

## Effects Of Transport Limitations On Pyrolysis Of Cellulosics

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### Introduction

The tendency of cellulosic materials to form chars during pyrolysis is well established. However the effects of sample density, size and grain orientation on char formation are not yet well established. In this work, the data obtained from different experimental systems are compared in order to deduce the effects of sample density, size and grain orientation on pyrolysis of cellulosics. It was noted that the overall pyrolysis process appears to be similar for a wide range of materials, sample densities and grain orientations, at least under high (fire-level) heat flux conditions.

### Experimental

The pyrolysis behavior of purified cellulose (pressed to three different densities), white pine and oak were investigated in a large scale pyrolysis apparatus (designed to simulate fire conditions), a standard TGA, a standard tube furnace and a heated wire gauze reactor. This work was motivated by a desire to establish whether the kinetics of pyrolysis, measured in TGA-type devices can apply to room fire-type situations.

The large scale pyrolysis apparatus is shown schematically in Figure 1. A sample is heated by radiative heaters as it is positioned atop an electronic balance. The heat flux from the radiative heaters was  $40 \text{ kW/m}^2$  in all tests reported here and all the tests were performed under nitrogen purge. It should be noted that not all of the incident heat flux was absorbed due to the heat losses from the surface (i.e. reflection, re-radiation and convection). Mass changes and/or temperatures within the sample were monitored continuously. Samples used in the large scale pyrolysis apparatus were cylindrical with diameter 38 mm and various thicknesses (typically about 10mm). Pressed cellulose samples had densities of  $0.475 \pm 0.025 \text{ g/cm}^3$ ,  $0.725 \pm 0.025 \text{ g/cm}^3$  and  $1.000 \pm 0.090 \text{ g/cm}^3$ , white pine a density of  $0.377 \text{ g/cm}^3$  and oak a density of  $0.734 \text{ g/cm}^3$ . For tests with cellulose and white pine there were two different grain orientations with respect to the axis of incident radiative flux: parallel and perpendicular. For tests with oak only a "tangential" (with respect to growth rings) orientation was used.

In order to establish the difference in behavior between large samples (as used in a large scale pyrolysis apparatus) and small samples of purified cellulose, some tests were performed in a TGA/FTIR system using  $3 \times 3 \times 3 \text{ mm}$  cellulose samples of same densities as in a large scale pyrolysis apparatus. The atmosphere was helium and the heating rate was  $60^\circ\text{C/min}$ . The wire gauze reactor was used in order to investigate the effect of grain orientation on the ultimate char yield. Samples for the wire gauze reactor were of  $1.0 \text{ g/cm}^3$  density,  $2.7 \times 27 \text{ mm}$  and different widths. The atmosphere was helium and the heating rate was  $60^\circ\text{C/min}$ .

### Results and Discussion

Figures 2a and 2b show mass loss as a function of time for different initial sample densities for perpendicular (tangential for oak) and parallel grain orientation recorded in the large scale pyrolysis apparatus, respectively. Despite the diversity of materials and their densities, the behavior, with respect to mass loss, appears similar. There is some small amount of mass loss observed before the actual heating started. This is probably due to the sample drying, since the samples were handled in air without any drying prior to a run, and the atmosphere in the apparatus was dry nitrogen from the moment the sample was placed in the apparatus.

It can be seen from Figures 2a and 2b that the point of first significant mass loss is a function of density. Higher density samples tend to start to pyrolyze later than the lower density samples, independent of the grain orientation. The reason for such behavior is a difference in heat transport. The higher the density of the sample, the more efficiently it serves as a heat sink (since thermal conductivity varies with density), and the more slowly the temperature of the surface rises. Since it is the surface layer that begins the process of pyrolysis, it is the temperature of the surface that matters. This hypothesis is supported by the data of Figure 3, which shows the behavior of small samples of cellulose in a TGA device. In this case, the samples are uniformly heated over their surface and the gas phase temperature histories are identical, but there is a trend, again, towards "earlier" pyrolysis in the lower density samples. The process is undoubtedly external heat transfer controlled, since there is absolutely no reason to believe that pressing density affects kinetics (all samples were pressed from the same powder).

The pine samples of Figures 2a and 2b behave in a manner quite similar to that of pure cellulose. This cannot be said for the oak sample, perhaps because the pine is much more homogenous than the oak (there are clearly observable inhomogeneities in the oak sample). The nature of sample inhomogeneity and its importance will be further discussed below.

It can be seen from Figures 2a and 2b that during the middle stage of pyrolysis mass loss is linear in time, as is often seen in the literature for this type of material [1, 2, 3, 4, 5]. The reason for such a behavior is that the process is heat conduction limited, with surface flux prescribed. The pyrolysis wave is "pushed" at constant velocity by the heat deposited on the surface at constant rate (vide infra).

Figure 2c depicts the temperature at the surface and at 10 mm from the surface for a 12.25 mm thick cellulose sample of 1.078 g/cm<sup>3</sup> density with perpendicular grain orientation, recorded in the large scale pyrolysis apparatus. The temperature profiles clearly establish that the pyrolysis process is heat transfer limited, in such a system. Note that the "kinks" in the profiles at between 300°C and 400°C are reproducible, and we believe indicate an endothermic step in the overall process (though not necessarily the main reaction process). This will be discussed elsewhere.

Figures 4a, 4b and 4c show cumulative amounts of carbon monoxide, carbon dioxide and methane, respectively from the TGA experiments of Figure 3. It is obvious that there is an effect of sample density. There is more gas evolved from higher density samples. This is probably due to the higher residence times of tars, such that there is a higher probability for their cracking to lighter gases prior to escape from the particles. By examining the starting point of gas evolution in these figures, it can be concluded that both carbon monoxide and carbon dioxide are the products of primary pyrolysis as well as of secondary cracking reactions whereas methane appears as a product of the secondary reactions alone (otherwise it should start to evolve immediately with the other gases).

Figure 5 shows the final char yield for the three different sample densities, examined in the TGA and large scale pyrolysis apparatus. Obviously the TGA data support the notion that with increasing density, there is an increasing tendency towards cracking reactions of tars, which leave behind a char product as well. The effect, while measurable, certainly cannot be termed large, over the range of densities explored. Thus for pyrolysis of cellulose in woody materials, there is a suggestion that density alone is not a key factor in determining pyrolysis char yields. The data from the large scale apparatus requires consideration of other factors, discussed below.

Figure 6 presents mass loss rates (averaged over the linear portions of mass loss curves only) as a function of initial sample density for cellulose samples with perpendicular and parallel grain orientation from experiments in the large scale pyrolysis apparatus and from the experiments in the TGA. The samples used for a TGA should not be affected by a grain orientation due to the uniform heating of the samples from all sides. The mass loss rate follows the same trend for both grain orientations used in the large pyrolysis apparatus. The rate of mass loss is linear in density. The actual mass loss rates are shown in Table I as the parameter B, where the relationship between sample mass M and time t is roughly:

$$M = M_0 - Bt$$

Again, this holds approximately over a large fraction of the sample's pyrolysis history. The fact that Figure 6 shows  $B$  to be linear in density ( $\rho$ ) suggests that the ratio  $(B/\rho)$  is constant, and these values are also shown in Table I. For a sample of constant cross-sectional area,  $(B/\rho)$  is proportional to the linear propagation velocity of a pyrolysis wave through the sample, viz:

$$(B/\rho) = V A$$

where  $V$  is the velocity and  $A$  is the cross-sectional ( $1134 \text{ mm}^2$ ). Thus it may be seen that the average propagation velocity is  $9.8 \times 10^{-3} / 1.134 = 8.6 \times 10^{-3} \text{ cm/s}$  or about  $0.5 \text{ cm/min}$ . It can be seen from Table I that the pyrolysis wave speed is fairly independent of density. All  $(B/\rho)$  values fall within the standard deviation of the mean (i.e.  $\pm 3 \times 10^{-3} \text{ cm}^2/\text{s}$ ). No clear trends are established by the limited data available. Again, the constancy of  $(B/\rho)$  is expected, if thermal conductivity is linear in density.

Mass loss rates (averaged over the linear portions of mass loss curves only), obtained in the TGA experiments are also shown in Figure 6. The effect of density is not pronounced but is certainly observable. These data show the opposite trend from the data recorded in the large scale pyrolysis apparatus. Of course there is a significant difference between the two situations. Consider the locus of resistance to heat transfer in the two cases. There is little doubt that in the large-scale pyrolysis system, the process is conduction-limited. A sample that is partially pyrolyzed and sectioned shows a sharp pyrolysis front separating a black char from a relatively white unpyrolyzed zone. In the case of the samples in the TGA, the process is not conduction limited within the sample. This may be easily shown by considering the Biot number for the sample  $Bi = hr/k_s$ , where  $h$  is the heat transfer coefficient,  $r$  is the radius of the sample (treated as an effective sphere) and  $k_s$  is its thermal conductivity. Taking  $h$  to be governed by the conduction limit,  $Nu = hd/k_g = 2$ , where  $d$  is the diameter of a particle and thus  $Bi = k_g/k_s$ . Since  $k_g \cong 0.2 \text{ W/mK}$  for helium near  $500\text{K}$ , and since  $k_s$  for woods (cellulosics) is of the same order of magnitude, then clearly the influence of external heat transfer cannot be neglected since  $Bi$  is of order unity. With a few particles in a sample pan, the system is not as well-defined, but the conclusion that external heat transfer limitations can influence results still stands, and a clear relationship between density and rate should not be expected, as was seen in the conduction limited case.

Figures 5 and 6 clearly reveal effects of sample orientation in the bulk samples used in the large scale pyrolysis apparatus. The bulk samples all have a distinctly anisotropic appearance, despite the fact that they are produced by pressing from fine powder. Bands run across the entire diameter of the sample, in a direction perpendicular to the direction from which pressing force is exerted. The band structure reveals itself during pyrolysis as well. When samples are pyrolyzed in which the bands are perpendicular to the incident radiative flux, the samples tend to crack or split in a direction parallel to the bands. In the case in which incident flux is parallel to the bands the cracking is also in a direction parallel to the bands.

Given the anisotropy of the samples there is little surprise then that pyrolysis is affected to some extent by band orientation. As Figure 5 reveals, char yield correlates with band orientation as well as with density in the bulk samples. Care must be exercised in interpreting these results, because what is termed "char" in these experiments in fact includes partially pyrolyzed material, due to existence of heat losses at the back face of the sample. But for present purposes, it is significant that when the volatiles must cross the pressing bands to escape the front surface of the sample, a higher amount of secondary reactions occur than when the volatiles can move parallel to the bands (the secondary reactions, again, are believed to deposit extra char). Note that the volatiles must escape the front face of the sample because the back and sides are enclosed in a ceramic cup.

The effect of band orientation relative to a surface flux is probably somewhat analogous to wood grain orientation to a surface flux. The ultimate effect of such a choice of orientation does not

appear to be very large, in terms of char yield - a percent or two at most in Figure 5. Again, mass transfer effects are seen, but they are not large, just as in the case of the density effect seen with the small samples examined in the TGA. The density effect on char yield appears to be large in the case of the large samples of Figure 5, but again this is probably in large part an artifact induced by the differences in temperature profiles for samples of different density.

The mass loss rate data of Figure 6 suggest that the samples with band structures parallel and perpendicular to the incident flux have roughly comparable mass loss rates at low density ( $<0.5\text{g/cm}^3$ ). Upon increasing the density above  $0.7\text{g/cm}^3$ , there begins to be apparent a slight tendency towards higher rates when the volatiles can move parallel the band structure. As was seen in Table I, the trend towards faster mass loss in parallel samples is not particularly pronounced, so that roughly comparable mass loss rates give rise to the conclusion of roughly comparable rates of thermal wave propagation, irrespective of orientation. The trend is nevertheless consistent with a slight retardation of volatiles escape from samples in which volatiles have to cross the bands.

The importance of with- and cross-band transport was explored in one further experiment. Figure 7 presents the variation of the ultimate char yield with sample width, obtained from thin samples pyrolyzed in a wire gauze reactor. These samples all had a thickness of 2.7 mm and a length of 27 mm, and all had a density of around  $1\text{g/cm}^3$ . The samples were heated at a rate of  $60^\circ\text{C}/\text{min}$  up to  $600^\circ\text{C}$ . The samples were thus thin rectangular parallelepipeds, and had been pressed in the direction of 2.7mm thickness. The pressing direction is again significant, as the work with the larger samples has revealed. There would be expected a slight difference in rates of escape of volatiles in a direction parallel to the main faces of the parallelepiped vs across the faces.

The results of Figure 7 were surprising in the magnitude of the effect they revealed. The work with the narrowest samples (2.3 mm) gave a char yield of just over 5.5%, perfectly consistent with the TGA results shown in Figure 5. Increasing the sample width (while keeping thickness constant at 2.7 mm and length constant at 27 mm) had a surprisingly large effect on char yield. These results strongly suggest that the volatiles in fact have a great deal of difficulty moving cross-band and must move parallel to the band to escape (otherwise the fact that the shortest dimension remained 2.7 mm should have dictated that there be little effect on yield). It should also be remembered that in these experiments the samples were heated from all sides, so a pathway to a cooler zone was not available, as it might be in larger samples.

Thus it must be concluded that the concept of "ultimate char yield" is somewhat meaningless, when applied to samples of characteristic dimensions more than a few millimeters, in view of the results of Figures 5 and 7.

## Conclusions

The behaviors of three different materials (purified cellulose, white pine and oak) with different grain orientations and different densities were investigated using different experimental approaches. The behavior of white pine and oak are seen to be quite similar to pure high density cellulose under heat-transfer controlled, fire-like conditions. The role of density is seen in its effect on heat transfer; higher density samples conduct better, and if the process is conduction limited, will pyrolyze faster. The density also affects the ability of volatiles to escape pyrolyzing samples, and this affects both char yields and volatile yields. These effects are considerably less important than the effect of density on heat transfer.

Sample band, or grain, structure also has some small effect on volatiles escape, but again, the effect is small. Sample particle size is seen to be important in several respects, as it influences both heat and mass transfer measurably, even when particles are a few millimeters in size. Applications of TGA data to modeling of fire situations must involve cognizance of such issues.

## Acknowledgments

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### References

1. Lee, C. K., Chaiken, R. F. and Singer, J. M. XVI Symp. (Int) on Combustion, 1976
2. Julien, S., Chornet, E., Tiwari, P. K. and Overend, R. P. Journal of Analytical and Applied Pyrolysis, 19, 81, 1991
3. Radlein, D., Piskorz, J. and Scott, D. S. Journal of Analytical and Applied Pyrolysis, 19, 41, 1991
4. Lipowicz, P. J. and Rothenberg, S. J. Combustion and Flame, 75, 217, 1989
5. Raissi, A. T., Mok, W. S. L. and Antal, M. J. Ind. Eng. Chem. Res., 28, 856, 1989

Table I: Pyrolysis Wave Speed in Large Scale Apparatus, 40 kW/m<sup>2</sup> flux, as a function of sample density and orientation for Cellulose, Oak and Pine

Orientation	Density (g/cc)	B (g/s)x10 <sup>3</sup>	B/p (cc/s)x10 <sup>3</sup>
Perpendicular	0.47	5.0	10.6
Perpendicular	0.46	5.3	11.5
Perpendicular	0.70	6.5	9.8
Perpendicular	0.73	7.1	9.7
Perpendicular	1.06	8.0	7.5
Perpendicular	1.06	8.9	8.4
Parallel	0.49	4.7	9.6
Parallel	0.72	8.0	11.1
Parallel	0.72	7.8	10.8
Parallel	0.93	8.3	8.9
Parallel	0.97	9.2	9.5
Perpendicular (Oak)	0.73	7.2	9.9
Perpendicular (Pine)	0.38	2.9	7.6
Parallel (Pine)	0.38	4.9	<u>12.9</u>
			9.8

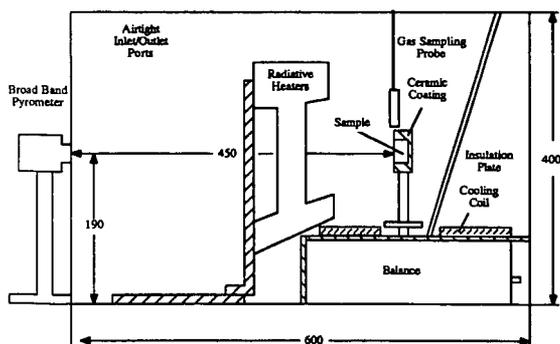


FIGURE 1: LARGE SCALE PYROLYSIS APPARATUS  
(All measure in millimeters)

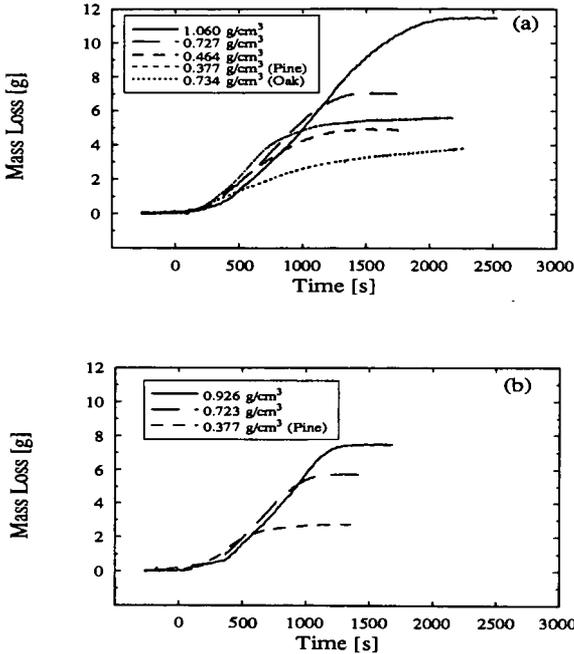


Figure 2: Mass loss as a function of time for (a)-perpendicular and (b)-parallel grain orientation from the large scale apparatus (flux was 40 kW/m<sup>2</sup>)

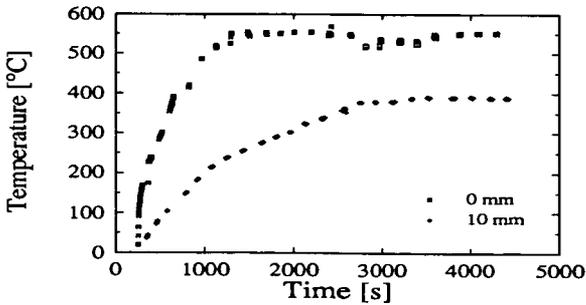


Figure 2c: Typical temperature profiles in a sample pyrolyzed in the large scale apparatus

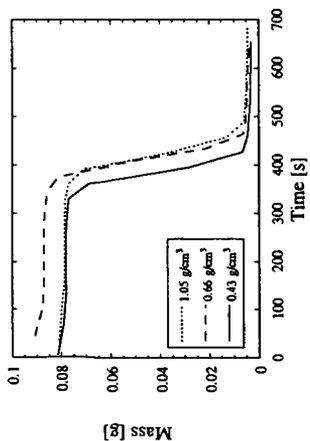


Figure 3: Mass loss as a function of time from the TGA (heating rate was 60°C/min)

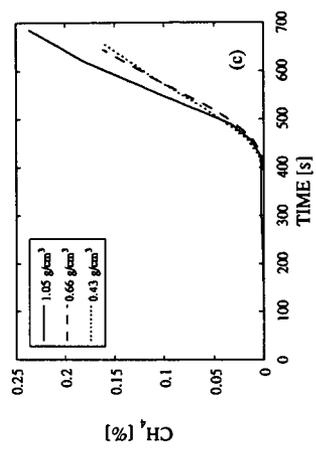
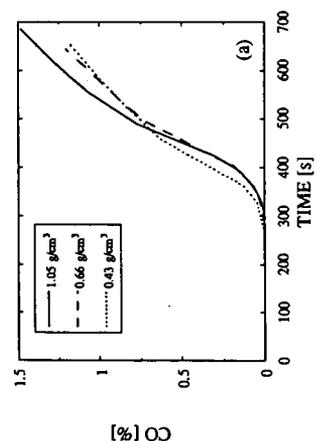
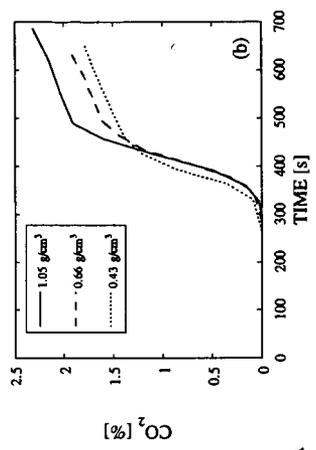


Figure 4: Cumulative amounts of a-CO, b-CO2 and c-CH4 as functions of time from the TGA (heating rate was 60°C/min)

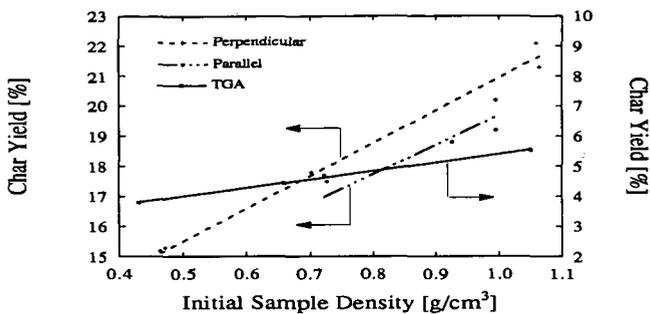


Figure 5: Cellulose char yield as a function of initial sample density for perpendicular and parallel grain orientation from the large scale apparatus and from the TGA

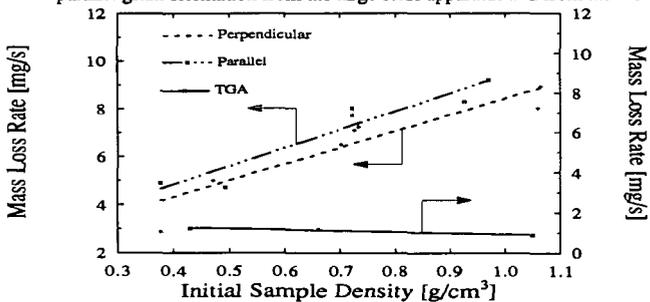


Figure 6: Mass loss rate as a function of initial sample density for perpendicular and parallel grain orientation from the large scale apparatus and from the TGA

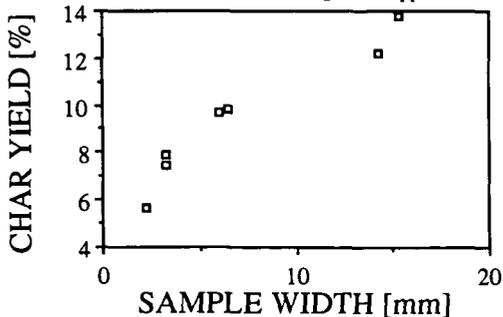


Figure 7: Cellulose char yield as a function of sample width from wire gauze reactor