

## Kinetics on the Thermal Decomposition of Cellulose

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### 셀룰로오스의 열분해반응속도론

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#### 초 록

Cellulose의 열분해 반응에 대한 Kinetic Parameter를 구하기 위하여 Thermogravimetry(TG)와 Differential Scanning Calorimetry(DSC)를 이용하는 네가지 비등온법을 고찰하였다.

그 결과 DSC에 의한 가열속도법과 TG에 의한 근사법이 가장 간편하였고 Kinetic Parameters의 신뢰도도 매우 높았다.

Cellulose 열분해 반응에서 반응차수는 1 / 2 차였고 활성화에너지는 42kcal/mol로 나타났다.

#### ABSTRACT

Four of non-isothermal methods evaluating kinetics have been studied by using differential scanning calorimetry(DSC) and thermogravimetry(TG) and applied for kinetics of the thermal decomposition of cellulose. It is concluded that the heating evolution methods with DSC and approximative methods with TG can lead to satisfactory kinetic analysis. Results calculating the reacting order and the activation energy of cellulose decomposition were 1/2 order and 42kcal/mol, respectively.

#### INTRODUCTION

The interaction between cigarette paper and tobacco is so complicated and dependent on many factors. One of the factors affecting smoke yields is a fiber composition of cigarette paper. Cigarette paper is basically interwoven with cellulose containing burning

chemicals and the burning rate of cigarette can be controlled by such chemicals. Majority of the works (1, 2, 4, 13) on cellulose combustion have centered on the use of burn-retardants. However, very few reports have dealt with accelerating chemicals for cellulose combustion. The reaction products by the thermal decomposition of cellulose gene-

rally fall into three distinct categories (14, 15, 16) : a series of permanent gases, primarily water and carbon dioxide; a solid carbonaceous char; tar, containing 1, 6-anhydro-glucopyranose (7, 25) as a main component which is further decomposed with the production of numerous flammable gases.

This study is to evaluate kinetic parameters for the thermal decomposition of cellulose. A comparison of several non-isothermal methods has been studied by using TG, DSC and derivative thermogravimetry (DTG).

### THEORY

Thermal analytical methods such as TG, DTG, DSC and differential thermal analysis (DTA) have been widely applied for kinetics on solid state chemical reactions. A number of methods for the kinetics have been developed. It has been found that, even with the same experimental data, different evaluation methods may result in different kinetic parameters such as activation energy, frequency factor, and reaction order. A few works (5,24) have made attempts to experimentally or mathematically compare the kinetic results obtained from different methods.

Non-isothermal methods for the evaluation have normally based on the Arrhenius equation,

$$k = A \exp\left(-\frac{E}{RT}\right) \dots\dots\dots (1)$$

where k is the temperature-independent rate constant, A the Arrhenius factor, E the activation energy, R the gas constant, and T the temperature.

Substituting eqn(1) into the formal kinetic equation,  $dx/dt = kf(\alpha)$ , one obtains

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \dots\dots\dots (2)$$

where  $\alpha$  is fractional conversion and  $f(\alpha)$  the function depending upon the reaction mechanism. Since temperature increases linearly with time, t, instead of operating isothermally, i. e. ,

$$T = T_0 + \phi t \dots\dots\dots (3)$$

where  $\phi$  is program rate, one obtains

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\phi} \exp\left(-\frac{E}{RT}\right) dt \dots\dots\dots (4)$$

Eqn(4) above has been widely used as the basis for kinetic evaluation. The integration methods of the right-hand side in eqn(4) may be divided into four groups:

- 1 . approximative methods,
- 2 . integral methods,
- 3 . differential methods,
- 4 . methods based on the maximum temperature shifts, i. e . , heating evolution methods.

1 . Approximative methods : Horowitz and Metzger (23, 29) introduced two alternative approximations into the equation suggested by Van Kravlen et al (27). The evaluation is made by using the following equation;

$$\ln[1 - (1 - \alpha)^{1-n}] = \ln(1-n) + \frac{E}{RT_m^2} \dots\dots\dots (5)$$

and with  $n=1$

$$\ln \ln\left(\frac{1}{1-\alpha}\right) = \frac{E}{RT_m^2} \theta \dots\dots\dots (6)$$

where  $T_m$  is the temperature at maximum rate, i. e. , the inflection point of DTG curve, n the reaction order, and  $\theta$  the difference between given temperature and  $T_m$ . Brodido's plots (3), that is,  $\ln \ln[1/(1-\alpha)]$  vs  $1/T$  also gives an excellent approximation to a straight line over the range  $0.999 > \alpha > 0.001$ . It

is noted that this method is slightly less accurate when decomposition temperature is broader (Method I).

2. Integral methods: For a reaction in which the order is unknown, Coats and Redfern (6) derived the following equations,

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right] = \ln\frac{AR}{E} \left(1 - \frac{2RT}{E}\right) - \frac{E}{RT} \dots\dots\dots (7)$$

and with  $n=1$

$$\ln\left(\frac{1}{1-\alpha}\right) = \ln\frac{AR}{E} \left(1 - \frac{2RT}{E}\right) - \frac{E}{RT} \dots\dots\dots (8)$$

Since first term of the right-hand side in eqn(7) and (8), in spite of containing the variable, T, is vanishingly small near constant, the left-hand side in eqn(7) and (8) against 1/T should result in a straight line having slope,  $-E/R$ , for a correct value of n. Since there is theoretical justification only for n of 0, 1/2, 2/3 and 1 in solid-state reactions, the correct order is assumed to lead to the best linear plots from which activation energy is also determined (method II).

3. Differential methods: One of the differential methods was developed by Freeman and Carroll (10). Taking logs and differentiating eqn(4), one obtains

$$\frac{\Delta \log(dw/dt)}{\Delta \log(w_\infty - w)} = n - \frac{E}{2.303R} \cdot \frac{\Delta(1/T)}{\Delta \log(w_\infty - w)} \dots\dots\dots (9)$$

where dw/dt is the rate of weight loss,  $w_\infty$  the maximum weight loss and w the weight loss upto time, t. The advantages of this method are it is possible to determine both values of n and E, and that considerably fewer experimental data are required. However, as Sestak (23) pointed it out, this method has several disadvantages leading to

uncertain and meaningless values for n (method III).

4. Heating evolution methods: During recent years, DSC has been proven useful for kinetics. Kinetic parameters are derived based on the linear relationship of  $\log \phi$  versus  $1/T_m$  (11, 19, 28).

Integrating eqn(4),

$$F(x) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{AE}{\phi R} \left( \frac{e^{-x}}{x} - \int_x^\infty \frac{e^{-u}}{u} du \right) \dots\dots\dots (10)$$

where  $u = E/RT$ .

Defining the function in the bracket in eqn(10) as p(x) (8, 21) and taking logs,

$$\log F(x) = \log \frac{AE}{R} - \log \phi + \log p(x) \dots\dots\dots (11)$$

where p(x) may be approximated by (18, 20)

$$\log p(x) \approx -2.315 - 0.457 \frac{E}{RT} \dots\dots (12)$$

Combining eqns(11) and (12), and taking the differential with respect to 1/T, then,

$$\log \phi + 0.457 \frac{E}{RT_m} = \text{constant} \dots\dots (13)$$

where  $T_m$  is the maximum temperature in DSC curves at the given program rate,  $\phi$ . Thus, plots of  $\log \phi$  versus  $1/T$  yield E. The advantages of this method include simplicity of operation and applicability to a wide variety of materials. It is noted that this method will not work in some materials which undergo an isomerization changes at reacting temperature and decompose with melting (method IV).

## MATERIALS and METHODS

1. Material: The cellulose used in this study was 98%  $\alpha$ -cellulose from Sigma, Ltd. and used as supplied.

2. Methods: All TG and DSC results in

this study were obtained by using DuPont 10-90 thermal analyzer with 951 thermogravimetric analyzer and 910 differential scanning calorimeter

The measurements in TG were carried out in a dynamic atmosphere of nitrogen at 8°C per minute program rate and in scale sensitivities of 0.5mg/cm and 20°C/cm. About 5mg of the samples were used for each experiment.

In DSC experiments for kinetic study, 5mg of samples were heated with a series of program rates ranging from 1° thru 20°C/min in a dynamic atmosphere of nitrogen. The scale sensitivity was 2.4mcal/cm. The temperature correction was obtained by calibrating the melting point of Indium metal.

The flow rate, 100ml/min, in both experiments of TG and DSC was chosen after testing whether this gas flow was good enough to prevent the oxidation of samples.

## RESULTS and DISCUSSION

As seen in Fig. 1, the TG curves obtained under the present experiment were very similar to the results of the previous investigations (9, 12, 22, 26). Cellulose decomposition occurred at a very slow rate until 250°C, followed by a rapid weight loss from 320° to 370°C at which the final weight loss was 84% with 13% char remained.

Kinetic parameters were computed by using the four non-isothermal methods. For the correct reaction order leading to the best linear plots and the determination of the correct values of activation energy, the estimations were made for each of  $n=1/2$ ,  $2/3$ , and 1.

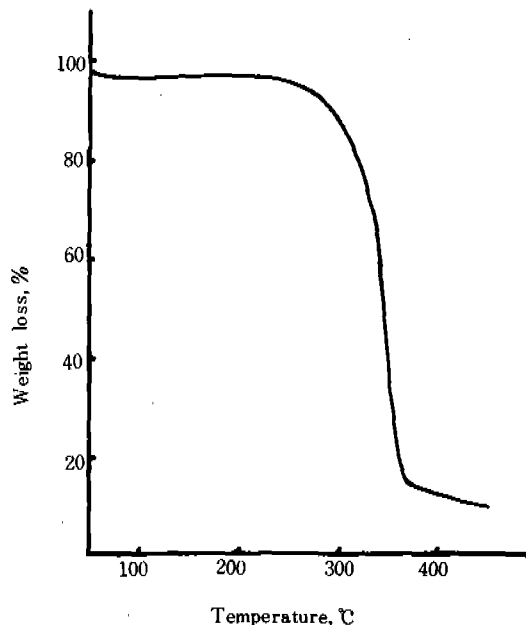


Fig 1. TG of Cellulose in nitrogen atmosphere.

Results obtained by method I and II with  $n=1/2$  are shown in Fig. 2.

As seen in Fig. 2, these methods yielded the linear plots with a most wide range when  $n=1/2$  and  $n=2/3$ . With  $n=1$  the range was less and the plots led to noticeable curvature at high values of  $\alpha$ .

Results obtained by method III are plotted in Fig. 3. The plots were more scattered than those in Fig. 2. The greater scatter in the data obtained by method III, when compared with method I and II, is largely due to the determination of three different functions, that is, rate of weight loss, weight loss and temperature over short temperature intervals. The line in Fig. 3 was obtained by least square method passing through

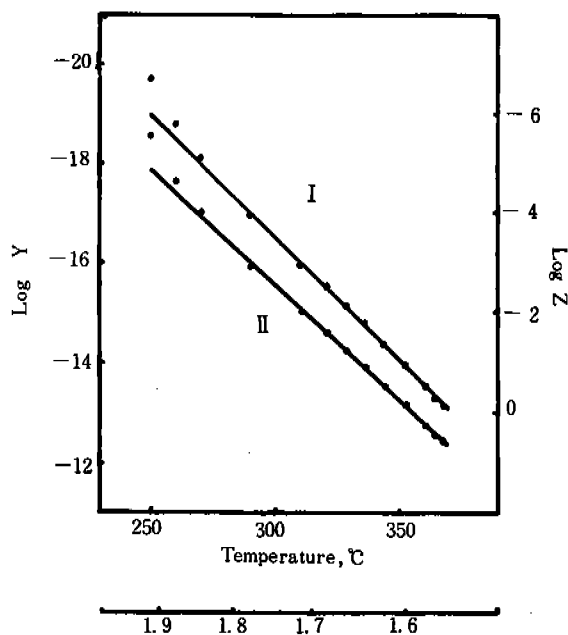


Fig. 2 Data calculated from method I &amp; II.

$$Y = [1 - (1 - \alpha)^{1/2}]$$

$$Z = 2[1 - (1 - \alpha)^{1/2}]/T^2$$

the ordinate axis at 0.53 corresponding to  $n=1/2$ .

Kinetic parameters calculated by means of least square method in method I thru IV are listed in Table 1.

As seen in Table 1, the value of  $E$  for cellulose decomposition is considered as 42 kcal/mol with  $n=1/2$  leading to the best linear plots. The values of  $E$  obtained by method II were remarkably smaller than those from the other methods. In method IV, a seven-sets of program rate and peak temperature data were plotted as seen in Fig. 4. The value of  $E$  obtained from the slope was refined by an iteration method. It is noted (18) that this method allows a precision for  $E$

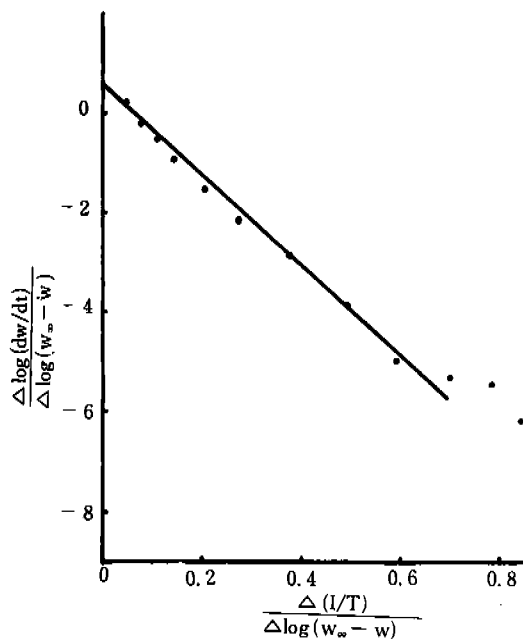


Fig. 3. Data calculated from method III.

Table 1. Kinetic parameters for pyrolysis of cellulose

	$n$	$E$ , Kcal/mol	Range of $\alpha$
Method I	1/2	41.5	0.01-0.97
	2/3	40.5	0.02-0.91
	1	44.2	0.04-0.82
Method II	1/2	33.1	0.01-0.97
	2/3	32.3	0.01-0.91
	1	36.0	0.02-0.82
Method III	0.53	42.4	0.26-0.72
Method IV		42.3	-

of 0.5-1 kcal/mol. The value of  $E$  calculated by Kissinger method (17) was 42.1 Kcal/mol.

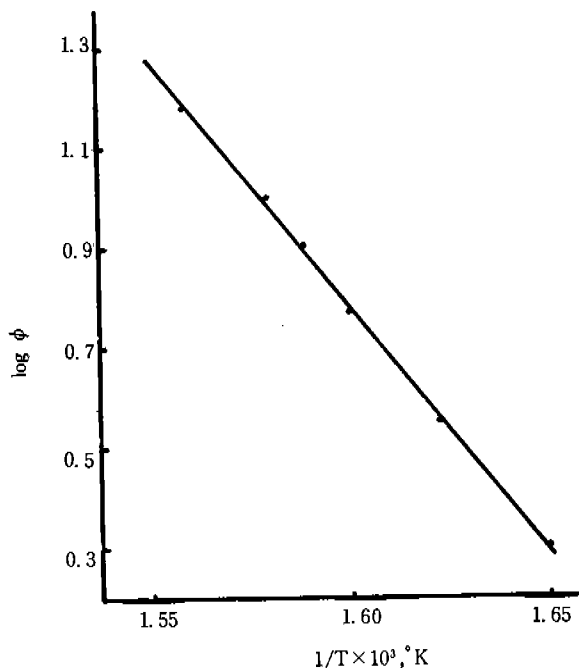


Fig 4. Data calculated from method IV.

## CONCLUSION

It is concluded that method I, II and IV can lead to satisfactory kinetic analysis. Method II is considered less satisfactory for determining E but reasonably accurate for n. The results under the present experiment conditions illustrate that n and E for cellulose decomposition are 1/2 and 42kcal/mol, respectively. The heating evolution method using non-isothermal DSC was significantly rapid and precise.

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