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Pressurized entrained-flow pyrolysis of microalgae: Enhanced production of hydrogen and nitrogen-containing compounds



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ABSTRACT

Pressurized entrained-flow pyrolysis of Chlorella vulgaris microalgae was investigated. The impact of pressure on the yield and composition of pyrolysis products were studied. The results showed that the concentration of H_2 in bio-gas increased sharply with increasing pyrolysis pressure, while those of CO, CO₂, CH₄, and C₂H₆ were dramatically decreased. The concentration of H2 reached 88.01 vol% in bio-gas at 900 °C and 4 MPa. Higher pressures promoted the hydrogen transfer to bio-gas. The bio-oils derived from pressurized pyrolysis were rich in nitrogen-containing compounds and PAHs. The highest concentration of nitrogen-containing compounds in biooil was achieved at 800 °C and 1 MPa. Increasing pyrolysis pressure promoted the formation of nitrogen-containing compounds such as indole, quinoline, isoquinoline and phenanthridine. Higher pyrolysis pressures led to increased sphericity, enhanced swelling, and higher carbon order of bio-chars. Pressurized pyrolysis of biomass has a great potential for poly-generation of H₂, nitrogen containing compounds and bio-char.

1. Introduction

Ever increasing global energy demand and depletion of fossil fuel resources and environmental concerns, particularly greenhouse gas emissions have motivated researchers to look for alternative energy resources. Microalgae are one of the most promising types of biomass due to their higher photosynthesis efficiency, simple cell structure, lowest sulphur content, and high CO2 capture capacity (Milano et al., 2016). In addition, the high-protein nature of microalgae makes it very suitable for production of various high-value nitrogen-containing fine chemicals (Huang et al., 2017; Maliutina et al., 2017).

Hydrogen is one of the most promising fuels with a very high energy density and numerous environmental and socio-economic advantages over fossil fuels (Kırtay, 2011; Sharma and Arya, 2017). Hydrogen is a clean source of energy as it does not form CO₂ when used in hydrogen fuel cells and the only by-product of its combustion is water (Azwar et al., 2014). Hydrogen is mainly produced by thermochemical conversion of fossil fuels such as natural gas, naphtha, heavy oils, and coal (Kirtay, 2011). Hydrogen is mainly used for production of fertilisers and petroleum refining (Konieczny et al., 2008), and can also be used for power generation or fuelling vehicles. Microalgae are promising sources for sustainable production of hydrogen, which can decrease the net CO₂ emissions to the atmosphere. However, the hydrogen production technologies from microalgae require further development to increase its competitiveness. One way to achieve this is development of a polygeneration approach for production of several value-added products. Pyrolysis of microalgae for co-production of hydrogen, nitrogen containing compounds, and bio-char may increase its competitiveness in energy market.

The conversion of microalgae into biofuels has been realized via thermochemical and biochemical conversion. However, the high cost and low efficiency of microalgae to biofuels techniques hinders the competitiveness of the biofuel produced from these methods with fossil fuels. An alternative approach is the production of value-added products from microalgae via pyrolysis. Pyrolysis of microalgae for coproduction of bio-oil, bio-gas, and bio-char has been reported in the literature. Miao et al. (2004) carried out fast pyrolysis of two different types of microalgae in a fluidized-bed reactor with a short vapor residence time of 2-3 s. Bio-oil was characterized by low oxygen content with a higher heating value of 29 MJ/kg, making it suitable as a fuel. In our previous study (Maliutina et al., 2017) the fast pyrolysis behavior of Chlorella vulgaris was investigated in an entrained-flow reactor. It was found that increasing the temperature greatly affected the product yields and composition. High protein nature of microalgae led to

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formation of nitrogen-containing compounds such as indole, imidazole, and pyridine in bio-oil. In another study by the authors (Huang et al., 2017) catalytic microwave pyrolysis of *Chlorella vulgaris* and *Spirulina* sp. was investigated for formation of nitrogen-containing compounds. It was found that activated carbon promoted the formation of nitrogen-containing aliphatics, while the yield of nitrogen-containing aromatic compounds was promoted in presence of magnetite. The formation of nitrogen-containing species during pyrolysis was also reported by other researchers (Li et al., 2017; Maddi et al., 2011; Trinh et al., 2013).

Reaction pressure may significantly affect the pyrolysis process in terms of product yield and composition. Thermogravimetric analysis (TGA), wire mesh reactor, fluidized-bed reactor, and entrained-flow systems have been used to investigate the influence of pressure on pyrolysis (Garcia-Nunez et al., 2017). Basile et al. (2014) investigated the effect of pressure on pyrolysis of biomass and reported that pyrolysis process may shift from endothermic (primary decomposition process, leading to the formation of volatiles) to exothermic (vaporsolid interactions, leading to secondary char formation) at higher pressures. Melligan et al. (2011) used a fixed-bad reactor for pyrolysis of Miscanthus under pressurized conditions. They observed that the surface area of char decreased significantly with increasing the pyrolysis pressure from atmospheric to 2.6 MPa. Wafiq et al. (2016) studied the pyrolysis of raw and torrefied Miscanthus in a drop tube reactor at 800 °C and pressures of 1–3 MPa. They reported that pressure significantly affected the yields of products, gas composition, and char structure for both raw and torrefied biomass. Ates et al. (2015) investigated the influence of pressure on dried distillers grains with soluble and canola seed press cake in a fixed-bed reactor and observed that at elevated pressures the yield of non-condensable gases and chars increased, while a lower yield was obtained for pyrolysis liquids. Qian et al. (2014) carried out pressurized pyrolysis of rice husk using a fixedbed reactor and reported that high pressure promoted the deoxygenation, dehvdration, and decarboxylation of bio-oil, while the concentration of methane increased in bio-gas. Mahinpey et al. (2009) studied pressurized pyrolysis of wheat straw using a tubular reactor at temperature of 500 °C and obtained the highest bio-oil and syngas (CO and H₂) yield at 40 psi and 20 psi, respectively. Large body of work has focused on pressurized pyrolysis of lignocellulosic and waste biomass and the impact of pressure on pyrolysis of microalgae is not fully understood. Furthermore, majority of pressurized pyrolysis experiments have been carried out using TGA, and small scale fixed-bed reactors, which suffer from low heating rates.

The composition of microalgae pyrolysis products at atmospheric pressures is very complex, which makes them very difficult to separate and purify. Therefore, new technologies need to be developed to increase the selectivity of the value-added products during pyrolysis process of microalgae. Pressurized entrained-flow pyrolysis of microalgae is a promising method to increase the selectivity of value-added products under single-particle heating mode and fast heating rates similar to that of industrial reactors. The present study aims to establish the influence of pressure on the yields and composition of microalgae pyrolysis tests were carried out in temperature range of 600–900 °C and pressures of 0.1–4 MPa and the impact of pressure on bio-oil, bio-gas, and bio-char yields and composition was systematically studied using various analytical techniques.

2. Materials and methods

2.1. Biomass characterization

Microalgae *Chlorella vulgaris* was supplied by Spirulina Bio-Engineering Co. Ltd., China with a particle size of $< 105 \,\mu$ m. Samples were dried at 105 °C for 24 h and stored in a desiccator to avoid the moisture reabsorption. The proximate analysis of microalgae were performed following ASTM standards of D3173 for the moisture, D3174 for the ash, and D3175 for the volatile matter, and the fixed carbon content was calculated by difference. The proximate analysis of microalgae was as follows: moisture (wt%, ar): 10.21; volatile matter (wt %, db): 80.41; ash (wt%, db): 5.54; and fixed carbon (wt%, db): 14.05%. The ultimate analysis of microalgae was carried out using a Euro Vector Euro EA elemental analyzer. The proximate analysis (wt% daf) of microalgae was as follows; C = 43.85%, N = 7.86%, H = 6.07%, S = 0.71%, O (by difference) = 41.61%. *Chlorella vulgaris* sample contained 56.44 wt% protein, 12.4 wt% lipids, and 17.3 wt% carbohydrates. The methods followed for calculating the protein, lipids, and carbohydrate contents in microalgae can be found elsewhere (Maliutina et al., 2017).

2.2. Pressurized entrained-flow pyrolysis experiments

The pressurized entrained-flow experimental setup used in this study can operate at a maximum pressure of 7 MPa and temperatures of up to 900 °C. The entrained-flow reactor had an inner diameter of 20 mm and was heated in an electric furnace with five heating zones. The total length of the heating zone was 1500 mm. The char collector at the bottom of the reactor was trace-heated to 250 °C. The reactor wall temperature was calibrated and found to be within \pm 10 °C of the furnace temperature. The pressure of the system was controlled by a pressure regulator and a back pressure valve.

Pressurized pyrolysis experiments were carried out at temperatures of 600, 700, 800, and 900 °C and pressures of 1, 2 and 4 MPa. The sample feeding rate was 0.5 g/min. High purity nitrogen (99.999%) with a flow rate of 5 L/min was used as the sweep gas during pyrolysis experiments. This led to a gas residence time of 5-6 s in the reactor. For each experimental run, approximately 30 g of dried microalgae was charged to the feeder. The carrier-gas was split into two streams. One stream was passed through the feeding system to prevent any contact between the sample and pyrolysis gas and the second stream was heated to 300 °C in a preheater before being fed directly to the pyrolysis reactor. After purging the feeder and the reactor for 1 h, the system was heated and pressurized to the desired temperature and pressure. The reactor outlet gas was then analyzed using a portable flue gas analyzer (Testo 350) to ensure an inert atmosphere inside the reactor. The pyrolysis vapors were passed through two water-cooled (a mixture of water and ethylene glycol at -5 °C) condensers. The dissolved organic bio-oil was separated from dichloromethane (Sinopharm Chemical Reagent Co., Ltd.) by distillation. The duration of each pyrolysis run was 30 min, after which the system was depressurized and the reactor was cooled to room temperature.

2.3. Product yields

The total volatiles matter yield and char yield during pyrolysis of microalgae under different experimental conditions was calculated using ash tracer method (Eq. (1)) (Lewis and Fletcher, 2013).

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% Mass Release_{Ash Tracer} (daf) =
$$\left[\frac{1 - \frac{X_{ash}^0}{X_{ash} char}}{1 - X_{ash}^0}\right]$$
(1)

where $x_{ash char}$ and x_{ash}^0 were the ash content of the char and microalgae, respectively. The yield of non-condensable gases was calculated from micro-GC measurements and the volume of gases produced in pyrolysis reactor. The bio-oil yield was calculated by difference.

2.4. Bio-gas analysis

A micro gas chromatography system (490 Micro-GC, Agilent Technologies Equipment) equipped with a thermal conductivity detector (TCD) with a 10 m (Molecule sieve) MS5A column and a 10 m (Polar Plot U) PPU column was used for the analysis of bio-gas derived

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