



The characteristic and evaluation method of fast pyrolysis of microalgae to produce syngas



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HIGHLIGHTS

- The bio-fuel (gas and bio-oil) yield became higher as the temperature increased.
- The highest emission of CO and H₂ could be gained at 800 and 900 °C, respectively.
- Higher temperature was beneficial to shorten the time of pyrolysis reactions.
- There was a significant impact on the syngas production under different temperatures.
- 800 °C was the optimal pyrolysis temperature to produce syngas.

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ABSTRACT

The fast pyrolysis of *Chlorella vulgaris* was carried out in a quartz tube reactor under different pyrolysis temperature levels. The product fractional yields, gaseous products and the evaluation method based on heating value and energy consumption were analyzed in order to obtain the optimal condition to produce syngas. The results indicated that the higher the pyrolysis temperature level was, the higher the bio-fuel yield was. 900 °C is the best temperature to obtain the maximum bio-fuel yield (91.09%, wt.%). And the highest emission of CO and H₂ were achieved under the pyrolysis temperature of 800 and 900 °C, respectively. According to the evaluation method based on heating value and energy consumption, there was a significant impact on the syngas production under different pyrolysis temperatures. Furthermore, the evaluation method based on energy consumption indicated that 800 °C was the optimal pyrolysis temperature to produce syngas.

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1. Introduction

Presently, energy consumption increased gradually as the living standard improved and social economy developed. However, the widely utilization of energy resources are still limited to fossil fuels (Pan et al., 2010), which are non-renewable resources, and their prices rise continually (Hu et al., 2012). Moreover, their usages obviously promote greenhouse gas (GHG) emission to the environment and cause serious environmental problems (Du et al., 2011; Hu et al., 2012). Therefore, according to the environment and energy crisis (Amin, 2009), it is necessary to develop new energies to substitute for fossil fuels (Haykiri-Acma et al., 2006). Due to the abundance of technology and resource, biomass energy is more potential to replace the traditional fossil fuels than the emerging energy such as wind energy, tidal energy and solar energy. Because of the biological CO₂ fixation and energy production (Amin, 2009), biomass energy can not only reduce the pollution on the ecological

environment but also alleviate the energy crisis (Guéhenneux et al., 2005). Therefore, as a renewable and environmentally friendly energy resource, biomass has attracted more and more attentions (Gerçel, 2002; Pan et al., 2010).

Among biomass resources, microalgae have been recommended to be very good candidates for fuel production because of the following advantages: (1) they have higher photosynthesis efficiency and higher biomass production, 5–30 times of conventional oil crops per unit surface area (Bae et al., 2011; Du et al., 2011; Pan et al., 2010; Schenk et al., 2008); (2) they can be cultivated on waste water or on non-arable land without occupying arable land, so they will not be a threat to traditional agricultural resources (Hu et al., 2012; Lee et al., 2010); (3) they have faster growth rate because their quantity can increase doubly within 24 h (Chisti, 2007; Muradov et al., 2010); (4) they can effectively reduce GHG in the atmosphere owing to their ability of fixing CO₂ (Chiu et al., 2009; Pan et al., 2010; Sawayama et al., 1995). Due to many advantages, the utilization and development of microalgae to produce bio-fuel can gain more and more environmental and economic benefits. Moreover, microalgae have been considered to be the

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most potential biomass resources to substitute for fossil fuels (Chisti, 2007; Hu et al., 2012). Therefore, it is very important and valuable to study the energy utilization of microalgae.

Pyrolysis has been recognized as the most efficient process for biomass conversion to replace the traditional fossil fuels (Miao et al., 2004). And biomass resources can be transformed into solid, liquid and gaseous products by pyrolyzing in the absence of air (Huber et al., 2006; Shie et al., 2010). Presently, more and more researchers focus on fast pyrolysis process for biomass to produce bio-fuel. The studies of fast pyrolysis of marine macroalgae (Bae et al., 2011), *Lemna minor* (Muradov et al., 2010), *Nannochloropsis* sp. (Pan et al., 2010) and *Chlorella protothecoides* (Miao et al., 2004) focus on the effects of temperature and catalysts on the bio-oil production yields and the characteristics of the bio-oil products. However, there are few discussions on the production of syngas (CO + H₂) by fast-pyrolyzing microalgae, as well as the evaluation method of syngas production. A new evaluation method based on heating value and energy consumption is introduced to obtain the optimal condition for syngas production. This evaluation method can combine the different effects of pyrolysis temperature on the gaseous emissions. Moreover, fast pyrolyzing biomass at the optimal condition obtained in this study can reduce much energy consumption. Therefore, the study on the evaluation method and production of syngas has a significant contribution to harnessing its energy potential under fast pyrolysis of microalgae.

This paper investigated the fast pyrolysis of *Chlorella vulgaris* under different temperature levels from 500 °C to 900 °C. The trend of CO and H₂ production were analyzed in order to obtain the optimal conditions based on a new evaluation method introduced by this paper.

2. Methods

2.1. Materials

In this paper, the samples of *C. vulgaris* were provided by Jiangmen Yuejian Biotechnologies Co., Ltd. (Jiangmen City, Guangdong Province, China). Pre-treatment of samples were carried out before the experiments. Firstly, the samples of *C. vulgaris* were dried in an oven at 105 °C for 24 h. Then they were finely pulverized by DFY-300 pulverizer (Wenling Linda Machinery Co., Ltd, Zhejiang Province, China). And then they were sieved to obtain uniform particle with a mesh size of less than 200 μm. Finally, the samples were stored in a desiccator for experiments. For consistent comparison, the amount of *C. vulgaris* used for each fast pyrolysis experiment was 0.100 g.

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

2.2. Experimental procedure

The fast pyrolysis of *C. vulgaris* was carried out in the quartz tube reactor with the internal diameter of 60 mm heated by a

SK2-4-13 tube furnace. The tube furnace was manufactured by Wuhan Yahua Furnace Co., Ltd.

The schematic diagram of fast pyrolysis experimental system is shown in Fig. 1. In this study, the tube furnace was heated by silicon carbide from the room temperature to a desired temperature (500, 600, 700, 800 and 900 °C). The temperature was controlled by a KSY-6D-16 temperature controller (Wuhan Yahua Furnace Co., LTD). In order to maintain anaerobic atmosphere, nitrogen was ventilated as inert carrier gas at a flow rate of 0.08 m³/h for 20 min before the experiment, and was used throughout the experiment. After that, when the tube furnace was heated to the desired temperature, the sample was placed in the crucible and then the crucible with sample was inserted into the quartz tube reactor. The sample was left in the quartz tube reactor at the desired temperature for 500 s. At the same time, the condensable volatiles were continuously collected using two condensers, and non-condensable gases were continuously collected using gas collecting bottles. In order to accurately assess the characteristic of syngas, the gaseous products in each fast pyrolysis experiment were on-line analyzed and recorded by a Testo 350-S flue gas analyzer, which was manufactured by Testo AG, Lenzkirch, Germany. The emissions of gaseous products were reported in the generally used unit of ppmv (part-per million by volume). The emission rate curves of CO and H₂ were obtained by differentiating the corresponding emission curves.

The production of solid residue was calculated from the weight of solid residue fraction whereas the bio-fuel (gas and liquid production) was calculated by difference based on the mass balance. The bio-oil produced by fast pyrolysis at high temperature was less, moreover the amount of each sample was only 0.100 g, and therefore the yields of solid residue and bio-fuel were just analyzed in this study. The yields of various products were calculated as follow:

$$Y_S = W_S/W_M \times 100 (\%) \quad (1)$$

$$Y_F = W_F/W_M \times 100 (\%) = 1 - Y_S \quad (2)$$

where Y_S denoted the yield of solid residue product; W_S , the weight of solid residue product; W_M , the weight of material; Y_F , the yield of bio-fuel product; W_F , the weight of bio-fuel product.

3. Calculation

3.1. Evaluation method based on heating value

As most researchers only studied the trends of CO and H₂ under pyrolysis processes, they could not carry out an overall evaluation on the syngas. Therefore, an evaluation method based on heating value was proposed to study the best condition of syngas production under different temperature levels. The recognized literature was consulted to determine the heating values of CO and H₂ (Yaws and Braker, 2001). The evaluation method based on heating value was calculated as follow:

$$\begin{aligned} HV_s &= HV_{CO} + HV_{H_2} \\ &= P_{CO} \cdot M_{CO} \cdot Q_{CO}/V_m + P_{H_2} \cdot M_{H_2} \cdot Q_{H_2}/V_m \end{aligned} \quad (3)$$

where HV_s denoted the heating value of syngas (ppmv kJ)/L; HV_{CO} , the heating value of CO in the syngas (ppmv kJ)/L; HV_{H_2} , the heating value of H₂ 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 (Yaws and Braker, 2001); V_m , the molar volume, L/mol; P_{H_2} , the emission of H₂, ppmv; M_{H_2} , the molar mass of H₂, kg/mol; Q_{H_2} , the heating value of H₂, 119,950.4 kJ/kg (Yaws and Braker, 2001).

Table 1

The elemental analysis and proximate analysis of *C. vulgaris*.

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

^a On dry ash free basis.

^b On wet basis.

^c Calculated by difference, O (%) = 100 - C - H - N - S.

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