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Pyrolysis kinetics of perfusion tubes under non-isothermal and isothermal conditions



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ABSTRACT

The waste-to-energy (WTE) conversion of solid waste including perfusion tubes becomes interesting, with potential advantages of reducing the volume and mass of solid waste, and exploiting new energy sources. First, the non-isothermal pyrolysis experiments of perfusion tubes with the heating rates (β) of 5, 10, 20, 40 °C min⁻¹ were conducted in a thermogravimetric analyzer (TGA) under nitrogen atmosphere. The TGA results indicated that the pyrolysis temperature of perfusion tubes is mainly between 200 °C and 500 °C, and the pyrolysis process of perfusion tubes under non-isothermal conditions can be divided into two stages. Next, the isothermal pyrolysis experiments of perfusion tubes were carried out on a batch fluidized bed at four temperatures (850, 875, 900, 925 °C), which is close to the practical pyrolysis processes of perfusion tubes. The batch fluidized bed results demonstrated that the pyrolysis process of perfusion tubes under isothermal conditions only has a rapid conversion stage, which is dissimilar to that under non-isothermal conditions (two-stage conversion). Last, the pyrolysis kinetic parameters of perfusion tubes under non-isothermal and isothermal conditions were calculated, respectively by the isoconversional methods (the Flynn-Wall-Ozawa (FWO) method and the Kissinger-Akahi ra-Sunose (KAS) method) and the isothermal model fitting methods. Noted that the isothermal pyrolysis kinetics of perfusion tubes were for the first time investigated according to the gas compositions at different isothermal conditions, and the contracting volume (R3) mechanism model was determined as the most probable model to describe the pyrolysis process of perfusion tubes among six potential mechanism models. The apparent activation energies of perfusion tube pyrolysis under non-isothermal conditions were between 97.81 and 209.62 kJ mol⁻¹ using the FWO method and between 85.63 and 214.28 kJ mol⁻¹ using the KAS method, while it was calculated as 74.54 kJ mol⁻¹ under isothermal conditions. The decrease of apparent activation energy in isothermal fluidized bed experiments could be due to less limitation to external transfer of mass and heat. Overall, these results suggested that this research can provide an understanding of pyrolysis kinetics of perfusion tubes and some useful information for the design of pyrolytic processing system using perfusion tubes as feedstock.

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1. Introduction

The management of solid wastes continues to be a major challenge in every country, particularly in the developing countries [1]. In recent years, more and more governments [2–6] realize that improper disposal of solid waste has huge social cost due to the spreading of communicable diseases and increased treatment costs for pollutants, and is an issue of increasing concern. Especially, the incineration of plastic wastes has been considered as a significant source of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), which is classified as hazardous wastes [7]. Besides, the world's reliance on the ever decreasing resources of fossil fuel energy has led to the necessity of exploiting new energy source [8]. It is well known that plastic waste has a high heating value [9] and its utilization as fuel would manifest a significant environmental and economical benefit [10].

The technologies for the primary thermal conversion of plastic waste (solid fuel) are combustion, gasification and pyrolysis [11]. Among these techniques, pyrolysis process is considered not only as a promising technology to convert plastic waste into chemicals and fuels with high efficiency in the absence of oxygen, but also as a precursor for combustion or gasification process of plastic waste [12,13]. These pyrolysis gases (H₂, CO, CO₂, CH₄, etc) of plastic waste could be also employed in internal combustion engines, gas turbine and other operating devices [14]. In addition, several

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potential benefits of plastic waste pyrolysis strengthen its practical significance, including the adequate utilization of contaminated plastic wastes [15] and the suppression of PCDD/Fs formation [16,17].

The pyrolysis kinetics of plastic wastes can provide deeper insights into the mechanism of pyrolysis [18] and it is important for the proper selection of reactor, optimization of the reactor design and operating condition [19]. The correctness of the kinetics expression heavily depends upon reliable evaluation of activation energy from the decomposition behavior under isothermal or non-isothermal conditions. Thermogravimetric analyzer (TGA) is an excellent tool for studying the thermal degradation kinetics and it has been widely used to investigate non-isothermal pyrolysis kinetics of solid fuel [20-22]. For example, Zhou et al. [23] used TGA to analyze the pyrolysis kinetics of coal and plastic blends through a first-order reaction model. Aboulkas et al. [20] analyzed the pyrolysis kinetics of moroccan oil shale and plastic mixtures using an isoconversional integral method according to these TG data. Biney et al. [25] used a new multi-stage kinetic model to calculate kinetic parameters for the thermal decomposition of three biomass fuels in a TGA. It is acknowledged that in most of the industrial processes fuel is usually introduced into a high temperature environment rapidly, where the pyrolysis of fuel would occur under nearly isothermal conditions [26-28]. Currently, fluidized beds have been widely used in the field of energy conversion due to their excellent mixing and gas-solid contact which improves the reaction rate as well as conversion efficiency remarkably [29–32]. However, little information is available about pyrolysis kinetics of plastic wastes under isothermal conditions, especially based on the pyrolysis process of plastic wastes in fluidized bed. More importantly, if the comparison of the isothermal pyrolysis kinetics (in fluidized bed) with the non-isothermal pyrolysis kinetics (in TGA) can be conducted for an identical plastic waste, more detailed knowledge for the pyrolysis process can be obtained.

In this work, a perfusion tube was selected as a representative type of plastic wastes and the pyrolysis experiments of perfusion tubes were first conducted in a TGA with four heating rates (β) of 5. 10. 20 and 40 $^{\circ}$ C min⁻¹ to explore the pyrolysis temperature of perfusion tubes. Next, the pyrolysis experiments of perfusion tubes were carried out on a batch fluidized bed at four isothermal conditions (850, 875, 900 and 925 °C) to detect the pyrolysis gas compositions of perfusion tubes. Last, the non-isothermal and isothermal pyrolysis kinetic parameters of perfusion tubes were calculated, respectively by the isoconversional methods (the FWO method and the KAS method) and the isothermal model fitting methods. It is for the first time to comparatively investigate the pyrolysis mechanism model under non-isothermal conditions and under isothermal conditions. Hopefully this study can help provide an understanding of the pyrolysis characteristics of plastic wastes and can provide useful information on the reutilization of plastic wastes.

2. Experimental

2.1. Material

A perfusion tube (which mainly includes polyethylene and polybutylene) as a typical type of plastic wastes has been selected in this work and it was provided by the Health Center of Huazhong University of Science and Technology (HUST). The sample was crushed and sieved into particles with a size range of 0.5–0.6 mm, which was dried for 24 h at 105 °C before experiments. The elemental composition, proximate analysis and calorific value of the sample are listed in Table 1, and its ash analysis is listed in Table 2. Note that the proximate analysis and the ultimate analysis

were conducted following the ASTM D5373 criterion and the GB212-91/GB212-84 criterion, respectively. The subscript "ad" means air dried basis. Therefore, M_{ad} , V_{ad} , A_{ad} and FC_{ad} mean the contents of moisture, volatile, ash and fixed carbon in the samples on air dried basis. C_{ad} , H_{ad} , N_{ad} , S_{ad} and Cl_{ad} mean the contents of C, H, N, S and Cl element in the samples on air dried basis. The contents of C_{ad} , H_{ad} , N_{ad} and S_{ad} were directly determined. The Cl_{ad} content was measured using an ion chromatograph (ICS-90) as follows: first, 0.2 g of perfusion tubes was placed within a furnace, and then, the furnace was heated to 1100 °C at 10 °C/min under air atmosphere. Next, the exhaust gas from the reactor was led into the NaHCO₃ saturated solution, where Cl_{ad} was measured by detecting the chloride ion concentration. Note that "else elements" in Table 2 mainly include P, Ti, Cr, K.

2.2. Apparatus and procedure

The pyrolysis characteristics of perfusion tubes were investigated in a simultaneous thermal analysis (WCT-1D). First, approximate 20 mg was loaded into a plate crucible made of Al₂O₃. Next, the sample was heated to 100 °C over 10 min and was maintained at 100 °C for 5 min for sample drying. Then, the sample was heated to 1000 °C for pyrolysis with four heating rates (β), i.e., 5 °C min⁻¹, 10 °C min⁻¹, 20 °C min⁻¹, 40 °C min⁻¹. For selecting heating rate, it is better to satisfy the requirement that the logarithm of heating rates are uniform, so four heating rates (5, 10, 20, 40 °C min⁻¹) were determined. The microbalance of the TGA apparatus has a nominal sensitivity of 0.1 µg and the gas flow into the TGA was controlled using an electronic mass flow regulator. Note that the ambient atmosphere during temperature-programmed pyrolysis was provided by a continuous nitrogen flow of 40 ml min^{-1} . Finally, the non-isothermal pyrolysis kinetics were calculated by two generally-used isoconversional methods (FWO method and KAS method) according to the change of sample weight at four heating processes.

Subsequently, the pyrolysis experiments of the perfusion tubes were carried out on a batch fluidized bed. An overview of the fluidized-bed system is presented in Fig. 1. A straight stainless steel tube (i.d. = 26 mm, length = 892 mm) with a porous distributor plate located 400 mm from the bottom was used as the reaction chamber. The reaction chamber was electrically heated by a furnace. This system has been detailedly described in other literatures [33–36]. First, 30 g of silica sand was placed within the reactor, and then, the furnace was heated to the designed temperatures (850, 875, 900, 925 °C). Note that the size range of silica sands is 0.2-0.3 mm and the minimum fluidisation velocity was calculated using Wen & Yu formula. After the furnace temperature was attained and maintained in the set-point temperature, 0.2 g of perfusion tubes was introduced into the furnace through a hopper which was inserted deep into the reaction region. Note that 600 mL min⁻¹ of nitrogen was introduced into the reactor and the working fluidisation velocity approximately is as twice larger as the minimum fluidisation velocity. Besides, the silica sands were used as the fluidized bed materials because the silica sands have higher heat capacities and better mixing efficiency. Next, the concentrations of CO₂, CO, CH₄, H₂, and O₂ were measured using on-line gas analyzers (Gasboard-3151). Then the exhaust gas was collected in a gas bag and the other gas components were subsequently measured by a gas chromatograph (Agilent 3000A micro-GC). HCl is the main chloride product and it is difficult to monitor HCl real-timely due to its corrosion and water-solubility. Because the pyrolysis process is mainly cutting carbon chain, the neglect of chlorine element does not cause some unacceptable errors. Last, the isothermal pyrolysis kinetics was then calculated according to the change of these gas concentrations under four isothermal conditions.

Table 1

Trowning of the period of the	Proximate analysis,	, ultimate analysis	(on wt.%, as received)	and lower heating	g value of the	perfusion tubes
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Sample	Proximat	Proximate (wt.%, as received)		LHV (MJ/kg, db)	LHV (MJ/kg, db)	Ultimate (wt.%, as received)				
	M _{ad}	FC _{ad}	V _{ad}	A _{ad}		C _{ad}	H _{ad}	N _{ad}	S _{ad}	Cl _{ad}
Perfusion tubes	0.03	0.08	93.79	6.1	33.87	73.89	10.82	0.72	0.16	4.92

Table 2

Ash analysis of the perfusion tubes (on wt.%, as received).

Sample	Component analysis (wt.%)								Else elements
	Al ₂ O ₃	SiO ₂	SO ₃	CaO	Mn_2O_3	Fe ₂ O ₃	CuO	ZnO	
Perfusion tubes	15.63	34.92	4.48	19.54	1.39	19.23	1.89	2.39	0.53



Fig. 1. Overview of the fluidized-bed reactor.

2.3. Data evaluation

The mass loss of perfusion tubes in TGA was defined as:

$$X = \frac{m_t}{m_o} \tag{1}$$

where m_o and m_t are the sample weights at the beginning and at time *t* of the pyrolysis stage, respectively.

For the batch fluidized-bed experiments, the volume flow rate of inlet N_2 (N_{N_2}) under the standard conditions was constant, and the gas concentrations of the outlet gases (X_i , $i = CO_2$, CO, CH₄, and H₂) were analyzed by the gas analyzer. $N_{i,out}$ was defined as the volume flow rate of gaseous product species *i*, which can be calculated via the N₂ balance.



Fig. 2. TG and DTG curves vs temperature at different heating rates.

$$N_{i,\text{out}} = \frac{N_{N_2}}{1 - \sum_i X_i} X_i \tag{2}$$

The cumulative volume of gas $i(V_{i,out})$ was first calculated (Eq. (3)). Subsequently the volume percentage of gas $i(v_{i,out})$ was obtained (Eq. (4)), avoiding the error from the sample mass of perfusion tubes at different temperature conditions.

$$V_{i,\text{out}} = \int_0^t N_{i,\text{out}} dt \tag{3}$$

$$\nu_{i,\text{out}} = \frac{V_{i,\text{out}}}{V_{\text{CO},\text{out}} + V_{\text{CO}_2,\text{out}} + V_{\text{CH}_4,\text{out}} + V_{\text{H}_2,\text{out}}}$$
(4)

3. Results and discussion

3.1. TGA result

The mass loss (TG) and the rate of mass loss (DTG) curves during the pyrolysis process of perfusion tubes at four heating rates (5, 10, 20, 40 °C min⁻¹) are shown in Fig. 2. It can be found that the DTG curves have two obvious mass loss peaks, which indicates that the pyrolysis process of perfusion tubes can be divided into two steps [22]. Also, it can be seen that the mass loss mainly occurs between 200 and 500 °C, and the decomposition temperature of perfusion tubes was prolonged 1000 °C. Factually, more than 95% of organic volatile components (see Table 1) can release promptly when temperature attains 500 °C. Furthermore, it can be seen that the DTG peaks move toward higher temperature and the absolute values of DTG peaks decrease with the increase of heating rate. The most reasonable explanation is that a greater heating rate delays the release of volatile matter and reduces the amount of volatile release at specific temperature, which is consistent with the previous achievements [12,37-39]. It is acknowledged that high temperature pyrolysis within the range of 650-850 °C can crack the primary de-volatilization products and the secondary gas phase for low molecular weight hydrocarbons (ranging from C_1-C_9) [22]. In order to adequately convert into gaseous products, higher temperatures of more than 850 °C (e.g., 850, 875, 900, 925 °C in this work) have been adopted as the isothermal pyrolysis temperature. Note that these determinated temperatures were mainly to ensure the precision of kinetic parameters derived from the isothermal experiments and the economical efficiency of perfusion tubes pyrolysis at these temperatures needs to be further investigated.

3.2. Batch fluidized bed result

The main pyrolysis products (CO₂, CO, CH₄ and H₂) of perfusion tubes at 850 °C, 875 °C, 900 °C and 925 °C were detected using an

on-line gas analyzer. Fig. 3 shows these gas concentrations of perfusion tube pyrolysis versus time at four temperatures and the main pyrolysis time-periods are within the first 100 s. Taking 900 °C for example (Fig. 3(c)), it is found that the CO concentration has the greatest peak values and the generation of H₂ was delayed approximate 20 s comparing with that of CO₂, CO and CH₄. One possible reason is that part hydrogen element can be first combined with the oxygen element in perfusion tubes at the initial stages. Another possible reason is that dealkylation reactions take place firstly and then aromatic decomposition. Note that these gases can be first detected 10 s later when perfusion tubes have been introduced into reactor, which was from the flue gas delay between reactor and gas analyzer. In order to evaluate the effect of temperature on gas compositions, the volume percentages were calculated according to Eq. (4), as shown in Fig. 4. It can be seen that the volume percentage of CH₄ presents a decreasing tendency with the increase of temperature, which should be mainly related with CH₄ decomposition at elevated temperatures [40]. Yet the volume percentages of the other gases do not emerge a prominent difference, which implied that these experimental conditions can adequately meet the requirements of perfusion tubes pyrolysis.

4. Pyrolysis kinetics

The rate of conversion $(d\alpha/dt)$ is often expressed using an Arrhenius type expression [38].

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_{\alpha}}{RT}\right) f(\alpha) \tag{5}$$

where A (s⁻¹), E_{α} (kJ mol⁻¹), R (kJ mol⁻¹ K⁻¹) and T (K) are the preexponential factor, the apparent activation energy, the universal gas constant, and the sample absolute temperature, respectively. $f(\alpha)$ represents the kinetic model that describes the rate of conversion dependence on the conversion.



Fig. 4. Gas components of perfusion tube pyrolysis at different temperatures.

4.1. Non-isothermal kinetics

For TGA experiments, the degree of conversion (α) of the pyrolysis process, which describes the change in sample weight, can be expressed as:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \tag{6}$$

where m_{∞} is the sample weights at the end of the pyrolysis stage.

Under a constant heating-rate ($\beta = dT/dt$), the time-dependence of the conversion rate can be used to rewrite the differential form (Eq. (7)) or the integral form (Eq. (8)) of the pyrolysis kinetic expression.

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(\frac{-E_{\alpha}}{RT}\right) f(\alpha) \tag{7}$$



Fig. 3. Gas concentrations of perfusion tube pyrolysis at different temperatures.

$$g(\alpha) = \int_0^T \frac{A}{\beta} \exp\left(\frac{-E_{\alpha}}{RT}\right) dT$$
(8)

By the kinetic method it is usually expected to derive an appropriate kinetic description of the process in terms of the E_{α} . In this work, apparent activation energy from dynamic data is obtained by the FWO method [38] and the KAS method [41–43] without knowledge of reaction mechanism. The FWO method and the KAS method are the isoconversional, integral methods. The FWO method is based on Eq.(9) using Doyle's approximation [22,24], and the KAS method is based on Eq.(10) [42–43]. This isoconversional method involves carrying out a series of experiments at different heating rates. More details can be found in the literatures [20,24]. Note that the work does not deny the existence of a more suitable isoconversional method and it is necessary to evaluate the accuracy of different isoconversional methods [41].

$$\ln \beta = \ln \left[\frac{AE_{\alpha}}{Rg(\alpha)} \right] - 5.331 - 1.052 \frac{E_{\alpha}}{RT_{\alpha}}$$
(9)

$$\ln(\beta/T_{\alpha}^{2}) = \ln\left[\frac{AR}{E_{\alpha}g(\alpha)}\right] - \frac{E_{\alpha}}{RT_{\alpha}}$$
(10)

For Eq. (9), $\ln\beta$ and $-1052/(RT_{\alpha})$ corresponding to each heatingrate are fitted into a straight line at each degree of conversion (α). The slope, ($E_{\alpha}/1000$), represents the apparent activation energy term, while the intercept is a coupled expression of the reaction model in the integral form, $g(\alpha)$, the apparent activation energy E_{α} , and the frequency factor, *A*. For Eq. (10), a plot of $\ln(\beta/T_{\alpha}^2)$ versus $1/T_{\alpha}$, obtained from thermal curves recorded at several heating rates, is a straight line whose slope allows evaluation of the apparent activation energy.

In the present study, four different heating rates (5, 10, 20 and 40 °C min⁻¹) were employed to calculate the apparent activation energies (E_{α}) using the FWO method and the KAS method. Nine conversions (α) were selected for the kinetic analysis corresponding to the perfusion tube pyrolysis. These conversions (α) include 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9. Nine straight lines are obtained and shown in Fig. 5(a) according to the FWO method, and these straight lines based on the KAS method are shown in Fig. 5(b). The apparent activation energy (E_{α}) values and linear correlation coefficient (R^2) are shown in Table 3 for each degree of conversion and the corresponding intercept of linear fittings are also listed in this table. As shown in Table 3, the linear correlation coefficients for getting the activation energy are in the range of 0.98149-0.9982 and the fitting is good for every linear plot. The apparent activation energies for perfusion tube pyrolysis were calculated and the range is between 97.81 kJ mol⁻¹ and 209.62 kJ mol⁻¹ using the FWO method and between 85.63 and



Fig. 6. Pyrolysis conversion (α) and pyrolysis rates ($d\alpha/dt$) of perfusion tubes vs time at different temperatures.

214.28 kJ mol⁻¹ using the KAS method. A similar rule for two methods can be found: there is a clear jump in the activation energy between 0.5 and 0.6 conversion corresponding to the change of TG curves, which should be derived from the transition side-chain to main-chain decomposition.

4.2. Isothermal kinetics

The product analysis such as gas, liquid, and solid is the significant criterion to evaluate these pyrolysis experiments. As shown in the Table 1, the content of volatile matter is 93.79%, which occupies the overwhelming proportion of perfusion tubes. The low content of fixed carbon (0.08%) illustrates that the influence from solid product is negligible. For the influence from liquid product, it is difficult for the isothermal pyrolysis experiments to detect the liquid yield real-timely. So in this study, only CO₂, CO, CH₄, and H₂ were considered as the pyrolysis products because the amount of other products were too low to be taken into account in these results (For example, the amount of all light hydrocarbons $C_x H_v$ ($x \ge 2$) is less than 1 vol.% when the pyrolysis experiment of perfusion tubes was conducted at 900 °C). It is undeniable that other gas compositions (like HCl, H₂O, SO₂, etc.) can release during the entire pyrolysis process of perfusion tubes, however, this simplification cannot cause an inadmissible error. One main reason is that Cad and Had are the primary elements of perfusion tubes, shown in Table 1. Another key factor is that the



Fig. 5. Isoconversional plot of the FWO method and the KAS method at different values of conversion.

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Table 3 Kinetic parameters obtained by using the FWO method and the KAS method.

Iso-conversional method	α	Intercept	E_{α} (kJ mol ⁻¹)	R ²
The FWO method	0.1	29.92889	117.77	0.99673
	0.2	28.48086	113.53	0.99602
	0.3	26.58377	107.16	0.99494
	0.4	23.8577	97.81	0.99663
	0.5	23.81412	112.06	0.99518
	0.6	36.56591	192.91	0.99368
	0.7	36.28605	196.29	0.99516
	0.8	36.2271	199.34	0.99377
	0.9	37.28806	209.62	0.98924
The KAS method	0.1	16.45871	120.02	0.9932
	0.2	14.3008	112.71	0.9982
	0.3	12.08932	104.53	0.99496
	0.4	6.19408	85.63	0.99265
	0.5	8.72817	108.99	0.99215
	0.6	22.35858	199.25	0.99557
	0.7	21.98901	201.29	0.98149
	0.8	21.15426	199.69	0.99542
	0.9	19.6508	214.28	0.99724

decomposition of perfusion tubes is a process of cutting off carbon chain, either the side chain or the main chain [44]. Hence the conversion including of almost all of C_{ad} and H_{ad} element release should be reliable. For the batch fluidized bed experiments, the degree of conversion (α) of the pyrolysis process, which describes the change of sample weight in reactor, can be expressed as:

$$\alpha = \frac{\int_{0}^{t} (28 \times N_{\text{CO,out}} + 44 \times N_{\text{CO}_2,\text{out}} + 16 \times N_{\text{CH}_4,\text{out}} + 2 \times N_{\text{H}_2,\text{out}})dt}{28 \times V_{\text{CO,out}} + 44 \times V_{\text{CO}_2,\text{out}} + 16 \times V_{\text{CH}_4,\text{out}} + 2 \times V_{\text{H}_2,\text{out}}}$$
(11)

The pyrolysis degrees (α) and pyrolysis rates ($d\alpha/dt$) of perfusion tubes versus time at four temperatures (850, 875, 900, 925 °C) were calculated according to Eq. (11), shown in Fig. 6. It can be found that four curves of conversion (α) do not emerge obvious difference when $\alpha < 0.1$, which should be derived from the warming process of sample particles. Also, it can be seen that higher temperature accelerated the pyrolysis process of perfusion tubes when $\alpha > 0.1$, which is coincident with the existing conclusions [45,46]. When α > 0.9, the progress of pyrolysis was too slow to meet the practical requirements. Hence only $0.1 < \alpha < 0.9$ has been considered for the subsequent pyrolysis kinetic calculation of perfusion tubes. Note that the pyrolysis process of perfusion tubes under isothermal conditions only has one conversion stage rather than two stages as that under non-isothermal conditions. The reasonable explanation is that two stages presented in non-isothermal conditions can be conducted simultaneously when a high temperature more than 850 °C was adopted.

Table 4

Algebraic expression for $f(\alpha)$ and $G(\alpha)$ for the most frequently used reaction mechanisms.



Fig. 7. Integral form expressions of six reaction mechanisms for perfusion tube pyrolysis at 900 $^\circ\text{C}.$

As known, the main purpose of the solid phase thermal degradation kinetic study is to evaluate the "kinetic triple" described by activation energy *E*, pre-exponential factor *A*, and the reaction model $f(\alpha)$. Kinetic parameters can be obtained from isothermal kinetic data using the rate law equation (Eq. (5)). And Eq. (13) can be obtained when Eq. (5) was coupled with Eq. (12) (where *k* is the rate constant).

$$k = A e^{-E/RT} \tag{12}$$

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{13}$$

Integrating (Eq. (13))

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = G(\alpha) = kt$$
(14)

The rate constant *k* can be determined by applying Eq. (14). The values of $G(\alpha)$ are first plotted with time *t* and then fitted by a linear line with the intercept equal to zero. The relation of *k* with the reaction temperature is established by the Arrhenius plots. It results in a straight line with the slope -E/R and an intercept that is the logarithm of pre-exponential factor *A*. Note that by taking the logarithm of Eq. (12) we have

$$\ln k = \ln A + \left(-\frac{E}{R}\right)\frac{1}{T}$$
(15)

Mechanism model	Different form $f(\alpha)$	Integral form $G(\alpha)$
Power law (accelerating $\alpha - t$ models)	$n\alpha^{(1-1/n)}$; $n = 1/2, 2/3, 1, 2, 3$	$\alpha^{1/n}$; $n = 1/2, 2/3, 1, 2, 3$
Exponential law	$\alpha/n; n = 1, 2$	$\ln \alpha^{n}; n = 1, 2$
Nuclei growth		
Avrami-Erofe'ev equation	$n(1 - \alpha)[-\ln(1 - \alpha)]^{(1-1/n)}; n = 1/4, 1/3, 2/5, 1/2, 2/3, 3/4, 1, 3/2, 2, 3, 4$	$[-\ln(1-\alpha)]^{1/n}$; $n = 1/4, 1/3, 2/5, 1/2, 2/3, 3/4, 1, 3/2, 2, 3, 4$
Chemical reaction		
Reaction order	$(1-\alpha)^n$; $n = 2, 3$	$(n-1)^{-1}(1-\alpha)^{(1-n)}; n = 2, 3$
Phase-boundary reactions		
Contracting area (R2)	$2(1-\alpha)^{1/2}$	$1 - (1 - \alpha)^{1/2}$
Contracting volume (R3)	$3(1-\alpha)^{1/3}$	$1 - (1 - \alpha)^{1/3}$
Diffusion		
1-D (D1)	1/2α	α^2
2-D (D2)	$[1 - \ln(1 - \alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha) + \alpha$
3-D (Jander) (D3)	$3/2 (1 - \alpha)^{2/3} / [1 - (1 - \alpha)^{1/3}]$	$[1 - (1 - \alpha)^{1/3}]^2$
3-D (Ginstling-Brounshtein) (D4)	$3/2[(1 - \alpha)^{-1/3} - 1]^{-1}$	$1 - (2\alpha 3) - (1 - \alpha)^{2/3}$

Table 5

Linear fitting parameters of	of six reaction	mechanisms	for the	pyrolysis	process of	perfusion	tubes at 9	00 °C.

Mechanism	Fitting line	R^2	Mechanism	Fitting line	R^2
R2	Y = -0.63616 + 0.02767X	0.99583	D2	Y = -0.82631 + 0.03055X	0.98686
R3	Y = -0.52437 + 0.02199X	0.99668	D3	Y = -0.35967 + 0.01278X	0.97089
D1	Y = -0.96287 + 0.03705X	0.99065	D4	Y = -0.2295 + 0.00836X	0.98283



Fig. 8. Integral form expression of Contracting volume (*R*3) for perfusion tube pyrolysis at four temperatures (a) 850 °C, (b) 875 °C, (c) 900 °C, (d) 925 °C.



Fig. 9. Plots of ln k vs 1000/T for perfusion tube pyrolysis at four temperatures (850 °C, 875 °C, 900 °C, 925 °C).

A variety of algebraic equations were derived to illustrate these models in a mathematical manner with relevant assumptions. The equations presented in Table 4 are the most frequently used reaction mechanisms [47–49].

Among these mechanism models, the phase-boundary reactions models and diffusion models should be the potential mechanism models to describe the pyrolysis process of perfusion tubes based on their physical meanings of these models. To determine the optimum kinetic model for these experimental data, six reaction models all were applied for the pyrolysis process of perfusion tubes at 900 °C, shown in Fig. 7. And corresponding linear fitting parameters were listed in Table 5. It can be found that the result from the contracting volume (R3) model can be fitted by a straight line ideally among these models. As previous mentioned, $G(\alpha)$ should be linear correlation with time *t* and the intercept should be equal or similar to zero. Note that the intercept of this fitting line based on the contracting volume (R3) model is not close to zero. The possible reason is that the heating process at the initial phase delays the transfer of heat. Finally, the contracting volume (R3) model has been considered as the most probable mechanism model. Subsequently, the rate constant k and the correlation coefficient (R^2) of four pyrolysis process at different temperatures were calculated, shown in Fig. 8. Note that these correlation coefficients (R^2) were more than 0.99071, which demonstrated the reliability of the contracting volume (R3) model. It is worth noted that pyrolysis mechanism model under non-isothermal conditions (TGA) was commonly described by $(1 - \alpha)^n$ [50–52] that is different from the contracting volume (R3) model under isothermal conditions in this work, which indicates that the pyrolysis process of perfusion tubes under isothermal conditions is different from those under non-isothermal conditions. Besides. the contracting volume (R3) model as the most probable mechanism model represents that the thermal decomposition (including the elimination of pendant groups and the decomposition of the main chain) of perfusion tube itself is the main factor for limiting the pyrolysis of perfusion tubes under isothermal conditions. In other words, the pyrolysis of perfusion tubes in the batch fluidized bed is less restricted by the external transfer of mass and heat.

As mentioned above, the linear regression analysis of the experimental data of ln k versus 1000/T was used to determine -E/R. Plots of ln k versus 1000/T are shown in Fig. 9 at different temperatures (850–925 °C). As expected, it was straight line with negative slopes, which is then used to estimate activation energy value. The obtained activation energy and pre-exponential factor are listed in Table 6. It was listed that the activation energy of perfusion tube pyrolysis in the batch fluidized bed is 74.54 kJ mol⁻¹, which is less than the results under non-isothermal conditions and some published results [46]. A reasonable explanation is that a worse transfer of heat and mass in the TGA experiments occurred than that in the batch fluidized bed experiments. In other words, the kinetic parameters obtained through the isothermal method in the batch fluidized bed reactor can be closer to the practical pyrolysis process of perfusion tubes and the reliable pyrolysis characteristics of perfusion tubes can be acquired. In addition, it should be pointed out that the kinetic parameters under isothermal conditions in this work were based on the gas concentrations of perfusion tube pyrolysis, and only the effect of temperature on the pyrolysis process was taken into account. The effect of sample quality, gas atmospheres and flow velocity on the pyrolysis kinetics of perfusion tubes should be further studied in the following study.

Table 6 Activation energy of perfusion tubes during the isothermal pyrolysis process.

Sample	Isothermal (°C)	Mechanism	Integral form $G(\alpha)$	E (kJ mol ⁻¹)	Α
Perfusion tubes	850, 875, 900, 925	Contracting volume (R3)	$1-(1-\alpha)^{1/3}$	74.54	45.70282

5. Conclusions

This work first conducts the pyrolysis experiments of perfusion tubes using a TGA in nitrogen atmosphere with four heating rates of 5, 10, 20 and 40 °C min⁻¹, which demonstrated that the perfusion tube pyrolysis mainly occurs between 200 °C and 500 °C. Also, isothermal pyrolysis experiments of perfusion tubes were carried out on a batch fluidized bed at four temperatures (850, 875, 900, 925 °C). These experimental results demonstrated that the pyrolysis process of perfusion tubes under isothermal condition only has one rapid conversion stage rather than two stages as under nonisothermal conditions. Last, the pyrolysis kinetic parameters of perfusion tubes under non-isothermal conditions were calculated by the FWO method and the KAS method, which are two widelyused isoconversional methods. For the batch fluidized bed experiments, six mechanism models were applied to determine the most probable model for describing the pyrolysis process of perfusion tubes at 900 °C, and finally the contracting volume (R3) mechanism model was determined. The apparent activation energies of perfusion tube pyrolysis obtained under isothermal conditions is 74.54 kJ mol⁻¹, which is less than that (97.81–209.62 kJ mol⁻¹ and 85.63–214.28 kJ mol⁻¹) obtained under non-isothermal conditions. In summary, these results demonstrated that the practical pyrolysis process of perfusion tubes under isothermal conditions is different from that under non-isothermal conditions and these kinetic data obtained under non-isothermal conditions can provide more reliable information for the design of pyrolytic processing system using perfusion tubes as feedstock.

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