



Analyzing the pyrolysis kinetics of several microalgae species by various differential and integral isoconversional kinetic methods and the Distributed Activation Energy Model



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ABSTRACT

The pyrolysis kinetics of the microalgae *Chlorella vulgaris* (CV), *Isochrysis galbana* (IG), *Nannochloropsis gaditana* (NG), *Nannochloropsis limnetica* (NL), *Phaeodactylum tricornutum* (PT), and *Spirulina platensis* (SP) were studied by non-isothermal thermogravimetric analysis conducted at nine different constant heating rates. The kinetic parameters of each microalgae species were calculated using several kinetic methods, such as those of Kissinger, Friedman, Ozawa-Flynn-Wall (OFW), Kissinger-Akahira-Sunose (KAS), Vyazovkin, and the simplified Distributed Activation Energy Model (DAEM). The results show that the kinetic parameters calculated from the integral isoconversional methods OFW, KAS and Vyazovkin are similar to those determined by applying the simplified DAEM. In contrast, application of the differential isoconversional method of Friedman led to moderate deviations in the activation energies and pre-exponential factors computed, whereas the unique values of the kinetic parameters determined by the Kissinger method resulted in the highest deviations.

1. Introduction

Pyrolysis of microalgae produces solid, liquid, and gaseous products of interest, which can be employed as sources of energy and/or chemicals. Pyrolysis is a process by which the biomass is thermally degraded in the absence of oxygen at moderate temperatures between 350 °C and 700 °C [1]. Knowledge of the thermal behavior of microalgae during the pyrolysis process, especially their apparent kinetics, is a crucial factor for the efficient use of this type of biomass as a source to produce biofuels [2]. A deeper knowledge of the pyrolysis process will serve as a useful tool for the design and operation of pyrolysis reactors with higher efficiency [3]. A widely used technique employed to study the pyrolysis of solid fuels is thermogravimetric analysis (TGA), which permits the calculation of pyrolysis kinetic parameters from the measurement of the evolution of the mass of a sample subjected to a temperature increase in an inert atmosphere. Based on TGA measurements, several mathematical models have been developed to describe the kinetic mechanism of the pyrolysis process, such as the Kissinger method [4,5], the single step model [6], the parallel reactions model [7], the three pseudo-components model [8], the sectional approach model [9], the Distributed Activation Energy Model (DAEM) [10], or

isoconversional methods [11]. Isoconversional methods can be further divided into two categories [12]: differential methods and integral methods. The most common differential method is the Friedman method [13], whereas there is a wide variety of integral methods, among which the most commonly used are the Ozawa-Flynn-Wall (OFW) method [14,15], the Kissinger-Akahira-Sunose (KAS) method [4,16], and the Vyazovkin method [17]. Integral methods are more universal due to their higher tolerance to experimental noise compared to differential methods, for which the use of derivatives propagates the effect of noise, reducing the accuracy of the results [18].

The kinetics of microalgae pyrolysis based on TGA measurements was recently reviewed by Bach and Chen [19]. The kinetics of multiple microalgae species has been studied applying either kinetic fitting or kinetic free models. For kinetic fitting models, the single reaction model, which assumes that microalgae are directly decomposed into char and volatiles, is very simple, but the fitting quality of this model to describe the pyrolysis of microalgae samples is quite poor [19]. Among the kinetic fitting models, multiple parallel reaction models are widely used to describe microalgae pyrolysis. These models were originally developed to characterize the pyrolysis of the three main components of lignocellulosic biomass, i.e., hemicellulose, cellulose and lignin [20].

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Nomenclature			
A	Pre-exponential factor [s^{-1}]	$S2_{(s)}$	Solid product
α	Conversion [%]	t	Time [s]
β	Heating rate [$K s^{-1}$]	T	Temperature [K]
E	Activation energy [$J mol^{-1}$]	T_0	Ambient temperature [K]
g	Stoichiometric coefficient within a reaction for a gaseous product [–]	T_{max}	Temperature at maximum rate of reaction [K]
$G_{(g)}$	Gaseous product [–]	Abbreviations	
k	Rate coefficient of a first order reaction [s^{-1}]	CV	<i>Chlorella vulgaris</i>
m	Mass of the sample remaining at time t [kg]	DAEM	Distributed Activation Energy Model
m_0	Initial mass of the sample [kg]	DTG	Derivative Thermogravimetric
m_f	Final mass of the sample [kg]	FAME	Fatty Acid Methyl Ester
n	Order of the pyrolysis reactions [–]	HHV	High Heating Value
N	Number of TGA curves obtained at different heating rates [–]	IG	<i>Isochrysis galbana</i>
R	Universal gas constant [$J mol^{-1} K^{-1}$]	KAS	Kissinger-Akahira-Sunose
s_1	Stoichiometric coefficient within a reaction for a solid reactant [–]	NG	<i>Nannochloropsis gaditana</i>
s_2	Stoichiometric coefficient within a reaction for a solid product [–]	NL	<i>Nannochloropsis limnetica</i>
$SI_{(s)}$	Solid reactant	OFW	Ozawa-Flynn-Wall
		PT	<i>Phaeodactylum tricornutum</i>
		SP	<i>Spirulina platensis</i>
		TGA	Thermogravimetric analysis

Due to differences in composition between lignocellulosic and microalgal biomass, the number of parallel reactions for the model was modified to account for the pyrolysis of carbohydrates, proteins, lipids, and other minor components of microalgae [21,22].

In contrast to fitting kinetic models, free kinetic models require no assumptions about the form of the conversion rate pyrolysis curve. Using kinetic free models to describe the pyrolysis of microalgae, the Vyazovkin method was applied by Gai et al. [23] to analyze the pyrolysis of *Chlorella pyrenoidosa* and *Spirulina platensis*, whereas the Kissinger method was employed to study the pyrolysis of periphytic microalgae [24] and the salt-water cord grass *Spartina alterniflora* [25]. The differential isoconversional method of Friedman was applied to describe the pyrolysis of the red algae *Kappaphycus alvarezii* [26], and the salt-water cord grass *Spartina alterniflora* [25]. The integral isoconversional methods of OFW and KAS have been applied to determine the pyrolysis kinetics of a broad range of microalgae species, including *Chlorella* sp. [27], *Chlorella vulgaris* [28–32], *Dunaliella tertiolecta* [33], *Kappaphycus alvarezii* [26], *Tetraselmis suecica* [27], and the salt-water cord grass *Spartina alterniflora* [27]. The simplified Distributed Activation Energy Model (DAEM) has also been widely applied to investigate the pyrolysis of several microalgal species, for instance *Chlorella humicola* [34], *Chlorella pyrenoidosa* [35], *Chlorella sorokiniana* [36], *Chlorella vulgaris* [37], *Dunaliella tertiolecta* [38], *Monoraphidium* [36], *Nannochloropsis oculata* [2], and *Tetraselmis* sp. [2]. Although many studies concerning the kinetics of microalgae pyrolysis are based on TGA measurements, they are limited in number compared to studies in other reactors such as fixed or fluidized beds [19]. Furthermore, most studies on the pyrolysis kinetics of microalgae available in the literature are based on a reduced number of TGA curves and, due to the limited number of investigation points on which they are based, these kinetic models cannot provide information about the fit quality of the models [19].

In this work, the pyrolysis kinetics of several microalgae species was investigated using non-isothermal thermogravimetric analysis (TGA). Six microalgae species were selected for the pyrolysis study to cover a broad range of biological and chemical properties, as well as growing conditions: *Chlorella vulgaris* (CV), *Isochrysis galbana* (IG), *Nannochloropsis gaditana* (NG), *Nannochloropsis limnetica* (NL), *Phaeodactylum tricornutum* (PT), and *Spirulina platensis* (SP). In contrast to studies available in the literature that are typically based on a reduced number of TGA curves, the TGA pyrolysis measurements were conducted for

each microalgae species, using nine different constant heating rates of 10, 13, 16, 19, 22, 25, 30, 35, and 40 K/min over a temperature range from 100 °C to 800 °C. The experimental results obtained from the TGA pyrolysis measurements were employed to calculate the pyrolysis kinetics parameters of the samples applying various kinetic methods: Kissinger, Friedman, OFW, KAS, Vyazovkin, and simplified DAEM. Moreover, the high number of TGA curves employed to analyze the pyrolysis kinetics of each microalgae sample permits characterization of the experimental measurements reliability and the fit capability of the kinetic models based on the quality of the linearization of the Arrhenius plots [39].

2. Pyrolysis kinetics

The kinetics of chemical reactions in solids, such as $s_1 SI_{(s)} \rightarrow s_2 S2_{(s)} + g G_{(g)}$, can be described by the rate of disappearance of the reactant SI [6], which is usually determined as a derivation of the law of mass action, originally proposed by Guldberg and Waage [40]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha), \quad (1)$$

where α is the conversion, t is the time, da/dt is the rate of reaction, $k(T)$ is the rate coefficient at an absolute temperature T , and $f(\alpha)$ is a function of α , with its exact form depending on the order of the kinetic model. The conversion α of the sample can be calculated from the mass loss of the sample during the chemical reaction:

$$\alpha = 1 - \frac{m - m_f}{m_0 - m_f} = \frac{m_0 - m}{m_0 - m_f}, \quad (2)$$

where m is the mass of the sample remaining at time t , m_f is the final mass of the sample when the reaction is completed, and m_0 is the initial mass of the sample.

The reaction rate coefficient $k(T)$ can be expressed as a function of the absolute temperature T using various equations [41], however, the most widely used expression for the rate coefficient is [42]:

$$k(T) = A \exp\left(-\frac{E}{RT}\right), \quad (3)$$

where A is the pre-exponential factor, E is the activation energy, and R is the universal gas constant.

Considering the Arrhenius relation for the rate coefficient and the

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