Antal, M. J., Jr.; Várhegyi, G.; Jakab, E.: Cellulose pyrolysis kinetics: Revisited.
Ind. Eng. Chem. Res. **1998**, *37* 1267-1275. *doi:* 10.1021/ie970144v

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Cellulose Pyrolysis Kinetics: Revisited

Michael Jerry Antal, Jr.*
Hawaii Natural Energy Institute and the Department of Mechanical Engineering,
University of Hawaii at Manoa, Honolulu, Hawaii 96822
Gábor Várhegyi and Emma Jakab
Research Laboratory for Inorganic Chemistry, Hungarian Academy of Sciences,
Pf. 132, Budapest 1518, Hungary

Abstract

In the same thermogravimetric analyzer (TGA) under identical conditions, samples of pure, ash-free cellulose (i.e. Avicel PH-105, Whatman CF-11, Millipore ash-free filter pulp, and Whatman #42) obtained from different manufacturers undergo pyrolysis at temperatures which differ by as much as 30 °C. Thus the pyrolysis chemistry of a sample of pure cellulose is not governed by a universal rate law, as is the case with a pure hydrocarbon gas (for example). Nevertheless, the pyrolytic weight loss of all the samples studied in this work is well represented by a high activation energy (228 kJ/mol), first order rate law at both low and high heating rates. These results do not corroborate the recent findings of Milosavljevic and Suuberg (1995). For a particular cellulose sample (for example Avicel PH-105), variations in the pre-exponential constant determined at different heating rates reflect uncontrolled, systematic errors in the dynamic sample temperature measurement (thermal lag).

Introduction

A recent review of the literature of cellulose pyrolysis (Antal and Várhegyi, 1995) concluded that the pyrolysis of a small sample of pure cellulose is characterized by an endothermic reaction governed by a first order rate law with a high activation energy (ca. 238 kJ/mol). We employed the terminology “high activation energy (ca. 238 kJ/mol)” to indicate that, even for a particular cellulose (e.g. Avicel), considerable uncertainty (± 10 kJ/mol or more) exists in any determination of the exact value of its activation energy (see below). Almost immediately after the review was published, these conclusions were contradicted by the findings of Milosavljevic and Suuberg (1995), who hypothesized the role of a high temperature, low activation energy (140 - 155 kJ/mol) step competing with a low temperature (below

327 °C), high activation energy (218 kJ/mol) reaction during the pyrolysis of a Whatman CF-11 fibrous cellulose powder. Milosavljevic and Suuberg argued that their findings were consistent with the results of earlier kinetic studies of many workers, which were summarized in Figures 1 and 2 of their paper. They used the kinetic data displayed in their Figure 1 to rationalize the existence of the purported high temperature, low activation energy (140 - 155 kJ/mol) reaction. We were surprised to find our high activation energy (205 kJ/mol) rate measurements at 80 K/min (Várhegyi et al., 1989) displayed in that figure, with no discussion of the fact that our data contradicted their hypothesis. Also included in their Figure 1 were the kinetics data of Tabatabaie-Raissi et al. (1989). But his measurements were made in a covered sample pan that greatly enhanced vapor-solid interactions; consequently, his experiments did not offer a true measurement of the primary rate of cellulose pyrolysis and should not have been used to assert the existence of a low activation energy reaction. Likewise, the early rate measurements of Antal et al. (1980) were used to argue the existence of the low activation energy step, but Antal and his co-workers later showed (Antal, 1985; Antal et al., 1985; Antal and Várhegyi, 1995) that his early measurements were compromised by heat transfer intrusions and did not represent a true determination of the temperature dependence of the rate law. In summary, our scrutiny of Milosavljevic and Suuberg’s Figure 1 left us with doubts about the role of a high temperature, low activation energy reaction in the pyrolysis of cellulose. To examine the matter further, we measured the rates of pyrolysis of the same cellulose employed by Milosavljevic and Suuberg (1995) in our equipment. We also studied the kinetics of other cellulose samples to learn if different pure celluloses evidence markedly different pyrolysis behavior. This paper documents the surprising results of our investigations.

Apparatus and Experimental Procedures

The Perkin Elmer TGS-2 thermobalance used in this work has been described in earlier publications (Várhegyi et al., 1988). Linear heating rates of 1, 10 and 65ºC/min were employed. Since the highest reaction rate of an experiment is roughly proportional to the heating rate, 0.3 mg sample masses were used at 65ºC/min to keep the heat and mass fluxes low. But for such a small sample mass, buoyancy and other base line shift effects distort the char yields; consequently the 0.3 mg experiments were corrected by subtracting a TG curve measured under identical conditions with an empty sample pan. We also carried out two test experiments at 1ºC/min with 0.35 mg CF-11 cellulose, where the char yield was not corrected in this way. (Accordingly, these two tests were not included in the comparison of char yields discussed below.) All the experiments described herein were conducted in high-purity argon with a flow rate of 140 mL/min.

We remark that we were able to measure the weight loss of samples as small as 0.3 mg because the Perkin Elmer thermobalance used in this work possesses a sensitivity of 0.1 μg. The Dupont 951 instrument employed by Milosavljevic and Suuberg (1995) possesses a sensitivity of only 2 μg. The low sensitivity of the Dupont 951 instrument necessitates the use of large sample sizes, which considerably alters the observed pyrolysis behavior (see below).

Professor Suuberg was kind enough to supply us with a sample of Whatman CF-11 fibrous cellulose powder (0.15 wt % ash) taken from the same lot as the samples employed in his work. Thus there can be no question concerning the influence of sample composition on results obtained in the two laboratories. In addition, we examined the pyrolysis behavior of a Millipore ash-free cellulose filter pulp, and a Whatman #42 cellulose filter paper (0.01 wt % ash). Finally, to facilitate comparison with our earlier work, we executed some studies of an Avicel PH-105 microcrystalline cellulose with an ash content of less than 10 ppm.

Results and Discussion

Systematic experimental errors. In this subsection we address the following questions. How accurate is the rate of weight loss measurement determined by the Perkin Elmer instrument? How accurate is the dynamic temperature measurement? Are weight loss vs. temperature measurements stable over time?

The decomposition of calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$) is a benchmark measurement in thermogravimetry. Figure 1 of Antal and Várhegyi (1995) displays a comparison of measured rates of gas evolution during the decomposition of calcium oxalate by the Perkin Elmer thermobalance and a Balzers QMG-511 mass spectrometer. The exact agreement of these two independent measurements indicates that the thermogravimetric determination of the rate of weight loss is extremely accurate. This result is consistent with the claimed high sensitivity (0.1 μg) of the Perkin Elmer balance. To detect and estimate systematic errors in temperature measurement we studied the behavior of a Nickel Curie-point calibrant furnished by Perkin Elmer. At a heating rate of 10 °C/min the measured Curie-point temperature was 358 °C: 4 °C above the actual Curie-point temperature of 354 °C. At a heating rate of 65 °C/min the temperature measurement error increased to 11 °C above the Curie-point value. These measurements illustrate the pervasive (but usually unappreciated) presence of thermal lag during thermogravimetric studies. We remark that heat demand during an endothermic pyrolysis event increases exponentially with temperature according to Arrhenius kinetics. The Curie-point phase transition is effectively autothermal. Consequently, Curie-point measurements of thermal lag only provide an accurate indication of the temperature measurement error associated with infinitely small samples of cellulose. Finite samples undergoing endothermic pyrolysis evoke larger thermal lags than those estimated by the Curie-point determination. Recent careful experimental measurements by Di Blasi and Lanzetta (1997) and Drummond and Drummond (1996), and numerical simulations by Narayan and Antal (1996) concur that thermal lag (i.e. the difference between the true sample temperature and the thermocouple temperature) increases dramatically with heating rate. The effects of this thermal lag on kinetic analysis will be discussed later.

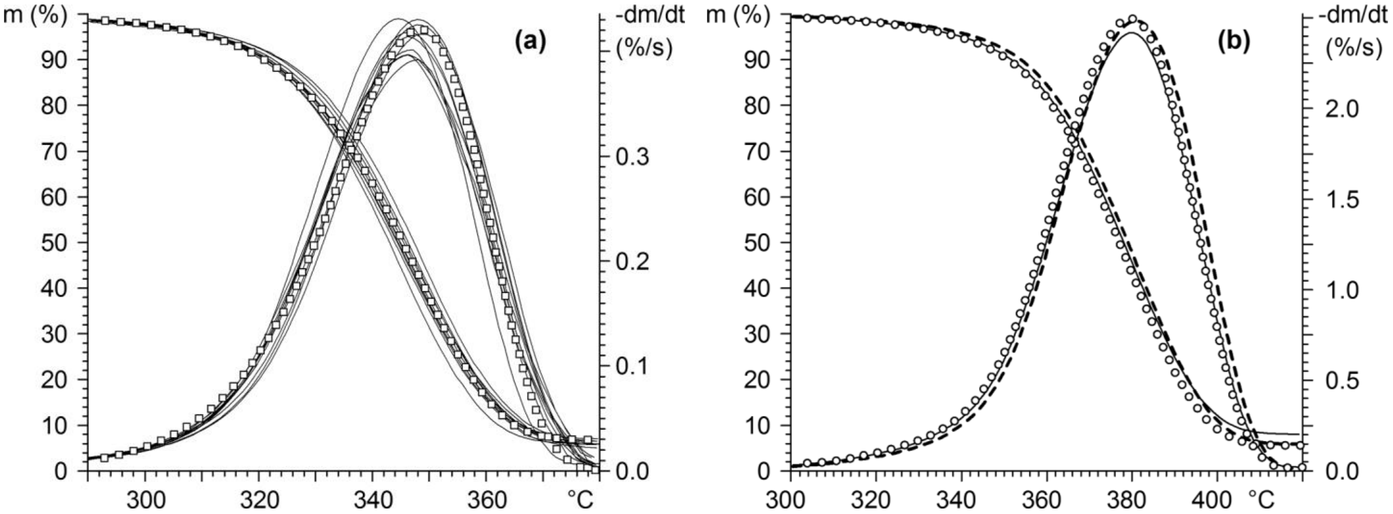

Figure 1. Reproducibility of the Avicel experiments. Panel A: 10 experiments executed over a ten year period at a nominal heating rate of 10 °C/min. Measured, actual heating rates were 9.6 ± 0.2 °C/min. A simultaneous kinetic evaluation of the TG curves, assuming identical kinetic parameters, resulted in E = 237 kJ/mol, log A/s^{-1} =18.0, n = 1, and m_f = 0.07. The simulated curve using these kinetic parameters at the average, actual heating rate is denoted by □. Panel B: 3 experiments at 65 °C/min measured within three consecutive days.

Figure 1a displays all the publishable quality weight loss measurements obtained in Budapest during the past ten years of 2 - 3 mg samples of Avicel PH-105 cellulose heated at 10 °C/min. The Avicel celluloses were taken from cans stored in Honolulu and opened in 1986, 1990, and 1996. The ten weight loss curves agree within 5 °C at a fixed value of weight loss. We call our readers' attention to the fact that most of the curves displayed in Figure 1a lie parallel to one another: each is systematically displaced by only a few degrees Celsius from the mean value. Moreover, the three omitted curves were also parallel to those displayed, but systematically shifted in temperature by an unacceptable amount. What is the cause of these systematic displacements of the weight loss curves? Over 15 years ago Antal et al. (1980) reported systematic temperature shifts of 20 to 25 °C at all heating rates in a Dupont 951 TGA, depending upon whether the sample thermocouple was slightly upstream or slightly downstream of the 2 mg cellulose sample. Thus, small changes in the placement of the thermocouple relative to the sample result in shifts of the weight loss curves identical to those shifts displayed in Figure 1a. The three curves which were omitted from Figure 1a were shifted by an unacceptable amount due to a misalignment of the thermocouple. These observations highlight the importance of periodic Curie-point calibrations of the TGA during an experimental campaign.

Figure 1b displays similar, recent data obtained at 65 °C/min. At this higher heating rate the data from the three Avicel PH-105 samples agree to within about 4 °C. We attribute this good agreement to the fact that the data was acquired over a two-day period, which involved no changes of the thermocouple's position.

Effects of systematic and random experimental errors on kinetic analysis. In this subsection we address the following questions. Recognizing our inherent inability to obtain perfectly reproducible weight loss curves, how should kinetic analysis of various weight loss curves (obtained under the same experimental conditions) be accomplished? Likewise, recognizing the increasing presence of thermal lag and the concomitant loss of accuracy in measuring temperature at higher heating rates; how should the kinetic analysis of data, obtained over a range of heating rates, be accomplished and interpreted?

Consider a kinetic analysis of the differential thermogravimetric curves (DTG curves) displayed in Figure 1a. For the sake of illustration, we employ the first-order rate equation:

$$d\alpha/dt = k\,(1 - \alpha) \qquad (1)$$

where $\alpha = (m(t) - m_f) / (m_0 - m_f)$, $k = A \exp(-E/RT)$, m(t) is the time dependent sample mass, m_0 is the initial sample mass, m_f is the amount of solid residue formed during cellulose decomposition, A is the pre-exponential constant, E is the apparent activation energy, R is the gas constant, and T is the sample temperature. A non-linear, least squares (NLS) fit of this rate equation to all the data displayed in Figure 1a offers the following values for the three free parameters employed in the rate equation: E = 227 kJ/mol, $\log A/s^{-1} = 17.17$, and $m_f/m_0 = 0.059$. As seen in Figure 1a, simulated TG and DTG curves, that employ these kinetic parameters with the first order rate equation, enjoy satisfying agreement with the experimental data. Thus no special problems arise in the kinetic evaluation of weight-loss curves obtained under the same experimental conditions. We believe that the small systematic discrepancy between the model and the experimental data in the temperature range 300 to 325 °C is due to the low temperature char forming pathway (Arseneau, 1971; Broido, 1976; Bradbury et al., 1979; Várhegyi et al., 1994) which is not included in the first order kinetic model. We discuss this matter further below.

Table 1: Kinetic evaluation of Avicel cellulose DTG curves at different heating rates (See Figures 2a and 2c).

	Independent evaluation (variable E)				Simultaneous evaluation (identical E)			
dT/dt (°C/min)	E (kJ/mol)	log A ($\log s^{-1}$)	m_f	fit (%)	E (kJ/mol)	log A ($\log s^{-1}$)	m_f	fit (%)
1	245	19.0	0.11	1.9	236	18.2	0.10	2.2
10	235	17.8	0.06	1.8	236	17.9	0.06	1.8
65	230	17.2	0.02	1.9	236	17.7	0.03	2.1

Figure 2a displays DTG curves for Avicel PH-105 cellulose at 1, 10 and 65 °C/min, together with simulated data using the first-order rate law with best-fit parameters E and log A determined individually at each heating rate (see Table 1). The gradual decline in the values of both E and log A with increasing heating rate is a benchmark conundrum of the field. Similar trends were reported by Antal et al. (1980) over fifteen years ago, and more recently by Font et al. (1991) using a Mettler TG50 thermobalance, and Williams and Besler (1994) using a Stanton-Redcroft 280 TGA. A vexing aspect of this problem is the fact that the values of E and log A decrease in such a way that their ratio remains constant. Chornet and Roy (1980) called attention to this phenomenon, known as the “compensation effect”, sixteen years ago.

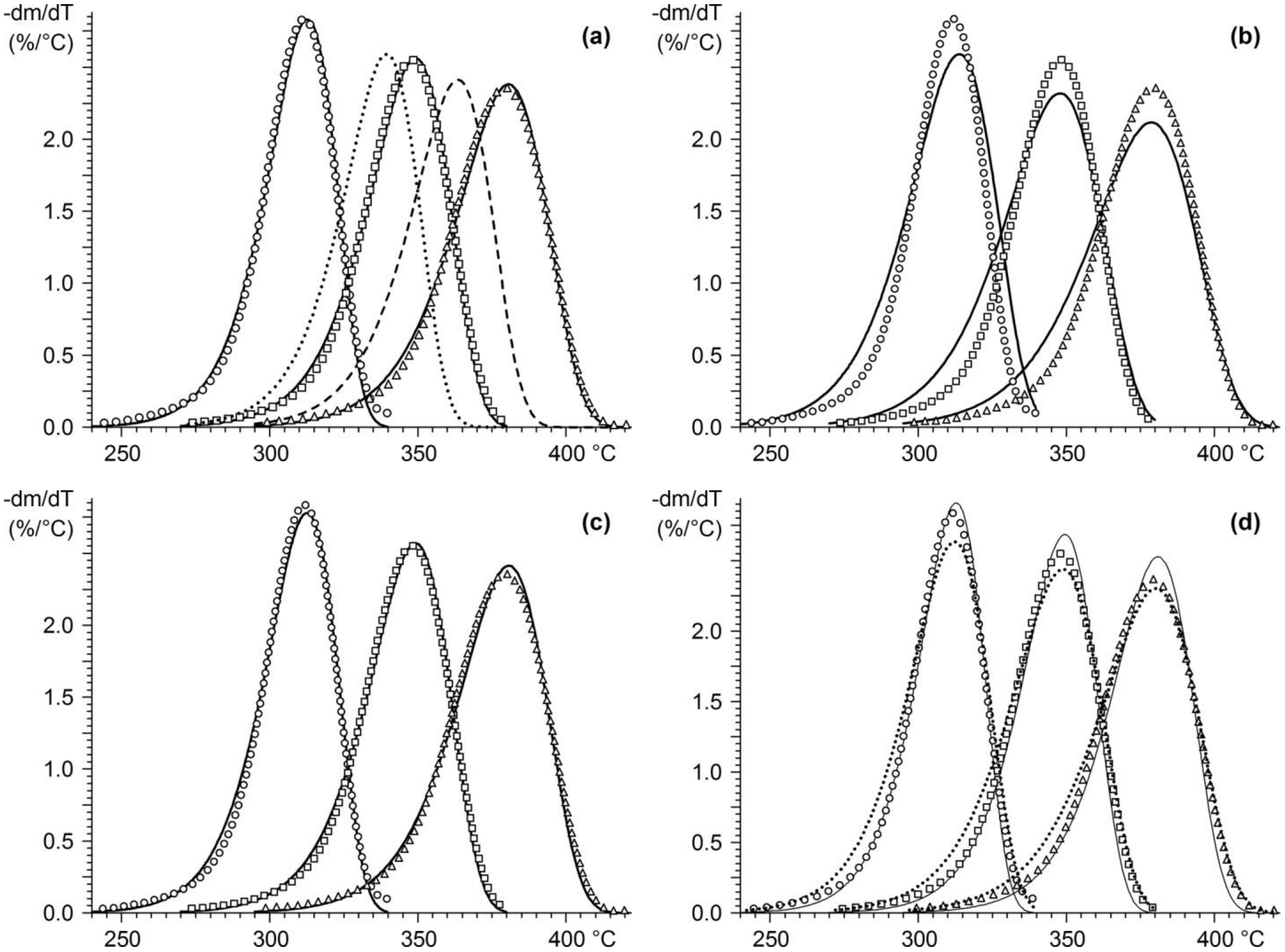

Figure 2. Kinetic evaluation of three Avicel DTG curves measured at 1 (○), 10 (□), and 65 (Δ) °C/min. Solid lines represent simulated data. Panel A: Solid lines represent simulated data from an independent evaluation of E and log A (see Table 1). Dotted and dashed lines represent simulated data at 10 and 65 °C/min using the best fit parameters (E = 245 kJ/mol, log A/s^{-1} = 19.0, m_f = 0.11) of the 1 °C/min experiment. Panel B: simultaneous evaluation with identical best fit parameters (E = 195 kJ/mol, log A/s^{-1} = 14.43). Panel C: simultaneous evaluation with identical values of E (see Table 1). Panel D: effect of a ± 10% change of the best fit value of E from panel C (see text).

What is the explanation of this strange decrease in E and log A? It would be easy to conclude that the mechanism for cellulose pyrolysis involves a transition from a high activation energy pathway to a less temperature sensitive pathway, but our earlier mass-spectrometric work (Várhegyi et al. 1988), and work of other researchers (Arseneau, 1971; Broido, 1976; Bradbury et al., 1979; Shafizadeh, 1985) offer no evidence to support this idea. Describing their results, Antal et al. (1980) hinted at another explanation: they complained about the severe effects of thermal lag on their determinations of E and log A. Very recently, Narayan and Antal (1996) showed by numerical simulations that increasing thermal lag in thermogravimetric analysis manifests itself as a decreasing apparent activation energy (and a decreasing pre-exponential constant) in the governing rate law. In fact, they showed that thermal lag alone is sufficient to explain the compensation effect described by Chornet and Roy (1980). Recall that Curie-point calibrations of our instrument plainly reveal increasing thermal lag with increasing heating rate.

Consequently, we attribute the declining values of E and log A displayed in Table 1 to thermal lag problems with our instrument, and not a shift in reaction pathways. Nevertheless, we freely admit that the single step, first order model is only a simple approximation of a very complex process (Várhegyi et al., 1994; Antal and Várhegyi, 1995). Our chief point is that the details of the complex process are obfuscated at increasing heating rates by systematic error (thermal lag), which must be recognized and corrected before the subtle, higher-temperature chemistry can be studied.

Even if we regard the decline in E and log A to be an artifact of instrumental error, the question remains: how should we use the data to deduce kinetics? There are a number of possibilities. One approach is to use NLS analysis to identify unique values of E and log A which give a best fit to the data at all 3 heating rates. Figure 2b displays the results of this approach. Unfortunately, the NLS values for E and log A result in a model that manifests broad DTG peaks which do not represent the pyrolytic behavior of cellulose. This unsatisfying result is the outcome of an attempt to force the rate law to mimic weight loss that occurs over an erroneously wide temperature range due to increasing values of thermal lag at higher heating rates. Any spread in the DTG peaks effectively increases the range over which weight loss appears to occur, which the rate law interprets to be a lower activation energy process. Thus the values E = 195kJ/mol and log A/s^{-1} = 14.43, which represent a best-fit of the rate law to the data, result in the ill-fitting curves displayed in Figure 2b. Similar observations were described by Cooley and Antal (1988), who reported the values E = 191 kJ/mol and log A/s^{-1} = 14.42 for Avicel cellulose heated in flowing helium at 1, 2, and 5 °C/min using a Setaram thermobalance.

Alternatively, we can select rate constants obtained at one heating rate to represent the true values and use those values to simulate the pyrolysis behavior at other heating rates. Figure 2a displays the results of this approach, using values of E and log A obtained at 1 °C/min. The shapes of the simulated DTG peaks, which result from the kinetic model, are identical to those of the experimental measurements, but the experimental curves at 10 and 65 °C/min are shifted systematically to higher temperatures (8 and 16 °C respectively) along the temperature axis. Note that the magnitude of these shifts are comparable to those detected by Curie point calibration (4 and 11 °C respectively, as discussed earlier), as well as the experimental measurements of thermal lag reported by Antal et al. (1980), and Di Blasi and her co-workers (Lanzetta et al., 1997; Di Blasi and Lanzetta, 1997). These uniform shifts in temperature are consistent with our opinion that thermal lag is an important, underlying cause for the decline in E and log A discussed above.

A similar approach, that possesses great intellectual appeal, is to use a kinetic analysis which employs weight loss curves obtained at different heating rates to deduce the dependence of the kinetic parameter E on weight loss. The Friedman method (Friedman, 1964) is an attractive, seemingly powerful tool for such work. Antal (1982) showed that the shapes of plots of E vs. weight fraction remaining (which he called “Friedman signatures”) can serve as a kind of Rosetta Stone (Antal et al., 1985) for interpreting complex, solid phase pyrolysis phenomenon when no thermal lag is present in the experimental datasets. The problem with this approach is that thermal lag is present in many datasets (particularly at high heating rates); hence the Friedman method necessarily mixes datasets compromised by differing amounts of systematic error (thermal lag). The Friedman mapping function is quite sensitive to datasets whose thermal lags increase systematically with increasing heating rate. When datasets are split (Myers, 1990) and analyzed with low heating rate results in one group and high heating rate data in another, the Friedman signature shifts dramatically downward by as much as 80 kJ/mol (Antal et al. 1985). Antal et al. (1985) showed that a numerical model for cellulose pyrolysis, which included the heat transfer characteristics of the TGA, generated weight loss data whose Friedman signatures at low and high heating rates were effectively identical to those obtained from the experimental data. Thus the downward shift in the Friedman signatures (activation energies) at higher heating rates can be attributed to heat transfer problems (thermal lag) within the TGA. In summary, we found the method of Friedman analysis to be virtually useless when applied to datasets with widely differing heating rates and thermal lags.

Let us suppose that the pyrolytic reaction chemistry is the same at 1, 10, and 65 °C/min. But in keeping with the observations discussed above, we also suppose that the observed reaction temperature is compromised by thermal lag, which increases in magnitude with increasing heating rates. It is well known that a small shift in temperature can be formally represented by a change in the value of log A. Hence, we search for a single value of E and different values of log A that provide a good fit to the DTG curves at the three different heating rates displayed earlier. In this way variations in log A are used to account for the inherent, systematic temperature measurement errors within our instrument. Figure 2c and Table 1 give the results of this approach. The fits displayed in Figure 2c are very nearly as good as those given in Figure 2a, and only one parameter (log A) was varied to account for the effects of thermal lag. Note that the value of E obtained by this method (236 kJ/mol) is somewhat lower than the value deduced from the low heating rate curve in Figure 2a. It also differs slightly (4%) from the value (227 kJ/mol) which gave a best fit to the data displayed in Figure 1a. Differences of this magnitude are unavoidable when datasets that involve different heating rates are analyzed, and reflect the fact that measurements of E by state-of-the art instruments include only two significant figures (see below). When we employ a model to fit data at many different heating rates (as in Várhegyi et al., 1994), we report a single value of E together with a mean value of log A and a standard deviation δ(log A). The magnitude of the δ(log A) term is an indication of the contribution of systematic temperature measurement errors to uncertainty in the log A term. Although this uncertainty appears small (δ(log A)/log A is typically in the range 0.01 – 0.02), it can represent temperature shifts of tens of degrees Celsius. Recently, this approach was successfully employed to model the oxidation of coal chars subject to several different heating programs and oxygen partial pressures (Várhegyi et al., 1996). If we are asked to provide a model which fits experimental data (that is probably compromised by thermal lag) at different heating rates, we currently employ this approach. We have not yet found a better way to represent the insidious effects of thermal lag on measured rate constants.

Others have reported similar methods to cope with the problems of thermal lag outlined above. For example, Gaur and Reed (1994) employed an Arrhenius-like rate law, wherein the pre-exponential factor was modified to include a power law dependence on the heating rate, to obtain improved fits to their cellulose TGA data. Thus, the effective pre-exponential "constant" used in their work was varied according to a power law dependence on heating rate to account for the effects of thermal lag on their TGA weight loss measurements. We differ with Gaur and Reed (1994) in that we attribute no fundamental chemical significance to such variations in the pre-exponential factor. These variations are simply an artifact of systematic experimental error in dynamic temperature measurements.

We must also comment on the precision of the parameters E and log A as determined by the procedures outlined above. Figure 2d displays the same data as given in Figure 2c, except that the simulated DTG curves employ values of E which are 10% larger and smaller than the value E = 236 kJ/mol used to create Figure 2c. Values of log A for each of the three heating rates presented in Figure 2d were selected to offer an optimum fit of the first order model to the data, given the values 260 and 213 kJ/mol for the apparent activation energy. Plainly a 10% reduction in E results in a simulated DTG curve which rises too quickly at low temperatures; whereas the higher activation energy model gives peaks which are too sharp and tall at the higher heating rates. Nevertheless, it is equally evident that smaller variations in E would result in a first order model that could fit the data reasonably well, especially in light of the reproducibility displayed in Figure 1. Consequently, we conclude that our reported values for the apparent activation energy and pre-exponential constant possess only two significant figures, although more are listed to avoid loss of accuracy during numerical computations.

Finally we address the question: if it were possible to purchase a thermobalance which did not suffer from the problems of thermal lag, what rate law would fit experimental data obtained at different heating rates using increasingly smaller samples of Avicel PH-105 cellulose? We believe that the experimental data obtained from this hypothetical instrument would be well represented by a first order rate law with values of E and log A quite near to those which are given in Table 1 at 1 °C/min.

Effects of sample mass. As mentioned earlier, Milosavljevic and Suuberg (1995) employed 30 mg samples of CF-11 cellulose in their studies. Our sample pan was not big enough to accommodate so large a sample: the most we could use was 9.2 mg which filled the pan to a depth of about 0.6 mm. Figure 3 displays our analysis of 9.2 mg of CF-11 at 65 °C/min, and duplicate runs of 0.3 mg samples at 1 and 65 °C/min. These samples were supplied to us by Professor Suuberg and are from the same batch which he employed in his work with Milosavljevic. Figure 3 clearly illustrates why the thermal analysis community prefers to work with small sample sizes: heat transfer and mass transfer problems with a large sample (aggravated by the high heating rate) delay the apparent onset of weight loss by about 40 °C.

Moreover, temperature inhomogeneities within the large sample cause the DTG curve to become much wider. The unhappy result of the wider DTG curve is that the apparent activation energy of the first order rate law describing weight loss falls precipitously. Thus a kinetic analysis of the 9.2 mg TG curve offers a low value of 174 kJ/mol; whereas the comparable values associated with the 0.3 mg sample are 209 kJ/mol at 65 °C/min and 249 kJ/mol at 1°C/min (see Table 2 and Figure 3). We emphasize that this decrease in the activation energy is largely due to temperature inhomogeneities in the sample at high heating rates which artificially broaden the DTG curves. In order to confirm our result, we asked our colleague Dr. Morten Grønli (Norwegian Institute of Technology, Trondheim, Norway), who employs a TA Instruments model SDT 2960 TGA in his work (Grønli. 1996), to check our analysis of the CF-11 cellulose. His results, displayed in Table 2, show excellent agreement with our determination of the activation energy and log A value.

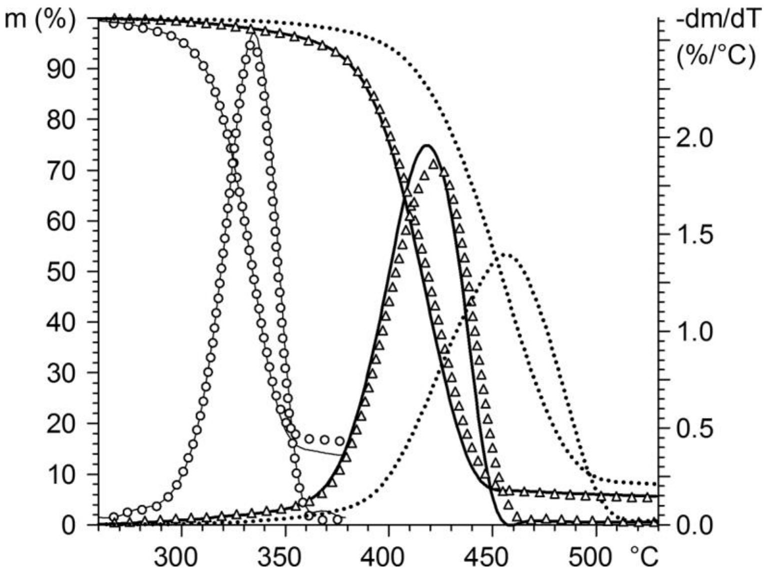

Figure 3. Experimental TG and DTG analyses of CF-11 cellulose. From left to right: two repeated 1 °C/min experiments with $m_0 \approx 0.35$ mg (—, ○); two repeated 65 °C/min experiments with $m_0 \approx 0.30$ mg (—, Δ); one 65 °C/min experiment with $m_0 = 9.2$ mg (····).

Table 2. Kinetic parameters for CF-11 cellulose as derived from TG curves

Source	E (kJ/mol)	log A (log s^{-1})	m_f	fit (%)
Milosavljevic & Suuberg[a], 30 mg, 0.1 - 1 °C/min	218	16.2	-	-
Milosavljevic & Suuberg[a], T>327°C	140 - 155	≈ 10	-	-
Present work, 9 mg at 65°C/min	174	11.1	0.09	0.4
Present work, 0.3 mg at 65°C/min	209	14.5	0.06	0.8
Grønli[b], 0.6 mg at 65°C/min	208	15.0	≈0.03	0.9
Grønli[b], 1.1 mg at 65°C/min	213	15.4	0.05	1.0
Present work, 0.3 mg at 1°C/min	249	18.5	0.15	0.4

[a] Milosavljevic and Suuberg, 1995. [b] M. Grønli, personal communication.

Table 2 also displays our results with small samples of CF-11 cellulose at 1 °C/min, where thermal lag problems are less severe. Mimicking the behavior of the Avicel cellulose, both the activation energy and the log A value increase together; however the increase in E (40 kJ/mol) is more than double the increase observed for Avicel (15 kJ/mol). We remark that the increase occurs in such a way that the E / log A ratio remains about constant at the two heating rates, in accord with the dictates of the compensation effect. As discussed above, it is known that the compensation effect is a manifestation of thermal lag (Narayan and Antal, 1996); hence it appears that the thermal lag problem is more severe with CF-11 than with Avicel. In a recent paper, Milosavljevic et al. (1996) have shown that the endothermic heat of pyrolysis for the CF-11 cellulose is larger than that observed for Avicel cellulose (Mok et al., 1992), and that the reaction remains endothermic over a very wide range of char yields. The large, endothermic heat of reaction associated with CF-11 pyrolysis would necessarily aggravate thermal lag problems, and thereby cause a larger drop in E (and log A) at elevated heating rates than observed with the Avicel cellulose. Thus the heat of reaction measurements of Milosavljevic et al. (1996) are consistent with the large falloff in E at high heating rates displayed in Table 2.

Much can be learned from a cursory examination of the char yields displayed in Figure 3. The reduction in sample size from 9.2 to 0.3 mg at 65 °C/min results in a decrease in the char yield at 520 °C from 8 to 6%. This is consistent with the fact that the reactive organic vapors produced during cellulose pyrolysis evidence a strong propensity to form char and light gases when held in the presence of the reacting solid sample (Mok and Antal, 1983; Várhegyi et al., 1988; Mok et al., 1992; Antal and Várhegyi, 1995). Values for the char yields obtained in our experiments are shown in Table 3. We report the char yield at two different temperatures for each experiment to show that a particular choice of a temperature value has only a small effect on the listed char yield. It is interesting to observe that the char yield increases with decreasing heating rate in all of our experiments. This increase can be attributed to the low temperature char-forming pathway (Arseneau, 1971; Broido, 1976; Bradbury et al., 1979; Várhegyi et al. 1994) mentioned earlier. Similarly, a 2-hour thermal pretreatment of the CF-11 at 260 °C, where the low temperature pathway dominates, also resulted in an increased char yield during subsequent heating at 65 °C/min. Other influences on the char yield from cellulose are discussed below.

Table 3: Residual char yield of the cellulose experiments[a]

Cellulose sample	dT/dt (°C/min)	Number of experiments	Residue (% of m_0)	
			T_1	T_2
Avicel	1	2	6.9	6.8
Avicel	65	5	2.3±0.3	2.2±0.3
CF-11 (3 mg)	1	3	10.4±0.4	10.2±0.3
CF-11 (0.3 mg)	65	3	6.3±0.8	6.0±0.8
CF-11 (0.3 mg) after 2 h preheating at 260°C	65	1	8.7	8.3
CF-11 (9.2 mg)[b]	65	1	8.3	7.9
Whatman #42 filter paper	1	3	9.3±0.1	9.1±0.1
Whatman #42 filter paper	65	3	3.8±0.6	3.6±0.6
Millipore filter pulp	1	1	7.3	7.0
Millipore filter pulp	65	2	3.1	2.9

[a] Values read from the TG charts at two different temperatures. At 1°C/min T_1=460 and T_2=480°C. At 65°C/min T_1=500 and T_2=520°C.

[b] When m_0=9.2 mg was employed at 65°C/min, T_1=520 and T_2=540°C were selected due to a shift of the TG curve to higher temperatures.

Comparisons of different celluloses. To our knowledge, no workers have reported back-to-back studies of the pyrolysis kinetics of different pure cellulose substrates in the archival literature. For this reason, we thought it would be instructive to compare the pyrolysis behavior of several different cellulosic materials, including Millipore ash-free filter pulp, Whatman #42 filter paper, the CF-11 cellulose employed by Milosavljevic and Suuberg, and the Avicel PH-105 cellulose that has been the focus of much of our work. Figures 4a and 4b, and Table 4 display the results of our analyses. The most striking thing about these figures is the wide range of temperatures over which the four different ash-free celluloses decompose. The Avicel powder is much less stable than the Whatman #42 filter paper: it pyrolyzes at temperatures 30 °C below the Whatman cellulose at 1 °C/min! This remarkable range in temperature sensitivities has not received sufficient attention, and points to the very strong influence of the chemical nature of the individual cellulose substrate on its pyrolysis behavior. Equally disconcerting is the range in char yields: 2 to 6% at 65ºC/min and 7 to 10% at 1ºC/min (Table 3). This difference cannot be ascribed to the ash content of the celluloses, since they are all low-ash materials. Evidently, there are “hidden variables” which exert a strong influence on the pyrolysis behavior of cellulose and have not yet been identified. These “hidden variables” may include the crystallinity (Pastorova et al., 1993) and degree of polymerization (Julien et al., 1991) of the cellulose substrate, but such a large effect as observed here would be quite surprising.

Table 4. Simultaneous evaluation of eight TG curves assuming identical E values (See Figure 4a.)

Substrate	dT/dt (°C/min)	E (kJ/mol)	log A (log s^{-1})	m_f	fit (%)
Avicel	1	228	17.4	0.10	0.8
Avicel	65	228	17.1	0.02	0.5
CF-11	1	228	16.6	0.14	1.0
CF-11	65	228	16.0	0.08	1.2
Whatman #42 filterpaper	1	228	16.4	0.12	1.2
Whatman #42 filterpaper	65	228	15.8	0.04	1.1
Millipore filterpaper	1	228	16.9	0.11	1.4
Millipore filterpaper	65	228	16.4	0.06	1.9

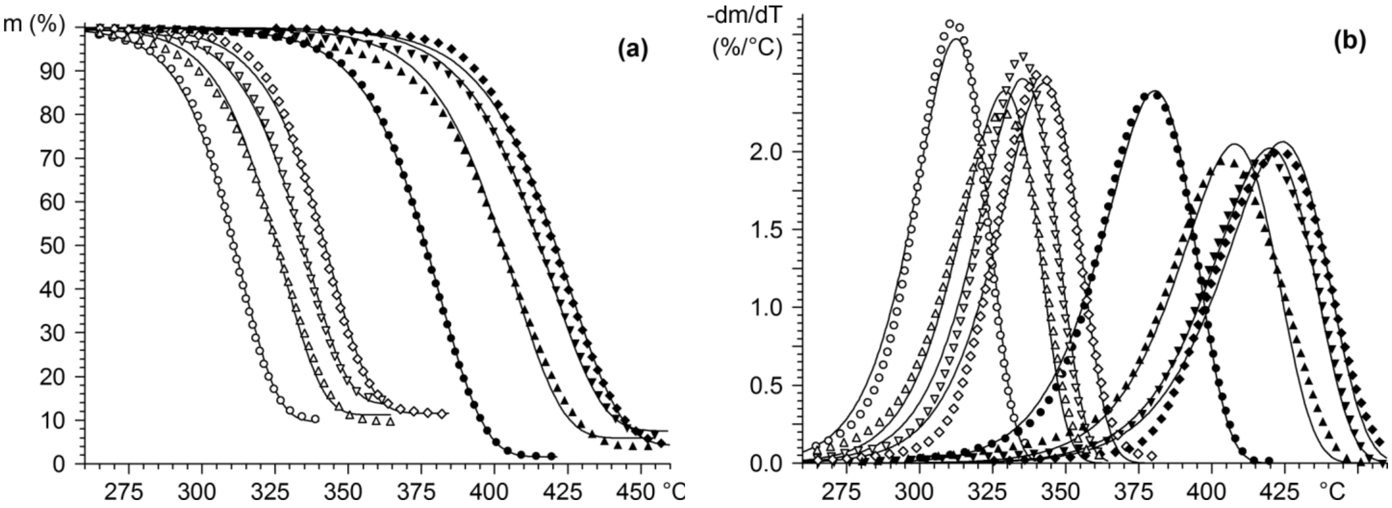

Figure 4. Simultaneous kinetic evaluation of TG (panel A) and DTG (panel B) experimental data for four different celluloses at 1 °C/min (open symbols) and 65 °C/min (filled symbols): Avicel cellulose (○,○), Millipore filter pulp (Δ,Δ), CF-11 cellulose (∇,∇), and Whatman #42 filter paper (◊,◊). Identical values of E were used for all simulated weight loss curves (see Table 4), which are displayed as solid lines.

Figures 4a and 4b also display the ability of a first order, high activation energy model (with a single activation energy and variable values of log A to account for varying thermal lag) to fit the weigh loss behavior of all four celluloses at both 1 and 65 °C/min. As observed earlier in this paper, the fit of the model to the Avicel data is very good. The model also offers a very good fit to the CF-11 data, except at low weight loss. The fit to the Millipore pulp data is less good, particularly during the early and late stages of weight loss. The Whatman #42 cellulose weight loss curve is somewhat sharper than the model.

Recognizing the fact that these four celluloses evidence intrinsic differences in their pyrolysis behavior, we also calculated best fit values of E and log A for each experiment (see Table 5); thereby accounting for increases in the thermal lag at the higher heating rate and the effects of this systematic error on both E and log A. In all cases the activation energy remains high (191 to 253 kJ/mol). Except for the CF-11 cellulose, the values of E and log A decrease only a small amount at the higher heating rate. As discussed above, the peculiar behavior of the CF-11 may be due to the highly endothermic nature of its pyrolysis chemistry. The fits of these models to the data are all excellent. The facts that the fits are all excellent, and the values E and log A do not change greatly at the elevated heating rate, but the value of E for each cellulose does differ significantly from the others, again emphasize the fact that all celluloses are not alike. Each cellulose is a unique material!

Table 5. Independent kinetic evaluation of the TG curves shown in Figure 4a.

Substrate	dT/dt (°C/min)	E (kJ/mol)	log A (log s^{-1})	m_f	fit (%)
Avicel	1	244	18.9	0.11	0.4
Avicel	65	234	17.6	0.02	0.3
CF-11	1	249	18.5	0.15	0.4
CF-11	65	209	14.5	0.06	0.8
Whatman #42 filter paper	1	253	18.5	0.13	0.7
Whatman #42 filter paper	65	243	17.0	0.05	0.9
Millipore filter pulp	1	198	14.2	0.10	0.4
Millipore filter pulp	65	191	13.4	0.04	0.8

Implications of this work for modelers. Recently there has been an upsurge of interest in numerical models capable of simulating biomass pyrolysis and gasification (Cozzani et al., 1996; Di Blasi, 1996a, b, c, d). Much progress has been made in representing the thermophysical aspects of the problem since the American Chemical Society sponsored sessions on mathematical modeling of biomass pyrolysis phenomenon over a decade ago (see Antal, 1985). Nevertheless, the findings presented in this paper, combined with our earlier work (Antal and Várhegyi, 1995), have important implications for modeling efforts. If the goal is to simulate the pyrolysis and gasification of whole biomass, the model must incorporate the catalytic influence of mineral matter (ash) on the pyrolysis kinetics. The authors know of no reliable treatment of this problem. The model should also incorporate the separate decomposition kinetics of the cellulose, hemicellulose and lignin components of the biomass. Since extraction procedures often compromise the chemical integrity of hemicellulose and lignin, models based on in-situ studies of hemicellulose and lignin pyrolysis are desirable, but few are available. We also remark that pyrolysis vapors are extremely reactive; consequently the model should include both the heterogeneous (see our earlier remarks regarding enhanced char formation during the pyrolysis of large samples) and homogeneous (Antal, 1983; 1985) reaction chemistry of vapors derived from the cellulose, hemicellulose, and lignin components of the biomass. Unfortunately, little knowledge of the heterogeneous reaction chemistry of these vapors exists. In summary, the development of models of whole biomass pyrolysis and gasification is an important goal for the community and we are excited by the progress reported by Di Blasi and her co-workers, but much experimental work is still needed to establish the chemical rate laws on which such models are based.

If the goal is simply to simulate the behavior of small particles of cellulose in a thermochemical reactor, the situation is less complex. Nevertheless, results presented herein clearly show that pure, ash-free celluloses obtained from different manufacturers manifest remarkably different responses to a thermal environment. Hints of such behavior were included in a recent review (Antal and Várhegyi, 1995), which revealed the extreme temperature sensitivity of the cellulose component of *Populus deltoides* and *Pinus radiata* (see also Grønli, 1996). Debate continues as to whether the Broido-Shafizadeh model (scheme 1 in Várhegyi et al., 1994), or the Arseneau-Várhegyi model (scheme 2 in Várhegyi et al. 1994), or a simple, single step model (as employed in this paper) better represents cellulose pyrolysis kinetics. For example, Di Blasi (1996a) writes "In most cases, kinetic models consist of a one-step global reaction whose data are estimated to best fit experimental weight loss curves. The main drawback of these kinetic models is that they are generally based on the assumption of a constant ratio of the final volatile to char yield. Consequently, they cannot predict, even from the qualitative point of view, the dependence of product yields on reactor temperature and heating rate, …". But as we have already seen, different pure, ash-free celluloses give dramatically different char yields when heated under identical conditions. Moreover, when Avicel cellulose pyrolysis is conducted in a covered pan with a pin-hole (Várhegyi et al., 1988) the char yield leaps to 19%! This extraordinary change in the char yield has nothing to do with the char forming pathways present in the Broido-Shafizadeh or the Arseneau- Várhegyi models (Várhegyi et al., 1994): it depends solely on vapor-solid reactions which are not well understood. Consequently, we view the debate about the utility of simple, single step models to be somewhat misleading. Product yields obtained from biomass in functioning thermochemical reactors depend largely upon reaction chemistry which remains to be elucidated by the scientific community. We believe the simple, one-step models represent an accurate statement of what is reasonably well known, and do not mislead the user into thinking that more is known than is actually the case. These remarks are not intended to detract from the remarkable progress made by modelers in the past decade. We simply emphasize that much remains to be learned.

Conclusions

1. Under identical conditions, samples of pure, ash-free cellulose obtained from different manufacturers undergo pyrolysis at temperatures which differ by as much as 30 °C. Consequently, when the kinetics of cellulose pyrolysis are discussed, they must be discussed in the context of a particular cellulose. Disagreements which exist in the literature concerning the rates of cellulose pyrolysis may reflect in part simple differences in the pure, ash-free cellulose samples themselves.

2. Nevertheless, the pyrolysis behaviors of the four cellulose samples discussed herein at low (1 °C/min) and high (65 °C/min) heating rates were well represented by a simple, single step, irreversible, first order rate law with a single, high activation energy (228 kJ/mol). Different values of log A were used in the model to fit the data. These differing values accounted for uncontrolled variations in systematic thermal lag (especially at the high heating rate) incurred during the experimental campaign, as well as inherent differences in the cellulose samples (mentioned above).

3. Recognizing the first conclusion listed above, together with the fact that thermal lag at high heating rates affects the observed values of E and log A for each cellulose, values of E and log A were calculated for each experiment with each cellulose. Except for the CF-11 material (see below), the values of E and log A did not change greatly at the higher heating rate. But in accord with our first conclusion, the values of E (and log A) varied greatly from one material to another (i.e. about 200 kJ/mol for Millipore filter pulp to about 250 kJ/mol for Whatman #42 filter paper).

4. At low heating rates (low temperatures) we find that Whatman CF-11 cellulose undergoes pyrolysis according to a high activation energy (ca 249 kJ/mol), first order rate law.

5. At higher heating rates (higher temperatures), we find that small samples (0.3 to 3 mg) of Whatman CF-11 cellulose undergo pyrolysis over a temperature range of 290 to 460 °C according to a first order rate law governed by a high activation energy (ca. 209 kJ/mol). This finding does not corroborate the work of Milosavljevic and Suuberg (1995). We attribute the modest decrease in the value of E (observed at the higher heating rate) to severe thermal lag problems that result from the unusually large endotherm associated with the pyrolysis chemistry of the CF-11 cellulose. Other explanations, such as a severe mass transfer limitation, may also explain the unusual behavior of the CF-11 cellulose.

6. Measured rates of weight loss for CF-11 pyrolysis are strongly influenced by the size of the sample. We find that an increase in sample size from 0.3 mg to 9 mg decreases the apparent activation energy from 209 to 174 kJ/mol. We believe that this decrease is due to temperature inhomogeneities within the large sample, which cause the DTG peak to widen and the activation energy to fall.

7. The community concerned with biomass pyrolysis is expressing increasing frustration with its inability to concur on measured rates of cellulose pyrolysis. This inability seems to result from unidentified, systematic temperature measurement errors which are accentuated at high heating rates. These systematic errors vary according to the design of the instrument and the skill of its user. We urge the community to undertake a round-robin study of a single, well-characterized, widely-available cellulose sample to gain insight into the influence of systematic errors on reaction rate measurements.

8. In light of the problems discussed above, and considering the needs of industry, we recommend that the community concerned with biomass pyrolysis shift its focus to studies of the in-situ behaviors of cellulose, hemicellulose, and lignin pyrolysis in whole biomass samples. A simple water wash suffices to remove much of the mineral matter, and modern methods of kinetic analysis are more than adequate to handle the complexity of heterogeneous materials (Antal and Várhegyi, 1995).

Acknowledgment

This research was funded by the National Science Foundation (Grant CTS95-21423), the U.S. Hungarian Joint Fund (Grant 93b-375), the Hungarian National Research Fund (Grant T 016173), and the Coral Industries Endowment of the University of Hawaii. We are particularly grateful to Dr. Morten Grønli (Norwegian Institute of Science and Technology) for allowing us to use his experimental data. We also thank Ms. Bonnie Thompson and Dr. Maria Burka (NSF) for their interest in this work, and Professor Eric Suuberg (Brown University) for his comments on this paper, and his gift of a sample of the CF-11 cellulose that he used in his research.

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