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Microwave pretreatment on microalgae: Effect on thermo-gravimetric analysis and kinetic characteristics in chemical looping gasification

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ABSTRACT

A new improvement of chemical looping gasification (CLG) process is based on microwave pretreatment, which is expected to obtain the kinetics analysis of CLG process for the utilization of microalgae. Thermo-gravimetric characteristics of CLG on *Chlorella vulgaris* are studied in a thermo-gravimetric analyzer under different heating rates and pretreatment conditions. TG characteristics, weight loss rate, reactivity rate, Homogeneous Model (HM) and Shrinking Core Model (SCM) were investigated in order to study the influence of microwave pretreatment on the CLG kinetics for the utilization of microalgae. The results indicated that microwave pretreatment would improve the TG characteristics and reactivity of microalgae. Moreover, the reactivity rate of CLG increased by 5.77% compared with SiO_2: *Chlorella* and it would increase by 6.79% after microwave pretreatment. Furthermore, the higher the heating rate was, the greater the reactivity and weight loss rate of microalgae were. Further, HM could simulate CLG better than SCM. Microwave pretreatment could reduce the activation energy of *Chlorella vulgaris* and promote CLG. As a result, microwave pretreatment was beneficial to CLG reaction.

1. Introduction

It is necessary to develop sustainable energy due to the increase of energy demands, the decline of fossil fuels reserve and the serious environmental problems. Many researchers indicate that microalgae has a great potential for bio-fuel supply among biomass [1]. Compared with the conventional biomass, there are many advantages for microalgae to produce bio-fuel as following: (1) higher photosynthesis efficiency [2]; (2) 5–30 times higher bio-fuel production [3]; (3) higher growth rate (increase double within 1 day) [4]; (4) stronger adaptability without occupying agricultural land [5].

Generally, thermo-chemical conversion includes pyrolysis, gasification, combustion, etc. Many researchers are attracted to a novel technology chemical looping gasification (CLG), which is developed from gasification and chemical looping combustion. CLG can be divided into oxidation stage and reduction stage. The gasifying agent of CLG is oxygen carrier (OC), while the gasifying agent of conventional gasification is air or O_2 [6]. Compared with the conventional gasification, there are three advantages for CLG as following [7,8]: (1) OC can be recycled and the cost of oxygen production can be saved. (2) OC can provide the catalytic effect on CLG process, thus CLG has a higher gasification efficiency. (3) OC can act as a heat carrier, which can transfer the heat from oxidation stage to reduction stage. Therefore, CLG is a promising thermo-chemical conversion technology.

In recent years, many researchers carried out CLG of biomass to produce syngas. The results indicated that natural iron ore was a good OC for CLG of biomass [9]. The addition of Fe_2O_3 into CuO-based OC could improve the characteristic of sintering resistance and porous structure of OC in CLG process [10]. Moreover, Tian et al. [11] investigated bimetallic Cu-Fe OC in CLG and they found Fe composition could enhance the decomposition of large molecular compounds in tar. Zeng et al. [12] used Fe-based OC in chemical looping pyrolysis-gasification and obtained a high H_2/CO syngas production. Multi-functional iron-based OC could promote biomass gasification in CLG process and expressed a stability of oxygen transportability and physical properties [13].

Recently, researchers focus on the modification of OC and pretreatment of material in order to improve the efficiency of chemical looping reactions. Inert substances were mixed with metal oxides as a OC in the chemical looping reaction, and the authors achieved a higher mechanical behavior and gasification efficiency [14]. Natural hematite was used as OC in CLG and it was obtained a good conversion efficiency and saved the cost of OC [15]. However, the modification of OC is partly limited by the number of redox cycles and mechanical behavior

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[16]. Pretreatment on material is another way to improve efficiency. Our previous paper [17] firstly focused on microwave pretreatment of microalgae to enhance the performance of CLG process. The results indicated that microwave pretreatment was beneficial to CLG reaction. This previous paper studied the syngas production, gasification efficiency and OC performance. In order to promote the syngas production and optimization of gasification conditions, it is necessary to carry out a deep kinetics analysis.

At present, the researches on gasification kinetics mainly focus on the gasification and catalytic gasification of coal and biomass char. Homogeneous Model (HM) was carried out to study the kinetics parameters of maple and pine woods chars under the conditions of H_2 and steam [18]. Standish et al. [19] carried out the gasification reaction on pyrolysis char of woods under CO_2 atmosphere and the results indicated that Shrinking Core Model (SCM) could describe the gasification reaction well. Matsumoto et al. [20] used the random pore model to calculate the kinetics parameters of gasification on biomass char under steam and O_2 atmosphere and the study revealed that the simulated results were consistent with the experimental results. The gasification studies on biomass char found that the gasification reactivity of biomass char was related to the added metal catalysts [21]. However, few study focuses on the gasification of biomass raw materials. Especially, no study focuses on kinetics analysis of CLG on microalgae.

Our previous paper studied the effect of microwave pretreatment on syngas production and gasification efficiency under different microwave powers and time in CLG. We found that 750 W and 60 s was the optimal microwave pretreatment condition to obtain the best performance of CLG. Generally, kinetics analysis is a key parameter in the process of biomass gasification. However, no study has focus on thermo-gravimetric analysis and kinetic characteristics of microwave pretreatment to enhance the performance of CLG process. Therefore, the objective of this paper is to study the influence of microwave pretreatment on the CLG kinetics for the utilization of microalgae. Based on our previous study, the characteristics of CLG on microalgae are studied in a thermo-gravimetric analyzer under different heating rates and pretreatment conditions. HM and SCM are adopted to calculate the kinetics parameters in order to analyze the effect of microwave pretreatment on CLG and obtain the better kinetics model. This study is expected to provide the theoretical basis for practical production and application of CLG in the future.

2. Materials and methods

2.1. Materials

The microalgae sample used in this paper is *Chlorella vulgaris*, which is provided by Jiangmen Yuejian Biotechnologies Co., Ltd.. Table 1 shows the proximate analysis and elemental analysis of *Chlorella vulgaris*.

Fe_2O_3 OC is cheaper and easier to obtain than the Co-based, Ni-based and Mn-based OC [22,23]. Further, it has a good capacity of oxygen-carrying. Furthermore, it is simple in the preparation process of Fe_2O_3, which will not produce secondary pollution. Therefore, Fe_2O_3 was used as an OC in this paper. The OC used in this paper is analytical Fe_2O_3 powder, which is provided by Guangzhou Chemical Reagent Factory. Table 2 shows the elemental composition analysis of analytical Fe_2O_3 powder. The elemental composition of Fe_2O_3 powder was measured by a X-Ray Fluorescence (XRF) analyzer (PANalytical B.V., Axios Pw4400, Netherlands).

Table 1
The proximate analysis and elemental analysis of *Chlorella vulgaris*.

Proximate analysis[a] (wt, %)		Elemental analysis[b] (wt, %)	
Moisture	6.54	C	53.32
Volatile	51.75	H	7.14
Ash	9.61	O[c]	27.87
Fixed Carbon	32.10	N	10.04
		S	1.63

[a] On wet basis.
[b] On dry ash free basis.
[c] Calculated by difference, O (%) = 100 – C – H – N – S.

Microalgae and OC samples were dried separately in a drying oven at 105 °C for 24 h. They were pulverized finely and then sieved with a mesh size of less than 200 µm. OC samples were calcined at 800 °C for 3 h under air atmosphere in order to oxidize sufficiently. *Chlorella vulgaris* was mixed with OC in the blending ratio of 1:1. The same amount of analytical SiO_2, an inert compound, was used instead of Fe_2O_3 as the comparison sample.

2.2. Possible application

IN Zaini et al. [24] and CC Cormos et al. [25] have discussed the possible integrated systems for harvest the energy from algae, and they skillfully converted algae/biomass into hydrogen and power in a integrated system. In order to enhance the efficiency of gasification, we proposed a new improvement of microwave pretreatment on microalgae. Moreover, microwave pretreatment could be applied in the above integrated systems. After the drying process, the dried microalgae were pretreated in the microwave pretreatment instrument. And then they were fed into the gasification process. In addition, the other processes were similar to the above integrated systems.

2.3. Experimental procedure

Microwave pretreatment was carried out in a microwave oven (CNWB-4SJ, Guangzhou Wancheng Microwave Equipment CO., LTD) with a maximum power of 3750 W at a frequency of 2450 MHz. A two-neck quartz reaction flask with 200 g microalgae samples were placed in the microwave oven. Nitrogen was ventilated into the reaction flask at a flow rate of 300 mL/min for 20 min before the experiment as well as during the experiment in order to maintain anoxic atmosphere. Microalgae samples were carried out microwave pretreatment under 750 W for 60 s. The efficiency of microwave reactor was 62%. So the power input of microwave pretreatment was 362.90 kJ/kg. Moreover, the LHV input of microalgae was 21,280 kJ/kg. Therefore, the total power input increased by 1.71% after microwave pretreatment.

The experiments were conducted in a thermo-gravimetric analyzer (Mettler Toledo, TGA/DSC 1/1600, Switzerland). Sample of 10 ± 0.5 mg was loaded to the ceramic pan of the TGA and heated from 30 to 1100 °C at 10, 20 and 40 K/min. As inert carrier gas, nitrogen with a purity of 99.999% was ventilated into the TGA at a flow rate of 80 mL/min during the experiment. Before the experiments, several blank experiments were carried out to obtain the baselines, which could calibrate the experiments with samples.

2.4. Methods

The equations of evaluation index for gasification reaction are shown as following [26,27].

The reactivity rate (R_r, s^{-1}) of biomass gasification is calculated as following:

$$R_r = \frac{1}{1-\alpha}\cdot\frac{d\alpha}{dt} \tag{1}$$

$$\alpha = \frac{m_0-m_t}{m_0-m_\infty} \tag{2}$$

where m_0 (mg) is the initial mass of the sample. m_t (mg) is the mass of the sample at time *t*. m_∞ (mg) is the residual mass of the sample after reaction.

The reactivity rate (R_{rs}, s^{-1}) of gasification is related to the required