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A study on experimental characteristic of microwave-assisted pyrolysis of microalgae

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ABSTRACT

The microwave-assisted pyrolysis of *Chlorella vulgaris* was carried out under different microwave power levels, catalysts and contents of activated carbon and solid residue. The products, pyrolysis temperature and temperature rising rate were analyzed in order to obtain the optimal conditions. The results indicated that the higher the microwave power level was, the higher the maximum temperature rising rate and pyrolysis temperature were. The maximum bio-oil yield (35.83 wt.%) and gas yield (52.37%) were achieved under the microwave power of 1500 W and 2250 W, respectively. And 2250 W was the optimal power to obtain bio-fuel product. High microwave power level and catalyst can enhance the production of gas. Catalysts can promote the pyrolysis of *C. vulgaris*, and activated carbon was the best among the tested catalysts followed by the solid residue. The optimal content of activated carbon is 5% with the maximum bio-fuel yield of 87.47%.

1. Introduction

As social economy developed and living standard improved, energy consumption increased gradually. According to "China Statistical Yearbook 2010" (China, 2011), the total energy consumption in 2009 was 3.06647 billion tons standard coal, the amount which was 2.1 times as in 2000. The data of last 30 years showed that energy consumption of fossil fuels accounted for about 90% of the total energy consumption in China. Fossil fuels are non-renewable resources and their prices rise continually. Moreover, their uses significantly promote greenhouse gas (GHG) emission to the environment (Ruan et al., 2011). Therefore, developing new energy to substitute for fossil fuels is imperative (Yaman et al., 2006). The emerging energy such as solar energy, nuclear energy, wind energy and tidal energy still cannot replace the traditional fossil fuels so far because of the limitation of resource and technology. Biomass energy, which results in zero emission of CO_2, is the most potential one among alternative energies. Being an emerging energy mostly applied in developing countries, biomass energy can not only alleviate the energy crisis but also reduce the pollution on the ecological environment (Guehenneux et al., 2005).

Compared with other biomass, microalgae have many advantages: (1) their growth cycle is short and generally their quantity can increase doubly within 24 h (Chisti, 2007); (2) their biomass production are higher, 5–30 times of traditional oil crops per unit surface area (Ruan et al., 2011; Schenk et al., 2008); (3) they are extremely rich in oil, over 60% by weight of dry biomass in some species (Gouveia and Oliveira, 2009; Ruan et al., 2011); (4) they do not pose a threat to traditional agricultural resources as they can be cultivated on non-arable land or on waste water without occupying agricultural land (Oh et al., 2010). So far, because of many advantages microalgae have been recognized as the most potential biomass resources to replace fossil fuels (Chisti, 2007). Therefore the study of microalgae energy utilization is very important.

Biomass can be converted into solid, liquid and gaseous products by thermo-chemical methods such as pyrolysis (Corma et al., 2006; Shie et al., 2010). Pyrolysis includes microwave-assisted pyrolysis and conventional pyrolysis such as muffle furnace, tube furnace, fixed bed and fluidized bed reactor (Czernik and Bridgwater, 2004; Meier and Faix, 1999; Mohan et al., 2006). Compared with conventional pyrolysis, microwave-assisted pyrolysis, which has shown advantages such as fast heating, even heating, easy control and selective heating, has been in good graces by many researchers. The studies of microwave-assisted pyrolysis of coffee hulls (Menendez et al., 2007), microalgae (Ruan et al., 2011), rice straw (Tsai et al., 2006) and corn stalk bale (Zhao et al., 2010) focus on the effects of temperature on the product yields and characteristics of the pyrolysis products. And there are some studies discuss the influence of microwave-assisted pyrolysis on pine wood (Chen et al., 2008) and corn stover (Wan et al., 2009) with the help of catalysts. Furthermore, many researchers believe that microwave-assisted pyrolysis will have a greater developing prospect in the transformation of biomass energy (Miura et al., 2004; Omar et al., 2011; Ruan et al., 2011, 2007). However, there

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are few discussions on the effects of temperature rising rate, different contents of catalysts. Therefore, under microwave-assisted pyrolysis, the study on the effects of temperature rising rate, different contents of activated carbon and solid residue of microalgae has a significant contribution to harnessing its energy potential.

This paper investigated the microwave-assisted pyrolysis of *Chlorella vulgaris* under different microwave power levels, catalysts and contents of activated carbon and solid residue. The products, pyrolysis temperature and temperature rising rate were analyzed in order to obtain the optimal conditions and maximize bio-fuel formation.

2. Methods

2.1. Materials

In this study, *C. vulgaris* was provided by Jiangmen Yuejian Biotechnologies Co. Ltd. (Guangdong Province, China). The elemental analysis, proximate analysis and low calorific value are shown in Table 1. The elemental analysis and proximate analysis were based on ASTM D5373 standard and GB212-91 standard, respectively. ASTM D240-92, ASTM D4809-95, ISO 1928 and BSI 1016 standards provided foundation for detecting the low calorific value. Pre-treatment of raw materials were carried out before the experiments. Firstly, the *C. vulgaris* sample was dried in oven at 105 °C for 24 h. Then it was milled and sieved to obtain uniform particle with a size less than 200 μm. Finally, the sample was stored in a desiccator for experiments.

In this study, activated carbon, CaO, SiC and solid residue were added as catalysts. Activated carbon, CaO and SiC belong to the AR (Analytical Reagent). The purity of activated carbon, CaO and SiC are higher than 99%, 98% and 98.5%, respectively. Solid residue was obtained by microwave-assisted pyrolysis 30 g pure *C. vulgaris* under 1500 W microwave power. The elemental analysis and proximate analysis of solid residue are shown in Table 2. The catalysts were dried in oven at 105 °C for 24 h, then milled and sieved to obtain uniform particle with a size less than 200 μm. According to different experimental set up conditions, the contents of catalysts were 5%, 10%, 20% and 30%, respectively. Test samples were either pure *C. vulgaris* or blended pure *C. vulgaris* with catalysts. For consistent comparison, sample size was 30 g.

2.2. Methods

The pyrolysis of *C. vulgaris* was carried out in a CNWB-4SJ microwave oven with the maximum power of 3750 W at a frequency of 2450 MHz. The microwave oven was manufactured by Guangzhou Wancheng Microwave Equipment Co. Ltd. The schematic diagram of microwave-assisted pyrolysis experimental system is shown in Fig. 1. The prepared sample was placed in the three-neck quartz reaction flask with a volume of 500 mL. In order to maintain anoxic atmosphere, nitrogen was ventilated as inert carrier gas at a flow rate of 300 mL/min for 20 min before the experiment as well as during the experiment. The thermocouple was inserted inside the sample without touching the flask bottom with the purpose of measuring the sample temperature accurately. At the same time, the condensable volatiles were continuously collected using three condensers, and non-condensable gases were continuously collected using gas collecting bottles. The experiment was completed when no obvious temperature change and volatiles were observed. The production of solid and liquid were calculated from the weight of each fraction whereas the gas production was calculated by difference based on the mass balance. Weight loss was calculated as the difference between 100% and the solid residue values. The temperature raising rate curves were obtained by differentiating the corresponding temperature curves. In this study, all experiments were performed three times to ensure the accuracy of the experimental results.

Table 1
The elemental analysis, proximate analysis and low calorific value of *Chlorella vulgaris*.

Elemental analysis[a] (wt.%)		Proximate analysis[b] (wt.%)		Low calorific value[a] (MJ/kg)
C	47.84	Moisture	6.54	21.88
H	6.41	Volatile	51.75	
O[c]	25.00	Ash	9.61	
N	9.01	Fixed carbon	32.10	
S	1.46			

[a] Dry basis.
[b] Wet basis.
[c] Calculated by difference, O (%) = 100 − C − H − N − S − Ash.

Table 2
The elemental analysis and proximate analysis of solid residue.

Elemental analysis[a] (wt.%)		Proximate analysis[b] (wt.%)	
C	49.08	Moisture	0.00
H	2.66	Volatile	7.89
O[c]	8.97	Ash	32.62
N	5.81	Fixed carbon	59.49
S	0.86		

[a] Dry basis.
[b] Wet basis.
[c] Calculated by difference, O (%) = 100 − C − H − N − S − Ash.

3. Results and discussion

3.1. Different microwave power levels

The weight of each sample was 30 g, and three microwave power levels were 750 W, 1500 W and 2250 W. Under different microwave power levels, the curves of pyrolysis temperature measured by thermocouple, the curves of temperature raising rate and product fractional yields are shown in Fig. 2(a)–(c), respectively.

As shown in Fig. 2(a), the entire microwave-assisted pyrolysis temperature of *C. vulgaris* is less than 200 °C when the microwave power is 750 W. However, the pyrolysis temperature increases rapidly after enhancing the microwave power. Further more, a phenomenon is shown that the stronger the microwave power, the higher the pyrolysis temperature. This may be because when the microwave power increases, the microwave density of cavity and the microwave energy absorption of *C. vulgaris* become greater, and then the heat from molecules intense movement is more. Thus the pyrolysis temperature becomes higher and the pyrolysis time becomes shorter. This trend of pyrolysis temperature curves is similar to those reported in the literature (Lo et al., 2010; Menendez et al., 2006; Ruan et al., 2011). The variations are mainly due to the differences of microwave cavity, heat insulation condition and sample. But it almost makes no impact on the analysis because the condition of each experiment is basically the same. The pyrolysis temperature curves show four stages except the curve for 750 W. The first stage is the section where temperature rises slowly. In this stage, the sample is dried and some volatiles are separated out. The second stage is the section where temperature rises rapidly. The dry solid residue produced from the first stage can promote the microwave absorption of *C. vulgaris*. So in this stage the temperature rises quickly and in the meantime, bio-oil and pyrolysis gas are evolved. The third stage is the temperature reduction section. It may be because the emission of bio-oil and pyrolysis gas which have taken away so much heat that the heat