



Thermogravimetric and kinetic analysis of bio-crude from hydrothermal liquefaction of *Enteromorpha prolifera*



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ABSTRACT

Bio-crude upgrading process by thermal treatment without the presence of neither catalysts nor hydrogen is a promising technique. Mechanism and kinetics of bio-crude thermal decomposition are crucial for the development of thermal upgrading process. In this paper, thermogravimetric and kinetic analysis of bio-crude from hydrothermal liquefaction of *Enteromorpha prolifera* was performed under non-isothermal conditions at different heating rates. A two-step reaction mechanism, a volatilization step followed by a thermal reaction step, was proposed based on the experimental results. The most probable reaction model was determined through a universal integral method, and the kinetic parameters were obtained simultaneously. At heating rate of 10 K/min, the volatilization step can be described by a 1-D diffusion model and the thermal reaction step followed apparent first-order reaction kinetics. The apparent activation energy was also estimated by using several isoconversional methods. However, further analysis proved that the basis of isoconversional method was violated.

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1. Introduction

Algae are considered as a more favorable feedstock for next generation biofuels. Algae biomass production can effect biofixation of CO₂. Nutrient for algae cultivation (especially nitrogen and phosphorus) can be obtained from wastewater [1]. Therefore, the potential advantages of algae-derived bio-fuels are not limited to energy conversion and utilization but also environmental impacts. Hydrothermal liquefaction (HTL) converts biomass feedstock into bio-crude in hot compressed water, and simultaneously produces an aqueous phase, solid residue and gas products [2]. Compared to traditional thermochemical conversion process, HTL dramatically reduces the energy input for dewatering and drying [2,3], therefore has been identified to be especially suitable for high moisture aquatic biomass such as algae.

Bio-crude has abundant heavy components according to the molecular weight distribution [4–6] and boiling range distribution [7,8]. Bio-crude is composed of hydrocarbons (almost no alkanes) [9] and various oxygenated and nitrogenous compounds, especially heterocyclic compounds [10]. Bio-crude contains a great number of functional groups and heteroatom bonds, and is high in both aromaticity and degree of unsaturation [10].

HTL in the presence of catalysts, or so-called catalytic liquefaction, does not distinctly improve bio-crude properties. Producing a useful biofuel directly from wet algae in one step and in one pot has not yet been demonstrated [3]. An upgrading process (hydrothermal catalytic

upgrading, catalytic hydrotreating or thermal upgrading) is suggested to follow the non-catalytic HTL. Yeh et al. [3] reviewed the development of hydrothermal catalytic upgrading of bio-crude. Elliott et al. [11] performed catalytic hydrotreating of bio-crude using a continuous-flow fix-bed reactor system. The literature shows that catalytic hydrotreating enjoys the advantages in properties of upgraded oil, however, it is constrained by reactor coking, catalysts cost and hydrogen consumption. Thermal upgrading operated at lower pressures does not require novel metal catalysts nor high pressure hydrogen, thus the equipment investment and operating cost can be greatly reduced. Roussis et al. [12] proposed a thermal treatment process of bio-crude. After thermal treatment at 673 K for 60 min, the density, acidity and boiling range distribution of bio-crude were all improved, the oxygen content was reduced to 0.2%, and the higher heat value (HHV) was elevated to 45 MJ/kg. The process yielded 81.9% of upgraded oil with pressure as low as 4.2 MPa. Eboibi et al. [8] improved bio-crude properties with vacuum distillation (353–373 K, 100 kPa). The process resulted in large reduction in metal contents and 97% deoxygenation of bio-crude, and the distilled bio-crude yield was up to 73%.

The thermal upgrading process and the coking or visbreaking process in residue processing are similar in terms of reaction temperature and reaction type. To further investigate the thermal upgrading process, it is crucial to understand the mechanism and kinetics of bio-crude thermal decomposition. Thermogravimetric analysis (TGA) is the most commonly applied thermal analytical technique in solid-state thermal decomposition studies [13]. Especially, using multiple sets of thermal data collected by performing experiments at multiple heating rates has gained widespread recognition in thermal studies of pyrolysis of

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biomass, coal, oil shale and other solid fuels [14–18]. However, to our knowledge, there has been no study wherein a kinetic study of HTL bio-crude was performed using non-isothermal methods. A critical review of kinetic models and mathematical approximations currently employed in solid-state thermal analysis was provided by White et al. [19]. Isoconversional and model-fitting methods for estimating kinetic parameters were comparatively evaluated. The influencing factors on kinetic parameters including process conditions, heat and mass transfer limitations, physical and chemical heterogeneity of the sample and systematic errors were discussed.

In this work, thermal decomposition of bio-crude from HTL of *Enteromorpha prolifera* was studied under non-isothermal conditions by using TGA. The reaction mechanisms were discussed based on the experimental results. The most probable reaction model was determined through a universal integral approach, and the kinetic parameters were simultaneously obtained. Different isoconversional methods were also used for estimating the apparent activation energy, and compared with the universal integral method. This kinetic study is expected to be valuable to the development of bio-crude thermal upgrading process or combustion in heavy oil boilers.

2. Materials and methods

2.1. Materials

Enteromorpha prolifera was directly collected from the silver beach, Qingdao China. *Enteromorpha prolifera* was first washed with tap water to remove solid particles, and then pulverized with a blender to obtain a slurry. The slurry was dried in air at 323 K for 24 h to a constant weight, then pulverized again to obtain powder of 80–300 mesh. The powder was used as a feedstock for bio-crude production. The elemental composition was analyzed using a CHNOS analyzer (Vario EL cube, Elementar, Hanau, Germany). Proximate analysis (ASTM 3172, ASTM 7582) and ultimate analysis of the feedstock are shown in Table 1.

2.2. Production of bio-crude

A GSH-0.3 L stainless steel autoclave with a magnetic drive stirrer (Shanghai Yan Zheng Experiment Instrument Co., Ltd., Shanghai, China) was used for the HTL experiments. In a typical run, 35.3 g of feedstock was mixed with 200 g of deionized water, and then filled in the reactor. Nitrogen gas was used to purge the residual air in the reactor, and pressure was raised to 1.0 MPa at room temperature to avoid water vaporization. The reactor was heated by an electric heater up to 573 K, and maintained for 30 min. Stirring at 500 rpm was applied throughout the reaction. After the reaction, the reactor was rapidly cooled to room temperature by flowing tap water through the cooling coil located inside the reactor. The products separation procedure is illustrated in Fig. 1. Once the reactor was cooled to room temperature, the gas products were vented and the reactor was opened. The solid–liquid mixture was rinsed from the reactor using 250 g of dichloromethane (DCM). The resulted suspension was filtered under a vacuum. The filtrate was transferred to a separatory funnel wherein the aqueous phase and the

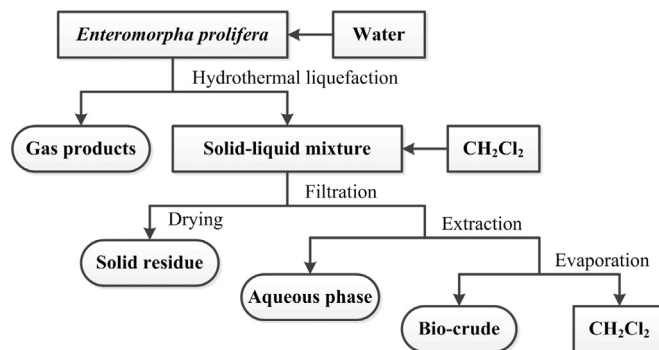


Fig. 1. HTL products separation procedure.

DCM phase were separated. The DCM phase was dried at 313 K for 6 h to a constant weight to remove the solvent, and the remaining was denoted as “bio-crude”. Five runs were performed and the bio-crude yield was $17.8 \pm 0.4\%$ on a dry basis. The elemental composition of the bio-crude is shown in Table 1, and the HHV was 32.93 MJ/kg according to the Channiwala and Parikh formula [20]: $\text{HHV}(\text{MJ/kg}) = 0.3491\text{C} + 1.1783\text{H} + 0.1005\text{S} - 0.1034\text{O} - 0.0151\text{N} - 0.0211\text{Ash}$.

2.3. Simulated distillation of bio-crude

The boiling range distribution of bio-crude was analyzed by simulated distillation (ASTM D7169) and the results are displayed in Table 2 and Fig. S1. An Agilent 6890 N gas chromatograph (Agilent Technologies, Santa Clara, CA) equipped with a flame ionization detector (FID) was used for the experiment. Boiling point calibration up to 1023 K was achieved by using a boiling point standard. The sample was prepared by dissolving 1 mg of bio-crude in 100 mg of CS_2 .

2.4. TGA of bio-crude

Thermogravimetric experiments were conducted on a thermogravimetric analyzer (TGA/DSC1, Mettler-Toledo, LLC, Columbus, OH). To avoid the heat transfer limitation generated by the sample itself, bio-crude of 2.75 ± 0.01 mg was heated from 313 to 1073 K at a linear heating rate of 5, 10, 20 or 40 K/min for each test. High purity argon gas at 50 mL/min was used as the carrier gas to suppress mass transfer effect to a minimum.

3. Theory of thermal analysis kinetics

3.1. Kinetic equation

The rate equation for non-isothermal solid-state reaction with a constant heating rate is shown below:

$$\frac{d\alpha}{dT} = \frac{1}{\beta} k(T) f(\alpha) \quad (1)$$

Table 1
Proximate analysis (air dry basis) and ultimate analysis (dry basis) of *Enteromorpha prolifera* and bio-crude.

Proximate analysis	% ^a	Ultimate analysis	% ^a	% ^b
Moisture	9.82	C	36.19	73.03
Volatile matter	66.64	H	6.27	7.66
Fixed carbon ^c	8.52	N	0.96	2.26
Ash	15.02	O ^c	39.92	14.49
		Ash	16.66	2.56

^a *Enteromorpha prolifera*.

^b Bio-crude.

^c Calculated by difference.

Table 2
Boiling range distribution of bio-crude.

Distillation range (K)	Bio-crude fraction (%)
<473	2.7
473–523	4.3
523–573	7.5
573–623	13.4
623–673	14.8
673–723	8.7
723–773	7.1
773–823	5.4
823–1023	9.4
Total	73.3

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