Thermochimica Acta, 90 (1985) 157-167
Elsevier Science Publishers B.V., Amsterdam - Printed in The Netherlands

KINETIC ANALYSIS OF LIGNIN PYROLYSIS USING NON-ISOTHERMAL TGA DATA

EITAN AVNI *

Department of Chemical Engineering, Florida State University, Tallahassee, FL 32306 (U.S.A.)

ROBERT W. COUGHLIN

Department of Chemical Engineering, University of Connecticut, Storrs, CT 06268 (U.S.A.)

(Received 15 February 1985)

ABSTRACT

The kinetics of lignin pyrolysis were investigated using TGA in the range 20-800°C at atmospheric pressure. The present study utilized an improved analytical technique for calculating the kinetic parameters from lignin pyrolysis data. The activation energy appears to depend linearly on conversion up to 0.4 conversion level ($E' = 13.96 + 69.42X'$, kcal g-mol^{-1}) and then the activation energy remains constant at 41 kcal g-mol^{-1}. It appears that a conversion-dependent activation energy model is simply a special case of a Gaussian distribution of an activitation energy model; both models suggest a variation in bond energies with the degree of ring condensation.

INTRODUCTION

The increased interest in wood and its components' conversion processes to produce clean chemicals and alternative fuels make it imperative to obtain a fundamental understanding of the pyrolysis, i.e., the initial step in combustion, gasification and liquefaction processes. The knowledge of the kinetics of thermal reactions is vital for understanding and predicting the pyrolysis behavior [1-8] and other thermal reactions of lignin, and related wood materials.

The pyrolysis behavior of lignin, wood and related biomass material is frequently studied by measuring the evolution of products [4,6,8,10] and/or by measuring the weight loss versus time and temperature [2,9]. This information, coupled with an Arrhenius-type equation is then used to estimate the activation energy, frequency factor, and reaction order of the pyrolysis reactions.

---

* To whom correspondence should be addressed.

Thermogravimetric analysis (TGA) is a powerful technique [11] that provides a semiquantitative analysis of the pyrolysis behavior under well-defined reaction conditions. Moreover, the usage of a small sample with fine particle size can minimize any mass or heat transfer resistance. TGA is usually carried out in an isothermal or a non-isothermal (dynamic) mode. Both techniques have a number of drawbacks [12–14], however, the advantages of the dynamic mode [11] are that considerably less experimental data is needed than the isothermal mode, and the pyrolysis kinetics can be followed versus the dynamic temperature.

Earlier kinetic studies of lignin pyrolysis have been conducted under a variety of experimental conditions resulting in a wide range of kinetic data. Even those carried out in TGA vary in their kinetic parameters due to different assumptions used in deriving the kinetic rates. This paper utilizes an improved analytical technique for calculating the kinetic parameters from lignin pyrolysis data, and it also presents a kinetic model for pyrolysis with an activation energy as a function of the lignin conversion.

EXPERIMENTAL

Lignin samples

Aspen wood lignin which was extracted from a dilute basic solution of steam-exploded Aspen wood, followed by precipitations with dilute HCl has been used in this study.

Thermogravimetric analyzer (TGA)

Apparatus

The Dupont 950 TGA (Fig. 1) was used with the electronic programming and recording facilities of the 900 differential thermal analyzer; it consisted of a fixed horizontal furnace with a null balance unit which slid into the furnace. The balance had an asymmetrical beam with a taut-band meter suspension which provided the restoring force. A quartz balance arm was fitted to the beam through a metal clip and together these compensated the weight measurement for expansion effects on heating. The arm carried a small sample holder in the center of the furnace close to the thermocouple; the opposite arm was counterbalanced (approximately by adding weights and accurately by electrical compensation) and carried the shutter of a photocell/shutter null detector.

The instrument could operate under ambient pressure or in a vacuum as low as 15 Torr. A sample weight of about 10 mg was pyrolyzed using the TGA. The results were plotted directly as weight or percentage of original weight and rate (dW/dt) versus temperature. The plot sensitivity could be

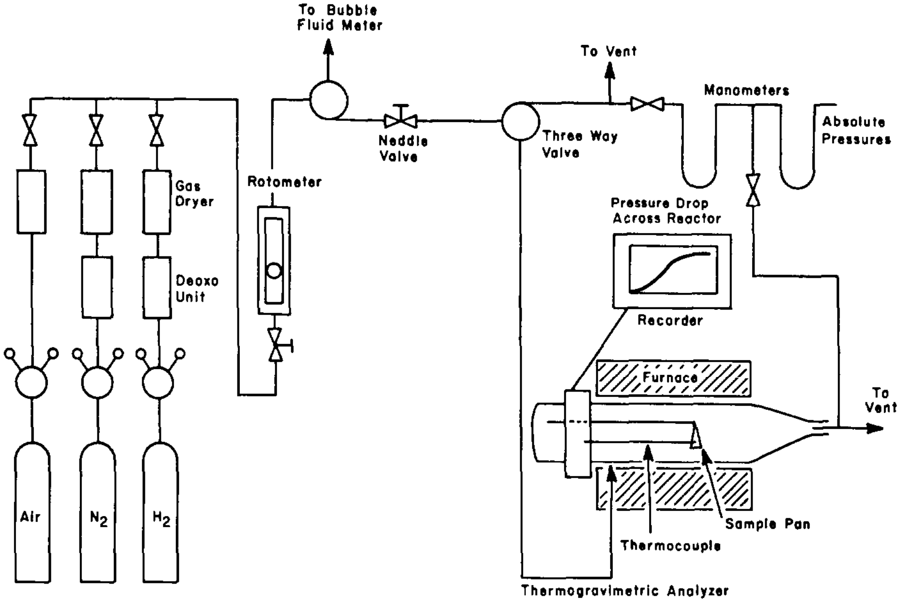

Fig. 1. Thermogravimetric analyzer flow system.

adjusted over the range 0.1–20 mg/in. of chart. The heating rate could be varied between 0.5 and 100°C min^{-1}. The TGA could be operated either under isothermal mode (static temperature) for a desired time or under dynamic mode (dynamic temperature) for a desired temperature range. The envelope of the TGA cell was modified by creating a second gas inlet in order to allow a flow of reactive gas atmosphere over the sample. When the TGA cell operated in a vacuum, the gas inlet was connected to a manometer while the gas outlet was connected to a vacuum pump.

Procedure

At the beginning of each day the balance was calibrated using calibration weights. The heating rate linearity as well as the recorded temperature were checked and calibrated accordingly. The recorded temperature was compared to a temperature measured by a J-type thermocouple inserted in the TGA envelope. The lignin sample was dried at 120°C for 24 h in a vacuum oven. The moisture content of the undried lignin was about 4–8 wt%, depending upon the lignin source.

The lignin (about 10 mg of 200 mesh particle size) was placed in the platinum sample pan, the envelope was connected to the balance using the threaded collar and the system was purged with dried nitrogen (2 ppm oxygen, Nixox catalyst) to remove all oxygen and moisture from the system. After purging the system for 10 min, the flow rates of the inert and the reactive gases were adjusted, and the lignin sample was weighed accurately (±0.05 mg). At the end of each run, oxygen was passed through the system in order to burn the coke deposits on the platinum pan and tar deposits on the envelope. Several runs were carried out using different heating rates of 0.5–100°C min^{-1} under different ambient atmospheres or in a vacuum. Each experiment was started at room temperature and terminated at 800°C. Several runs (at least three) were carried out at the same heating rate in order to assure reproducible TGA data.

REACTION KINETICS

Many investigators studying the pyrolysis kinetics of carbonaceous materials found it rather difficult to study the complex thermolysis, and the mass and heat transfer resistances involved in the pyrolysis process. Thus, the pyrolysis process, which is comprised of multiple elementary reaction pathways, was described by the general equation of the form

$$-\frac{\mathrm{d}W}{\mathrm{d}t} = k\mathrm{f}(W) \tag{1}$$

where W is the sample weight at time t, $\mathrm{f}(W)$ is a function of W, and k is the rate constant given by the Arrhenius equation

$$k = k_0\,\mathrm{e}^{-E/RT} \tag{1a}$$

where k_0 = frequency factor (min^{-1}), E = activation energy (kcal g-mol^{-1}), R = gas constant (kcal g-mol^{-1} K^{-1}), T = absolute temperature (K).

Many investigators [15,16] assumed that $\mathrm{f}(W) = W^n$, and $n = 1$, while others based their analysis on the fraction of non-decomposed material or conversion (X'), which was expressed by Van Krevelen's equation [17–19]

$$+\frac{\mathrm{d}X}{\mathrm{d}t} = k\left(1 - \frac{X'}{X'_\infty}\right)^n;\ 0 \leqslant \frac{X'}{X'_\infty} \leqslant 1 \tag{2}$$

where X' = conversion at $t = \infty$. The above kinetic models were analyzed by a wide variety of both dynamic and isothermal temperature methods. Most of the kinetic studies of lignin pyrolysis used eqns. (1) and (2) to calculate the apparent kinetic parameters (single, first-order reaction model). Table 1 compares the apparent kinetic parameters for the pyrolysis of lignin from different studies. The activation energy varied from 6 to 38.4 kcal mol^{-1},while the frequency factor varied from 5.6×10^0 to 4.3×10^{12} min^{-1}. The wide range of the frequency factor and the activation energy among the investigators is due to different methods of analysis, experimental apparatus and heat and mass transfer. All the investigators but the second one used the TGA as the pyrolysis reactor.

All the previous investigators have assumed a first-order process and a rate constant with an Arrhenius-type temperature dependence. This assumption is troublesome because of the lignin's inhomogeneity. This inhomogene-

TABLE 1

Comparison of apparent kinetic parameters for lignin pyrolysis

	Temp. (°C)	k_0(min^{-1})	E (kcal g-mol^{-1})
Present study	25–800	2.66×10^8	$13.96 + 69.42X'$ for $0 < X' < 0.4$ 41 for $0.4 < X' < 0.6$
Stamm [15]	95–250	8.4×10^{11}	23
Krieger and Chen [21]	160–680	4.7×10^2	6
	410–1890	9×10^1	7.3
Tang and Eickner [20]	280–344	9.9×10^5	21
	344–435	5.6×10^0	9
Ramiah [22]	245–330	–	13.0
Hirata [31]	280–300	4.3×10^{12}	34.8

ity typically produces a distribution of rates rather than a single sharp rate for any chemical reaction. Such a distribution can be understood from the work of Stein et al. [29] and Vernon [30] which suggests a variation in bond energies with the degree of ring condensation. Using a two-parameter fit to define a rate has contributed to the wide variation in published rates.

MODEL AND ANALYSIS

Since it is impossible to identify all the elementary chemical reactions in the pyrolysis of a complex polymer such as lignin, most reported models are based on either the original weight of the lignin or its final weight. Following the first convention, the conversion is defined as a fraction

$$X' = (W_0 - W)/W_0 \tag{3}$$

For pyrolysis of a large and complex molecule like lignin, it is convenient to assume that the apparent activation energy is dependent on the extent of pyrolysis which involves many parallel and competitive chemical reactions. Here, the apparent activation energy is a function of conversion

$$E' = \mathrm{f}(E'_0, X') \tag{4}$$

where E'_0 = activation energy at zero conversion, X' = conversion. The activation energy dependency on conversion can be assumed to follow a simple equation

$$E' = E'_0 + aX' \tag{5}$$

where a = constant. The rate of weight loss is then assumed to follow the simple kinetic rate law

$$-(1/W_0)(\mathrm{d}W/\mathrm{d}t) = k_0 \exp(-E'/RT)\ \mathrm{F}(W) \tag{6}$$

where $\mathrm{F}(W)$ = function of residue.

According to the logarithmic form of eqn. (6), plotting $\ln(-1/W_0)$ (dW/dt) versus $1/T$ (K) for constant values of W or X' will give values of the activation energy, E', at different conversions. Knowing the activation energy, temperatures and the rate of weight loss at various conversions, one can calculate the values of $\ln(k_0 F(W))$. If one assumes that $F(W) = (W/W_0)^n$, a plot of $\ln[k_0 F(W)]$ versus $\ln(W/W_0)$ yields the frequency factor and the order of reaction.

Gardner et al. [23] used thermobalance techniques to study the hydrogasification of coal over the temperature range 0–1200°C and a pressure range of 0–1000 psia. A model in which the activation energy was assumed to be the linear function of the extent of reaction was fitted to the experimental data.

Chermin and Van Krevelen [24] theorized that a secondary evolution from the semicoke of coal became progressively more difficult as the reaction proceeded. This behavior was represented by the conversion-dependent activation energy in the following rate equation

$$dV/dt = k_0(V^* - V)\exp\{-[E_{\max} - a(V^* - V)/RT]\} \tag{7}$$

where V^* = volatile lost up to time $t = \infty$ (ultimate yield), fraction of original weight, V = volatile lost, fraction of original weight at time t, $V^* - V = 1 - X'$, a = constant.

It can be shown that eqn. (7) is simply a special case of eqn. (8a), proposed by Pitt [26].

$$(V^* - V)/V^* = \int_0^{\infty} \exp[-k_0 t \exp(-E/RT)] f(E) dE \tag{8a}$$

$f(E)$ = Gaussian distribution function

$$f(E) = [\sigma(2\pi)^{1/2}]^{-1} \exp[-(E - E_0)^2/2\sigma^2] \tag{8b}$$

where σ = standard deviation (kcal mol^{-1}), E_0 = mean activation energy (kcal mol^{-1}).

Pitt [26] assumed thermal decomposition of coal to consist of a large number of independent chemical reactions. Differences in the strength of chemical bonds throughout the molecule would cause marked differences in the temperatures at which the various bonds rupture.

If one approximates the overall process as a first-order rate equation [25]

$$dV_i/dt = k_i(V_i^* - V_i) \tag{9a}$$

or in an integrated form at constant temperature

$$V_i^* - V_i = V_i^* \exp[-k_0 t \exp(-E/RT)]_i \tag{9b}$$

The problem can be simplified by assuming that the k_i values differ only in activation energy ($k_{i0} = k_0$ for all i) and that the number of reactions is large enough to permit E to be expressed as a continuous distribution function, $f(E)$, with $f(E)dE$ representing the function of the potential volatile loss, V^*, which has an activation energy between E and $E + \mathrm{d}E$. Therefore, V^* can be written as

$$\mathrm{d}V^* = V^* \mathrm{f}(E)\mathrm{d}E \text{ with } \int_0^\infty \mathrm{f}(E)\mathrm{d}E = 1 \tag{10}$$

Integrating eqn. (10)

$$\int_0^V \mathrm{d}V^* = V^* \int_{E_{\max}}^{E} \mathrm{f}(E)\mathrm{d}E$$

while assuming that

$$\mathrm{f}(E) = (E_{\max} - E_{\min})^{-1} \text{ and } a = (E_{\max} - E_{\min})/V^*$$

will result in $E = E_{\max} - a(V^* - V)$, which is the conversion-dependent activation energy shown in eqn. (7). Chermin and Van Krevelen [24] estimated values for the uniform distribution using data on the residual volatile content of chars. The shape of Chermin and Van Krevelen's distribution curve is very different from those formed by Pitt [26] and Anthony and Howard [27].

RESULTS AND DISCUSSION

Figure 2 shows typical TGA experimental results for lignin pyrolysis at different heating rates under a nitrogen atmosphere. The heating rates used in the study do not appear to affect the final conversion, however, it slightly influences the reaction rates. When eqn. (6) is divided by $\mathrm{d}T/\mathrm{d}t = \mathrm{HR}$ (heating rate) we get a new equation

$$(-1/W_0)(\mathrm{d}W/\mathrm{d}T) = (k_0/\mathrm{HR}) \exp(-E'/RT)\,(W/W_0)^n \tag{11}$$

This equation predicts that at higher heating rates, higher temperatures

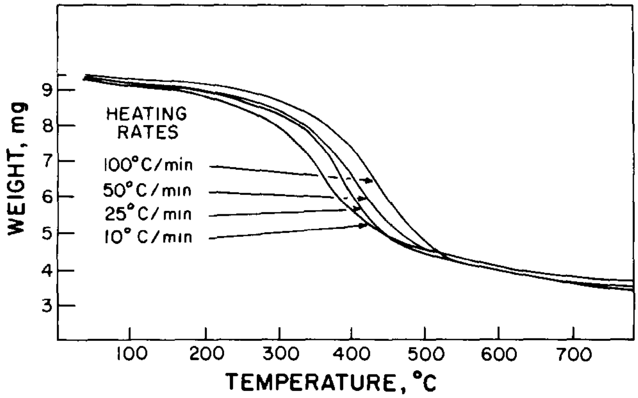

Fig. 2. TGA curves of Iotech lignin at different heating rates; 1 atm N_2.

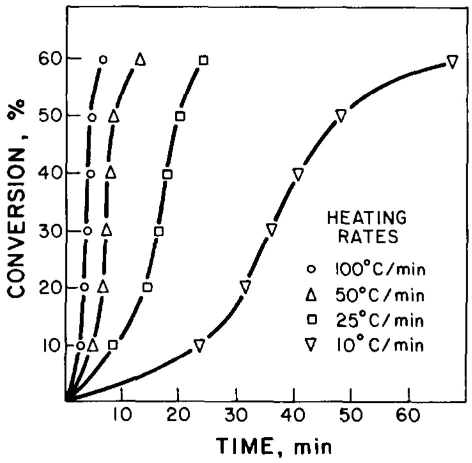

Fig. 3. Conversion of Iotech lignin versus time at different heating rates; 1 atm N_2.

are required to achieve the same conversion level. Figures 3 and 4 show the conversion at different heating rates (dynamic pyrolysis) versus time and temperature, respectively. Figure 5 shows the Arrhenius plots of $\ln[-(1/W_0)(dW/dt)]$ versus $1/T$ (K) at constant conversions but different heating rates. It indicates that E' is insensitive to heating rate. In the proceeding step of the kinetic analysis, E' and $\ln[k_0 F(W)]$ were estimated by using a regression analysis package. Figure 6 shows a plot of the activation energy obtained by the above analysis of lignin pyrolysis (in nitrogen) versus conversion. The activation energy appears to depend linearly on conversion up to 0.4 conversion level, and then the activation energy remains constant, probably since the bonds in the remaining char are

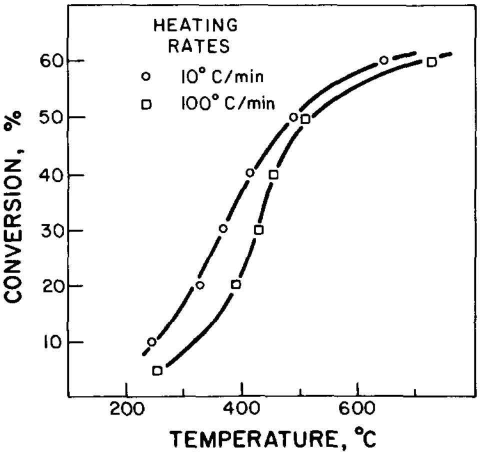

Fig. 4. Conversion of Iotech lignin versus dynamic temperature; 1 atm N_2.

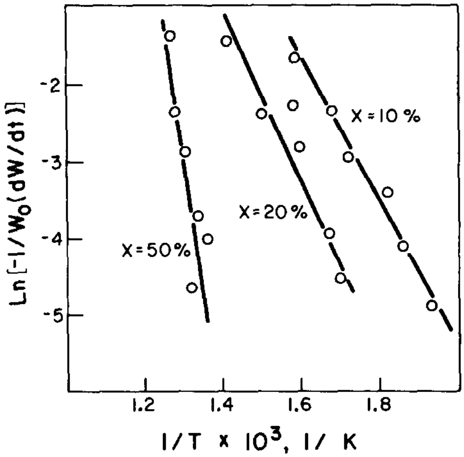

Fig. 5. Arrhenius plot at different conversions; Iotech lignin; 1 atm N_2.

relatively homogeneous in strength. The activation energy can be correlated as $E' = 13.96$ kcal g-mol^{-1} + $69.42X'$; over the conversion range 0–0.4.

Estimates of the reaction order ($n = 1.09$) and pseudo rate constant ($k_0 = 2.60 \times 10^8$ min^{-1}) are computed from the knowledge of $\ln[k_0 F(W)]$ at different conversion levels (see Fig. 5). Figure 7 depicts the plot of $\ln[k_0 F(W)]$ versus $\ln(W/W_0)$.

Comparison of the apparent first-order rate constant for lignin pyrolysis obtained in this study to those obtained in other studies of lignin pyrolysis are summarized in Table 1. The "apparent kinetic rate" appears to vary with

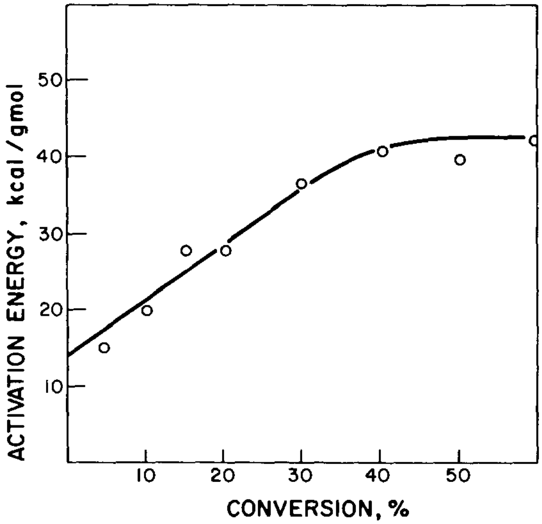

Fig. 6. Activation energy versus conversion; Iotech lignin; 1 atm N_2.

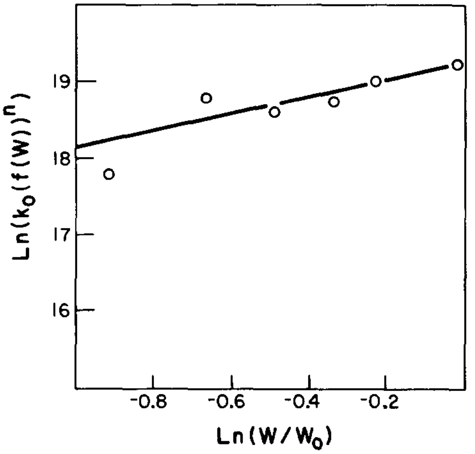

Fig. 7. Determination of reaction rate constant and reaction order; Iotech lignin; 1 atm N_2.

the experimental configuration and method of analysis. One reason for a variation in rates is that the experiments differ in pressures and rates of heat and mass transfer. Our pyrolysis experiments with seven lignins indicate the insensitivity of the species evolution rates [4,6] to the lignin source or extraction processes. Krieger and Chen [21] and Tang and Eickner [20] analyzed the rates at two temperature ranges (see Table 1) and estimated different apparent kinetic parameters for the two temperature ranges. A similar analysis of the rates was found by Van Krevelen and Fitzgerald [25]. The Arrhenius plot for the methane evolution in coal pyrolysis was calculated using eqn. (9) which is a single, first-order rate equation.

The estimation of V^*, the ultimate volatility, is a difficult task. Krieger and Chen took V^* as the cumulative volatiles at infinite time. Other investigators analyzed their data using ultimate volatiles (V^*) that depend on the temperature–time history [28].

In the present study we assume that the activation energy is a function of conversion, which indicates a linear distribution of activation energies for lignin weight loss rather than a single rate. The rate constant is a function of conversion (X'), the frequency factor (k_0), and activation energy at zero conversion (E_0'), while in the Gaussian distribution of the activation energy model (see eqn. 7) the three kinetic parameters are: frequency factor (k_0), average activation energy (E_0) and the standard deviation (σ) of activation energy which is assumed to follow a Gaussian distribution.

REFERENCES

1 T. Milne, Pyrolysis—the thermal behavior of biomass below 600°C, SERI/TR-33-23d, II, Chap. 5, 1979.

2 W.K. Tang and W.K. Neill, J. Polym. Sci., 6 (1984) 65.
3 W.S.L. Mok and M.J. Antal, Jr., Thermochim. Acta, 68 (1983) 155, 165.
4 P.R. Solomon, H.H. King, E. Avni and R.W. Coughlin, ACS Fuel Div. Prepr., 28 (1983) 319, 307.
5 E. Avni and R.W. Coughlin, Holzforschung, 39 (1985) 33.
6 E. Avni, R.W. Coughlin, P.R. Solomon and H.H. King, Fuel, in press.
7 P.C. Lewellen, W.A. Peters and J.B. Howard, 16th Symp. of Combustion, The Combustion Institute, Pittsburgh, PA, 1977, p. 1471.
8 F. Thurner and U. Mann, IEC Proc. Des. Dev., 20 (1981) 482.
9 M.J. Antal, Jr., H.L. Friedman and F.E. Rogers, Combust. Sci. Technol., 21 (1980) 141.
10 R.J. McCarter, J. Appl. Polym. Sci., 17 (1973) 183.
11 E.S. Freeman and B. Caroll, J. Phys. Chem., 62 (1958) 394.
12 A. Blazek, in J.F. Tyson (Ed.), Thermal Analysis, Van Nostrand Reinhold, London, 1973.
13 T. Daniels, Thermal Analysis, Wiley, New York, 1972.
14 W.W. Wendlandt, Thermal Methods of Analysis, Wiley, New York, 1974.
15 A.J. Stamm, Ind. Eng. Chem., 48 (1956) 413.
16 F.C. Beall, Wood Fiber, 1 (1967) 215.
17 D.W. Van Krevelen, C.V. Van Heerden and F.J. Huntjens, Fuel, 20 (1951) 253.
18 K. Akita and M. Kase, J. Polym. Sci., Part A, 5 (1967) 833.
19 J.N. Barooah and V.D. Long, Fuel, 55 (1976) 116.
20 W.K. Tang and H.W. Eickner, For. Prod. Res. Lab. Rep. 82, Madison, WI, 1964.
21 B.B. Krieger and R.W.C. Chen, J. Appl. Polym. Sci., 26 (1981) 153.
22 M.V. Ramiah, J. Appl. Polym. Sci., 19 (1970) 1323.
23 N. Gardner, E. Samuels and K. Wilks, Adv. Chem. Ser., 131 (1974) 217.
24 H.A.G. Chermin and D.W. Van Krevelen, Fuel, 36 (1957) 85.
25 D.W. Van Krevelen and D. Fitzgerald, Fuel, 38 (1959) 17.
26 G.J. Pitt, Fuel, 41 (1962) 267.
27 D.B. Anthony and J.B. Howard, 15th Symp. of Combustion (International), 1975, p. 1303.
28 D.Q. Tran and G. Rai, Fuel, 57 (1978) 293.
29 S.E. Stein, D.M. Golden and S.W. Benson, J. Phys. Chem., 81 (1977) 314; S.E. Stein and B.D. Barton, Thermochim. Acta, 44 (1981) 265.
30 L.W. Vernon, Fuel, 59 (1980) 102.
31 T. Hirata, Mokuzi Gakkaishi, 19 (1973) 451.