

Communication

Kinetic Analysis of Algae Gasification by Distributed Activation Energy Model

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Received: 30 June 2020; Accepted: 21 July 2020; Published: 2 August 2020



Abstract: Conversion of algal biomass into energy products via gasification has attracted increasing research interests. A basic understanding of the gasification kinetics of algal biomass is of fundamental importance. Distributed activation energy model (DAEM), which provides the information of energy barrier distribution during the gasification process, is a promising tool to study the kinetic process of algae gasification. In this study, DAEM model was used to investigate *Chlorella vulgaris* and *Spirulina* gasification. The activation energy of *Chlorella vulgaris* gasification was in the range from 370 to 650 kJ mol⁻¹. The range of activation energy for *Spirulina* gasification was a bit wider, spanning from 330 to 670 kJ mol⁻¹. The distribution of activation energy for both *Chlorella vulgaris* and *Spirulina* showed that 500 kJ mol⁻¹ had the most components, and these components were gasified at around 300 °C. The DAEM algorithm was validated by the conversion and conversion rate from experimental measurement, demonstrating that DAEM is accurate to describe the kinetics of algal biomass gasification.

Keywords: algal biomass; gasification; kinetics; activation energy distribution

1. Introduction

The dependency of fossil fuels in recent centuries has significantly contributed to the carbon emission and the consequent global warming. Climate change, together with the declining reservation of fossil fuels, is urging the environment and energy research community to seek alternative energy sources that are renewable and have lower environmental impact. Among possible options, biomass, which could be thermally converted into various bio-fuels, for instance oil and syngas via pyrolysis and gasification, have attracted great research attention, not only because of the renewability but also due to the carbon neutrality throughout its life cycle.

Biomass could be generally divided into three generations. The first generation of biomass includes those from terrestrial plants such as rice, potato, corn, bean, wheat, maize, oil palm, sugarcane and food wastes [1]. However, extensive conversion of first-generation biomass to bio-fuel might endanger our

food stock security [2]. Energy production at the expense of food supply should never be encouraged. The majority of second-generation bio-resources are non-food waste and lingo-cellulosic materials such as grass, husk, wood, municipal solid waste and sewage sludge [3]. These feedstocks do not sacrifice the food supplies. In addition, the bio-fuel yield from this type of biomass is generally higher than that from the first generation of biomass [1]. In spite of these advantages, they still have some barriers to reaching commercial-scale conversion, such as the transportation, collection networks and the cost-effective pre-treatment. The third generation is algal biomass, which could avoid the deficiencies mentioned above for the first- and second-generation biomass. Cultivating the third-generation biomass does not require cultivatable land. They do not compete with traditional food crops either [4]. Compared to normal plants, microalgae show exceptionally rapid growth rates and exceptional photosynthetic efficiency [5]. Microalgae can be grown in ponds or photo-bioreactors with nutrients [6] or wastewater supply [7–9], which is another advantage over the first- and second-generation biomass that heavily rely on agricultural resources such as fertile soil and fertilizer.

In view of the advantages of algal biomass over other types of biomass, converting algal biomass into value-added energy products has attracted increasing research attention. A great number of studies has successfully converted algal biomass to syngas, hydrocarbon oils and biochar via some common thermochemical techniques such as liquefaction [10], torrefaction [11], pyrolysis [12] and gasification [13]. Among them, producing hydrogen-rich syngas by gasification is of great interest in the energy and environmental community. Díaz-Rey et al. gasified *Scenedesmus almeriensis* algae with a Ni-based catalyst below 700 °C and produced hydrogen-rich syngas, which has a calorific value of about 25 MJ Nm⁻³ [14]. Onwudili et al. conducted hydrothermal gasification of *Chlorella vulgaris*, *Spirulina platensis* and *Saccharina latissima* at 500 °C and 36 MPa, and the hydrogen yield was more than 10 mol kg⁻¹-algae [15]. Duman et al. employed steam gasification of algae and obtained almost 45 mol hydrogen from per gram *Fucus serratus* [16].

Gasification of algal biomass is an endothermic process that requires considerable thermal energy input. Biomass generally consists of large molecules including cellulose, hemicellulose and lignin. The bonds in those large molecules need to be ruptured before converting to oil or gases, and there is always some energy barrier to activate the bond breakage. The energy barrier called activation energy is a good indicator of energy requirement for a process to occur. Because of the complex nature of real biomass, the value of activation energy generally spreads in a large range instead of being a fixed number [17]. Therefore, studying the activation energy distribution is essential in many aspects for algal biomass gasification, such as evaluating the conversion efficiency and assessing the effectiveness of the catalyst [18]. This study will apply distributed activation energy model (DAEM) to inspect the distribution of activation energy for *Chlorella vulgaris* and *Spirulina* gasification.

2. Method

2.1. Experimental Test

Chlorella vulgaris and *Spirulina* powders, purchased from Xi'an Snooker Biotech Co., Ltd., China, were selected as algal biomass samples in this study. The characteristics of the *Chlorella vulgaris* and *Spirulina* including bio-chemical composition, proximate analysis and ultimate analysis could be found in our previous study [19]. The gasification rate was measured in the TA-SDT-Q600 thermo-gravimetric analysis (TGA) instrument. In each test, around 2–3 mg sample in a fine powder state was loaded in the TGA crucible. The temperature was raised from 30 °C to 600 °C with different heating rates of 10, 20 and 30 °C min⁻¹. The conversion of biomass gasification was defined as

$$\alpha = \frac{m - m_0}{m_\infty - m_0} \quad (1)$$

where m is the mass of sample during gasification, m_0 is the original mass before the gasification and m_∞ is the final mass after gasification. The gasifying agent was composed oxygen and argon with a

volumetric ratio of 20%:80%, and the flow rate of gas gasifying agent was maintained at 500 mL min⁻¹. More experimental details about the kinetic test were described in our previous publication [20].

2.2. Model Development

The early development of distributed activation energy model was to study the activation energy for coal pyrolysis [21,22]. However, the method to obtain the activation energy distribution is universally applicable to thermal treatment of other complex organics. The basic assumption for algae gasification is that the algae is composed of a series of constituents that have different activation energies.

If the total volatile of algae is denoted as V^* , the constituent of which activation energy equals E_i is V_i^* .

$$V_i^* = V^* f(E_i) \Delta E \quad (2)$$

where $f(E_i)$ is the activation energy distribution. According to Arrhenius law and the hypothesis of first order law, the decomposition rate of this constituent is

$$\frac{d(V_i/V_i^*)}{dt} = k_i \left(\frac{V_i^* - V_i}{V_i^*} \right) = A_i \exp\left(-\frac{E_i}{RT}\right) \left(\frac{V_i^* - V_i}{V_i^*} \right) \quad (3)$$

where V_i is the decomposed volatile in V_i^* , T is temperature and R is gas constant. Upon integration of Equation (3), we get

$$V_i = V_i^* \left\{ 1 - \exp\left[-\int_0^t A_i \exp\left(-\frac{E_i}{RT}\right) dt\right] \right\} \quad (4)$$

Summation of all the constituents together leads to

$$V = V^* - \sum_{i=1}^n \exp\left[-\int_0^t A_i \exp\left(-\frac{E_i}{RT}\right) dt\right] V_i^* f(E_i) \Delta E \quad (5)$$

Since the total conversion $\alpha = V/V^*$, Equation (4) is rearranged to

$$1 - \alpha = \sum_{i=1}^n \exp\left[-\int_0^t A_i \exp\left(-\frac{E_i}{RT}\right) dt\right] f(E_i) \Delta E \quad (6)$$

If the temperature is raised at a constant rate β , Equation (6) is then rewritten as

$$1 - \alpha = \sum_{i=1}^n \exp\left[-\frac{A_i}{\beta} \int_{T_0}^T \exp\left(-\frac{E_i}{RT}\right) dT\right] f(E_i) \Delta E \quad (7)$$

For simplicity, a function $\phi(E, T)$, which means the unconverted fraction of group with activation energy E at temperature T , is defined as

$$\phi(E, T) = \exp\left[-\int_0^T \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT\right] \quad (8)$$

By converting the continuous temperature data to discretization form, Equation (7) is then transformed to matrix form

$$\begin{bmatrix} 1-\alpha_1 \\ 1-\alpha_2 \\ \vdots \\ 1-\alpha_j \\ \vdots \\ 1-\alpha_m \end{bmatrix} = \begin{bmatrix} \phi(E_1, T_1) & \phi(E_2, T_1) & \dots & \phi(E_n, T_1) \\ \phi(E_1, T_2) & \phi(E_2, T_2) & & \vdots \\ \vdots & \vdots & \ddots & \vdots \\ \phi(E_1, T_m) & \vdots & \dots & \phi(E_n, T_m) \end{bmatrix} \begin{bmatrix} f(E_1)\Delta E \\ f(E_2)\Delta E \\ \vdots \\ f(E_n)\Delta E \end{bmatrix} \quad (9)$$

If the activation energy and temperature are divided into the same number of divisions ($m = n$), the reverse matrix of $[\phi(E, T)]$ could be mathematically obtained as $[\phi(E, T)]^{-1}$. Theoretically, by multiplying $[\phi(E, T)]^{-1}$ on both sides of Equation (9), the distribution of activation energy could be expressed as Equation (10)

$$[\phi(E, T)]^{-1}[1-\alpha] = [f(E)\Delta E] \quad (10)$$

However, a number of studies pointed out that $\phi(E, T)$ is almost a step function to E , which means progressing from 0 to 1 sharply, so $[\phi(E, T)]$ is nearly a singular matrix. As a consequence, $[\phi(E, T)]^{-1}$ could not be calculated, thus obtaining distribution of activation energy by Equation (10) is mathematically impossible. However, if the distribution of activation energy is already known, calculating the algae conversion by the matrix method is very convenient.

The actual activation energy distribution is continuous rather than discrete, and the integration form of Equation (7) is

$$1-\alpha = \int_0^{\infty} \phi(E, T)f(E)dE \quad (11)$$

Differentiating Equation (11) with respect to E , together with the boundary conditions $f(0) = f(\infty) = 0$, $\phi(0, T) = 0$ and $\phi(\infty, T) = 1$, we get

$$\frac{d\alpha}{dE} = -\frac{d}{dE} \int_0^{\infty} \phi(E, T)f(E)dE = -\int_0^0 \phi(E, T)d[f(E)] - \int_1^0 f(E)d[\phi(E, T)] = f(E) \quad (12)$$

Thus, the distribution of activation energy could be obtained from Equation (12).

After obtaining the distribution of activation energy, it is used to calculate the conversion by Equation (9), and the conversion rate could be obtained subsequently. To validate the model, the conversion rates computed from DAEM model and measured from the experiment are compared. The root-mean-square error is defined as

$$RMSE = \sqrt{\frac{\sum_{i=1}^n \left(\left(\frac{d\alpha}{dt} \right)_{DAEM} - \left(\frac{d\alpha}{dt} \right)_{EXP} \right)^2}{n}} \quad (13)$$

3. Results and Analysis

3.1. Thermo-Gravimetric Analysis

The profiles of thermogravimetry (TG) and differential thermogravimetry (DTG) data during the gasification are shown in Figure 1. The TG of *Chlorella vulgaris* was almost stable when the temperature was above 500 °C, down to the minimum of ~10 wt.%. The TG of *Spirulina* after 500 °C also hardly presented any mass variation and stabilized around 14 wt.%. The final values of TG were in good agreement with the ash and fixed carbon values in proximate analysis [20]. The DTG profiles showed three major mass loss processes at around 300, 420 and 450 °C for *Chlorella vulgaris*. For *Spirulina*

gasification, there were two major peaks at ~ 300 and 450 °C and one minor peak at ~ 420 °C. From the perspective of distributed activation energy, the phenomenon that volatile components are decomposed or gasified at different temperatures was due to the different activation energies. The volatiles gasified at higher temperature generally have higher energy barriers to be activated than those gasified at lower temperature [23].

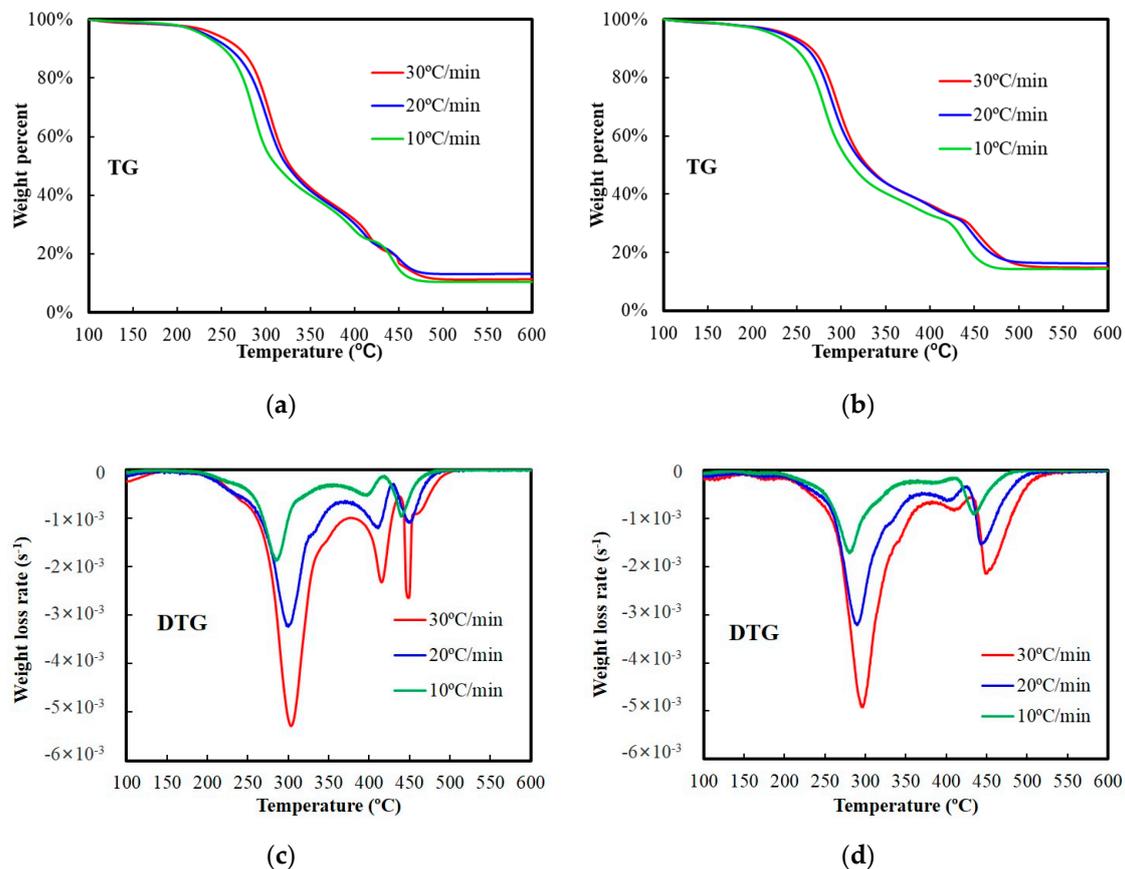


Figure 1. Thermogravimetry (TG) and differential thermogravimetry (DTG) profiles of *Chlorella vulgaris* and *Spirulina* gasification. (a) TG of *Chlorella vulgaris*; (b) TG of *Spirulina*; (c) DTG of *Chlorella vulgaris*; (d) DTG of *Spirulina*.

3.2. The Distribution of Activation Energy

With the thermogravimetry data and the DAEM model developed above, the distributions of activation energy for *Chlorella vulgaris* and *Spirulina* gasification could be obtained. As displayed in Figure 2, the activation energy of *Chlorella vulgaris* gasification covered the range from 370 to 650 kJ mol⁻¹. The activation energy range for *Spirulina* gasification was a bit wider, spanning from 330 to 670 kJ mol⁻¹. Both *Chlorella vulgaris* and *Spirulina* had a significant number of constituents with activation energy around 500 kJ mol⁻¹. Owing to the lower activation energy, this part of algae was relatively easier to be gasified, and the gasification of this part corresponded to the first major peak in DTG. The range of activation energy presented in Figure 2 covered the main activation energy values for decomposition of *Chlorella vulgaris* (208–546 kJ mol⁻¹) [24] and *Chlorella variabilis* (133–876 kJ mol⁻¹) [25] but was slightly higher than the activation energy values reported in thermal treatment of other algae such as *Cladophora glomerata* (177 kJ mol⁻¹) [26], *Chlorococcum humicola* (140–240 kJ mol⁻¹) [27] and *Kappaphycus alvarezii* (61–312 kJ mol⁻¹) [28]. Since the feedstocks are not the same, the difference was likely due to the variations of compound types and contents. In addition, the different algorithms in DAEM model and iso-conversional model-free method also lead to the difference in activation energy.

In the iso-conversional method assuming a reaction model is not necessary, but in DAEM the reaction model is under the order-law frame [18].

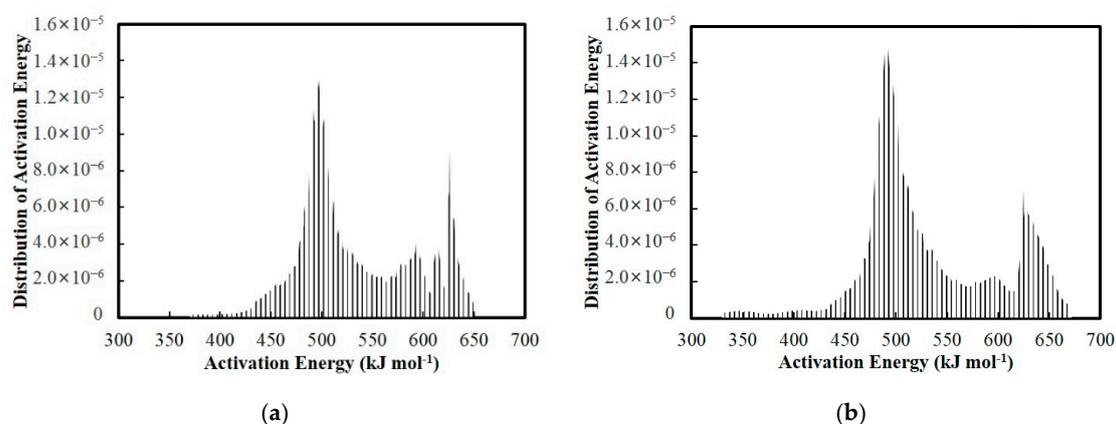


Figure 2. The distributed activation energy of (a) *Chlorella vulgaris* and (b) *Spirulina* gasification.

The upper bound of *Spirulina* gasification was a bit higher than *Chlorella vulgaris* gasification, indicating that *Spirulina* had some constituents that were difficult to decompose. As observed in the TG and DTG profiles (Figure 1), the gasification of *Chlorella vulgaris* completed before 500 °C, but there was still ongoing gasification above 500 °C for *Spirulina*. This was highly likely due to the constituents with activation energy higher than 650 kJ mol⁻¹ in Figure 2b. According to our previous study, *Spirulina* has 60.23% protein, and *Chlorella vulgaris* has 51.51% protein [19]. The higher protein content in *Spirulina* might be owing to its higher activation energy.

3.3. DAEM Model Validation

To evaluate the validity of the derived distribution of activation energy, the conversion calculated from DAEM model should be compared with the experimental results. Once we have the distribution of activation energy, the conversion of the gasification process can be computed from the activation energy distribution according to Equation (9) and then compared with the conversion measured by TGA. The comparison between experimental conversion and modeling data is displayed in Figure 3. The conversions match each other well with marginal deviations only for the case of 10 °C min⁻¹, indicating the reliability of activation energy distribution derived above.

Another pathway to validate the activation energy distribution is to examine the conversion rate. The conversion rate is actually the first-order derivative of conversion with respect to time. After performing the differentiation of α to t , the conversion rates are further compared in Figure 4, and the DAEM conversion rates also closely fit the experimental conversion rates. Figure 4 showed some insignificant difference. The root-mean-square errors are only 3.04×10^{-4} (10 °C min⁻¹), 2.44×10^{-4} (20 °C min⁻¹) and 4.17×10^{-4} (30 °C min⁻¹) for *Chlorella vulgaris*. For *Spirulina*, the values are 3.17×10^{-4} (10 °C min⁻¹), 2.04×10^{-4} (20 °C min⁻¹) and 3.09×10^{-4} (30 °C min⁻¹). The insignificant difference between experimental and DAEM model values might arise from the neglect of thermal-lag effect due to the mismatch of temperature values. The peaks of experimental conversion rates did not appear at the same temperature, and it seemed that the peaks were delayed at higher heating rates. This phenomenon is generally because the heat transfer inside the biomass particle is not sufficiently quick. In DAEM model, the thermal-lag effect was not considered, thus almost all the conversion rate peaks arrived at the same temperature. As a consequence, the conversion rate from DAEM model cannot perfectly fit all the conversion rates from the three heating rates.

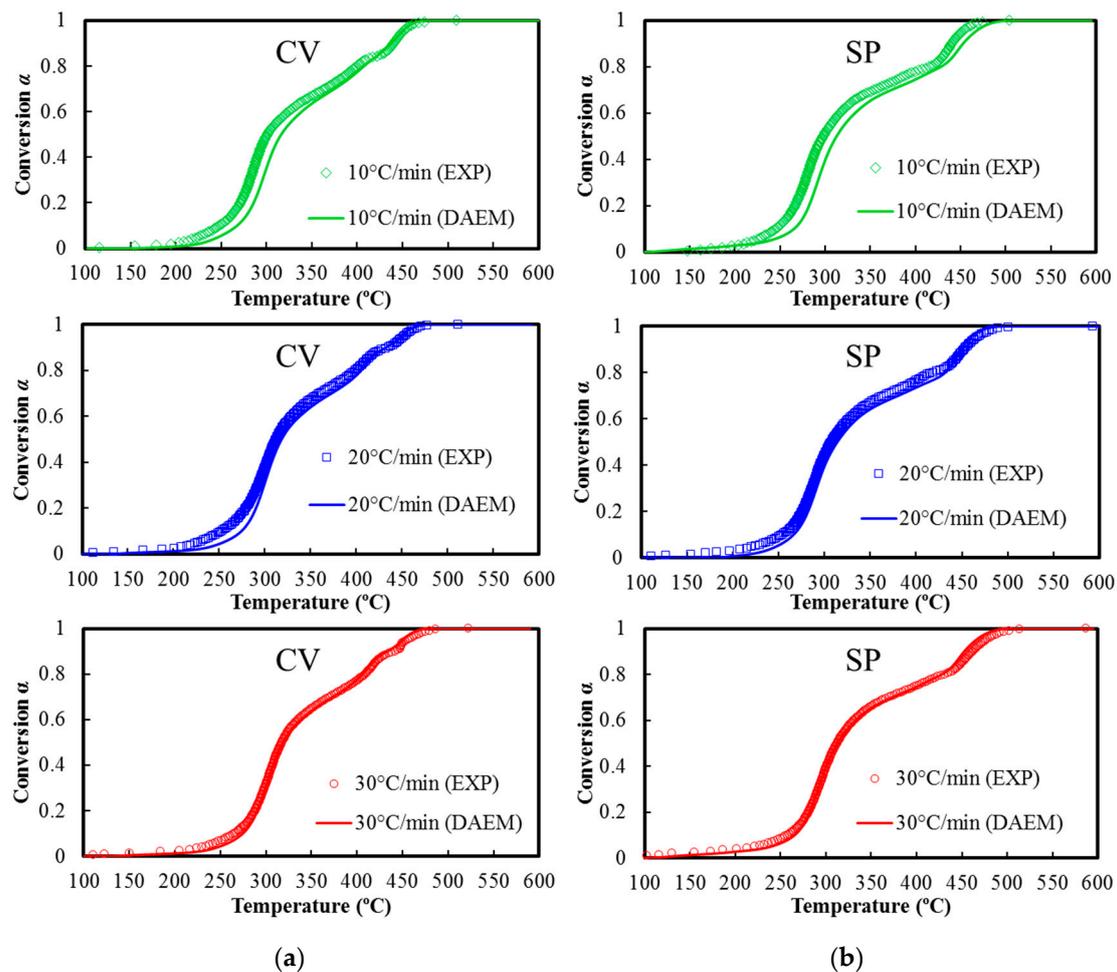


Figure 3. Comparison of conversion value between experimental measurement and DAEM model. (a) *Chlorella vulgaris*; (b) *Spirulina*. EXP: experimental data; DAEM: model data from DAEM model.

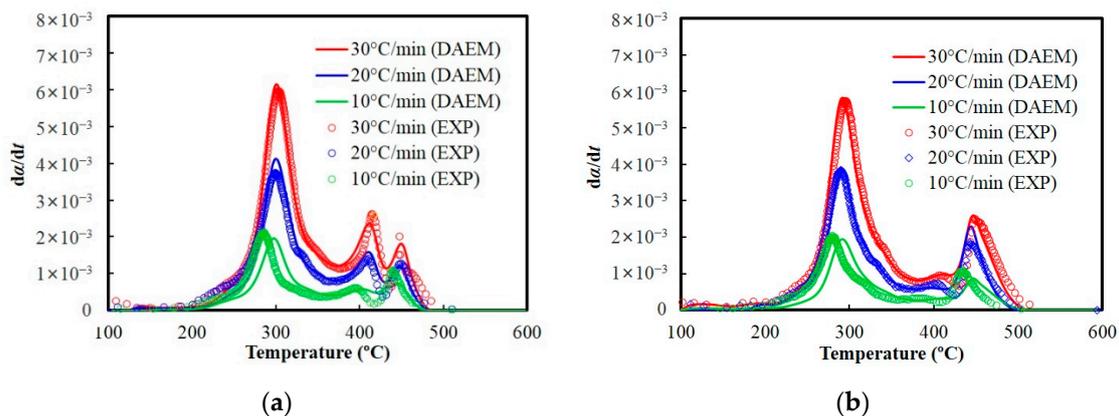


Figure 4. Comparison of conversion rate between experimental measurement and DAEM model. (a) *Chlorella vulgaris*; (b) *Spirulina*.

4. Conclusions

Distributed activation energy model (DAEM) was applied to study the gasification of *Chlorella vulgaris* and *Spirulina*. Both *Chlorella vulgaris* and *Spirulina* showed complex behaviors during gasification, as the DTG profiles presented multiple major peaks at different temperature ranges. By using the DAEM model, it was found that both *Chlorella vulgaris* and *Spirulina* had a significant number

of components with activation energy close to 500 kJ mol^{-1} , and this part of components was gasified around $300 \text{ }^\circ\text{C}$. *Spirulina* had more components with high activation energy, which explained the ongoing gasification above $500 \text{ }^\circ\text{C}$. The conversion and conversion rate from DAEM model could accurately reproduce the experimental conversion and conversion rate, demonstrating the validity of applying DAEM to algal biomass gasification.

Author Contributions: Conceptualization, G.J. and Z.Z.; Methodology, G.J., A.R. and W.D.; Validation, G.J., B.Q. and M.Z.; Formal Analysis, X.W. and Y.G.; Investigation, G.J. and Z.Z.; Resources, Z.Z.; Writing-Original Draft Preparation, G.J. and Z.Z.; Writing-Review & Editing, W.F. and W.D.; Visualization, G.J.; Supervision, A.L.; Funding Acquisition, G.J. and Z.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by [Open Foundation of Key Laboratory of Industrial Ecology and Environmental Engineering, Ministry of Education] grant number [KLIEEE-19-01] and [the Fundamental Research Funds for the Central Universities] grant number [DUT18RC(3)036].

Conflicts of Interest: The authors declare no conflict of interest.

Nomenclature

A	Pre-exponential factor
E	Activation energy
$f(E)$	Distribution of activation energy
m	Mass of algal biomass
m_0	Initial mass of algal biomass
m_∞	Final mass of algal biomass
R	Gas constant
t	Time
T	Temperature
T_0	Initial temperature
V	Quantity of gasified biomass
V^*	Total convertible biomass

Greek letters

α	Biomass conversion
β	Heating rate
ϕ	The unconverted fraction of biomass

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