

Pyrolysis Simulation of Plastic Wastes in Actual Situation

Zijian Wang

Abstract—Nowadays, the physical and chemical qualities of the same type of plastic goods can vary significantly due to production conditions and manufacturing processes, making it difficult to categorize discarded plastic products and increasing the difficulty of recycling. In this paper, three thermoplastics: polypropylene (PP); polystyrene (PS); and high-density polyethylene (HDPE), are used to detect and analyze the pyrolysis properties of waste plastics using Thermogravimetric Analysis (TGA) and to calculate the kinetic parameters of thermoplastics in the pyrolysis reaction. It is found that the mixed pyrolysis of plastics facilitates the pyrolysis reaction, but the required activation energy of the reaction increases if the content of more stable HDPE gains. The optimum pyrolysis temperature range and activation energy of pyrolysis are discovered by modelling the real proportion of waste plastics and pyrolyzing them. And the results will predict and guide the engineering development for mass waste plastic pyrolysis.

Index Terms—Plastic waste, plastic pyrolysis, activation energy.

I. INTRODUCTION

Plastic has become one of the indispensable application materials in people's life. The broad acceptance of single-use plastics, such as gloves, masks, and medical packaging, during the current COVID-19 outbreak illustrates this [1]. Flexible, low-cost, and long-lasting properties of plastics have aided their extensive use in packaging materials, agriculture, electronics, automobile, and other industries [2]. Worldwide plastic production has exceeded about 280 million tons per year and continues to grow every year [3]. Plastics' physical qualities and timeliness enable vast amounts of waste to be generated, and the complex composition of plastic compounds makes waste separation and disposal difficult. Plastic trash disposal has a tremendous environmental impact today, with marine pollution being particularly serious. Nearly 5.21 trillion pieces of plastic debris (mostly microplastics less than 5 mm in diameter) have been found to exist in detectable seas. Statistics show that 45,700 microplastic debris exist per square mile of ocean, weighing approximately 270,000 tons, and 7.99 million tons of plastic debris enter the ocean each day [4]. Total waste exceeded 6.2 billion tons in 2016, of which plastic waste generated nearly 238 million tons, accounting for 11.8% of municipal solid waste [5].

Non-biodegradable plastic products in landfills will pollute the soil, and incineration of waste plastics will pollute the air by producing toxic gases such as dioxins and hydrogen chloride, as well as increasing particulate matter and carbon dioxide in the air [6]. In comparison to typical waste plastics

technology, pyrolysis offers great processing efficiency and environmental friendliness, and is more in line with waste treatment methods in terms of reduction and harmlessness. Despite the fact that some believe this technique is unsustainable, pyrolysis has significant environmental benefits over other waste plastic recycling methods, as it produces no dioxins and can cut greenhouse gas emissions [7]. Ibrahim Dubdub *et al.* studied the pyrolysis of mixed plastics: polypropylene (PP); polystyrene (PS); and high-density polyethylene (HDPE). They found that the pyrolysis temperature periods of pure plastic samples at different heating rates were ranked as: PS<PP<HDPE, as well as the pyrolysis temperature periods of mixed plastics increase when the amount of HDPE increases [8]. Their sample ratios are ideal, which may not fit with the actual ones. The pyrolysis temperature periods under the actual plastic ratios cannot be predicted. C. McCaffrey *et al.* conducted mixed plastic pyrolysis experiments using PS, PE plastic waste ratios in US and discovered that polyethylene could be degraded by free radical processes [9]. However, their reference ratios are relatively simple. the ratios may have large errors, which may lead to large mistakes in predicting the real situation.

In this study, Pure material pyrolysis experiments are performed to verify the temperature regularity of pyrolysis, and ternary mixtures are pyrolyzed to observe pyrolysis temperature, reaction activation energy and the relationship between plastic samples containing substituents and branched chains (PP, PS), and linear plastic samples (HDPE). Since China is a major plastic consuming country, this study decides to ration the raw materials by plastic annual world and Chinese plastic consumption, and experimentally simulate the actual plastic waste pyrolysis process to restore the actual situation of plastic ratios as much as possible, so that the results will predict the actual plastic pyrolysis temperature and kinetic parameters.

II. EXPERIMENTAL MATERIALS AND PREPARATION

A. Material Properties

PP, HDPE, and PS are used for plastic pyrolysis. PP as a matrix material has the advantages of better insulation, high temperature resistance, high transparency, high dimensional stability and excellent composite properties, which broadens its application. PP is one of the most promising raw materials for the creation of natural synthetic polymer composites because it is well suited for industrial applications as a reinforcing and hybrid material [10]. HDPE has the advantages of linear, acid and alkali resistant substances, good chemical stability, high degree of crystallization and low branching volume, which exhibits better mechanical properties than other types of polyethylene [11]. PS is a

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widely used general thermoplastic with high chemical stability, mechanical properties, good chemical inertness and excellent processing performance [12].

B. Experimental Procedure

The experiment is conducted with nitrogen as carrier gas, and the weighed samples are put into the pyrolyzer. The initial temperature of the reaction is set at 25 °C and stabilize for 40 minutes, and then thermogravimetric curves of the sample are drawn at different heating rates (the heating temperature gradient selected is 20°C, 25°C, 30°C, 35°C, 40°C, 45°C). After the final temperature is raised to 650 °C and stabilize for 20 minutes, the pyrolysis reaction is completed and the heating furnace is reduced to room temperature by cooling water circulation device. The pyrolysis kinetics is analyzed and calculated in the appropriate prolysis temperature range, and the activation energy is calculated.

III. MATH EXPERIMENTAL AND DATA PROCESSING METHODS

A. Experimental Methods

This study mainly adopts thermogravimetric analysis, which is a method to test the change of material quality with temperature under the condition of programmed temperature. The prolysis experiment finally obtains the pattern of sample mass decreasing with temperature through the connected computer, which is called the thermogravimetric (TG) curve. The thermal gravimetric method can not only observe the appropriate pyrolysis temperature range and mass change by comparing the pyrolysis start temperature (Tonset), peak temperature (Tpeak) and end temperature (Tendset), but also derive the temperature (or time) by TG curve according to the thermal gravimetric data to obtain the derivative thermogravimetric (DTG) curve [13].

B. Data Processing Methods

It is assumed that the initial mass of the sample is m_0 , and the residual mass after the pyrolysis reaction is m_f . When the temperature rises to a certain time (t), the mass is m , and the decomposition rate can be expressed as:

$$\frac{dx}{dt} = \beta \times \frac{dx}{dT} = K(T) \times f(x) \quad (1)$$

where β is heating rate, °C / min, x is the mass conversion rate of reactants, $x = (m_0 - m) / (m_0 - m_f)$.

For the simple reaction $f(x) = (1 - x)^n$, n is the reaction order, substituting the Arrhenius equation into Eq.(1) the kinetic equation is :

$$\frac{dx}{dt} = \beta \times \frac{dx}{dT} = A \exp\left(-\frac{E}{RT}\right) \cdot (1-x)^n \quad (2)$$

In the above reaction kinetics equations, the methods for approximate calculation of kinetic parameters are Kissinger method, Coats-Redfern (C-R) method, Achar method and Friedman method. This study selected C-R method, Friedman method for calculation.

C-R method is a common model fitting method, which needs to assume or select the dynamic model in advance [14]. When the selected model is accurate, the calculation results are better, but limited by different assumed models. The following equation can be obtained by transforming Eq.(2).

$$\ln\left[\frac{g(x)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\right] - \frac{E}{RT} \quad (3)$$

The two items containing $1/T$ in the equation are used as the strain and independent variables of straight line, respectively. When the reaction order and the appropriate reaction mechanism $g(x)$ are determined, the activation energy E and frequency factor A can be calculated by the slope and intercept of the straight line.

Friedman method is used to calculate the activation energy E by the change rate of different weight loss rates obtained under the same conversion rate on the DTG curves of different heating rates:

$$\ln \beta \cdot \frac{dx}{dT} = \ln A + \ln(1-x) - \frac{E}{RT} \quad (4)$$

Friedman method is one of the most commonly used methods in thermal decomposition kinetics. This method does not need to assume the reaction order, which can greatly simplify the dynamic analysis process [15].

IV. UNITS EXPERIMENTAL RESULTS AND DISCUSSION

A. Selection of Experimental Conditions

China is a major consumption of plastic, with an annual production and sales volume of 21 million tons, and annual production is still increasing. In Table I, it is decided to conduct the experiment by using the annual consumption ratio of plastics in China and the world as the estimated value, and The Table II is obtained by normalizing the data of Table I.

TABLE I: THE ANNUAL CONSUMPTION RATIO OF PLASTICS

	HDPE(wt.%)	PP(wt.%)	PS(wt.%)
Worldwide	35.00	23.00	10.00
China	24.40	17.80	2.10

TABLE II: CALCULATION RESULTS OF THREE RAW MATERIAL RATIO

	HDPE(wt.%)	PP(wt.%)	PS(wt.%)
Worldwide	51.50	33.80	14.70
China	55.10	40.20	4.70
Average	53.30	37.00	9.70

B. Thermal Analysis of Single Component Plastic

Thermographic analysis of single component plastic. The TG curves of the single component plastic polymer samples (PP, PS, HDPE) are shown in Fig. 1. In general, if the thermogravimetric curves of the samples are similar and the ash content is neglected, it can be assumed that these completely degraded pure plastic samples are controlled by a single degradation step. By reviewing the book, Polymer

degradation and stability, and considering the correlation coefficients and experimental data, it is considered that the reaction order $n = 1.0$ is more suitable for the actual situation [16]. Because of the similar TG curves between the plastic samples, it is assumed that the pyrolysis reaction of single component plastics (PP, PS, HDPE) is the first order reaction.

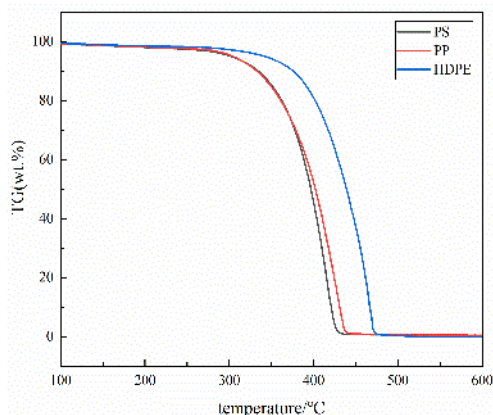


Fig 1. Thermogravimetric curve of single component samples at 25 °C/min.

During polymer pyrolysis, the reaction is initiated to break the macromolecular polymer into free radicals, and in the

propagation reaction, free radicals and various polymer molecules further break into smaller free radicals and molecules. Finally, free radicals combine to form stable molecules and the reaction terminates [17]. It can be seen from Fig. 1. that the pyrolysis characteristic temperatures of single component plastic samples are in this order: PS<PP<HDPE. In addition, studies have shown that at low temperatures, substituents and branched-chain plastics (such as PP, PS, etc.) are easier to decompose than linear plastic polymers (HDPE).

Calculation of Pyrolysis Kinetic Parameters (PP). Fig. 2 shows that the kinetic curves are calculated by C-R method and Friedman method at different heating rates. It can be seen that the heating degree of the samples varies with heating rate, so the activation energy required for the pyrolysis reaction is different. The corresponding activation energy and frequency factor can be obtained by linear fitting of PP pyrolysis at different heating rates. In C-R method, The activation energy of PP pyrolysis is between 106.22 kJ / mol and 117.11 kJ / mol. The average activation energy (E1) of PP pyrolysis is 111.34 kJ / mol. In Friedman method, the activation energy (E2) of PP pyrolysis is calculated between 84.52 kJ / mol and 129.16 kJ / mol. The average activation energy required for the reaction is 110.10 kJ / mol.

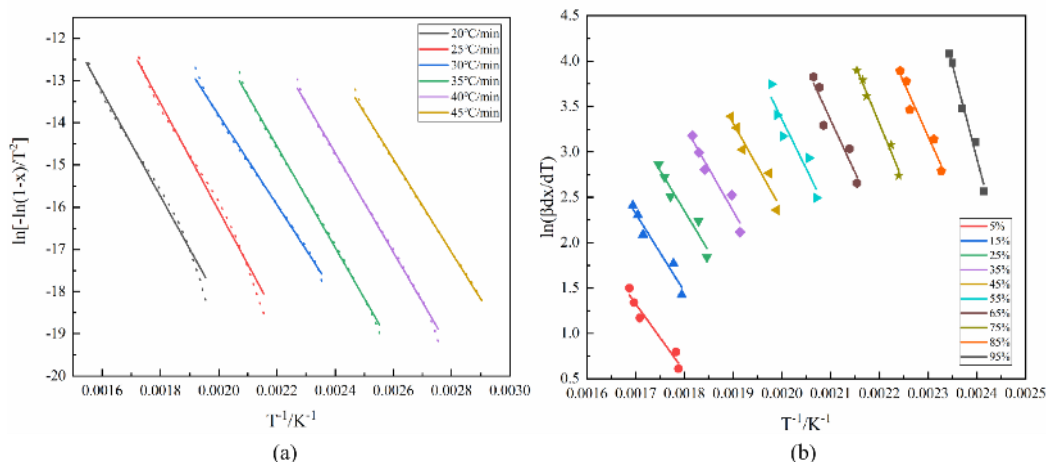


Fig 2. (a) Fitting results of Coats-Redfern method for PP with different heating rate. (b) Fitting results of Friedman method at different conversion rates of PP.

The activation energy data of PS and HDPE, which are obtained with the same method of thermal analysis as PP. (E1, PS=109.72 KJ/mol; E1, PS=108.58 KJ/mol; E1, HDPE=190.70 KJ/mol; E2, HDPE=178.50 KJ/mol) It is seen from the experimental results that HDPE is the most difficult to pyrolyze and has the largest activation energy among the three plastics due to its relatively stable structure. The activation energy of PP pyrolysis is significantly lower than that of HDPE, indicating that the existence of branched chain greatly affects its thermal stability.

C. Thermal Analysis of Three Component Plastic

Thermographic analysis of three component plastic. As shown in Fig. 3, the TG curve shows a downward trend and the temperature distribution is similar to that of the single component pyrolysis, and is suitable for the first order reaction. The pyrolysis temperature of PP/PS/HDPE isometric mixture is between 318.52°C and 448.32°C, and have the maximum pyrolysis rate at 424.53°C (a). HDPE in

single component plastics has the highest stability and is not easy to crack. When the HDPE content in the three plastics increases (from 33.3% to 53.3%), the Tonset of pyrolysis lags behind that of the three components mixed with equal ratio. The pyrolysis temperatures of the actual PP/PS/HDPE ratios range from 323.5 °C to 462.4 °C, with the maximum weight loss rate occurring at 431.7 °C (b).

Calculation of Pyrolysis Kinetic Parameters (PP/PS/HDPE) The activation energy of pyrolysis of PP/PS/HDPE with the actual ratio is determined by the Coats-Redfern (C-R) method in the range of 102.38 kJ/mol to 113.07 kJ/mol with an average reaction activation energy of 108.01 kJ/mol, which is higher than the average activation energy of isometric PP/PS/HDPE (105.31 kJ/mol) as shown in Fig. 4(a). In Fig. 4(b), Similar results are obtained by Friedman method, with the required activation energy of PP/PS/HDPE ranging from 98.92 kJ/mol to 117.79 kJ/mol and an average reaction activation energy of 107.10 kJ/mol, which is slightly higher than the reaction activation energy of the isometric mixed

PP/PS/HDPE (106.35 kJ/mol). This result shows that the mixed pyrolysis of three component plastics promotes the

reaction and reduces more activation energy.

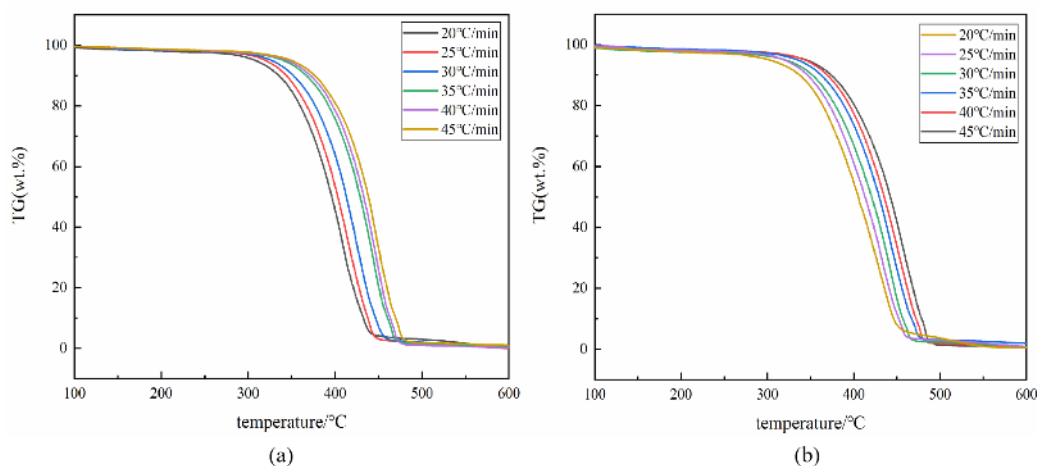


Fig. 3. (a) Thermogravimetric curves of equiproportional mixture at different heating rate. (b) Thermogravimetric curves of actual mixture at different heating rate.

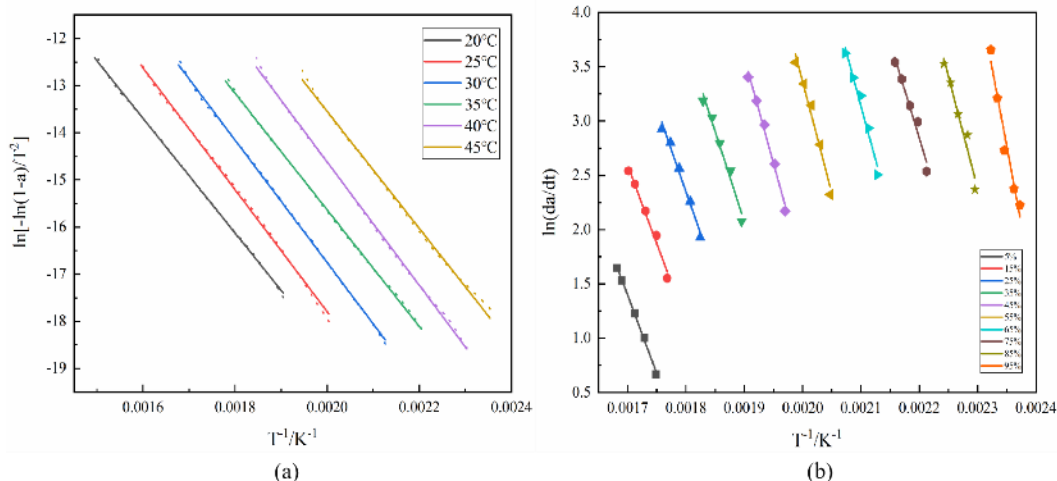


Fig. 4. (a) Fitting results of the C-R method for PP/PS/HDPE at different heating rate. (b) Fitting results of PP/PS/HDPE at different conversion rates by Friedman method.

V. CONCLUSION

A conclusion section is usually required. Although a conclusion may review the main points of the paper, do not replicate the abstract as the conclusion. A conclusion might elaborate on the importance of the work or suggest applications and extensions. The result shows that pure HDPE has the largest pyrolysis temperature and the highest weight loss peak temperature, followed by PP and PS. With the increase of plastic components, the activation energy of mixed pyrolysis gradually decreases. The law Following the mixed pyrolysis of plastics is expected to promote the reaction while lowering the activation energy. In the actual situation, the mixed pyrolysis of plastic waste has the lowest reaction activation energy (108.01 l~107.10 kJ/mol), indicating that in the future industry, the pyrolysis reaction can be completed with a lower reaction activation energy than an equiproportional mixture of plastics.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

There is only one author for this work.

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