

CELLULOSE DECOMPOSITION KINETICS - GLOBAL KINETICS FOR FUELS PROCESSING AND FIRE MODELING APPLICATIONS

Ivan Milosavljevic* and Eric M. Suuberg
Division of Engineering, Brown University
Providence, RI 02912

Keywords: Pyrolysis, Cellulose, Kinetics

Introduction

There has been an ongoing debate in the literature concerning the "true" global kinetics of cellulose pyrolysis. The global kinetics are of interest in modeling cellulose decomposition in many applications in which trying to represent the full complexity of the cellulose degradation process makes no sense. Roberts noted that the activation energy data on the pyrolysis of wood and related materials tended to cluster around two values, one at about 235 kJ/mol, and the other 125 kJ/mol [1]. Various reasons were advanced, including the possible role of catalysis and sample-size related issues. Lipska and coworkers reported values for cellulose near 176 kJ/mol [2, 3], while Shafizadeh reported 113 kJ/mol [4], although they concluded elsewhere [5] that the process can be divided into an initiation step (243 kJ/mol) followed by competitive pathways to volatiles (198 kJ/mol) and char (153 kJ/mol). Broido and Weinstein obtained 230 kJ/mol and an a pre-exponential of $5.25 \times 10^{17} \text{ s}^{-1}$, using a TGA technique [6]. Meanwhile Lewellen et al. obtained a much lower activation energy of 140 kJ/mol, and a pre-exponential of $6.79 \times 10^9 \text{ s}^{-1}$ using a much higher heating rate [7]. Rogers and Ohlemiller obtained a similar value of activation energy, 163 kJ/mol, but at low heating rates, in a TGA [8]. Recently, Varhegyi et al. [9] obtained 234 kJ/mol and a pre-exponential of $3.9 \times 10^{17} \text{ s}^{-1}$, also in a TGA system at low heating rates (10 K/min).

Thus there is not particularly good agreement as to the global kinetics of the process. The kinetics often appeared to depend upon the heating rate employed in the experiments used to deduce them. For our purposes, involving fire modeling, we were in a range of heating rates between those studied by many workers and we felt it necessary to establish more clearly what the applicable kinetics were. In addition to the question about Arrhenius parameters, there is also uncertainty concerning the order of reaction. While there is often a tendency to model the decomposition using first order decompositional kinetics, some careful studies clearly suggest fractional order kinetics are more appropriate. In this paper, we explore this subject using thermogravimetric analysis (TGA). We have also employed differential scanning calorimetry (DSC) to study the problem, and these results will be presented elsewhere.

Experimental

This work was carried out as part of a larger experimental program, concerned with the behavior of cellulosic materials under simulated fire conditions. Other results from this work have been reported previously [10]. The interest in the behavior of bulk solids under fire conditions dictated the general range of heating rates to be below 100 K/min, but we extended this to 1000 K/min for some experiments.

The pyrolysis behavior of purified cellulose in one case was studied in a standard TGA (DuPont Instruments Model 951). All TGA experiments were conducted in an inert gas environment (nitrogen). Temperature calibration of the TGA was of particular concern, since in this device the thermocouple was not in direct contact with the sample. The temperatures reported by the "standard" instrument thermocouple were observed to be significantly in error (over 20 K) depending upon how the experiments were performed (i.e., depending upon heating rate and amount of sample, gaseous environment). To obtain correct temperatures, an experimental protocol was adopted in which two identical experiments were performed, one in which a fine thermocouple was actually embedded in the sample powder. Using this procedure, we obtained much more satisfactory results, in terms of agreement with other careful work reported in the literature, as well as with our own DSC kinetics.

The cellulose used for all TGA work was a Whatman CF-11 fibrous cellulose powder that was used as-received. This cellulose is prepared from high purity cotton of 99% alpha cellulose content. The ash content is 0.009% by mass. The molecular weight of this material is in the range 36,000 to 45,000 daltons. The diameter of the fibres was 10 to 30 μm .

For some experiments, a heated wire mesh reactor was used, in order to achieve higher heating rates than are available from the TGA. This reactor consists of a thin wire gauze which is stretched between electrodes that provide current for resistively heating the gauze. The sample is held between two layers of gauze, and is uniformly heated. The apparatus is described in more detail elsewhere [11]. The samples used in this work consisted of either the same powders as used in the TGA work, or acid-washed filter paper (Munkteill's OK/S2-80-200), with an ash content of 0.007%. The paper had a thickness of $168 \pm 8 \mu\text{m}$, and was cut into rectangles approximately 1 x

* Present address: Advanced Fuel Research, Inc., East Hartford, Ct.

2cm. Since the powder and paper gave virtually identical results but had much different characteristic dimensions, this suggested that in-sample transport limitations were not important in this work, even at high heating rates. This will be further discussed below.

Results and Discussion

Figure 1 shows the results of experiments performed at high heating rates in the heated wire mesh reactor. Each datum represents the char residue yield (and thus one minus the total volatiles yield) from an isothermal experiment in which the sample is heated at the indicated rate to the abscissa temperature, and then allowed to cool at a rate of between 200 to 400 K/s. Mass loss during cooling is generally quite small compared to that during heating. The highest of the heating rates in Fig. 1 would be closer to the conditions that obtain in pulverized biomass combustion or pyrolysis, though still quite a bit lower. Nevertheless, there is good agreement with similar experiments performed at even higher heating rates [7,12]. The curves were calculated, assuming a typical moisture level of about 6%, from the parameters of [7], which were shown to apply to heating rates of 400 to 10,000 K/s. Thus the range for these global parameters is seen to now extend from about 1.7 K/s (100 K/min) to 10,000 K/s. As we have previously reported [13], there is, however, difficulty in applying these kinetic parameters at 5 K/min, as Fig. 1 also clearly shows. There is a significant underprediction of volatiles release rates observed at these heating rates.

Cellulose decomposition data from many other low heating rate studies also cannot be fit by the high heating rate parameters. Generally, activation energies of over 200 kJ/mol have been required, as noted above. Since we were interested in fire safety applications that put us in between the high and low heating rate ranges, we carried out an examination of the kinetics in this zone. This work could be carried out using TGA techniques. Two different types of experiments were performed. One type employed the ordinary constant temperature ramping techniques common in TGA work, and the other involved experiments in which the temperature was ramped at a fixed rate up to a particular temperature, and then the sample was held isothermally. Typical results of the latter ("isothermal") experiments are seen in Figure 2. The data of Fig. 2 could be analyzed to obtain kinetic parameters for a particular constant level of conversion. This is important in a case in which the kinetics change with conversion. The Arrhenius expression for a general n-th order reaction is:

$$\frac{d\left(\frac{M - M_f}{M_0 - M_f}\right)}{dt} = - \left(\frac{M - M_f}{M_0 - M_f}\right)^n A \exp\left(-\frac{E_a}{RT}\right) \quad (1)$$

where M is the mass of cellulose or char at any time, the subscripts 0 and f denote initial and final, A is the Arrhenius pre-exponential, E_a the activation energy, R the gas constant, T temperature and t time. By taking the natural logarithm of (1), and then taking the derivative with respect to reciprocal temperature, the activation energy is calculable independently of any assumptions of order, if the calculations are performed at constant conversion. There is an issue of what to use for M_f in this case, since char yield can be a function of experimental conditions. In our TGA work, the value did not vary particularly much from 10%, and in testing our parameters for sensitivity to the assumed value, the variation proved unimportant.

Results obtained from the above calculations, using isothermal data of the type in Fig. 2, are shown in Table 1. It is observed that the values obtained at these low heating rates (1 K/min) are different from those from high heating rate experiments, and that they do not depend upon conversion. The values cluster near many others reported in the literature for slow-heating experiments. The pre-exponential factors, A , may also be calculated if a reaction order of unity is assumed, and are also shown in Table 1. The values are too high to represent unimolecular decompositions, as has been noted by others as well. Clearly the decomposition process does not involve rate control by a single step, in this range of conditions. Also, for comparison, a "typical" pair of kinetic parameters derived by this approach are used to try to fit the data of Figure 1. While a fair fit may be claimed at 5 K/min and 100 K/min, a very poor fit is obtained to the 1000 K/min data. Clearly such parameters are not appropriate for high heating rate modeling.

Figure 3 shows the values of activation energy obtained from the type of experiments as shown in Fig. 2, but involving heating at a rate of 60 K/min. Several features were very different from those observed at lower heating rates. First, the attempts at fitting the data with a single activation energy failed. Rather, it was found that there were two different activation energy regimes. It was decided on the basis of observed behavior to divide the results into two regimes, one above 600 K and the other below. The regime below 600 K was seen to be characterized by an activation energy (and associated pseudo-first-order pre-exponential) that was quite similar to those obtained in the slow heating experiments, and shown in Table 1. The higher temperature regime was found to be characterized by a non-constant activation energy, but the values of apparent activation energy seemed to bracket those of the high heating rate experiments. It should be recalled that since the method of fitting the data attempts to avoid questions of reaction order change, an apparent temperature dependence of mechanism is the most plausible reason for the shift.

It may be noted from Fig. 2 that the major part of the decomposition is completed below about 600 K in all cases. This lends support to the idea that there is a shift in mechanism that takes place above that temperature, since Fig. 2 gave no evidence of two distinct kinetic steps. The higher the

heating rate, the more quickly the transition temperature of 600 K is exceeded and the more the higher temperature mechanism would show itself. As heating rates become so high as to force most conversion to occur in the high temperature regime, the kinetics again begin to look more simple. Unfortunately, it has been historically the heating rate regime between 1 and 10 K/min that has been the most explored, and this has put investigators squarely between the high and low temperature regimes in many experiments. We believe that this has led to many apparently contradictory results being reported.

The more traditional heating-ramp experiments also supported the two-regime proposal. Typical data are shown in Figure 4. These data were obtained from different non-isothermal TGA results, by determining the actual mass loss rates at different heating rates for a constant value of conversion (60% in Figure 4). These mass loss rates are the tangents to the mass loss curve at any time. It is clear from Figure 4, there is a point that fits neither curve cleanly, at around 600 K. From the data obtained at low heating rate conditions (0.1 and 1 K/min), the activation energy is calculated to be between 205 and 252 kJ/mol, varying randomly with conversion. For the data obtained at high heating rates (15 and 60 K/min), the activation energy varies between 137 and 180 kJ/mol. Depending upon how the point near 600 K in Fig. 4 is "counted", considerably higher values of apparent activation energy could be obtained.

Some analyses have been performed to address the question of reaction order. Letting $\phi = [(M-M_f)/(M_0-M_f)]$, then generally speaking for any arbitrary n-th order reaction at constant temperature:

$$d\phi/dt = - [A \exp(-E_a/RT)]\phi^n = -k\phi^n \quad (2)$$

Integrating yields different expressions for different values of n:

$$\phi = -k_0t + C_0 \quad (3)$$

$$\ln(\phi) = -k_1t + C_1 \quad (4)$$

$$1/\phi = k_2t + C_2 \quad (5)$$

where the subscripts on the constants indicate the orders assumed. The results of the isothermal experiments were examined for order, using these expressions. For convenience, a function $f(M/M_0)$ is defined such that:

$$f(M/M_0) = (F-F_{\min})/(F_{\max}-F_{\min}) \quad (6)$$

where F represents the values of the left hand sides of (3), (4) and (5). The order may be determined from the data by examining which assumed order gives the best approximate fit to linear, per (3), (4) or (5). Figure 5 shows a typical result, for an experiment at 584 K, following heatup at 1 K/min. Clearly first order is the best approximation to the data after an initial period of zero order. This result obtained in most low temperature (< 600 K) cases, and is consistent with earlier results in the literature [2,14]. The results of the experiments at higher temperatures did not give as clearcut results, and appeared to imply second order reaction might be involved, perhaps consistent with another report of near second order behavior [15]. Clearly this topic warrants further study.

Finally, we consider the question of transport effects as possibly responsible for the apparent shift in kinetic parameters. We believe this to be unlikely for several reasons. First, considering the analysis by Hajaligol et al. [16], it appears that despite of the endothermic nature of the pyrolysis reactions involved, the particles examined here are too small to be subject to a heat transfer limitation. Further, it is difficult to rationalize why use of a single heating rate could result in the behavior seen in Fig. 3, if a heat transfer limitation were involved. Thus it seems quite unlikely that a heat transfer limitation is the cause of the observed variation in kinetic parameters.

Conclusions

It appears as though the confusing state of the literature on global kinetics of cellulose pyrolysis has as its cause a previously unrecognized shift in mechanism near 600 K. Depending upon the heating rate used to examine the kinetics, different values can easily emerge. We believe that the low temperature regime is characterized by an activation energy around 224 kJ/mol and an order that seems to go from zero, early in the process, towards first. The high temperature regime is characterized by neither constant activation energy nor order, and the apparent activation energy is centered near 140 kJ/mol. Together with an assumption of first order, a value of activation energy around 140 kJ/mol is clearly the most reasonable for applications involving pulverized combustion or pyrolysis of small cellulose particles. For fire modeling applications, both kinetic regimes may be of interest.

Acknowledgments

The support from the Center for Fire Research of NIST under grant 60NANB0D1042 is gratefully acknowledged.

References

1. Roberts, A.F., *Combustion and Flame*, 14, 261 (1970).
2. Lipska, A.E. and Parker, W.J., *J. Appl. Polymer Sci*, 10, 1439 (1966).

3. Lipska, A.E. and Wodley, F.A. *J. Appl. Polymer Sci*, 13, 851 (1969).
4. Shafizadeh, F. and Bradbury, A.G. *J. Appl. Polymer Sci*, 23, 1431 (1979).
5. Bradbury, A.G., Sakai, Y., and Shafizadeh, F. *J. Appl. Polymer Sci*, 23, 3271 (1979).
6. Broido, A. and Weinstein, M., *Comb. Sci. and Tech.*, 1, 279 (1970).
7. Lewellen, P.C., Peters, W.A., and Howard, J.B., *16th Symp. (Int.) on Comb.*, p 1471, The Combustion Institute, Pittsburgh, 1977.
8. Rogers, F.E. and Ohlemiller, T.J. *Comb. Sci. and Tech.*, 24, 129 (1980).
9. Varhegyi, G., Antal, M.J., Jr., Szekely, T., Szabo, P., *Energy and Fuels*, 3, 329 (1989).
10. Milosavljevic, I. and Suuberg, E.M., *ACS Div. Fuel Chem. Prepr.*, 37(4), 1567 (1992).
11. Suuberg, E.M., Peters, W.A. and Howard, J.B., *I&EC Proc. Des. Dev.*, 17, 37 (1978).
12. Hajaligol, M., Howard, J.B., and Peters, W.A., *I&EC Proc. Des. Dev.*, 21, 457 (1982).
13. Suuberg, E.M. and Dalal, V.F., *Proc. Eastern States Sect. Comb. Inst.*, 65-1, Nov., 1987.
14. Tang, W.K. and Neill, W.K., *J. Polymer Sci. C*, 6, 65 (1964).
15. Kashiwagi, T. and Nambu, H., *Comb. and Flame*, 88, 345 (1992).
16. Hajaligol, M., Peters, W.A., and Howard, J.B., *Energy and Fuels*, 2, 439 (1988).

Table 1. Kinetic Parameters for Cellulose Decomposition from Isothermal Experiments with 1 K/min Heating

Remaining Mass (%)	E_a [kJ/mol]	A [1/s]
80	225	4.82×10^{16}
70	215	5.77×10^{15}
60	224	5.39×10^{16}
50	215	8.80×10^{15}
40	212	5.59×10^{15}
30	214	1.15×10^{16}
20	225	4.69×10^{16}

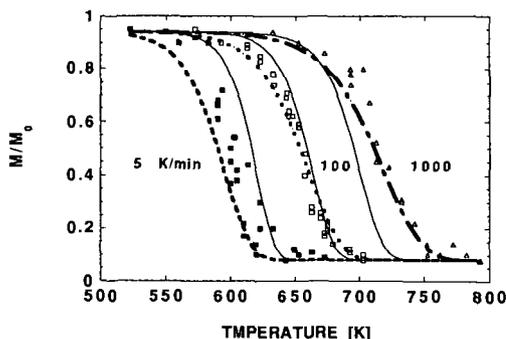


Figure 1. Comparison of char yield data obtained at indicated heating rates with model predictions. Broken lines are for kinetic parameters from [7], $A = 6.79 \times 10^9 \text{ s}^{-1}$, $E_a = 140 \text{ kJ/mol}$. Solid lines are for $A = 4.12 \times 10^{16} \text{ s}^{-1}$ and $E_a = 224 \text{ kJ/mol}$.

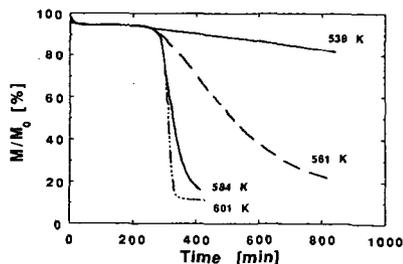


Figure 2. Typical isothermal experiment results, for 1 K/min heating to final temperature.

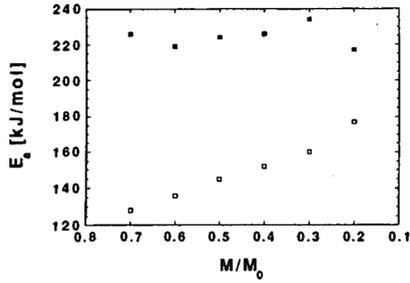


Figure 3. Activation energies obtained as a function of conversion in isothermal experiments involving heating at 60 K/min to final temperature. The open points are for results obtained for temperatures above 600 K and the solid points for temperatures below 600 K.

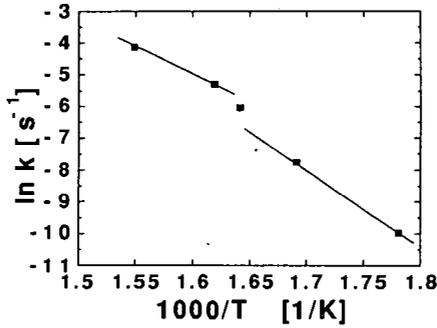


Figure 4. Arrhenius plot for $M/M_0 = 0.6$, from data obtained under nonisothermal conditions, at heating rates of 0.1, 1, 6, 15 and 60 K/min.

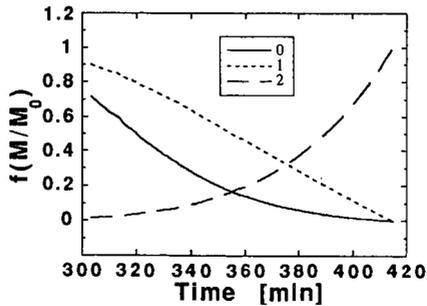


Figure 5. Test of different reaction orders on TGA data obtained in an isothermal experiment at 584 K.