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A comprehensive study on pyrolysis kinetics of microalgal biomass

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ABSTRACT

Pyrolysis of microalgal biomass for biofuels production has attracted much attention. However, detailed degradation mechanism and kinetics of the process have not been fully explored yet. In this study, a non-isothermal pyrolysis of microalga *Chlorella vulgaris* ESP-31 is thermogravimetrically investigated. Several kinetic models, from a single reaction to seven parallel reactions, are tested to fit the experimental pyrolysis data for finding out the optimal pyrolysis model. The results show that the pyrolysis behavior of the microalga is somewhat different from that of lignocellulosic biomass, stemming from the inherent difference in their compositions. Overall, the kinetic modeling processes show that increasing the number of reactions improves the model fit quality. Curve fitting results indicate that the models consisting of three and less than three reactions are not suitable for microalga pyrolysis. The four-reaction model, via considering the pyrolysis of carbohydrate, protein, lipid and others, can be employed for modeling the thermal degradation; however, it cannot precisely predict the thermal degradation of the shoulder and the small peak. The conducted seven-reaction model further partitions the decomposition processes of carbohydrate and protein into two stages, and explains the thermal degradation well. The model indicates that the devolatilization peak is attributed to the combined degradation of *Protein I* and *Carbohydrate II*. The seven-reaction model offers the highest fit quality and is thus recommended for predicting the microalga pyrolysis processes.

1. Introduction

Biomass is a potential source of renewable energy, which is receiving a great deal of attention due to its advantages over other alternative energy sources [1]. Biomass derived fuels can be categorized into first, second, and third generation biofuels. First generation biofuels are produced from food crops such as sugarcane, corn, potato, wheat, and sugar beet. This directly affects human food supplies and biodiversity [2]. Second generation biofuels are produced from non-food or lignocellulosic biomass and biomass residues such as switchgrass, grass, jatropha, miscanthus, husk, wood chips, leaves and stump. Non-food biomass does not threaten food supplies; however, its planation will compete with arable lands for food crops and influence nutrient cycles and soil conservation [3]. The disadvantages of first and second generation biofuels can be overcome by exploiting algal biomass, which is considered as the potential feedstock for third generation biofuels. Unlike land-based lignocellulosic biomass, algal biomass can be cultivated in fresh, saline, or waste water [4], and thus requires no land allocation. Moreover, compared to terrestrial biomass, algal biomass, including microalgae and macroalgae, has higher growth rate and photosynthetic efficiency, and hence can absorb more CO_2 during its growth [5,6]. This enables more efficient reduction in the greenhouse gas emissions [7], and even achieves CO_2 utilization [8].

Many thermochemical conversion processes can be employed to convert microalgal biomass into energy-dense biofuels such as bio-oils and biochars [9–11]. Pyrolysis is a thermal conversion route in which microalga is heated at elevated temperatures (400–800 °C) and in an oxygen-free atmosphere [12]. The pyrolysis products include bio-oils and biochars as well as a small fraction of permanent gases, and their distribution usually depends on the operating parameters such as temperature (or heating rate) and residence time [13]. Pyrolysis at high temperatures with short residence times yields more bio-oil. On the other hand, biochar production is favored for pyrolysis at low temperatures with long residence times. Both bio-oils and biochars can be used directly for combustion to produce heat and power. Bio-oils can be further upgraded to produce liquid transport fuels and bio-chemicals, while biochars can be used as activated carbon, soil enhancer, fertilizer, etc.

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Nomenclature

Abbreviations

daf	dry and ash free basis
db	dry basis
DTG	differential thermogravimetric
TG	thermogravimetric
TGA	thermogravimetric analysis
wt	weight
LTSC/HTSC	low/high thermal stable components
Comp	component
FWO	Flynn-Wall-Ozawa model
KAS	Kissinger-Akahira-Sunose model
DAEM	distributed activation energy model
SSGM	single-step global model
Cal.	calculated data
Exp.	experimental data

Symbols

A	pre-exponential factor (s^{-1})
c	contribution factor
$k(T)$ or k	reaction rate constant (s^{-1})
m	sample mass at any time (g)
m_0	initial sample mass (g, at 105 °C)
m_f	final residual mass (g, at 700 °C)
R	universal gas constant (=8.314 $J \cdot mol^{-1} \cdot K^{-1}$)
T	absolute temperature (K)
t	conversion time (s)
α	conversion degree

Subscript

i	ith component

As an important conversion of microalgal biomass into biofuels, pyrolysis has received great attention recently. The number of works on microalgae pyrolysis has been increasing in order to assess the chemical, physical and fuel properties of microalgae bio-oils and to compare with lignocellulosic biomass bio-oils. It has been reported that bio-oils produced from microalgal biomass are more stable than those from lignocellulosic biomass [10]. Moreover, microalgae bio-oils contain less oxygen and have greater heating value than lignocellulosic biomass bio-oils [14]. In addition to researches on the properties of microalgae bio-oils, kinetic studies have been also conducted to investigate the pyrolysis behavior of microalgae. In practice, pyrolysis kinetics is highly related to chemical reaction control and reactor design. For this purpose, thermogravimetric technique has become a proven method and been widely used by many researchers [15–21]. It has been pointed out that microalgae pyrolysis undergoes three stages. In the first stage, water is removed from microalgae. The mass loss in this stage is associated with the moisture content of the feedstock. Main microalgal components, including carbohydrate, protein and lipid, are thermally degraded in the second stage, which accounts for most of the mass loss during pyrolysis. In the last stage, only slight mass loss is observed which is attributed to the decomposition of carbonaceous matters in the solid residues. In some studies [22], the thermal decomposition of lipid is partitioned from that of carbohydrate and protein, whereby four-stage thermal degradation of microalgae is defined.

Although pyrolysis kinetic researches of microalgal biomass are active, most of the available studies employed simplified kinetics models. In other words, deep knowledge about the reaction mechanism from the obtained kinetic data is insufficient. A number of recent studies regarding pyrolysis kinetic of various microalgae are summarized in Table 1 in which a variety of methods were conducted. As can be seen from the table, the available studies employed several approximation and transformation of the Arrhenius expression to estimate the values of activation energy and pre-exponential factor at different conversion rates. As a result, the values of the two kinetic parameters are normally in a range, from which mean values can be calculated and they represent the whole microalgal biomass, even though the microalgae contain several components whose reactivity and kinetic parameters are different. In addition, these models cannot reproduce the predicted thermogravimetric curves or provide any information about the fit quality between the modeled and experimental data. Consequently, the evaluation of these models is difficult. More complex kinetic models, e.g., multiple reaction models, are available and have been successfully applied to analyze the pyrolysis behaviors of several lignocellulosic biomass materials [23–26]. However, applicability of these models for microalgae pyrolysis is still unclarified because the main components of microalgae (i.e., carbohydrates, proteins and lipids) differ from those of lignocellulosic biomass (i.e., hemicellulose, cellulose and lignin). In order to address this issue, a variety of microalga pyrolysis models are tested in this study, from which more comprehensive information and better understanding of microalga pyrolysis mechanism can be obtained.

In this study, various kinetic models from a single to multiple parallel reactions are tested in order to figure out the optimal pyrolysis model which is applicable for microalgal biomass pyrolysis. For this purpose, microalga *Chlorella vulgaris* ESP-31 was pyrolyzed in a nitrogen atmosphere along with a non-isothermal

Table 1
Summary of recent pyrolysis kinetic studies on various microalgae.

Feedstock	Method[a]	Main results	Refs.
Dunaliella tertiolecta	FWO, KAS	Mean activation energy: 145.7 kJ/mol in KAS method and 146.4 kJ/mol in FWO method	[15]
Chlorella spp.	Freeman-Carroll	Activation energy: 71.3–79.2 kJ/mol Pre-exponential factor: $1.47–1.62 \times 10^6$ min^{-1}	[16]
Chlorella vulgaris	FWO, KAS, regression	Mean activation energy: 66.7 kJ/mol in KAS method and 61.7 kJ/mol in FWO method	[17]
Chlorella pyrenoidosa (CP) and *Spirulina platensis* (SP)	Vyazovkin	Activation energy: 8.85–114.5 kJ/mol for CP and 74.35–140.1 kJ/mol for SP	[18]
Scenedesmus almeriensis (SC), *Nannochloropsis Gaditana* (NG) and *Chlorella vulgaris* (CV)	Órfão	Activation energy: 63.5 kJ/mol for CV, 128.1 kJ/mol for NG, 79.6 kJ/mol for SC	[19]
Nannochloropsis oculata (NO) and *Tetraselmis* sp. (TS)	Simplified DAEM	Highest activation energy: 152 kJ/mol for NO and 334 kJ/mol for TS	[20]
Chlorella pyrenoidosa	SSGM, simplified DAEM	Mean activation energy: 143.7 kJ/mol in SSGM and 100.6 kJ/mol in simplified DAEM	[21]

[a] Abbreviations are explained in Nomenclature.