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Thermal analysis kinetics of dioscorea saponin by mechanical activation

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Abstract. Dioscorea saponin isolated from the rhizome of *Dioscorea nipponica* Makino was activated by AGO mill. On the basis of TG–DSC analysis, two endothermic peak of dioscorea saponin after mechanical activation both moved back, and it had finished weightlessness in advance due to the accelerated decomposition. According to thermal analysis kinetics, the average thermal decomposition activation energy of dioscorea saponin after mechanical activation increased, and the maximum activation energy at different conversion rates moved back. According to the determining results of kinetic mechanism function, the thermal decomposition kinetics mechanism functions of dioscorea saponin before and after mechanical activation both fitted the Jander formula. After mechanical activation, the thermal decomposition kinetic mechanism of dioscorea saponin transformed from three–dimensional to two–dimensional diffusion.

1. Introduction

Dioscorea saponin, a type of white crystal, is made by the raw material of *dioscorea nipponica*, and it is obtainable by separation and purification. Dioscorea saponin can increase coronary flow, improve coronary circulation, and resist atherosclerosis in arterial circulation. Water–soluble and active dioscorea saponins are favored by the market because they can be easily absorbed by receptors ^[1–3]. Dioscorea saponin can also be used to prepare dioscorea diosgenin, which is the initial material used for synthetic steroid hormone drug intermediation and thus regarded the “mother” of the hormone ^[4, 5]. Considerable researches on dioscorea saponin have focused on its pharmacological effects ^[6, 7], but no relevant articles have been reported on its mechanical activation. The activation of dioscorea saponin not only improves the effects of efficacy, but also speeds up the hydrolysis process, increases hydrolysis rate, and reduces acid dosage, which can subsequently reduce the preparation cost of dioscorea diosgenin and reduce the pollution of the environment. In this study, dioscorea saponin isolated from the laboratory was mechanically activated, and the thermal decomposition kinetics mechanism functions of dioscorea saponin before and after mechanical activation were analyzed.



2. Materials and methods

2.1. Materials

The dioscorea rhizomes of *Dioscorea nipponica* Makino were purchased from Yangjiang (Guangdong Province, China). The content of each basic component of the dioscorea rhizome is shown in Table 1.

Table 1. Basic components of dioscorea rhizome

Component	Fiber	Starch	Protein	Saponin	Water soluble	Others
Content/%	30–35	40–45	5–10	5–10	10–15	5

Isolated in the laboratory, dioscorea saponin is a white crystalline with chemical formula of $C_{45}H_{72}O_{16}$, molecular weight of 869.05, and melting point of 294 °C–296 °C. Dioscorea saponin is soluble in acetic acid, methanol, and ethanol; and slightly soluble in acetone and samyl alcohol; insoluble in water, petroleum ether, and benzene. Dioscorea saponin is a screw-type saponin, and the structure formula of dioscorea saponin is shown in Figure 1.

2.2. Mechanical activation method

Dioscorea saponin (10 g) was taken from the tank and ground by AGO mill for two minutes. Then, the mechanically activated dioscorea saponin was placed into a dryer for detection. Dioscorea saponin before mechanical activation was represented by S_a , and dioscorea saponin after mechanical activation was represented by S_b .

2.3. Thermal decomposition method

The temperature and heat coordinates were calibrated with high purity indium, and the whole process was conducted under the drying nitrogen. The purge nitrogen flow rate was 20ml/min. Dioscorea saponin samples before and after mechanical activation (5.0 ± 0.1) mg were accurately weighed, and placed into aluminum crucibles whose lids with hole in the center. The same empty crucibles were used as the reference. Then heating rates (5 °C, 10 °C, 15 °C, and 20 °C) were set respectively, heated to 600 °C, and kept the temperature for five minutes.

3. Results and discussion

3.1. TG–DSC analysis

The TG–DSC curves of dioscorea saponin are shown in Figure 2(a). Two obvious endothermic peaks appear on DSC curves. One of the endothermic peaks (358 °C) represents the bond rupture between RMB glycosides and sugar-based glycosides. The other endothermic peak (498 °C) represents the pyran ring ready to be opened. The TG curve of dioscorea saponin before 300 °C corresponds to 5% weightlessness (i.e., moisture volatilized weightlessness). After 300 °C, the dioscorea saponin began to rapidly lose weight due to the disintegrating sugar-based glycosides. Then, much more decomposition, material carbonization, and gasification were observed. Before reaching 580 °C, the cumulative weightlessness of the sample was 99%. The TG–DSC curve of the dioscorea saponin after mechanical activation is shown in Figure 2(b), in which two endothermic peaks move toward 343 °C and 463 °C. Before reaching 480 °C, the mechanically activated sample had 99% weightlessness, which was ahead of the 100 °C.

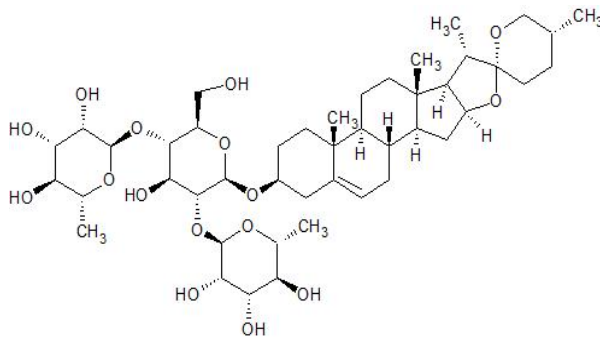
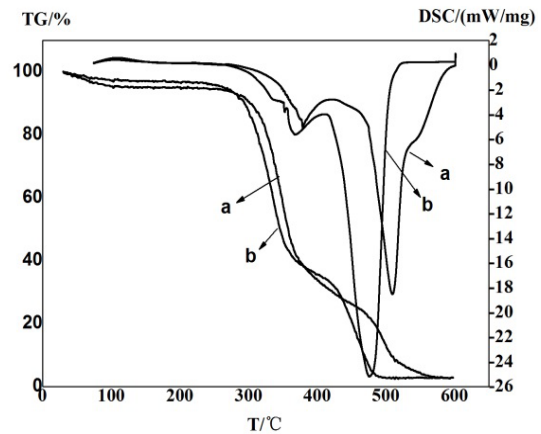


Figure 1. Structure of dioscorea saponin

Figure 2. TG–DSC curves (a S_a , b S_b)

3.2. Kinetic analysis

3.2.1. Kinetic data processing method

According to the isothermal kinetics theory, the dynamic formula of solid decomposition reaction can be expressed as follow Formula 1. In the formula, α is conversion rate (%); A is pre-exponential factor; E is thermal decomposition activation energy (kJ·mol); R is universal constant; T is temperature (K); and $f(\alpha)$ is differential form of kinetic mechanism function.

$$\frac{d\alpha}{dt} = A e^{-\frac{E}{RT}} \cdot f(\alpha) \quad (1)$$

In the thermal analysis test, the heating rate is a fixed value ($\beta = \frac{dT}{dt}$), which is substituted into Formula 1, can obtain the non-isothermal kinetic formula as in Formula 2.

$$\frac{d\alpha}{dt} = \left(\frac{A}{\beta}\right) e^{-\frac{E}{RT}} \cdot f(\alpha) \quad (2)$$

After derivation of Formula 2 through differential and deformation, formulas corresponding to Flynn–Wall–Ozawa method and Friedman method can be obtained [8, 9] as in Formula 3 and Formula 4.

$$\ln \beta = \ln \left(\frac{AE}{RG(\alpha)} \right) - 5.3305 - 1.0516 \frac{E}{RT^2} \quad (3)$$

$$\ln \left[\left(\frac{d\alpha}{dt} \right) \beta \right] = \ln [Af(\alpha)] - \frac{E}{RT} \quad (4)$$

Through substituting $\alpha = \frac{H_t}{H_0}$ (H_0 is the total heat, H_t is the heat at a certain temperature) and

$T = T_0 + \beta t$ (T_0 is the starting point temperature) into Formula 1, the formula of the Kissinger maximum rate method can be deduced after differentiation and deformation as in Formula 5.

$$\ln \frac{\beta_i}{T_{\max i}^2} = \ln \left(\frac{A_k R}{E_k} \right) \frac{1}{T_{\max i}} \quad (5)$$

Formula 4 can also be changed as in Formula 6.

$$\ln \left[\left(\frac{d\alpha}{dt} \right) \beta \right] - \ln f(\alpha) = \ln A_s - \frac{E_s}{RT} \quad (6)$$

In the thermal decomposition curve of β_i ($i=1, 2, 3, \dots$), the corresponding E_s and A_s can be calculated by 30 kinds of common kinetics mechanism functions (as shown in Table A of appendix). If E_s meet the conditions ($0 < E_s < 400 \text{ kJ}\cdot\text{mol}^{-1}$), the E_s and $\ln A_s$ would be considered reasonable^[10, 11]. E_s was compared to E_0 (the average thermal decomposition activation energy calculated by the Flynn–Wall–Ozawa method and Friedman method), and kinetics mechanism functions which met the conditions ($\left| \frac{E_0 - E_s}{E_0} \right| \leq 0.1$) would be found out. $\ln A_s$ was compared to $\ln A_k$ (calculated by the Kissinger method), and kinetics mechanism functions which met the conditions ($\left| \frac{\ln A_s - \ln A_k}{\ln A_k} \right| \leq 0.2$) would be found out. According to the R^2 value, the comparison results of E_s and E_0 , $\ln A_s$ and $\ln A_k$, the best screening result of the thermal decomposition kinetic mechanism function of dioscorea saponin would be determined.

3.2.2. Kinetic parameters calculation

Graphing $\ln \beta$ of $\frac{1}{T}$ and $\ln \left[\left(\frac{d\alpha}{dT} \right) \beta \right]$ of $\frac{1}{T}$ according to multivariate linear fitting by Flynn–Wall–Ozawa method and Friedman method (α in the range of 0.2–0.8), the thermal decomposition activation energy (E) can be obtained. Diagrams of $\ln \beta$ plotted against $\frac{1}{T}$ (Flynn–Wall–Ozawa method) and $\ln \left[\left(\frac{d\alpha}{dT} \right) \beta \right]$ plotted against $\frac{1}{T}$ (Friedman method) of dioscorea saponin before and after mechanical activation in different α are shown in Figure 3.

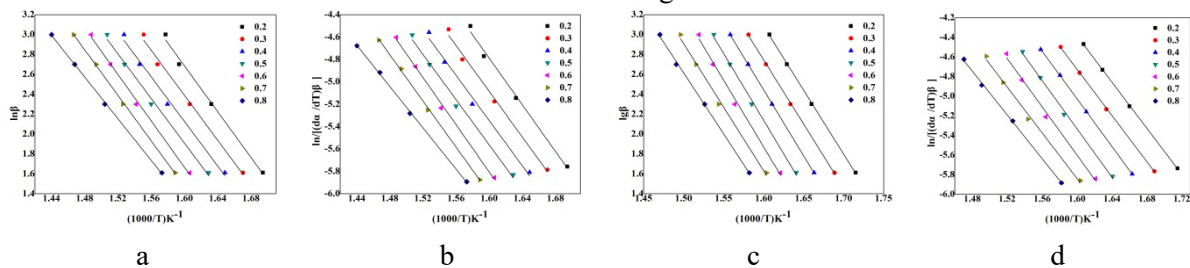


Figure 3. TG–DSC processing datas of dioscorea saponin before and after mechanical activation were

plotted against $\frac{1}{T}$ (a $\ln \beta - \frac{1}{T}$ (Flynn–Wall–Ozawa, S_a), b $\ln \left[\left(\frac{d\alpha}{dT} \right) \beta \right] - \frac{1}{T}$ (Friedman, S_a), c

$\ln \beta - \frac{1}{T}$ (Flynn–Wall–Ozawa, S_b), d $\ln \left[\left(\frac{d\alpha}{dT} \right) \beta \right] - \frac{1}{T}$ (Friedman, S_b))

The fitting curves of thermal decomposition activation energy at different conversion rates obtained by Flynn–Wall–Ozawa method and Friedman method are shown in Figure 4. The thermal decomposition activation energy of dioscorea saponin after mechanical activation at different conversion rates was higher than that of dioscorea saponin. The maximum value of dioscorea saponin

after mechanical activation had been reached when the conversion rate of increment was 0.5, which was 0.15 ahead of dioscorea saponin.

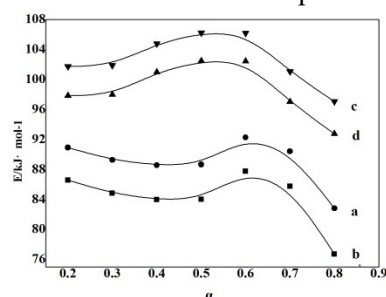


Figure 4. Fitting curves of thermal decomposition activation energy of different conversion rates of dioscorea saponin before and after mechanical activation (a (Flynn–Wall–Ozawa, S_a), b (Friedman, S_a), c (Flynn–Wall–Ozawa, S_b), d (Friedman, S_b))

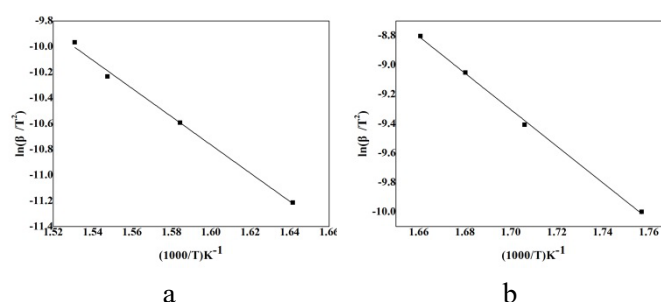


Figure 5. TG–DSC processing datas of dioscorea saponin before and after mechanical activation were

plotted for $\frac{1}{T} \left(a \ln \frac{\beta_i}{T_{\max i}^2} - \frac{1}{T_{\max i}} \right)$ (Kissinger, S_a) ,

b $\ln \frac{\beta_i}{T_{\max i}^2} - \frac{1}{T_{\max i}}$ (Kissinger, S_b))

The thermal decomposition activation energy calculated results of two calculation methods are listed in Table 2. The results (\bar{E}) calculated by Flynn–Wall–Ozawa method and Friedman method were similar whether dioscorea saponin mechanically activated or not. The average thermal decomposition activation energy of dioscorea saponin (\bar{E}_{a0}) was 86.60 ± 3.74 kJ·mol. After mechanical activation, the average thermal decomposition activation energy (\bar{E}_{b0}) was 100.73 ± 3.57 kJ·mol.

Table 2. Results of the thermal decomposition activation energy of dioscorea saponin before and after mechanical activation calculated by Flynn–Wall–Ozawa method and Friedman method

Activation energy	S_a		S_b	
	Flynn–Wall–Ozawa	Friedman	Flynn–Wall–Ozawa	Friedman
\bar{E} /kJ·mol	88.98 ± 2.8	84.22 ± 3.37	102.69 ± 3.04	98.77 ± 3.22
\bar{E}_0 /kJ·mol	86.60 ± 3.74		100.73 ± 3.57	

Graphing $\ln \frac{\beta_i}{T_{\max i}^2}$ of $\frac{1}{T_{\max i}}$ according to linear fitting by Kissinger method (α in the range of 0.2–

0.8), the thermal decomposition activation energy E_k can be obtained. Diagrams of $\ln \frac{\beta_i}{T_{\max i}^2}$ plotted

against $\frac{1}{T_{\max i}}$ of dioscorea saponin before and after mechanical activation in different α are shown in

Figure 5.

The calculated results of Kissinger method are listed in Table 3. The thermal decomposition activation energy of dioscorea saponin (E_{ak}) was 91.32 kJ·mol. After mechanical activation, the

thermal decomposition activation energy (E_{bk}) was 103.43 kJ·mol. The result of $\ln A_{ak}$ was 9.21 min⁻¹, and $\ln A_{bk}$ was 14.38 min⁻¹. The variances (R^2) were 0.9889 and 0.99794.

Table 3. Results of dioscorea saponin before and after mechanical activation calculated by Kissinger method

	S_a			S_b		
	$E_k/\text{kJ}\cdot\text{mol}$	$\ln A_k/\text{min}^{-1}$	R^2	$E_k/\text{kJ}\cdot\text{mol}$	$\ln A_k/\text{min}^{-1}$	R^2
Value	91.32	9.21	0.98889	103.43	14.38	0.99794

3.2.3. Kinetic mechanism function determination

Combined with 30 kinds of common kinetics mechanism functions $f(\alpha)$, the thermal decomposition activation energy E_s can be obtained through graphing $\ln \left[\left(\frac{d\alpha}{dT} \right) \beta \right] - \ln f(\alpha)$ of $\frac{1}{T}$ according to multivariate linear fitting. The calculated results (E_s , $\ln A_s$ and R^2) are shown in Figure 6.

The value of No.5, No.12, No.14, No.17 and No.23 (E_{as}) were close to E_{a0} in Figure 6a, and only No.5, No.12 and No.23 met the requirements ($0 < E_{as} < 400 \text{ kJ}\cdot\text{mol}^{-1}$ and $\left| \frac{\ln A_{as} - \ln A_{ak}}{\ln A_{as}} \right| \leq 0.2$).

The value of No.5, No.12, No.14, No.17 and No.23 ($\ln A_{as}$) were close to $\ln A_{ak}$ in Figure 6b, and only No.5, No.12, No.14 and No.23 met the requirements ($\left| \frac{\ln A_{as} - \ln A_{ak}}{\ln A_{as}} \right| \leq 0.2$). According to the

R^2 value in Figure 6c, and refer to the comparison results of E_{as} and E_{a0} , $\ln A_{as}$ and $\ln A_{ak}$, No.5 was the best screening result of the thermal decomposition kinetic mechanism function of dioscorea saponin. In the same way, No.6 was the best screening result of the thermal decomposition kinetic mechanism function of dioscorea saponin after mechanical activation.

According to Table A of appendix, the thermal decomposition kinetics mechanism functions of No.5 and No.6 both were Jander formula. The kinetic mechanism function of dioscorea saponin was $f(\alpha) = 6(1 - \alpha)^{2/3} \left[1 - (1 - \alpha)^{1/3} \right]^{1/3}$, and this was regarded the mechanism of three-dimensional diffusion. After mechanical activation, the kinetic mechanism function of dioscorea saponin was $f(\alpha) = 4(1 - \alpha)^{1/2} \left[1 - (1 - \alpha)^{1/2} \right]^{1/2}$, and this was regarded the mechanism of two-dimensional diffusion.

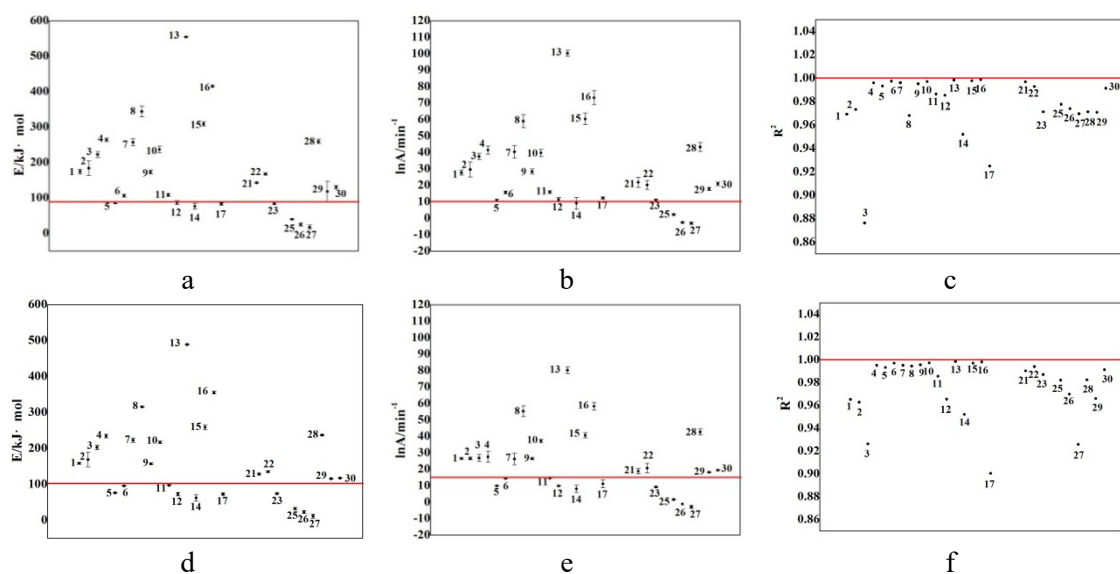


Figure 6. Diagram of E_s , $\ln A_s$ and R^2 obtained from 30 kinds of kinetics mechanism functions of dioscorea saponin before and after mechanical activation (a E_{as} , b $\ln A_{as}$, c R_a^2 , d E_{bs} , e $\ln A_{bs}$, f R_b^2)
^{a,d} The red lines represent the average thermal decomposition activation energy of dioscorea saponin (\overline{E}_{a0} and \overline{E}_{b0}) in Figure 6a and Figure 6d

^{b,e} The red lines represent the value of $\ln A_{ak}$ and $\ln A_{bk}$ in Figure 6b and Figure 6e

^{c,f} The red lines represent R^2 wireless approaching the value 1 in Figure 6c and Figure 6f.

4. Conclusion

(1) According to the TG–DSC analytical results, two endothermic peaks of dioscorea saponin after mechanical activation moved back 15 °C and 35 °C respectively, and it had 99% weightlessness ahead of 100 °C. After mechanical activation, the thermal decomposition of dioscorea saponin was accelerated.

(2) According to the results of thermal analysis kinetics, the average thermal decomposition activation energy of dioscorea saponin before and after mechanical activation were 86.60 ± 3.74 kJ·mol⁻¹ and 100.73 ± 3.57 kJ·mol⁻¹, which showed 13.45 kJ·mol⁻¹ activation energy of dioscorea saponin increased after mechanical activation. The maximum activation energy at different conversion rates also changed, which moved from 0.65 to 0.5.

(3) According to the determining results of kinetics mechanism functions, the thermal decomposition kinetics mechanism functions of dioscorea saponin before and after mechanical activation both fitted Jander formula. The kinetic mechanism function of dioscorea

saponin was $f(\alpha) = 6(1-\alpha)^{2/3} \left[1 - (1-\alpha)^{1/3} \right]^{1/3}$, and the kinetic mechanism function of dioscorea saponin after mechanical activation was $f(\alpha) = 4(1-\alpha)^{1/2} \left[1 - (1-\alpha)^{1/2} \right]^{1/2}$. After mechanical activation, the decomposition mechanism of dioscorea saponin transformed from three-dimensional to two-dimensional diffusion.

Appendice

Table A. 30 kinds of common kinetics mechanism functions

No.	Name	Mechanism	$f(\alpha)$
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1	Parabola rule	One-dimensional diffusion, 1D	$1 / 2\alpha^{-1}$
2	Valensi formula	Two-dimensional diffusion, Cylindrical symmetry, 2D	$\left[1 - \ln(1 - \alpha)\right]^{-1}$
3	G-B formula	Three-dimensional diffusion, Cylindrical symmetry, 3D	$3 / 2 \left[(1 - \alpha)^{-1/3} - 1 \right]^{-1}$
4~5	Jander formula	Three-dimensional diffusion, 3D	$3 / n (1 - \alpha)^{2/3} \left[1 - (1 - \alpha)^{1/3} \right]^{-(n-1)}$ (n=2,1/2)
6	Jander formula	Two-dimensional diffusion, 2D	$4 (1 - \alpha)^{1/2} \left[1 - (1 - \alpha)^{1/2} \right]^{1/2}$
7	Jander formula	Three-dimensional diffusion, Sphere symmetry, 3D	$3 / 2 (1 - \alpha)^{2/3} \left[(1 + \alpha)^{1/3} - 1 \right]^{-1}$
8	Z-L-T formula	Three-dimensional diffusion, 3D	$3 / 2 (1 - \alpha)^{4/3} \left[1 / (1 - \alpha)^{1/3} - 1 \right]^{-1}$
9	Mample single rule	Random nucleation and growth, each particle should has only one core	$1 - \alpha$
10~16	Avrami-Erofeev formula	Random nucleation and growth,	$1 / n (1 - \alpha) \left[-\ln(1 - \alpha) \right]^{-(n-1)}$ (n=2/3,1/2,1/3,4,1/4,2,3)
17	P-T formula	Auto-catalysis, Ramifor nucleation, A_u	$\alpha (1 - \alpha)$
18~22	Reaction series	n=1/2,3,2,4,1/3,1/4	$1 / n (1 - \alpha)^{-(n-1)}$ (n=3,2,4,1/3,1/4)
23~27	Mampel Power rule	n=1,3/2,1/2, 1/3,1/4	$1 / n \alpha^{-(n-1)}$ (n=1,3/2,1/2, 1/3,1/4)
28	Second order	Chemical reaction, F_2	$(1 - \alpha)^2$
29	Contraction cylinder	Phase boundary reaction, Cylindrical symmetry, R_2	$2 (1 - \alpha)^{1/2}$
30	J-M-A formula	Random nucleation and growth, A_3	$2 / 3 (1 - \alpha) \left[-\ln(1 - \alpha) \right]^{1/3}$

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