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Application of the distributed activation energy model to the kinetic study of pyrolysis of *Nannochloropsis oculata*

Daniel Viju, Ribhu Gautam, R. Vinu*

Department of Chemical Engineering and National Center for Combustion Research and Development, Indian Institute of Technology Madras, Chennai 600036, India

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ABSTRACT

Pyrolysis of algae is a promising route to produce high quality bio-oil and renewable chemicals. Owing to its complex structural composition, multiple pseudo-components are required to describe its thermal decomposition in a wide temperature range and evaluate the reaction kinetics. In this study, the pyrolysis behavior of the microalga, *Nannochloropsis oculata* (*N. oculata*), was studied by means of a thermogravimetric analyzer at various heating rates. A four-parallel-reaction scheme characterizing the pyrolysis of carbohydrate, protein, lipid and the secondary decomposition of char was employed to model thermal degradation using distributed activation energy model (DAEM). The average and standard deviation of activation energy, pre-exponential factor, and composition of the model components for pyrolysis of *N. oculata* were estimated. The model mass loss and differential mass loss profiles matched well with the experimental data at different heating rates. Based on the model predictions, the decomposition of proteins, carbohydrates, lipids and char occurred in the temperature regimes of 200–450 °C, 200–300 °C, 400–500 °C, and 750–900 °C, respectively. To gain valuable insights on the pyrolysate composition at various temperature regimes, analytical pyrolysis-gas chromatography/mass spectrometry experiments were performed. Indole and phenol, aliphatic and aromatic hydrocarbons, and long chain oxygenates were observed as the major pyrolysates in the temperature regimes of 30–350 °C, 350–600 °C and 600–1000 °C, respectively.

1. Introduction

A thorough understanding of the physico-chemical properties and chemistry of transformation of renewable and carbon neutral species like microalgae are inevitable for their efficient utilization for biofuels production, and design of efficient systems for processing them [1,2]. In recent years, *Nannochloropsis* sp. has been proposed as an excellent candidate for biofuel production due to their ability to generate high quantity of lipids [2]. The bio-chemical composition of algae is fundamentally different from terrestrial biomass. Cellulose, hemicellulose, and lignin constitute lignocellulosic biomass, while microalgae are made up of proteins, lipids, carbohydrates and nucleic acids [3]. A wide variety of products are possible from the conversion of microalgae, as lipids, after extraction, can be converted to biodiesel, and carbohydrates, via fermentation, can be converted to bio-ethanol [4].

Pyrolysis, which involves heating the feedstock at moderate temperatures (400–600 °C) in the absence of oxygen, has gained significant attention, as this thermochemical process converts the whole of microalgae into liquid bio-oil [5]. Microalgae pyrolysis results in bio-oil with better properties than that derived from lignocellulosic biomass [6]. For effective utilization of microalgae via thermochemical technologies, an understanding of their thermal behavior and pyrolysis kinetics is necessary. This understanding can be applied to reactor design and to decide the optimum operating parameters for better process efficiency [6]. The inherent composition of the microalgae leads to lower decomposition temperatures than lignocellulosic biomass during thermochemical conversion [7]. Global kinetic schemes are used to explain the mass volatilization and to capture the overall yields of bio-oil, gas, and char from pyrolysis. Investigating the intrinsic (or mechanistic) kinetics of algae pyrolysis is complicated due to its complex composition. Recently, Ranzi and co-workers developed a multi-step semi-detailed kinetic mechanism of algae pyrolysis using different reference compounds, and validated the model with the experimental data obtained under dynamic and isothermal slow and fast pyrolysis conditions [8].

Thermogravimetric analysis (TGA) is extensively used to study the thermal behavior and evaluation of apparent kinetic parameters of decomposition. TGA precisely gives the mass loss data as a function of time and temperature at low heating rates (5–100 °C min^{-1}). TG data obtained at single or multiple heating rates are used to calculate the

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* Corresponding author.
E-mail address: vinu@iitm.ac.in (R. Vinu).

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Nomenclature

A	pre-exponential (or frequency) factor (s^{-1})
c_i	mass fraction of the i-th pseudo component
E	activation energy (J mol^{-1})
E_0	mean activation energy of the Gaussian distribution (J mol^{-1})
$f(E)$	activation energy distribution (mol J^{-1})
n_d	number of data points used
R	universal gas constant (J mol^{-1} K^{-1})
S	objective function for differential thermogravimetric data (K^{-2})
S_1	objective function for conversion data
T	temperature (K)
T_0	initial temperature (K)
α	degree of conversion
β	linear heating rate (K min^{-1} or °C min^{-1})
σ	standard deviation of the activation energy distribution (J mol^{-1})

apparent kinetic parameters via integral or differential isoconversional methods and n-th order model fitting techniques [9]. TG data is useful not only to determine the kinetic parameters, but also to understand the overall pyrolysis mechanisms involved [10]. Owing to the complexity of microalgae pyrolysis and the involvement of multiple parallel reactions, it is difficult to describe the entire process with a single-step reaction kinetic model. Kim et al. [11] utilized a differential TG and evolved gas analysis–mass spectrometric technique to identify the decomposition regimes of carbohydrates (< 300 °C), proteins and lipids (301–380 °C) and secondary cracking of proteins and lipids (> 380 °C) during pyrolysis of *Porphyra tenera*. In another study, apparent activation energies for pyrolysis of *Chlorella* sp. (~300 kJ mol^{-1}) and *Tetraselmis suecica* (~100 kJ mol^{-1}) were evaluated using TGA employing isoconversional methods, and found to be lower than lignocellulosic biomasses [12].

Vo et al. [13] described *Aurantiochytrium* sp. pyrolysis using a lumped model involving three reactions, which included algae → bio–oil → gases, and algae → gases. The apparent activation energy of bio-oil formation was found to be 71.16 kJ mol^{-1}. Bach and Chen [14] utilized one, two, three, four and seven-reaction models, and found that the seven-reaction model described well the pyrolytic mass loss profiles of *Chlorella vulgaris*. Bui et al. [15] used five pseudo–component mechanism to model the pyrolysis of *Chlamydomonas* sp. and -*Chlorella sorokiniana*, and determined the apparent kinetic parameters. A multi-step model involving devolatilization and oxidation to describe the pyrolysis of *Nannochloropsis gaditana*, *Scenedesmus almeriensis* and *Chlorella vulgaris* is reported to fit the pyrolysis mass loss data [16]. In a recent study by Gautam et al. [17], first order and one-dimensional diffusion models matched the experimental data obtained under isothermal fast pyrolysis conditions in the temperature range 400–700 °C for *Nannochloropsis oculata*, *Chlorella vulgaris*, *Arthrospira platensis* and *Schizochytrium limacinum*. The models employed in these studies are based on a simplified assumption that each microalgae component decomposes with a single activation energy. Nevertheless, the complex structure of the components requires a range of activation energies to describe the dissociation of various types of bonds present in proteins, carbohydrates and lipids.

Distributed activation energy model (DAEM) is a multiple reaction model, which is widely used to describe the decomposition behavior of solid and liquid fuels [18]. The model assumes that decomposition occurs via large number of independent, parallel, first-order reactions with different activation energies reflecting the varying bond strength of the species [19]. Models based on three parallel first-order reactions corresponding to the decomposition of hemicellulose, cellulose and lignin have been successfully used to describe the pyrolysis of lignocellulosic biomass [20]. The DAEM has been successfully extended for the kinetic study of pyrolysis of the freshwater alga, *Chlorococcum humicola* [21]. Ceylan and Kazan [22] investigated the pyrolysis behavior and kinetics of *Nannochloropsis oculata* and *Tetraselmis* sp. The devolatilization behavior was explained using a simplified DAEM approach. In a recent study, Simao et al. [23] used multiple models such as Miura-Maki DAEM, independent parallel reaction model and isoconversional kinetic models of Friedman and Flynn-Wall-Ozawa to study the pyrolysis behavior of *Spirulina maxima*. The use of zeolites was found to enhance the production of aromatic hydrocarbons by five times. Soria-Verdugo et al. [24] comprehensively applied and compared isoconversional models and DAEM to study the pyrolysis behavior of six different microalgae species, viz., *Chlorella vulgaris*, *Isochrysis galbana*, *Nannochloropsis gaditana*, *Nannochloropsis limnetica*, *Phaeodactylum tricornutum*, and *Spirulina platensis*.

In this study, a four-parallel-reaction DAEM is developed to describe the pyrolysis kinetics of *Nannochloropsis oculata*. As the fundamental composition of microalgae is different from lignocellulosic biomass, TG mass loss experiments of bovine serum albumin, starch and sunflower oil, representing protein, carbohydrate and lipid, respectively, were first conducted to map the decomposition of the pseudo-components to the primary constituents in the algae. This study is unique as the decomposition regimes of the pseudo-components described by the model were validated using the experimental composition of the pyrolysis products obtained at different temperature regimes. More importantly, the high temperature decomposition regime at 800–1000 °C observed for this microalga was assigned to the fourth pseudo-component, which is nothing but secondary decomposition of char, based on both model and experimental product composition data. The decomposition regimes were then deconvoluted and the kinetic parameters were obtained for the pseudo-components.

Table 1
Characterization of *N. oculata* used in this study. The data are presented as the mean ± S.D., $n = 3$.

Proximate analysis[a]			Ultimate analysis[a]					Nutritional analysis[c,d,e]			HHV (MJ kg^{-1})
VM (%)	FC (%)	A (%)	C (%)	H (%)	N (%)	S (%)	O[b] (%)	Proteins (%)	Lipids (%)	Carbohydrates (%)	
64.9 ± 2.4	30.8 ± 1.3	4.3 ± 0.2	35.6 ± 1.2	6.7 ± 0.1	5.2 ± 0.2	0.5 ± 0.06	47.7 ± 2.0	69	21	10	18.0 ± 0.5

VM = volatile matter, FC = fixed carbon, A = ash. All percentages are wt%.

[a] % dry basis

[b] By difference, O(%) = 100 − C − H − N − S − ash.

[c] Algal bio-chemical composition from http://www.oilgae.com/algae/comp/comp.html (accessed on 9 Jun 2018).

[d] Reed Mariculture Inc. reedmariculture.com/support_algae_nutritional_proximate_profile.php (accessed on 9 Jun 2018).

[e] Dry ash free basis.