



Thermal degradation of carbohydrates, proteins and lipids in microalgae analyzed by evolutionary computation



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ABSTRACT

The kinetics of microalgae pyrolysis is investigated to analyze the thermal degradation of carbohydrates, proteins and lipids in different species of microalgae. The pyrolysis processes of microalgae *Chlorella vulgaris* ESP-31, *Nannochloropsis oceanica* CY2, and *Chlamydomonas* sp. JSC4 are examined by thermogravimetric analysis (TGA), and independent parallel reaction (IPR) model is adopted to approach the pyrolysis kinetics. To maximize the fit quality between the established kinetic models and experimental data, particle swarm optimization (PSO), a kind of evolutionary computation, is employed. The thermal degradation characteristics of the three microalgal species are compared with each other. The results suggest that the thermal degradation curves of the three microalgae can be predicted with a fit quality of at least 97.9%. The activation energies of carbohydrates, proteins, and lipids in the microalgae are in the ranges of 53.28–53.30, 142.61–188.35, and 40.21–59.23 kJ mol⁻¹, respectively, while the thermal degradation of carbohydrates, proteins, and lipids are in temperature ranges of 164–497, 209–309, and 200–635 °C, respectively. It is proved in this work that the IPR model and the calculation of the PSO can be used to predict the pyrolysis kinetics of microalgae to a good level of fitness.

1. Introduction

Renewable energy sources are becoming more and more important as alternatives to fossil fuels. Bioenergy is one of the largest parts of renewable energy. Different types of materials have been investigated as biomass resources, including microalgae, crop residues, manure, and lignocellulosic biomass [1,2]. Many routes for utilizing biomass have been developed to produce different phases of biofuel, including gasification, liquefaction, carbonization, and pyrolysis. Among these, pyrolysis, which is applied to remove the volatile matter of biomass under an atmosphere without oxygen, is considered as a fundamental process, and it is thus important to study the characteristics of related reactions and products [3]. Thermogravimetric analysis (TGA) has become the most widespread technique to achieve this, due to its advantage in identifying the weight and temperature of the samples continuously and precisely. Furthermore, the data from TGA could be used to obtain derivative thermogravimetric (DTG) analysis to inspect the degradation behavior of biomass in a thermal conversion process.

Microalgae have been applied as a promising biomass feedstock, because of their wide distribution, high growth rates, and less

competition with terrestrial crops in cultivated land [4,5]. Microalgae are microorganisms that can perform photosynthesis at high efficiency, which means they can capture CO₂ from the atmosphere and even faster than terrestrial plants [6]. Generally, there are three main components in microalgae: carbohydrates, proteins, and lipids. Depending on the species of microalgae, the mass contents of these main components and other elements are different, which means the characteristic of the biofuel produced by microalgae would be affected by the species used. Additionally, microalgae are considered to have a high potential to take the place of fossil fuels for power generation and transportation, thus reducing CO₂ emissions [7]. Pyrolysis and thermochemical liquefaction are the most technically practical methods for the conversion of algal biomass-to-biofuels, after the extraction of oils from algae [8].

Accurate kinetic models are needed to investigate the details of thermal decomposition processes. Such models are practical tools to predict not only the biomass pyrolysis, but also the torrefaction process, which can be used to describe the mass loss of the components during the conversion process using calculations [9]. Due to the adoption of the Arrhenius equation, the activation energy (E_a) and the pre-exponential factor (A) are two important parameters to build models for

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Nomenclature			
α	conversion degree	$\left(\frac{d\alpha}{dT}\right)_{exp,i}$	the conversion rate of the experiment ($^{\circ}\text{C}^{-1}$)
A	pre-exponential factor (s^{-1})	$\left(\frac{d\alpha}{dT}\right)_{cal,i}$	the conversion rate of the calculation ($^{\circ}\text{C}^{-1}$)
Ea	activation energy (kJ mol^{-1})	v_i	the velocity of the i -th particle
R	the universal gas constant ($= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)	x_i	the position of the i -th particle
T	absolute temperature (K)	N_{var}	the number of variables
m_i	the mass at initial temperature (mg)	k	the number of iterations
m_T	the mass at given temperature (mg)	β_c, α_c	the momentum constant
m_f	the mass at final temperature (mg)	φ_1	the cognitive learning rate
β	the heating rate ($^{\circ}\text{C s}^{-1}$)	φ_2	the social learning rate
c_i	the mass fraction of each composition	$rand()$	random number
N	the number of the components	$pbest_i$	the best position of the i -th particle
OBJ	objective function	$gbest$	the global best position
		$N_{particle}$	the number of particles

non-isothermal conversion. Many kinds of models have been developed and applied to establish the kinetics of pyrolysis, including single-step model [10], multiple parallel reaction model [11], sectional approach model [12], distributed activation energy model (DAEM) [13], and so on. However, if a precise result is needed then a single-step model is not recommended due to its simplicity [11], and thus a multiple parallel reaction model is selected in this study. Research has shown that such a model could build a simulated DTG curve that perfectly coincided with the experimental one [11]. It has also been proven that the pyrolysis kinetics of microalgae could be simulated by multiple pseudo-components models [14].

Evolutionary computation (EC) is a well-known technique applied to design, simulate, and solve optimization problems. The concept of EC is based on the mechanism of natural evolution. Compared with traditional algorithms, EC can solve optimization problems with more parameters due to its characteristic based on particle numbers. The execution steps with EC can generally be divided into three parts: (1) identify the expressing form of the target problem; (2) select the method to calculate the fitness value of the particles to target problem; (3) define the appropriate selection and variation operators [15]. Various kinds of EC have been developed, such as the genetic algorithm (GA), differential evolution (DE), ant colony optimization (ACO), and particle swarm optimization (PSO). As described earlier, the pyrolysis reaction of biomass is fairly complicated, and thus EC is a potential tool to solve the large number of parameters involved in pyrolysis kinetics. Different types of EC have been applied in the field of pyrolysis kinetics for different materials [16–19].

TGA has been extensively performed to figure out the thermal

degradation characteristics of microalgae. In general, carbohydrates and proteins are thermally decomposed at lower temperatures, whereas lipids have higher degradation temperatures. However, it appears that the thermal degradation temperatures of the three constituents in microalgae have not been defined completely. Particle swarm optimization (PSO), a kind of EC, is a technique that finds the optimal solution by comparing the empirical position of each particle with regard to a fitness value. PSO was first proposed by Kennedy and Eberhart in 1995 [20], and the mechanism is based on the social behaviors of the groups of animals, assuming each particle has the abilities of memory and sharing knowledge [21], such as the flocking process of birds [22]. PSO has the merits of low CPU and memory demands, and the program can be simply implemented [22]. To the best of the authors' knowledge, PSO has not been applied in the field of pyrolysis kinetics, and is thus employed to construct the pyrolysis kinetics of microalgae in the present work. The application of PSO [22–26] is shown in Table 1. In this study, the pyrolysis kinetics of three different microalgae are evaluated. Based on the obtained results, the thermal decomposition temperatures of carbohydrates, proteins, and lipids are analyzed to provide useful information for the pyrolysis of microalgae.

2. Methods

2.1. Materials

Three different microalgae, including *Chlorella vulgaris* ESP-31 (*C. vulgaris* ESP-31), *Nannochloropsis oceanica* CY2 (*N. oceanica* CY2), and *Chlamydomonas* sp. JSC4 (*C. sp.* JSC4), were chosen as feedstocks in this

Table 1
Applications of PSO.

Method	Application Fields	Equation	Target	Reference
Novel momentum-type PSO	Engineering optimization	$\vec{v}_i^{k+1} = \vec{V}_i^k + \beta_c \times \Delta \vec{v}_i^k$ $\vec{x}_i^{k+1} = \vec{x}_i^k + \alpha_c \times \vec{v}_i^{k+1}$ $\vec{V}_i^k = \varphi_1 rand() (pbest_i - \vec{x}_i^k) + \varphi_2 rand() (gbest - \vec{x}_i^k)$	Unconstrained and constrained problems	[22]
DPSO	Ship hydrodynamics problems	$\vec{v}_i^{k+1} = \chi [\vec{v}_i^k + \varphi_1 (pbest_i - \vec{x}_i^k) + \varphi_2 (gbest - \vec{x}_i^k)]$ $\vec{x}_i^{k+1} = \vec{x}_i^k + \vec{v}_i^{k+1}$ (χ is the constriction factor.)	Resistance to weight ratio	[23]
PSO	Distribution systems with wind turbine generators	$\vec{v}_i^{k+1} = w \vec{v}_i^k + \varphi_1 rand()_1 (pbest_i - \vec{x}_i^k) + \varphi_2 rand()_2 (gbest - \vec{x}_i^k)$ $\vec{x}_i^{k+1} = \vec{x}_i^k + \vec{v}_i^{k+1}$ (w is the inertia weight which is normally in the range of 0–1)	Minimized power losses	[24]
PSO-ICA	Optimal reactive power dispatch	$\vec{v}_{ij}^{k+1} = w \vec{v}_{ij}^k + \varphi_1 rand()_{1j} (pbest_{ij} - \vec{x}_{ij}^k) + \varphi_2 rand()_{2j} (gbest - \vec{x}_{ij}^k)$ $\vec{x}_i^{k+1} = \vec{x}_i^k + C \vec{v}_i^{k+1}$ (j is the dimension of the particle, C is the constriction factor.)	Minimized power losses and voltage distribution	[25]

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