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EFFECTS OF PRESSURE ON BIOMASS PYROLYSIS. I. CELLULOSE PYROLYSIS PRODUCTS

WILLIAM S.-L. MOK and MICHAEL J. ANTAL, JR. *

Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08544 (U.S.A.)

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ABSTRACT

A three phase research program, using a tubular, laminar flow, micro reactor system, was undertaken to study the effects of pressure on biomass pyrolysis. Results of the first two phases indicate that increasing pressure increases the yields of char and CO_2, and decreases the yields of CO, CH_4, C_2H_6 and C_3H_6. Increased volatile residence time favors the formation of char, and increases yields of C_2H_6 at the expense of CO and C_3's. The addition of small amounts of O_2 reduces the yields of all hydrocarbons, but has little effect on char formation.

INTRODUCTION

Various reactors, designed to pyrolyze and gasify biomass and solid wastes, are presently in commercial operation or running on a pilot scale. Many design considerations, such as improving throughput, reducing the cost of product gas compression, and increasing reaction rates, underlie the development of high pressure reactors. The effects of pressure on pyrolysis chemistry, product distribution, and heat demands are thus of great interest for reactor design.

An extensive literature search reveals, however, scarce and scattered data regarding the effects of pressure on biomass pyrolysis and gasification. Cellulose pyrolysis at atmospheric pressure reportedly produces a higher char yield and a lower levoglucosan yield than pyrolysis under a vacuum [1,2]. Studies conducted by the Wright Malta Corporation [3] on their high pressure biomass gasifiers show opposing influences of pressure in the steam gasification of biomass. In the lower range, increasing pressure promotes reactions between water and char by increasing the steam concentration and forming aqueous films on the char particles. But above 300–400 psi, increas-

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* Present address: University of Hawaii, Hawaii Natural Energy Institute, Honolulu, HI 96822, U.S.A.

ing pressure shifts the product distribution towards the formation of higher molecular weight tar and char. It is also reported that the overall gasification process is more endothermic at lower pressures [3].

To study systematically the effects of pressure on biomass pyrolysis, a three-phase 2-year research program was undertaken. The following is an overview of the three-phase effort.

Phase 1: a study of the effects of pressure and residence time on the overall pyrolysis product distribution.

Phase 2: a study of the effects of the addition of a small amount of oxygen on the pyrolysis product distribution detailed in the phase 1 studies.

Phase 3: a study of the effects of pressure on the heat demand and mechanism of pyrolysis reactions.

Cellulose, the major component of most biomass materials, was used in the first two phases. Other biomass materials were included in the phase 3 studies. In this paper, results from phase 1 and 2 experiments will be discussed.

EXPERIMENTAL

Apparatus

An overall schematic of the experimental apparatus, designed to cover the uses required throughout the three phases of research, is provided in Fig. 1. This system can be divided into three main parts: (1) 2 micro reactors, partly embedded in a differential scanning calorimeter for solid phase pyrolysis studies, and partly in a heating block for gas phase cracking; (2) a system to generate pressure using either steam or an inert gas (argon); and (3) an exit system with product gas collection. The dual reactor design was adopted since the DSC requires both a sample and a reference reactor. However, the DSC was not used during the first two phases of experimentation. Instead, heater tapes were used to raise the temperature of the solid phase pyrolysis zone.

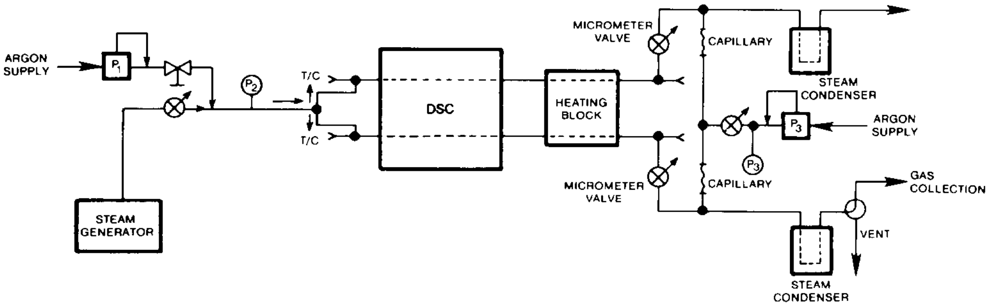

Fig. 1. Overall schematic of the pressurized DSC reactor system.

Tubular micro reactors

The two micro reactors, with an internal diameter of 4.64 mm, were fabricated from type 316 stainless steel, capable of repeated operations at 25 atm and 800°C. For all the experiments described in this paper, the flows through the gas phase zone of the reactors were laminar, with Reynolds numbers ranging from 3 to 16.

Sample holder

The identical sample holders, one for each reactor, were also constructed from type 316 stainless steel. Geometrically, each was a horizontal cylinder (diameter 3 mm, length 12 mm) with an open top. Each cup was welded onto the end of a type K (chromel–alumel) thermocouple with a stainless steel sheath, which monitored the sample temperature and positioned the cups within the reactors.

Gas phase heating block

Eight heater cartridges were symmetrically located within a block of stainless steel 3 in. in length. The center of the block housed the gas phase zones of the micro reactors. The heating cartridges were controlled directly by a Love proportional temperature controller with fast cycling solid state output (Model 49-844).

Pressure and flow system

The reactors were pressurized by steam, supplied by a Steam Master PP-6 steam generator which set an upper pressure limit of 6 atm. Steam also served as the carrier gas. Argon was used to purge the system of air. During phase 2, controlled amounts of oxygen were introduced via the argon supply inlet of Fig. 2.

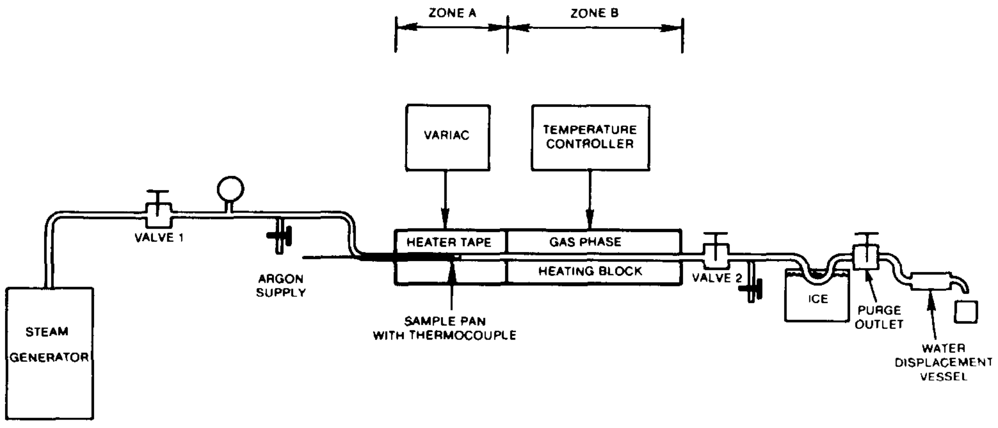

Fig. 2. Flow diagram of the pressurized flow reactor as used in phase 1 experiments.

Exit system and product gas collection

Nupro bellows metering valves (SS-413MW), which allow fine flow control at high temperatures, were used at the reactor exits. After passing through an ice trap, the remaining permanent gases were collected within a water displacement vessel. Concerns regarding the solubility of permanent gases led to a careful evaluation [4] of the potential displacement fluids. It was concluded that if gas samples were withdrawn within 20 min of collection, distilled water is as suitable a displacement fluid as any other potential fluid.

Gas chromatograph

Product gases were transferred by syringes to a Hewlett Packard 5840 gas chromatagraph for analysis, using both flame ionization and thermal conductivity detectors to detect various hydrocarbons and other fixed gases. A 10 ft. Poropak QS 50–80 mesh column (1/8 in. diameter) in series with a 6 ft. Porasil A 80–100 mesh column was used in conjunction with a mixture of 91.5% He and 8.5% H_2 as the carrier gas, flowing at a rate of 30 cc min^{-1}. The temperature history of the analysis consisted of an initial 2 min hold at -50°C, followed by a 30°C min^{-1} rise to 240°C, and finally a 10 min hold at 240°C.

Samples

The following cellulose samples were used: Whatman No. 1 filter paper (0.06% ash) cut into rectangular strips (10 mm × 2 mm), and Avicel PH102 microcrystalline cellulose from the FMC corporation.

Procedures

First, the steam flow was calibrated to achieve the desired reactor pressure and gas phase residence time by adjusting micrometer valves 1 and 2 (see Fig. 2). The material was then placed in the sample holder and inserted into the middle of zone A (for solid phase pyrolysis), which was maintained at 150°C before pyrolysis. Zone B (for gas phase cracking) was maintained at 700°C. Pyrolysis was initiated by electrically heating zone A, which rose to 500°C in approximately 4 min. The experiment was terminated when no gas evolution was detected for 15 min. Gas products were collected by water displacement after condensation of the steam, and were analyzed by gas chromatography. The sample holder was then removed and the char weighed. The C, H, O fractions of char were determined by an independent laboratory to be 0.78, 0.4 and 0.18, respectively. Tar collection was not possible with this apparatus. However, a previous study [5] showed that tar formation is small under the present experimental conditions.

For the phase 2 experiments, a measured flow of O_2 was introduced into the reactor via the argon supply inlet of Fig. 2. The oxygen was mixed with the steam before entering zone A. The rest of the procedures were similiar to those described above.

RESULTS AND DISCUSSION

Phase 1

Initial experiments were conducted with the Avicel cellulose at 1, 2, 3 and 5 atm pressure and a gas phase residence time of about 1 s. The resultant yields of CO_2, CO, H_2, CH_4, C_2H_4, C_2H_6, C_3H_6 and fractions of carbon converted to permanent gas species (i.e. g of C in gas/g of C in feed) are presented in Figs. 3–5.

The collected data are very scattered. This scattering can be explained by noting some experimental difficulties. The setting of pressure and residence time was done by simultaneously adjusting valves 1 and 2 (Fig. 2). Since a pressure regulator for steam was not available, it was difficult to adjust the reactor pressure to the desired value while at the same time maintaining a predetermined residence time. Further, after the reactor was calibrated and the sample inserted, the heating of the solid phase pyrolysis zone altered the calibrated pressure, and hence the residence time. The new pressure was reported by the pressure gauge, but the new residence time had to be calculated using the amount of steam collected during the duration of the

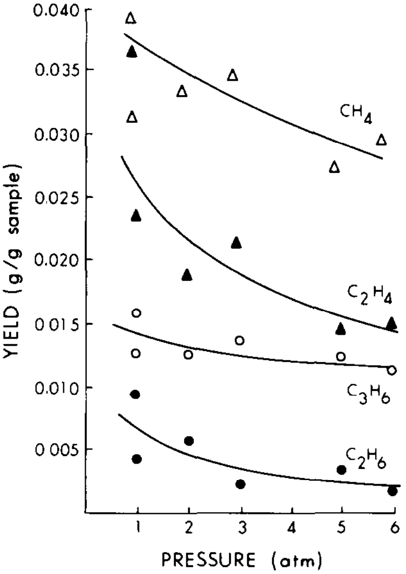

Fig. 3. Yields of hydrocarbons from cellulose pyrolysis as a function of pressure. Residence time = 1 s. △, CH_4; ▲, C_2H_4; ○, C_3H_6; ●, C_2H_6. Lines indicate trend only.

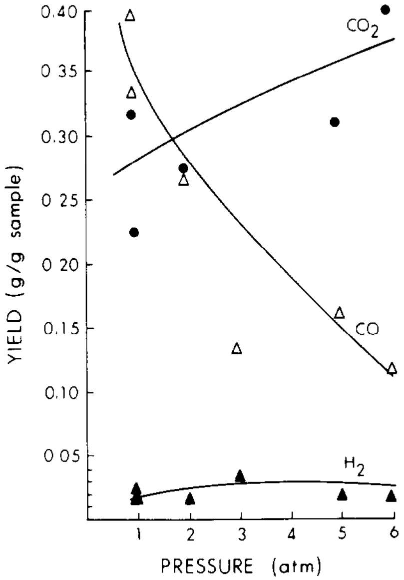

Fig. 4 Yields of CO(△), CO_2(●) and H_2(▲) from cellulose pyrolysis as a function of pressure. Residence time = 1 s. Lines indicate trend only.

experiment. Therefore, although pressure was the only desired parameter, the effect of an accompanying change in residence time was difficult to avoid. Repeated experiments at 1 atm pressure showed differences of more than 30% between the gas yields from two experiments under supposedly identical experimental conditions. However, trends of gas yields as a function of pressure are discernable despite the scatter.

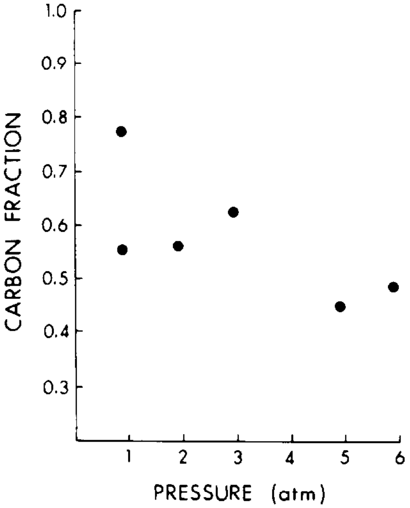

Fig. 5. Fraction of feed carbon found in gas species.

The trends displayed in Figs. 3–5 can be summarized as follows: increasing pressure decreases yields of CO, CH_4, C_2H_6, C_2H_4 and C_3H_6, but increases yields of CO_2 and H_2. Overall, the fractions of feed carbon contained in the effluent gases decrease as pressure increases. As will be explained later, we were unable to measure the char yields from Avicel cellulose accurately. However, the decreasing total gas yields suggest an increasing char yield with pressure.

A previous study [5] has shown that the effects of increasing residence time on the gas yields asymptote at about 1 s under atmospheric pressure. The present work investigates whether the gas yields asymptote similarly under increased pressure.

A comparison of gas yields with 1 and 10 s residence time at 5 atm is given in Table 1. No gross differences in the yields of H_2, CH_4, and C_2H_4 were observed. However, a drastic decrease in CO was evident, accompanied by a non-negligible increase in C_2H_6, and a decrease in C_3H_6.

The material balances of all the above experiments were unsatisfactory, averaging only 0.6. Normally, this would indicate gross experimental errors and lead to serious doubts concerning the validity of the collected data. However, if the poor material balances could be accounted for by a loss of char, then the validity of the reported gas trends could be maintained. Avicel cellulose was originally chosen so that comparison could be made with earlier research in this laboratory. Unfortunately, the Avicel cellulose is extremely powdery and the resultant char was easily blown away. To show that the material balances could be closed by collecting all the char, another set of experiments was conducted using Whatman No. 1 filter paper as the cellulose sample. The results are summarized in Table 2. As shown in Table 2, the structural integrity of the Whatman filter paper enabled the char to remain in the sample cup, thus permitting adequate char collection and an improved closure of the carbon balance. A char yield as high as 23% was observed, and the carbon balance was in the order of 85%. A phenomenon not observed previously was a definite increase of char yield with increasing residence time.

Results given in Table 2 also verify that an extended residence time effects a decreased yield of CO and C_3H_6, but an increased yield of C_2H_6. An

TABLE 1

Comparison of gas yields from pyrolysis and gasification of Avicel cellulose at residence times of 1 and 10 s and 5 atm total pressure

Residence time(s)	Gas yields (g/g sample)						
	CO_2	CO	H_2	CH_4	C_2H_6	C_2H_4	C_3H_6
1	0.304	0.148	0.018	0.027	0.003	0.014	0.012
10	0.355	0.009	0.014	0.028	0.013	0.012	0.004

TABLE 2

Effects of gas phase residence time on pyrolysis and gasification of Whatman filter paper at 5 atm pressure

Residence time (s)	Gas yields (g/g sample)							Char (%)	Carbon balance
	CO_2	CO	H_2	CH_4	C_2H_6	C_2H_4	C_3H_6		
1	0.323	0.167	0.018	0.035	0.012	0.022	0.015	15	0.78
5	0.516	0.097	0.023	0.040	0.017	0.024	0.013	16	0.87
15	0.579	0.004	0.018	0.040	0.027	0.013	0.003	22	0.89
18	0.485	0.004	0.011	0.036	0.023	0.014	0.005	23	0.85

increase in CO_2 and a decrease in C_2H_4 yields were also observed. No apparent effect of residence time on H_2 and CH_4 formation was detected.

Phase 2

This phase consisted of a series of experiments to study the effect of the presence of a small amount of free oxygen on the pyrolysis process. The goal was to identify the conditions which would maximize the yields of CO and H_2, and minimize CO_2 formation. Experiments were conducted at 1 and 5 atm, using 10 mg samples of Whatman filter paper.

To determine a suitable rate of oxygen flow, the time needed for pyrolysis was first determined by examining previous thermogravimetric experiments. Using the NASA thermochemical equilibrium program [6], the equilibrium product mixture as a function of feed-to-oxygen ratio was then calculated, and the ratio which would yield maximum CO vs. CO_2 was determined. Dividing the amount of oxygen needed to achieve the maximum CO_2: CO ratio by the time of pyrolysis, a flow rate of 2 cc min^{-1} was determined.

In Table 3, the results of these experiments are summarized and compared with previous experiments without the additional oxygen. The various material balances reported in Table 3 have as their denominators the relevant amount contained in the solid sample, and not the total material input. Because any H_2O formed as a pyrolysis product is not distinguishable from the carrier steam, it is not included as part of the material output. Consequently, it is not surprising to find an oxygen balance of more than 100% due to the additional input of free oxygen, and a very low hydrogen balance due to oxidation resulting in water.

The effect of pressure on pyrolysis in the presence of oxygen can be seen by comparing lines 1 and 2 of Table 3. Consistent with results from previous pyrolysis experiments without the oxygen, high pressure increases the char yield and decreases the gas yields. However, contrary to previous results, there is a slight decrease in the CO_2 yield.

TABLE 3

Results of cellulose pyrolysis in the presence of oxygen, compared with similar results without free oxygen input

Pressure (atm)	Gas yields (g/g sample)							Char (%)	Balances		
	CO_2	CO	H_2	CH_4	C_2H_6	C_2H_4	C_3H_6		C	H	O
With free oxygen											
1	0.491	0.456	0.011	0.019	0.003	0.021	0.005	9	0.99	0.39	1.3
5	0.451	0.261	0.012	0.021	0.002	0.015	0.007	15	0.87	0.42	1.0
Without free oxygen											
1	0.316	0.395	0.021	0.039	0.009	0.037	0.016	[a]			
5	0.323	0.167	0.018	0.035	0.012	0.022	0.015	15	0.78	0.66	0.72

[a] Avicel cellulose used. Balance and char not recorded due to loss of char. Whatman filter paper used for other experiments.

The effects of the free oxygen can be seen by comparing lines 1 and 3 and 2 and 4 in Table 3. The oxygen has led to significant increases in the yields of CO_2 and CO, and decrease in H_2. The yields of the lower hydrocarbons (CH_4, C_2H_4, C_2H_6) have also decreased while the higher hydrocarbons (C_3's and C_4's) have been reduced to trace amounts. This clearly indicates a combustion phenomenon. The higher hydrocarbons are first broken down to form smaller ones, followed by oxidation to form CO and finally to CO_2. The loss of hydrogen suggests a preferential oxidation of the hydrogen to form water. The effect of oxygen on the char yield is not very significant, and suggests the participation of the free oxygen to be minimal in the solid phase reactions, when compared to the participation in the gas phase reactions.

CONCLUSIONS

Increasing pressure favors the formation of char and CO_2, and reduces the yields of CO and all hydrocarbons from the pyrolysis of cellulose in steam. An extended residence time increases the formation of C_2H_6 at the expense of CO and C_3's; it also favors the formation of char. With the addition of oxygen, a gas phase combustion phenomenon can be observed. The presence of the free oxygen has little effect on the solid phase pyrolysis reactions.

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