



A kinetic study on the effects of alkaline earth and alkali metal compounds for catalytic pyrolysis of microalgae using thermogravimetry



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HIGHLIGHTS

- Alkali and alkaline earth metals compounds can promote the degradation of microalgae organic matters.
- Alkali and alkaline earth metals compounds can increase the initial decomposition temperatures of microalgae pyrolysis.
- Alkali and alkaline earth metals compounds can affect the microalgae pyrolysis overall activation energy.

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ABSTRACT

In this paper, thermogravimetric (TG) analysis and kinetic modeling are applied to study the effects of alkaline earth and alkali metal compounds on catalytic thermal decomposition of microalgae. When alkaline earth and alkali metal compounds are added, the initial thermal degradation temperatures increased by about 3.2–10.2 K, and the final temperatures reduced by about 3.5–9.4 K. The results show that CaO, MgO, K₂CO₃, BaCO₃ and Na₂CO₃ may shorten the time of pyrolysis, implying that alkaline earth and alkali metal compounds may promote the process of thermal degradation of organic matters. The first maximum weight loss rate is in the order of Na₂CO₃ > CaO > K₂CO₃ > BaCO₃ > MgO > no additive. E_m (weight means activation energy) varies from 99.60 to 134.05 kJ mol⁻¹, which implies ignorable overall activation energies (E_m) after alkaline earth and alkali metal compounds are added.

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1. Introduction

Biofuel receives increasingly concerns from governments and scientists all over the world, due to its ease of treatment, storage and transportation [1]. At present, grain, a common raw material for biofuel production, becomes a threat to food supply, which further, affects the social and economic stability. It is clearly stated in the “Corn processing project on strengthening the management of emergency notice” that China will insist on promoting non-grain-based biofuel industry [2]. Microalgae are single-cell algae and rich in fat, protein and carbohydrates, besides it can effectively convert CO₂, H₂O, and inorganic salts into organic substances through solar energy. Compared with other biomass resources, microalgae has the following distinctive characteristics [3–6]: high photosynthetic efficiency and environmental adaptability, short

growth cycle, independence from soil, automatic breeding process, capability to produce high-molecular-weight hydrocarbons with high calorific value and very little sulfur and nitrogen.

To make the best use of all algae cells, several researchers began to convert algae into high-energy-density liquid biofuel through thermal degradation technology. In 1993, Ginzburg [7] successfully applied thermal decomposition of microalgae for low-nitrogen liquid substance, which produced a high-quality low-sulfur bio-oil. Other researchers have made further studies and progresses in the microalgae pyrolysis of biofuel [8–11]. According to previous research results, in order to produce liquid biofuel from microalgae, the maximum liquid biofuel production portion of heterotrophic microalgae is 57.9% and autotrophic microalgae is 35.83%, with others as gas or solid. Therefore, further exploration is necessary to improve the overall bio-oil yield (conversion level).

The application of alkali and alkali-earth salts in coal and other biomass catalytic pyrolysis has been extensively studied [12–15]. The results show that the oil production rate is higher, with the addition of catalyst in the process of biomass pyrolysis. With

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intermediate temperatures, K^+ and Ca^{2+} catalytic pyrolysis mainly occurs in the solid phase, and only a very small amount of liquid or gas is generated. Different categories of ion selective catalytic reaction are formed and the process of molecular bond breaking in fission and disproportionation reaction is accelerated. This feature provides a guarantee for the preparation of bio-oil conditions. Therefore, catalyst can improve the conversion rate of biomass pyrolysis process. However, the catalysis of alkaline earth and alkali metal compounds for microalgae thermal decomposition has not been addressed and is worth for further studies.

This paper will discuss the microalgae catalytic pyrolysis with alkaline earth and alkali metal compounds. The powdery microalgae was mixed with alkaline earth and alkali metal compounds (including $BaCO_3$, K_2CO_3 , Na_2CO_3 , MgO , and CaO), respectively. The catalytic thermal degradation was conducted by a TG analyzer. The heating rate of TG analyzer is $10\text{--}30\text{ K min}^{-1}$, the reaction atmosphere is nitrogen (N_2), and the temperature range is from ambient temperature to $1000\text{ }^\circ\text{C}$. The kinetic parameters are decided by Flynn Wall Ozawa (FWO) and Kissinger Akahira Sunose (KAS) methods, to evaluate the effects of catalytic pyrolysis.

2. Materials and methods

2.1. Materials

The microalgae used in this study were *Chlorella vulgaris* produced by Jiangmen City Yue Jian Biotechnologies Company Limited in China. Barium Carbonate ($BaCO_3$), potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3), Magnesia (MgO) and calcium oxide (CaO) were used as catalyst in the experiments.

Samples of *Chlorella vulgaris*, alkaline earth and alkali metal compounds were kept in a $105\text{ }^\circ\text{C}$ drier for about 24 h, were then grinded into particles with no more than 200 microns. After the above pretreatment, the samples were laid in a container with desiccant.

Additives were mixed on microalgae through mechanical mixing method, the specific processes are as follows: take samples that weigh 200 g, and additive that weighs 2 g, then they were poured into a mortar in order to mix them thoroughly, and were then grinded; finally, the mixed microalgae sample was placed in a vacuum oven for 14 h, and dried at $80\text{ }^\circ\text{C}$.

The ultimate analysis and proximate analysis were tested according to GB/T212-2008, GB211-84 and ASTM D5373-08, respectively. Heat figures were valued based on ASTM D5468-02 and ASTM E870-82. The proximate analysis, ultimate analysis and low calorific value were listed in Table 1.

2.2. Equipment and experimental procedures

A thermogravimetric Analyzer (model: NETZSCH STA 409 PC Luxx) was used for TG analysis. A crucible, placed on sample carrier, was made of Al_2O_3 . The thermocouple of type S was welded on heating metal coil in a furnace, with the temperature reproducibility $\pm 3\text{ }^\circ\text{C}$, and the temperature precision was $\pm 0.1\text{ }^\circ\text{C}$. The

Table 1
Ultimate, proximate analyses and calorific value of *Chlorella vulgaris* (wt.% on dry basis).

Ultimate analysis (wt.%)					Proximate analysis (wt.%)			LCV (MJ kg ⁻¹)
C	H	O	N	S	Volatile	Ash	Fixed carbon	
47.84	6.41	25	9.01	1.46	55.37	10.28	34.35	21.88

Note: LCV, low calorific value.

balance mass precision was 0.001 mg. In the crucible, about 3.5 mg samples were placed uniformly, and the temperature was linearly raised from ambient temperature (about $35\text{ }^\circ\text{C}$) to $1000\text{ }^\circ\text{C}$ with a heating rate of $30\text{ }^\circ\text{C min}^{-1}$. There was no additional hold at a temperature. The pyrolysis atmosphere of desired gas flow rate was a constant of 100 mL min^{-1} . Transmission error of the experimental system was 0.01%.

2.3. Characteristic parameters of temperatures and increment of weight loss

The onset and end thermal degradation temperatures represent how severe the reaction was. The peak temperature (T_p), corresponding to the maximum weight loss rate ($d\alpha/dt$), was related to the fuel property. The onset temperature (T_0) of microalgae thermal decomposition was defined as the temperature at a weight loss rate of 5%. The end decomposition temperature (T_f) was defined as the temperature at a weight loss rate of 95%. DTG_p was the differential thermalgravity value at a peak temperature.

Δm [16] was obtained to further explain the effectiveness of these five additives on the conversion of microalgae samples as.

$$\Delta m = m_c - m_w \quad (1)$$

where Δm as the increment of weight loss after mixing alkali and alkaline earth with microalgae samples, m_c as the weight loss of microalgae samples with the addition of additives, and m_w as the weight loss of the microalgae samples under a uniform temperature. Δm represented the 'level' of catalytic impact of additive, such as alkali and alkaline earth. TG weightlessness unit was wt.%.

2.4. Kinetic analysis of the microalgae pyrolysis

The conversion rate of single reaction model [17] can be described as follows:

$$\frac{d\alpha}{dt} = A(1 - \alpha)^n \exp\left(-\frac{E}{RT}\right) \quad (2)$$

α is the fractional conversion of combustible in microalgae at the time t , and is given as $\alpha = (m_0 - m)/(m_0 - m_\infty)$; m_0 , m_∞ , m refer to the onset, end residual amount, and present of microalgae specimen, respectively; R , which equals to $8.314\text{ J mol}^{-1}\text{ }^\circ\text{C}^{-1}$, is a universal gas constant, and n is reaction order and T is Kelvin temperature.

In this paper, an isoconversional model was used to carry out all experimental data with different heating rates. The activation energy was figured out from a series of dynamic data according to the isoconversional model by Flynn Wall Ozawa (FWO) and Kissinger Akahira Sunose (KAS).

The following formula is based on FWO:

$$\ln \beta = \ln \left[\frac{0.0048AE_\alpha}{g(\alpha)R} \right] - 1.0516 \frac{E_\alpha}{RT} \quad (3)$$

where, α is a constant, $\ln \beta$ vs. $1/T$ obtained at three heating rates obtain a straight line, and the slope evaluates apparent activation energy.

The following formula is based on KAS:

$$\ln \left(\frac{\beta}{T^2} \right) = \ln \left[\frac{AR}{g(\alpha)E_\alpha} \right] - \frac{E_\alpha}{RT} \quad (4)$$

E_α for different fractional conversion can be figured out from a plotting $\ln(\beta/T^2)$ vs. T^{-1} .

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