

Contents lists available at ScienceDirect

Journal of the Energy Institute

journal homepage: www.elsevier.com/locate/joei



Comparison between two-step and single-step kinetic models for non-isothermal CO₂ gasification of biomass char generated by fast pyrolysis

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ARTICLE INFO ABSTRACT Handling Editor: Dr. Paul Williams Kinetic analysis plays a critical role in the gasification process. The kinetics of CO₂ gasification for various wood chars, which were prepared in a single particle reactor (SPR), were studied using a non-isothermal method in a Keywords: thermogravimetric analyzer. To statistically derive significant conclusions, the data obtained from the gasifi-Kinetics modeling cation of fast pyrolyzed chars are used to compare the performance of the volumetric model (VM), grain model CO₂ gasification (GM), random pore model (RPM), integrated core model (ICM), and two-step (first step: VM; second step: ICM) Biomass char parallel model. The obtained results show that most |DDTG| curves show one local minimum, representing at Fast pyrolysis least one reaction step. When combined with the TG curves, the gasification process exhibits a distinct devolatilization and char gasification component. ICM has a better performance compared to the other single-step models. The two-step model significantly improves over the single-step model due to the additional equation. The two-step model's average deviation DEV(X) is 0.95 %, which shows an 80 % improvement compared to ICM (DEV(X) = 4.64 %). The predicted activation energy (devolatilization: 54.8–76.2 kJ/mol; gasification: 185.7-247.5 kJ/mol) falls within a reasonable range, which is consistent with the findings reported in the literature.

1. Introduction

In recent years, the extensive use of fossil fuels has caused serious environmental problems [1]. Biomass chemical conversion technology plays a crucial role in addressing climate and environmental concerns [2,3]. Among the several thermochemical conversion processes, gasification is generally considered the most promising and practical process, which can convert various types of biomass into syngas [4–6]. The gasification process consists of two main stages: initial pyrolysis and subsequent char gasification, with the latter stage controlling the overall conversion [7,8]. Therefore, the enhancement of gasifier design and process efficiency is closely connected to the study of reactivity and kinetic modeling [7].

Kinetic analysis plays a critical role in the gasification process, and comprehending the kinetics of gasification enables a profound understanding of the reaction process [9]. It has thereby been the focus of numerous early and recent research [10]. The single-step models, which represent the kinetic behavior of gas-solid reactions, are considered the most elementary models [11] and can represent the gas-solid reaction at a temperature below 1000 °C well [11]. Therefore, single-step models are extensively applied for the kinetic modeling of gasification [12]. The volumetric model (VM), grain model (GM), random pore model (RPM), and modified random pore model (MRPM) are the commonly used gasification kinetic models [13]. Among these models, RPM is the typical theoretical one, which takes into account pore growth and coalescence during reaction simultaneously [11] and predicts the maximum reaction rate at conversion levels below 0.393 [8]. The model has achieved significant success in modeling gasification reactions of coal char [8]. However, there are evident deviations between the experimental and fitted curves by traditional RPM due to the catalytic or inhibiting effect of inherent inorganic elements in samples [13], especially for cases in which the peak reaction rate takes place at a higher conversion rate stage(>0.393) [7]. Therefore, the MRPM was proposed to consider the influence of inorganic elements on catalysis [8]. Wang et al. [14]

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https://doi.org/10.1016/j.joei.2023.101450

Received 22 September 2023; Received in revised form 19 October 2023; Accepted 24 October 2023 Available online 27 October 2023 1743-9671/© 2023 Energy Institute. Published by Elsevier Ltd. All rights reserved.

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described the kinetics of four herbaceous residue chars and two wooden residue chars using VM, GM, RPM, and MRPM. The findings suggested that for biomass chars, MRPM and RPM showed better suitability, with MRPM performing better in a high conversion range. However, the use of RPM may not be suitable for analyzing gasification kinetics without considering 1) the changing gas mixture effect and 2) the reduction in char surface area caused by the experimental procedure. Instead, ICM may have a better fitting performance than RPM [15,16]. On the whole, the VM, GM, RPM, and ICM models are among the most often used models that have been proven by substantial researches [14–16] to accurately describe the conversion of biomass char.

The complexity of the phenomena in the majority of non-isothermal experiments requires models built from multiple kinetic equations (each kinetic equation considers the kinetics of several zones or pseudocomponents [17]). Most of the published non-isothermal kinetic analyses are based on oversimplified single-step models [18]. Di Blasi et al. [17] used single-step, two-step, and three-step models to describe the kinetics of the conventional beech wood chars. The single-step model showed the worst fitting performance, especially for the conversion rate curves (deviations up to 18%), but the deviation of the two-step and three-step models was only 5.4 %. Table 1 summarizes extensive research on the multi-step model. As shown in Table 1, previous studies of the multi-step model have focused on devolatilization and oxidation but lacked research on gasification. It is also noted that previous work has sometimes unreasonably increased the number of steps of the multi-step model (related to the peaks and shoulders of the DTG curves [19]) in pursuit of better fitting performance.

We found that the gasification process exhibits a distinct devolatilization and gasification component, which fits the two-step model originally proposed by Di Blasi [17,20]. This suggests that the two-step model can theoretically provide a better description of the kinetics of fast pyrolyzed chars compared to the single-step model. Therefore, the current study attempts to compare VM, GM, RPM, ICM, and two-step (first step: VM; second step: ICM) parallel model based on gasification data of fast pyrolysis chars [4] to draw statistical conclusions.

2. Materials and methods

2.1. Samples and char preparation

The wood samples were collected, processed, and shaped into uniform cubic particles measuring 3*3*3 mm with a smooth surface. The data of char yield and proximate analysis are shown in Table S1. The results of proximate analysis, ultimate analysis, biomass components analysis, ash composition analysis, and other detailed information are provided in our previous work [4]. The chars were generated by fast pyrolysis of the wood particles using a single particle reactor (SPR). The hydrogen flame temperature inside the SPR was approximately 1523K, with a heating rate of around 200K/s. These conditions closely resembled those observed in industrial entrained flow reactors [31]. The reactor and the experimental procedures were comprehensively described elsewhere [31–33].

2.2. Gasification tests

The char particles were meticulously pulverized using a mortar and pestle. In this work, the thermogravimetric analyzer (TGA, Netzsch STA 449F1 Jupiter) was used to test the reaction kinetics of char powder in a CO₂ atmosphere. To avoid the effects of gas dispersion caused by the switching of gases, the experiments were conducted using a non-isothermal approach with a heating rate of 10 °C/min from 110 °C to 1100 °C. The gasification rate is ensured to be unaffected by external diffusion by setting the total gas flow rate at 100 mL/min. The sufficient reactant flow, moderate heating rate, and a small sample mass ensure the elimination of self-heating effects and limitations caused by mass transfer [20,34]. Duplicate tests showed good reproducibility. The maximum range of standard errors between the measured weight loss curves is always within 0.5 %.

Table 1

Kinetic parameters of the multi-step model. ("1 + 1" means one-step devolatilization and one-step oxidation; "parallel"/"sequential" means parallel/sequential reaction. Only the final temperature is shown in the temperature range because the initial temperature is not mentioned in the reference.)

Ref	Fuel	Multi-steps kinetic model	Activation energy(kJ/mol)		Atmosphere	Temperature	Charring condition
			Devolatilization	Oxidation		range (K)	
[21]	Beech char, fir char, spruce char	1 + 1(oxidation, parallel)	122.4–143.4	180.8–205.1	Air	600–800	800K, packed-bed
[17]	Beech char and Douglas fir char	1,1 + 1,2 + 1, (oxidation, parallel)	114.5–140	114.5–182.6	Air	500-850	800K, fluidized sand-bed
[20]	Beech wood char, fir wood char	1 + 1(oxidation, parallel)	125.1–142.6	186–207	Air	580-800	800K , packed-bed
[22]	4 secondary biomass chars (BTG, Dynamotive, Ensyn, Pyrovac)	3 + 1(oxidation, parallel)	84–118	163–211.6	Air	The final temperature is 873K.	5 K/min from ambient temperature up to 600 K and an isothermal section at 600 K for 1500s , TGA
[23]	Banana peel	2 + 2(oxidation, parallel)	78.4–87.4	107.6–193	Air	350–950	
[24]	Wheat Straw	5(devolatilization, parallel)	101.1–125.7		N ₂	400–773	
[25]	Beech wood	3(devolatilization, parallel)	146.7–148.6		Inert atmosphere	300-800	
[<mark>26</mark>]	4 hardwoods and 5 softwoods	5(devolatilization, parallel)	46–236		N ₂	423–723	
[27]	4 biomass fast pyrolysis oils (BTG, Dynamotive, Ensyn, Pyrovac)	8(devolatilization, parallel)	46.5–102		Air	The final temperature is 600K.	
[28]	Beech and Douglas fir	3 + 1(oxidation, sequential)	106–226	183	Air	400–873	
[29]	Intumescent laminate	3 + 1(oxidation, sequential)	83–140.1	182.2	Air	The final temperature is 873K.	
[30]	Rigid polyurethane foam	3(oxidation, sequential)		81–180	Air	The final temperature is	

2.3. Gasification kinetic models

The gasification reaction characteristics are described by the char conversion X, which is defined as Eq. (1):

$$X = \frac{m_0 - m_t}{m_0 - m_\infty}$$
(1)

where m_0 , m_t , and m_∞ are the initial mass, the mass of the char at a specific moment in time t, and the final ash residue mass.

Char gasification is a gas-solid non-catalytic heterogeneous reaction completely controlled by the chemical reaction step, and the overall reaction rate can be expressed as following Eq. (2):

$$\frac{dX}{dt} = k(T)f(X) \tag{2}$$

where k is the apparent gasification reaction rate constant, which is determined by temperature (*T*) and f(X), which explains the changes in physical or chemical properties resulting from the reaction. The apparent gasification reaction rate constant can be expressed by the Arrhenius equation as Eq. (3):

$$k = Ae^{-\frac{E}{RT}} \tag{3}$$

where *A* is the pre-exponential factor, *E* is the activation energy, and *R* is the conventional gas constant.

To assess the evolution of the sample reactivity with conversion, four single-step kinetic equations were used to describe the kinetic of the fast pyrolyzed char gasification, corresponding to VM, GM, RPM, and ICM.

The VM model is the simplest model, assuming that the reaction occurs uniformly with the volume of the char particle [4]. The GM model postulates that the initial reaction occurs on the external surface of grains, subsequently progressing inwardly [4]. The RPM model, which considers the effects of pore growth and coalescence during reaction simultaneously, typically provides better prediction and enables to show a peak for the reaction rate at conversion levels below 0.393 [4]. The ICM model is an empirical model that improves the GM and VM by introducing a second parameter n [16]. These four models provide various formulations for f(X), with their fundamental equations shown in the following Eqs. (4)–(7):

$$\frac{dX}{dt} = k_{VM}(1 - X) \tag{4}$$

(2) GM model

$$\frac{dX}{dt} = k_{GM} (1 - X)^{\frac{2}{3}}$$
(5)

(3) RPM model

$$\frac{dX}{dt} = k_{RPM}(1-X)\sqrt{1-\psi\ln(1-X)}$$
(6)

(4) ICM model

$$\frac{dX}{dt} = k_{ICM} (1 - X)^n \tag{7}$$

where ψ and *n* are structural parameter related to the internal pore structure and reaction order, respectively.

The samples were heated at a consistent rate, a, using the non-

isothermal method in a thermogravimetric analyzer. The relationship between, T, and heating time, t, can be expressed by Eq. (8):

$$T = T_0 + at \tag{8}$$

After a series of transformation, the corresponding conversions of the above four kinetic equations were expressed as follows in Eqs. 9–12:

$$VM: X = 1 - \exp\left(-\frac{RT^2}{aE}Ae^{-\frac{E}{RT}}\right)$$
(9)

$$GM: X = 1 - \left(1 - \frac{RT^2}{3aE}Ae^{-\frac{E}{RT}}\right)^3$$
(10)

$$RPM: X = 1 - \exp\left\{-\frac{RT^2}{aE}Ae^{-\frac{E}{RT}}\left[1 + \frac{\Psi}{4}\left(\frac{RT^2}{aE}\right)Ae^{-\frac{E}{RT}}\right]\right\}$$
(11)

$$ICM: X = 1 - \left[1 - \frac{(1-n)RT^2A}{aE} \exp\left(-\frac{E}{RT}\right)\right]^{\frac{1}{1-n}}$$
(12)

The thermogravimetric curves, as depicted in Fig. 1, exhibit two distinct stages: devolatilization and gasification. Therefore, the two-step kinetic model, which consists of two parallel reactions for char devolatilization and gasification, was used to provide better description of the fast pyrolyzed char gasification kinetics.



Where V_i (i = 1,2) are the lumped volatile products.

From the chemical point of view, R1 is essentially associated with char devolatilization, and R2 is associated with char gasification (peak in the rate curve). A parallel reaction (instead of a sequential reaction) mechanism has been chosen because it appears to be more flexible to take into account the overlap between the reaction zones. The reaction rates present the usual Arrhenius dependence on temperature (E_1 , E_2 are the activation energies, and A_1 , A_2 the pre-exponential factors), and a linear (devolatilization) or power-law (gasification, n reaction order) on the solid mass fraction (Y_1 and Y_2) [22]. The latter treatment takes into account the evolution of the pore surface area during conversion [22]. Their equations are listed as the following Eq. (13).

$$\frac{lY_1}{dt} = -A_1 \exp\left(-\frac{E_1}{RT}\right) Y_1, Y_1(0) = \alpha$$
(13a)

$$\frac{dY_2}{dt} = -A_2 \exp\left(-\frac{E_2}{RT}\right) Y_2^n, Y_2(0) = 1 - \alpha$$
(13b)

$$Y = 1 - X \tag{13c}$$

Where α is the mass fraction of volatiles released during devolatilization.

Furthermore, the ratio of *E* to *R* (*E*/*R*) and *A* were obtained by the nonlinear regression method between the experimental data and the kinetic models. The numerical procedure is implemented within the framework of Python. The deviation (DEV) between the experimental and fitted curves was calculated using Eqs. 14 and 15 to assess the performance of the kinetic models.

$$\text{DEV}(X)(\%) = 100 \times \frac{\left(\sum_{i=1}^{N} \left(X_{cal,i} - X_{exp,i}\right)^2 / N\right)^{\frac{1}{2}}}{\max X_{exp}}$$
(14)



Fig. 1. TG curves (a) and DTG curves (b) of fast pyrolyzed chars generated from various wood varieties. The TGA experiment was conducted in a CO₂ environment, with the temperature ranging from 580 to 1273 K and a heating rate of 10 K/min.

$$\text{DEV}\left(\frac{dX}{dt}\right)(\%) = 100 \times \frac{\left(\sum_{i=1}^{N} \left(\left(\frac{dX}{dt}\right)_{cal,i} - \left(\frac{dX}{dt}\right)_{exp,i}\right)^2 / N\right)^{\frac{1}{2}}}{\max\left(\frac{dX}{dt}\right)_{exp}}$$
(15)

where i is the experimental (exp) or the calculated (cal) variable at the time t; N represents the number of experimental points. The term 'max' indicates the maximum value.

3. Results and discussion

3.1. Non-isothermal gasification curves

The measured global weight loss curves of the fast pyrolyzed chars were plotted during the linear non-isothermal gasification. However, due to the strange secondary weight loss behavior in five of the samples compared to the others, which has only been reported in DDGS [35,36] and banana peel [23]. There is no clear explanation for this, which requires further analysis, which is beyond the scope of this study.

Fig. 1 shows the non-isothermal conversion and DTG curves for different wood varieties. All the observed trends are qualitatively similar. The TG curves in Fig. 1a exhibit two distinct main regions (Y \approx 1–0.9 for devolatilization and Y \approx 0.9–0 for gasification), which are referenced to the average value of α from the two-step model in Table S2. It can be observed that the mass fraction of the sample undergoes a slow decline (with near-linear change) from the initial temperature to T₁₀ (approximately 900K–1016K), followed by a rapid decline (with exponential change). Then the conversion curve reaches a flattened part and the reaction rate drops to 0. The fast pyrolyzed chars generated from different types of wood exhibit varying gasification reactivities, with T₅₀ ranging widely between 1016 and 1184 K. However, qualitatively speaking, all the curves have the same shape, which means that they are suitable to be described by the same kinetic model.

The |DDTG| curves (shown in Fig. 2) help to determine the appropriate number of steps for the multi-step model of the fast pyrolyzed chars. It is generally believed that a complex reaction consists of several apparent sub-reactions, which are denoted by several peaks and shoulders on the overall DTG curves [19]. Most |DDTG| curves in Fig. 2 show one local minimum, which represents at least one reaction step. When combined with the TG curves, the gasification process exhibits a distinct devolatilization and gasification component, which fits well with the two-step model proposed originally by Di Blasi [17,20]. Given that the char produced in the dynamic flame environment (Sect.2.1) was not sufficiently soaked at high temperatures, it seems reasonable to assume that some macro-components may not have been fully decomposed. The above discussion suggests that, in theory, the two-step model can provide a better description of the kinetics of fast pyrolyzed chars compared to the single-step model. The following attempts to systematically compare different single-step models and two-step models using the data obtained from the gasification of fast pyrolyzed chars.

3.2. Kinetic analysis

The present study examines four single-step kinetic models (VM, GM, RPM, and ICM) and one two-step kinetic model to analyze char reactivity variation in CO_2 gasification experiment using the gasification data of fast pyrolyzed chars. It is noteworthy that a similar fitting trend was observed among all fast pyrolyzed wood chars. To make better comparisons from the perspective of model fitting performance, only the figures for the best (wood 34), worst (wood 40), and average (wood 38) fits are shown.

3.2.1. Performance of VM, GM, RPM, and ICM models

VM, GM, and RPM are the three most typical single-step kinetic models, and most previous studies have concluded that RPM has the best fitting performance because it can establish the correlation between reaction behavior and internal pore structure and enable to predict a peak for the reaction rate observed in some experiments [4]. However, the gasification reactivity of most chars studied increased with conversion or reached a peak in the high conversion range, and RPM fails to explain these peculiarities [8]. Undoubtedly, RPM falls short of being an optimal model; subsequent studies have demonstrated that ICM describes the gasification curve of char under a CO₂ atmosphere better than RPM [15,16]. To derive statistically significant conclusions, the data of fast pyrolyzed wood chars is used to compare these four models.

Fig. 3a–d shows the experimental and predicted curves of mass fraction and conversion rate for three representative wood chars to VM, GM, RPM, and ICM. The performances of VM, GM, RPM, and ICM are quite similar overall. The mass fraction above Y = 0.7 and below Y = 0.3



Fig. 2. Experimental curves of |DDTG| of fast pyrolyzed char generated from (a)woods 1–45, (b)woods 1–22, (c)woods 23–45, and (d)woods 34,38, and 40.

cannot be predicted well by all of them, and they tend to overpredict the mass fractions in these ranges, independent of the feedstock effect. The sharp peak exhibited in the experimental curve is not accurately captured by any of the four single-step models. This is particularly evident when the peaks are sharper. It is worth noting that the ICM can fit the sharper peak better compared to the other three models. When plotted against conversion, these four models are also unable to describe the maximum conversion rate in the experimental curve. The initial acceleration can be attributed to the increasing temperature used in the non-isothermal method, while the subsequent deceleration is a result of the reduction of residue mass available for the reaction.

For a better quantitative comparison, Table 2 lists the deviation and the regression coefficients (R^2) for three selected samples predicted by VM, GM, RPM, and ICM. As shown in Table 2, the RPM and ICM demonstrate slightly better fitting performance compared to the VM and GM, which can be explained by the increase in the variables of the RPM and ICM model equations. In addition, VM has the worst fitting performance among them. As illustrated in the supplemental material (Tables S4 and S5), ICM outperformed the majority of wood types and even outperformed all of the wood types in terms of DEV(X). As shown in

Table 3, it can be found that on the whole, ICM has a better performance compared to RPM. The average DEV(X) of ICM is 4.64 %, which is 0.2 % lower than that of RPM. Furthermore, the average DEV(dX/dt) of ICM is 6.07 %, which shows a 15.34 % improvement compared to RPM. Moreover, the performance of RPM and GM is similar overall. When assessing the performance of various models, including VM, GM, and RPM in describing char CO₂ gasification, some authors have reached similar conclusions [2,37]. The ICM improved the GM with a second parameter (n), which can be simultaneously adjusted with the rate coefficient [16]. The superior performance of ICM compared to RPM can be explained. The performance varied among different single-step models; however, overall it was still poor, particularly in terms of devolatilization fitting. Therefore, it is necessary to study the two-step model.

3.2.2. Performance of two-step model

The experimental data appear to be better described by the multistage reaction mechanism, where each reaction considers the kinetics of several regions or pseudo-components in the conversion curve [38]. As shown, the TG curves exhibit two distinct main regions ($Y \approx 1-0.9$ for



Fig. 3. Comparison between predicted and measured curves of mass fraction (left), conversion rate (middle) versus temperature, and conversion rate versus conversion (right) for three representative wood chars: a VM; b GM; c RPM; d ICM.

Table 2

Estimated kinetic parameters, adjustable parameters, deviation, and regression coefficients (R^2) of four single-step models (VM, GM, RPM, and ICM) for three representative wood varieties.

Sample number	34	38	40
VM			
E(kJ/mol)	226.5	224.4	235.6
$A(s^{-1})$	1.32E+09	1.33E+09	1.34E + 09
DEV(X)(%)	3.92	5.20	6.27
DEV(dX/dt)(%)	7.01	8.74	10.54
$R^2(X)$	0.9906	0.9841	0.9703
$R^2(dX/dt)$	0.9460	0.8504	0.5064
GM			
E(kJ/mol)	208	206.1	216.3
$A(s^{-1})$	1.32E+09	1.33E+09	1.34E+09
DEV(X)(%)	3.98	5.08	5.92
DEV(dX/dt)(%)	7.17	6.67	9.04
$R^2(X)$	0.9904	0.9850	0.9741
$R^2(dX/dt)$	0.9499	0.9230	0.6800
RPM			
E(kJ/mol)	194.3	192.2	202.1
$A(s^{-1})$	3.02E+08	2.74E+08	2.21E + 08
Ψ	0.26	0.65	2.85
DEV(X)(%)	3.35	4.81	5.94
DEV(dX/dt)(%)	5.32	7.58	8.81
$R^2(X)$	0.9929	0.9863	0.9738
$R^2(dX/dt)$	0.9650	0.8818	0.7009
ICM			
E(kJ/mol)	193.3	191.3	201
$A(s^{-1})$	2.84E+08	2.64E+08	2.01E + 08
Ν	0.95	0.82	0.26
DEV(X)(%)	3.29	4.73	5.65
DEV(dX/dt)(%)	6.01	7.82	6.57
$R^2(X)$	0.9931	0.9866	0.9768
$R^2(dX/dt)$	0.9576	0.8760	0.8653

Table 3

Deviation and the regression coefficients (R^2) between the experimental and models (VM, GM, RPM, and ICM) predicted conversion and gasification rate data.

	Average	Max	Min
VM			
DEV(X)(%)	5.17	6.48	3.92
DEV(dX/dt)(%)	9.04	10.63	7.01
$R^2(X)$	0.9815	0.9906	0.9536
$R^2(dX/dt)$	0.7680	0.9460	0.5064
GM			
DEV(X)(%)	4.89	6.28	3.83
DEV(dX/dt)(%)	7.07	9.37	5.15
$R^2(X)$	0.9836	0.9913	0.9564
$R^2(dX/dt)$	0.8716	0.9556	0.6800
RPM			
DEV(X)(%)	4.84	6.12	3.35
DEV(dX/dt)(%)	7.17	9.72	5.27
$R^2(X)$	0.9839	0.9929	0.9588
$R^2(dX/dt)$	0.8677	0.9650	0.7009
ICM			
DEV(X)(%)	4.64	6.01	3.29
DEV(dX/dt)(%)	6.07	9.50	4.53
$R^2(X)$	0.9851	0.9931	0.9622
$R^2(dX/dt)$	0.9149	0.9609	1.79 0.7879

devolatilization and Y \approx 0.9–0 for gasification). These two main regions are more distinguished than in the research of Di Blasi [20]. The gasification process fits well with the two-step model originally proposed by Di Blasi [17,20]. Therefore, the two-step model shows potential for a better description of the kinetics of the fast pyrolyzed chars.

Fig. 4 shows the measured and predicted global weight loss curves for three representative wood chars to the two-step model. Compared to the single-step model, the two-step model can predict the mass fraction well; the two-step model captures the sharp peak shown in the experimental curve better, and even the sharp peak of wood 34 can be captured completely. When plotted against conversion, the two-step model performs better in describing the maximum experimental rate. The ICM, representing the single-step model, is compared with the twostep model in Fig. 5 for better comparison. As shown, the single-step model cannot fit the devolatilization region well. Because it needs to fit both the devolatilization region and the gasification region simultaneously, the fitting of the single-step model is influenced by the devolatilization region, thereby affecting its accuracy in fitting the gasification region. Conversely, the two-step model circumvents these issues and enables a more precise fit for devolatilization region and the gasification region by using VM model (the VM model is generally considered to be more suitable for fitting the devolatilization region [22].) to fit the devolatilization region and ICM model (the ICM model is generally considered to be more suitable for fitting the subsequent conversion region [22].) to fit the gasification region, respectively. In addition, the whole DTG curve tended to move toward the upper right, thereby implying the two-step model performs better when it exhibits a maximum value in the high conversion rate range.

Table 4 lists the deviation and the regression coefficients (R^2) for three representative wood chars predicted by the two-step model. As demonstrated in Table 4, the two-step model shows better fitting performance compared to the single-step model due to an increase in the number of equations. As expected, shown in the supplemental material (Tables S4 and S5), the two-step model outperformed the majority of wood types, and even substantially outperformed all of the wood types in terms of DEV(X). As shown in Table 5, it can be found that on the whole, the two-step model has a better performance compared to singlestep models. The two-step model's average DEV(X) is 0.95 %, which shows an 80 % improvement compared to ICM. Furthermore, the average DEV(dX/dt) of the two-step model is 5.47 %, which is 0.6 % less than that of ICM. It is worth noting that although the two-step model shows significant improvement over the single-step model in terms of DEV(X) value, there is not such a substantial improvement in DEV(dX/dXdt) value. Additionally, the DEV(dX/dt) value is significantly higher than the DEV(X) value, which is consistent with the findings reported in the literature [39,40].

3.2.3. Estimation kinetic coefficient

Table S2-S5 provide full data on the fitted kinetic parameters of fast pyrolyzed chars in CO₂ gasification estimated by five models (VM, GM, RPM, ICM, and two-step), together with R^2 and the mean DEV values. The performance of the model is typically evaluated by either R^2 or some form of deviation index, such as the mean DEV values utilized in this study. It should be noted that DEV values are significantly lower than R^2 values. In addition, DEV(X) is generally lower than DEV(dX/dt).

The results in Table S2 show that ICM performs slightly better than the other single-step models in terms of the feedstock-average regression coefficient $R^2(X)$ (0.9851 for ICM compared to 0.9815, 0.9836, and 0.9839 for the others). Additionally, ICM has a significant advantage in terms of the average regression coefficients of the feedstock-average regression coefficient $R^2(dX/dt)$ (0.9149 for ICM compared to 0.7680, 0.8716, and 0.8677 for the others), confirming its superior predictive accuracy. The two-step model, as expected, exhibited the best performance, with average regression coefficients R^2 (X) and R^2 (dX/dt) of 0.9989 and 0.9372, respectively, which are significantly higher than those of the single-step model. The minimum regression coefficients between the experimental and the model predicted conversion are 0.9536 for VM, 0.9564 for GM, 0.9588 for RPM, 0.9622 for ICM, and 0.9866 for the two-step model. The high regression coefficient confirms the correctness of the model fitting and the estimated kinetic parameter [6,41,42].

Table 6 indicates the statistics of the *E* and *A* fitted by four single-step models (VM, GM, RPM, and ICM) and a two-step model for fast pyrolyzed wood chars. The average *E* values for VM, GM, RPM, and ICM are 228.2 kJ/mol, 209.1 kJ/mol, 195.8 kJ/mol, and 194.7 kJ/mol respectively. The ranges of *E* values for VM, GM, RPM, and ICM are



Fig. 4. Comparison between measured and the two-step model predicted curves of mass fraction (a), conversion rate (b) versus temperature, and conversion rate versus conversion (c) for three representative wood chars.

210.4–247.5 kJ/mol, 193.1–219.9 kJ/mol, 185.7–211.9 kJ/mol, and 185.7–211.2 kJ/mol respectively. The feedstock-average activation energies of E_1 and E_2 in the two-step model are 66.8 and 202.4 kJ/mol, respectively. The values range from 54.8 to 76.2 kJ/mol and from 191.4 to 211.3 kJ/mol. In this study, the results obtained are undeniably reliant on the kinetic models used. The trend of obtaining higher E values with VM and lower E values with RPM is consistent with the literature [43,44]. Based on the evaluation of model prediction accuracy, it remains uncertain which value is more suitable for describing the CO₂ gasification of fast pyrolyzed char.

Currently, the literature has reported a wide range of activation energies for biomass char in CO_2 gasification. In the review conducted by Di Blasi [45], a range of activation energies was reported, with values ranging from 88 to 250 kJ/mol. Notably, a significant portion of these values clustered around the range of 200–250 kJ/mol. A recent review from 2014 to 2020 [46] also found a similar range (100–247 kJ/mol) for CO_2 gasification of biomass char. The activation energies predicted by the single-step models and the E_2 of the two-step model in this study fall within reported values. Nevertheless, it is noteworthy that the values obtained by VM all fall within the reasonable range(200-250 kJ/mol) indicated by Di Blasi, and the values obtained by GM and the E_2 of the two-step model are also very close to this range. In addition, the predicted activation energies (E_1) of the two-step model all fall within the normal scope, and its maximum value does not exceed 88 kJ/mol, which proves the correctness of the two-step model in this study. The wide range of reported E values may be due to various factors, including biomass properties, pyrolysis, and gasification conditions (temperature range and temperature-programmed used, gasifying agent concentration), or reactor types. Furthermore, the choice of kinetic model and analysis method can significantly impact the determination of kinetic parameters [46]. Therefore, this study utilized the same experimental equipment to prepare the char and deduce the kinetic parameters for different wood types under consistent experimental and model-fitting conditions. According to Tables 6 and it appears that the reactive



Fig. 5. Comparison between measured, ICM, and the two-step model predicted curves of mass fraction (left), conversion rate (middle) versus temperature, and conversion rate versus conversion (right) for three representative wood chars: **a** wood 34; **b** wood 38; **c** wood 40.

Table 4
Estimated kinetic parameters, adjustable parameters, deviation, and regression
coefficients (R^2) of the two-step model for three representative wood chars.

Sample number	34	38	40
Two-step model			
$E_1(kJ/mol)$	75.4	54.8	59.2
$A_{I}(s^{-1})$	5.46E+02	4.78E+01	7.30E+01
$E_2(kJ/mol)$	200.1	200.3	221.3
$A_2(s^{-1})$	4.64E+08	5.25E+08	1.56E + 09
Ν	0.66	0.44	0.05
A	0.08	0.09	0.10
DEV(X)(%)	0.47	0.93	1.70
DEV(dX/dt)(%)	3.00	5.58	6.50
$R^2(X)$	0.9998	0.9994	0.9866
$R^2(dX/dt)$	0.9966	0.9746	0.8760

Table 5

Deviation and the regression coefficients (R^2) between the experimental and the two-step model predicted conversion and gasification rate data.

	Average	Max	Min
Two-step model			
DEV(X)(%)	0.95	1.70	0.47
DEV(dX/dt)(%)	5.47	7.52	3.00
$R^2(X)$	0.9989	0.9998	0.9866
$R^2(dX/dt)$	0.9372	0.9966	0.8664

behavior of the biomass was impacted by its inherent characteristics.

4. Conclusion

Kinetic analysis plays a critical role in the gasification process. The

Table 6

The maximum, minimum, and average estimated kinetic parameters of wood char samples fitted by four single-step models (VM, GM, RPM, and ICM) and a two-step model.

	Average	Max	Min
VM			
E(kJ/mol)	228.2	247.5	210.4
$A(s^{-1})$	1.33E+09	1.35E+09	1.30E + 09
GM			
E(kJ/mol)	209.1	219.9	193.1
$A(s^{-1})$	1.29E+09	1.34E+09	5.77E+08
RPM			
E(kJ/mol)	195.8	211.9	185.7
$A(s^{-1})$	2.42E+08	4.13E+08	1.95E+08
ICM			
E(kJ/mol)	194.7	211.2	185.7
$A(s^{-1})$	2.31E+08	4.73E+08	1.89E + 08
Two-step model			
$E_1(kJ/mol)$	66.8	76.2	54.8
$A_1(s^{-1})$	7.63E+02	4.68E+03	3.10E + 01
E ₂ (kJ/mol)	202.4	221.3	191.4
$A_2(s^{-1})$	5.29E+08	1.59E+09	6.32E+07

kinetics of CO_2 gasification for various wood chars, which were prepared in a single particle hydrogen flame reactor, were studied using a non-isothermal method in a thermogravimetric analyzer. Four singlestep models and one two-step (first step: VM; second step: ICM) parallel model were used to calculate the kinetic parameters. The main conclusions are summarized below.

- (1) The char gasification process exhibits a distinct devolatilization and gasification component, which fits well with two-step model proposed originally by Di Blasi [17,20].
- (2) Compared to the ICM with the best fitting performing among single-step models, the two-step model's average DEV(X) is 0.95 %, which shows an 80 % improvement compared to ICM (DEV (X) = 4.64 %). The average DEV(dX/dt) of the two-step model is 5.47 %, which is 0.6 % less than that of ICM. The minimum regression coefficient between the experimental and the model predicted conversion is 0.9866 for the two-step model. The high regression coefficient confirms the correctness of the model fitting and the estimated kinetic parameter.
- (3) The predicted activation energy (devolatilization:54.8–76.2 kJ/mol; gasification:185.7–247.5 kJ/mol) falls within a reasonable range, which is consistent with the findings reported in the literature.

Author contribution

Jianfeng Cai: investigation, methodology, data curation, writing – original draft. Zhimin Lu: conceptualization, funding acquisition, supervision, writing – review and editing. Jinzheng Chen: laboratory analysis and writing – review and editing. Jing Chen: investigation. Zhengyan Bao: writing – review and editing. Shengyuan Guo: writing – review and editing – review and

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.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (52276190) and the Fundamental Research Funds for the Central Universities (2022ZFJH004).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.joei.2023.101450.

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