PYROLYSIS KINETICS OF POTASSIUM-IMPREGNATED BIOMASS ANALYZED BY EVOLUTIONARY COMPUTATION

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ABSTRACT

Potassium is a natural catalyst in biomass thermochemical conversion and plays an essential role in plant's growth. To figure out the catalytic effects of potassium on the thermochemical behaviors of biomass, the pyrolysis characteristics of rubber wood are comprehensively studied using a thermogravimetric analyzer where the biomass is impregnated by different concentration of potassium carbonate (K_2CO_3=0.004 M, 0.008 M, and 0.012 M). The thermal degradation with independent parallel reaction (IPR) model is adopted. To maximize the fit quality between the established kinetic models and experimental data, particle swarm optimization (PSO), a kind of evolutionary computation, is employed. The results suggest that the thermal degradation curves of the raw and impregnated rubber wood can be predicted with a fit quality of at least 97.5%. It is proved in this work that the IPR model and the calculation of the PSO can be used to predict the pyrolysis kinetics of impregnated biomass to a good level of fitness.

Keywords: Potassium catalyst, Pyrolysis, Independent parallel reaction model, particle swarm optimization.

1. INTRODUCTION

In recent years, there is a growing awareness of environmental issues such as air pollution, deteriorated atmospheric greenhouse effect, global warming, and climate change that are the consequences of fossil fuel combustion. To mitigate the aforementioned energy and environment issues, the development of clean and sustainable energy has received increasing attention over the past decades. Among all the developed renewable energy sources, bioenergy, derived from abundant resources like wood, livestock dung, algae, sewage sludge, and municipal solid waste, is currently the fourth largest primary energy source worldwide. When plants grow, carbon is absorbed by biomass from the atmosphere to synthesize its essential nutrients, and is then returned to the environment when it is burned or digested. On account of having a zero net carbon emission, biomass is considered as a carbon-neutral fuel. Compared to fossil fuels, biomass is characterized by its short life cycle and can be thought of as a renewable and environmentally friendly substitute to the non-renewable fuels.

Pyrolysis has been a potential method to produce biofuel which is regarded as an important and sustainable alternative in fuel production, carbon storage, and soil amendment. A number of studies have investigated the effects of inorganic metals such as K, Mg, Ca, Na, etc. on biomass thermal degradation, and showed that they might act as catalysts in thermal reactions of biomass, thereby affecting char formation, pyrolysis products distribution [1, 2]. However, the kinetic models need to be investigated to evaluate the influence of different conditions in the biomass. Such models are practical tools to predict the biomass pyrolysis, which can be used to describe the mass loss of the components during the conversion process using calculations.

Therefore, the objective of this study was to investigate the influence of the rubber wood impregnated with K_2CO_3 on the thermal degradation. Therefore, the pyrolysis kinetics of the impregnated rubber wood is developed using an independent parallel reaction (IPR) model along with the particle swarm

optimization (PSO) to predict its thermal degradation phenomenon. The developed kinetic model can be used to describe the mass loss of the wood during the decomposition process and is conducive to the reactor design. Moreover, the obtained results are capable of providing useful insights into the potential for bioenergy production and application with rubber wood.

2. MATERIALS AND METHODS

2.1 Material

The biomass used in this study was rubber wood obtained from Chinese Petroleum Corporation (CPC) in Taiwan. The raw biomass was ground by a crusher and sieved between 60 and 120 mesh (125–250 μm). The sieved sample was then dried in an oven at 105 °C for 24 h for subsequent treatment. When preparing potassium-enriched biomass, potassium was loaded into dried biomass samples by chemical impregnation, which has been widely adopted in the literature [3].

Potassium carbonate (K_2CO_3) was chosen as the source of potassium for the impregnation. The K_2CO_3 solutions were prepared by mixing deionized water and anhydrous K_2CO_3 (Katayama Chemical Inc) according the required concentrations. Impregnation was done by putting 5 g of dried rubber wood sample into the prepared K_2CO_3 solution in a beaker at a mixing ratio of 10 mL g^{-1}, followed by mixing the mixture using a stirrer for 1 h at room temperature. Afterward, the impregnated samples were filtered and dried at 105 °C for 24 h. The samples were then placed in sealed plastic bags and stored in an electronic cabinet at room temperature until experiments were carried out. In this study, three low K^+ concentrations (K_2CO_3=0.004 M, 0.008 M, and 0.012 M) were selected.

2.2 Thermogravimetric analysis

To understand the thermal properties of the raw and impregnated rubber wood, their thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) analysis were conducted using a thermogravimetric analyzer (TG, SDT Q600 TGA, TA Instruments). In each test, around 5 mg of the bio-oil was loaded in an alumina crucible. Then, nitrogen gas and air at a flow rate of 100 mL min^{-1} were individually used as carrier gases to analyze the pyrolysis characteristics of the samples [4, 5]. In each analysis, the sample was first heated from room temperature to 105 °C and then held for 5 min to provide a dry-basis for pyrolysis analysis. Afterward, the sample was heated from 105 °C to 800 °C at a heating rate of 20

°C min^{-1}. The instantaneous sample weight during the analysis was detected and recorded at a frequency of 2 Hz for further analysis.

2.3 Pyrolysis kinetics

The independent parallel reaction (IPR) model has been successfully applied to demonstrate the pyrolysis processes of different materials [6, 7], and was thus employed to analyze the thermal degradation process of the impregnated rubber wood. This model assumed that the wood had a number of components, and their decomposition behaviors were described by individual Arrhenius equations [8], in terms of their mass fractions (c), pre-exponential factors (A), and activation energies (Ea). To optimize the predicted DTG curves, the non-linear least squares method was used to minimize the sum of the square differences between the experimental and calculated data, which was defined as the objective function (OBJ). Then, the fit quality between actual and modeled data was calculated to validate the optimization or the curve fitting process. The algorithm of momentum-type PSO proposed by Liu et al. [9] was used to optimize the objective function which had been adopted in a previous study [8].

3. RESULTS AND DISCUSSION

3.1 Pyrolysis characteristic

The degradation characteristic of raw and potassium-impregnated rubber woods have been described in previous study [10]. For the raw rubber wood, the whole pyrolysis process can be partitioned into three stages. The first stage or the first shoulder (200-330 °C) might be attributed to the decomposition of hemicellulose [11]. The second stage (330-400 °C) contains a peak at about 360 °C and height of 0.926 % °C^{-1}, which is the main pyrolysis process. This is due to the thermal decomposition of cellulose. The third stage (400-750 °C) is mainly constructed by the second shoulder, presumably stemming from the decomposition of lignin [12]. In regard to the DTG curves of the potassium-impregnated samples, the peak shifts toward lower temperature with increasing K^+ concentration, and the shoulder has a trend to disappear. This phenomenon is mainly due to the modification of the cellulose structure in biomass by potassium which increases the reactivity of cellulose [13].

3.2 Kinetics of rubber wood pyrolysis

The predicted results of the four-reaction model compared to the experimental data of rubber wood are

shown in **Fig. 1**. The detailed results of the kinetics parameters and fit qualities of the samples are shown in **Table 1**. The values for raw and potassium-impregnated rubber woods are 99.23%, 97.52%, 99.33 and 99.17%, respectively, implying that, overall, the fit quality can reach over 97.5%.

The first group (group I), decomposing at temperatures between 170 and 380 °C, accounts for 33% (i.e., cI=0.33 in Table 1). This might be assigned to the decomposition of hemicellulose [11]. The activation energies of raw and potassium-impregnated rubber wood are similar, which are in the ranges of 105.39 to 107.40 kJ mol^{-1}. However, it seems that the decomposed onset temperature of group I decreases as the K$^+$ concentration increases, which also observed in the study of Macedo et al. [3]. The second group thermally degrades in the temperature range of 250-400 °C. It is attributed to the thermal decomposition of cellulose. The activation energies was decreasing vigorously as increasing the K$^+$ concentration from 0.004M to 0.012M, which causing the peak shifts toward lower temperature. This phenomenon is mainly due to the modification of the cellulose structure in rubber wood by potassium which increases the reactivity of cellulose [13].

The reaction of the third group (group III) occurs at temperatures between 110 to 580 °C, as a consequence of the weight loss of lignin with no significantly change of activation energies (35.23 to 37.86 kJ mol^{-1}). However,

the composition of group III was increasing as increasing K$^+$ concentration. It may attribute to the decomposing component from cellulose.

4. CONCLUSIONS

The results indicate that the experimental DTG curve of the impregnated rubber woods could be predicted well, with a fit quality of at least 97.5%. Using the IPR model, the thermal degradation of each component with increasing temperature could be predicted separately. It is found that the activation energies of group II are decreasing from the 223.86 kJ mol^{-1} to 204.14 kJ mol^{-1}, which are in good agreement with the data reported in the literature. This illustrated that K$_2$CO$_3$ played a major roles in the pyrolysis of cellulose. Overall, the kinetics of potassium-impregnated rubber wood pyrolysis can thus be simulated readily to a certain fit quality using the IPR model and the calculations obtained from PSO. The common kinetic model for the impregnated rubber wood devolatilization is hoped to facilitate the future development of comprehensive models for the simulation of practical conversion systems.

Table 1 The calculated kinetics parameters of four-reaction model.

Concentration	Group	Kinetic parameters			Temperature range (°C)	Fit quality (%)
		Ea (kJ mol^{-1})	A (s^{-1})	c		
Raw	I	105.57	2.84×10^7	0.33	200-380	99.23
	II	223.86	3.80×10^{16}	0.43	290-400	
	III	36.78	3.22×10^0	0.14	110-580	
	IV	34.27	3.06×10^{-1}	0.10	190-800	
0.004	I	105.39	2.65×10^7	0.34	180-380	97.52
	II	226.31	5.94×10^{16}	0.44	260-400	
	III	37.86	3.80×10^0	0.16	110-580	
	IV	32.69	3.80×10^{-1}	0.06	280-800	
0.008	I	107.04	3.64×10^7	0.32	180-380	99.33
	II	209.53	3.89×10^{15}	0.42	250-400	
	III	37.26	3.81×10^0	0.19	110-570	
	IV	33.76	2.06×10^{-1}	0.07	210-800	
0.012	I	107.02	3.74×10^7	0.33	170-380	99.17
	II	204.14	1.99×10^{15}	0.38	250-390	
	III	35.23	2.83×10^0	0.21	110-570	
	IV	31.95	1.75×10^{-1}	0.08	190-800	
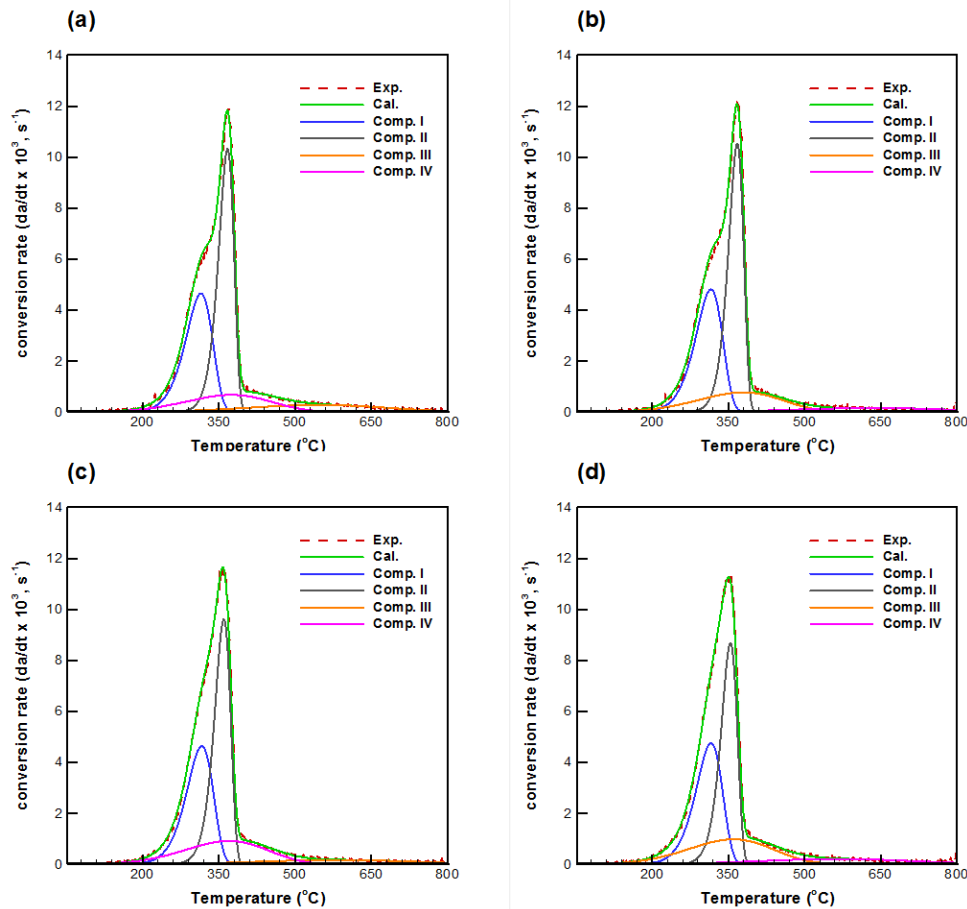
Fig. 1 Comparison of experimental and predicted data for (a) untreated rubber wood, and potassium-impregnated with (b) 0.004M, (c) 0.008M, and (d) 0.012M rubber woods.

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