Misuse of pre-exponential factor in the kinetic and thermodynamic studies using thermogravimetric analysis and its implications

Imtiaz Ali

Department of Chemical and Materials Engineering, King Abdulaziz University, Rabigh, Saudi Arabia

Keywords: Second derivative method; Pre-exponential factor; Model-free methods; Isoconversional methods

E-mail address: imtiaz_che@hotmail.com

Abstract

This paper describes the misuse of Arrhenius pre-exponential factor in the kinetic and thermodynamic studies using thermogravimetry. Standard test method (ASTM E698) has been used recently by many researchers to calculate the pre-exponential factor. ASTM E698 is reserved for differential scanning calorimetry (DSC) and impose many restrictions which have being overlooked by many recently. The obtained pre-exponential factors have been used to describe the thermodynamic behavior during the course of thermal conversions. The objective of this paper is to inform the readers that the pre-exponential factor obtained from the restricted equation can mislead and generate some false thermodynamic data.

Theoretical Background

ASTM E698-16 describes the standard method to evaluate the kinetic parameters from Flynn/Wall/Ozawa method using Differential Scanning Calorimeter (DSC)(ASTM International, 2016). It is mentioned in the limitation section of the standard that this method can not be used for simultaneous and consecutive reaction steps. Besides this there are many other assumptions which are made to reach the final form of the equation and should be taken care off. To explain the limitations, let's consider the general rate equation with reaction model $f(\alpha)$ as

$$\frac{d\alpha}{dt} = \mathrm{A} \cdot \exp\left(-\frac{E_\alpha}{RT}\right) \cdot f(\alpha) \tag{1}$$

Differentiating Eq. 1 with respect to time while considering A as constant

$$\frac{d^2\alpha}{dt^2} = \mathrm{A} \cdot \frac{\mathrm{d}}{\mathrm{dt}}\left[\exp\left(-\frac{E_\alpha}{RT}\right) \cdot f(\alpha)\right] \tag{2}$$

Eq 2 can be expanded further as

$$\frac{d^2\alpha}{dt^2} = \mathrm{A} \cdot \left\{\exp\left(-\frac{E_\alpha}{RT}\right) \cdot \frac{\mathrm{d}}{\mathrm{dt}}[f(\alpha)] + f(\alpha) \cdot \frac{\mathrm{d}}{\mathrm{dt}}\left[\exp\left(-\frac{E_\alpha}{RT}\right)\right]\right\} \tag{3}$$

$\frac{\mathrm{d}}{\mathrm{dt}}[f(\alpha)] = \frac{\mathrm{d}}{\mathrm{d}\alpha}[f(\alpha)] \cdot \frac{d\alpha}{dt} = f'(\alpha) \cdot \frac{d\alpha}{dt}$ can be introduced in the equation to get

$$\frac{d^2\alpha}{dt^2} = \mathrm{A} \cdot \exp\left(-\frac{E_\alpha}{RT}\right) \cdot f'(\alpha) \cdot \frac{d\alpha}{dt} + \mathrm{A} \cdot f(\alpha) \cdot \exp\left(-\frac{E_\alpha}{RT}\right) \cdot \frac{E_\alpha}{RT^2}\frac{\mathrm{dT}}{\mathrm{dt}} \tag{4}$$

For constant heating rate $\beta = \frac{dT}{dt}$ experiment using Eq. 1, one obtains

$$\frac{d^2\alpha}{dt^2} = \left[\mathrm{A} \cdot \exp\left(-\frac{E_\alpha}{RT}\right) \cdot f'(\alpha) + \frac{\beta E_\alpha}{\mathrm{RT}^2}\right]\frac{d\alpha}{dt} \tag{5}$$

35 The reaction model $f(\alpha)$ and corresponding first derivative $f'(\alpha)$ can be used from Table 1.

36 Table 1 Common reaction model and corresponding derivatives

Reaction Model	**Symbol**	$\boldsymbol{f(\alpha)}$	$\boldsymbol{f'(\alpha)}$
Power law $\left(n = \frac{1}{4}\right)$	$P_{\frac{1}{4}}$	$4\alpha^{\frac{3}{4}}$	$3\alpha^{-\frac{1}{4}}$
Power law $\left(n = \frac{1}{3}\right)$	$P_{\frac{1}{3}}$	$3\alpha^{\frac{2}{3}}$	$2\alpha^{-\frac{1}{3}}$
Power law $\left(n = \frac{1}{2}\right)$	$P_{\frac{1}{2}}$	$2\alpha^{\frac{1}{2}}$	$\alpha^{-\frac{1}{2}}$
Power law $\left(n = \frac{3}{2}\right)$	$P_{\frac{3}{2}}$	$\frac{2}{3}\alpha^{-\frac{1}{2}}$	$-\frac{1}{3}\alpha^{-\frac{3}{2}}$
One-dimensional diffusion (Parabola law)	D_1	$\frac{1}{2}\alpha^{-1}$	$-\frac{1}{2}\alpha^{-2}$
Mampel $(n = 1)$	F_1	$1-\alpha$	-1
Mampel (nth order)	F_n	$(1-\alpha)^n$	$-n(1-\alpha)^{n-1}$
Avrami-Erofeev $(n = 4)$	A_4	$4(1-\alpha)[-\ln(1-\alpha)]^{\frac{3}{4}}$	$[4\ln(1-\alpha)+3][-\ln(1-\alpha)]^{-\frac{1}{4}}$
Avrami-Erofeev $(n = 3)$	A_3	$3(1-\alpha)[-\ln(1-\alpha)]^{\frac{2}{3}}$	$-[3\ln(1-\alpha)+2][\ln(1-\alpha)]^{-\frac{1}{3}}$

Avrami-Erofeev ($n = 2$)	A_2	$2(1-\alpha)[-\ln(1-\alpha)]^{\frac{1}{2}}$	$[2\ln(1-\alpha)+1][-\ln(1-\alpha)]^{-\frac{1}{2}}$
Three-dimensional diffusion (Jander model)	D_3	$\frac{3}{2}(1-\alpha)^{\frac{2}{3}}\left[1-(1-\alpha)^{\frac{1}{3}}\right]^{-1}$	$\frac{1}{2}\left[(1-\alpha)^{\frac{1}{3}}-2\right]\left[(1-\alpha)^{\frac{1}{3}}-1\right]^{-2}(1-\alpha)^{-\frac{1}{3}}$
Contracting sphere	R_3	$3(1-\alpha)^{\frac{2}{3}}$	$-2(1-\alpha)^{-\frac{1}{3}}$
Contracting cylinder	R_2	$2(1-\alpha)^{\frac{1}{2}}$	$-(1-\alpha)^{-\frac{1}{2}}$
Two-dimensional diffusion (Valensi model)	D_2	$[-\ln(1-\alpha)]^{-1}$	$[-\ln(1-\alpha)]^{-2}(\alpha-1)^{-1}$
SB model	SB	$\alpha^m(1-\alpha)^n[-\ln(1-\alpha)]^p$	$\frac{[-\ln(1-\alpha)]^p(1-\alpha)^n\alpha^{m-1}\{[(n+m)\ln(1-\alpha)+p]\alpha-m\ln(1-\alpha)\}}{(\alpha-1)\ln(1-\alpha)}$

37

38 At peak-maximum temperature $T = T_m$, $\alpha = \alpha_m$ and $\frac{d^2\alpha}{dt^2} = 0$

$$\mathrm{A}\cdot\exp\left(-\frac{E_a}{RT_m}\right)\cdot f'(\alpha_m)+\frac{\beta E_a}{\mathrm{RT_m^2}}=0 \qquad (6)$$

39 Rearranging equation 6, yields (Vyazovkin et al., 2011)

$$\mathrm{A} = -\frac{\beta E_a}{\mathrm{RT_m^2} f'(\alpha_m)} \exp\left(\frac{E_a}{RT_m}\right) \tag{7}$$

Now for a first order reaction $f(\alpha) = 1 - \alpha$ and $f'(\alpha) = -1$

$$\mathrm{A} = \frac{\beta E_a}{\mathrm{RT_m^2}} \exp\left(\frac{E_a}{RT_m}\right) \tag{8}$$

This equation is exactly the same as Eq. 3 of ASTM E698-16. The widespread use of this method is due to the fact that pre-exponential factor is obtained directly from activation energy. It is clear from the derivation that the final form of the equation is based on certain assumptions which are as follows

1. A is constant
2. E_a is constant
3. $f(\alpha) = 1 - \alpha$, reaction follows 1st order kinetics
4. $T = T_m$, iterating that the DTG contains single peak for a specific β

Activation energy can be obtained if Eq. 4 is transformed at peak-maximum temperature taking $\frac{d^2\alpha}{dt^2} = 0$ as

$$f'(\alpha_m) \cdot \left.\frac{d\alpha}{dt}\right|_m = -f(\alpha_m) \cdot \frac{E_a}{RT_m^2} \cdot \beta \tag{9}$$

Rearranging Eq. 9, one can get

$$E_a = -\frac{RT_m^2 \cdot f'(\alpha_m)}{\beta \cdot f(\alpha_m)} \cdot \left.\frac{d\alpha}{dt}\right|_m \tag{10}$$

For a first order reaction

$$E_a = \frac{RT_m^2}{\beta(1-\alpha_m)} \cdot \left.\frac{d\alpha}{dt}\right|_m \tag{11}$$

E_a will be obtained for a peak-maximum conversion rate $\left.\frac{d\alpha}{dt}\right|_m$ for all the limitations mentioned above. Friedman obtained similar expression and mentioned it as second derivative method (Friedman, 1964).

Natural logarithm of Eq. 6 yields Kissinger's equation which is valid for a single peak, constant A and constant E_a for any reaction model

$$\ln\left(\frac{\beta}{\mathrm{T_m^2}}\right) = \ln\left[\frac{-\mathrm{AR}f'(\alpha_m)}{E_a}\right] - \frac{E_a}{R\mathrm{T_m}} \tag{12}$$

Taking 1st order kinetics into consideration, Eq. 9 takes the widely used form of Kissinger's equation (Kissinger, 1957)

$$\ln\left(\frac{\beta}{\mathrm{T_m^2}}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{R\mathrm{T_m}} \tag{13}$$

This equation has been used for the determination of E_a from the slope of the regression line fitted on $\ln\left(\frac{\beta}{\mathrm{T_m^2}}\right)$ vs inverse $\mathrm{T_m}$ plot. Eq. 13 assumes the same limitations for the calculation of E_a as does Eq. 8 for the estimation of A.

Discussions

(Kim et al., 2010) estimated pre-exponential factor from Eq. 8 using thermogravimetric conversion data, it seems that the authors referred ASTM standard D 698 mistakenly instead of E 698. They used the equation without specifying reaction model, moreover the activation energy of their samples varied greatly with conversion. The criteria for the use of

this equation was therefore not fulfilled. Although it was a key mistake but they deduced a single A value for each one of their samples. The real problem arose when (Maia and de Morais, 2016) used this equation and varied the peak temperature (T_m) in their calculation (cf. Table 2). Instead of obtaining a single value of A corresponding to T_m, they obtained evolution of A with conversion. During the pyrolytic conversion of red pepper waste, the variation of E_a was significant moreover reaction order was not specified or evaluated.

Table 2 Peak maximum temperature used by (Maia and de Morais, 2016)*

Conversion	$T_1, (K)$ 5 °C/min	$\boldsymbol{T_2, (K)}$ **7.5 °C/min**	$T_3, (K)$ 10 °C/min	$E_a, \left(\frac{kJ}{mol}\right)$	$\boldsymbol{T_m, (K)}$ **From eq. 8**	$\boldsymbol{T_i = \frac{E_a - \Delta H}{R}, (K)}$
0.10	460.13	**463.17**	471.62	97.04	**409.96**	**465.48**
0.15	491.28	**496.79**	499.52	123.88	**446.97**	**497.96**
0.20	508.40	**515.20**	519.41	107.99	**455.47**	**517.20**
0.25	524.68	**533.32**	537.44	108.48	**468.87**	**534.04**
0.30	536.83	**545.75**	551.59	96.93	**473.00**	**547.27**
0.35	551.02	**559.93**	565.54	97.16	**483.62**	**560.50**
0.40	562.83	**571.32**	578.38	96.35	**491.73**	**571.33**
0.45	575.82	**583.04**	591.93	79.31	**489.29**	**588.16**
0.50	590.26	**601.48**	613.07	147.25	**542.84**	**606.21**
0.55	617.81	**627.64**	644.39	47.83	**477.16**	**637.48**
0.60	648.46	**662.96**	676.26	71.77	**539.65**	**673.56**
0.65	675.65	**689.04**	700.84	92.17	**577.29**	**695.21**
0.70	690.78	**704.29**	712.76	104.51	**596.37**	**706.04**
0.75	699.39	**711.74**	722.21	110.67	**607.66**	**714.46**
0.80	704.86	**720.17**	728.20	67.73	**564.83**	**721.67**
0.85	710.24	**724.96**	735.38	101.33	**609.54**	**728.89**

0.90	717.59	**731.53**	740.77	29.49	**470.04**	**736.11**

* Permission to reuse the data has been obtained under license no. “4330930581283” dated April 16, 2018

In following works, some of the authors kept T_m constant in Eq. 8 and obtained the evolution of A as a function of E_a (Yuan et al., 2017; Müsellim et al., 2018; Barbanera et al., 2018; Mallick et al., 2018; Özsin and Pütün, 2018; Rasool et al., 2018). Taking for example the recent work of (Mallick et al., 2018) on rice husk and saw-dust (RH+SD) blend pyrolysis. The variation of E_a was insignificant, hence peak- maximum T_m= 351 ^{o}C and E_a =158.12 kJ/mol can be used to calculate A from Eq. 8 and corresponding thermodynamics parameters can be evaluated thereafter. *Table 3* summarizes the kinetic and thermodynamic parameters for the pyrolysis of RH+SD blend at 10 ^{o}C /min using Ea from Friedman method.

Table 3 Comparison of kinetic and thermodynamic for rice husk and saw-dust (RH+SD) blend pyrolysis at 10 ^{o}C /min using activation energy from Friedman method at any instant and peak-maximum (Mallick et al., 2018)*

Measurement	Mechanism	$\alpha,(-)$	$E_a,\left(\frac{kJ}{mol}\right)$	$T,(K)$	$A,(s^{-1})$	$\Delta H,\left(\frac{kJ}{mol}\right)$	$\Delta G,\left(\frac{kJ}{mol}\right)$	$\Delta S,\left(\frac{kJ}{mol-K}\right)$
Instant	**F1**	0.2	152.57	598.99	4.63E+10	147.59	181.82	-54.85
		0.3	155.32	585.76	7.97E+10	150.45	181.73	-50.08
		0.4	163.86	558.10	4.38E+11	159.22	181.45	-35.64
		0.5	178.27	612.22	7.66E+12	173.18	181.01	-12.55
		0.6	164.52	625.45	4.97E+11	159.32	181.43	-35.43
		0.7	161.14	631.47	2.55E+11	155.89	181.54	-41.11

		0.8	166.55	645.90	7.47E+11	161.18	181.37	-32.34
Average			**163.18**		**1.39E+12**	**158.12**	**181.48**	**-37.43**
Peak-maximum	**F1**	**0.57**	**158.12**	**624.15**	**1.39E+11**	**152.93**	**181.66**	**-46.03**
	F2				1.63E+11		180.86	-44.74
	F3				2.53E+11		178.56	-41.06

* Permission to reuse the data has been requested under order no. “501391286” dated April 19, 2018

It is clear from the comparison that the value of A depends on the reaction mechanism so are the values of ΔG and ΔS. Therefore, it is necessary to establish reaction mechanism using methods described elsewhere (Vyazovkin, 2018; Vyazovkin et al., 2011). Besides ΔG for F1, average values of other parameters don’t match with the peak-maximum results. A single set of parameters exist for a single peak and that is for a particular reaction mechanism only. The evolution of kinetic and thermodynamic parameters using Eq. 8 with conversion is therefore nothing more than a misconception.

Ahmad et al. adopted slightly different methodology, they kept T_m constant (607.4K) for estimation of both A and ΔH for Para grass pyrolysis (Ahmad et al., 2017a). Although the degradation showed a multicomponent decomposition, they varied A using the changes in E_a as a function of conversion without specifying reaction order. Same methodology was adopted in many other studies (Khan et al., 2016; Mehmood et al., 2017; Ahmad et al., 2017c, 2017b; Kaur et al., 2017; Afzal et al., 2018; Ye et al., 2018; Ahmad et al., 2018). In case of complex degradations, components should be deconvoluted and dealt separately for the kinetic analysis (Ali et al., 2018; Koga, 2018).

With all the limitation of the Eq. 8 manipulations such as described above may implicate further the kinetic and thermodynamic evaluations.

Conclusions

With mathematical derivation it is explained that use of second derivative method for the pre-exponential factor (A) impose certain restrictions. Strictly speaking, single value for a single component can be obtained. Equation. 8 does not allow evolution of A with conversion neither by replacing peak-maximum temperature (T_m) with conversion temperature (T_i) nor by keeping T_m constant with varying activation energy (E_a). Use of A without understanding the limitations of the Eq. 8 may end-up with misleading kinetic and thermodynamic data and interpretations.

References

1. Afzal, I., Ahmad, M.S., Malik, S., Ibrahim, M., Al-Ayed, O.S., Qadir, G., Al, H.D., Gull, M., 2018. Bioenergy potential of Eichhornia crassipes assessed via thermodynamics and kinetics analyses. Protein Pept. Lett. https://doi.org/10.2174/0929866525666180122104237
2. Ahmad, M.S., Mehmood, M.A., Al Ayed, O.S., Ye, G., Luo, H., Ibrahim, M., Rashid, U., Arbi Nehdi, I., Qadir, G., 2017a. Kinetic analyses and pyrolytic behavior of Para grass (Urochloa mutica) for its bioenergy potential. Bioresour. Technol. 224, 708–713. https://doi.org/10.1016/j.biortech.2016.10.090
3. Ahmad, M.S., Mehmood, M.A., Liu, C.-G., Tawab, A., Bai, F.-W., Sakdaronnarong, C., Xu, J., Rahimuddin, S.A., Gull, M., 2018. Bioenergy potential of Wolffia arrhiza appraised through pyrolysis, kinetics, thermodynamics parameters and TG-FTIR-MS study of the evolved gases. Bioresour. Technol. 253, 297–303. https://doi.org/10.1016/j.biortech.2018.01.033

4. Ahmad, M.S., Mehmood, M.A., Taqvi, S.T.H., Elkamel, A., Liu, C.-G., Xu, J., Rahimuddin, S.A., Gull, M., 2017b. Pyrolysis, kinetics analysis, thermodynamics parameters and reaction mechanism of Typha latifolia to evaluate its bioenergy potential. Bioresour. Technol. 245, 491–501. https://doi.org/10.1016/j.biortech.2017.08.162
5. Ahmad, M.S., Mehmood, M.A., Ye, G., Al-Ayed, O.S., Ibrahim, M., Rashid, U., Luo, H., Qadir, G., Nehdi, I.A., 2017c. Thermogravimetric analyses revealed the bioenergy potential of Eulaliopsis binata. J. Therm. Anal. Calorim. 130, 1237–1247. https://doi.org/10.1007/s10973-017-6398-x
6. Ali, I., Naqvi, S.R., Bahadar, A., 2018. Kinetic analysis of Botryococcus braunii pyrolysis using model-free and model fitting methods. Fuel 214, 369–380. https://doi.org/10.1016/j.fuel.2017.11.046
7. ASTM International, 2016. ASTM E698-16 - Standard Test Method for Kinetic Parameters for Thermally Unstable Materials Using Differential Scanning Calorimetry and the Flynn/Wall/Ozawa Method. 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959. United States.
8. Barbanera, M., Cotana, F., Di Matteo, U., 2018. Co-combustion performance and kinetic study of solid digestate with gasification biochar. Renew. Energy 121, 597–605. https://doi.org/10.1016/j.renene.2018.01.076
9. Friedman, H.L., 1964. Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic. J. Polym. Sci. Part C Polym. Symp. 6, 183–195. https://doi.org/10.1002/polc.5070060121
10. Kaur, R., Gera, P., Jha, M.K., Bhaskar, T., 2017. Pyrolysis kinetics and thermodynamic parameters of castor (Ricinus communis) residue using thermogravimetric analysis. Bioresour. Technol. 250, 422–428. https://doi.org/10.1016/j.biortech.2017.11.077
11. Khan, A.S., Man, Z., Bustam, M.A., Kait, C.F., Ullah, Z., Nasrullah, A., Khan, M.I., Gonfa, G., Ahmad, P., Muhammad, N., 2016. Kinetics and thermodynamic parameters of ionic liquid

155 pretreated rubber wood biomass. J. Mol. Liq. 223, 754–762.
156 https://doi.org/10.1016/j.molliq.2016.09.012
157 12. Kim, Yong Sang, Kim, Young Seok, Kim, S.H., 2010. Investigation of Thermodynamic
158 Parameters in the Thermal Decomposition of Plastic Waste−Waste Lube Oil Compounds.
159 Environ. Sci. Technol. 44, 5313–5317. https://doi.org/10.1021/es101163e
160 13. Kissinger, H.E., 1957. Reaction Kinetics in Differential Thermal Analysis. Anal. Chem. 29,
161 1702–1706.
162 14. Koga, N., 2018. Chapter 6 - Physico-Geometric Approach to the Kinetics of Overlapping Solid-
163 State Reactions, in: Vyazovkin, S., Koga, N., Schick, C. (Eds.), Handbook of Thermal Analysis
164 and Calorimetry, Recent Advances, Techniques and Applications. Elsevier Science B.V., pp.
165 213–251. https://doi.org/10.1016/B978-0-444-64062-8.00012-7
166 15. Maia, A.A.D., de Morais, L.C., 2016. Kinetic parameters of red pepper waste as biomass to
167 solid biofuel. Bioresour. Technol. 204, 157–163.
168 https://doi.org/10.1016/j.biortech.2015.12.055
169 16. Mallick, D., Poddar, M.K., Mahanta, P., Moholkar, V.S., 2018. Discernment of Synergism in
170 Pyrolysis of Biomass Blends using Thermogravimetric Analysis. Bioresour. Technol.
171 https://doi.org/10.1016/j.biortech.2018.04.011
172 17. Mehmood, M.A., Ye, G., Luo, H., Liu, C., Malik, S., Afzal, I., Xu, J., Ahmad, M.S., 2017.
173 Pyrolysis and kinetic analyses of Camel grass (Cymbopogon schoenanthus) for bioenergy.
174 Bioresour. Technol. 228, 18–24. https://doi.org/10.1016/j.biortech.2016.12.096
175 18. Müsellim, E., Tahir, M.H., Ahmad, M.S., Ceylan, S., 2018. Thermokinetic and TG/DSC-FTIR
176 study of pea waste biomass pyrolysis. Appl. Therm. Eng. 137, 54–61.
177 https://doi.org/10.1016/j.applthermaleng.2018.03.050
178 19. Özsin, G., Pütün, A.E., 2018. Co-pyrolytic behaviors of biomass and polystyrene: Kinetics,
179 thermodynamics and evolved gas analysis. Korean J. Chem. Eng. 35, 428–437.
180 https://doi.org/10.1007/s11814-017-0308-6

20. Rasool, T., Srivastava, V.C., Khan, M.N.S., 2018. Bioenergy Potential of <Emphasis Type="Italic">Salix alba</Emphasis> Assessed Through Kinetics and Thermodynamic Analyses. Process Integr. Optim. Sustain. 1–10. https://doi.org/10.1007/s41660-018-0040-7
21. Vyazovkin, S., 2018. Chapter 4 - Modern Isoconversional Kinetics: From Misconceptions to Advances, in: Vyazovkin, S., Koga, N., Schick, C. (Eds.), Handbook of Thermal Analysis and Calorimetry, Recent Advances, Techniques and Applications. Elsevier Science B.V., pp. 131–172. https://doi.org/10.1016/B978-0-444-64062-8.00008-5
22. Vyazovkin, S., Burnham, A.K., Criado, J.M., Pérez-Maqueda, L.A., Popescu, C., Sbirrazzuoli, N., 2011. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. Thermochim. Acta 520, 1–19. https://doi.org/10.1016/j.tca.2011.03.034
23. Ye, G., Luo, H., Ren, Z., Ahmad, M.S., Liu, C.-G., Tawab, A., Al-Ghafari, A.B., Omar, U., Gull, M., Mehmood, M.A., 2018. Evaluating the bioenergy potential of Chinese Liquor-industry waste through pyrolysis, thermogravimetric, kinetics and evolved gas analyses. Energy Convers. Manag. 163, 13–21. https://doi.org/10.1016/j.enconman.2018.02.049
24. Yuan, X., He, T., Cao, H., Yuan, Q., 2017. Cattle manure pyrolysis process: Kinetic and thermodynamic analysis with isoconversional methods. Renew. Energy 107, 489–496. https://doi.org/10.1016/j.renene.2017.02.026