Comparative study on pyrolysis of lignocellulosic and algal biomass using a thermogravimetric and a fixed-bed reactor

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HIGHLIGHTS

- Pyrolysis behaviors of algal and lignocellulosic biomass were compared.
- Activation energy for pyrolysis of biomass samples was estimated by FWO and KAS methods.
- H_2 and CH_4 concentrations increased with increasing pyrolysis temperature.
- Bio-oil from lignocellulosic biomass contained more phenolic compounds.
- Bio-oil from microalgae showed a higher content of nitrogen containing compounds.

ARTICLE INFO

ABSTRACT

Pyrolysis characteristics of four algal and lignocellulosic biomass samples were studied by using a thermogravimetric analyzer (TGA) and a fixed-bed reactor. The effects of pyrolysis temperature and biomass type on the yield and composition of pyrolysis products were investigated. The average activation energy for pyrolysis of biomass samples by FWO and KAS methods in this study were in the range of 211.09–291.19 kJ/mol. CO_2 was the main gas component in the early stage of pyrolysis, whereas H_2 and CH_4 concentrations increased with increasing pyrolysis temperature. Bio-oil from *Chlorella vulgaris* showed higher content of nitrogen containing compounds compared to lignocellulosic biomass. The concentration of aromatic organic compounds such as phenol and its derivatives were increased with increasing pyrolysis temperature up to 700 °C. FTIR analysis results showed that with increasing pyrolysis temperature, the concentration of OH, C—H, C=O, O—CH₃, and C—O functional groups in char decreased sharply.

1. Introduction

Growing concerns over increasing energy demand and environmental impact due to the utilization of fossil fuels have resulted in calls for more renewable and alternative energy sources. Biomass is one of the main renewable energy resources widely available and provides the only source of renewable liquid, gaseous and solid fuels (Bridgwater et al., 1999). Biomass is considered as CO_2 neutral with low contents of sulfur. Biomass can generally be divided into lignocellulosic and algal biomass. Lignocellulosic biomass is mainly composed of hemicellulose, cellulose, and lignin. Among biomass species, microalgae is considered as a promising source of energy because of faster growth, higher yields, higher efficiency in CO_2 capture and photosynthesis, and non-competitiveness with food crops. Microalgae contain three main components, namely carbohydrates, proteins and lipids (Tahmasebi et al., 2013). The ash content and concentration of alkali and alkali earth metals (AAEM) in microalgae depends on the type and culturing methods of microalgae. If microalgae with high ash content are used directly in gasification and combustion, it can cause slagging and fouling.

An alternative is thermochemical conversion of microalgae by fast pyrolysis. Fast pyrolysis is a promising process for conversion of biomass into value-added fine chemicals and fuel. Fast pyrolysis has the potential to achieve high yields of liquid at temperatures around 500 °C (Trinh et al., 2013). Several biomass pyrolysis studies focusing on the effects of biomass components (cellulose, hemicelluloses and lignin) (Wang et al., 2008; Yang et al., 2007, 2006), different types of lignocellulosic biomass (Barneto et al., 2011; Stenseng et al., 2001), and algae (Bae et al., 2011; Rizzo et al., 2013) has been reported in the literature.

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Value-added chemicals can be produced through fast pyrolysis of biomass (Abdullah and Gerhauser, 2008). Liquid fuels, petrochemical phenols, adhesives, or resins are other promising products from biomass pyrolysis (Trinh et al., 2013). Bio-char is also a valuable product and can be used to enhance natural rates of carbon sequestration in soils, reduce farm waste, and substitute renewable energy sources for fossil-derived fuel inputs (McHenry, 2009). Gas derived from biomass can be used as syngas for internal-combustion engines, in power stations and heat supply (Raveendran and Ganesh, 1996).

The information on the difference between the behavior of algal and lignocellulosic biomass during fast pyrolysis and the composition of pyrolysis products is scarce in the literature. In order to develop an efficient biomass pyrolysis technology, a better understanding of pyrolysis characteristics of different kinds of biomass is critical. Previous investigations were concerned on the pyrolysis conditions required to obtain a maximum bio-oil yield as well as pyrolysis kinetics. Therefore, a systematic and comparative investigation of pyrolysis characteristics of algal and lignocellulosic biomass using a TGA and a fixed-bed reactor was carried out in this study. The effect of pyrolysis temperature and biomass type on the yields and composition of pyrolysis products (bio-oil, gas, and char) was systematically studied to investigate the possibility of production of fine chemicals and synthesis gas from different biomass feedstock. The char, oil and gas products were analyzed by Fourier transform infrared spectroscopy (FTIR), gas chromatography–mass spectrometry (GC–MS), and gas chromatography (GC), respectively. Since both algal and lignocellulosic biomass samples with different compositions were used, the results obtained in this study can also help in understanding the influence of the biomass feedstock on pyrolysis bio-oil and gas composition.

2. Methods

2.1. Sample preparation

The microalgae *Chlorella vulgaris* (*C. vulgaris*) sample was obtained from Spirulina Bio-Engineering Co. Ltd., China in powder form. The peanut shell, corncob and pine needle samples were from North China. Air-dried peanut shell, corncob and pine needle samples were crushed and sieved into 74–140 μm particle size. The samples were then dried in a vacuum oven at 105 °C for 12 h to remove the moisture and then stored in desiccators. The proximate and ultimate analyses of the samples are given in Table 1.

2.2. Thermogravimetric experiments

TGA has been used for identifying the range of temperatures required in pyrolysis (Park et al., 2008). The TGA experiments in this study were carried out in a NETZSCH STA 449 F3 in non-isothermal condition. In order to avoid diffusion limitations, a sample size of 10 mg was heated at heating rates of 5, 10, and 20 °C/min from room temperature to 800 °C under nitrogen with a flow rate of 100 ml/min for estimating the kinetic parameters and evaluation of pyrolysis characteristics of biomass samples. Experiments for each test were repeated twice in order to confirm the reproducibility of the results. The temperature of the sample was measured with a type S thermocouple with an accuracy of ±1.5 °C.

TGA and DTG profiles obtained during pyrolysis and combustion experiments were used to determine characteristic parameters. T_1 was defined as the temperature at which pyrolysis process commenced and was taken as the point where the weight loss reached to 10% of total sample weight loss. T_2 was the temperature corresponding to the peak of the derivative thermogravimetric (DTG) curve. T_3 represents the temperature at which sample pyrolysis was completed. It was taken as the point immediately before weight loss reached to 90% of the total weight loss of the sample (Meng et al., 2013a).

2.3. Kinetics modeling

In the non-isothermal experiments, the sample mass loss was recorded as a function of the temperature. The rate of conversion, $d\alpha/dt$, can be written as (Tahmasebi et al., 2013):

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where α is the conversion degree, t is time, T is the absolute temperature, $k(T)$ is the temperature-dependent rate constant, and $f(\alpha)$ is the temperature-independent function of conversion. In Arrhenius equation, k as a function of T can be written as:

$$k = A \exp\left(-\frac{E}{RT}\right) \tag{2}$$

where A is pre-exponential or frequency factor, E is the activation energy, and R is the universal gas constant. The function $f(\alpha)$ is expressed as:

$$f(\alpha) = (1-\alpha)^n \tag{3}$$

where n is the reaction order.

The conversion (α) is expressed as:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \tag{4}$$

where m_0 is the initial mass of the sample, m_t the mass of sample at time t and m_∞ is the final indecomposable mass of the sample in the reaction.

The combination of Eqs. (2)–(4) gives:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \tag{5}$$

If the temperature of the sample is changed by a controlled and constant heating rate, $\beta = dT/dt$, the re-arrangement of Eq. (5) gives:

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right)dT \tag{6}$$

Three heating rates (β) of 5, 10, and 20 °C/min were used in this study. The integrated form of Eq. (6) is generally expressed as:

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right)dT \tag{7}$$

$$T = T_0 + \beta T \tag{8}$$

Table 1
Proximate and ultimate analysis of biomass samples.

Sample	Peanut shell	Pine needle	*C. vulgaris*	Corncob
Moisture (wt%, ar)	8.03	8.81	6.26	6.33
Volatile matter (wt%, ar)	58.38	60.09	76.13	51.64
Fixed carbon (wt%, ar)	22.29	18.86	11.50	12.53
Ash (% wt ar)	11.31	12.24	6.11	29.51
C (wt%, daf)	37.87	46.28	47.32	22.49
H (wt%, daf)	5.185	5.804	6.899	3.303
N (wt%, daf)	1.57	0.72	8.48	0.51
S (wt%, daf)	0.137	0.164	0.848	0.017
O[a] (wt%, daf)	55.238	47.032	36.453	73.68
H/C[b]	1.64	1.50	1.75	1.76
O/C[b]	1.09	0.76	0.58	2.46

ar: as received; daf: dry ash free.
[a] Calculated by difference.
[b] Molar ratio.