Analysis and Kinetics of Co-Pyrolysis of PE and Enteromorpha

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Abstract. In order to study the better disposal of the main components of waste plastics, co-pyrolysis it with Enteromorpha in a nitrogen atmosphere, with the increase of the mass fraction of Enteromorpha, the main co-pyrolysis temperature range of polyethylene (PE) and Enteromorpha shifts toward the high temperature zone. Polyethylene (PE) and Enteromorpha co-pyrolysis have a certain inhibitory effect. When the polyethylene (PE) mass fraction is 75%, the relative inhibition value can reach 19.4%. The kinetic analysis shows that the first-order kinetic model can well describe the co-pyrolysis process of the two, and there is a dynamic compensation effect.

1. Introduction
Plastics have always been the primary problem in the process of waste disposal. Plastics in landfills are not easily degraded. Incineration of plastics is prone to high-risk pollutants such as dioxins [1-2]. Therefore, plastic pyrolysis has attracted extensive attention from scholars at home and abroad. Its advantage is that it can produce liquid cleaning resources similar to fossil fuels during pyrolysis, and the pollutants generated by pyrolysis can be further controlled [3-5]. Liu Yibin [6], Xiao Zhiwei [7] and others investigated the pyrolysis process of several typical plastic components and found that plastic is a substance that is difficult to be normally pyrolyzed. Further research has found that adding a certain amount of addition to the typical components of plastics. The material can produce a certain synergistic effect, reduce the pyrolysis temperature of the plastic, and improve the pyrolysis efficiency. Yao Dingding [8] believes that plastics have a large amount of hydrogen during the co-pyrolysis process, which can provide a large amount of hydrogen to the Enteromorpha during the co-pyrolysis process, thereby generating a large amount of volatiles and improving pyrolysis efficiency. In the study of the co-pyrolysis process of plastics and additives, Liu Shiqi [9-12] studied the co-pyrolysis process of main woody biomass, such as charcoal, lignin, cellulose, wood powder and other plastics, and found that they all promote the pyrolysis process of plastics. Zhao Yu [13] studied the co-pyrolysis process of non-woody biomass, such as straw and other typical components of waste plastics, and found that a certain amount of straw additives can make the main pyrolysis zone of plastic move toward the low temperature zone and improve pyrolysis efficiency.

Li Houyang et al [14-15] found that whether plastics and other substances are mixed and co-pyrolysis can produce synergistic effect, the main factor is that the main pyrolysis interval of the additive coincides with the pyrolysis interval of plastic. At the same time, plastics are co-pyrolysis with other substances. In reality, the material must be large and easily available to meet the needs of
plastic co-pyrolysis. Nowadays, the microalgal resources in the ocean are more and more valued by humans. The third largest biomass resource after grain and lignocellulosic resources is widely used for its large reserves, short growth cycle, and efficient photosynthesis. There have been studies on co-pyrolysis of typical components of microalgae and plastics. Wu Hao [16] deeply studied the co-treatment process of Dunaliella salina and polypropylene, and found that there is a significant promotion effect in the process of co-pyrolysis. At present, there are few studies on the typical components of microalgae and plastics. The reaction mechanism of co-pyrolysis of plastics and biomass is still unclear. Based on this, this paper examines a co-pyrolysis process of a combination of microalgae and plastic that has not been reported in the literature (Enteromorpha and polyethylene (PE)), and perform the Kinetic analysis and establish the reaction kinetic model.

2. Experimental materials and methods
Polyethylene (PE) was used as the experimental material in the experiment, which was mechanically crushed and sorted by a 200-mesh vibrating screen; For Enteromorpha, it was placed in a dry box and dried at 120 °C for four hours, mechanically crushed, and sieved using an 80-mesh vibrating sieve; Finally, the treated polyethylene (PE) and the Enteromorpha are mechanically blended in proportion (25%, 50%, 75%) to ensure uniform mixing. For the thermal analysis of polyethylene (PE) and Enteromorpha samples, the sample quality is about 10 mg, the heating rate is 20 °C/min, the upper temperature limit is 950 °C, the experimental atmosphere is nitrogen, the gas pressure is 0.1 MPa, and the flow rate is 0.1 MPa. 40 mL/min. Since the time from sample preparation to the start of the experiment is short, the effect of ambient temperature and humidity on the sample during this period is negligible.

The thermogravimetric experiment uses a ZTC-B type integrated (synchronous) thermal analyzer to combine thermogravimetric analysis and differential thermal analysis, and can simultaneously obtain the thermogravimetric and differential thermal information of the measured substance in one experiment.

The average pyrolysis rate is calculated by equation (1):

$$\left( \frac{dm}{dt} \right)_{\text{mean}} = \beta \cdot \frac{\alpha - \alpha_h}{T_h - T_i}$$

The sample weight loss rate W is calculated by equation (2):

$$W = \frac{m_0 - m_1}{m_0} \times 100\%$$

The conversion rate x is calculated by equation (3):

$$X = \frac{\alpha_0 - \alpha}{\alpha_0 - \alpha_h}$$

The degree of synergy ΔW is calculated by equation (4):

$$\Delta W = W_{\text{Blend}} - (X_1 W_1 + X_2 W_2)$$

The symbolic interpretation is shown in Table 1.
Table 1. Symbolic interpretation table

| Symbol   | Interpretation                                      | Unit          |
|----------|-----------------------------------------------------|---------------|
| $\beta$  | Heating rate                                       | °C/min        |
| $\alpha_i$ | Quality score when starting pyrolysis               | %             |
| $\alpha_h$ | Quality score at completion of pyrolysis            | %             |
| $T_b$    | Temperature at completion of pyrolysis               | °C            |
| $T_i$    | Mass fraction at pyrolysis                          | %             |
| $\alpha_0$ | Mass fraction of sample after loss of water         | %             |
| $\alpha$  | Quality score of the sample at any one time         | %             |
| $W_{blend}$ | Weight loss rate of PE/ Enteromorpha mixture       | %             |
| $X_i$    | The mass fraction of PE in the mixture              | %             |
| $X_2$    | The mass fraction of Enteromorpha in the mixture    | %             |
| $W_1$    | Corresponding weight loss rate when PE is separately pyrolyzed | % |
| $W_2$    | Corresponding weight loss rate when the Enteromorpha is pyrolyzed separately | % |
| $\Delta W$ | Degree of synergy                                  | %             |

3. Thermogravimetric test results and analysis
Before studying the co-pyrolysis process of polyethylene (PE) and Enteromorpha, the two experimental materials were analyzed by separate pyrolysis process, and the pyrolysis characteristic curve is shown in Figure 1.

![TG curve of two materials separately pyrolyzed](image)

a) TG curve of two materials separately pyrolyzed
Observing the TG and DTG curves of Enteromorpha, the pyrolysis process of Enteromorpha can be divided into three stages. The first is the evaporation of free moisture in the Enteromorpha particles and the loss of gas adsorbed on the surface of the particles. This stage can be regarded as the drying stage of the Enteromorpha particles, and the main temperature range is room temperature - 200 °C. Then, it is the main pyrolysis stage of Enteromorpha, and the polysaccharide macromolecules, fat molecules and macromolecular proteins in the Enteromorpha are pyrolyzed in sequence, and the main temperature range is 200-650 °C. Finally, the fixed carbon C-C fracture in the Enteromorpha granules and the metal salt ions are further decomposed, and the main temperature range is 650-950 °C.

Observing the TG and DTG curves of polyethylene (PE), it can be observed that the TG curve has a significant decrease, and the DTG curve shows a significant weight loss peak with a peak temperature of 480 °C. When the pyrolysis temperature rises to 292 °C, weight loss begins to occur. At about 590 °C, the pyrolysis reaction is almost completed. The entire pyrolysis reaction process only shows a weight loss peak at 480 °C, indicating that the PE pyrolysis reaction is completed in one step. Polyethylene (PE) is essentially free of moisture compared to the enteromorpha pyrolysis process, so there is no drying stage. The mechanically blended polyethylene (PE) and the Enteromorpha mixture were pyrolyzed, and the TG and DTG curves are shown in Figure 2.
b) DTG curves

Figure 2. Polyvinyl chloride and enteromorpha are blended with pyrolysis TG-DTG curves in different proportions

It can be seen from the figure that the co-pyrolysis TG curves of polyethylene (PE) and Enteromorpha is mainly between the curves of polyethylene (PE) and Enteromorpha alone pyrolysis, which are distributed in a stepped manner. As the polyethylene (PE) mass fraction increases, the more the mass fraction decreases, the weight loss rate gradually increases. The co-pyrolysis DTG curve can observe obvious weight loss peaks with a temperature range of 400-600 °C. It can be inferred that polyethylene (PE) dominates in the process of co-pyrolysis of Enteromorpha with polyethylene (PE). As the mass fraction of Enteromorpha increased, the weight loss peak gradually became smaller, and the corresponding mass change rate became smaller. It can be observed that the peak temperature of the weight loss peak gradually shifted toward the high temperature region.

In order to further investigate the co-pyrolysis synergy of polyethylene (PE) and Enteromorpha, the $\Delta W$ of the two is calculated and expressed as shown in the figure3.

Figure 3. $\Delta W$ curve of polyethylene (PE) and enteromorpha mixed in different proportions

Observing the $\Delta W$ curve of co-pyrolysis of polyethylene (PE) and Enteromorpha, it is found that there is no obvious change in the temperature range of room temperature - 200 °C, indicating that there is no synergy between the two. This is mainly because there is no structural change between Enteromorpha and polyethylene (PE) in this temperature range. The Enteromorpha only undergoes its drying stage, and Polyethylene (PE) has not been pyrolyzed. In the range of 200-600 °C, it can be observed that the $\Delta W$ curve of the two has obvious fluctuations, and with the increase of the
polyethylene (PE) mass fraction, it shows a certain inhibition effect. When the mass fraction of polyethylene (PE) reaches 75%, the relative value of the inhibition is 19.4%. There is no synergy between the two in the range of 600-950 °C. The main reason is that both of them have been completely pyrolyzed and no longer have synergistic effects.

4. Dynamics analysis

Under the condition that the heating rate is kept constant, the basic equation of dynamics can be calculated by equation (5):

\[
\frac{dX}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) \cdot \left(1 - X^n\right)
\]

The co-pyrolysis of polyethylene (PE) / Enteromorpha is regarded as the first-order kinetic reaction, and the above formula can be converted into the formula (6) by the Coats-Redfern approximation method:

\[
\ln\left[-\ln\left(\frac{1-X}{T^2}\right)\right] = \ln\left[\frac{AR}{\beta E} \cdot \left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT}
\]

The symbolic interpretation is as shown in Table 2, and the complete pyrolysis process of polyethylene (PE)/ enteromorpha is calculated. The kinetic analysis of the pyrolysis process, the results of the polyethylene (PE) / enteromorpha kinetic parameters are shown in Table 3 and Table 4, and the kinetic compensation effect is shown in the figure4.

### Table 2. Symbolic interpretation table

| Symbol | Interpretation | Unit |
|--------|----------------|------|
| x      | Conversion rate | %    |
| A      | pre exponential factor | —    |
| E      | Reaction activation energy | J/mol |
| R      | Molar gas constant | J/(mol·K) |
| T      | Thermodynamic temperature | K    |
| n      | reaction order | —    |
| a      | compensation parameters | —    |
| b      | compensation parameters | —    |

### Table 3. Calculation results of first-stage kinetic parameters of co-pyrolysis of polyvinyl chloride and enteromorpha

| Polyethylene (PE) share | Imitative straight line equation | correlation coefficient | pre exponential factor A | Reaction activation energy E /kJ·mol⁻¹ |
|-------------------------|---------------------------------|------------------------|--------------------------|-----------------------------------|
| 75%                     | \( y = -32793.61262x + 29.42856 \) | 0.98223                | 3.95804E+18              | 272646.0953                        |
| 50%                     | \( y = -22278.18038x + 15.6478 \) | 0.98731                | 2.78396E+12              | 185220.7917                        |
| 25%                     | \( y = -13118.70486x + 3.87095 \) | 0.95558                | 12590795.84              | 109068.9122                        |
Table 4. Calculation results of second-stage kinetic parameters of co-pyrolysis of polyvinyl chloride and enteromorpha

| Polyethylene (PE) share /% | Imitative straight line equation \( y = ax + b \) | correlation coefficient \( R \) | pre exponential factor \( A \) | Reaction activation energy \( E \) /kJ∙mol\(^{-1}\) |
|---------------------------|---------------------------------|-------------------------------|-----------------|------------------|
| 75%                       | \( y = -14501.43633x + 9.61767 \) | 0.92913                      | 4358549931      | 120564.9416      |
| 50%                       | \( y = -9349.49611x + 2.08451 \) | 0.98721                      | 1503520.63      | 77731.71066      |
| 25%                       | \( y = -7314.03231x - 1.10599 \) | 0.97103                      | 48401.80037     | 60808.86463      |

From the results of the kinetic parameters calculated in Table 3 and Table 4, it is known that the correlation coefficients calculated in the two pyrolysis stages are all above 0.92. The experimental data and the first-order kinetic model can be well fitted, which can well describe the co-pyrolysis reaction process of polyethylene (PE) and Enteromorpha. In the process of co-pyrolysis of polyethylene (PE) and Enteromorpha, as the mass fraction of polyethylene (PE) increases, the mass fraction of Enteromorpha decreases, and the value of activation energy \( E \) increases continuously. When polyethylene (PE) and Enteromorpha are co-pyrolysis, as the mass fraction of polyvinyl chloride (PE) increases, the reaction requires higher temperature and longer time. Therefore, under the same factors, as the mass fraction of polyethylene (PE) increases, the mass fraction of Enteromorpha decreases, and the pyrolysis of the mixture gradually becomes difficult, that is, the initial temperature of pyrolysis increases. Data processing on \( E \) and \( A \) shows that there is a good linear relationship between \( E \) and \( \ln(A) \), as shown in Figure 4. The squares of the correlation coefficients \( R^2 \) are 0.9999, 0.9996, 0.9994 and 0.9999, respectively. The two can be well fitted, that is, there are dynamic compensation effects.

\[
\ln A = a + bE
\]  
(7)

It is reasonable to describe the pyrolysis process of polyethylene (PE) / Enteromorpha using this kinetic model.

![Graph showing the relationship between ln(A) and E](image-url)
5. Conclusion

During the co-pyrolysis of polyethylene (PE) and Enteromorpha, the two have a certain inhibitory effect. When the polyethylene (PE) mass fraction reaches 75%, the relative value can reach 19.4%. Ethylene (PE) will vitrify during pyrolysis, entraining canola, hindering its pyrolysis.

The kinetic analysis shows that the two-stage first-order kinetic model can well describe the co-pyrolysis of polyethylene (PE) with Enteromorpha. The correlation coefficient between the kinetic model and the experimental data is above 0.92. There is a linear relationship between E and ln (A), and the correlation coefficients are all above 0.999, indicating that there is a dynamic compensation effect.

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