

# Study of synergistic effects during co-pyrolysis of cellulose and high-density polyethylene at various ratios

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## ABSTRACT

The mechanism of synergistic effects occurred during co-pyrolysis of cellulose (CE) and high-density polyethylene (HDPE), mixed at various mass ratios (3:1, 1:1, 1:3 w/w), was studied by thermogravimetric analysis coupled with mass spectrometry (TG-MS) and pyrolysis-gas chromatography coupled with mass spectrometry (Py-GC/MS). The TG analysis showed that the co-pyrolysis process was divided into two-stages: the first stage was the decomposition of CE (at 260 °C–410 °C), and the second stage between 410 °C and 527 °C was mainly the decomposition of HDPE. The experimental mass loss values of the mixtures were greater than the estimated values, which confirmed a synergistic effect in the co-pyrolysis of CE and HDPE. The results of MS and Py-GC/MS indicated that the effects of co-pyrolysis promoted the release of small-molecule volatile ( $\text{H}_2\text{O}$ ,  $\text{CO}/\text{C}_2\text{H}_4$ ,  $\text{CO}_2$ ), and the promotion effect was strongest when the ratio was 1:3. Hydrogen transfer from the scission of HDPE could be provided for the decomposition of CE, and the oxygen-containing compounds from CE could promote the chain scission and cracking of HDPE. When the CE/HDPE ratio was less than 1:1, the production of carbohydrate, aldehyde, ketone, and furan groups assigned to CE pyrolysis was suppressed, and the production of alkane and alkene groups was promoted. The decomposition pathways in the co-pyrolysis process of CE and HDPE were proposed.

## 1. Introduction

The problem of municipal solid waste (MSW) disposal is growing worldwide as a result of economic growth, increasing human populations and continued urbanization. MSW pyrolysis is considered an innovative alternative for treating MSW. In a process involving pyrolysis, energy can be obtained more cleanly than is possible from conventional MSW incineration plants, and the waste component can be converted to liquid fuel and chemical feedstocks, potentially reducing secondary pollution problems.

Many studies [1–5] on individual components of MSW have been performed in recent years, and the pyrolysis characteristics of individual components were obtained. However, MSW is a complex heterogeneous mixture and there are interaction among the components during pyrolysis, some researchers [6–9] investigated the characteristics of the pyrolysis products resulting from mixed components of MSW and the co-pyrolysis between biomass and plastics has attracted many researcher's attention, because of the high proportion of biomass

and plastics. Chen et al. [10] investigated the interaction mechanism and the yields of alcohols and hydrocarbons during co-pyrolysis of waste newspaper (WP) and high density polyethylene (HDPE), and found that hydrogen supplements by HDPE could cause aldehydes and ketones convert into branched hydrocarbons, and radicals from WP decomposition could result in the formation of linear hydrocarbons with low carbon number. Saidak et al. [11] investigated the co-pyrolysis effects between polypropylene and two types of biomass, and indicated a synergy in the co-pyrolysis, which related to the reactions between the radicals formed from the co-pyrolysis process and the depolymerisation of cellulose, hemicellulose and lignin. According to the previous studies, the co-pyrolysis between biomass and plastics could promote a higher yield of bio-oil and improve the properties of the bio-oil, which the carbon and hydrogen contents were increasing and oxygen content was decreasing as well as an increase in the calorific value. This was because plastics contain large amounts of carbon and hydrogen content, and may be a hydrogen donor during co-pyrolysis with biomass [12].

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**Table 1**  
Proximate analysis and ultimate analysis of samples.

Sample		CE	CP-31	CP-11	CP-13	HDPE
Proximate analysis (wt%)	Volatile	93.75	94.48	98.30	99.96	100
	Ash	0.06	0.03	0.02	0.01	0
	FC <sup>a</sup>	6.19	5.49	1.68	0.03	0
Ultimate analysis (wt%)	C	42.23	53.96	64.00	75.49	85.81
	H	6.36	8.15	9.59	11.16	12.30
	N	0.03	0.03	0	0	0.02
	S	0.03	0.03	0	0	0
	O <sup>b</sup>	51.34	37.85	26.39	13.34	1.83

FC: fixed carbon.

<sup>a,b</sup> The FC and O content was calculated by difference.

In fact, biomass is consisted of three major components include cellulose, hemicellulose and lignin, generally represent, respectively, 40–60, 20–40 and 10–25 wt% [13]. The pyrolysis mechanisms occurring during pyrolysis of biomass is closely depended on the proportion and the form of three main components [14]. Părpăriță et al. [15] studied the decomposition of polypropylene/biomass composites by TG/FT-IR/MS, reported that the main composites of gaseous products obtained from decomposition of polypropylene/biomass were H<sub>2</sub>O, CO<sub>2</sub>, CO, methane, methanol, formaldehyde, acetic acid and formic acid, and indicated that the biomass type and its composition in main constituents were the dominant factors affecting the composites. In order to understand the synergistic effects of co-pyrolysis thoroughly, the co-pyrolysis of plastics with biomass components has been studied. Jin et al. [16] studied the co-pyrolysis of lignin with low density polyethylene (LDPE) and found that lignin could promote the decomposition of polycarbonate. LDPE may restrain the cracking of the aryl-OCH<sub>3</sub> bond in the co-pyrolysis of lignin with LDPE. Sanjana D. [17] investigated the synergies in the processes of devolatilization and condensation during co-pyrolysis of LDPE with cellulose, the results were the synergistic effect will increased the liquid yield and the char will catalyzed LDPE to form liquid during condensation. During condensation, gas-gas and gas-liquid interactions enhanced the generation of liquid products. Piotr [18] studied the influence of polystyrene addition to cellulose on chemical structure and properties of bio-oil obtained during pyrolysis, found that the chemical composition of bio-oils from blends was more similar to the liquid products obtained from polystyrene, and oxygen content of compounds was in a smaller level. As for the co-pyrolysis of biomass component and plastics, previous studies haven't illuminated how the synergistic effects affect the process

of co-pyrolysis, and what's the interaction between biomass component and plastics related to the different conversion paths of cellulose and plastics.

Cellulose, one of the major component of biomass, has a primary structure consisting of two  $\beta$ -glucopyranose units linked by  $\beta$ -1,4-glycosidic bonds, where the glucopyranose comes from the hemiacetal reaction of D-glucose between the C-1 and C-5 positions [19,20]. In addition, cellulose derived compounds are rich in hydroxyl and aldehyde groups [21]. Polyethylene is a widely used plastic and a common type of MSW; moreover, it has a high carbon content of 85 wt% and an extremely low oxygen content of 0.15 wt% [10]. Therefore, cellulose and high density polyethylene were selected as raw materials for the co-pyrolysis experiment.

In this work, the co-pyrolysis mechanism of cellulose and high density polyethylene, and the influence of the different proportion on the synergistic effect at various ratios were studied by TG-MS and Py-GC/MS. During the co-pyrolysis process, samples of cellulose and high density polyethylene were mixed in 3:1, 1:1 and 1:3. TG-MS was used to explore the mass loss characteristics, and the evolution characteristics of the volatile small-molecule products (H<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O, CO, C<sub>2</sub>H<sub>4</sub>, CO<sub>2</sub>) with temperature [12,22], and Py-GC/MS was performed to determine the pyrolytic product distributions, which could speculate the co-pyrolysis reactions [23].

## 2. Materials and methods

### 2.1. Materials

In this study, high density polyethylene (HDPE) was supplied by Dushanzi Petrochemical Branch of PetroChina Co., Ltd., and cellulose (CE) was from Aladdin Industrial Co. (CAS number: 9004-34-6). For the samples to be fully dried, the HDPE and CE feedstocks were dried at 105 °C for 12 h, then mixed them in different weight ratios (1:0, 3:1, 1:1, 1:3, 0:1) and finally milled with a ball mill and sieved through 100 mesh to obtain uniform mixtures. Proximate analysis and ultimate analysis of the samples were performed by GB/T 212-2008 method and elemental analyzer (vario EI cube), and the results were shown in Table 1.

In this paper, the samples of 100% cellulose, 75% cellulose/25% high density polyethylene, 50% cellulose/50% high density polyethylene, 25% cellulose/75% high density polyethylene and 100% high density polyethylene were designated CE, CP-31, CP-11, CP-13 and HDPE, respectively.

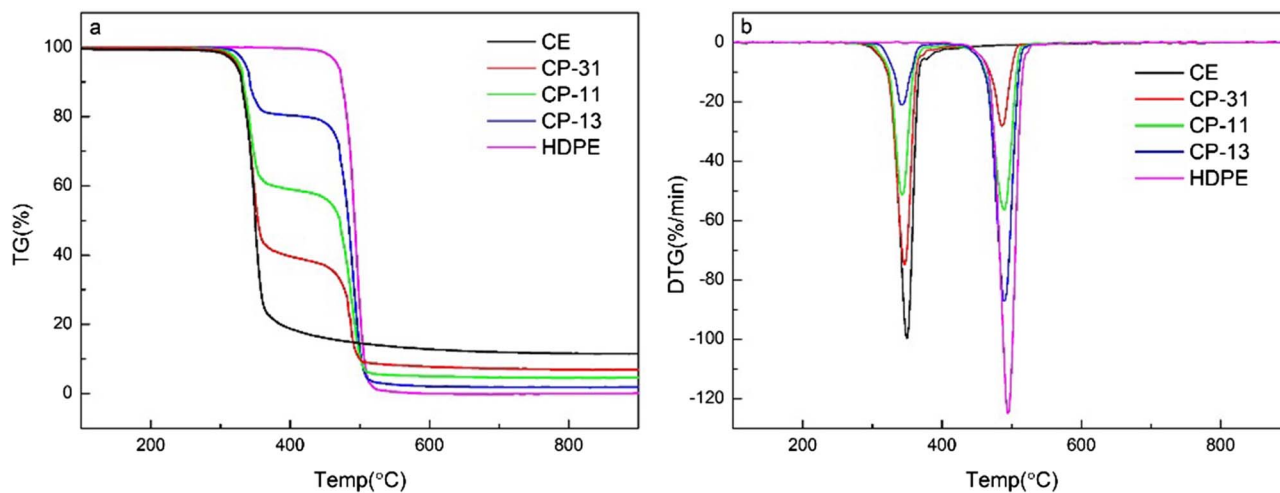


Fig. 1. TG (a) and DTG (b) curves of the samples.

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