

CHARACTERISTICS OF THE PYROLYSIS AND GASIFICATION OF LOW-DENSITY POLYETHYLENE (LDPE)

Zheng Jiao*, Chi Yong

*Institute for Thermal Power Engineering, State Key Lab of Clean Energy Utilization,
Zhejiang University, Hangzhou 310027, China
E-mail: msw_2@zju.edu.cn*

1. Introduction

Plastic waste was considering as one of the most harmful component of municipal solid waste, due to its non-biodegradability. However, on the other hand, plastics contain large quantity of energy and shows great potential to be used as some raw material or energy source[1]. Worldwidely, polyethylene is the most common used plastics, it takes about 25% of total plastic production of the world[2].

Nowadays, pyrolysis and gasification were developed to be one of the most effective way of recycling and energy utilization of solid wastes. Previous studies uncovered some characteristics of PE pyrolysis and gasification, such as kinetic modeling[3,4] or products distribution[5,6]. This work try to find the basic access of the decomposition of LDPE under both pyrolysis and gasification condition by comparing the TGA/FTIR and fluidized bed gasification experiments.

2. Experimental

2.1 Material

The raw material used in this study was LDPE particles produced by Sinopec Yangzi petrochemical company with the particle size of 3mm, the density of 0.920g/cm³ and the melting point of 130~145°C. Tab.1 shows the proximate and ultimate analysis of the material. Powdered LDPE was used for TGA/FTIR experiment and original particles were directly used to carry out the fluidized bed gasification.

Tab. 1 Proximate and ultimate analysis of material/%

M_{ad}	A_{ad}	V_{ad}	FC_{ad}	$Q_{b,ad}/kJ\cdot kg^{-1}$	C_{ad}	H_{ad}	N_{ad}	S_{ad}	O_{ad}
0.02	0.15	99.83	— ^①	46362	85.83	14.38	0.16	0.07	— ^①

^①Not detected.

2.2 TGA/FTIR

The Nicolet Nexus 670 spectrometer and Mettler Toledo TGA/SDTA851e thermo analyzer were coupled by a Thermo-Nicolet TGA interface model, of which the stainless transfer line and gas cell (20cm path length) were set to 180 C to minimize the change of evolved gas. Heating rate was set to 15K/min, nitrogen was used as the purge gas for both TGA and spectrometer. Resolution in FTIR was set as 4cm^{-1} , number of scans per spectrum was set as 20 times/min, and the spectral region was set as $4000\sim 400\text{cm}^{-1}$.

2.3 Fluidized bed gasification

A fluidized bed gasifier with the capacity of 10kg/h was used in this study. Fig. 1 shows the schematic diagram of the facility. The height of the gasifier is 5m, and the inner diameter is 0.1m.

The sampling point was located at horizontal section at the exit of the gasifier. The detail description of sampling point is showed at Fig. 2. The filter was used to catch the entrained ash/char and the condensable products were collected by the condenser, ice water was used as the coolant, the composition of syngas was detected by the gas analyzer. The sampling process was strictly in accordance with the requirements of isokinetic sampling. The equivalent rate for gasification was set to 0.4 and the temperature was $550\sim 750^\circ\text{C}$.

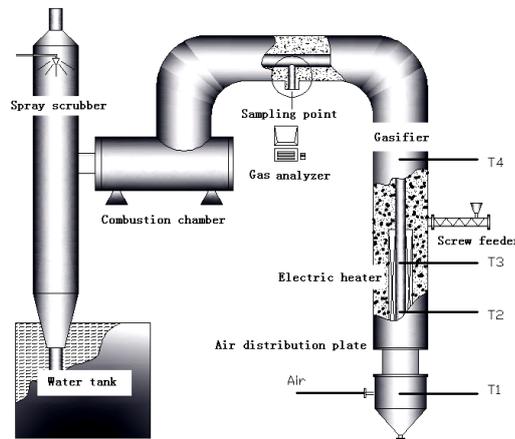


Fig. 1 Schematic diagram of the experimental facility

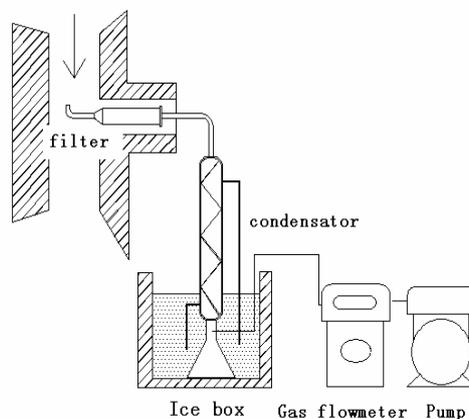


Fig. 2 Schematic diagram of the Sampling point

3. Results and discussion

3.1 Pyrolysis behaviour and products

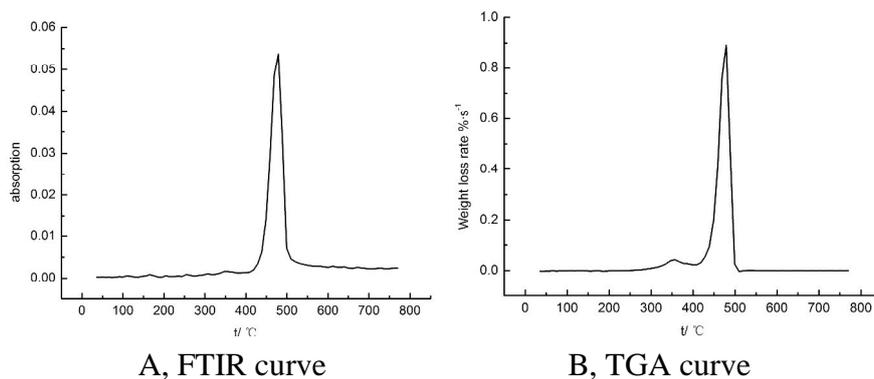


Fig. 3 TGA/FTIR curves of pyrolysis of LDPE

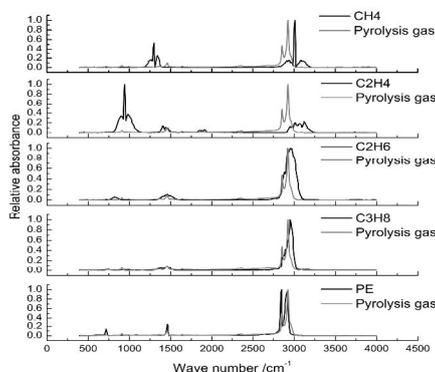
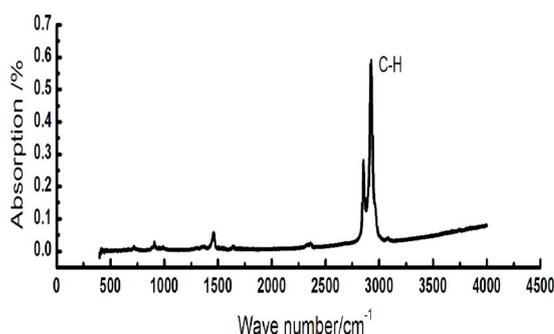


Fig. 4 FTIR spectra of the product of LDPE pyrolysis

Fig. 5 FTIR spectra comparing

Fig. 3 shows the TGA/FTIR curves of pyrolysis of LDPE, the decomposition takes place in a very narrow temperature range, from 450°C to 550°C and the maximum conversion speed reached 0.9%/s at 500°C. As expected the FTIR curve presented the similar figure, a narrow absorption peak represents the gaseous product generated at the temperature range of 450~550°C, as well. Fig. 4 shows the FTIR spectra of the product of LDPE pyrolysis, some mixture of alkanes (bands in the regions 2964-2885 and 2853 cm^{-1}) can be indentified. Comparing with this FTIR spectra with methane, ethene, ethane, propane and polyethylene as shown in Fig. 5. It is found that the similarity increased with the molecular weight, that means high molecular weight products takes a great part of the products of LDPE pyrolysis. Therefore, the pyrolysis progress was deduced as following: LDPE $[\text{C}_2\text{H}_4]_n$ is a kind of mixture caused by the switch of 'n' in a certain range. As the increase of 'n' some physical characteristic such as density, soften temperature and boiling temperature can be raised slightly.[7] Under the high temperature condition, some small 'n' ones vaporized first and as the raising of temperature the decomposition decreased the number of 'n', that means most of the small molecular products was generated by the decomposition of the steam of small 'n' PE.

PART II GASIFICATION

However, the experimental condition was not so good for the sufficient decomposition of LDPE, because, the heating rate was only 20k/min and the residence time of gas in the reactor was not long enough. In another words, when the steam leave the reactor, the temperature is only a little higher than the boiling point. That's why a lot of wax was found in the condensed products of PE pyrolysis[8].

3.2 Distribution of products of fluidized bed gasification

Tab.2 Mass and energy distribution of LDPE gasification

Temperature /°C	Mass distribution / %				Energy distributio / %		
	Syngas	Water	Tar	Ash/Char	Syngas	Tar	Ash/Char
550	73.75	3.42	0.86	1.12	79.93	1.31	3.26
650	88.70	4.35	1.09	0.53	81.03	1.67	1.50
750	93.30	5.20	1.04	0.32	80.70	1.61	0.86

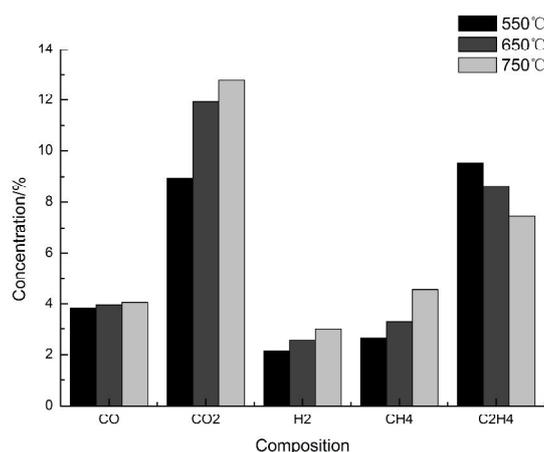


Fig. 6 The composition of the syngas

Tab. 2 shows the mass and energy distribution of LDPE gasified in fluidized bed. Either for mass or energy, syngas was the main product takes about 80% of energy and 90% of mass of the products. Fig. 6 shows the composition of the syngas, ethene is the main combustible component of syngas, takes about 10% vol. Obviously, the decomposition of LDPE in fluidized bed was much more sufficient than in TGA/FTIR condition.

There may be three possible reasons for achieving sufficient decomposition, they are higher heating rate, long residence time and the effect of oxygen. As shown by TGA/FTIR the decomposition of LDPE which can generate small molecules such as ethene, should take place in the gaseous phase, therefore the temperature of gaseous phase is very important for achieving sufficient decomposition. In despite of the residence time of gaseous phase in fluidized bed can not be very long, the dramatically high heating rate can be helpful to heat the gaseous phase and make the decomposition sufficient. The exist of oxygen burn out some

gas products and the high temperature tail gas directly increased the temperature of gaseous phase. On the other hand, the incomplete oxidation of LDPE or the high molecular products such as tar or wax also generated some small molecules. That's why the decomposition under gasification condition can be much more sufficiently than pyrolysis condition at low temperature, although the reactors are both fluidized bed[9].

4. Conclusions

Comparing with the TGA/FTIR study and the fluidized bed gasification some conclusion was drew as flowing:

(1) The decomposition of LDPE take place at about 450~550°C and generate a lot of high molecular products;

(2) The temperature of gaseous phase is the key parameter of decomposition. Since the residence time of gas can not be very long in both TGA/FTIR condition or fluidized bed gasification, high temperature and heating rate can be very helpful for achieving sufficient decomposition.

(3) The incomplete oxidation of both LDPE and it's decomposition products is good for heating the gaseous phase to promote the reaction of decomposition and generate small molecules as well.

(4) The gasification of LDPE can be very sufficient in fluidized bed reactor at low temperature (about 550°C). Among the products, syngas takes more than 80% for both mass and energy. Ethene is the main combustible component of the syngas, takes about 10% of the volume.

Reference

- [1] D. S. M. El-Haggar, Recycling of Municipal Solid Waste Rejects, in Sustainable Industrial Design and Waste Management, *Academic Press Oxford*, **2007**,197-222.
- [2] L. Lundquist, et al., Plastics Recovery and Recycling, in Life Cycle Engineering of Plastics.*Elsevier Science Ltd*, **2000**,39-75.
- [3] T. Faravelli, et al., Kinetic modeling of the thermal degradation of polyethylene and polystyrene mixtures. *Journal of Analytical and Applied Pyrolysis*, **2003**,70(2), 761-777.
- [4] M. Wallis, S. K. Bhatia, Kinetic study of the thermal degradation of high density polyethylene. *Polymer Degradation and Stability*, **2006**, 91(7),1476-1483.
- [5] T. Faravelli, et al., Gas product distribution from polyethylene pyrolysis. *Journal of Analytical and Applied Pyrolysis*, **1999**, 52(1), 87-103.
- [6] M. He, et al., Syngas production from catalytic gasification of waste polyethylene: Influence of temperature on gas yield and composition. *International Journal of Hydrogen Energy*, **2009**. 34(3),1342-1348.
- [7] D. Seth, A. Sarkar, Thermal pyrolysis of polypropylene: effect of reflux-condenser on the molecular weight distribution of products. *Chemical Engineering Science*, **2004**. 59(12), 2433-2445.

PART II GASIFICATION

- [8] A. E. S. Green, S. M. Sadrameli, Analytical representations of experimental polyethylene pyrolysis yields. *Journal of Analytical and Applied Pyrolysis*, **2004**. 72(2), 329-335.
- [9] M. L. Mastellone, et al., Fluidized bed pyrolysis of a recycled polyethylene. *Polymer Degradation and Stability*, **2002**. 76(3),479-487.