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# THE KINETICS OF XYLAN PYROLYSIS *

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## ABSTRACT

The study concerned itself with the investigation of the kinetics of xylan in an inert atmosphere. It was found that there were two basic mechanisms for degradation in the temperature range studied, nucleation and diffusion. The range of temperatures studied was 200—290°C. By comparison to several theoretical models the correct theoretical interpretation was based on the best statistical fit of the data. In this way, it was discovered that a first order nucleation mechanism prevailed over the temperature range 200—235°C. A least squares program was developed from an IBM Statistical Package in which each model was subject to the same analysis.

A Carter—Valensi model was obeyed from 240 to 255°C. This model is a diffusion type model. In this case, the product layer develops at the surface of the particle. Finally, an Avrami—Erofeyev equation was found as the best fit for the temperature range 270—290°C. It is surmised that polymer degradation in the solid state follows heterogeneous mechanisms rather than, as previously thought, by *n*th order homogeneous mechanisms.

## INTRODUCTION

There are conflicting opinions on the nature of polymer degradation mechanisms. Many past analyses have assumed an *n*th order mechanism resembling homogeneous gas phase kinetics [1—4]. On the other hand, there is speculation by many investigators [5—7] that polymers degrade by heterogeneous solid state mechanisms and, in fact, the classical equation $d\alpha/dt = k(1 - \alpha)^n$ is applicable only in certain highly specific cases [8,9] and will in general be invalid. To completely describe the decomposition of any solid it is necessary to know the rate of formation and spatial distribution of the nuclei in nucleation mechanisms, and the depth of growth in diffusion mechanisms. Hence, the full mathematical formulation of the rate process must in general be expressed in terms of both spatial and time coordinates. The material used in this study was xylan, an extract of wood and similar in structure to cellulose. In the course of achieving a kinetic expression for the kinetics of decomposition, several new analytical techniques were created

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and perfected, including a new instrumental method of analysis, and a new statistical technique for the analysis of the kinetic data.

## PREVIOUS RESEARCH ON THE PYROLYSIS OF XYLAN

It appears that only one paper has been published on the kinetics of xylan degradation to date. Shimizu et al. [10] have investigated the thermal degradation of xylan from an isothermal and non-isothermal point of view. The xylan used was an extract from beech wood. Analysis of the sample was performed on a thermogravimetric analyzer.

### *Non-isothermal kinetics*

It was observed that the weight loss of xylan commenced at 200°C and rapidly decomposed, terminating at about 300°C. There was a resultant 70% loss in weight of the initial sample leaving a char as residue. Shimizu et al. [10] postulated that the reaction followed the form

$$\mathrm{A} \rightarrow \mathrm{B} + \mathrm{C} \tag{1}$$

The rate expression assigned to this reaction for the weight loss is

$$-\mathrm{d}w/\mathrm{d}t = kW_{\mathrm{R}}^{n} \tag{2}$$

where, $k$ is the specific rate, $n$ is the order of the reaction, and $W_{\mathrm{R}}$ is the weight remaining as reactant.

The rate constant expression follows the usual Arrhenius form

$$k = A\mathrm{e}^{-E/RT} \tag{3}$$

where, $A$ is the pre-exponential factor, $E$ is the energy of activation, $R$ is the gas constant, and $T$ is the absolute temperature.

Combining eqns. (2) and (3) and taking the logarithms of both sides, we arrive at

$$\log(-\mathrm{d}w/\mathrm{d}t) - n \log W_{\mathrm{R}} = \log A - E/2.303RT \tag{4}$$

If two thermograms are used the following equation can be obtained

$$n = \frac{\log(-\mathrm{d}w/\mathrm{d}t)_2 - \log(-\mathrm{d}w/\mathrm{d}t)_1}{\log W_{\mathrm{R}_2} - \log W_{\mathrm{R}_1}} \tag{5}$$

By this method of analysis, these investigators concluded that for the temperature range 232—290°C, the reaction followed first order kinetics. It was also discovered that below 232°C the value of $n$ was considerably less than 1 and above 290°C greater than 1. It was postulated that xylan degraded by more than one mechanism in the temperature range studied. Above 232°C it was found that a simple reaction order could not be fitted to the data. A solution to this problem was obtained by progressively fitting the kinetics with selected orders of reaction as shown in Table 1.

TABLE 1

Kinetic parameters of pyrolysis for xylan obtained by the Chatterjee method

| | Zero order reaction 201–232°C | First order reaction | | |
|---|---|---|---|---|
| | | I | II | III |
| | | 232–245°C | 245–267°C | 267–290°C |
| Wt. loss of reactant (%) | 10 | 17 | 39 | 29 |
| | 39.9 | 29.6 | 17.7 | 43.6 |
| log $A$ | 17.4 | 11.4 | 6.3 | 16.8 |

## *Isothermal kinetics*

It was assumed from the beginning that xylan followed a first order mechanism and therefore the governing kinetic expression used was

$$-\mathrm{d}w/\mathrm{d}t = kW'_{\mathrm{R}} \tag{6}$$

Integrating and rearranging, we obtain

$$2.303 \log W'_{\mathrm{R}} = -kt \tag{7}$$

where $W'_{\mathrm{R}}$ is weight remaining calculated according to the following expression

$$W'_{\mathrm{R}} = [(W - W_{\infty})/(W_0 - W_{\infty})] \times 10.0 \tag{8}$$

where, $W_{\infty}$ is the weight of char, $W$ is the weight of residue, and $W_0$ is the initial amount of residue.

It was found that the data obtained from the isothermal technique demonstrated that the pyrolysis of xylan obeyed zero order kinetics around 200°C, subsequently followed by a first order mechanism. Shimizu et al. [10] admit the failure of trying to fit the kinetic data by an $n$th order

TABLE 2

Reaction constant and energy of activation for pyrolysis of xylan obtained by isothermal method

| | Isothermal temp. (°C) | Specific reaction constant ($\mathrm{min}^{-1}$) | Energy of activation (kcal $\mathrm{mole}^{-1}$) |
|---|---|---|---|
| Primary first order | 204 | 0.0102 | |
| | 216 | 0.0206 | 25.7 |
| | 221 | 0.0257 | |
| Secondary first order | 204 | 0.0053 | |
| | 216 | 0.0090 | 21.9 |
| | 221 | 0.0119 | |

expression. Discrepancies were found below 245°C and above 280°C in which the kinetic equations did not follow a simple first order expression. Table 2 shows the reaction constant and energy of activation for the degradation of xylan by the isothermal technique.

## EXPERIMENTAL

### *Apparatus*

The instrument used in this study is the DuPont 990 modular thermal analysis system. The two functional units are a temperature programmer-controller and an $X$—$Y$—$Z$ recorder. The temperature of the sample under analysis is controlled by the programmer-controller. Variance in the sample property, energy absorption or release, weight or dimensional change, etc., is read on the $Y$ or $Y'$ axis as a function of sample temperature on the $X$ axis of the recorder.

### *Materials*

The sample used in this study was xylan from larchwood composed of $\beta$-1,4 linked xylopyranose residues. The xylan was obtained from the Sigma Chemical Company, St. Louis (product number, X3875). According to the manufacturers' catalog, the molecular weight of this species of xylan was evaluated as approximately 20 000.

### *Procedure and methods*

The following procedure was used for each run.

(1) An empty aluminum pan, provided by the Dupont deNamours Company, was weighed in a Mettler balance. The xylan sample (powdered form) was then poured into the pan and subsequently weighed.

(2) The desired isothermal program was set. The cell was heated to the program temperature and allowed to equilibrate. Purge gas (argon) was then admitted to the sample chamber through an orifice in the block wall positioned midway between the two raised platforms on the left.

(3) The sample pan was quickly placed in the cell and the cover of the cell placed immediately afterwards and the recorder started.

(4) A two-pen sensitivity range was used in order that the entire analog plot remained on paper.

(5) When the pen(s) achieved a horizontal position after a great length of time (indicating the reaction was completed) the recorder and DSC were turned off.

(6) The sample pan was taken from the cell and weighed. The final residue weight was recorded.

*Analysis of raw DSC thermograms*

The first step in the kinetic analysis of xylan degradation is to determine the baseline of the analog output. This is done by extending the horizontal position of the curve till it meets the initial part of the curve. Partial areas were determined at pre-designated time intervals by an Amsler planimeter. Each interval of time had five area measurements, in which the mean value of the area was chosen as the final value for the kinetic analysis. If one takes the partial areas and divides them by the total area under the curve, one may obtain values of $\alpha$ for the selected temperature. Plotting the fraction reacted, $\alpha$, vs. time gives us the classical decomposition curve. The set of $\alpha$ vs. time values were then fed into the least squares polynomial program to find the model of best fit.

## TECHNIQUE OF ANALYSIS

This technique expands the right-hand side of the general equation for the kinetics of solids. Let us assume that the general differential form for any solid decomposition reaction is

$$\frac{d\alpha}{dt} = k f(\alpha) \tag{9}$$

Integrating the above equation gives us

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = k \int_0^t dt \tag{10}$$

or

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = kt \tag{11}$$

If we were to plot $g(\alpha)$ on the $y$ axis and time, $t$, on the $x$ axis, we would notice slight or major deviations from the predicted straight line. This method fits a polynomial equation to the data by means of a least squares analysis, whereby several curve fitting tests are applied in order to determine which mathematical model agrees with the data. In this method the independent variable $t$, is expanded in a power series and then subjected to a variety of statistical tests to determine the extent of its linearity. Obviously, from inspection of the empirical polynomial equation one can see from the magnitude of the coefficients its deviation from a straight line. In addition, from a purely mathematical analysis, we can also conjecture about the physical phenomenon that the xylan sample underwent. For example, if we subject the data to an Avrami—Erofeyev equation and perceive deviations from linearity at large values of time, we can conclude that the kinetics of the reaction are no longer obeyed when those deviations become manifest. In other words, we can conclude that either the model does not fit the data accurately, leading to the assumption that the sample reacts by a completely different mechanism, or there is a change in mechanism occurring at some interval, in which the mathematics is detecting its incipient deviation. Since the mechanics of polynomial regressions are well established, the power series type formula was chosen for both methods. All of the expansions reduce to a power series form, thus facilitating handling of the data. A tremendous saving in computer time comes about because the same functional relationship is used for all the final statistical analyses. The following derivation of the power series as it is used in the polynomial analysis will be given below.

Let us represent the general power series in the following form

$$\sum_{k=0}^{\infty} a_k t^k = a_0 + a_1 t + a_2 t^2 + \cdots \qquad (12)$$

where, $t$ is the time reacted, and $a_k$ is the coefficient of the series.

We shall concern ourselves with the problem of approximating to a given function.

$$y = f_n(t) \qquad (13)$$

where, $g(\alpha)$ is the integrated form of the solid state model $= y$

$$kt = f_n(t)$$

by means of a sequence of polynomials $f_n(t)$ of the form

$$f_n(t) = a_0 + a_1 t + a_2 t^2 + \ldots + a_n t \qquad (14)$$

This approach was used throughout the study.

## DISCUSSION AND CONCLUSIONS

We will take the analysis of one typical run to show the technique of analysis as well as give a clearer understanding of the results. For example, let us

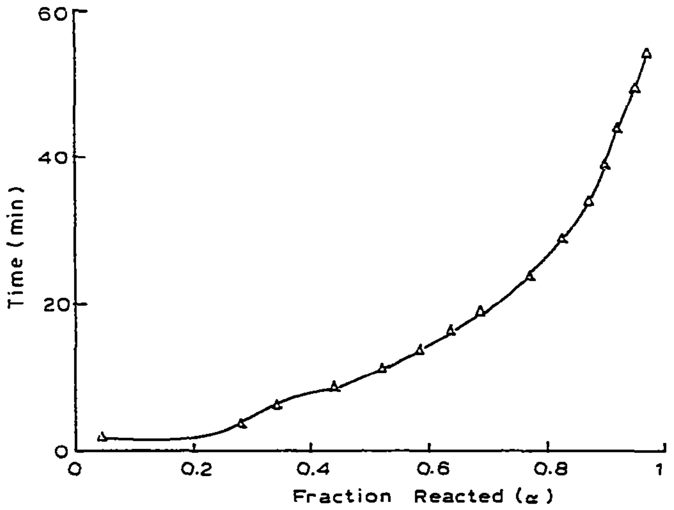

Fig. 1. Fraction reacted at 240°C.

TABLE 3

Kinetic models used in this study

(1) First order nucleation

$\ln(1-\alpha) = k't$

(2) Prout Tompkins mechanism

$\ln[\alpha/(1-\alpha)] = kt$

(3) Zhuravlev and Lesokhin mechanism

$$\left[\frac{1}{(1-\alpha)^{1/3}} - 1\right]^2 = \frac{2kD}{r^2}t$$

(4) Jander diffusion

$[1-(1-\alpha)^{1/3}]^2 = 2kD/r^2 \times t$

(5) Kroger—Ziegler mechanism

$[1-(1-\alpha)^{1/3}]^2 = 2k/r^2 \times \ln t$

(6) Contracting geometry where $n = \frac{1}{3}$

$1-(1-\alpha)^{1/3} = kt$

(7) Contracting geometry where $n = \frac{1}{2}$

$1-(1-\alpha)^{1/2} = kt$

(8) Two dimensional diffusion controlled

$(1-\alpha)\ln(1-\alpha) + \alpha = kt$

(9) Ginstling Brounstein mechanism

$1-\frac{2}{3}\alpha-(1-\alpha)^{2/3} = kt$

(10) Power law where $n = 1$

$\alpha = kt$

(11) Komatsu and Uemura mechanism

$$[(1+\alpha)^{1/3}-1]^2 = \frac{2kD}{r^2}t$$

(12) Avrami—Erofyev model where $r = 2$

$\ln(1-\alpha)^{-1} = kt^2$

(13) Avrami—Erofyev model where $r = 3$

$\ln(1-\alpha)^{-1} = kt^3$

(14) Zero order mechanism

$1-(1-\alpha) = kt$

(15) Second order mechanism

$$\frac{1}{1-\alpha} - 1 = kt$$

(16) Avrami—Erofyev model where $r = 4$

$\ln(1-\alpha)^{-1} = kt^4$

TABLE 3 (continued)

(17) Avrami—Erofyev model where $r = \frac{1}{2}$

$\ln(1 - \alpha)^{-1} = kt^{0.5}$

(18) Avrami—Erofyev model where $r = 1.5$

$\ln(1 - \alpha)^{-1} = kt^{1.5}$

(19) Avrami—Erofyev model where $r = 2.5$

$\ln(1 - \alpha)^{-1} = kt^{2.5}$

(20) Carter—Valensi model where $z = 0.1$—$0.9$ and $1.1$—$1.9$

$$\frac{z - (z - 1)(1 - \alpha)^{2/3} - [1 + (z - 1)\alpha]^{2/3}}{(z - 1)} = \frac{2ktD}{r^2}$$

(21) Hulbert model where $z = 0.1$—$0.9$

$$\frac{z - [(1 + (z - 1)\alpha]^{2/3} - (z - 1)(1 - \alpha)^{2/3}}{(z - 1)} = \frac{2k \ln t}{r^2} = kt$$

(22) Empirical order where $n = 1.1$—$1.9$

$$\frac{1}{n - 1}\left[\frac{1}{(1 - \alpha)^{n-1}} - 1\right] = kt$$

(23) One dimensional diffusion

$\alpha^2 = kt$

(24) Exponential rule

$\ln \alpha = kt$

(25) Power law where $n = 2$

$\alpha^2 = kt$

(26) Power law where $n = 3$

$\alpha^3 = kt$

(27) Power law where $n = 4$

$\alpha^4 = kt$

(28) Empirical exponential law

$\ln \alpha = \ln t$

take the isothermal run at 240°C. The first step in the analysis of the data is to find the $\alpha$ vs. time values. These values were obtained as shown earlier, and are shown in Fig. 1. The next step is the statistical analysis of the data according to the method outlined in the Techniques of Analysis. As explained earlier, the data were treated according to a power series technique because of its inherent simplicity and its amenability to computer methods. The program developed was a least squares polynomial program. Table 3 lists the set of kinetic models used in this study. The final result of the analysis of variance for the least squares statistical regression of the data shows the progres-

TABLE 4

Polynomial regression of degree 1 by the Carter—Valensi model where $z = 0.9$ at 240°C: table of residuals.

| Observation no. | *t* value (min) | g(α) value | g(α) estimate | Residual |
|---|---|---|---|---|
| 1 | 2.00000 | 0.00022 | −0.00575 | 0.00597 |
| 2 | 4.00000 | 0.00483 | 0.00400 | 0.00083 |
| 3 | 6.50000 | 0.01403 | 0.01620 | −0.00217 |
| 4 | 9.00000 | 0.02507 | 0.02840 | −0.00332 |
| 5 | 11.50000 | 0.03759 | 0.04059 | −0.00300 |
| 6 | 14.00000 | 0.04970 | 0.05279 | −0.00309 |
| 7 | 16.50000 | 0.06220 | 0.06498 | −0.00278 |
| 8 | 19.00000 | 0.07565 | 0.07718 | −0.00153 |
| 9 | 24.00000 | 0.10578 | 0.10157 | 0.00421 |
| 10 | 29.00000 | 0.13049 | 0.12596 | 0.00453 |
| 11 | 34.00000 | 0.15575 | 0.15036 | 0.00539 |
| 12 | 39.00000 | 0.17667 | 0.17475 | 0.00192 |
| 13 | 44.00000 | 0.19335 | 0.19914 | −0.00580 |
| 14 | 49.00000 | 0.22181 | 0.22353 | −0.00173 |
| 15 | 54.00000 | 0.24849 | 0.24793 | 0.00057 |

sive fit of the g(α) vs. time for polynomials of degree one or higher. The program terminates when the polynomial of the best fit as determined by the improvement in terms of the sum of squares is reached. It should be pointed out that the highest polynomial of any physical meaning is that equation of order one with respect to time. Therefore, even though the program terminated with a third degree polynomial, we may only take the analysis of variance for a first degree polynomial. Theoretically, the value of the intercept should be zero. Unfortunately, due to machine as well as human error, slight deviations from that value will almost inevitably occur. The slope of the line represents the pseudo rate constants as shown in Table 3. What is the criterion for selecting one model over another? This question can be answered as follows. The *F* value is often used as a statistical fit test in many analyses. This same approach was used here in which it was found that comparing the *F* values of the different models and choosing the largest *F* value (the larger the *F* value the closer is the curve to a straight line) a uniform rule was established to determine goodness of fit.

As an example, we shall look at the results of a run taken at 240°C, in which it was found by the method above that the Carter—Valensi model for $z = 0.9$ fitted the data best, as shown in Table 4 and graphically in Fig. 2. The first column is the data point count. The second column, *t*, represents the time parameter (in min) for the reaction. The third column represents the value of g(α) for each value of α from Fig. 1. This is the integrated function of the solid state differential equation. In this case, the function is a diffusion model. The last column is the difference between the experimental g(α) and the "calculated" g(α).

Proceeding in like fashion through a wide range of temperatures we can slowly establish an overall picture of the reaction mechanism. Changes of mechanism can be detected by the inability of fitting the data to a first order

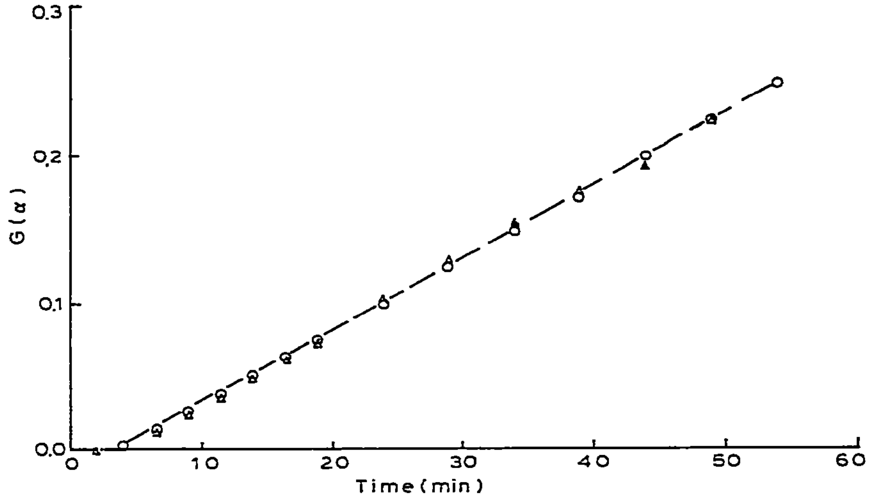

Fig. 2. Polynomial regression of the Carter—Valensi model where $z = 0.9$ at 240°C. △, $g(\alpha)$; ○, estimated $g(\alpha)$.

regression. In this case, we would note where the incipient deviation from a straight line is located and apply the computer program at that point to search for the best model. Thus, a history of the reaction is developed on a logical basis. By this technique the following conclusions have been reached on the pyrolysis of powdered xylan.

### *First order nucleation mechanism for the range 200—235° C*

In this range of temperatures, pyrolysis times ranged from about 79 to 80 min in extent. In all isothermal runs a large exothermic peak manifested itself early in the reaction.

It appears that the nucleation mechanism commences at sites on the particle in which imperfections of a physical nature are present. The undulating features of the reacted particle seem to bear out the hypothesis that trapped gas attempts to escape from the particle early in the reaction. The sites appear to form in a random fashion.

### *The Carter—Valensi model for the range 240—255° C*

The derivation and discussion for this model are given elsewhere [11]. Once again, the same procedures were used as in the nucleation models to find the best fit and compared to evaluate the difference between the corresponding empirical equations. It must also be pointed out that no empirical equation of the power type had an integral exponent, leading to the assumption that a more complex mechanism exists. The DSC plots show the exothermic peak shifting closer to the beginning of the reaction and inevitably becoming larger and steeper.

### *The Avrami—Erofyev model for the range 275—290° C*

This model where $r = 1/2$ is the special case of one dimensional growth. Here, there is a zero nucleation rate (saturation of point sites). In addition, the slopes of the DSC output were almost vertical with respect to the exothermic peak.

It is clear that, although an empirical order can be fitted to the data at any temperature, it should be understood that any value of the exponent, $n$, for the kinetic expression $d\alpha/dt = k(1 - \alpha)^n$ which is not integral or which has not been derived from some mathematical model has no physical meaning and thus cannot help us to understand the mechanism.

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## REFERENCES

1 H.C. Anderson, J. Polym. Sci., Part C, 6 (1965) 175.
2 H.L. Friedman, J. Polym. Sci., Part C, 6 (1965) 183.
3 K.E.J. Barrett, J. Appl. Polym. Sci., 11 (1967) 1617.
4 B. Carroll and E.P. Manche, J. Polym. Sci. 9 (1965) 1895.
5 T.A. Clarke and J.M. Thomas, Nature (London) 219, (1968) 1149.
6 K. Kishore, V.R. Pai Verneker and M.N.R. Nair, J. Appl. Polym. Sci., 20 (1976) 2355.
7 A.R. Allnatt and P.W.M. Jacobs, Can. J. Chem., 46 (1968) 111.
8 P.W.M. Jacobs and F.C. Tompkins, in W.E. Garner (Ed.), Chemistry of the Solid State, Butterworths, London, 1955, pp. 184—267.
9 B.N.N. Achar, G.W. Brindley and J.H. Sharp, Proc. Int. Clay Conf., Jerusalem, Israel, Vol. 1, 1966.
10 K. Shimizu, F. Teratani and K. Miyazaki, J. Jpn. Wood Res. Soc. 16 (1969) 114.
11 R.E. Carter, J. Chem. Phys., 34(6) (1961) 2010.