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Co-pyrolysis Characteristics of Biomass and Polyethylene by Thermogravimetry–Mass Spectrum

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Abstract: To study the synergetic effects and variations in small molecule gas products, which occur during co-pyrolysis of main biomass components and plastics, a thermogravimetry–mass spectrum (TG–MS) method was used to study co-pyrolysis characteristics of cellulose, xylan, lignin, and polyethylene. The blending ratio of each co-pyrolysis sample was 1:1 (w/w). Weight loss intervals of single components as well as mixed components were obtained via TG analysis, wherein theoretical and experimental values were obtained by fitting TG data of individual components. A synergetic effect occurred during the co-pyrolysis process and this effect promoted the decomposition of samples. MS experimental data showed that the presence of polyethylene may facilitate decomposition of biomass components and increase the yield of small molecule gas products during the co-pyrolysis process. The presence of H_2O and CO_2 in the small molecular products was increased during pyrolysis of cellulose with polyethylene. Xylan and polyethylene promoted mutual decomposition during the co-pyrolysis process, while the yield of H_2O, CH_4, H_2, and C_2H_4 was increased. Thus, co-pyrolysis between lignin and polyethylene may increase the yields of CO, C_2H_4, and H_2.

Key words: cellulose, xylan, lignin, polyethylene, co-pyrolysis

1 Introduction

Advancements in science and technology have enabled the increased consumption of non-renewable energy sources, such as coal and petroleum [1,2]. Biomass is composed of many complex high-molecular organic compounds. The main components are cellulose, hemicellulose, and lignin, together with certain extracts and minerals [3]. Generally, in dry-based biomass feedstocks, cellulose, hemicellulose, and lignin account for 46 wt%–60 wt%, 20 wt%–40 wt%, and 10 wt%–25 wt%, respectively [4]. Biomass can be converted into energy and clean fuel by thermochemical and biochemical methods. Pyrolysis is a very effective thermochemical method to convert biomass into fuel [5], thereby reducing potential secondary pollution issues [6].

To improve the yield of pyrolysis products and to obtain high value-added products, many studies have been conducted on the co-pyrolysis of biomass and plastics in recent years [7–13]. Due to high hydrogen and low oxygen contents, plastics are used as co-reagents with biomass in co-pyrolysis [8]. Moreover, plastic waste pollutes the environment, and co-pyrolysis of biomass and plastics provides a very effective method to dispose of plastics. Brebu et al. [11] conducted experiments on the co-pyrolysis of pine corn with low density polyethylene (LDPE), polypropylene (PP), and polystyrene (PS), and reported that the energy of pyrolysis oil from mixed samples was higher than that from any single component of pine corn. Önal et al. [10] studied the yield of bio-oil from co-pyrolysis of almond shells and high density polyethylene (HDPE). The results indicated that the yield was enhanced by 23%, and that the bio-oil obtained had high hydrogen content, low oxygen content, and high calorific value. However, the complexity of biomass components has hindered the study of the mechanisms underlying co-pyrolysis. Biomass is

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mainly composed of three major components. Presently, co-pyrolysis of these three components and plastic was investigated to assess potential synergistic effects during co-pyrolysis.

Polyethylene is a widely used plastic, and is commonly found in municipal solid waste. It has a high carbon content and low oxygen content. Therefore, it is a raw material of biomass, which is suitable for use in co-pyrolysis studies. In this study, thermogravimetry–mass spectrum (TG–MS) analysis was carried out to investigate the co-pyrolysis process of cellulose, hemicellulose, and lignin with polyethylene. Potential synergistic effects, generation of small molecule gas products, and weight loss in different samples, were explored by comparing experimental yields with estimated yields of pyrolysis products,

2 Materials and methods

2.1 Materials

The samples used in this experiment were cellulose, hemicellulose, lignin, and polyethylene. Cellulose (CAS number: 9004-34-6) is α-cellulose powder, and lignin (CAS number: 8068-05-1) is an alkaline lignin. Both were purchased from Sigma-Aldrich Corporation. Xylan (CAS number: 9014-63-5) is a model compound of hemicellulose derived from corncob. It was purchased from Macklin Corporation. All single samples were dried at 105 ºC for 12 h and then mixed with polyethylene in different ratios (1:0, 1:1, 0:1), milled with a ball mill, and sieved through a grade 100 mesh to obtain uniform mixtures. High density polyethylene was supplied by Dushanzi Petrochemical Branch of PetroChina Co., Ltd. Proximate and ultimate analyses of the samples were performed via the GB/T 212—2008 method using an elemental analyzer. The results are shown in Table 1.

Sample names are simplified in Figs. 1–3, Table 2, and Figs 7–9. Cellulose, xylan, lignin, and polyethylene were designated as C, X, L and PE, respectively, and the mixed samples were designated as CP-11, XP-11, and LP-11, respectively.

2.2 TG-MS analysis

A thermogravimetric analyzer (NETZSCH STA 449 F3) coupled with a mass spectrometer (Oministar^{TM}GSD 320) were used to perform pyrolysis experiments. In the TG experiment, 10 ± 0.1 mg of samples were heated from 25°C to 1000°C at a heating rate of 30°C/min. In all experiments, the purge gas used was argon with a 40 ml/min flow rate. TG and MS were connected by a gas transmission pipeline, and maintained at 200°C in order to avoid gas condensation. In this study, the mass spectra 2, 16, 18, 28, and 44 were assigned to represent H_2, CH_4, H_2O, CO/C_2H_4, and CO_2, respectively.

3 Results and analyses

3.1 Pyrolysis TG/DTG curves of samples

The heating rate of single and mixed components of cellulose, xylan, lignin, and polyethylene was 30°C/min. The TG curves and differential thermal gravimetry (DTG) curves of samples were obtained (Figs. 1–3). The weight loss process of biomass pyrolysis is generally categorized into two stages: (i) decomposition of unstable compounds and (ii) continuous devolatilization [14].

The weight loss stage of cellulose was 280–400°C, and the maximum weight loss rate (105.28 %/min) occurred at 350°C. This was mainly due to depolymerization of the sample, where more than 80% of the sample was decomposed into volatiles, including most of its component organic compounds such as furan, levoglucosan, and other molecules [15]. Following the decomposition reaction, CO, CO_2, aldehydes, and ketones are generated. Charring occurs at a temperature range of 400–900°C, during which the sample loses weight gradually but continuously [16]. The weight loss stage of HDPE occurs between 440–530°C, and the maximum weight loss occurs at 490°C with a maximum weight loss rate of 127.43%/min. The pyrolysis products were mainly alkanes and alkenes. The trend was similar for the mixed samples. Weight loss could be divided into two stages, the first stage is the pyrolysis of biomass components and the second stage is mainly the pyrolysis of HDPE. The TG/DTG curve of the pyrolysis of xylan is shown in Fig. 2. The weight loss stage was at 220–350°C. Maximum weight loss occurred at a temperature close to 300°C with a small peak around 260°C. This small peak corresponded to the fragmentation and decomposition of certain side chain groups. The weight loss stage of xylan consisted mainly of the depolymerization and fracturing of major structures, as well as the generation of certain volatiles due to secondary reactions, such as those of CO and CO_2 [17]. Above 350°C, weight loss resulted mainly from the charring process,

Table 1. Proximate and ultimate analysis of samples.

Sample	Ultimate analysis (%)					Proximate analysis (%)		
	C	H	O	N	S	Volatiles	Ash	Fixed carbon
Cellulose	42.23	6.36	51.31	0.04	0	93.75	0.06	6.19
Xylan	41.10	6.54	51.44	0.01	0	92.79	0.91	6.30
Lignin	49.99	4.87	24	0.08	3.76	45.64	17.30	37.06
HDPE	85.81	12.30	1.86	0.02	0	99.99	0.01	0

which included reforming of multi-ring structures. The pyrolysis residue of xylan was 16.99%. The TG/DTG curves of pyrolysis of lignin indicated that the main weight loss stage was 200°–530°C, and that the maximum weight loss occurred at 322°C, with a maximum weight loss rate of 7.79%/min (Fig. 3). The main reason behind the weight loss was cleavage of unstable chains in lignin, such as alkyl chains and methoxy groups. Some volatiles, such as CO_2, CO, H_2O, and CH_4, may be generated during this process [18].

To obtain the weight loss characteristics in co-pyrolysis, experimental and estimated values of TG/DTG curves of the blends were compared. Estimated values were calculated as:

$$M_{es} = 0.5M_b + 0.5M_p \quad (1)$$

where M_{es} is the estimated mass percentage of blends in the co-pyrolysis process, M_b is the mass percentage of biomass components in the individual process, and M_p is the mass percentage of HDPE in the individual pyrolysis process.

Comparisons between the experimental and estimated values of TG/DTG curves are shown in Figs. 4–6), and the characteristics points are listed in Table 2. The process of co-pyrolysis had little effect on the pyrolysis temperature in each stage of the samples. However, the experimental values of maximum weight loss rate were lower than the estimated values. Moreover, experimental values of residues of the blends were lower compared to estimated values. These findings indicate the existence of a synergistic effect in the co-pyrolysis of cellulose, xylan, and lignin with polyethylene, where the effect promoted decomposition of the samples.

3.2 MS data analysis

In the pyrolysis process, samples decompose into small molecular volatiles. In this experiment, the volatiles were analyzed in real time via MS, and six major small molecule gas products were detected. They were $m/z = 2$ (H_2), $m/z = 16$ (CH_4), $m/z = 18$ (H_2O), $m/z = 28$ (CO, C_2H_4), $m/z = 44$ (CO_2) (m represents the proton number and z represents the charge number).

The pyrolysis gas products of polyethylene were mainly

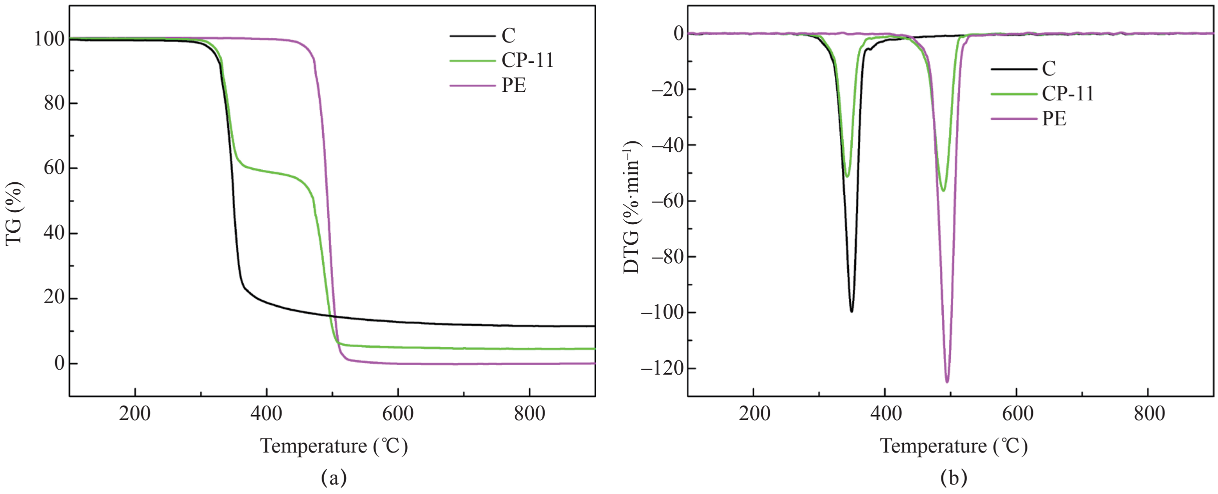


Fig. 1. TG and DTG curves of C, PE, and CP-11.

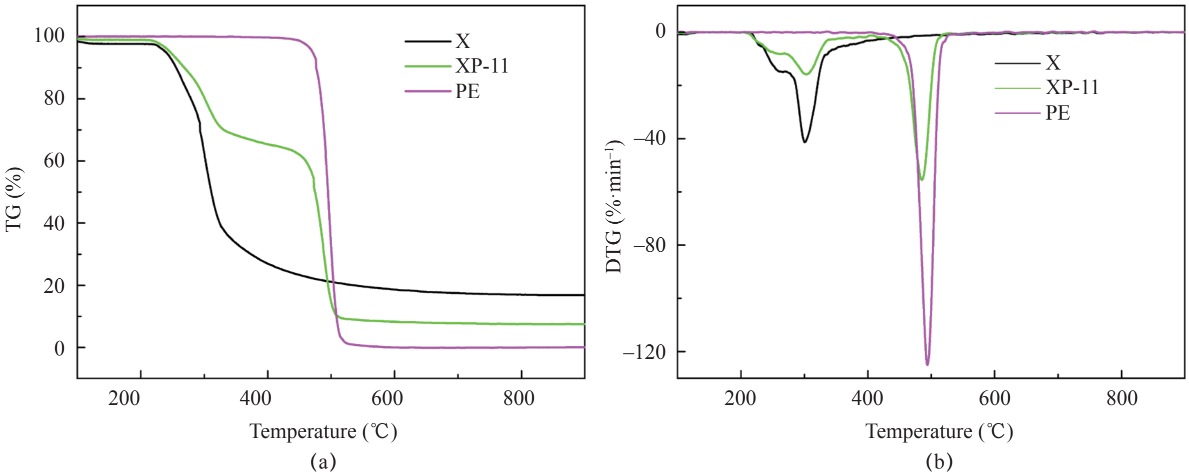


Fig. 2. TG and DTG curves of X, PE, and XP-11.

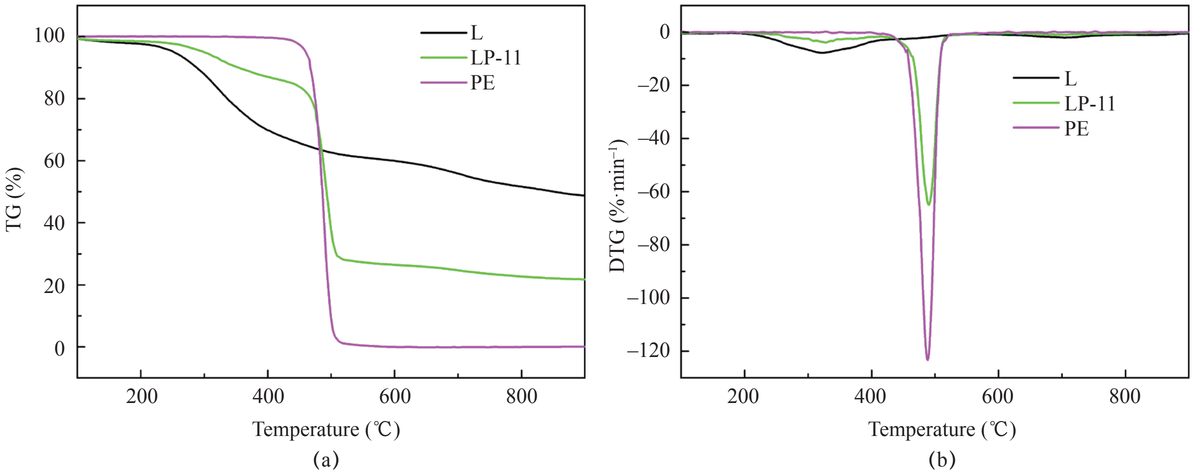


Fig. 3. TG and DTG curves of L, PE, and LP-11.

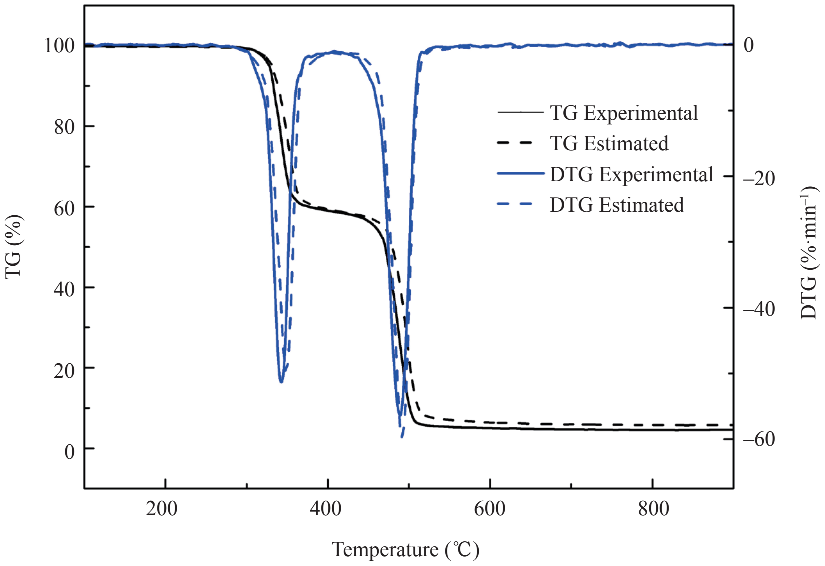


Fig. 4. Experimental and estimated TG and DTG curves of the mixture of C with PE.

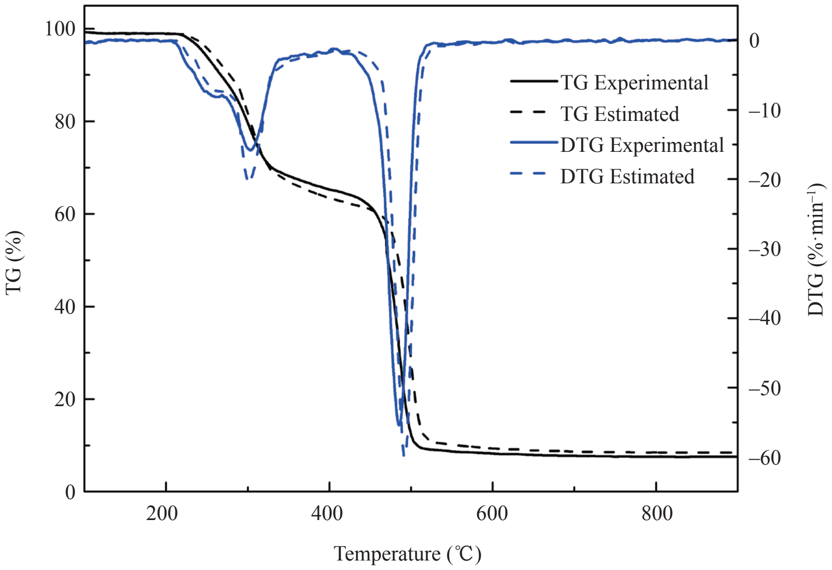


Fig. 5. Experimental and estimated TG and DTG curves of the mixture of X with PE.

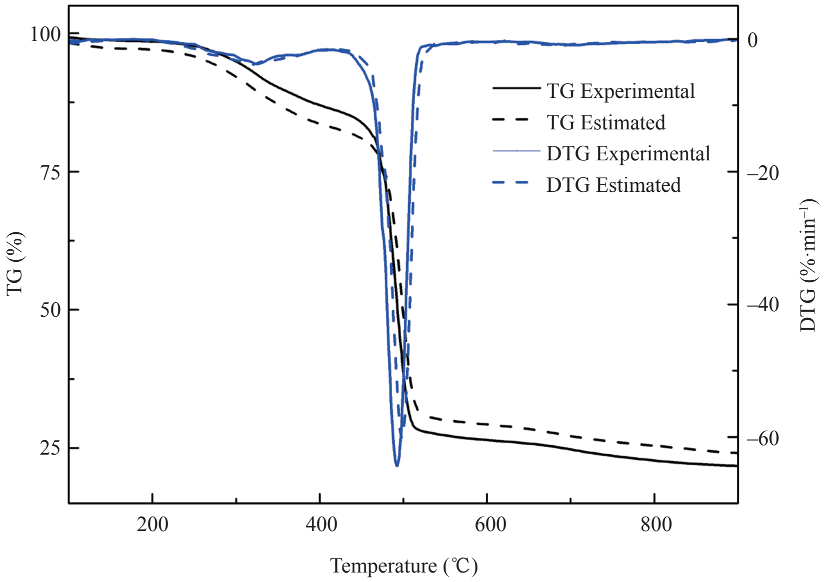


Fig. 6. Experimental and estimated TG and DTG curves of the mixture of L with PE.

Table 2. Experimental and estimated values of characteristic points of the TG and DTG curves of the mixtures.

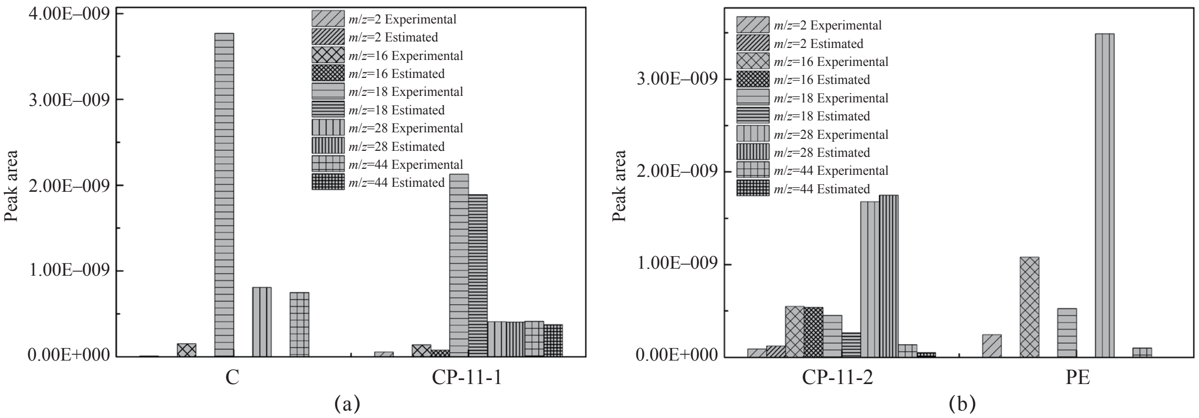
Sample		T_{max1} (°C)	D_{max1} (%/min^{-1})	T_{max2} (°C)	D_{max2} (%/min^{-1})	Residue (%)
CP-11	Experimental	343.06	−52.16	490.83	−56.95	4.81
	Estimated	349.57	−49.73	491.46	−59.66	5.91
XP-11	Experimental	305.40	−15.83	488.40	−55.42	7.68
	Estimated	301.22	−20.48	492.08	−60.01	8.58
LP-11	Experimental	327.87	−3.86	490.57	−64.90	21.66
	Estimated	318.29	−3.92	498.65	−60.16	23.89

T_{max1} and T_{max2} represent temperatures corresponding to the maximum weight loss rates of the first and second stages; and D_{max1} and D_{max2} represent the maximum weight loss rates of the first and second stages respectively.

C_2H_4, CH_4, and H_2O during the weight stage of 440–530°C. These results were due to breakage of C—C bonds between the polyethylene monomers, which corresponds to the generation of CH_4. While C=C bonds are difficult to break, their breakage results in the generation of a large amount of C_2H_4 during pyrolysis. In the weight loss range of 260–410°C, the main gas products of cellulose were H_2O, CO, and CO_2, which could be attributed to dehydration of cellulose and the depolymerization of the polymer. Pyrolysis products of xylan in the weight loss range of 220–350°C were mainly H_2O, CO_2, CO, and a small amount of CH_4, which were attributed to dehydration and depolymerization reactions and intermolecular bond rupture. Pyrolysis of lignin in the weight loss range between 200°C and 530°C produced gaseous products, including H_2O, CO_2, and CH_4, while CO was observed between 530 and 900°C. This may be due to a secondary reaction in the charring process, during which CO is produced from a reaction of CO_2 with C.

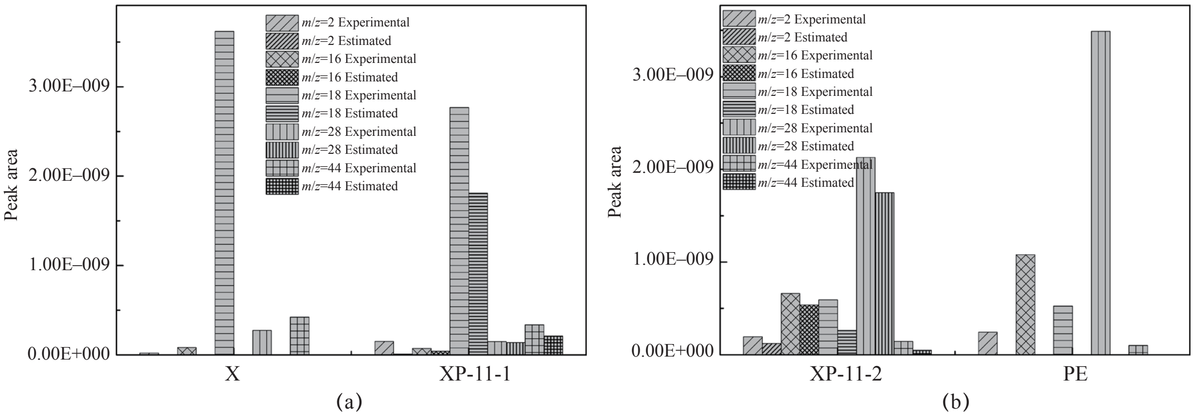
To better understand the effect of co-pyrolysis on the distribution of pyrolysis products, the peak areas of corresponding gas products was obtained by integrating the MS curve. The theoretical value of the peak area was calculated using formula (1) and compared with the experimental value. The effect of co-pyrolysis on pyrolysis gas products was obtained by comparing experimental values of the peak area with the theoretical values. The MS curves could be divided into two stages. The first stage was represented by the MS curve of the pyrolysis product of cellulose in co-pyrolysis. The second stage was the pyrolysis product MS curve of polyethylene. The results are shown in Figs. 8 and 9. Since lignin undergoes considerable weight loss during the charring process, more CO and H_2 is generated during the 530–900°C stage. Therefore, comparison of experimental and estimated peak areas of lignin MS curves led to the calculation of the peak area of the whole pyrolysis process.

Comparison of experimental and estimated peak areas of all samples are shown in Figs. 7–9). The experimental values of H_2O and CO_2 were clearly higher than the theoretical values in the first stage of the co-pyrolysis of cellulose and polyethylene. The same trend was observed in the second stage, which indicated that the presence of polyethylene may promote dehydration and depolymerization of cellulose to produce H_2O and CO_2. The experimental values of H_2O, CH_4, and H_2 were higher than the theoretical values in the first stage of co-pyrolysis of xylan and polyethylene, and the same trend was seen in the second stage (Fig. 8). Moreover, the experimental value of the gas product



(a) (b)

Fig. 7. Comparison of experimental and estimated peak areas of C, PE, and CP in two stage decomposition processes.



(a) (b)

Fig. 8. Comparison of experimental and estimated peak areas of X, PE, and XP in two stage decomposition processes.

corresponding to m/z=28 was larger than the theoretical value. The gas product was C_2H_4, produced by the decomposition of polyethylene, confirming that the presence of xylan promoted the production of C_2H_4. These results indicate that co-pyrolysis of xylan and polyethylene may promote decomposition of both, resulting in the production of more gas products. Comparison of peak area experimental values and theoretical values of the pyrolysis products was done referring to the MS curves of the pyrolysis process of lignin and polyethylene (Fig. 9). The yield of m/z=28 (CO, C_2H_4) and H_2 was very high in the pyrolysis of mixed samples. The major changes noticed were that the experimental values were greater than the estimated values, and that there were slight changes in other gas products. The experimental value of H_2O was greater than the theoretical value, while the experimental value of CH_4 was less than the theoretical value. This indicated that co-pyrolysis of lignin and polyethylene may promote the production of CO, C_2H_4, and H_2 gases.

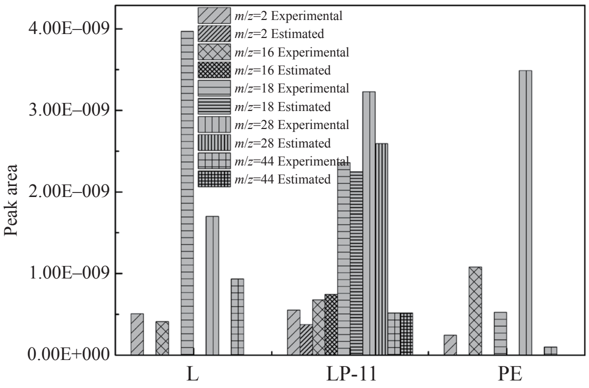


Fig. 9. Comparison of experimental and estimated peak areas of L, PE, and LP in decomposition processes.

4 Conclusions

In this study, co-pyrolysis characteristics between cellulose, xylan, lignin and polyethylene were analyzed via TG–MS. The main weight loss range of cellulose was 280–400°C, and the maximum weight loss rate was reached at 350°C. The weight loss range of xylan was 220–350 °C and the maximum weight loss was observed at 260°C and 300°C, respectively. The main weight loss range of lignin was 200–530°C, and the maximum weight loss rate was reached at 322°C. The weight loss range of polyethylene was 440–530°C, and the maximum weight loss rate was observed at 490°C.

Comparison of experimental and theoretical values of characteristic points of the TG/DTG curve of each sample indicated very little effect on the pyrolysis temperature of each stage during the co-pyrolysis process. However, there was an effect on the maximum weight loss rate, as demonstrated by experimental values that were generally smaller than the theoretical values. All experimental values of the pyrolysis residues of mixed samples were lower than the theoretical values. This result indicated that a synergistic effect occurred during the co-pyrolysis process, and that this effect may have promoted the decomposition of the samples.

In the co-pyrolysis process, the existence of polyethylene promoted the dehydration and depolymerization of cellulose to produce H_2O and CO_2. Co-pyrolysis of xylan and polyethylene promoted decomposition of both and produced more gas products, where H_2O, CH_4, H_2, and C_2H_4 all displayed higher yields. Co-pyrolysis of lignin and polyethylene promoted the production of CO, C_2H_4, and H_2.

Co-pyrolysis of biomass components and polyethylene facilitated the decomposition of the sample, resulting in more gaseous products and pyrolysis products with a higher added-value, Therefore, due to the high hydrogen content and low oxygen content of plastics, it may be favorable to add plastic materials in co-pyrolysis with biomass to improve the quality and yield of pyrolysis gas products.

References

[1] Naik S, Goud V V, Rout P K, et al. Characterization of Canadian biomass for alternative renewable biofuel [J]. Renewable Energy, 2010, 35 (8): 1624–1631.

[2] Zhou H, Long Y, Meng A, et al. The pyrolysis simulation of five biomass species by hemi-cellulose, cellulose and lignin based on thermogravimetric curves [J]. Thermochimica Acta, 2013, 566 (16): 36–43.

[3] Yu J, Paterson N, Blamey J, et al. Cellulose, xylan and lignin interactions during pyrolysis of lignocellulosic biomass [J]. Fuel, 2017, 191: 140–149.

[4] Mckendry P. Energy production from biomass (part 1): Overview of biomass [J]. Bioresource Technology, 2002, 83 (1): 37–46.

[5] Wang C, Li D, Hao Q L , et al. Pyrolysis characteristics of pine biomass in a powder-particle fluidized bed [J]. Journal of Fuel Chemistry and Technology, 2012, 40(2): 156–163. Chinese.

[6] Jin W, Shen D, Liu Q , et al. Evaluation of the co-pyrolysis of lignin with plastic polymers by TG-FTIR and Py-GC/MS [J]. Polymer Degradation and Stability, 2016, 133: 65–74.

[7] Zhang X S, Lei H W, Chen S L , et al. Catalytic co-pyrolysis of lignocellulosic biomass with polymers: A critical review [J]. Green Chemistry, 2016, 18 (15): 4145–4169.

[8] Oyedun A O, Tee C Z, Hanson S , et al. Thermogravimetric analysis of the pyrolysis characteristics and kinetics of plastics and biomass blends [J]. Fuel Processing Technology, 2014, 128 (1): 471–481.

[9] Chen W, Shi S, Zhang J, et al. Co-pyrolysis of waste newspaper with high-density polyethylene: Synergistic effect and oil characterization [J]. Energy Conversion and Management, 2016, 112: 41–48.

[10] Önal E, Uzun B B; Pütün A E. Bio-oil production via co-pyrolysis of almond shell as biomass and high density polyethylene [J]. Energy Conversion and Management, 2014, 78(1): 704–710.

[11] Brebu M, Ucar S, Vasile C, et al. Co-pyrolysis of pine cone with synthetic polymers [J]. Fuel, 2010, 89(8): 1911–1918.

[12] Chen W, Shi S, Chen M, et al. Fast co-pyrolysis of waste newspaper with high-density polyethylene for high yields of alcohols and hydrocarbons [J]. Waste Management, 2017, 67: 155–162.

[13] Yang J, Rizkiana J, Widayatno W B, et al. Fast co-pyrolysis of low density polyethylene and biomass residue for oil production [J]. Energy Conversion and Management, 2016, 120: 422–429.

[14] Idris S S, Rahman N A, Ismail K, et al. Investigation on thermochemical behaviour of low rank Malaysian coal, oil palm biomass and their blends during pyrolysis via thermogravimetric analysis (TGA) [J]. Bioresource Technology, 2010, 101(12): 4584–4592.

[15] Wang S, Guo X, Wang K, et al. Influence of the interaction of components on the pyrolysis behavior of biomass [J]. Journal of Analytical and Applied Pyrolysis, 2011, 91(1): 183–189.

[16] Gunasee S D, Danon B, G Rgens J F, et al. Co-pyrolysis of LDPE and cellulose: Synergies during devolatilization and condensation [J]. Journal of Analytical and Applied Pyrolysis, 2017, 126: 307–314.

[17] Wu S, Shen D, Hu J, et al. Cellulose-lignin interactions during fast pyrolysis with different temperatures and mixing methods [J]. Biomass and Bioenergy, 2016, 90: 209–217.

[18] Liu Q, Wang S, Zheng Y, et al. Mechanism study of wood lignin pyrolysis by using TG–FTIR analysis [J]. Journal of Analytical and Applied Pyrolysis, 2008, 82 (1): 170–177.