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Research Paper

Kinetic study on pyrolysis of waste phenolic fibre-reinforced plastic

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HIGHLIGHTS

- Pyrolysis tests of waste phenolic FRP are conducted in a wide heating rate range.
- A two-step consecutive reaction model describing the pyrolysis process is proposed.
- Genetic algorithm is used to optimize all the kinetic parameters simultaneously.
- The predicted results fit well with the experimental thermogravimetric curves.
- The applicability of optimized parameters is validated for wider heating rates.

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ABSTRACT

Pyrolysis is considered to be a promising method to recycle waste plastics for fuel or chemical feedstock. In order to provide guidance for reactor design and pyrolysis process management for recycling waste phenolic fibre-reinforced plastic (FRP), the pyrolysis behaviors of waste phenolic FRP is studied employing thermogravimetric analysis (TGA) over a wide heating rate range from 10 K/min to 70 K/min in nitrogen. A two-step consecutive reaction model is proposed to characterize the pyrolysis process. A global optimization algorithm called genetic algorithm (GA) coupled with the two-step consecutive reaction model is used to obtain all the kinetic parameters simultaneously based upon the experimental thermogravimetric data at heating rates of 10, 20 and 30 K/min. The predicted MLR and conversion curves using the optimized kinetic parameters and the two-step consecutive reaction model fit well with the experimental results not only at heating rates of 10, 20 and 30 K/min, but also at heating rates of 50, 60 and 70 K/min which are not used to obtain the kinetic parameters. The optimized kinetic parameters and the two-step consecutive reaction model may be applicable to the pyrolysis of waste phenolic FRP under more practical and complex thermal conditions that can be characterized by various heating rates.

1. Introduction

Fibre-reinforced plastic (FRP) is a representative thermosetting plastic. It mainly contains phenolic FRP and polyester FRP according to the resin type. Owing to prominent thermal insulation, impact resistance and absorption characteristics, it is increasingly applied in buildings, aircrafts, ships and automobiles. Meanwhile, large amounts of waste FRP are generated from the equipment renewal. In general, landfill, incineration and pyrolysis are the major methods to dispose such solid waste [1,2]. Therein, landfill and incineration are cheaper than pyrolysis. However, landfill will occupy large amounts of valuable soil. Incineration will release hazardous gases. As one of the pivotal thermo-chemical conversion technologies, pyrolysis has proved to be effectively convert the raw heterogeneous feedstock into homogeneous and more energy dense products in absence of oxygen without pollution to environment [3–8]. Hence, pyrolysis may be a promising method to recycle waste FRP. In order to effectively utilize waste FRP for energy and chemical feedstock recycling through pyrolysis, it is of great importance to obtain the pyrolysis kinetics of waste FRP. In addition, conducting kinetic modeling of waste FRP is of considerable benefit to characterize practical pyrolysis process and then optimize the reactor design.

As to the pyrolysis kinetics of waste FRP, Yun et al. [9] employed Friedman method [10] to calculate the pre-exponential factor and activation energy of polyester FRP pyrolysis with assumption of reaction order. Yu et al. [11] used Friedman method [10], Kissinger method

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[12,13], Ozawa method [14] and modified Coats-Redfern method [15,16] to calculate the pre-exponential factor, activation energy and reaction order of polyester FRP pyrolysis. The above two research focused on the pyrolysis kinetics of polyester FRP. The pyrolysis kinetics of phenolic FRP receives little attention to date to the best knowledge of the authors. Since phenolic FRP possesses much higher fire performance than that of polyester FRP, increasing application of phenolic FRP may occur as an alternative of polyester FRP. Therefore, it is necessary to investigate the pyrolysis kinetics of phenolic FRP.

In addition, in the research of Yun et al. [9] and Yu et al. [11], the three key kinetic parameters namely the pre-exponential factor, activation energy and reaction order are not able to be calculated simultaneously. For example, the pre-exponential factor cannot be calculated without known activation energy in the research of Yu et al. [11]. Thus, if the activation energy is calculated mistakenly, then the calculated pre-exponential factor will be also wrong. Furthermore, for solid materials with complex compositions such as the waste phenolic FRP in the present study, several physical and chemical reactions may simultaneously or consecutively occur in the pyrolysis process. It requires relatively complex kinetic schemes to model their pyrolysis. And these kinetic schemes require a large number of parameters. These parameters cannot be easily determined by the traditional kinetic methods used in the research of Yun et al. [9] and Yu et al. [11].

For the abovementioned reason, global optimization methodologies such as genetic algorithm (GA) coupled with thermogravimetric analysis (TGA) have been employed to parametrize the kinetic schemes and obtain the kinetic parameters of some intricate thermoplastics such as polyurethane (PU) [17,18], polystyrene (PS) [17]. In their research, the kinetic parameters were calculated simultaneously. In addition, the calculated kinetic parameters can be used to well reproduce the experimental thermogravimetric curves. However, to date, GA coupled with TGA is merely applied to study the pyrolysis kinetics of the thermoplastics. Since there are large differences between the pyrolysis process of thermosetting plastics and thermoplastics, it is necessary to investigate the applicability of GA coupled with TGA to obtain the pyrolysis kinetics and conduct kinetic modeling of thermosetting plastics such as phenolic FRP in the present study.

In order to provide guidance for reactor design and pyrolysis process management for the waste phenolic FRP pyrolysis recycling and analyze the applicability of GA coupled with TGA to obtain the pyrolysis kinetics of thermosetting plastics, the present study employs TGA to investigate the pyrolysis behaviors of the waste phenolic FRP at heating rates from 10 to 70 K/min in nitrogen. Based upon part of the thermogravimetric data (10, 20 and 30 K/min), GA coupled with a two-step consecutive reaction model is used to optimize all the kinetic parameters simultaneously. Using the optimized kinetic parameters, the two-step consecutive reaction model is applied to predict the thermogravimetric curves at the remained heating rates (50, 60 and 70 K/min) to evaluate the applicability of the approach.

2. Experimental and kinetic modeling

2.1. Experimental

2.1.1. Material

The waste phenolic FRP adopted in the present study was provided by Shanghai FRP Research Institute. According to the technical data provided by the supplier, the phenolic FRP consists of approximately 50% phenolic resin and 50% fiberglass (mass fraction). Phenolic resin was obtained by the condensation polymerization of phenol and formaldehyde. Proximate and ultimate analyses, as shown in Table 1, were conducted to further determine the composition of the specimen. The basic properties of the specimen are illustrated in Table 2. Therein, the density ρ was provided by the supplier. The specific heat c and thermal conductivity λ were obtained employing a hot disk TPS2500s. These three thermophysical parameters will be used in the optimization process by GA. The specimen was kept in a drying oven with constant temperature of 373 K for 24 h before tests.

Table 1
Proximate and ultimate analyses of the specimen.

Proximate analysis (wt%)[a]			Ultimate analysis (wt%)[a]					
Volatile matter	Fixed carbon	Ash	C	H	O	N	S	Other elements[b]
28.26	14.42	57.32	37.52	3.37	10.76	0.05	0.86	47.44

Note: a: dry basis; b: by difference.

Table 2
Basic properties of the specimen.

Category	Value
Density ρ (kg/m^3)	1970
Specific heat c (J/(kg·K))	932
Thermal conductivity λ (W/(m·K))	0.357

2.1.2. Thermogravimetric tests

The thermogravimetric tests were performed using a SDT Q600 thermal analyzer with gas flow rate of 100 ml/min in nitrogen. Typical heating rates including 10, 20, 30, 50, 60 and 70 K/min were selected for tests. The program temperature was increased from room temperature (RT) to 1056 K at the end. The specimen was grinded to powder with mass of approximately 9 mg in each test.

2.2. Kinetic modeling

2.2.1. Kinetic reaction scheme

As illustrated in Section 2.1.1, phenolic resin is the major composition to be decomposed in the pyrolysis process of waste phenolic FRP. According to the previous studies concerning the pyrolysis of phenolic resin [19–21], the pyrolysis process of phenolic resin may be mainly divided into three consecutive stages: formation of crosslinking between phenol derivatives, scission of the crosslinking and stripping off hydrogen atoms from the aromatic rings. Moreover, the former two stages mainly contribute to the pyrolysis of phenolic resin. Note that each of these consecutive stages does not represent an elementary reaction but rather a relatively complicated set of reactions. And it may be modeled by an apparent overall kinetic expression [20]. If this apparent overall kinetic expression is established, the pyrolysis of the waste phenolic FRP may be quantitatively characterized. Therefore, the pyrolysis process of waste phenolic FRP may be made up of a series of consecutive reactions, as expressed as Eq. (1).

$$A \rightarrow B \rightarrow C \rightarrow \ldots \tag{1}$$

In the present study, it is assumed that the pyrolysis process of waste phenolic FRP is divided into $i = 1, 2, \ldots, n_{reaction}$ consecutive stages. Each stage may be characterized by a nominal single-step nth order Arrhenius-type decomposition reaction which yields residue and volatiles. Note that this nominal reaction may actually contain a relatively complicated set of reactions, as illustrated above. Then, a nominal consecutive reaction scheme may be established as follows:

$$Component_i \rightarrow \nu_i residue + (1-\nu_i) volatiles \tag{2}$$

where for ith reaction, $Component_i$ represents the nominal reactant. ν_i denotes the nominal residue yield (also called reaction stoichiometry coefficient). Note that the residue generated in ith reaction may be the reactant in the $(i + 1)$th reaction. Based upon the nth order Arrhenius-type decomposition reaction, the condensed-phase reactive rate for Eq. (2) can be calculated by: