



Thermal behavior and kinetics of co-pyrolysis of cellulose and polyethylene with the addition of transition metals



Zhanghong Wang^{a,b}, Dekui Shen^{a,*}, Chunfei Wu^{b,*}, Sai Gu^c

^a Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, Southeast University, Nanjing 210096, PR China

^b School of Engineering and Computer Science, University of Hull, Hull HU6 7RX, United Kingdom

^c Faculty of Engineering and Physical Sciences, University of Surrey, Guilford GU2 7XH, United Kingdom

ARTICLE INFO

Keywords:

Catalytic co-pyrolysis
Cellulose
Polyethylene
Transition metal
Thermal behavior

ABSTRACT

The influence of the addition of transition metals involving nickel (Ni), cobalt (Co), iron (Fe) and manganese (Mn) on the thermal behavior and kinetic of co-pyrolysis of cellulose (CL) together with polyethylene (PE) was investigated according to thermogravimetric analysis (TGA). It is found that the involvement of transition metals acting as catalysts could promote the decomposition of individual component (CL and PE) in the mixture. The initial decomposition temperature of CL and PE in the mixture is reduced by 91–136 °C and 8–15 °C, respectively, after the addition of transition metals in comparison with that of the mixture of CL and PE. Meanwhile, transition metals could intensify the synergistic interactions between CL and PE, especially during the pyrolysis stage assigned to CL decomposition. The maximum difference of weight loss in this stage is –9.30% to –14.10% for transition metals treated-mixtures while that of the mixture without transition metal treatment is –2.99%. Kinetic results show that the co-pyrolysis of transition metal-involved CL/PE mixtures can be well described as two consecutive first order reactions. The activation energy (E) of CL and PE in the mixture is reduced by 53.21–80.53 kJ/mol and 8.23–12.36 kJ/mol, respectively, as transition metals were involved. In addition, the content of transition metal makes a large influence on the thermal behavior and kinetics of co-pyrolysis of CL/PE mixture.

1. Introduction

Biomass is considered to be one of the most important renewable sources in nature. It is estimated that the world's annual biomass production is up to 146 billion tons [1]. At the same time, biomass is largely produced as a by-product of industry, agriculture and forestry such as bioethanol fermentation, pulp and paper manufacturing, grain planting, and forest mining [2]. For example, biomass waste derived from agricultural production is estimated to be as many as 30 billion tons per year and that from pulp and paper industry can reach 70 million tons per year as well [3]. On the other hand, plastics are extensively used in our daily lives to bring us considerable convenience. It is reported that the global annual production of plastics in 2015 was estimated to have come to 322 million tons [4]. As a consequence, large amount of plastic related wastes are generated causing serious environmental issues due to their high biochemical stability in environment. Although various conventional methods for the disposal of biomass and plastics have been developed, the management of these wastes is still challenging. Moreover, the technology to process these wastes such as incineration and landfill would bring about many

potential secondary hazards to the health of human being and the environment [5,6]. Accordingly, it appears much urgent to develop some green and available approaches to deal with the increasing production of biomass and plastic wastes.

Co-pyrolysis is a promising technique to simultaneously process biomass and plastic and produce high-value added products such as bio-oil and chemicals [7,8]. It is reported that the bio-oil directly derived from biomass generally presented a nature of high oxygen content, acidity, instability, viscosity and corrosion which highly restricted its applications [1,9]. On the contrary, plastic contains high hydrogen content presenting a high effective hydrogen to carbon ratio [10]. Plastic can provide biomass with abundant hydrogen atoms (serving as hydrogen donor) to intensify the thermal decomposition of biomass and reduce the polycondensation of the intermediate products as it was employed to co-pyrolyze with biomass. Meanwhile, the oxygenated compounds originated from biomass during the co-pyrolysis process could promote the chain scission and cracking of plastic in return [11]. As a result, the quality and yield of targeted products (bio-oil or chemicals) were significantly improved. It is reported by Dorado et al. that the yield of alkyl benzenes from the catalytic fast pyrolysis of CL along

* Corresponding authors.

E-mail addresses: 101011398@seu.edu.cn (D. Shen), c.wu@hull.ac.uk (C. Wu).

with polyethylene terephthalate was greatly enhanced compared with CL alone [12]. Kositkanawuth et al. found that co-pyrolysis of biomass with polystyrene led to the improvement of the quality and quantity of the oil compared to pyrolysis of Sargassum alone [13]. Particularly, the oil quantity increased from 3% for Sargassum alone to 29% for the mixture of 67% Sargassum and 33% polystyrene.

It is notable that the involvement of catalyst during the co-pyrolysis of biomass and plastic would further improve the quality of bio-oil compared to that without catalyst. The presence of catalyst can serve active sites for the decomposition of raw materials and the interaction of the intermediates. For example, the surface acid sites of HZSM-5 zeolite can promote the catalytic cracking and refining reactions of biomass and its mixture together with plastic to de-oxygenate bio-oil, favoring the production of hydrocarbon products [14]. At the same time, the catalyst with unique porosity structure is efficient to enhance the selectivity of desired products. Kim et al. found that HY zeolite with a large pore size ($7.4 \times 7.4 \text{ \AA}$) and cavities could be favorable for the diffusion of reactant molecules from the co-pyrolysis of CL and polypropylene into internal pores, resulting in the enhancement of the yields of aromatic hydrocarbons [15]. On the contrary, using a catalyst with pore size smaller than raw material (CL with a kinetic diameter of 8.6 \AA) resulted in the reactions mainly occurred at external surface of the catalysts which greatly restricted the catalytic reaction [15]. Up to date, the catalysts employed are those with unique physicochemical characteristics mainly concerning zeolites and metal oxides [7,16–18]. For example, LOSA-1, spent FCC and $\gamma\text{-Al}_2\text{O}_3$ were employed as catalysts during a catalytic co-pyrolysis of PE and black-liquor lignin for the production of petrochemicals and these catalysts were consequently proven to be effective in the catalytic conversion [17]. In the co-pyrolysis of CL and polypropylene, microporous zeolites (ZSM-5) was found to be more favorable in the formation of aromatic hydrocarbons in comparison with mesoporous Al-SBA-15 [16].

Transition metals especially for Ni, Co, Fe and Mn have been widely applied in various fields such as catalytic pyrolysis of biomass for the preparation of high quality bio-oil [19,20]. It was found that the involvement of Ni and Fe could simultaneously catalyze rearrangement reactions and promote depolymerization of biomass which were favorable for the preparation of desired pyrolysis products such as fuels, chemicals [21]. Meanwhile, transition metals are the necessary minerals for the growth of plant, which are extensively disperse in biomass [22,23]. In this work, transition metals have been used for the co-pyrolysis of biomass and plastic. We aims to develop a new, low-cost and high-efficient catalyst for the catalytic co-pyrolysis of biomass and plastic blend, and assess the effect of natural biomass with intrinsic transition metals on its co-pyrolysis process. Particularly, CL and PE were employed as the representatives of biomass and plastic, respectively. The thermal behavior and kinetics of co-pyrolysis of the mixtures affected by the type of transition metals (Ni, Co, Fe and Mn) and the

concentration of catalyst (Ni) were investigated according to TGA at ambient temperature to $750 \text{ }^\circ\text{C}$ under nitrogen atmosphere.

2. Materials and methods

2.1. Raw materials

Commercially available CL (CAS number 9004-34-6) in the form of microcrystalline powders was purchased from Sigma-Aldrich Corporation (St. Louis, MO, USA). PE powder (CAS number 9002-88-4) with average M_w and M_n of ~ 4000 and ~ 1700 by GPC, respectively, was provided by Sigma-Aldrich Corporation (St. Louis, MO, USA). The detailed elemental composition and chemical structure of CL and PE are presented in Table S1 and Fig. S1. Transition metal nitrates including nickel nitrate hexahydrate (Ni), cobaltous nitrate hexahydrate (Co), iron nitrate nonahydrate (Fe) and manganese nitrate tetrahydrate (Mn) were purchased from Sigma-Aldrich Corporation (St. Louis, MO, USA).

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.enconman.2018.07.010>.

2.2. Experimental procedure

2.2.1. Preparation of samples

For the preparation of Ni-involved CL/PE mixture, 1 g CL powder was immersed into a 20 mL of 0.1 mol/L Ni solution. The mixed suspension was stirred at $60 \text{ }^\circ\text{C}$ for 3 h to evaporate and then dried at $105 \text{ }^\circ\text{C}$. Afterward the dried powder was collected and mixed with 1 g PE powder in an agate mortar via manual grinding for 20 min. The as-grinded powder was the targeted mixture of CL and PE in a ratio of 1:1 with a Ni concentration of 1 mmol Ni/g mixture, which was labeled as CL/PE-Ni-1. CL/PE mixture with different dosage of Ni (0, 0.25, 0.5, 0.75 and 1 mmol Ni/g mixture) and different type of transition metals as catalysts (Ni, Co, Fe, Mn) were prepared in the similar process via regulating the concentration of Ni solution and catalyst solution type, respectively. For comparison, CL/PE mixture without catalyst and CL with 1 mmol/L transition catalyst (i.e., CL-Ni-1, CL-Co-1, CL-Fe-1 and CL-Mn-1) were also prepared.

2.2.2. Thermogravimetric analysis

The pyrolysis experiments were carried out in a thermogravimetric analyzer (Mettler Toledo 188 TGA/SDTA 851, Switzerland) to investigate the thermal decomposition profiles of CL and PE and their mixtures with or without catalysts. About 10 mg of sample was pyrolyzed under $0.1 \text{ m}^3/\text{min}$ N_2 flow at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ from room temperature to $750 \text{ }^\circ\text{C}$. More than two parallel runs were carried out for all the experiments to ensure low relative errors (below 5%).

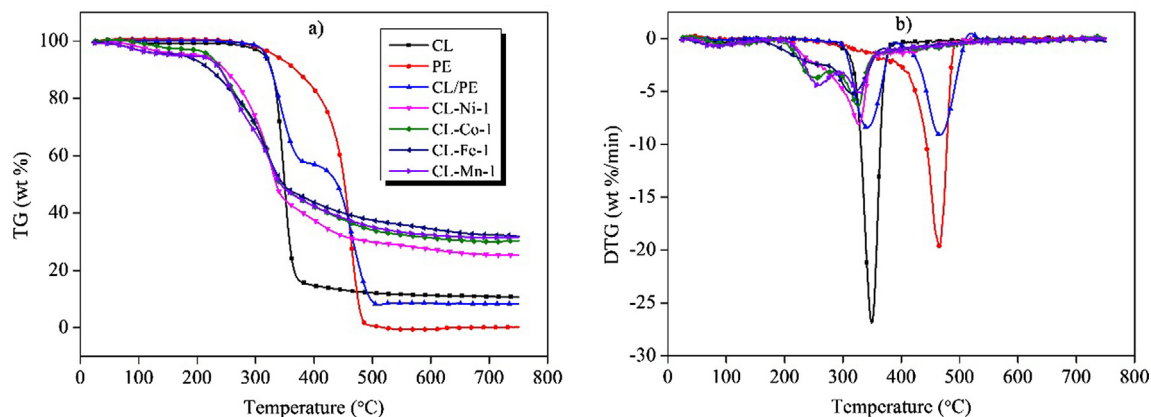


Fig. 1. Pyrolytic behavior of CL with or without transition metals catalysts, PE and CL/PE mixture: (a) TG curves, (b) DTG curves.

Download English Version:

<https://daneshyari.com/en/article/7157959>

Download Persian Version:

<https://daneshyari.com/article/7157959>

[Daneshyari.com](https://daneshyari.com)