Kinetic study for the co-pyrolysis of water hyacinth biomass with waste polystyrene

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Abstract. Co-pyrolysis behavior of water hyacinth (WHC) and waste PS using thermogravimetric analysis to determine kinetic parameters was investigated. TG and DTG results indicated that the pyrolysis of WHC and mixture of WHC and waste PS could be divided into three stages. It was found that co-pyrolysis of WHC and waste PS delayed the pyrolysis process with a wider decomposition temperature range, when compared with the pyrolysis of PS. The results compared with the pyrolysis of individual components revealed a positive synergistic interaction between WHC and waste PS according to the difference in weight loss. Coats-Redfern method was applied in the second stage to evaluate the activation energy (Ea) and pre-exponential factor (A) from the data of weight loss using three major reaction mechanisms. Two conversion temperature zones, zone I of 240-400 °C and zone II of 400-530 °C, were identified and a best-fit model describing the co-pyrolysis behavior of mixture was achieved. The addition of waste PS to WHC led to a slight decrease in the activation energy in the first zone and then the activation energy significantly reduced in the second zone. Chemical reaction and diffusion-controlled reaction mechanisms could be kinetically examined and enabled good explanation of the co-pyrolysis behavior of the mixture of WHC and waste PS as well as individual pyrolysis.

1. Introduction

The solid waste management and energy crisis are of critical concern and require further attention. Presently, plastics are major contributors in solid waste and are found to be one major pollutant to the environment. Direct combustion of post-consumer plastics is not encouraged because of the formation of toxic pollutants. Therefore, it becomes a great challenge to deal with the large amount of solid waste in an environmentally friendly and pollution-free approach. Waste plastics can be converted into energy to help address issues on both waste disposal and energy needs [1-2]. Among all the renewable energy sources, biomass wastes are considered as one of the attractive sources with the advantages of low greenhouse gas emission and carbon neutral, biodegradable, renewable and huge reserves [3-4]. Biomass conversion to energy is classified into thermochemical and biochemical routes. In the biochemical process, biomass is decomposed into lower molecular-weight compound using enzyme or bacteria as catalysts, requiring a long time for conversion of biomass into value added products. The thermochemical conversion technologies include pyrolysis, combustion, gasification, cofiring, and liquefaction. In the thermochemical process, biomass is decomposed into smaller molecular-weight
compounds using heat [5]. Among them, pyrolysis has the potential to decompose biomass very quickly in the absence of oxygen into solid biochar, liquid fuel (known as bio-oil or pyrolysis oil), and gas fuel. However, bio-oil obtained from the pyrolysis of biomass has high oxygen content (~40 wt%) because of high oxygen content contained in the original biomass. Mostly, high oxygen content results in a fuel with low heating value, corrosiveness and thermal instability as well as limits the widespread application of the bio-oil [6]. Plastics with high hydrogen contents (polyethylene, polypropylene and polystyrene) could act as hydrogen donor to the biomass during pyrolysis process which leads to an increase and improvement in yield and quality of the produced oil [1]. Hence, co-pyrolysis of biomass and plastics might be a promising alternative for bio-oil upgrading and sustainable usage of improved bio-fuels. Studies have shown that co-pyrolysis of biomass and plastics compounds could increase bio-oil quantity and quality compared with pyrolysis of separate components [7-9]. Kinetic analysis of biomass and plastic waste is necessary before the conversion of biomass and plastic wastes into fuel, which provides information for the mathematical modeling simplification, process parameter optimization, and design of thermochemical equipment (e.g. pyrolysis reactor). The kinetic parameters include pre-exponential factor (A), activation energy (Ea), and order of the reaction (n). Thermogravimetric (TGA) analysis is the simplest analytical tool to investigate co-pyrolysis characteristics and determine kinetic parameters of organic materials or different types of thermochemical process. For the commercialization of the co-pyrolysis process in bio-oil production, an important further research is needed for better understanding of the reaction kinetics. The objective of current work is to investigate the thermal decomposition behavior, kinetics, pyrolysis of individual wastes, and co-pyrolysis of water hyacinth and waste polystyrene using TGA at different heating rates. Model-fitting methods were applied to evaluate kinetic parameters and find the most appropriate kinetic reaction mechanism using Coats-Redfern model.

2. Experimental

2.1. Materials and sample preparation

The biomass sample used in this study is water hyacinth (WHC) and it was collected from a canal located in Kanchanaburi, Thailand. The sample was washed with distilled water to remove impurities and then dried at 80 °C for 72 h. Dried water hyacinth was crushed and sieved to obtain particle size ranging from 75 to 100 μm as well as dried before experiments. Waste polystyrene (oriented PS (OPS)) was collected from several food service locations in Sanam Chandra Palace Campus, Silpakorn University, Thailand. The PS waste was washed and dried, followed by cutting into small pieces with approximately 1 mm² and using in the thermal pyrolysis reaction.

2.2. Experimental technique

Co-pyrolysis of water hyacinth with waste PS was examined using TGA (Mettler Toledo TGA/DSC1 STARe Thermogravimetric Analysis System) with horizontal balance, which was equipped for simultaneous thermogravimetric analysis. All the tests in this study were run under nitrogen carrier gas flowed at a constant rate of 50 mL/min. The samples were placed in an alumina crucible forming a small fixed bed with an initial mass of approximately 6 mg at mixing ratios (WHC:PS (w/w)) of 100:0, 90:10, 0:100. The samples were heated from 50 °C to 1000 °C and sets of experiments at different heating rates of 10, 15, 25 and 50 °C/min were carried out for every sample. The repeated data obtained from TGA experiment were used for kinetic parameter analysis.

2.3. Kinetic study

The conversion degree (α) reflects the thermal decomposition and is defined by the following equation [10]:

\[
α = \frac{m_a - m_t}{m_a - m_f}
\]
where \( m_0, m_t, \) and \( m_f \) are the initial, instantaneous and final masses during thermal decomposition, respectively. The rate of conversion with respect to time \( (d\alpha/dt) \) for a heterogeneous solid-state thermal decomposition can be expressed as:

\[
\frac{d\alpha}{dt} = k(T)f(\alpha)
\]  

(2)

where \( f(\alpha) \) is the mechanism function and is only a function of conversion. \( T \) and \( k \) are the absolute temperature and rate coefficient, respectively. According to the Arrhenius equation, the rate constant \( k(T) \) can be established as:

\[
k(T) = A e^{\left(\frac{-E_a}{RT}\right)}
\]  

(3)

where \( A, E_a \) and \( R \) are the pre-exponential factor, apparent activation energy and universal gas constant \((8.314 \text{ J/mol.K})\), respectively.

For constant heating rates \( \beta = \frac{dT}{dt} \), therefore equations (2) and (3) can be given in the combined form [11]:

\[
\frac{d\alpha}{dt} = \frac{A}{\beta} e^{\left(\frac{-E_a}{RT}\right)} f(\alpha)
\]  

(4)

The integrated form for \( f(\alpha) \) in equation (4) is generally stated in the following equation:

\[
g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T e^{\left(\frac{-E_a}{RT}\right)} dT
\]  

(5)

where \( g(\alpha) \) is an integral form of reaction model.

A model-fitting method, Coats-Redfern model, is widely used to estimate the pre-exponential factor and activation energy and to predict the order of reaction \( (n) \). The basic equation for Coats-Redfern method can be expressed as [11]:

\[
\ln \left[ \frac{g(\alpha)}{T^2} \right] = \ln \frac{A R}{\beta E_a} - \frac{E_a}{RT}
\]  

(6)

Activation energy can be achieved by drawing a graph between \( 1/T \) and \( \ln[g(\alpha)/T^2] \) and by finding slope from drawn straight line. The pre-exponential factor can be evaluated from the intercept of this graph and \( g(\alpha) \) can be varied according to different developed model and reaction mechanisms. Most of the solid-state degradation reactions could fall into three categories which are shown in Table 1. In Criado method, the experimental data were compared with the data calculated by reaction mechanism function. Therefore, the kinetic reaction mechanism of the pyrolysis process could be identified. The equation of this method obtained from equation (4) and (6) can be given below:

\[
\frac{x(\alpha)}{x(0.5)} = \frac{f(\alpha)g(\alpha)}{f(0.5)g(0.5)} = \left( \frac{T_\alpha}{T_{0.5}} \right)^2 \left( \frac{d\alpha/dt}{(d\alpha/dt)_{0.5}} \right)
\]  

(7)

where \( T_{0.5} \) and \( (d\alpha/dt)_{0.5} \) are the temperature and conversion rate at \( \alpha=0.5 \). The left-hand side \( f(\alpha)g(\alpha)/f(0.5)g(0.5) \) is a theoretical curve referring to the characteristic of each reaction mechanism listed in Table 1. The right-hand side of equation (7) is the reduced rate curve, which was
attained from experimental data. By comparing the theoretical curve with the reduced rate curve, it is definitely to determine the most appropriate reaction mechanism [12].

Many methods were developed to determine the pre-exponential factor and reaction order in a direct way due to the variation in reaction models. These methods are explained below: when the model-fitting method is applied for a single heating rate, a large variation in kinetic parameters are acquired when using different reaction models. These values can be correlated by compensation effect since activation energy is partially or completely compensated by changing pre-exponential factor [13]. The relation is shown in the following expression:

\[
\ln(A) = a + bE_a
\]  

(8)

where a and b are constant known as the compensation effect parameters.

**Table 1.** The common solid-state reaction kinetics models.

| Code | Reaction mechanism | Differential form \(f(\alpha)\) | Integral form \(g(\alpha)\) |
|------|--------------------|---------------------------------|---------------------------|
| Fm   | Chemical reaction order |                               |                           |
| F1   | First order        | \(1 - \alpha\)                 | \(-\ln(1 - \alpha)\)     |
| F2   | Second order       | \((1 - \alpha)^2\)             | \((1 - \alpha)^{-1} - 1\) |
| F3   | Third order        | \((1 - \alpha)^3\)             | \([(1 - \alpha)^{-1} - 1]/2\) |
| Dm   | Diffusion          |                                |                           |
| D1   | 1D diffusion       | \(1/2\alpha^{-1}\)             | \(\alpha^2\)              |
| D2   | 2D diffusion       | \([-\ln(1 - \alpha)]^{-1}\)   | \((1 - \alpha) \ln(1 - \alpha) + \alpha\) |
| D3   | 3D Diffusion-Jander| \(3/2(1 - \alpha)^{2/3}\)     | \([1 - (1 - \alpha)^{1/3}]^2\) |
| D4   | 3D, Ginstling-Brounshtein | \(3(1 - \alpha)^{1/3}^{-1}\)  | \(1 - 2\alpha/3 - (1 - \alpha)^{2/3}\) |
| D5   | 3D, Zhuravlev, lesokin, Tempelman | \(3/2(1 - \alpha)^{4/3}\)     | \([(1 - \alpha)^{1/3} - 1]^2\) |
| D6   | 3D, Anti-Jander    | \(3/2(1 + \alpha)^{2/3}\)     | \([(1 + \alpha)^{1/3} - 1]^2\) |
| Am   | Volume reaction model (Avarami-Erofe’ev) | \(\frac{3}{2}(1 - \alpha)[-\ln(1 - \alpha)^{1/3}]\) | \([-\ln(1 - \alpha)^{2/3}]\) |
| A3/2 |                     | \(2(1 - \alpha)[-\ln(1 - \alpha)^{1/2}]\) | \([-\ln(1 - \alpha)^{1/2}]\) |
| A2   |                     | \(3(1 - \alpha)[-\ln(1 - \alpha)^{2/3}]\) | \([-\ln(1 - \alpha)^{1/3}]\) |
3. Results and discussion

3.1. Thermal degradation of the mixture of WHC biomass and waste PS

The conversions of WHC, PS and 90WHC:10PS were shown in Figure 1 at four heating rates (10, 15, 25, and 50 °C/min). Figure 1(a) shows the TGA curves of WHC, PS and 90WHC:10PS at a heating rate of 50 °C/min. The pyrolysis process of WHC could be divided into three stages including dehydration, devolatilization, and decomposition. The major macromolecules (cellulose, hemicellulose and lignin) with the interaction between these moieties in WHC result in a multi-staged decomposition. These findings were in accordance with various reported works [14-15]. The conversion for the thermal decomposition of WHC and 90WHC:10PS demonstrated three stages: stage I from 50 to ~200 °C, stage II from ~200 °C to ~530 °C, and stage III from ~530 °C to 800 °C. These stages indicated various processes during the thermal decomposition of WHC which is the main component in 90WHC:10PS. When the samples WHC and 90WHC:10PS were heated, moisture was first released at stage I, a primitive peak is observed at ~100 °C indicating the removal of moisture and lower volatile matter which accounts for 5.75% for WHC and for 5.29% for 90WHC:10PS of the total weight loss. As the temperature continued to rise, hemicellulose and cellulose in WHC were then decomposed at stage II. This stage mainly involves the generation of volatile compounds with high oxygen content by random fragmentation of glucosidic bonds in hemicellulose and cellulose, leaving a lignin rich carbonaceous matrix (biochar) [16]. This stage was the main reaction stages of WHC and 90WHC:10PS, with the highest mass loss of 52.46% for WHC and 47.52 % for 90WHC:10PS (~390 °C). The breakdown of hemicellulose occurred in the range of 200-300 °C by dehydrating its methoxy and acetyl bond. Because hemicellulose consists of short-chain heteropolysaccharides with low polymerization and an amorphous and branched structure, it becomes less stable in the thermal decomposition [17]. On the other hand, the dominant peak is observed at 339 °C, which appeared due to breakage of glucosidic bonds in cellulose. Since cellulose is a linear macromolecule polysaccharide containing D-glucosyl groups with high polymerization and hydrolysis resistance, its thermal degradation was more difficult than that of hemicellulose in the thermal conversion [18]. The solid residue was 42.26% for WHC and 46.73% for 90WHC:10PS (~390 °C). In contrast, the thermal decomposition of PS occurred at 360-510 °C. It was found that PS was completely degraded without the formation of a solid residue. At the same time, the weight loss of 90WHC:10PS accounted for 19.83% (390-530 °C), and the solid residual quantity was only 26.90% (36.00% for WHC). These results suggested that the presence of PS had a strong influence on the degradation temperature. The presence of PS inhibited coke formation from cellulose during co-pyrolysis, and the solid residue of the mixture of WHC and PS was also decreased. The lower ash content directed to convenient for burning fuel. Moreover, the ash content has a direct relationship with the heating value of fuel, indicating that lower the ash, higher the heating value of the fuel [19]. Lignin was decomposed throughout the process of pyrolysis. However, the decomposition of lignin became dominant at stage III. Because lignin is a complex organic polymer containing aromatic rings constituents and is present in the cross-linking of cellulose and hemicellulose [18]. Therefore, thermal decomposition of lignin was more difficult than that of hemicellulose and cellulose.

Figure 1 (b)-(d) show the comparison of the conversion at four heating rates. It was found that the temperature decomposition of all the samples increased with the heating rates. The higher heating rate revealed that the samples reach higher temperature with shorter residence time, eventually generating instability. With an increase in heating rate from 10 to 50 °C/min, it was observed that DTG thermograms of all the samples shifted to higher temperature zone. The decomposition rate was slower at the increased heating rate due to heat constraint between WHC biomass and/or PS, unlike the situation at lower heating rates. Furthermore, at the lower heating rate, heat stayed in the particles of biomass and/or PS for a longer time, leading to intense heat transfer between biomass and/or PS particles. Compared with the pyrolysis of individual wastes, the DTG data for co-pyrolysis demonstrated two DTG peaks as shown in Figure 1(d). It was probably because the decomposition of WHC affected the co-pyrolysis process and responded for the first DTG peak at about 200-400 °C (zone I), and the
pyrolysis of PS resulted in the second DTG peak at a wider temperature range of 400 to 530 °C (zone II). Additionally, the first DTG peak of the co-pyrolysis was higher than the second DTG peak (Figure 1(a)), which might be attributed to the faster weight loss of WHC at 200-390 °C than the decomposition of PS at 390-530 °C. The maximum temperature from the DTG curves for co-pyrolysis in zone II was higher than that for pyrolysis of PS (Table 2). Similar trend has also been observed by other works [2, 20]. These results described that co-pyrolysis delayed the pyrolysis process in comparison with the pyrolysis of individual PS, indicating the possible interaction between WHC and PS during co-pyrolysis process.

The synergistic effect during the co-pyrolysis of WHC and PS was analyzed using equation (9) by comparing the difference of weight loss from TGA (\(\Delta W\), wt%) between the experimental and calculated results:

\[
\Delta W = W_{\text{exp}} - W_{\text{cal}}
\]

(9)

where \(W_{\text{exp}}\) is the experimental weight loss from TGA measurement. As shown in equation (9), \(W_{\text{cal}}\) was calculated from the sum of the weight loss from TGA pyrolysis of individual WHC or PS [21]:

\[
W_{\text{cal}} = \chi_1 W_{\text{WHC}} + \chi_2 W_{\text{PS}}
\]

(10)

where \(\chi_1\) and \(\chi_2\) are the mass proportion of WHC and PS in corresponding co-pyrolysis sample, and \(W_{\text{WHC}}\) and \(W_{\text{PS}}\) are the TGA weight loss of individual WHC and PS, respectively.

![Figure 1.](image-url)
To further demonstrate the synergistic effect between WHC biomass and waste PS, the difference of weight loss ($\Delta W$) as the synergistic index parameter for co-pyrolysis of WHC and PS was defined. $\Delta W > 0$ indicates a passive synergistic effect. Meanwhile, $\Delta W < 0$ indicates an accelerated co-pyrolysis process and a positive synergistic effect [20]. Figure 2 represents the variation of $\Delta W$ with temperature at a heating rate of 50 °C/min. It can be seen that for 90WHC:10PS, the weight loss difference is less than ±1% at below ~250 °C. This difference exists because at this temperature stage, the WHC was not decomposed, and no interaction between WHC and PS occurred. It was seen that $\Delta W$ was not equal to zero at this stage, which may have resulted from experimental errors such as different initial weights and thermal conductive conditions. In the temperature range of 280-440 °C, $W_{exp}$ is less than $W_{cal}$ implying that the weight loss was more in the case of the mixture. This indicates a positive synergistic effect between WHC and PS during the co-pyrolysis. The value of $\Delta W$ was started to decrease at 280 °C and increased sharply at 460 °C after peaking at 320 °C. This characteristic behavior of the mixture can be described by the physical state of PS. Firstly, PS was softened and followed by a plastic state which could inhibit the release of volatile compounds from WHC by the formation of a coating layer on the WHC surface. With further increase of temperature, PS began to decompose quickly, leading to the rapid increase of the $\Delta W$. The $\Delta W$ value is less than ±1% at above 460 °C since the devolatilization process was completed.

Table 2. Characteristic temperatures of pyrolysis and co-pyrolysis processes.

| Sample         | Zone 10 °C/min | Zone 15 °C/min | Zone 25 °C/min | Zone 50 °C/min |
|----------------|----------------|----------------|----------------|---------------|
| WHC            | 1 319.16 °C    | 326.89 °C      | 331.7 °C       | 338.96 °C     |
| PS             | 2 416.94 °C    | 425.72 °C      | 434.09 °C      | 445.38 °C     |
| 90WHC:10PS     | 1 318.69 °C    | 322.68 °C      | 330.70 °C      | 337.73 °C     |
|                | 2 421.57 °C    | 429.94 °C      | 439.74 °C      | 453.40 °C     |

Figure 2. Experimental and calculated (from equation (9)) TGA curves for 90WHC:10PS at heating rate of 50 °C/min of (a) weight loss as a function of temperature and (b) $\Delta W$. 
3.2. Evaluation of kinetic parameters

Model-fitting methods provide the activation energy (E_a) and pre-exponential factor (A) by fitting different reaction models (Table 1) into the used equation (6). The model that yields the best statistical fit is chosen as the model of choice from which the activation energy and pre-exponential factor can be calculated. This method assumes constant kinetic parameters, as well as uses a single heating rate. The best fit was confirmed by a linear correlation coefficient value of ~ 1 and master plot. The use of different reaction models gives different pairs of E_a and A. However, the compensation effect can be utilized to estimate the actual kinetics parameters. The Coats-Redfern method was used to evaluate the kinetic parameters for single heating value. Figure 3 shows the activation energy for WHC, PS and 90WHC:10PS using the direct differential method. The deviation of the results between different models is because of different assumptions and mathematical derivation of the used reaction models in solid-state kinetics. Table 3 demonstrates the values of the most accurate models with the highest R^2 from Figure 3. It can be shown that the models with the highest R^2 are the Diffusion models (D1, D2, D3, D4 and D6) and the Reaction-order models (F1) for WHC and 90WHC:10PS (zone I). The highest R^2 is approximately 1 and obtained by the Avarami-Erofe'ev and First-order model for PS, whereas the maximum R^2 for 90WHC:10PS is obtained by F2 and F3 (zone II). Figure 4 suggests an n-order reaction model for WHC, PS and 90WHC:10PS when comparing the theoretical (z(α)/(z(0.5) vs α) and experimental curves. A reaction model of D3 controls the decomposition steps of WHC (Figure 4(a)) and 90WHC:10PS in zone I as shown in Figure 4(c), meanwhile F2 controls the decomposition step of 90WHC:10PS in zone II (Figure 4(d)). Model of F1 controls the decomposition step of PS in Figure 4(b). The pre-exponential factor and reaction model were achieved from the compensation effect and master plot, respectively, by using the values of E_a obtained from Coats-Redfern method. The determination coefficients (see Figure 5) of the compensation effect equation were higher than 0.9979 for all the samples. Therefore, the equations in Figure 5 present a linear relationship between the values of A and E_a and the compensation effect parameters can be applied to estimate the values of A. The compensation parameters and E_a value of each pseudo-component were replaced in equation (8). Therefore, Figure 5 illustrates the linear fit obtained by the compensation effect and the master plot curves for each decomposition of WHC, PS and 90WHC:10PS. Compensation effect was used to correlate the obtained values to get the actual values of the kinetic parameters. The pre-exponential factors of WHC, PS, and 90WHC:10PS (zone I and zone II) were 4.21E+10, 9.83E+20, 2.59E+10, and 8.79E+13, respectively. In the pyrolysis zone II, the value of pre-exponential factor (A) was highest for PS and reduced for 90WHC:10PS which may affect changes in Gibbs free energy and in entropy [22].
Table 3. The best-fit models of pure glycerol using Coats-Redfern method

|       | WHC               | PS               | 90WHC:10PS        |
|-------|-------------------|------------------|-------------------|
|       | R²    | Ea [kJ/mol] | A [1/min] | R²    | Ea [kJ/mol] | A [1/min] | R²    | Ea [kJ/mol] | A [1/min] |
| F1    | 0.990 | 67.623     | 7.47E+05   | 0.999 | 277.230     | 7.88E+20  | 0.991 | 66.455       | 2.90E+06   |
| F2    | -     | -          | -         | -     | -           | -         | -     | -             | -         |
| F3    | -     | -          | -         | -     | -           | -         | -     | -             | -         |
| D1    | 0.997 | 112.778    | 2.19E+09  | -     | -           | -         | -     | -             | -         |
| D2    | 0.998 | 121.849    | 8.82E+09  | -     | -           | -         | 0.996 | 342.815      | 1.50E+27   |
| D3    | 0.996 | 132.882    | 2.45E+10  | -     | -           | -         | -     | -             | -         |
| D4    | 0.998 | 125.491    | 4.51E+09  | -     | -           | -         | -     | -             | -         |
| D5    | -     | -          | -         | 0.991 | 752.271     | 4.67E+54  | -     | -             | -         |
| D6    | 0.994 | 103.599    | 2.83E+07  | -     | -           | -         | -     | -             | -         |
| A3/2  | -     | -          | -         | 0.999 | 180.799     | 7.15E+13  | -     | -             | -         |
| A2    | -     | -          | -         | 0.999 | 132.591     | 2.33E+10  | -     | -             | -         |
| A3    | -     | -          | -         | 0.999 | 84.376      | 7.21E+06  | -     | -             | -         |

Figure 3. Activation energy of (a) WHC, (b) PS, (c) 90WHC:10PS (zone I) and (d) 90WHC:10PS (zone II) obtained by Coats-Redfern method at 50 °C/min.
Figure 4. The curves obtained from Criado method at a heating rate of 50 °C/min of (a) WHC, (b) PS, (c) 90WHC:10PC (zone I) and 90WHC:10PS (zone II).

Figure 5. Kinetic compensation effect plot showing a linear dependency between $E_a$ and $\ln(A)$ for a multi-component model.
4. Conclusions
In this study, co-pyrolysis of biomass with waste synthetic polymer was examined to understand the kinetics of the synergistic effects between the waste materials. Oriented polystyrene was used as a model plastic investigated with water hyacinth as a representative of lignocellulosic biomass. TGA/DTG analysis showed that there was a synergistic effect when WHC and PS were pyrolyzed together. During co-pyrolysis, WHC biomass showed an insignificant change in the activation energy compared with individual pyrolysis of WHC, while the activation energy drop of ~21% (48 kJ/mol) with respect to PS was observed for the WHC:PS (90:10) mixture. The apparent activation energy of neat WHC, PS and the mixture of 90WHC:10PS (zone I and zone II) derived from the model-fitting methods was 133, 227, and 130 (in zone I) and 179 (in zone II) kJ/mol, respectively. The thermal decomposition of the mixture 90WHC:10PS followed a diffusion (D3) model in the conversion range of zone I (same as WHC) and second-order chemical reaction kinetics in the conversion range of zone II, whereas the thermal decomposition of PS followed first-order chemical reaction kinetics. The co-pyrolysis of WHC with waste PS enhanced the conversion efficiency of pyrolysis reaction.

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References
[1] Cao B, Sun Y, Guo J, Wang S, Yuan J, Esakkimuthu S and Wang Q 2019 Fuel. 246 319.
[2] Burra KG and Gupta AK 2018 Appl. Energ. 220 408.
[3] Yuan R, Yu S and Shen Y 2019 Waste Manage. 87 86.
[4] Wang X, Jin Q, Wang L, Bai S, Mikulčič H, Vujanović M and Tan H 2019 J. Environ. Manage. 339 306.
[5] Boateng AA, Weimer PJ, Jung HG and Lamb JFS 2008 Energ. Fuel. 22 2810.
[6] Van Nguyen Q, Choi YS, Choi SK, Jeong YW and Kwon YS 2019 J. Environ. Manage. 237 24.
[7] Lopez G, Artetxe M, Amutio M, Bilbao J and Olazar M 2017 Renew. Sust. Energ. Rev. 73 346.
[8] Uzoejewwa BB, He X, Wang S, El-Fatah Abomohra A, Hu Y and Wang Q 2018. Energ. Convers. Manage. 163 468.
[9] Yang J, Rizkiana J, Widayatno WB, Karnjanakom S, Kaewpanha M, Hao X and Guan G 2016 Energ. Convers. Manage. 120 422.
[10] Vuppaladadiyam AK, Zhao M, Memon M Z and Soomro AF 2019 Sustain. Energ. Fuels. 3 1283
[11] Naqvi SR, Tariq R, Hameed Z, Ali I, Naqvi M, Chen WH and Shahbaz M 2019 Renew. Energy. 131 854.
[12] Xu F, Wang B, Yang D, Hao J, Qiao Y and Tian Y 2018 Energ. Convers. Manage. 171 1106.
[13] Almazrouei M and Janajreh I 2020 Renewable Energy. 145 1693.
[14] Huang H, Liu J, Liu H, Evrendilek F and Buyukada M 2020 Energ. Convers. Manage. 207 112552.
[15] Alves JLF, da Silva JCG, da Silva Filho VF, Alves RF, de Araujo Galdino WV and De Sena RF 2019 Biomass Bioenergy. 121 28.
[16] Siddiqi H, Kumari U, Biswas S, Mishra A and Meikap BC 2020 Energy. 204. 117933.
[17] Sobek S and Werle S 2020 Fuel 261 116459.
[18] Yu J, Paterson N, Blamey J and Millan M 2017 Fuel. 191 140.
[19] Mishra RK and Mohanty K 2020 Bioresour Technol. 311 123480.
[20] Alam M, Bhavanam A, Jana A, Viroja JKs and Peela NR 2020 Renew. Energy. 149 1133.
[21] Hu Q, Tang Z, Yao D, Yang H, Shao J and Chen H 2020 J. Clean. Prod. 260 121102.
[22] Naqvi SR, Ali I, Nasir S, Alí Ammar Taqvi S, Atabani AE and Chen WH 2020 Fuel. 278 118259.