Study on the co-pyrolysis of high density polyethylene and potato blends using thermogravimetric analyzer and tubular furnace

Sijiang Xiong, Jiankun Zhuo*, Hui Zhou, Renzhong Pang, Qiang Yao

Key Laboratory of Thermal Science and Power Engineering, Tsinghua University, Beijing 100084, PR China

ABSTRACT

The interactions between high density polyethylene (HDPE) and potato during their primary and secondary co-pyrolysis process were investigated by a thermogravimetric analyzer (TGA) and a tubular furnace. Kinetic analysis has shown that the devolatilization of potato was relatively faster compared to those of cellulosic materials, which has been ascribed to the multi-side-chain structure and lower polymerization degree of starch. The pyrolysis process of potato can be divided into three stages, and the main thermal degradation took place between 178 and 378 °C, while the HDPE decomposition occurred in a single stage in the temperature range of 380–517 °C. In the case of blends, the weight loss differences (ΔW) between experimental and theoretical ones were less than ±8% in all cases, and the co-pyrolysis process of potato and HDPE can be described as two consecutive first order reactions, the apparent activation energies of blends were almost invariable, suggested that only physical step limitation was found in the primary co-pyrolysis process of potato and HDPE. On the contrary, the results of tubular furnace experiment showed that due to the relatively long gas resident time, the interaction occurred in the gas phase not only favored the formation of gaseous products, but also improved the bio-oil quality by significantly reducing the oxygen-to-carbon ratios (O/C) of the pyrolysis oil.

1. Introduction

As an attractive materials which are extensively used in our daily lives, the worldwide production and use of plastics has grown rapidly over the last decades, the total plastic consumption in China has exceeded 60 million tons every year [1]. Polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinylchloride (PVC) and polyethylene terephthalate (PET) are found to be the main plastics which arise in the municipal solid waste (MSW). Although various methods for the recycling of waste plastic have been developed, pyrolysis appears to be a promising way both for environmental protection and sustainable development. Especially the polyolefins (contain only carbon and hydrogen i.e., PE and PP) of various origins are considered to be a desirable pyrolysis feedstock. A free radical degradation mechanism of the polymer chain is proposed to explain the pyrolysis patterns, which involving thermal initiation, depropagation, intramolecular and intermolecular transfer and termination of radicals [2–4]. Meanwhile, another type of MSW that raises environmental problems is biomass waste. Numerous studies on the pyrolysis of biomass, in particular, agricultural residue

and lignocellulose materials, have been carried out [5–7]. It has been found that the amount of oxygen present in the pyrolysis oil from biomass can range from ∼35 to 50%, resulting in the corrosion and instability of the oil [8].

It is known that the polyolefins not only contain high hydrogen-to-carbon ratios (H/C), but also have no oxygen, they could provide hydrogen during the co-pyrolysis process with biomass, upgrading the pyrolysis oil by balance the C, H and O in the feedstock [9]. Several studies on the co-pyrolysis of plastic and biomass have been carried out [10–13]. Some researchers claimed that since biomass has a lower thermal stability compares to plastics, they would show their inherent individual characteristics during the co-pyrolysis process, while others believed that there were obvious interactions and synergistic effects between biomass and plastics in the co-process [14–16]. Although these contradictory versions may have been caused by the composition and origins of raw material, the extent of interaction between biomass and plastics still remains ambiguous and unclear. Furthermore, except for a few studies [15,17,18], the co-pyrolysis of HDPE with biomass has not been sufficiently investigated, and as an important resource of kitchen waste, the researches on starch biomass, such as potato, rice and wheat, were rather limited as well. Therefore, the co-pyrolysis of starch biomass and HDPE needs a further study, in order to under-

Table 1
Proximate and ultimate analysis of potato and HDPE.

Samples	Proximate analysis/%				Ultimate analysis/%				
	M_{ad}	A_{ad}	VM_{ad}	FC_{ad} [a]	C_{daf}	H_{daf}	O_{daf} [a]	N_{daf}	S_{daf}
Potato	4.24	3.02	77.04	15.70	44.48	6.56	46.49	1.82	0.65
HDPE	0	0	100.00	0	85.11	14.57	0	0.32	0

M: moisture; A: ash; VM: volatile matter; FC: fixed carbon, ad: air dried basis, daf: dry ash-free basis.
  [a] calculated by difference.

stand their thermal degradation behaviors and to investigate the mutual effect between the sample species in the blends.

Potato is an essential food crop in the world. As the world's largest potato producer, China produces over 80 million tons of potato every year, it also makes potato becomes an important part of kitchen waste. In the present work, potato and HDPE were, respectively, selected as starch biomass and polyolefins. The extent of interaction between two species with respect to their thermal behavior and the characteristics of co-pyrolysis products were evaluated with a TGA and a tubular furnace. The experimental weight loss for the blends, and the amount of co-pyrolysis products were compared with the theoretical values which were obtained by linear combination of the data of pure materials. Meanwhile, special attention was directed to the clarification of the synergistic effects during their primary and secondary co-pyrolysis process.

2. Experimental method

2.1. Materials

In this work, potato was obtained from a local market (Beijing, China). It was cooked and oven dried overnight at 102 °C, crushed to particle size of less than 0.4 mm, and stored in a desiccator. Commercially available HDPE (Youngling Technology Corporation, Shanghai, China) with particle size of less than 75 μm was used as polyolefin material. Blended samples of potato and HDPE in the ratio of 75%: 25%, 50%: 50% and 25%: 75% (by weight) were used in this study. The homogeneity of blends was achieved by mixing in a mortar. The properties of potato and HDPE were presented, respectively, in Table 1.

2.2. Thermogravimetric analysis

In each experiment, approximately 20 mg sample was placed in a ceramic crucible of a TGA (STA 409 C/3/F, Netzsch, German). High purity argon was used for the experiments at a flow rate of

100 ml min^{-1}. The argon flow was started 20 min prior of starting the experiments, in order to ensure an inert atmosphere. The samples were heated from room temperature to 900 °C at heating rate of 10, 20 and 30 °C min^{-1}, respectively. The weight loss in response to temperatures was recorded automatically to plot TG and derivative thermogravimetric (DTG) curves. All experiments were replicated two times.

2.3. Tubular furnace pyrolysis

The pyrolysis of HDPE, potato and their blends was performed with the use of a horizontal quartz reactor with 1200 mm length and 65 mm inner diameter under atmospheric pressure. Fig. 1 shows the schematic diagram of the experimental installation. Before each experiment, 25 g sample was put in a porcelain boat located in the left side of the reactor, and was introduced into the center of the furnace by a long thermocouple at 500 °C, by which the actual temperature of the process can be monitored at the same time. To obtain an inert atmosphere, the reaction occurred under a high grade pure argon with a flow rate of 0.42 L min^{-1}, and the system was purged for 30 min prior to the experiments. The duration of each thermal treatment was 60 min.

The volatiles evolved from the sample passed through two consecutive condensers immersed in two ice baths, by which the condensed fraction was collected. And then the non-condensable gas passed through two filters which were filled with absorbent cotton in order to remove the remaining impurities. Finally, the clean gas was collected in a tedlar sample bag. One microlitre of non-condensable gas was analyzed in a gas chromatograph Agilent 3000 equipped with thermal conductivity detectors.

After each experiment, the solid residue was collected and directly weighted as solid fraction, the amount of condensed products was obtained by taking the difference between the weight of reactor, condensers and connecting pipes before and after the beginning of the experiment. The condensed and solid fraction
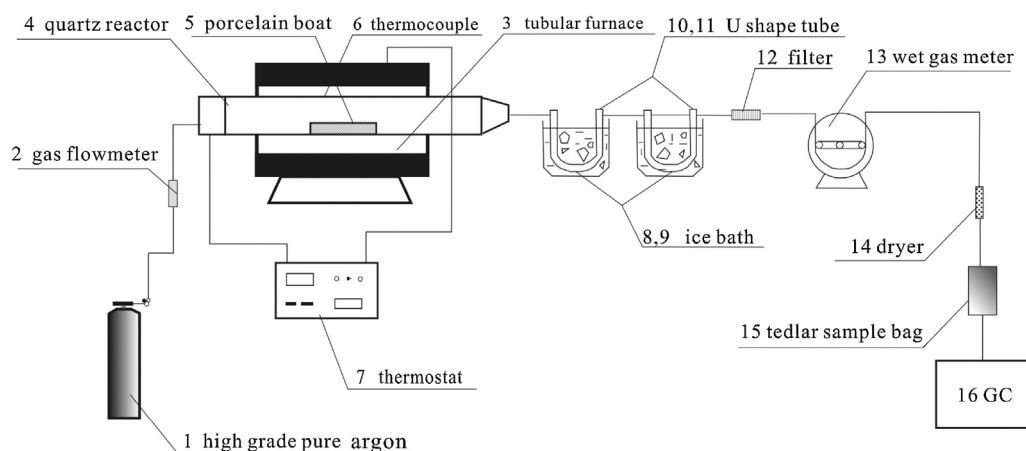
Fig. 1. Schematic diagram of tubular furnace pyrolysis system.