

The Effect of Temperature on Liquid Product Composition
from the Fast Pyrolysis of Cellulose

Donald S. Scott, J. Piskorz, A. Grinshpun and R.G. Graham

Department of Chemical Engineering
University of Waterloo
Waterloo, Ontario, Canada N2L 3G1

Introduction

In recent years, a good deal of attention has been focused on the thermal conversion of biomass to gases and liquids, and in particular, on the products obtainable from short time, high temperature pyrolysis of wood and other lignocellulosics. This flash pyrolysis is usually carried out at or near atmospheric pressures, while hydrolypyrolysis commonly employs hydrogen pressures to 20 MPa.

Residence times of only a few seconds or less with reaction at high temperatures requires a reactor configuration capable of very high heating rates. Two of the most appropriate designs are the entrained flow reactor, and the fluidized bed reactor. Many flash pyrolysis studies have employed one or the other of these reactor types.

In general, two approaches to flash pyrolysis of biomass have been used by various workers. One approach has the objective of producing a maximum yield of a desirable gas, which in atmospheric pressure non-catalytic pyrolysis processes is usually ethylene, or other olefins. Examples of processes for this purpose, such as "ultrapyrolysis" (10)(17), "ablative pyrolysis" (7), the flash pyrolysis process described by Antal (2) and the fluidized bed process of Kuester (14) have been studied in recent years for the production of olefins. These processes are characterized by high temperatures $>650^{\circ}\text{C}$ and residence times of 1 second or less.

A second approach to flash pyrolysis has been described by Scott and Piskorz (19)(20) and Scott et al. (21). In these publications the development has been outlined of an atmospheric pressure flash pyrolysis process utilizing a fluidized bed of solid as heat carrier. The process studied has as a primary objective the determination of conditions for maximum yield of liquids from biomass, particularly forest materials. Results indicated that at apparent vapor residence times of about 0.5 seconds, organic liquid yields of 60%-70% on a moisture free basis could be obtained from hardwoods such as aspen-poplar and maple. Lower but still high yields of organic liquids (40%-60%) could be obtained from agricultural wastes such as wheat straw, corn stover and bagasse.

More recently, Knight et al. (11) have described the operation of an entrained flow reactor for the production of liquids. A somewhat different upflow entrained pyrolyzer for the production of liquids from wood has been described by Beaumont (5). Kosstrin (12) has also used a fluidized bed for thermal conversion of biomass to liquid. In general, processes for the attainment of high liquid yields operate at much lower temperatures, commonly 450°-550°C than do processes to yield gaseous products, but at about the same vapor residence times of about 500 ms.

In rapid pyrolysis processes, the rate of heat transfer is all-important. Ideally, in such a process, the time required for a biomass particle to reach about 95% of the reaction temperature would be much less than the particle residence time itself. The residence times normally quoted in thermal pyrolysis studies are usually mean gas residence times, that is, the net empty reactor volume divided by the volumetric flow rate, usually taken at reactor inlet conditions. Particle residence times are not as precisely known, and will vary with the reactor configuration and type. Measurement of mean particle residence times has not been done in the majority of fast pyrolysis process studies. However, Berruti (6) measured these residence times in a fluidized sand bed for 1 mm wood particles, and found that these varied from 2 to 6 s depending on the gas residence time (400 to 800 ms). Recently, Solomon et al. (22) reported measurements of the velocity of fine coal particles in a downward flow entrained reactor and found these were only about 40% of the gas velocity over most of the reaction period. Therefore, although the residence time of particles is generally not known very precisely in fast pyrolysis processes, it will likely be from 2 to 10 times the apparent gas residence time for most of the applicable reactors, that is, for entrained flow, fluid bed, spouted bed or cyclonic reactors. It is likely, therefore, that given a reactor capable of high heat flux, and particles of appropriate size with the "normal" gas residence time of about 500 ms, the heat-up time may not be a large fraction of the total particle residence time.

It is likely that each process will have its limits such that inadequate heat transfer causes marked changes in the distribution of the pyrolysis products. However, within these limits (which may not differ very much for different reactors capable of high heat transfer rates), the product distribution at a given gas residence time might be expected to be a function of the final reaction temperature only, especially if particles are smaller than about 1 mm and are reasonably dry. The principal criterion for this to be true is that the heat-up time for the particle should be considerably less than the time spent near reaction temperature, possibly only 20% of the total particle reaction time. As a result, the kinetic rate of reaction will probably be the rate limiting process. An equivalent criterion due to Lidén (16) would be to require that a particle reach decomposition temperature e.g. 450°C before any significant weight loss is observed.

Experimental

For this work, two completely different pyrolysis reactors were used, operated by two different research groups. The "ultraprolysis" entrained flow reactor was developed by workers at the University of Western Ontario, and was capable of operation to 1000°C with gas residence times of 50 ms to 900 ms (10). The second reactor was the fluidized bed pyrolysis unit developed at the University of Waterloo for thermal conversion of biomass to liquids (20). It operated up to 750°C with gas residence times of 300 to 1500 ms. Typical operating ranges for the two reactors are summarized in Table 1. Detailed descriptions of the respective apparatus and procedures are given in the two articles cited.

Table I Range of Experimental Parameters

	Ultraprolysis	Fluid Bed
Temperature, °C	700-1000	400-750
Reactor Residence Time (Gas), ms	50-900	300-1500
Maximum Feed Rate, kg/hr	1.0	3.0
Estimated Heating Rates, °C/s	10^4 - 10^5	10^4 - 10^5
Pressure, atm abs.	1.0	1.0
Reaction Atmosphere	N ₂	N ₂ or Product Gas

In all tests reported here, only one feed material was used, Avicel PH-102 microcrystalline cellulose. Both groups of experimenters used samples from the same lot, which at time of use had moisture content from 2.9-4.0%, with ash <0.1%, and C 44.24, H 6.16, O 49.6. Particle size range was -250 +40 µm with a mean particle diameter of 100 µm.

Results

The pyrolysis experiments in the fluid bed were all carried out at gas residence times of 450-550 ms. In this range, yields of liquid, gas and char show only a small variation with time. Pyrolysis in the transport reactor over the reaction time span of 350-900 ms, showed that the yields of liquid, char and gas became nearly independent of residence time in the reactor. Accordingly, yields from the transport reactor in this asymptotic range at 500 ms were compared to data from the fluidized bed pyrolyzer. All data were reported as percent by weight of the moisture free feed of total liquids (including water of reaction), gas and

char. Yields were normalized to 100% by correcting the liquid yield. In all experiments, material balances were generally $\pm 5\%$ or better, and the major errors were considered to reside in losses of the most volatile liquids during liquid recovery, and inaccuracies in the water balance. Also, methanol was normally used as the solvent for recovery of tars from lines and condensers, which means that methanol yields could not be determined.

The results of pyrolysis experiments with Avicel cellulose are shown in Figures 1-4 with all data presented on a dry feed basis. Figure 1 shows that over the temperature range of 450°C-900°C the yields of gas, char and liquids from two different reactors, operated by two different research groups, are in very close agreement. Figures 2 and 3 show the variation in CO and CO₂ yields with temperature over the same range. Again, agreement of the two sets of results is very good. Yields of hydrocarbon gases are shown in Figure 4, and the good agreement of data from the two reactors is again evident for both CH₄ yield and C₂H₄ + C₂H₂ yield.

Liquid products from the pyrolysis tests were obtained over a temperature range of 375°-700°C. These liquids were analyzed for specific chemical components using methods described elsewhere (18). Results for nine of the more significant components obtained in a water extract of the tars are shown in Figures 5-8. All of these results were obtained using the fluid bed pyrolysis system of the University of Waterloo. It is apparent that at a constant reaction time, well defined and fairly narrow optimal temperature ranges exist corresponding to the maximum yields for each component.

Discussion

In order to determine if the criterion of the ratio of heat-up time to time at reaction temperature is $\ll 1.0$, it is necessary to estimate heat transfer rates in the reactors and for the particles used. If the ideas of Kothari and Antal (13) are accepted, the time required for the centre of a particle to approach 500°C would represent the heat-up time. Lede (15) comes to similar conclusions for pyrolysis at high heat fluxes, but sets the decomposition temperature at 466°C for wood. The most extreme case, that is, the longest heat-up time in the present work, would be for the largest particles at the lowest reactor temperatures. The center point temperature was calculated for 600 μm and 100 μm particles for the heating conditions of a fluidized bed (16), for a reactor temperature of 500°C with feed at 20°C. The time required for the particle mid-point temperature to reach 450°C was found to be 618 ms for the 600 μm particle and 62 ms for the 100 μm particle. Inasmuch as the solid particle residence times for the larger particles were from 2 to 6 seconds in the fluidized bed, and for smaller particles in the transport reactor were at least 500 ms, the criterion of ratio of heat-up time/available reaction time $\ll 1$ is well satisfied for all the work reported here.

Another approach was taken by Lidén (16) to estimate the importance of the heat-up period. On the basis of low temperature pyrolysis results reported in the literature, and the results obtained in our laboratory, it was assumed that if the particle temperature reached at least 450°C before more than 10% of the wood decomposed (as measured by a rate-of-weight loss kinetic expression) then excessive char production would be avoided, and the condition for high tar yields would be met, since tar decomposition would be minimized by the rapid volatilization and removal of tar components. Assuming a first order weight loss expression, this heat-up time criterion can be expressed as

$$\ln \left[\frac{1}{0.9} \right] \geq \int_0^{t_c} k [T(t)] dt \quad (1)$$

where t_c is the time required for the particle centre to reach 450°C and $T(t)$ are the set of functions describing the particle centre temperature as a function of time after introduction of feed into the reactor. The value of the first order rate constant, k , used should be one which is applicable for the rate of weight loss of the biomass species used. For the purposes of evaluating the above criterion, the kinetic parameters for the rate expression describing the total decomposition of wood as given by Thurner and Mann (23) were used, that is

$$k = 2.468 (10^6) \exp - 106.5/RT \quad s^{-1} \quad (2)$$

where the activation energy is given in kJ/mole.

Numerical integration of the right hand side of equation (1) for hardwood particles in a fluidized bed reactor at 500°C shows that for all particle sizes less than 2 mm diameter the criterion will be satisfied. It follows that for all the data presented here for the two reactors, the particles were heated throughout to at least 450°C, even at the lowest reaction temperatures, before any appreciable weight loss occurred from them. Under these conditions, then, the product distribution from either reactor for the same gas residence times could be expected to be a function of reactor temperature only, even though biomass solids were well mixed in one reactor, and in plug flow in the other.

Recently, Lidén (16) and Diebold (8) using different reactor configurations have presented very similar kinetic models for the secondary decomposition of primary pyrolysis tars from biomass. The kinetic steps for which rate constants were evaluated are proposed to be parallel initial first order decompositions, one yielding volatile liquids, while the other yields char and gas, with respective rate constants k_1 and k_2 . The ratio of k_1/k_2 in both models was assumed to be a constant with respect to temperature and to represent a theoretical maximum (ultimate) liquid (or tar) yield. The volatile organics were then assumed to decompose by another first order process to lower molecular

weight products, because experimental results for short time pyrolysis suggest that little secondary char is formed in this step (see Figure 1). Experimental results also suggest that the primary decomposition step is largely completed before significant loss of tar yield occurs, as evidenced by a nearly minimum char yield at the maximum liquid yield, as well as low gas yields at this point. As tar yield decreases due to secondary decomposition reactions, gas yield increases proportionally. It becomes possible, then, to neglect the rate of the tar forming step and to express the change of tar yield due to secondary reactions by a simplified kinetic expression, given by both Lidén (16) and Diebold (8) as

$$x = \frac{x_0 [1 - \exp(-k_3 \theta)]}{k_3 \theta} \quad (3)$$

where x is the fractional tar yield, x_0 is the theoretical "ultimate" tar yield, k is the first order constant for the tar decomposition step and θ is the reaction time for the vapor phase. The values used for the reaction parameters for tar decomposition were

Lidén $k_3 = 3.1 \times 10^6 \exp(-107500/RT) \text{ s}^{-1}$ $x_0 = 0.703$

Diebold $k_3 = 1.551 \times 10^5 \exp(-87634/RT) \text{ s}^{-1}$ $x_0 = 0.78$ or 0.76

Liden's parameters are based on experimental data from hardwood (poplar) pyrolysis in a fluidized bed, while Diebold's values are obtained from measurements of the ablative pyrolysis of softwood followed by thermal cracking of the pyrolysis vapors.

Equation (3) was applied to the results from the pyrolysis of Avicel cellulose with prediction as shown in Figure 9. In applying equation (3) to these results, the ultimate yield, x_0 , was assumed to be 100%, although the low temperature results suggest a value slightly less than this might be more appropriate. Similarly, the yield of water was neglected, although it ranges from 2%-5%. The predicted tar yields as shown in Figure 9 are in remarkably good agreement with experiment, considering the assumptions of the model, and the fact that parameters derived from wood pyrolysis are being used to predict yields from the pyrolysis of a microcrystalline cellulose. Further, no effort was made to optimize values of the parameters with the experimental data, but only to use the values of Lidén or Diebold.

In summary, equation (3) appears to give a reasonable description of the complex cracking reactions in which biomass pyrolysis tars are converted to gaseous products, at least over the temperature range of about 500°-900°C, and for short vapor phase reaction times.

The yields of individual components shown in Figures 5-8 suggest strongly that a series of sequential decomposition steps is occurring. However, it is not clear from these results what

the precursor for any particular compound may be, or what system of parallel or sequential reactions can satisfactorily explain the nature of the variation of yield with temperature. More extensive analyses of these data are now underway.

Acknowledgement

The authors wish to extend their thanks to the National Research Council of Canada for the financial support of this work.

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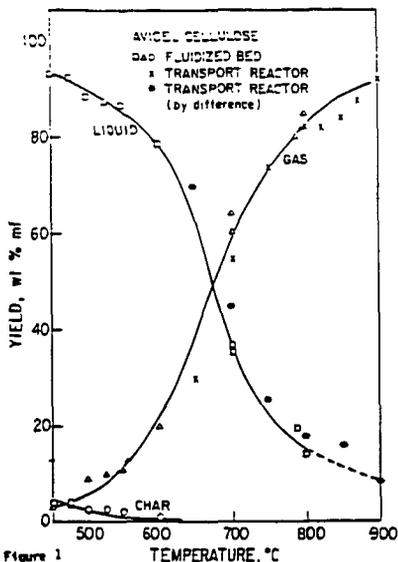


Figure 1 Product Yields from Avicel Cellulose for Two Reactors

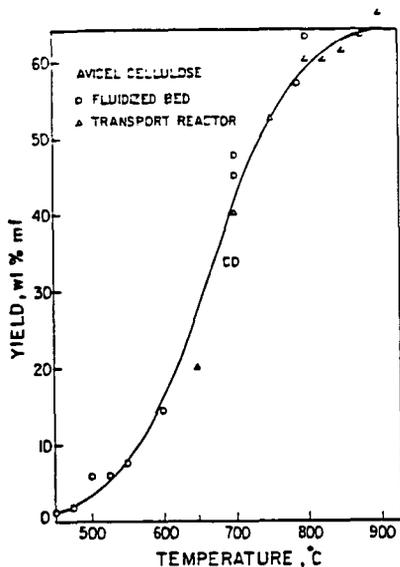


Figure 2 Yield of CD from Avicel Cellulose

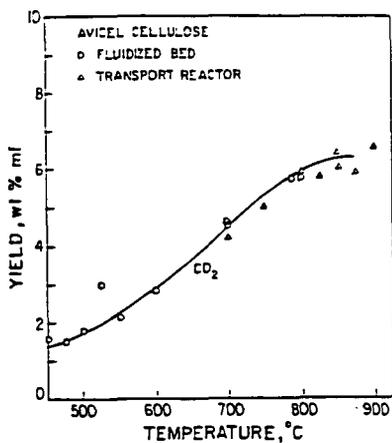


Figure 3 Yield of CO₂ from Avicel Cellulose

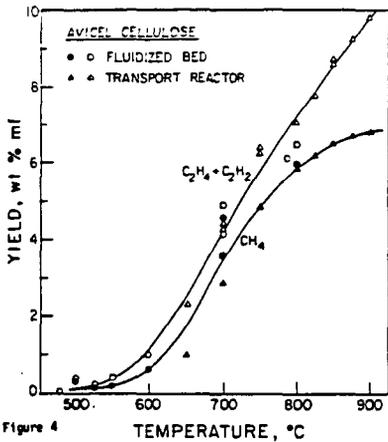


Figure 4 Yield of Hydrocarbon Gases from Avicel Cellulose

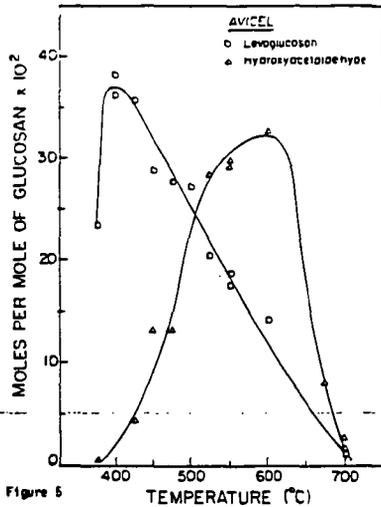


Figure 5 Yields of Levoglucosan and Hydroxyacetaldehyde, 800 ms, Fluidized Bed

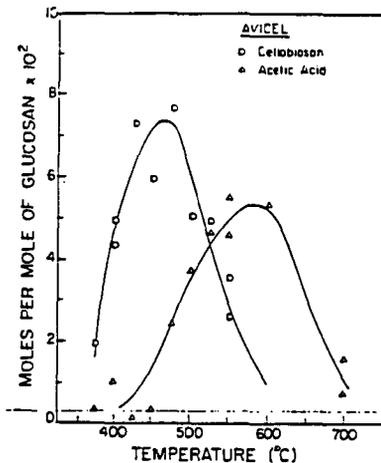


Figure 6 Yields of Cellobiosan and Acetic Acid, 500 ms, Fluidized Bed

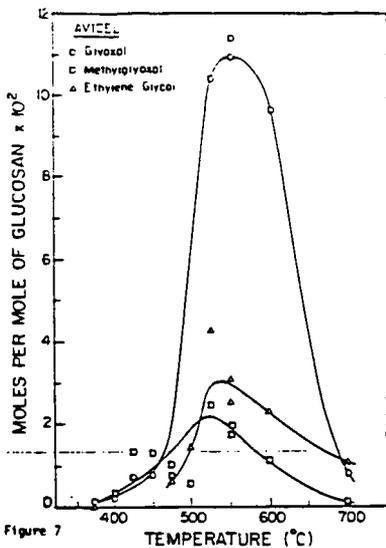


Figure 7 Yields of Glyoxal, Methylglyoxal and Ethylene Glycol, 500 ms, Fluidized Bed

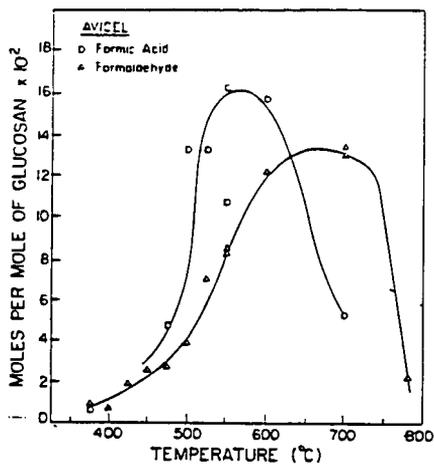


Figure 8 Yields of Formic Acid and Formaldehyde, 500 ms, Fluidized Bed

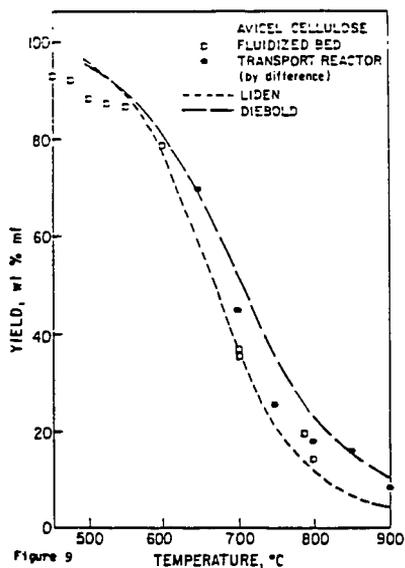


Figure 9 Prediction of Total Liquid Yields from Avicel Cellulose