



Study on pyrolytic kinetics and behavior: The co-pyrolysis of microalgae and polypropylene



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HIGHLIGHTS

- PP can interact with CO₂ or carbonyl groups and lower the CO₂ production.
- PP lowers the activation energy of microalgae from 166.9 to 144.2 kJ mol⁻¹.
- The strongest interaction of PP and *D. tertiolecta* happens when their ratio is 6:4.
- The particle size of PP has great effect on interaction of PP and *D. tertiolecta*.
- TG–FTIR and TG–MS were used to monitor the distribution of pyrolysis gas products.

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ABSTRACT

In the current work, the co-pyrolysis kinetics of *Dunaliella tertiolecta* and PP were investigated via TGA, while TG–FTIR and TG–MS were used for the analysis of gas-phase components and volatiles transition. The TGA results show that PP with certain small particle size accelerates the pyrolysis process of the microalgae, while the existence of *D. tertiolecta* delayed that of PP. This significant interaction achieves maximum when mass ratio of PP and *D. tertiolecta* is 6:4. The activation energy estimated from FWO kinetic model also supports this interaction. The TG–FTIR and TG–MS results show that a significant decrease of CO₂ occurs at PP and *D. tertiolecta* mass ratio of 6:4, indicating that small molecules (such as radicals) released by PP might react with CO₂ produced by *D. tertiolecta* or carbonyl groups in the microalgae.

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1. Introduction

The modern industry has evolved to an immense scale, and resulting in resource shortage and environmental problems. The depletion of fossil fuels and environmental pollution caused by overuse of fossil fuels has forced researchers to seek renewable, sustainable and environmental friendly sources of energy (Upadhye et al., 2011; Zhang et al., 2014). Of all alternatives, bio-oils produced from biomass resources are regarded as a substitutable candidate for petroleum (Chen et al., 2012; Yu et al., 2014). Among the biomass resources, microalgae have been considered as a potential optional feedstock for bio-oil production due to superior photosynthetic efficiency, higher growth rate, area-specific yield, efficient carbon dioxide fixation (Zou et al., 2010).

Furthermore, microalgae can be cultivated on a large scale in either freshwater or saline environments, and do not compete with the use of agriculturally productive or environmentally sensitive land (Yu et al., 2011).

So far, thermochemical conversion of microalgae biomass has been carried out to produce bio-oil (Shihadeh and Hochgreb, 2002). However, some disadvantages of bio-oil obtained from biomass pyrolysis such as higher oxygen content, lower high-heating value (HHV), lower volatile, and delayed ignition time in engine severely hinder its use in practice (French and Czernik, 2010). Hence, it is necessary to explore how to improve the quality of the bio-oil. At present, there are main two pathways to improve the quality of bio-oil: (1) Upgrading of bio-oil, including high-pressure hydrogenation processing and catalytic cracking (Marin et al., 2002); (2) Co-pyrolysis of plastic and biomass (French and Czernik, 2010; Han et al., 2013). The latter have received much attention in recent years because it provides an alternative way to convert cellulose (or lignin)-derived materials and plastic into high-quality fuels or high-value chemicals

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Table 1
Analysis results of *D. tertiolecta*.

Industrial analysis/wt.%		Chemical composition analysis/wt.%		Elemental analysis/wt.%	
Moisture W_{ar}	1.60	Lipids	5.18	C	43.31
Volatiles V_{ar}	64.70	Proteins	30.63	H	5.96
Ash A_{ar}	16.50	Carbohydrates	52.31	O ^a	29.90
Fixed carbon C_{Far}	17.20	Others ^a	11.88	N	4.33
				Empirical formula	CH _{1.65} O _{0.52} N _{0.09}
				HHV (MJ kg ⁻¹)	17.81

^a Calculated by difference.

(Sørum et al., 2001). Since plastics, like polyethylene (PE) and polypropylene (PP), contain a large amount of hydrogen (approximately 14 wt.%), and could provide hydrogen during its co-pyrolysis process with biomass and lead to an increase of liquid production and improvement of oil quality (Bhattacharya et al., 2009). Moreover, the high-pressure hydrogenation of the subsequent upgrading process can be avoided, resulting in safer bio-oil production. At the same time, co-pyrolysis can handle waste plastic efficiently, which is the arch-criminal of the white pollution. To this end, the co-pyrolysis process of plastics and microalgae biomass has the broad application prospect.

Literatures published have proved that co-pyrolysis of plastics and biomass is a very promising method in the field of renewable energy research (French and Czernik, 2010). As reported by Zhou et al. (2006), the mixture of wood-PE or wood-PP can be successfully converted into liquids fuel via co-pyrolysis. Obvious synergistic effect, which led to the increase in the mass loss rate of the blends under high temperature, can be found during the co-pyrolysis process. Similar results were obtained by other researchers (Çit et al., 2007). To date, publications mainly focused on the co-process of plastics with terrestrial biomass (mainly consists of cellulose, hemicellulose and lignin) (Suriapparao et al., 2014), however, the co-process of plastics and microalgae (mainly consists of protein, lipid and carbohydrate) involved scarcely. Pei et al. (2012) and Duan et al. (2015) studied the co-process of microalgae with high density PE and waste rubber tire, respectively. Positive synergistic effect was observed in the co-pyrolysis process. Nevertheless, the reaction dynamics research, which is very important for the effective design and operation of thermochemical conversion units, is not included in these studies. Tang et al. (2011) studied the co-pyrolysis characteristic of microalgae and municipal solid waste (mainly plastic) under different atmospheres using TGA. They found the addition of microalgae could promote the pyrolysis of municipal solid waste. However, detailed interaction information of microalgae and plastic was not discussed, which needs further research.

The objective of this paper is to study the interaction between plastic (PP) and microalgae (*Dunaliella tertiolecta*). Thermogravimetric analysis (TGA) is chosen to estimate the pyrolysis behavior and kinetic parameters, such as apparent activation energy (E) and pre-exponential factor (A) in the current work. In addition, in order to investigate the detailed interaction of *D. tertiolecta* and PP, TG–FTIR and TG–MS were used to monitor the distribution of gas products of co-pyrolysis.

2. Experimental

2.1. Materials

D. tertiolecta (Xi'an Victory Biochemical Co. China) is an important green microalgae and already is mass cultivated mainly in China for its β -carotene content. The elemental composition of the materials is listed in Table 1. The microalgae was dried at 105 °C for 24 h, ground and sieved to obtain fraction under 120

mesh (<125 μ m). The volatiles of PP (Shanghai Yangli Electromechanical Science and Technology Ltd., China) are 100%, and the content of H and C are 13.58% and 84.55%, respectively. PP was first dissolved in *o*-xylene at 120 °C, and then precipitated by anhydrous ethanol to get PP foams. The foams were washed with ethanol and dried at 80 °C for 24 h, and subsequently ground and sieved to get fraction under 120 mesh. The obtained PP and *D. tertiolecta* were mixed uniformly at different weight ratios of 10:0, 8:2, 6:4, 4:6, 2:8 and 0:10.

2.2. Thermogravimetric analysis

The thermogravimetric analyzer (TG Instruments SDT-Q600) was used for these experiments. In a typical experiment, 10 mg of sample was evenly placed into an alumina crucible and pyrolyzed under a high purity nitrogen flow of 50 mL/min. Temperature was raised from room temperature to 800 °C at different heating rates of 5, 10, 20 and 40 °C/min. The experimental errors are lower than 3% by three runs repeatedly at the same conditions.

2.3. TG–FTIR

The TG–FTIR was carried out in STA449F3 (NETZSCH-Gerätebau GmbH, Germany) and VETTEX 70 V (Bruker, Germany). In a typical run, 10 mg sample was used and temperature was raised from room temperature to 800 °C under a heating rate of 10 °C/min in Ar atmosphere with a flow rate of 60 mL/min. The transfer line between the TGA and FTIR apparatuses was made by polytetrafluoroethylene with an internal diameter of 2 mm and length of 1.5 m, the temperature of the transfer line was 200 °C. The spectral region of the FTIR is 4 cm⁻¹ and the resolution is 4000–650 cm⁻¹, the scanning times of spectrum is 16. The experimental data was collected at every 25 °C during the experiment.

2.4. TG–MS

TG–MS was performed by STA449F3 (NETZSCH-Gerätebau GmbH, Germany) coupled with a quadrupole mass spectrometer (QMA 403, Balzers). 10 mg sample was put in an alumina crucible for each batch, and temperature was raised from room temperature to 800 °C at a heating rate of 10 °C/min. The purge gas used was Ar with a flow rate of 60 mL/min. This study primarily discusses the small molecules like H₂, CH₄, H₂O, C₂H₄, C₃H₈, and CO₂, with the $m/z = 2, 15, 18, 28, 43, 44$, respectively. It is notable that the $m/z = 28$ was assigned to represent C₂H₄ because no CO was found in the results of TG–FTIR analysis (see Fig. S2).

2.5. Kinetic methods

A fundamental rate equation was used to analyze the non-isothermal kinetic data from TG analyzer showed as follows:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

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