Wang, Zhi; Hostikka, Simo; Wang, Jian

**Pyrolysis behavior and kinetic analysis of waste polypropylene-based complex for cable filler**

Published in:  
Case Studies in Thermal Engineering

DOI:  
10.1016/j.csite.2022.102261

Published: 01/09/2022

**Document Version**  
Publisher's PDF, also known as Version of record

**Published under the following license:**  
CC BY-NC-ND

Please cite the original version:  
https://doi.org/10.1016/j.csite.2022.102261
Pyrolysis behavior and kinetic analysis of waste polypropylene-based complex for cable filler

Zhi Wang a,*, Simo Hostikka b, Jian Wang c

a State Key Laboratory of Coal Resources and Safe Mining, China University of Mining and Technology, No. 1 University Road, Xuzhou, Jiangsu, 221116, China
b Department of Civil Engineering, Aalto University, Espoo, 02150, Finland
c State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei, Anhui, 230026, PR China

ARTICLE INFO

Keywords:
Cable filler waste
Thermogravimetric analysis
Pyrolysis kinetics
Parameter optimization
Reaction modeling

ABSTRACT

To better understand the thermochemical conversion for the pyrolysis recycling of cable waste, the pyrolysis kinetics of the typical cable filler was investigated in detail. Thermogravimetric experiments were conducted at different heating rates ranging from 5 °C/min to 40 °C/min. Three degradation stages were observed in the process of pyrolysis. The influence of air on the superposition of the first two peaks was also identified. The activation energy at different heating rates was calculated using three commonly used model-free methods. A three-component reaction scheme was proposed to describe the whole degradation process. The first one was associated with the stearic acid decomposition, the second was dominated by the polypropylene decomposition, while the third was attributed to the calcium carbonate decomposition. The created reaction model combined with an optimization algorithm was applied to determine the kinetic parameters. The values of activation energy estimated by this method were in accordance with those by isoconversional methods, which verified the accuracy of the parameter calculation by the optimization algorithm. The predicted results based on the optimized parameters agreed well with the experimental data. Finally, the whole kinetics process was deconstructed into three independent reactions corresponding to all reactants and products.

1. Introduction

Large amounts of cables widely contribute to the fields of power transmission, information transfer, and equipment control [1,2]. Generally, the industrial cables are composed of several parts mainly including sheath, insulation, filler, and copper. Therein, the polymer component (sheath, insulation, and filler) is considered an important contributor to the mass fraction and total heat release of the whole cable [3,4]. In the meantime, more and more cable waste is increasingly generated owing to the failure/retirement of cable [5]. It is a critical issue how to deal with the cable waste. Landfill, incineration, and pyrolysis are the main strategies to dispose of such plastic waste [6–8]. Considering the shortcomings of low efficiency for landfills and hazardous gas emissions for incineration, pyrolysis is regarded as a promising method to efficiently covert the solid waste into valuable fuel or chemical feedstock without polluting the environment [9,10]. Therefore, the pyrolysis approach is employed to recycle cable waste [5,11,12].

To the researchers’ knowledge, the pyrolysis kinetics of the main components in materials can devote to understanding not only the energy conversion but also the gasification and combustion processes of whole materials [13,14]. Numerous studies have been...
extensively conducted on the decomposition behavior and kinetic mechanism of the insulation and sheath in cable waste [2,15,16]. However, cable filler is another important flammable material in cable [1,3], and little attention was paid to the pyrolysis of cable filler waste. The polypropylene-based complex is one of the most commonly used cable filler, consisting of stearic acid (SA), polypropylene (PP), and calcium carbonate (CC). Most previous work focused on the thermal degradation behavior and decomposition kinetics of SA [17–19], PP [20–22], and CC [23–25], respectively. The kinetic parameters and reaction model were calculated and determined using the common thermodynamic methods. Whereas, the total pyrolysis process of cable filler with intricate components will include complex multi-step reactions and require relatively more kinetic parameters to characterize the degradation. It is considerably difficult for the simply traditional kinetics methods to solve this problem. Accordingly, the optimization method, involving Genetic Algorithms (GA) [26–28], Differential Evolution [29] and Shuffled Complex Evolution (SCE) [30] is the best choice, which has been employed successfully to estimate the kinetic parameters for plastics and wood. Especially, SCE algorithm can provide a more robust and efficient convergence to obtain a global optimum with a relatively limited amount of available target data [31,32].

In this study, we mainly conducted the thermogravimetric measurements of commercial cable filler waste at different heating rates in nitrogen atmosphere. The activation energy at various conversion rates was determined by three commonly applied isoversional methods. The pyrolysis process of cable filler waste can be divided into several independent sub-reactions. The SCE algorithm was applied to obtain the kinetic parameters of each reaction for cable filler. Finally, three independent reactions separated from the whole reaction mechanism corresponded to the consumption of all reactants and the generation of residue.

2. Materials and methods

2.1. Materials

The sample used in this study was obtained from the waste flame-retardant PVC cable. The formula was typical for cable filler materials, mainly composed of SA, PP, and CC. The sample was ground to less than 0.2 mm to eliminate the temperature gradient within the particles during the pyrolysis process. Before testing, all samples were dried at 80 °C for about 24 h to completely remove the free water.

2.2. Thermogravimetry

The thermogravimetric measurements were conducted on a TA instrument SDT Q600 thermal analyzer from 23 °C to 950 °C with five heating rates of 5, 10, 20, 30 and 40 °C min\(^{-1}\) under pure nitrogen gas with a flow rate of 50 ml min\(^{-1}\). The heating rates employed in current work are acceptable after considering the research needs and most previous similar studies comprehensively. Approximately a 4 mg sample was evenly placed in an alumina crucible at each heating rate. The maximum deviation between the recorded mass loss data for repeated tests was less than 0.5%. The test corresponding to the different operating conditions was conducted at least three times.

2.3. Kinetic methods

Thermogravimetric data provides some information on the overall kinetics of the thermal decomposition reactions [33,34]. The pyrolysis process can be characterized by a function of the arithmetic product of chemical reaction rate constant \(K(T)\) and kinetic model \(f(\alpha)\) [35]. \(K(T)\) has the form of the Arrhenius law, \(f(\alpha)\) depends on conversion rate \(\alpha\). So, the reaction rate of the solid materials under non-isothermal condition can simply be written as the following equation,

\[
\frac{da}{dt} = \beta \frac{da}{dT} = K(T)f(\alpha) = A_e \exp\left(\frac{-E_a}{RT}\right)f(\alpha)
\]

where \(t\) is the reaction time, \(\beta\) is the heating rate, \(T\) is the sample temperature, \(A_e\) is the pre-exponential factor, \(E_a\) is the apparent activation energy, and \(R\) is the gas constant. Here, three most commonly used model-free methods (including Kissinger-Akahira-Sunose (KAS) [36,37], Flynn-Wall-Ozawa (FWO) [38,39] and Friedman [40] methods) were employed to calculate the kinetic parameters at multiple heating rates. The expressions of these methods are listed in Table 1.

2.4. Parameters optimization

SCE algorithm is considered as a promising way to solve the global optimization problems based on the principle of racial evolution. The core of this method is Competitive Complex Evolution (CCE) algorithm [32]. It has been applied widely and successfully in parameter optimization in the field of hydrology [41] and flammability [42]. A brief description of the procedure about SCE algorithm

<table>
<thead>
<tr>
<th>Method</th>
<th>Expression</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAS</td>
<td>(\ln(\frac{\beta}{T^\alpha}) = \ln(A_e R / E_a g(\alpha)) - \frac{E_a}{RT})</td>
<td>(\ln(\beta/T^\alpha) \text{ vs } 1/T)</td>
</tr>
<tr>
<td>FWO</td>
<td>(\ln \beta = \ln(A_e E_a / Rg(\alpha)) - 5.331 - 1.052 \frac{E_a}{RT})</td>
<td>(\ln \beta \text{ vs } 1/T)</td>
</tr>
<tr>
<td>Friedman</td>
<td>(\ln(\frac{\beta \cdot da}{dT}) = \ln(f(\alpha)) - \frac{E_a}{RT})</td>
<td>(\ln(\beta(da/dT)) \text{ vs } 1/T)</td>
</tr>
</tbody>
</table>
applied to materials’ pyrolysis property estimation is involved in several previous work [13,18]. In current work, SCE algorithm was compiled by Visual Basic and implemented through a Microsoft Excel user interface. The detailed description about all necessary computations involved in this method can be found in previous literature [13,31,32]. The procedure was performed using an Intel Xeon E5-2680 v3 CPU (2.50 GHz, 2*12 cores) in Aalto high performance computing cluster.

3. Results and discussion

3.1. Thermogravimetric analysis

Fig. 1 (a) shows the curves of mass loss and mass loss rate at the five heating rates of 5, 10, 20, 30 and 40 °C min⁻¹ under nitrogen atmosphere. Almost the same trends can be observed at the five heating rates, because there are the same chemical compositions and structures. With the increase of heating rate, a lateral shift to higher temperatures occurs in mass loss and mass loss rate curves. The
combined effects of the heat hysteresis and the change of the decomposition kinetics will be responsible for the pyrolysis delay under a high heating rate [20,43]. Three stages in mass loss curves and three peaks in mass loss rate curves indicate that the pyrolysis occurs in a three-step process. The first step (167–395 °C) is attributed to the decomposition of SA. The second step occurs between 378 °C and 521 °C, which is related to the degradation of PP. The decomposition of CC happens at a higher temperature range (536–805 °C), which corresponds to the third step. Table 2 lists the onset temperature of pyrolysis (Tonset), the temperature corresponding to the maximum rate of mass loss (Tpeak), the end temperature of the main mass loss (Tend) and the maximum mass loss rate (MLRpeak) in each step for all the heating rates. The values of MLRpeak for each step also increase with the heating rate.

Fig. 1 (b) compares the mass loss and mass loss rate curves in nitrogen and air at the heating rate of 10 °C min⁻¹. It is found that there is a main two-step pyrolysis process with three peaks, and the first two peaks clearly overlap and gradually merge under the air atmosphere. It appears that the second peak shifts to the lower temperature side. This point is consistent with the finding that PP begins to pyrolyze at low temperature in air atmosphere [22]. The presence of oxygen in air can complicate the degradation mechanisms and promote the random scissions of polymers, resulting in the change of pyrolysis process [44]. Besides, there is no significant change in the pyrolysis behavior of the third step except the residue mass and the value of the peak mass loss rate.

3.2. Kinetic analysis

Fig. 2 (a)-(c) shows the model-free method plots (KAS, FWO and Friedman plots) at different conversion rates ranging from 0.05 to 0.95, where three regions can be clearly identified. The correlation coefficients of linear fitting are closed to 1 except α = 0.15 and 0.45 in the transition region. It implies that the values of Eα at α = 0.15 and 0.45 are less reliable, ignored in the activation energy analysis. The Eα will be determined from the slopes of these plots. The dependence of Eα on the conversion rate for α = 0.15–0.95 is depicted in Fig. 2 (d). The obtained Eα ranges 96.8–216.3 kJ mol⁻¹ for KAS, 100.1–217.4 kJ mol⁻¹ for FWO and 97.9–219.2 kJ mol⁻¹ for Friedman. The standard error of activation energy ranges from ±4.2 to ±11.4 kJ mol⁻¹. The difference in the value of Eα at the same conversion rate for three methods is due to various approximations and mathematical formulation [45,46]. However, it is possible to distinguish the three regions corresponding to pyrolysis process of each component. Assume that the first region (α =0.05–0.10) is related to the SA degradation, while the second region (α =0.20–0.40) corresponds to the PP degradation and the CC degradation.
contributes to the third region ($\alpha = 0.50–0.95$). It is evident that the values of $E_\alpha$ are independent of the conversion rates in each region. The calculated average $E_\alpha$ for the first step, second step and third step are 99.5, 214.7 and 186.9 kJ mol$^{-1}$, respectively. The average values of activation energy in the three stages are in accordance with the previous studies about the only SA [18], PP [20], and CC [25], respectively.

### 3.3. Reaction kinetic model

Based on the cable filler pyrolysis analysis mentioned above, a three-component chemical kinetics mechanism is proposed, associated with the decomposition of SA, PP, and CC. The scheme proposed in the present work has physically representative because the three components account for more than 95% of the cable filler. A similar study associated with wood has been conducted widely and verified carefully [47,48]. Fig. 3 shows the profiles of heat release, oxygen consumption and gaseous product. There are two peaks of heat release rate (HRR), coinciding with the two peaks in the curve of oxygen consumption. Besides, three stages of gas emissions appear during the pyrolysis process. It indicates that SA pyrolysis corresponds to the first HRR peak (or oxygen consumption) and the first stage of gas release, PP pyrolysis should be mainly responsible for the second HRR peak (or oxygen consumption) and the second stage of gas release, while CC pyrolysis occurs over a broad temperature range without heat release. Referring to the above discussion, the kinetic reactions can be represented by,

$$\text{Reaction 1} \quad \text{SA} \rightarrow \nu_s \text{residue} + (1 - \nu_s) \text{gas} \quad (2)$$

$$\text{Reaction 2} \quad \text{PP} \rightarrow \nu_p \text{residue} + (1 - \nu_p) \text{gas} \quad (3)$$

$$\text{Reaction 3} \quad \text{CC} \rightarrow \nu_c \text{residue} + (1 - \nu_c) \text{gas} \quad (4)$$

where subscript $s, p$ and $c$ represent SA, PP and CC, respectively. Previous studies have concluded that the residue of SA and PP degradation is negligible [19,22]. Thus, the values of $\nu_s$ and $\nu_p$ can be considered as zero.

**Table 3**

Values of pyrolysis characteristic parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Optimized value</th>
<th>Reaction 1</th>
<th>Reaction 2</th>
<th>Reaction 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y/\cdot$</td>
<td>0.083 ± 0.001</td>
<td>0.154 ± 0.002</td>
<td>0.763 ± 0.002</td>
<td></td>
</tr>
<tr>
<td>$A/\cdot$</td>
<td>2.38 ± 0.02E8</td>
<td>1.18 ± 0.02E12</td>
<td>4.17 ± 0.03E6</td>
<td></td>
</tr>
<tr>
<td>$E/\cdot$</td>
<td>105 ± 5</td>
<td>204 ± 7</td>
<td>176 ± 8</td>
<td></td>
</tr>
<tr>
<td>$n/\cdot$</td>
<td>2.75 ± 0.03</td>
<td>0.11 ± 0.01</td>
<td>0.18 ± 0.02</td>
<td></td>
</tr>
</tbody>
</table>

![Fig. 4](image-url) Predicted data (dash lines) compared with experimental data (symbols).
3.4. Optimized results and reaction deconstruction

In this study, the $n$-order kinetic model was adopted in the optimization method, which can be expressed as,

$$f(\alpha) = (1 - \alpha)^n$$  \hspace{1cm} (5)

Based on Eqs. (1)–(5), the decomposition rate of each component can be written as,

$$\frac{d y_i}{d T} = -\frac{1}{\beta_i} \left( \frac{y_i}{y_{i,0}} \right)^n A_{i,j} \exp \left( -\frac{E_{a,i}}{R \theta_{i,j}} \right)$$  \hspace{1cm} (6)

$$\frac{d y_{\text{residue}}}{d T} = -\sum_{i=1}^{n} \beta_i \frac{d y_i}{d T}$$  \hspace{1cm} (7)

where $y_i$, $y_{i,0}$ and $y_{\text{residue}}$ denote the mass fraction of $i$-th component, the initial mass fraction of $i$-th component and the residue mass fraction. The total mass loss rate can be defined as the sum of the reaction rate of each component, expressed as the following formula,

$$MLR = \sum MLR_i + MLR_{\text{residue}} = \sum_{i=1}^{n} \frac{d y_i}{d t} + \frac{d y_{\text{residue}}}{d t}$$  \hspace{1cm} (8)

where $MLR_i$ is the mass loss rate of $i$-th component. $MLR_{\text{residue}}$ is the mass loss rate of residue. This kinetic model combined with the SCE algorithm is applied to estimate the kinetic parameters and reconstruct the pyrolysis process. The application of the optimization method will be described as follows.

The experimental data at four heating rates (5, 10, 30 and 40 °C min$^{-1}$) were employed to simultaneously optimize kinetic parameters of each reaction by means of the SCE algorithm. The optimized parameters could be obtained as listed in Table 3. Note that the value of activation energy for each reaction estimated by the optimization algorithm is in agreement with those calculated by
model-free methods. This indicates that it is reliable to calculate the kinetic parameters of cable filler by SCE algorithm to some extent. Fig. 4 shows the comparison between predicted values and experimental data at various heating rates. It is found that the model results based on optimized parameters provide very good agreement with the experimental data. The correlation coefficients are more than 0.99 for all data at four heating rates. To determine the applicability of these optimized parameters to predict the experimental data at other heating rates, the model values for one experiment at the heating rate of 20 °C min⁻¹ were calculated using these kinetic parameters. Fig. 5 (a) shows the prediction results and experimental data at the heating rate of 20 °C min⁻¹. It is noted that the predicted data by the optimized parameters fit well with experimental results with a fit of 0.994, though there is a slight over-prediction of the peak values. Fig. 5 (b) shows the deconstruction of pyrolysis reaction by SCE algorithm. Three reactions mainly contribute to the total mass loss rate. The degradation of SA occurs over 160 °C for reaction 1, and PP begins to decompose above 370 °C for reaction 2. The above reactions only produce gaseous products. The degradation of CC starts from 530 °C in reaction 3 with the formation of the only eventual residue signified by the negative part. Overall, it has been proved that the optimized parameters could be applied to well estimate the thermogravimetric data of cable filler under the different conditions involving those used/not used to optimize these values, and possibly even more complex programs. We should keep in mind that the more realistic set of the kinetic parameters may be obtained when the thermogravimetric data for more heating rates are used to optimize parameters. However, the difference in optimized values between these procedures is acceptable.

4. Conclusions

In the present study, a series of thermogravimetric tests at 5, 10, 20, 30 and 40 °C min⁻¹ in nitrogen and 10 °C min⁻¹ in air were performed to examine the pyrolysis kinetics of typical cable filler waste. The degradation process can be clearly divided into three independent steps, which is attributed to the decomposition of stearic acid, polypropylene, and calcium carbonate, respectively. The overlapping phenomenon of the first two steps occurs in air due to the complex oxidation reaction. The average activation energy obtained by multiple model-free methods is around 99.5, 214.7 and 186.9 kJ mol⁻¹ for the three stages, respectively. A three-component reaction model was proposed based on the analysis of the pyrolysis characteristics. The Shuffled Complex Evolution algorithm was applied to optimize the kinetic parameters of the reaction scheme. The activation energy (105, 204 and 176 kJ mol⁻¹) estimated by the optimization algorithm in each stage presents very good agreement with that calculated by model-free methods. Based on the assumption of the n-order kinetic model for each stage, the predicted results using the optimized parameters are considerably consistent with the experimental data. Besides, it is also found that the optimized parameters can be applied to reconstitute experimental data at other heating rates. All three reactions are responsible for the total mass loss rate. In summary, the application of these kinetic parameters optimized by Shuffled Complex Evolution algorithm may be expanded to the complex pyrolysis scenarios. However, we should stress that the limitations of the existing application are impossible to avoid for the present work because of the complexity and diversity of cable fillers in the real situation. Besides, the dependence of the calculation accuracy on the experimental data used to optimize kinetic parameters should be paid more attention. To better understanding the pyrolysis mechanisms, the detailed analysis for pyrolysis products by the TG-FTIR and gas chromatography-mass spectrometry (MC-GS) is also indispensable. We will study the relevant aspects in detail in our future work. All above may provide guidance for thermochemical degradation and second-life applications of the retired cables.

Author statement

Zhi Wang: Conceptualization, Data curation, Data collection, Investigation, Methodology, Writing-original draft, Writing-review & editing. Simo Hostikka: Conceptualization, Methodology, Software, Writing-review & editing. Jian Wang: Project administration, Funding acquisition, Supervision, Validation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgements

The authors would like to acknowledge valuable discussion with Dr. Aleksi Rinta-Paavola and financial support sponsored by the Fundamental Research Funds for the Central Universities (No. 2022QN1009) and National Key R&D Program of China (No. 2018YFC0809500) and China Scholarship Council (CSC) as well as the computing support provided by Aalto high performance computing cluster.

References
