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Synthetic Effects and Economic Accounting of Low-temperature Pyrolysis Process of Typical Medical Waste based on Kinetics Analysis

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Abstract. The thermogravimetric (TG) analysis was adopted to study the pyrolysis characteristics of two typical medical wastes at different heating rates (10, 20, and 50 ℃/min), and the kinetic parameters were analyzed by the Coats-Redfern method. Finally, the economic evaluation of the technology was carried out. The results showed that the two typical medical wastes both have only one weight loss peak. The syringes and bamboo sticks pyrolysis ranged from 264.80 to 554.07 ℃ and from 205.66 to 487.05 ℃, respectively. With the increase of the heating rate, the initial, final and peak temperatures of the two raw materials shifted to higher values. The pyrolysis reaction mechanisms of the syringes and bamboo sticks were summarized as the nucleation growth model (A2.5) and the second-order model (F2). The total investment of medical waste pyrolysis project is 59 million yuan, and the annual net gain is 11.85 million yuan. The investment recovery period of the project takes five years.

1 Introduction

With the improvement of medical enterprise, a large quantity of medical wastes have been generated. According to statistics, there were about 843,000 tons of medical wastes produced in China in 2019, and the production increased by 4-8% annually [1]. Due to the high infectivity and pathogenicity of medical waste, rapid harmless treatment has attracted the attention of the whole society.

Medical waste contains more than 80% organic fractions [2]. Concretely speaking, it includes 39.30-50.00% plastics, 14.32-45.10% biomass and 3.40-6.60% rubber [3]. And the calorific value is higher than 4000 kcal/kg [4-5], so it has the potential to be converted into energy through thermal treatment. Pyrolysis can break medical wastes into high value products such as coke, combustible gas and tar in an oxygen-free or anoxia environment [6]. Compared with traditional incineration technology, pyrolysis technology has been considered to have obvious advantages in producing energy, high value products and in reducing pollution [6-8].

The prerequisite and key to the development and design of the pyrolysis process lies in the thorough understanding of the pyrolysis characteristics of medical waste. The complexity and variability of medical waste result in the extremely complex pyrolysis process. Therefore, in order to understand the overall pyrolysis characteristics of medical waste, it is necessary to grasp the pyrolysis behavior of single component. Thermogravimetric analysis has been widely applied in researching the thermal analysis and kinetic parameters of organic matter [9], and the Coats-Redfern method is a general method for the thermal kinetic analysis of coal, biomass and solid wastes [10]. The Coats-Redfern method can simultaneously calculate the activation energy, pre-exponential factor and reaction mechanism function [11]. Therefore, the Coats-Redfern method can be used to obtain kinetic parameters and reaction mechanisms.

In this study, syringes and bamboo sticks were selected as typical components of plastic and biomass in medical wastes. The pyrolysis characteristics of raw materials with different heating rates were studied by TG. Based on thermogravimetric data, the Coats-Redfern method was used to calculate the kinetic parameters and determine the most appropriate reaction mechanism. Pyrolysis behaviors and kinetic analysis grasped in this paper are helpful to the selection and optimization of the reactors as well as the setting of operation parameters in the industrial pyrolysis process.

2 Materials and methods

2.1 Materials

Two typical medical waste components, syringes and

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bamboo sticks were selected in this study, which were purchased from Jiangsu Zhiyu Medical Instrument Co., Ltd. and Qingdao Hainuo Biological Engineering Co., Ltd. respectively. The samples were crushed to powder with a particle size of less than 0.5 mm, and then dried in an oven at 105 ℃ for 3 h. The proximate analysis was performed according to the Chinese National Standard GB/T212-2008, and the ultimate analysis was tested by elemental analyzers (Elementar Vario Micro cube, Germany and Euro Vector EA3000, Italy). The test results are shown in Table 1.

Table 1. Proximate analysis and ultimate analysis of samples

Sample	Proximate analysis/wt.%			Ultimate analysis/wt.%				
	Ad	Vd	FCd	Cd	Hd	Nd	Sd	Od
Syringes	0.02	99.10	0.88	85.90	13.53	0.00	0.00	0.55
Bamboo sticks	8.64	83.33	8.03	44.58	5.73	0.28	0.19	40.58

2.2 Experiment methods

The pyrolysis experiment was carried out on a thermogravimetric analyzer (STA 449 F3 Jupiter, NETZSCH Company, Germany). About 10 mg of samples were placed in an alumina crucible and heated from 25 to 600 ℃ at heating rates of 10, 20 and 50 ℃/min. A nitrogen flow rate of 20 ml/min was applied during the entire heating process. For the sake of reducing the system error, the blank experiment of each heating rate was carried out before the actual experiments.

2.3 Coats-Redfern kinetic method

The Coats-Redfern (CR) method [12] was used for kinetic analysis in this study, whose equation was as follows:

$$\ln\frac{G(\alpha)}{T^2}=\ln\frac{AR}{\beta E}-\frac{E}{RT} \tag{1}$$

Therefore, the values of activation energies and pre-exponential factors can be obtained by the slope and intercept of the fitted regression equation. The most suitable reaction mechanism was determined by comparing activation energies with model-free method.

3 Results and discussion

3.1 Thermogravimetric analysis

The TG and DTG curves of samples at different heating rates (10, 20, 50 ℃/min) are displayed in Fig. 1. Both of two kinds of samples had only one weight loss peak, indicating that both of them had one-step thermal degradation characteristics. The initial pyrolysis temperature (Ti), maximum weight loss rate pyrolysis temperature (Tp), final pyrolysis temperature (Tf) and mass residue (mf) were summarized in Table 2. From Fig. 1 and Table 2, syringes had a rapid reaction rate and a narrow temperature range. The pyrolysis interval of syringes with different heating rates was 364.80-554.07 ℃, and the peak temperature of DTG was 459.41 ℃ for the heating rate of 10 ℃/min, 467.94 ℃ for the heating rate of 20 ℃/min and for the heating rate of 50 ℃/min, respectively. Syringes produced almost no

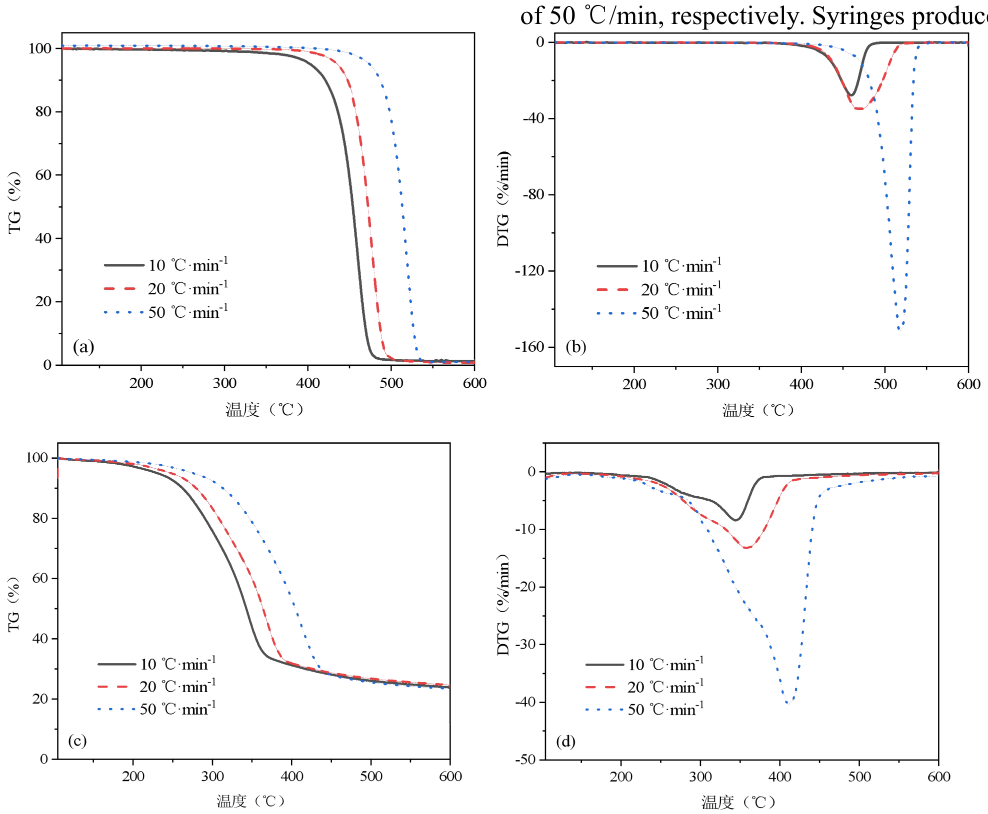

Fig. 1. TG/DTG curves of two samples: (a)(b) Syringes；(c)(d) Bamboo sticks

coke after pyrolysis, and the mass residues at three heating rates were less than 1.3 wt.%. Compared with syringes, bamboo sticks appeared to have a slower weight loss rate and a wider pyrolysis temperature range. The pyrolysis process of bamboo sticks started at 205.66-220.83 ℃, and finished at 410.18-487.03 ℃. It can be found that the DTG curves of bamboo sticks were asymmetrical, and there was an obvious shoulder on the left half of every DTG curve, which may be caused by the pyrolysis of different components in bamboo sticks.

Table 2. Pyrolysis characteristics of two samples

Sample	β/℃·min-1	To/℃	Tp/℃	Tf/℃	mf/%
Syringes	10	364.80	459.41	496.44	1.25
	20	374.50	467.94	529.87	0.73
	50	394.06	518.95	554.07	0.98
Bamboo sticks	10	205.66	344.53	410.18	23.92
	20	210.94	358.43	439.97	24.72
	50	220.83	410.76	487.03	23.52

Noteworthily, the initial, final and peak temperatures of the two raw materials shifted to higher temperatures with the increase of heating rate from 10 to 50 ℃/min. From the DTG curves, it was not difficult to find that the maximum weight loss rates under high heating rates were higher than those under low heating rates, indicating that the higher the heating rate was, the more intense the pyrolysis reaction was.

3.2 Kinetic analysis

The determination of pyrolysis reaction models and kinetic parameters is very important to study the pyrolysis mechanisms of materials. The common solid reaction mechanism functions were substituted into the Coats-Redfern method for calculation, and activation energies E, pre-exponential factors A and correlation coefficients R2 of syringes and bamboo sticks were obtained and summarized in Table 3 and 4, respectively. As shown in Table 3 and 4, the correlation coefficients of all reaction mechanism functions exceeded 0.9, which demonstrated that the kinetic parameters calculated by the Coats-Redfern method were credible. Meanwhile, the kinetic parameters of different reaction mechanism function models fluctuated greatly. For example, The values of activation energy were distributed in 78.51-629.71 KJ/mol and 12.71-122.48 KJ/mol for syringes and bamboo sticks, respectively. It was obvious that the difference between the maximum and minimum was nearly 9 times, which showed that not all mechanism function models were applicable to the selected samples.

The activation energies of syringes calculated by the A2.5 mechanism at three heating rates were 96.60-135.95 KJ/mol, which were close to the values calculated by the FWO, KAS and Friedman method. Thus, it can be inferred that the pyrolysis behavior of syringes follows the nucleation growth model (A2.5), and the integral form of the mechanism function is G(α)=[-ln(1-α)]2/5. It shows that during the pyrolysis process of syringes, several active sites for the decomposition reaction were first formed at the reaction interface. The decomposition products formed the nuclei of the product around these active sites, and the surrounding materials then reacted on the nuclei. As the pyrolysis reaction proceeded, the reaction nuclei continued to increase and grow [13] until the pyrolysis reaction was completed. For bamboo sticks, the values of activation energy with three heating rates obtained by the F2 model ranged from 87.49 to 91.18 KJ/mol, similar to the values estimated by model-free models. Therefore, the second-order model (F2) may be the most suitable mechanism of the pyrolysis behavior of bamboo sticks, whose integral form is G(α) =(1-α)-1-1.

Table 3. The kinetic parameters of syringes at different heating rates by CR method

Model	β=10 ℃·min-1			β=20 ℃·min-1			β=50 ℃·min-1			Average
	E/KJ·mol-1	A/min-1	R2	E/KJ·mol-1	A/min-1	R2	E/KJ·mol-1	A/min-1	R2	E/KJ·mol-1
F1	259.41	1.92×1018	0.9887	343.36	1.23×1024	0.9995	359.30	1.93×1024	0.9943	320.69
F2	347.56	9.40×1024	0.9560	468.02	1.54×1033	0.9828	481.30	5.56×1032	0.9670	432.29
F3	454.76	1.15×1033	0.9165	620.60	1.87×1044	0.9537	629.71	9.77×1042	0.9308	568.36
D1	397.99	8.53×1027	0.9981	513.87	5.07×1035	0.9887	547.88	3.17×1036	0.9973	486.58
D2	435.65	3.05×1030	0.9981	565.91	1.59×1039	0.9950	599.97	6.44×1039	0.9992	533.84
D3	481.71	2.05×1033	0.9950	630.26	1.70×1043	0.9992	663.70	3.62×1043	0.9984	591.89
D4	450.85	9.55×1030	0.9974	587.13	1.24×1040	0.9969	621.00	4.07×1040	0.9993	552.99
A2	123.74	1.89×108	0.9876	165.53	2.42×1011	0.9995	173.18	4.65×1011	0.9939	154.15
A2.5	96.60	1.71×106	0.9871	129.96	6.31×108	0.9994	135.95	1.26×108	0.9937	120.84
A3	78.51	7.10×104	0.9865	106.25	1.15×107	0.9994	111.13	2.37×107	0.9935	98.63
R1	193.03	1.59×1013	0.9980	250.78	1.92×1017	0.9881	267.47	7.45×1017	0.9972	237.09
R2	223.55	1.75×1015	0.9967	293.14	1.27×1020	0.9976	309.68	3.36×1020	0.9992	275.46
R3	234.89	8.60×1015	0.9948	308.98	1.24×1021	0.9991	325.38	2.79×1021	0.9984	289.75

Table 4. The kinetic parameters of bamboo sticks at different heating rates by CR method

Model	β=10 ℃·min-1			β=20 ℃·min-1			β=50 ℃·min-1			Average
	E/KJ·mol-1	A/min-1	R2	E/KJ·mol-1	A/min-1	R2	E/KJ·mol-1	A/min-1	R2	E/KJ·mol-1
F1	57.82	1.51×104	0.9900	63.17	6.50×104	0.9938	65.51	1.06×105	0.9919	62.17
F2	87.49	1.59×107	0.9791	90.91	3.61×107	0.9590	91.18	2.70×107	0.9542	89.86
F3	124.62	7.93×1010	0.9545	125.14	7.55×1010	0.9165	122.48	2.04×1010	0.9097	124.08
D1	84.02	1.22×106	0.9655	96.12	1.87×107	0.9909	103.22	5.20×107	0.9973	94.46
D2	95.20	8.48×106	0.9780	107.25	1.18×108	0.9966	114.06	2.67×108	0.9997	105.51
D3	109.71	5.46×107	0.9878	121.27	6.14×108	0.9981	127.39	1.01×109	0.9982	119.46
D4	99.97	5.70×106	0.9821	111.87	7.41×107	0.9978	118.46	1.51×108	0.9997	110.10
A2	23.98	8.33×100	0.9850	26.59	2.55×101	0.9919	27.47	4.94×101	0.9895	26.01
A2.5	17.01	1.50×100	0.9985	17.82	3.13×100	0.9970	19.86	9.17×100	0.9877	18.23
A3	12.71	4.85×10-1	0.9756	14.39	1.35×100	0.9887	14.79	2.76×100	0.9853	13.96
R1	37.09	9.61×101	0.9546	43.06	5.69×102	0.9881	46.32	1.47×103	0.9963	42.16
R2	46.36	4.77×102	0.9799	52.19	2.50×103	0.9977	55.12	5.33×103	0.9995	51.22
R3	49.93	7.57×102	0.9848	55.63	3.75×103	0.9978	58.41	7.36×103	0.9981	54.66

3.3 Economic analysis

Based on the kinetic calculations and experimental results, taking the medical waste pyrolysis project with a treatment capacity of 100 t/d as an example, the rotary kiln pyrolysis gasification device was selected. A minimum of 1,500 m3 gas can be generated per ton of medical waste, and the calorific value of the gas is about 6.3 MJ/Nm3. The heat consumption rate of the unit is calculated as 10 MJ/kW·h. Eight 600 GFZ1 automatic shut-type high-pressure gas generator sets were selected for the power plant, whose continuous output was about 4000 kW. The total investment of the power plant was 59 million yuan, of which the medical waste pyrolysis gasification system was about 37 million yuan and the power plant system was about 22 million yuan.

(1) Electricity selling profit:

According to the above settings, the annual output power can be calculated as:

4000 kW×8400 h (350 D) /10000=33.6 million kW·h

The average self-consumed rate of the power plant was calculated by 6%, the total power consumption of the medical waste pyrolysis gasification device was about 225 kW, and the on-grid price was budgeted by 0.65 yuan/(kW·h). Therefore, the electricity selling profit per year can be computed as:

0.65×[33.6×(1-6%)-0.225×8.4]=19.3 million yuan

(2) Metal recovery:

On the basis of investigation results, the metal content in medical waste was about 0.5%, and the metal recovery rate was estimated as 0.4%. Thus, metal recovery from waste disposal is 140 tons per year. Considering the market price of 940 yuan/ton of scrap iron, the annual income is 131,600 yuan.

(3) Saving transportation cost:

35,000 tons of medical waste disposed in situ per year can save 6,000 times transportation. Pressing 50 yuan per time can save a total of 300,000 yuan. The fuel charge can save up to 1.35 million yuan, which was calculated by 300,000 km of transportation distance and 5.64 yuan per liter of diesel prices. As a whole, the transportation cost can be saved by about 1.65 million yuan.

(4) Operating cost:

The gas making equipment lifetime is approximately 10 years, and the repair cycle is about 1 year. 0.5 million and 2 million yuan are required per year for the system maintenance and operation respectively. For the operation of the system and the management of the power plant, 25 people are needed, and the annual salary and social insurance for each of them is 50,000 yuan. Together with management cost of 300,000 yuan per year, the annual operating cost totals 4.05 million yuan.

(5) Depreciation cost:

The depreciation of houses and buildings is calculated based on 25 years, while machinery equipment and other fixed assets are depreciated for 10 years. The ratio of the remaining value is 5%, and the calculated depreciation rate is 9.5%. The depreciation cost is about 5.18 million yuan per year.

According to the above economic benefit analysis, the total investment of the medical waste pyrolysis gasification project is 59 million yuan, and the total annual expenditure is 9.23 million yuan. Without considering government subsidization, the income is 21.08 million yuan and the project investment payback period takes five years. If the government grants a medical waste treatment subsidy of 83 yuan/ton, the project investment recovery period will be four years.

4 Conclusion

The pyrolysis behaviors of two typical components of medical wastes (syringes and bamboo sticks) were investigated at three heating rates by TG. According to TG and DTG curves, the Coats-Redfern method was employed to determine the suitable reaction mechanisms and kinetic parameters. The main conclusions are as follows:

(1) It can be observed from TG and DTG curves that the pyrolysis process of two kinds of samples was only one stage. The pyrolysis reaction rate of the syringes was relatively fast, and the pyrolysis mainly occurred at 264.80-554.07 ℃. Bamboo sticks covered a decomposition temperature that ranged from

205.66-487.05 ℃, and there was an obvious shoulder on the left half of every DTG curve, which may be the result of the pyrolysis of different components in bamboo sticks. The initial, final and peak temperatures of the two raw materials shifted to higher temperatures as the heating rate increased.

(2) It is found that the activation energies of syringes calculated by the A2.5 model (96.60-135.95 KJ/mol) and bamboo sticks obtained from the F2 mechanism function (87.49-91.18 KJ/mol) were similar to values estimated by model-free models. Therefore, the pyrolysis kinetic reaction mechanisms of syringes and bamboo sticks followed as nucleation growth model (A2.5) and second-order model (F2), respectively.

(3) The total investment of 100 t/d medical waste pyrolysis gasification project is 59 million yuan, and the total annual expenditure is 9.23 million yuan. Without considering government subsidization, the income is 21.08 million yuan, and the investment recovery period of the project needs five years. If the government grants 83 yuan per ton of medical waste treatment subsidies, the project investment recovery period is four years.

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