.; Ong, H. C.; Ling, T. C.; Chen, W. H.; Ng, E. P.; Chang, J. S. Recent Developments on Algal Biochar Production and Characterization. Bioresour. Technol. 2017, 246, 2–11.
(15) Koçer, A. T.; Mutlu, B.; Özçimen, D. Investigation of Biochar Production Potential and Pyrolysis Kinetics Characteristics of Microalgal Biomass. Biomass Convers. Bioref. 2020, 10, 85–94.
(16) Elbour, A. Y.; Alghyamah, A. A.; Shaikh, H. M.; Poulose, A. M.; Al-Zahrani, S. M.; Anis, A.; Al-Wabel, M. I. Effect of Pyrolysis Temperature on Biochar Microstructural Evolution, Physicochemical Characteristics, and Its Influence on Biochar/Polypropylene Composites. Appl. Sci. 2019, 9, 1149.

(17) Li, T.; Wang, L.; Ku, X.; Güell, B. M.; Lovás, T.; Shaddix, C. R. Experimental and Modeling Study of the Effect of Torrefaction on the Rapid Devolatilization of Biomass. Energy Fuels 2015, 29, 4328–4338.

(18) Ku, X.; Li, T.; Lovás, T. Effects of Particle Shrinkage and Devolatilization Models on High-Temperature Biomass Pyrolysis and Gasification. Energy Fuels 2015, 29, 5127–5135.

(19) Jayaraman, K.; Kök, M. V.; Gökalp, I. Combustion Mechanism and Model Free Kinetics of Different Origin Coal Samples: Thermal Analysis Approach. Energy 2020, 204, 117905.

(20) Emre Altun, N.; Hicyilmaz, Ç.; Kök, M. V. Effect of Particle Size and Heating Rate on the Pyrolysis of Silopi Asphaltite. J. Anal. Appl. Pyrolysis 2003, 67, 369–379.

(21) Vyazovkin, S.; Burnham, A. K.; Criado, J. M.; Pérez-Maqueda, L. A.; Popescu, C.; Shirzadzouli, N. ICTAC Kinetics Committee Recommendations for Performing Kinetic Computations on Thermal Analysis Data. Thermochem. Acta 2011, 520, 1–19.

(22) Coats, A. W.; Redfern, J. P. Kinetic Parameters from Thermogravimetric Data. Nature 1964, 201, 68–69.

(23) Wang, C.; Du, Y.; Che, D. Reactivities of Coals and Synthetic Model Coal under Oxy-Fuel Conditions. Thermochem. Acta 2013, 553, 8–15.

(24) Jayaraman, K.; Kok, M. V.; Gokalp, I. Thermogravimetric and Mass Spectrometric (TG-MS) Analysis and Kinetics of Coal-Biomass Blends. Renewable Energy 2017, 101, 293–300.

(25) Hu, M.; Chen, Z.; Wang, S.; Guo, D.; Ma, C.; Zhou, Y.; Chen, J.; Laghari, M.; Fazal, S.; Xiao, B.; Zhang, B.; Ma, S. Thermogravimetric Kinetics of Lignocellulosic Biomass Slow Pyrolysis Using Distributed Activation Energy Model, Fraser-Suzuki Deconvolution, and Iso-Conversional Method. Energy Convers. Manage. 2016, 118, 1–11.

(26) Sharma, P.; Pandey, O. P.; Diwan, P. K. Non-Isothermal Kinetics of Pseudo-Components of Waste Biomass. Fuel 2019, 253, 1149–1159.

(27) da Silva, J. C. G.; de Albuquerque, J. G.; Galdino, W. V. d. A.; de Sena, R. F.; Andersen, S. L. F. Single-Step and Multi-Step Thermokinetic Study–Deconvolution Method as a Simple Pathway for Describe Properly the Biomass Pyrolysis for Energy Conversion. Energy Convers. Manage. 2020, 209, 112653.

(28) Buys, T. S.; De Clerk, K. Bi-Gaussian Fitting of Skewed Peaks. Anal. Chem. 1972, 44, 1273–1275.

(29) Gogoi, M.; Konwar, K.; Bhuyan, N.; Borah, R. C.; Kalita, A. C.; Nath, H. P.; Saikia, N. Assessments of Pyrolysis Kinetics and Mechanisms of Biomass Residues Using Thermogravimetry. Bioreour. Technol. Rep. 2018, 4, 40–49.

(30) Qin, K.; Thunman, H. Diversity of Chemical Composition and Combustion Reactivity of Various Biomass Fuels. Fuel 2015, 147, 161–169.

(31) Sobek, S.; Werle, S. Kinetic Modelling of Waste Wood Devolatilization during Pyrolysis Based on Thermogravimetric Data and Solar Pyrolysis Reactor Performance. Fuel 2020, 261, 116459.

(32) Yang, Z.; Zhang, L.; Zhang, Y.; Bai, M.; Zhang, Y.; Yue, Z.; Duan, E. Effects of Apparent Activation Energy in Pyrolytic Carbonization on the Synthesis of MOFs-Carbon Involving Thermal Analysis Kinetics and Decomposition Mechanism. Chem. Eng. J. 2020, 395, 124980.

(33) Chen, T.; Ku, X.; Lin, J. CFD Simulation of the Steam Gasification of Millimeter-Sized Char Particle Using Thermally Thick Treatment. Combust. Flame 2020, 213, 63–86.

(34) Buys, T. S.; De Clerk, K. Bi-Gaussian Fitting of Skewed Peaks. Anal. Chem. 1972, 44, 1273–1275.

(35) Sydney, E.B.; Novak, A.C.; de Carvalho, J.C.; Soccol, C.R. Potential Carbon Fixation of Industrially Important microalgae. In Biofuels from Algae; Elsevier: Amsterdam, 2019; pp. 67–88.

(36) Masojídek, J.; Torzillo, G. Mass Cultivation of Freshwater Microalgae. Reference Module in Earth Systems and Environmental Sciences; 2014, Elsevier, DOI: 10.1016/B978-0-12-409548-9.09373-8.