Co-pyrolysis of the mixtures of polyethylene and lignin with various ratios using thermogravimetric analysis-mass spectroscopy (TG-MS)

J. Gu[1,2], H.R. Yuan[1,2*] and Y.Z. Wang[1,2]

[1]Key Laboratory of Renewable Energy, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, China

[2]Guangdong Key Laboratory of New and Renewable Energy Research and Development, Guangzhou 510640, China

Abstract

High density polyethylene (PE) due to the high hydrogen content (14%), low oxygen content, low-cost and largely existed and alkali lignin (AL) one of main constituents in biomass, were employed in this study. PE and AL were mixed at various ratios, which were 3:1, 1:1 and 1:3 (mass ratio) respectively, using planetary ball mill. TG-MS was used to study the thermal mass-loss characteristics and the evolution character of syngas of the mixture of PE and AL in an inert atmosphere. There was a distinct mass loss stage (420-526 °C) during the co-pyrolysis of the mixtures, the temperature corresponding to the maximum mass loss rate was lower than the estimated value which was calculated from the experimental data of individual component pyrolysis regarding the mixing ratio, and the maximum mass loss rate was larger than the estimated value, which indicated that PE and AL could promote each other to decompose. The mass loss of the thermal degradation process was approximately linear to the ratio of PE. The main gaseous products of PE were CO, CH_4, H_2O, and little H_2, while the ones of AL were H_2O, CO_2, CH_4 and CO. The corresponding peak areas of CO and H_2O was larger than the estimated value in the co-pyrolysis of the mixtures, which indicated that there was a mutual promotion between PE and AL.

Keywords: co-pyrolysis, polyethylene, lignin, TG-MS

1 Introduction

Combustible solid waste, which includs vast plastic and biomass, is an important component of municipal solid wastes, accounting for approximately 30 % of all the municipal solid waste [1]. A number of studies are about the waste-to-energy of combustible solid waste using various thermochemical processes, such as combustion [2], pyrolysis [3] and gasification [4]. Both pyrolysis and gasification, which has been paid highly attention in recent years, are suggested as a feasible alternative to combustion for the inhibition of the emissions of dioxin precursors due to reducing conditions, strong reduction of volume and weight and the improvement of resource recovery [5-7]. Pyrolysis is the thermochemical treatment of solids to produce char, tar and syngas under an inert atmosphere [8-10], and the syngas produced from pyrolysis can be easily integrated into current energy technologies, such as the steam power generation technology with conventional burner and the advanced gas-steam combined cycle power generation technology. However, the thermal characteristics of the plastic and biomass vary greatly, resulting in a series of problems such as difficulties in the design of the pyrolyzer and relevant processes and complexity in controlling the thermal treatment. Therefore, it becomes very necessary to study the synergic interaction between plastic and biomass in the co-pyrolysis process.

Thermogravimetric analysis (TG) has been widely used to study the thermal mass-loss characteristics and reaction kinetics of various solids (coal, biomass and plastic et al.), which are influenced by heating rate [11], atmosphere [12], pretreatment [13] and so on. Furthermore, the combination of mass spectroscopy (MS) and TG is one of the best way to the real-time analysis on the evolved gases, in order to study the mechanisms of thermochemical processes [14-15].

In this work, TG-MS was employed to study the co-pyrolysis characteristics and gas evolution data of the high density polyethylene (PE) and the alkali lignin (AL), which were the typical components of plastic and biomass. This study attempted to compare their different behaviors with the thermal characteristics to obtain the mutual influence between plastic and biomass.

2 Materials and Methods

2.1 Raw materials

PE was obtained from Dushanzi Petrochemical Branch of PetroChina Co Ltd. AL which from Sigma-Aldrich Co. LLC., is employed as co-pyrolysis reagent. PE and AL were milled in 3:1 (3PE1AL), 1:1 (1PE1AL) and 1:3 (1PE3AL) wt ratio. In order to advance the uniformity, the binary

mixtures were prepared by Planet-Ball-Grinding machine. All samples were dried for 6 hours before experiments. The proximate and ultimate analyses of the samples are shown in Table 1.

Table 1 shows that PE is a thermoplastic resin with the highest volatile content, approximately 99 %, while AL has the highest ash content (~16 %) and the lowest carbon content, approximately 20 %. The ash content of the mixtures vary in the proportion of weight, which indicated that PE and AL were blended well.

Table 1 Proximate analysis and ultimate analysis of PE, AL and their mixtures

Samples		PE	3PE1AL	1PE1AL	1PE3AL	AL
Proximate Analyses	Ad %	0.00	3.74	7.50	12.16	16.18
	Vd %	99.99	89.91	76.66	65.36	48.64
	FCd %	0.01	6.35	15.84	22.48	35.17
Ultimate Analyses	Cd %	85.81	69.58	52.75	36.23	20.65
	Hd %	12.30	10.59	8.15	5.38	2.61
	Nd %	0.02	0.07	0.18	0.29	0.40
	Sd %	0.00	0.83	1.93	3.03	4.11
	Od %	1.87	15.82	30.58	44.46	56.05

2.2 Experimental methods

Co-pyrolysis experiments between PE and AL were performed using a STA449 F3 TG analyzer (Erich Netzsch GmbH & Co., KG., Selb, Germany) coupled with an OMNISTAR GSD301 mass spectrometer (Pfeiffer Vacuum Technology AG, Asslar, Germany). A 10 mg sample was heated from 40 °C to 1000 °C at a constant heating rate of 30 °C/min with an Ar flow (100 mL/min). Before heating, the temperature was held at 40 °C for 1 h to remove the air and stabilize the baseline of MS. TG and MS data were recorded at the same time during the heating process, and a multiple ion detection (MID) model was adopted in the MS. This work examined the important ions [16] at 2, 16, 18, 28 and 44 (m/z), designated H_2, CH_4, H_2O, CO and CO_2, respectively.

3 Results and discussion

3.1 Thermogravimetric analysis

Fig. 1 presents the TG and DTG curves for PE, AL and their mixtures under Ar atmosphere at heating rate of 30 °C/min, and Table 2 lists the characteristic parameters of the samples, which highlight the differences between these samples.

3.1.1 TG-DTG of PE and AL in Ar atmospheres

Since the volatile content of PE was close to 100 %, only one mass loss peak was generated with a maximum mass-loss rate of 127.5 %/min in Fig. 1. At 440-531 °C, the pyrolytic mass loss of PE in Ar was 98.1 %, with a complete off-the-chain depolymerization reaction. Two distinct mass-loss stages appeared during the pyrolysis of AL. The first DTG peak occurred at 323 °C, and the mass loss at 180-549 °C was 36.81 %, which was largely due to the evolution of the volatile substances. The second DTG peak occurred at 704 °C and the mass loss at 549-938 °C was 12.92 %, which was possibly due to the decomposition of the residual volatile.

3.1.2 TG-DTG of the binary mixtures in Ar atmospheres

As displayed in Fig. 1, the co-pyrolysis of 3PE1AL, 1PE1AL and 1PE3AL under Ar atmosphere exhibited three main peaks and the third peak was not obvious. In the second mass-loss stage (420-526 °C) of the binary mixtures, where the pyrolysis of PE and AL occurred, the temperature corresponding to the maximum mass loss rate was lower than PE, and the mass loss was higher than the estimated value which was calculated from the experimental data of individual component pyrolysis regarding the mixing ratio (Fig.2), which indicated that PE and AL could promote each other to decompose. These results were consistent with those of previous reports, such as Jakab et al. [17] and Sajdak [18]. Besides, in the first mass-loss stage (183-420 °C) of the binary mixtures, where only pyrolytic reactions of AL happened, the initial temperature was higher than AL and the mass loss was lower than the estimated value, which indicated that PE could inhibit AL to decompose.

The mass loss of the thermal degradation process was reduced with the reduction of PE proportion and was approximately linear to the ratio of PE. By means of mathematical treatment, the formula was got as follows:

$$massloss(\%) = 0.482 \times PE + 49.73 \tag{1}$$

The correlation coefficient (R^2) was 0.991, indicating that the simulation effect was good. The mass loss of the mixture of PE and AL in random wt ratio will be calculated by the formula, which can predict the thermal degradation process of binary mixtures.
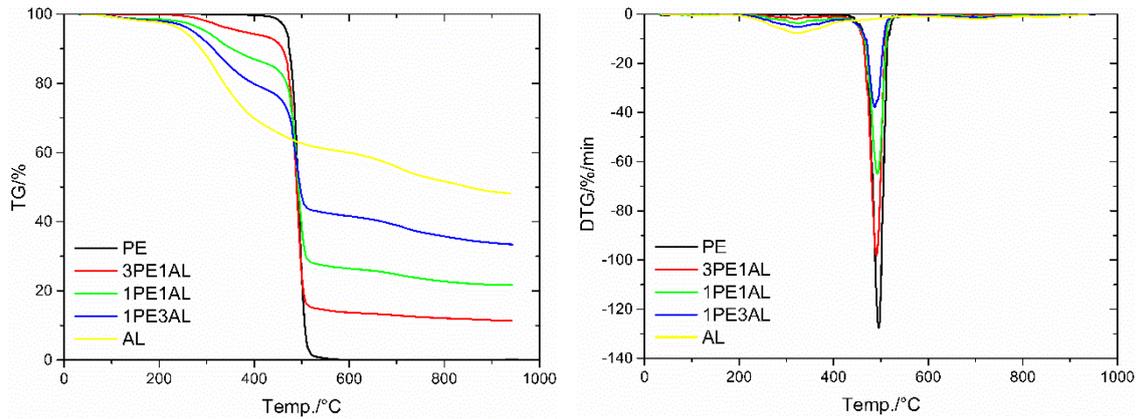
Fig.1. TG and DTG curves of PE, AL and their mixtures

Table 2 Characteristic parameters of TG and DTG curves

Samples	1			2			3		
	Temperature range /°C	Temperature peak /°C	Mass loss /%	Temperature range /°C	Temperature peak /°C	Mass loss /%	Temperature range /°C	Temperature peak /°C	Mass loss /%
PE	\	\	\	440-531	495.4	98.1	\	\	\
3PE1AL	205-414	318.42	5.96	414-526	490.66	78.87	526-941	701.08	3.65
1PE1AL	183-416	326.91	12.36	416-525	493.03	58.27	525-943	705.8	6.32
1PE3AL	189-420	322.99	19.59	420-526	487.29	35.38	526-943	709.45	9.77
AL	180-549	322.54	36.81	\	\	\	549-938	704.19	12.92
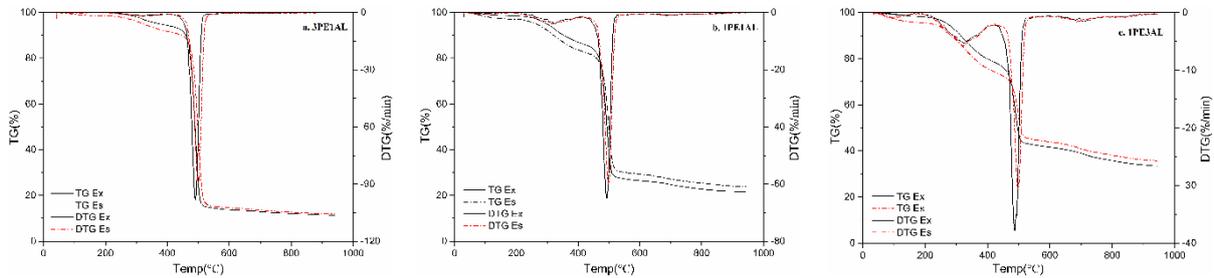
Fig.2. The experimental and estimated TG-DTG curves of the mixtures

3.2 Evolved gas analyses

To analyze the evolved gases in real time, MS was combined with TG, and focusing on the evolution of selected gases such as H_2, CH_4, H_2O, CO and CO_2. As shown in Figs. 3, the MS curves of the evolved gas of the samples were synchronous with the DTG curves, and the peak of the main gas products appeared within the vicinity of the DTG peak temperature.

As shown in Fig. 3a, the main gaseous products of PE were CO, CH_4 and H_2O, and little H_2 was generated at 440-531 °C, which may be due to the decomposition of long-chain molecules. In the pyrolysis of AL, H_2O, CO_2, CH_4 and CO were mainly generated at 180-549 °C, and the release of CO was observed at 549-938 °C, which were the main components of the volatile.

In Fig. 3b-3d, the main gaseous products generated during the first main mass-loss stage (183-420 °C) of the mixtures were H_2O and CO_2, and the peak area of H_2O was lower than the estimated value, which indicated that PE could suppressed the decarboxylation and decarbonylation of AL, as mentioned above. During the second mass-loss stage (420-526 °C) of the mixtures, the main gaseous products generated included CO, H_2O and CH_4. The corresponding peak areas of CO was larger than the estimated value, which may be attributed to the cracking of PE promoted by the CO_2 from AL[19], and the corresponding peak areas of H_2O was larger than the estimated value which could be attributed to the decomposition of AL enhanced by the H_2 from PE[20]. These results indicated that there are synergic interactions between PE and AL.
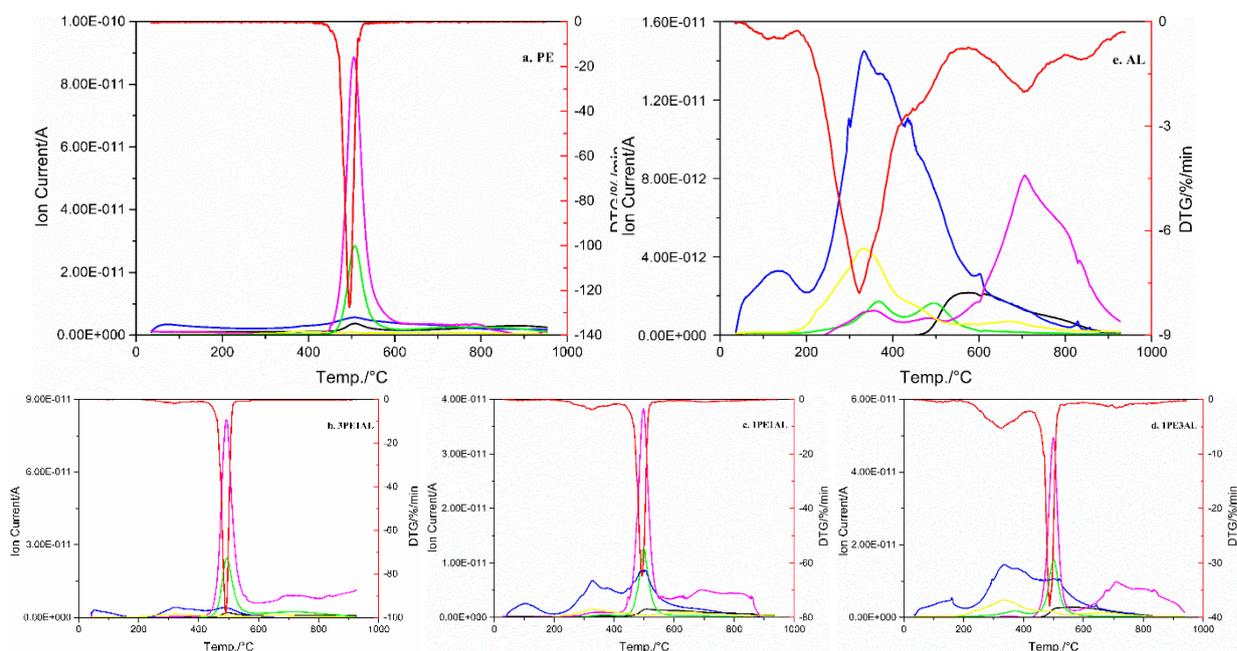
Fig.3. MS and DTG curves of PE, AL and their mixtures

(━m/z=2,━m/z=16,━m/z=18,━m/z=28,━m/z=44)

4 Conclusions

TG-MS was used to study the thermal mass-loss characteristics and the evolution character of syngas from co-pyrolysis of the mixture of PE and AL (3:1, 1:1 and 1:3 wt ratio). The co-pyrolysis of the binary mixture divided into three stages, and the mass loss of the thermal degradation process was approximately linear to the ratio of PE. The main gaseous products of the mixtures were CO, H_2O and CH_4 during the second mass-loss stage (420-526 °C) .The mutual promotion between PE and AL in co-pyrolysis process should be considered.

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