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The catalytic pyrolysis of microalgae to produce syngas ☆

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ABSTRACT

The pyrolysis of *Chlorella vulgaris* was carried out in a quartz tube reactor with different catalysts and contents of activated carbon. The solid residue yield, gaseous products and the evaluation method based on higher heating value and energy consumption were analyzed in order to obtain the optimal condition to produce syngas. The results indicated that catalysts obviously affected the pyrolysis products. Activated carbon was a good choice of catalyst to obtain the minimum solid residue yield (10.79 wt.%), and mixing with a higher content of activated carbon could produce a lower solid residue yield; meanwhile, the effect of each 1% activated carbon will be worse. According to the evaluation methods, there was a certain impact on the syngas production under different catalysts and contents of activated carbon. Furthermore, the $HV_{e,s}$ indicated that activated carbon was the optimal catalyst and 3% is the optimal content of activated carbon to produce syngas.

1. Introduction

In recent years, energy consumption increased gradually as the social economy developed and the living standard improved. However, the conventional fossil fuels, as non-renewable resources, are still the most widely used energy resources [1]. Moreover, their prices rise continually and their usages remarkably cause serious environmental problems promoting CO_2 emission to the environment [1]. Therefore, in order to solve the energy crisis and environmental problems [2], it is necessary to develop a renewable energy for the conventional fossil fuels substitution [3]. Biomass has attracted great interests for its stable energy supply ability, as it can be derived from biomass wastes and cultivation of energy crops, and by harvesting forestry and other plant residues [2]. Furthermore, biomass can absorb a large amount of CO_2 during its growth [4]. Because of the energy production and the biological CO_2 fixation [2], biomass energy can not only alleviate the energy crisis but also reduce the pollution on the ecological environment [5]. Therefore, thanks to the advanced technology and the abundant resource, biomass energy, as an environmental-friendly and renewable energy resource, has more potential to replace the conventional fossil fuels and produce fuels than other renewable energy resources and has attracted more and more attentions [1,6,7].

Compared with other biomass resources, microalgae has been widely considered to be the most potential biomass resources to replace the conventional fossil fuels [8,9] because of the following advantages: (1) they have higher biological CO_2 fixation so they can effectively reduce the CO_2 emission in the environment during their growth [1,10,11]; (2) they can increase twofold within 24 h so they have higher growth rate [4,8,9]; (3) they can be cultivated on waste water, aquatic medium and non-arable land without threatening traditional agricultural resources [12,13]; (4) they have higher photosynthesis efficiency and higher biomass production, 5-30 times of conventional oil crops per unit surface area [1,13–16]. Hence, the development in a proper utilization of microalgae would be of great economic and environment benefits. Therefore, it is valuable and important to study the energy utilization of microalgae.

Among many conversion processes, pyrolysis has been recognized to be an efficient technology for biomass conversion, by which biomass resources can be converted to solid, liquid and gaseous products [17–20]. Presently, many researchers focus on pyrolysis technology of biomass for energy conversion. The studies of pyrolysis of wood chips [21], rice husk [7], *Lemna minor* [4], marine macroalgae [14] and *Chlorella protothecoides* [17] focus on the effects of temperature on the bio-oil production yields and the characteristics of the bio-oil products. And there are some studies discuss the influence of catalysts on *Nannochloropsis* sp. [1], lignocellulosic biomass [22], plant biomass [18] and *Chlorella* [23]. Due to the lack of discussions on the syngas ($CO + H_2$) production and

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evaluation method of syngas production, a previous paper [13] was given to obtain the optimal temperature for syngas production and introduce a new evaluation method based on higher heating value and energy consumption. However, there are few discussions on the syngas production by catalytic pyrolysis of microalgae. Therefore, the study on the optimal condition of syngas production has a significant contribution to harnessing its energy potential under catalytic pyrolysis of microalgae.

This paper investigated the pyrolysis of *C. vulgaris* under different catalysts and different contents of activated carbon at 800 °C. The trends of CO and H_2 production were analyzed in order to obtain the optimal conditions with the help of the evaluation method based on the higher heating value and energy consumption.

2. Materials and methods

2.1. Materials

The microalgae used in this paper were *C. vulgaris*, which were provided by Jiangmen Yuejian Biotechnologies Co., Ltd. (Jiangmen City, Guangdong Province, China). The *C. vulgaris* was cultivated in fresh water. We have washed it before pretreatment. Pretreatments of *C. vulgaris* were carried out before the experiments. Firstly, the samples of *C. vulgaris* were dried in an oven at 105 °C for 24 h, and then finely pulverized by DFY-300 pulverizer (Wenling Linda Machinery Co., Ltd., Zhejiang Province, China). Finally, they were sieved with a mesh size of less than 200 μm, and then stored in a desiccator.

The proximate analysis and elemental analysis are shown in Table 1 and were based on GB212-91 standard and ASTM D5373 standard, respectively.

In this study, activated carbon, $ZnCl_2$, SiC and MgO were used as catalysts. Activated carbon, $ZnCl_2$, SiC and MgO belong to the AR (Analytical Reagent). The purity of activated carbon, $ZnCl_2$, SiC and MgO are greater than 99%, 98%, 98.5% and 98.5%, respectively. The catalysts were dried in oven at 105 °C for 24 h, then ground and sieved below 200 μm. According to different experimental conditions, the contents of $ZnCl_2$, SiC and MgO were 5%, and the contents of activated carbon were 3%, 5% and 10%, respectively. Test samples were either pure *C. vulgaris* or blended pure *C. vulgaris* with catalysts. For consistent comparison, the amount of sample used for each experiment was 0.100 g.

2.2. Experimental procedure

The schematic diagram of pyrolysis experimental system is displayed in Fig. 1. In this study, the catalytic pyrolysis of *C. vulgaris* was carried out in the quartz tube reactor with the internal diameter of 60 mm. The quartz tube reactor was controlled by the tube furnace with a KSY-6D-16 temperature controller, which was heated by silicon carbide from the room temperature to 800 °C. In order to maintain anoxic atmosphere, nitrogen was ventilated as inert carrier gas at a flow rate of 0.08 m^3 /h for 20 min before and during the experiment. When the tube furnace was heated to 800 °C, the crucible with sample was placed into the quartz tube reactor for 500 s. At the same time, a Testo 350-S flue gas analyzer was operated to analyze and record the gaseous products in each experiment. The emissions of gaseous products were reported in the generally used unit of ppmv (part-per million by volume). The Testo 350-S flue gas analyzer, with an accuracy of 10 ppmv and a resolution of 1 ppmv, is tested regularly by Testo AG.

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.

2.3. Methods

The yields of solid residue, liquid and gaseous product were calculated as following:

$$Y_S = [(W_S - W_C)/W_M] \times 100\ (\%) \quad (1)$$

$$Y_F = (W_F/W_M) \times 100\ (\%) = 100 - Y_S\ (\%) \quad (2)$$

Y_S, the yield of solid residue product, %;
W_S, the weight of solid residue product, g;
W_C, the weight of catalyst, g;
W_M, the weight of material, g;
Y_F, the yield of liquid and gaseous product, %;
W_F, the weight of liquid and gaseous product, g.

The evaluation method based on higher heating value and energy consumption was proposed in the previous paper [13]. In order to obtain the optimal condition of catalytic pyrolysis of *C. vulgaris*, this paper studied the catalytic pyrolysis of *C. vulgaris* based on the evaluation method as the followings:

$$\mathrm{HV}_s = \mathrm{HV}_{\mathrm{CO}} + \mathrm{HV}_{\mathrm{H2}} = P_{\mathrm{CO}} . M_{\mathrm{CO}} . Q_{\mathrm{CO}}/V_m + P_{\mathrm{H2}} . M_{\mathrm{H2}} . Q_{\mathrm{H2}}/V_m \quad (3)$$

$$W_T = P_T . t = P_{T,100} . S \cdot t = P_T, 100 \cdot \pi \cdot D \cdot L \cdot t/100 \quad (4)$$

$$\mathrm{HV}_{e,s} = HV_s/W_T \quad (5)$$

HV_s, the higher heating value of syngas, (ppmv kJ)/L;
$\mathrm{HV}_{\mathrm{CO}}$, the higher heating value of CO in the syngas, (ppmv kJ)/L;
$\mathrm{HV}_{\mathrm{H2}}$, the higher heating value of H_2 in the syngas, (ppmv kJ)/L;
P_{CO}, the emission of CO, ppmv;
M_{CO}, the molar mass of CO, kg/mol;
Q_{CO}, the heating value of CO, 10103.9 kJ/kg [24];
V_m, the molar volume, L/mol;
P_{H2}, the emission of H_2, ppmv;
M_{H2}, the molar mass of H_2, kg/mol;
Q_{H2}, the heating value of H_2, 119950.4 kJ/kg [24];
W_T, the electrical work at 800 °C, W h;
P_T, the electrical power at 800 °C, W;
t, the time of pyrolysis, h;
$P_{T,\ 100}$, the electrical power per 100 cm^2 at 800 °C, 130 W [25];
S, the heating surface of tube furnace, cm^2;
π, pi;
D, the diameter of the quartz tube, cm;
L, the heating length of the quartz tube, cm;
$\mathrm{HV}_{e,s}$, the higher heating value of syngas based on energy consumption, (ppmv kJ)/(L W h).

3. Results and discussion

3.1. The effect of catalysts on the solid residue yield of C. vulgaris

Based on the previous paper [13], the optimal pyrolysis temperature of *C. vulgaris* is 800 °C. Hence each experiment was operated at 800 °C in this paper to obtain the optimal condition of catalytic pyrolysis of *C. vulgaris*. In this section, the content of