

Flash Pyrolysis of Cellulose in a Micro Fluidized Bed

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INTRODUCTION

Short contact time or flash pyrolysis is one of the alternatives under consideration for the conversion of biomass into liquid or gaseous fuel, or perhaps into chemicals feedstock. A variety of compounds are formed in flash pyrolysis so that it would be desirable to be able to predict yields of at least the major products as a function of the pyrolysis device and operating conditions such as heating rate of the biomass, final temperature, particle size, gas phase composition. As a contribution to this goal, this paper considers the flash pyrolysis of micro crystalline cellulose powder and particles in a fluidized bed. By flash pyrolysis, we refer to heating rates (at the particle surface) greater than 100°C/s, final temperatures generally greater than 500°C and contact times of the order of 1-2 seconds or less. Compared with the vast literature on slow pyrolysis of cellulose the literature on flash pyrolysis is very small. A few studies have been made using a Pyroprobe or a Curie point pyrolyzer (Iglauer et al. (1974); Ohnishi et al., (1975) Hileman et al., (1979) and a fluidized bed (Barooah and Long, 1976); Maa and Bailie, (1978); Scott and Piskorz, (1981.) Irradiation was used by Martin (1965) and Shivadev and Emmons (1974) as a heat source. Lewellen et al. (1977) and Hajaligol et al. (1982) pyrolyzed filter paper suspended between two massive electrodes. The latter team succeeded in producing quite a wide range of temperatures and heating rates. Unfortunately, in most past studies, weight loss measurement and analysis of volatile products were not carried out simultaneously. Indeed, identification of volatile products usually came from investigations where the pyrolysis reactions went nearly to completion. In such cases, the product distribution might result from not only cellulose pyrolysis but also from secondary cracking and perhaps even char gasification.

EXPERIMENTAL SYSTEM, ANALYTICAL TECHNIQUES AND STUDY MATERIALS

Figure 1 shows the fluidized bed system used in this study. Details of the bed itself are given in Figure 2. The assembly shown in Figure 2 was built by Scott and Piskorz (1981) and used by them to study the flash pyrolysis of coal and wood.

Pyrolysis occurs in a bed of fluidized sand supported by a porous stainless steel distribution plate. The net reactor volume is 23 mL. Fluidizing gas is introduced from the bottom through a preheating tube 1 meter in length. As Figure 1 shows, the reactor sits in a three-zone Lindberg electric tube furnace, 91 cm in length. The reactor was located in the upper zone and the preheating tube of the reactor was situated in the bottom two zones and was sufficient to heat up the fluidizing gas to bed temperature before it entered the reactor.

The low rate of cellulose feed needed for the system was achieved using an entrainment feeder described by Scott and Piskorz (1981). Feed rate

could be adjusted from 5 to 100 g/h with this unit. Cellulose entrained in carrier gas entered the bed through the central, downwardly directed tube in Figure 2. The tip of this tube was immersed in the fluidized sand. The concentric tube, terminating in a 6.3 mm o.d. outlet was originally supposed to introduce a cold quench gas into the reactor. In this study, it served as sampling line to a Carle G.C. with a heated sampling loop. This G.C. periodically sampled the off gas and was used to insure the assembly operated at steady state.

Most of the volatile products and gas introduced to fluidize the sand bed and to entrain the cellulose feed left the reactor through the 12.7 mm o.d. outlet seen in Figure 2. This outlet was connected to the first of three, water-cooled glass condensers by about 40 cm of Teflon tubing. Almost all the tar formed and the char eluted from the bed was trapped in the condensers or in the connecting tubing. The remaining tar was caught in a glass-wool-filled column. After passing through two further columns to strip out water, the gas was collected in an inflatable bag.

A run using this equipment lasted about 30 minutes once steady state was established. Weighing provided the amount of cellulose fed to the fluidized bed and the char caught in the bed. Washing of the glass wool, tubing and condensers with ethanol provided a measure of the char eluted (by weighing the residue on filtering the solvent) and of the tar formed by weighing the residue after filtering and evaporating the solvent. GC analysis of the gas bag content and measurement of the gas volume gave the non-condensable, volatile products produced.

Analyses were performed using a dual channel GC equipped with a 1.83-m 100/120 mesh Porapak T column on one channel and a 1.83-m 80/100 mesh Porapak Q column in the other. Both channels used FID's and temperature programming was employed. A second chromatograph equipped with a 1.83-m mesh 5A molecular sieve column was also used on the gas bag to measure CO, CO₂ and water.

Tar samples were treated with N-trimethyl silylimidazole in pyridine. This reagent creates a volatilizable compound from levoglucosan; other tar compounds are also converted to volatilizable substances by silylation. Silylated tar solution was injected onto either a 1.83-m 6% OV-101 on 80/100 mesh Chromosorb column or a similar Chromosorb column treated with 6% SE-52. Peak identification was by means of pure levoglucosan dissolved in N-trimethyl silylimidazole.

A microcrystalline cellulose (MCP) furnished as a 200/270 mesh powder was the primary test material. Cellulose particles, as a 20/40 mesh material were made by pelletizing the MCP in a press, crushing the pellets, and then sieving. The particles permitted a test of a particle size on product distribution and pyrolysis rate to be made. Limitations of attainable fluidization velocity limited the size to 20/40 mesh.

Cellulose conversion and product distribution were measured at fluidized bed temperatures between 310 and 770°C. Most experiments were performed in an N₂ atmosphere, but measurements were made as well with CO, CO₂ and a H₂-N₂ mixture as the fluidizing gas. Contact time of cellulose in the bed was not less than 0.5 s (the residence time of the fluidizing gas in the bed), and probably did not exceed 2 to 3 seconds. Based on work with coal,

Tyler (1979) estimates that the heating rate of fine particles in a fluidized bed must be greater than 1°C/ms.

EXPERIMENTAL RESULTS

CO, CO₂ and H₂ pyrolysis yields from cellulose powder are shown in Figure 3. The carbon oxides are the major products. H₂ yields are the same order of magnitude as the hydrocarbon yields. A transition in behaviour occurs around 500°C. Above this temperature the CO yields increase at slower rate but the CO₂ yields level off. Char yields were less than 10 wt% of the sample fed above 500°C so that pyrolysis is essentially complete. The abrupt change in the CO₂ yield reflects, evidently, completion of the cracking reaction.

Yields of light hydrocarbon by carbon number vs temperature appear in Figure 4. A change in slope at about 500°C is evident. With the exception of flattening of the C₃ and C₄ yields above 700°C, the light hydrocarbon behaviour resembles the yield behaviour seen for CO. Probably cracking of C₃⁺ hydrocarbons at 700°C+ accounts for the flattening observation.

The major liquid oxygen-bearing molecules detected were acetaldehyde, acrolein, furan and acetone. While Hajaligol et al. (1982) measured relatively high methanol yields, 1 wt% of the pure cellulose sample, the yields in this study were as low as 0.1 wt% of the sample. Figure 5 shows yields of acetaldehyde while Figure 6 shows those of acetone plotted versus temperature. Data for MCP powder and 20/40 mesh pellets are plotted together. Particle size quite clearly does not affect yield. Measurements taken in different atmospheres are also shown. Once again, the atmosphere surrounding the pyrolyzing material does not change the yield temperature behaviour. Both these observations apply to the CO, CO₂ and H₂ yields and for the light hydrocarbons.

Acetaldehyde yield data (Figure 5) resembles that for CO, while the acetone yields are much more like the data obtained for CO₂ (Figure 3). Indeed, of the other two oxygen containing hydrocarbon which could be accurately measured, acrolein and furan, the former exhibited the CO behaviour with temperature while the latter appeared to show the CO₂ behaviour.

The yields of levoglucosan are shown in Figure 7. Particle size and fluidizing atmosphere do not affect the yields. Replotting the data against weight loss of the original MCP or cellulose particles permits a comparison with the yields data obtained by other workers for slow pyrolysis. Figure 8 provides the comparison. Yields found in this study were smaller by a factor of 2 to 3 than yields measured under slow pyrolysis. It is surprising that the agreement among the data of different investigators is so poor.

The difference between our data and others shown in Figure 8 is that heating and contact times in our study were perhaps an order of magnitude greater than those used by the others. If levoglucosan is a primary product of cellulose pyrolysis, as has been proposed, shorter contact times should increase not decrease yields. Evidently, at high temperatures, some of the cellulose molecules can be directly decomposed into smaller weight fragments and these free radicals can combine to form volatile products. Levoglucosan would not be formed as an intermediate for this route to the lower molecular weight products. This may be the explanation for the deviation of our data from those

obtained by Tsuchiya and Somi (1970) and some of the data of Shafizadeh et al. (1978a, 1979b).

Closure of the material balances to about 2% when MCP was pyrolyzed, permits a reliable picture to be drawn of the product distribution between solid tar, liquid and gas for flash pyrolysis in a fluidized bed. This distribution is shown as a function of temperature in Figure 9. Pyrolysis atmosphere and the particle size of cellulose up to 20 to 40 mesh do not affect the distributions. The levoglucosan product is also shown.

It is clear from the figure that the liquid-tar fraction of the products can be maximized by operating between 450 and 650°C. Higher temperatures increase gas production while lower temperatures result in large char residues.

The remarkably similar yield vs. temperature behavior seen in Figures 3 to 6 suggest cross plotting of the yield data. When this is done it is found that all the pyrolysis products with the exception of levoglucosan and other tar components plot as simple logarithmic functions of the form

$$Y_x = a Y_{CO}^b \quad (1)$$

against CO yield (Y_{CO}) or against CO_2 yield. Examples of such plots appear in figures 10 and 11. The functions are independent of temperature, gas atmosphere, and particle size. Linear relationships on these log-log plots hold very closely from CO yields of from 0.5 to 20 weight percent. Data of other studies, including Tsuchiya and Sumi (1970) who worked with slow pyrolysis, also give linear cross plots and both for furan and the light hydrocarbons these data agree quite well with what was observed in this study even though the pyrolysis technique differed substantially. Probably then, Equation 1 and its parameters are independent of the type of flash pyrolysis unit. Agreement was poorer for other products so probably Equation 1 cannot be generalized to slow pyrolysis. Yield relationships appear to offer a useful means of predicting product distribution in flash pyrolysis operations. The relationships are developed and discussed in more detail in a recent paper by Funazukuri et al. (1984).

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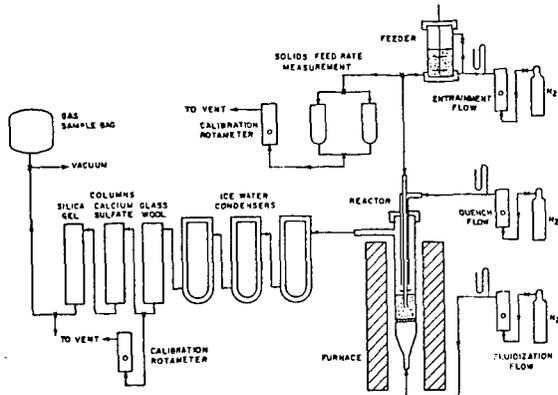


Figure 1 Micro Fluidized bed pyrolysis system (Scott and Piskorz, 1981)

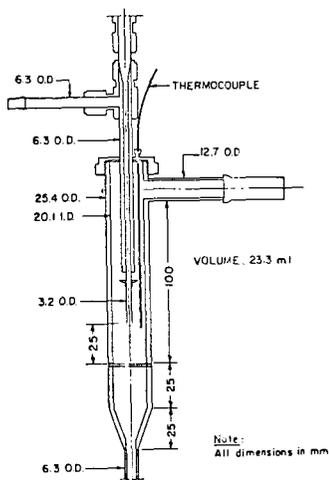


Figure 2 Construction details of fluidized bed (Scott and Piskorz, 1981)

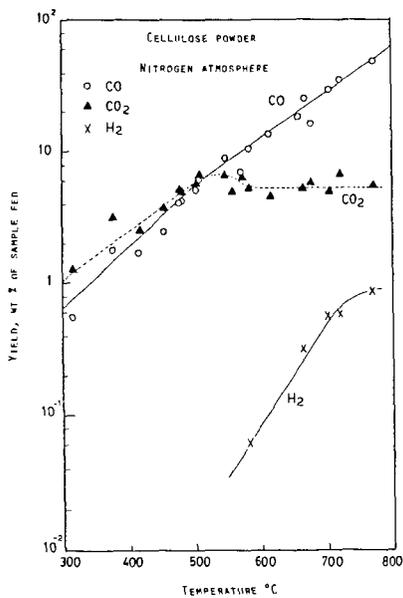


Figure 3 Light gas pyrolysis yield from MCP

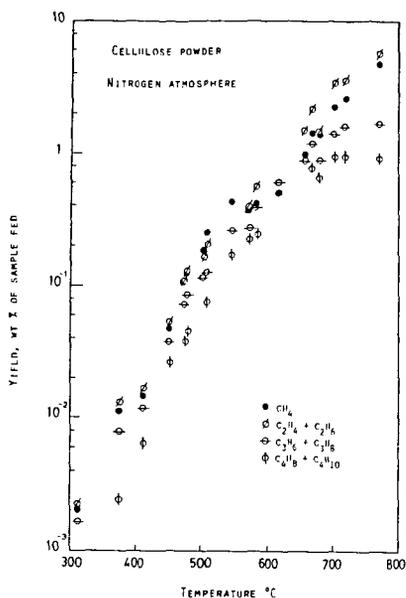


Figure 4 Yield of light hydrocarbon from MCP

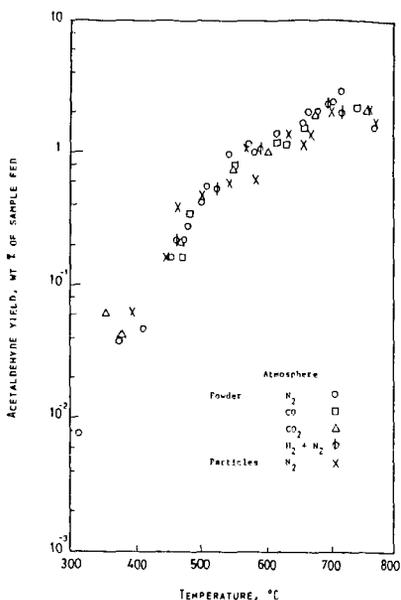


Figure 5 Yield of acetaldehyde from MCP and Cellulose particles

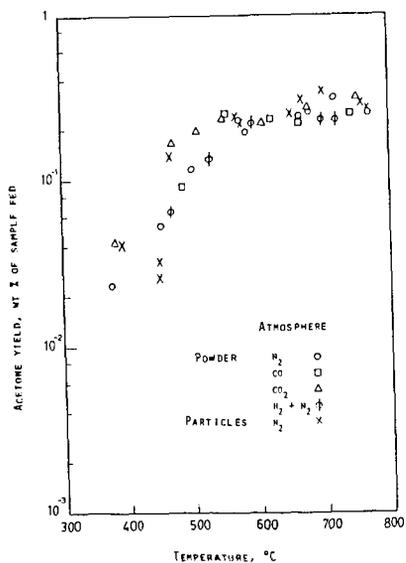


Figure 6 Yield of acetone from MCP and cellulose particles

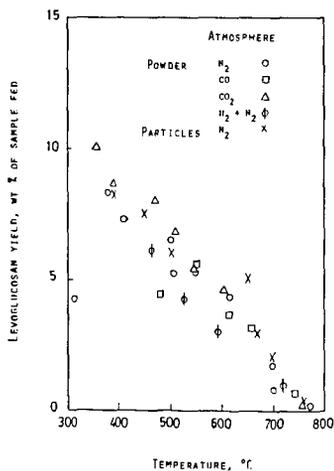


Figure 7 Yield of levoglucosan from MCP and cellulose particles

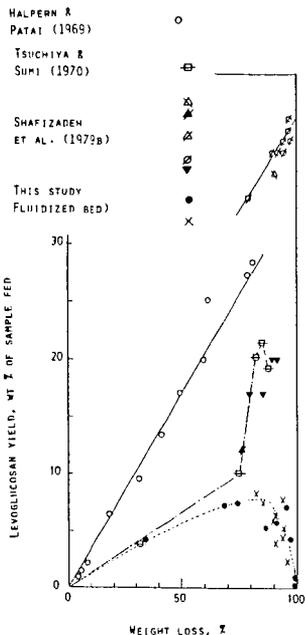


Figure 8 Levoglucosan yield as a function of weight loss with a comparison with slow pyrolysis data

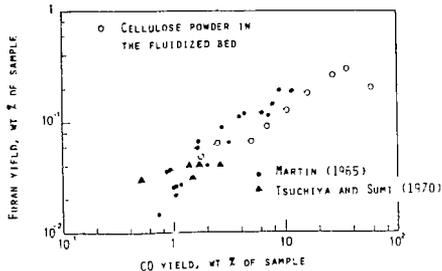


Figure 11 Cross plot of furan yields and CO yields from MCP

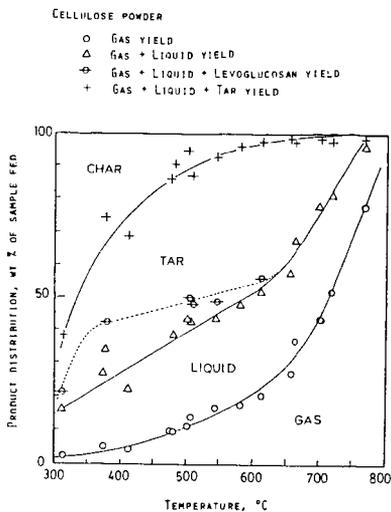


Figure 9 Product distribution in flash pyrolysis of MCP

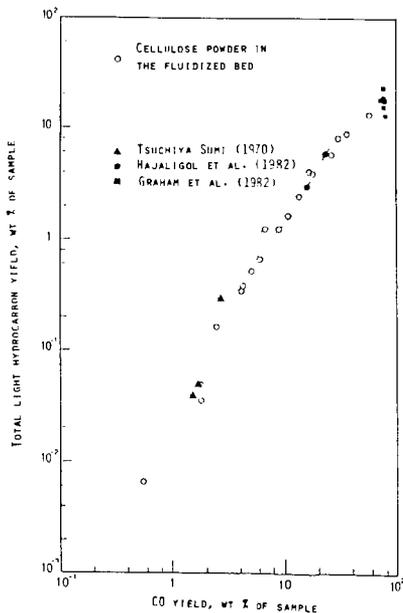


Figure 10 Cross plot of light hydrocarbon yields and CO yield from MCP