STEAM GASIFICATION OF COTTONWOOD (BRANCHES) IN A FLUIDIZED BED

Satish K. Singh, Walter P. Walawender,
and *L. T. Fan*

Department of Chemical Engineering

and

Wayne A. Geyer

Department of Forestry
Kansas State University
Manhattan, KS 66506

ABSTRACT

Cottonwood (branches) were gasified in the presence of steam in a 5.08 cm I.D. bench-scale fluidized bed reactor, over a temperature range of 850 to 1,075 K. The objective of the study was to investigate the effect of reactor temperature on the produced gas composition, yield, heating value, energy recovery, and carbon conversion. The results were compared with data obtained from alpha-cellulose in the same reactor to gain insight into the secondary gas phase reactions that occur in biomass gasification.

The major components of the produced gas were CO, CO_2, H_2, and CH_4, which comprised over 90% of the gas. The gas yield, energy recovery, and carbon conversion all increased with increasing temperature: from 0.23 to 1.59 m^3/kg dry ash-free feed, 15.0 to 96.8%, and 16.9 to 87.1%, respectively. The higher heating value of the gas ranged from 12.4 to 11.6 MJ/m^3. The dependence of the gas composition on temperature indicated the existence of two regimes for the secondary gasification reactions with a transition occurring over the temperature range of 930–950 K. The first regime (below this temperature range) was dominated mainly by the cracking of cellulose tar. The extent of lignin tar cracking was small compared to that of cellulose tar in this regime. The second regime was dominated by the water gas shift reaction. Cellulose tar cracking was essentially complete in the second regime, and the relative amount of lignin tar cracking was small. Thus the gas composition was primarily determined by the shift reaction in the second regime. The observed behavior for wood gasification was similar to that for alpha-cellulose, although the transition from one regime to the other was not as sharp. Steam, when present in large amounts, was found to be an active gasification agent in the second regime.

Keywords: Cottonwood, steam gasification, fluidized bed, temperature dependence, tar cracking, shift reaction.

INTRODUCTION

Gasification offers an attractive method for converting wood into a clean gas, usable for either chemical synthesis or as a utility fuel. Currently, wood provides about 2% of our total energy needs and could contribute up to 8% within the next decade (Zerbe 1981). The annual harvest of woody biomass amounts to about 1.4 billion tons in the U.S. alone. Over 700 million tons of the harvested material is not used because it is not of the right species, size, fiber length, or fiber morphology (Goldstein 1978). Branchwood is a prime example of this type of wood waste. The potential for the conversion of wood wastes to provide an alternate supply of fuel and chemicals is significant.

Destructive distillation of wood has been practiced for centuries. The process

was originally used to produce charcoal, but in the later part of the nineteenth century, emphasis shifted towards the recovery of chemicals such as methanol, acetic acid, and acetone from the pyrolignious acid. However, with the development of the petrochemicals industry, the use of wood as a source of organic chemicals has declined.

Fluidized beds were first studied for wood pyrolysis about 30 years ago. Among the early reports on fluidized bed pyrolysis was an investigation by Morgan et al. (1953), in a batch reactor fluidized by nitrogen. They pyrolyzed powdered hardwood and obtained a charcoal yield of 32% at 673 K after 30 minutes of operation. Kilburn and Levelton (1963) used a bed of incandescent charcoal, fluidized by air, to produce charcoal from sawdust in a continuous operation.

More recent work has focused on gas production in a fluidized bed. Rensfelt et al. (1978) conducted basic gasification studies in a flash pyrolysis unit to determine biomass fuel characteristics. The gas mass yield was observed to be strongly dependent on the residence time and temperature of the volatiles. Their results demonstrated the importance of the secondary gas phase reactions of the primary volatiles produced during rapid heating. The extent of the secondary reactions depended on the residence time in the heated zone, temperature, temperature profile, and chemical composition of the pyrolysis environment. It was concluded that steam was an active gasification agent, and was consumed through steam reforming of the hydrocarbons produced in the primary reactions and/or char gasification.

Feldman et al. (1981) studied the gasification of wood in a multi-solid fluidized bed gasifier, consisting of two fluidized beds with solids circulation between them. They examined the effects of gasifier temperature, wood feed rate, steam rate, entrained-phase recycle rate, dense-phase particle size, wood particle size, and moisture content. Temperature was found to have the most influence on the performance of the system. The gas heating value, energy recovery, and carbon conversion increased with increasing temperature. They observed that tar production was negligible, and that steam was not consumed over a temperature range of 963 K to 1,172 K (steam to wood ratio 0.8).

Schoeters et al. (1981) gasified wood shavings, under partial oxidation conditions, in a bed fluidized with air and mixtures of air and steam. An increase in the air-factor, defined as the ratio of the actual flow rate of air to the air flow rate for complete combustion, caused the gas yield to increase, the higher heating value (HHV) of the gas to pass through a maximum, and the energy recovery to be almost unchanged. High steam rates were found to lower the HHV, gas yield, and energy recovery. It was also shown that the freeboard temperature had a considerable influence on the gas yield, gas composition, and HHV. The concentrations of CO_2 and H_2 increased, while that of CO decreased with an increase in the freeboard temperature. This behavior was attributed to the water gas shift reaction.

Using sawdust, Lian et al. (1982) studied air-blown wood gasification in a set of fluidized bed reactors of various sizes. After examining a number of variables (temperature, feed rate, air flow rate, and residence time), they found that the ratio of the total carbon-to-nitrogen in the dry gas correlated best with the important properties of the produced gas including the %C, $\%H_2$, and gas heating value. Their results indicated that at a given total carbon-to-nitrogen ratio, the gas quality was only slightly affected by wide variations in the size of the reactor,
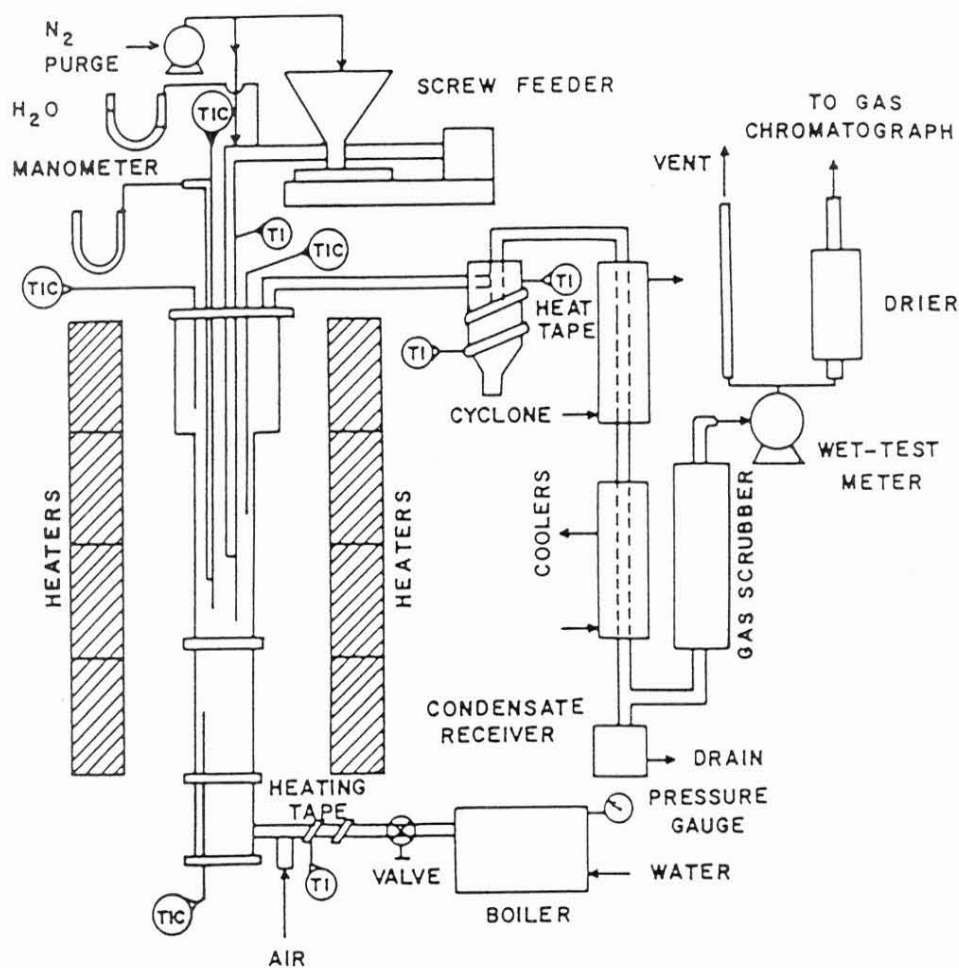
Fig. 1.   Bench-scale reactor system.

the existence of thermal steady state, type of feed, residence time, and the bed temperature. However, these variables did influence char and tar formation.

Wood pyrolysis in a bench-scale reactor, with nitrogen as the fluidizing gas, was investigated by van den Aarsen et al. (1985). They used data from the literature for pyrolysis of small wood particles under high heating rates (250–1,000 K/s) to derive the kinetics of fluidized bed pyrolysis and determined the fast pyrolysis product distribution. The gas yield was found to increase with increasing temperature at the expense of condensate yield due to increased tar cracking with increasing temperature. The pyrolysis of a 1-mm wood particle was predicted as being essentially complete in 2 seconds with a heating rate of about 500 K/s. The char yield was found to decrease with an increase in heating rate and decrease in particle size.

Apart from using the produced gas for fuel, another major use is as a starting material for methanol or ammonia synthesis. Normally, the produced gas needs to be processed further to render it suitable for chemical synthesis. However, catalysts have been successfully employed to promote gasification and shift re-

TABLE 1. *Reactor operating parameters.*

Reactor temperature range	850–1,075 K
Fluidizing gas	Steam
Superficial velocity	0.15–0.20 m/sec
Condensate rate	9.5–15.6 cc/min
Feed rate (average)	1.55 DAF g/min
Particle size (feed)	−28 +50 mesh
Particle size (bed)	
Sand (75 weight %)	−30 +50 mesh
Limestone (25 weight %)	−7 +50 mesh
Gas residence time	2.00–2.35 sec

actions to obtain a methanol synthesis gas with a favorable CO/H_2 ratio (Mudge et al. 1981).

Wood sawdust, being a waste product, has been commonly used for the generation of energy. However, branchwood, which does not satisfy the requirements of the traditional wood users (lumber, paper, furniture, and construction industries) also represents a waste that can be used as a source of energy. The objective of this work was to examine the steam gasification of cottonwood (branches) in a fluidized bed, with continuous feed under steady-state conditions. The gas composition and other properties of the gas were examined as functions of temperature, with the gas residence times being held relatively constant. The specific properties examined included the gas heating value, gas yield, carbon conversion, and energy recovery. Comparison was made with data for alpha-cellulose gasification, obtained from the same reactor under similar operating conditions.

EXPERIMENTAL FACILITIES AND PROCEDURE

Facilities and procedure

A schematic of the bench-scale fluidized bed gasifier used in this study is shown in Fig. 1. The reactor had an I.D. of 5.08 cm, and the bed material was a mixture of 25 wt % limestone and 75 wt % silica sand. The bed had a static height of 8 cm and an expanded height of about 11 cm.

A detailed description of the experimental set-up has been given by Walawender et al. (1985a, b). The present set-up differed only in the way the reactor heaters were controlled and the way the steam was generated. The top three pairs of heaters were controlled by three Omega (model 49K-814) three-mode controllers instead of simple thermostats. Steam was generated in a Sussman Hot-Shot boiler (model MB-6) and was supplied to the distributor/preheater section at approximately 400 K and 202.6 kPa.

The experimental procedure was similar to that described by Walawender et al. (1985a). A typical experimental run lasted between 100 to 130 minutes with the last 40 to 50 minutes yielding steady gas chromatograph readings.

Chemical analyses

Analyses of the dry off-gas were conducted with an Applied Automation (Optichrom 2100) on-line process gas chromatograph (GC). The components of interest were H_2, CO, CO_2, CH_4, C_2H_6, C_2H_4, C_3H_6, O_2, and N_2. Moisture and ash
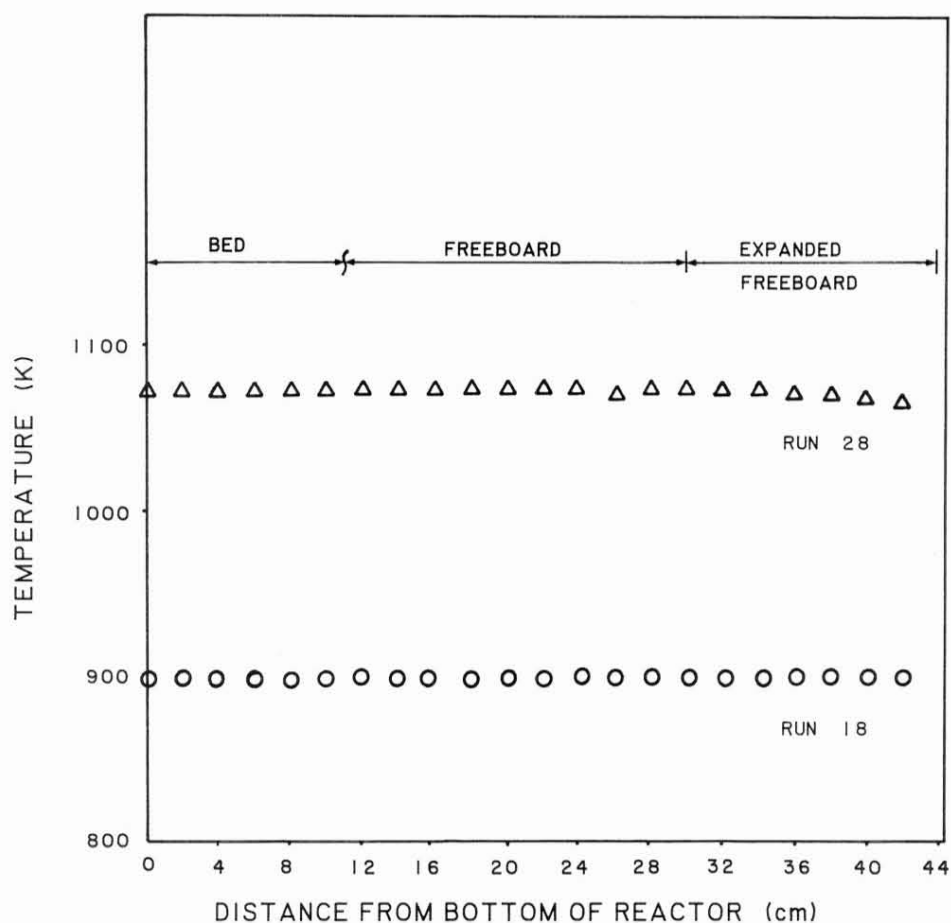
FIG. 2.   Typical temperature profiles in reactor.

analyses of the feed material were performed according to standard ASTM procedures in a ventilated oven and muffle furnace, respectively. Elemental analyses of the feed were conducted with a Perkin-Elmer (model 240b) elemental analyzer. Analyses of the feed for cellulose, hemicellulose, and lignin were conducted by an independent laboratory. Neutral-detergent (cell wall), acid-detergent fiber, and permanganate lignin tests, as described by Goering and Van Soest (1970), were used for these determinations.

Operating conditions

The operating conditions for all the experimental runs are summarized in Table 1. By adjusting the steam rate with the temperature of the run, it was possible to maintain a fairly constant gas phase residence time for all the runs. The gas phase mean residence time, which ranged from 2.0 to 2.4 seconds, was estimated on the basis of reactor temperature, total dry gas flow rate, and steam rate. The observed average feed rate varied between 1.56 and 1.98 g/min, although the screw-feeder setting was the same for all the experimental runs. An average for all the experiments gave a feed rate of 1.77 g/min (1.55 g dry ash-free/min). The

TABLE 2. *Analyses of feed—cottonwood (branches).*

Ultimate analysis (% dry basis)[*]		Component analysis (% dry basis)[**]	
Ash	5.9	Ash	5.5
C	48.6	Cellulose	37.2
H	6.0	Hemicellulose	13.2
N	0.5	Lignin	25.1
O[1]	39.0	Extractives[1]	19.0
Average moisture content		4.8%	
Empirical formula		$C_6H_{8.82}O_{3.62}$	
Heat of combustion (DAF basis)[2]		19.1 MJ/kg	
Heat of combustion (DAF basis)[3]		18.9 MJ/kg	

[*] Average of 6 samples.
[**] Average of 3 samples.
[1] By difference.
[2] Dulong's Formula.
[3] Measured.

principal experimental variable was temperature, with a uniform axial temperature profile being maintained in all the experiments. Typical reactor temperature profiles are shown in Fig. 2.

Feed material

Cottonwood is a medium- to light-weight wood having a specific gravity of 0.32 to 0.37. The cottonwood (*Populus deltoides* Bartr) used in this study was obtained from the branches of three trees—all 12 years old with trunk diameters of about 30 cm. Branches up to 8 cm in diameter and 1 to 12 years old were used. The branches (wood and bark) were first run through a Morbark chipper and then ground in a hammer mill. The −28 + 50 mesh fraction (0.595 mm to 0.297 mm), separated by sifting, was used as the feed material. The separation removed fibrous material that would result in bridging in the feed hopper. Typical elemental and component analyses of the feed material are presented in Table 2.

TREATMENT OF DATA

Calculations

All of the calculations were based on the average of gas composition data obtained during the last 40 to 50 minutes of each run. The GC readings were adjusted (to correct for nitrogen used as feeder purge gas) to evaluate the produced gas composition. The gas composition in turn was used to calculate the higher heating value (HHV) of the gas using the standard heat of combustion for each component. The feed rate used for the calculation of gas yield, energy recovery, carbon conversion, and mass yield was the average value for all the experiments. The volumetric flow rate of the produced gas was determined from the difference in the rates measured by a wet-test meter with and without feeding. The volumetric gas yield of dry produced gas (at 288 K and 101.3 kPa) per unit mass of dry ash-free (DAF) feed was calculated by dividing the produced gas volume flow rate by the feed rate. The energy recovery was calculated as the ratio (expressed as a percentage) of the product of the gas yield per unit mass of DAF feed and the gas HHV to the heat of combustion of a unit mass of DAF feed. The carbon conversion was determined as the ratio (expressed as a percentage) of the mass of carbon in

TABLE 3. *Statistical analysis (Regression models).*

y	R^2	Prob. > F-value	Significant regression model[1]
mole % CO	0.95	0.0001	$y = 64.98 - 5.22*10^{-2}T$
mole % CO_2	0.82	0.0001	$y = 2566.35 - 7.66T + 7.68*10^{-3}T^2 - 2.55*10^{-6}T^3$
mole % H_2	0.97	0.0001	$y = -4246.43 + 12.89T - 1.29*10^{-2}T^2 + 4.31*10^{-6}T^3$
mole % CH_4	0.86	0.0001	$y = 142.78 - 2.73*10^{-1}T + 1.36*10^{-4}T^2$
HHV	0.47	0.0033	$y = 6.12 + 1.60*10^{-2}T - 1.01*10^{-5}T^2$
Gas yield	0.96	0.0001	$y = -21.86 + 4.17*10^{-2}T - 1.85*10^{-5}T^2$
Energy recovery	0.94	0.0001	$y = -1500.01 + 2.90T - 1.32*10^{-3}T^2$
Carbon conversion	0.93	0.0001	$y = -1240.59 + 2.40T - 1.08*10^{-3}T^2$
Mass yield	0.95	0.0001	$y = -17.14 + 3.27*10^{-2}T - 1.44*10^{-5}T^2$

[1] T is reactor temperature in Kelvin.

the gas produced from a unit mass of DAF feed to the mass of carbon in a unit mass of DAF feed. Finally, the mass yield of the gas was calculated by converting the volumetric yield to a mass basis.

Statistical analysis

All the dependent variables were fit to polynomial functions of temperature using the SAS (Statistical Analysis System) package. For each dependent variable, the square of the correlation coefficient (R^2), the probability of falsely rejecting the proposed regression model (Pr. F-value > F-statistic in F-test for significance of regression), and the significant regression model were determined. The model parameters are summarized in Table 3. Compositions of the major gas components (H_2, CO, CO_2, CH_4) were also related to temperature by splines (two lines with a common joint point) for comparison with the alpha-cellulose data from Wala-wender et al. (1985a, b). Linear regression models with different parameters in each temperature region were used to determine the common points. These common points were estimated using a search technique in which various points were tested to determine the ones that gave the minimum sum of the squares of the residuals (Hudson 1966). The common points were found to be close to 930 K for all four major gas components and thus 930 K was used. The model coefficients and statistics for the splines are given in Table 4.

RESULTS

Produced gas composition

The variations in the concentrations of the major gas components, H_2, CO, CO_2, and CH_4, as functions of temperature are shown in Fig. 3. The solid lines represent the spline regression of the data, while the dot-and-dash lines represent the polynomial regression. The concentration of H_2 increased with increasing temperature from 32.3% at 850 K to 48.9% at 1,075 K. The concentration of CO_2 ranged from 33.7% at 850 K to 32.4% at 1,075 K with a minimum of 28.6% at 930 K. The CO concentration decreased linearly with increasing temperature from 20.6% at 850 K to 8.9% at 1,075 K. The methane concentration decreased from 9.3% at 850 K to 6.9% at 1,075 K. The concentrations of the minor gas components (C_2H_6, C_2H_4, and C_3H_6) all decreased with increasing temperature. Their compositions are not plotted since they represent a small part of the gas

TABLE 4. *Statistical analysis (Splines).*

	Model parameters					t test Ho: $\beta_1 = 0$ Prob > |t|	t test Ho: $\beta_2 = 0$ Prob > |t|	F test Ho: $\beta_1 = \beta_2$ Prob > F
y^1	α_1	β_1	α_2	β_2	R^2			
CO	73.235	$-6.14*10^{-2}$	61.30	$-4.86*10^{-2}$	0.96	0.0001	0.0001	0.2885
CO_2	86.56	$-6.27*10^{-2}$	-1.10	$3.15*10^{-2}$	0.76	0.0001	0.0001	0.0001
H_2	-104.78	$1.62*10^{-1}$	31.85	$1.51*10^{-2}$	0.96	0.0001	0.0092	0.0001
CH_4	42.88	$-3.93*10^{-2}$	3.98	$2.58*10^{-3}$	0.89	0.0001	0.1597	0.0001

$$^1 y = \begin{bmatrix} \alpha_1 + \beta_1 \cdot T : T < T^* \\ \alpha_2 + \beta_2 \cdot T : T \geq T^* \end{bmatrix} T^* = 930 \text{ K}.$$

(C_2H_6 0.82% to 0.24%; C_3H_6 0.91% to 0.30%; C_2H_4 2.9% to 1.5%). The broken lines shown in Fig. 3 are the corresponding gas compositions for alpha-cellulose gasification in the same reactor.

Produced gas higher heating value and yield

The HHV of the gas as a function of temperature is shown in Fig. 4. The solid line represents the polynomial regression. The HHV decreased with increasing temperature from 12.4 MJ/m³ at 850 K to 11.6 MJ/m³ at 1,075 K. The variation in the heating value was small, and the average value was 11.8 MJ/m³. The broken line represents the alpha-cellulose data. The variation in the volumetric yield of the gas is shown in Fig. 5 as a function of temperature. The solid line again represents the polynomial regression. The gas yield increased from 0.23 m³/kg DAF feed at 850 K to 1.59 m³/kg DAF feed at 1,075 K. The broken lines are the results for alpha-cellulose.

Energy recovery and carbon conversion

The energy recovery represents the percentage of energy content of the feed that appears as combustible gas. Figure 6 shows the energy recovery plotted against temperature and fitted by polynomial regression (solid curve). The energy recovery increased from 15.0% at 850 K to 96.8% at 1,075 K. The broken lines are the alpha-cellulose results. The carbon conversion as a function of temperature is shown in Fig. 7. The polynomial regression is shown by the solid curve. The carbon conversion increased with temperature from 16.9% at 850 K to 87.1% at 1,075 K. The broken lines are the results for alpha-cellulose gasification.

Produced gas mass yield

The mass yield of gas as a function of temperature is shown in Fig. 8. The polynomial regression is represented by the solid curve. The mass yield of gas increased from 0.24 kg gas/kg DAF feed at 850 K to 1.35 kg gas/kg DAF feed at 1,075 K. The broken lines are the results for alpha-cellulose.

DISCUSSION

All of the experiments in the present study were conducted under steady-state conditions with a well-defined axial temperature profile and gas phase residence time. The feed particles were small (0.595 mm to 0.297 mm), resulting in essentially instantaneous devolatilization (Maa and Bailie 1973; Antal et al. 1978; Antal 1979; Raman et al. 1981a, b; van den Aarsen et al. 1985). In addition, the range
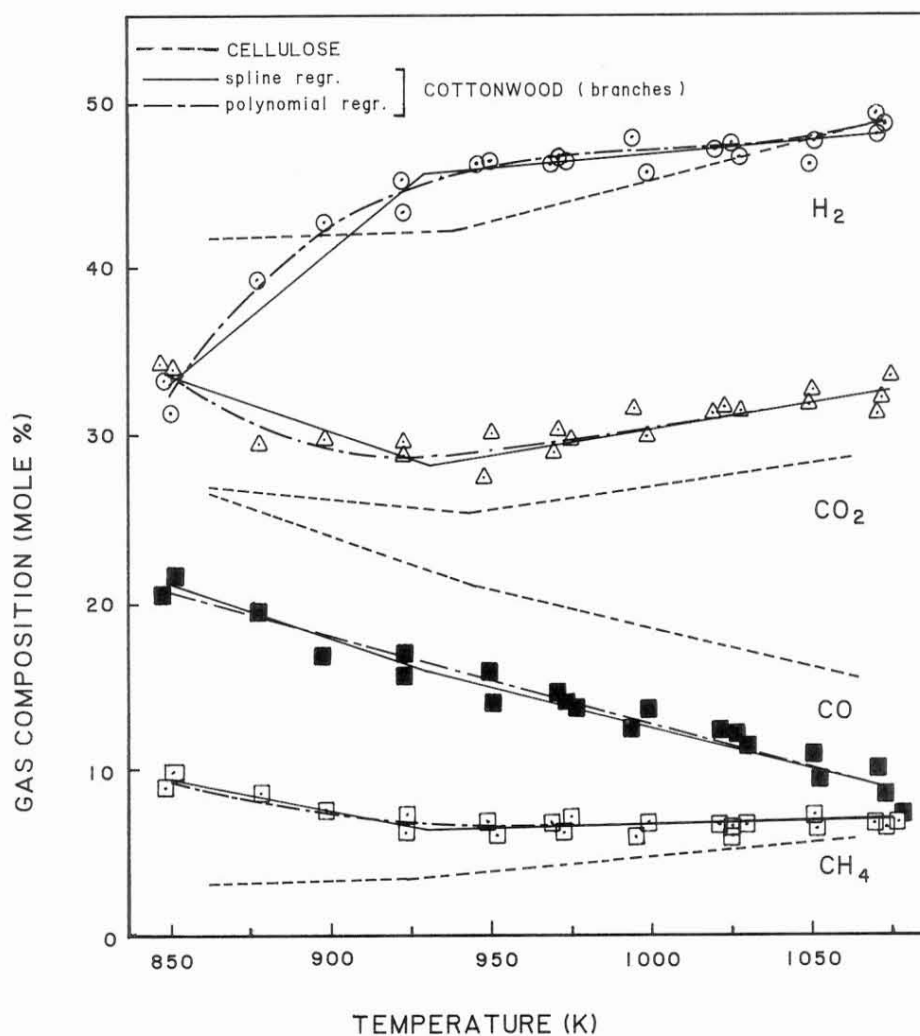
FIG. 3. Gas composition vs. temperature.

of temperatures used was such that char gasification was not important in these experiments (Antal et al. 1978; Rensfelt et al. 1978). Consequently, the results of the experiments reflect the influence of temperature on the secondary gas phase reactions. The results could also be compared with those from Walawender et al. (1985a, b) for alpha-cellulose, which was gasified in the same reactor under very similar conditions.

The component analysis of the cottonwood (branches) used in the experiments was 37.2% cellulose, 25.1% lignin, 13.2% hemicellulose, 5.5% ash, and 19.0% extractives. Shafizadeh and McGinnis (1971) conducted a TGA study on cottonwood and its components and showed that while cellulose and hemicellulose were almost completely devolatilized at 773 K, lignin lost only half of its weight at this temperature. The heating rates used by them were of the order of 15 K/min. In contrast, the heating rates in a fluidized bed are of the order of 1,000 K/s. Con-
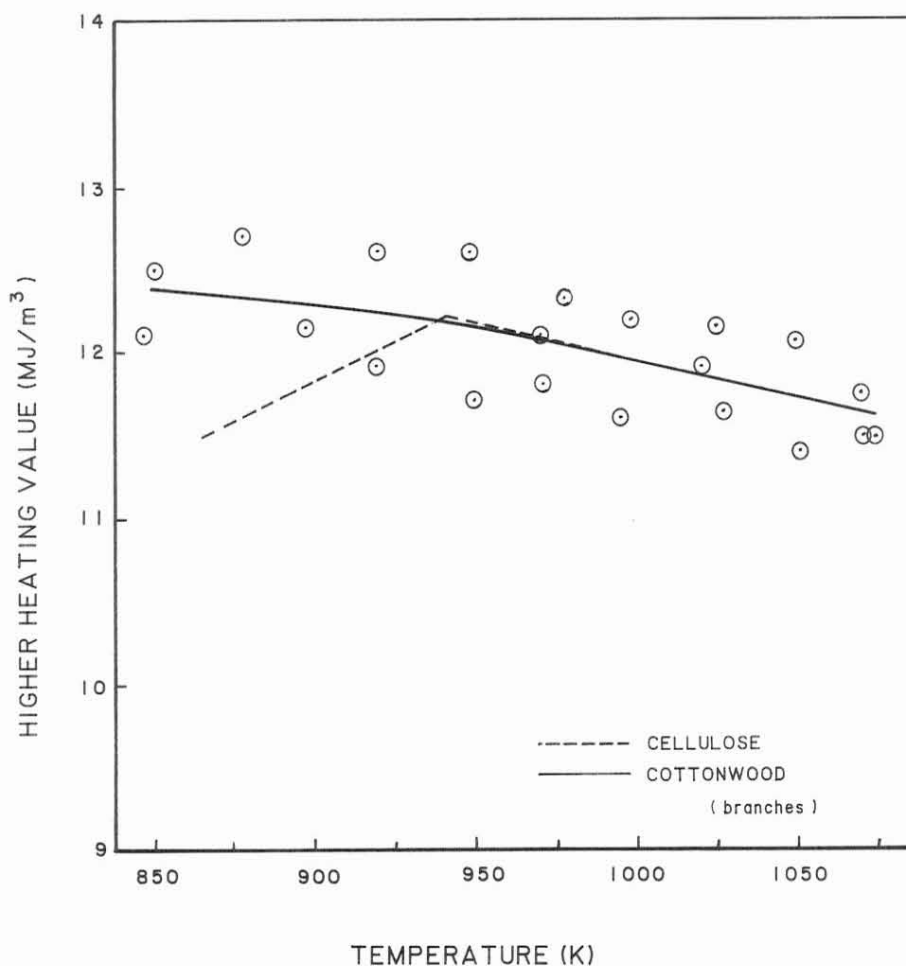
FIG. 4.   Higher heating value vs. temperature.

sequently, the extent of devolatilization in the present work is expected to be higher and the char yield less than the 12% obtained by them. Char yields of the order of 6–8% can typically be expected for wood in a fluidized bed (Rensfelt et al. 1978; van den Aarsen et al. 1985). Although the char yields were not measured in the experiments, visual observation of the amount of char produced indicated that the yields from wood were significantly higher than those from cellulose.

Tar yields also were not measured in the experiments; however, visual observations showed that the tar yields from wood and cellulose were different. Estimates, using the wood component data from Antal (1983, 1985) and the experimental wood composition, indicate that while the tar from lignin in the wood was present even at 1,023 K, its amount (as percent of the dry-ash free wood) did not change appreciably: from 5.8% at 923 K to 3.8% at 1,023 K. The calculations also show that the amount of lignin tar decreased linearly with increasing temperature. The incremental amount of lignin tar cracked between any two temperatures was small relative to the increment in the produced gas mass yield.
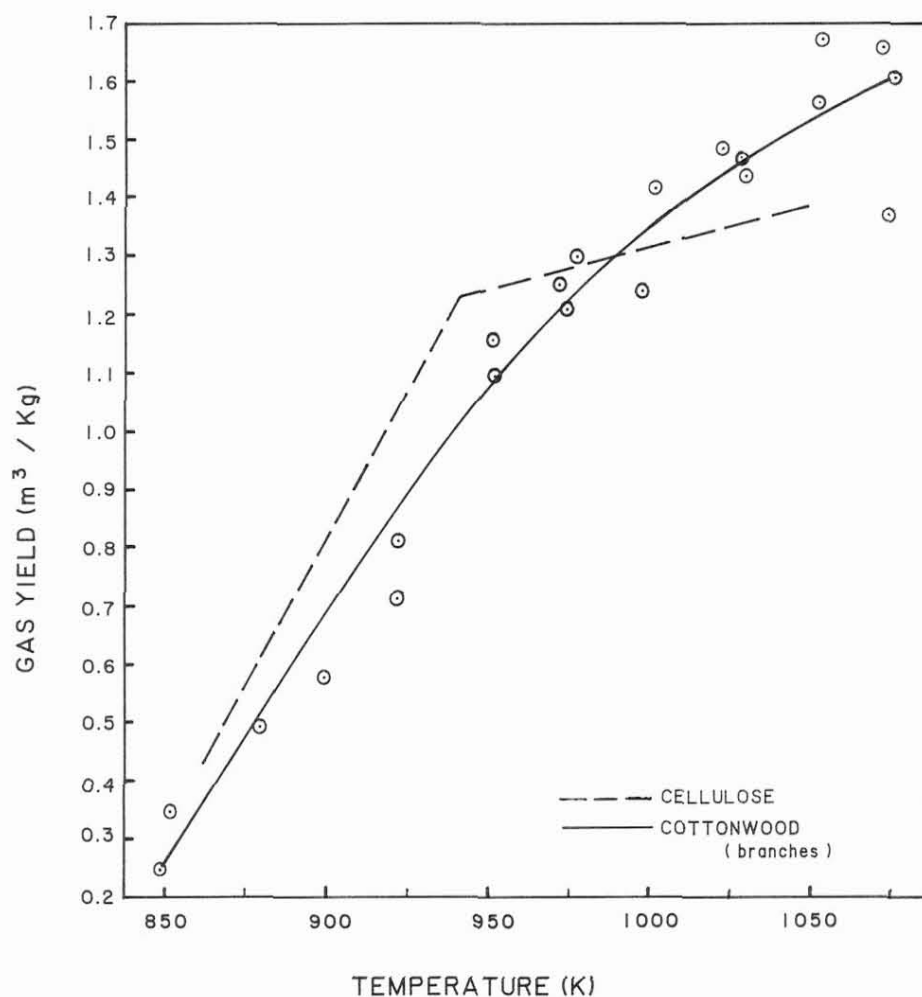
FIG. 5. Volumetric gas yield vs. temperature.

Furthermore, the total lignin tar present relative to the mass yield of gas decreased slowly with increasing temperature: from 8% at 923 K to 3% at 1,023 K. Similar estimates for cellulose show that while the amount of tar from cellulose in the wood was large at 873 K (20% of the wood feed), it decreased rapidly with increasing temperature up to 950 K. The amount of tar from cellulose between 950 K and 1,023 K was almost constant at about 2% of the wood feed. These calculations show that the cracking of cellulose tar was essentially complete by 950 K, although not all the tar was cracked. While similar calculations could not be performed for the hemicellulose, it was expected that hemicellulose would give even less tar than cellulose (Milne 1979). Figure 9 presents the results of the calculations for the above analysis.

Walawender et al. (1985a, b) conducted experiments on the gasification of alpha-cellulose in the same reactor used in the present work under similar operating conditions. They observed that the secondary reactions for volatiles generated
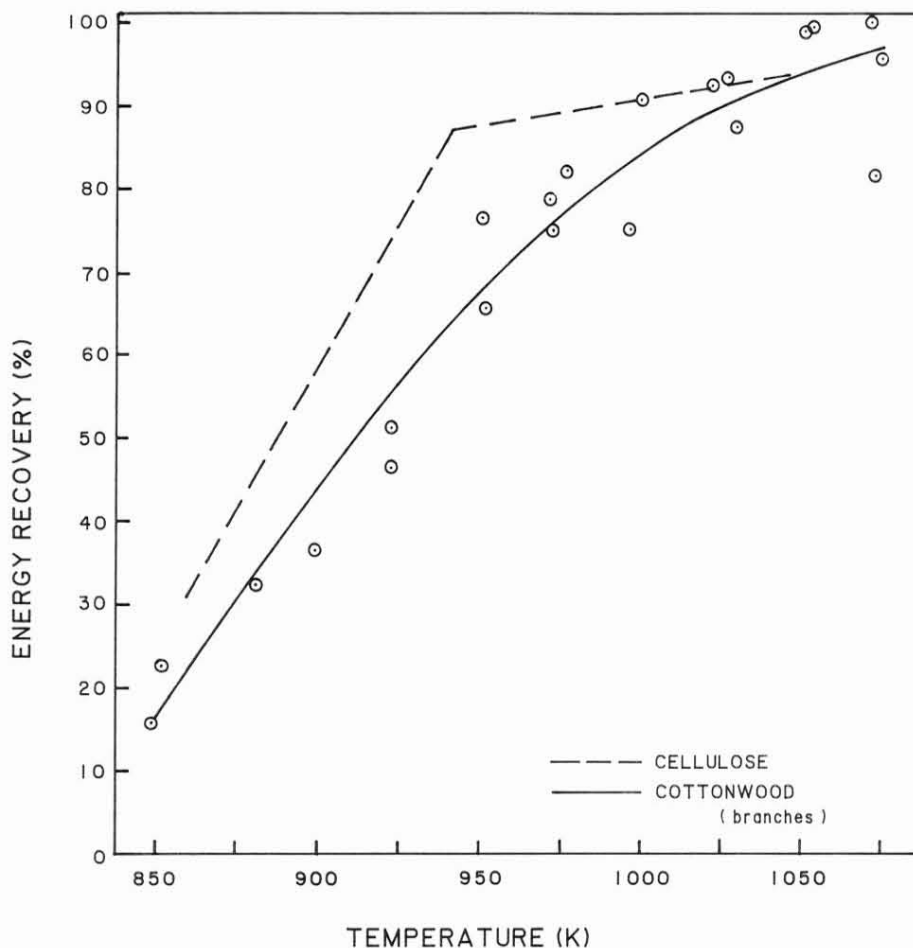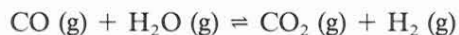
FIG. 6.   Energy recovery vs. temperature.

from cellulose could be described by two distinct regimes with a transition point at 940 K. The first regime, below 940 K, was identified to be dominated by tar cracking. The second regime, above 940 K, was identified to be dominated by the water gas shift reaction. The water gas shift reaction is represented by

$$CO\ (g)\ +\ H_2O\ (g)\ \rightleftharpoons\ CO_2\ (g)\ +\ H_2\ (g)$$

Information about its heat of reaction and equilibrium constants at different temperatures may be found in various standard references (see e.g., United Catalysts Inc. 1969) or calculated from ΔH^f and ΔG^f values (see e.g., Barin and Knacke 1973).

In the present work, sharp transition points at 940 K, as observed in the cellulose experiments, were not seen (Figs. 4–7). However, the transition point was approximated in the gas composition data as indicated in Fig. 3. Even though a distinct transition point was not observed, the evidence presented in the remainder of this section suggests that the two respective regimes dominate in the case of wood as well.
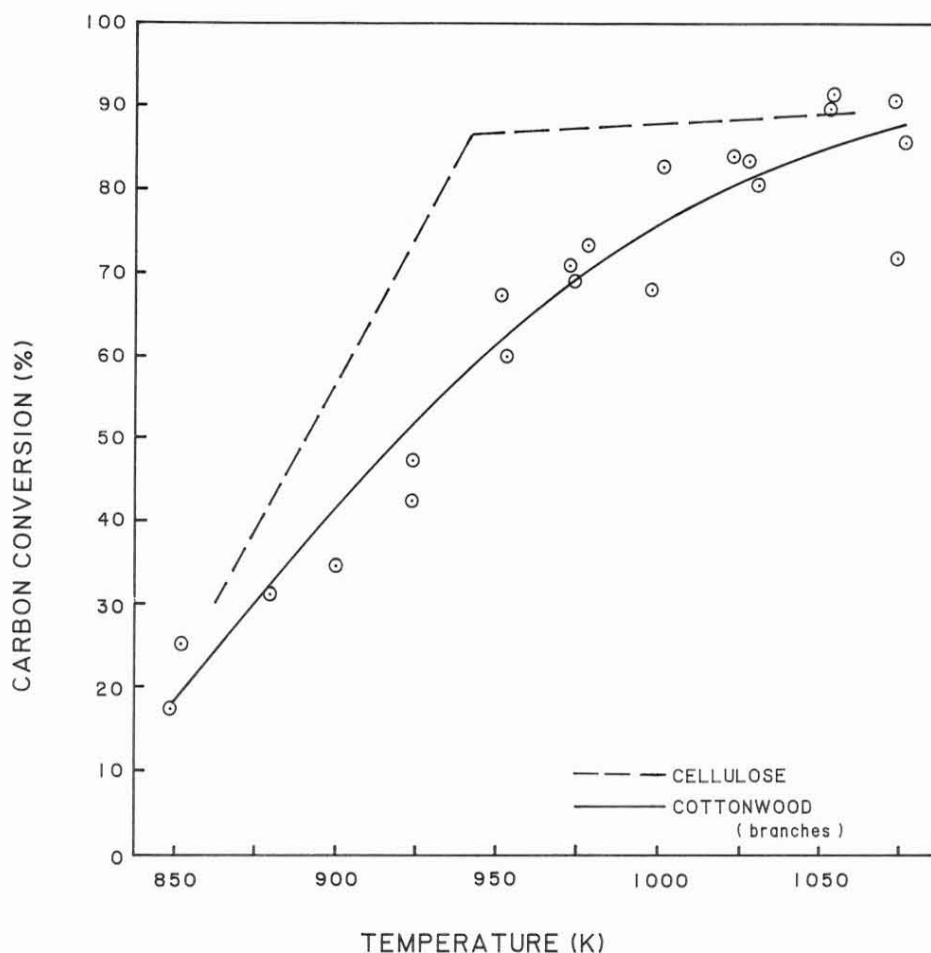
FIG. 7.   Carbon conversion vs. temperature.

In the upper temperature regime, the mass yield of gas was greater than one for both wood and cellulose. This result can be explained by the water gas shift reaction. The large amounts of steam in the experimental system provide a high driving force for this reaction. Calculations of the partial pressure ratios show that the system was far removed from equilibrium for both feedstocks. Estimates at the highest operating temperatures reveal that over 50% of the gas yield came from steam that is shifted to CO_2 and H_2. The condensate measurements were not sufficiently accurate to determine the precise amount of water consumed. Nevertheless, the condensate rate was observed to progressively decrease with increasing temperature over the course of the second temperature regime.

The gas composition versus temperature plots presented in Fig. 3, reveal that the slopes for CO_2 and CO from wood closely parallel those from cellulose over the second temperature regime. For hydrogen, the parallel in slopes is apparent only for temperatures greater than 1,000 K. It is interesting to note that the common points in the splines for wood are fairly close to the common points for cellulose. If the water gas shift reaction is the sole controlling factor, then the
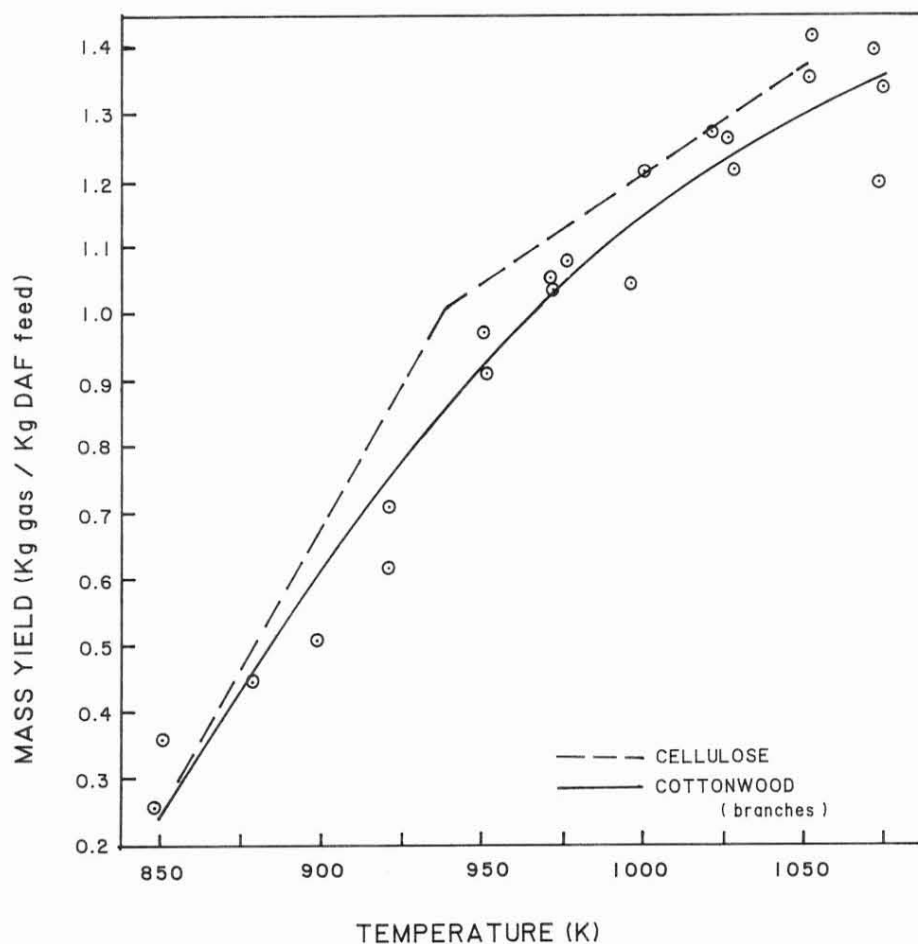
FIG. 8.   Mass yield of gas vs. temperature.

absolute slopes of the three components, CO, CO_2, and H_2, should be in a 1:1:1 proportion. Force fitting of the data for the three gas components from wood, to the theoretical proportions, revealed that all the data could be described by the force fit with a maximum deviation of 2.5%. The cellulose data gave similar results.

The above findings lend strong support to the hypothesis that the water gas shift reaction dominates the second temperature regime. However, it is not the sole factor because the carbon conversion for wood increases in this regime by more than a minor amount, unlike that for cellulose (Fig. 7). A possible explanation for the differences between the observed results for wood and cellulose can be found by examining the cracking behavior of pyrolytic tars from cellulose and lignin. Figure 9 presents the estimated amounts of tar from a unit mass of DAF cottonwood as a function of temperature for both the cellulose component and the lignin component. In the second temperature regime, the amount of cellulose tar is essentially constant while the amount of lignin tar continues to decline. Although the change in the amount of lignin tar appears to be small, estimates
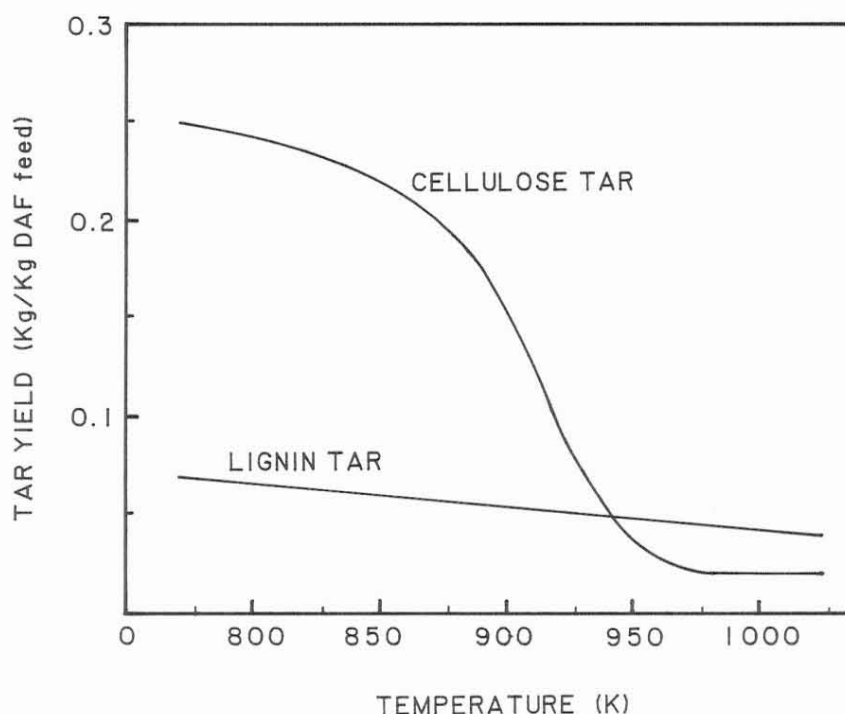
FIG. 9. Estimated tar yield from gasification of cottonwood (branches) vs. temperature.

based on Antal's data (Antal 1983, 1985), reveal that significant changes in carbon conversion can result from tar cracking due to its high carbon content.

Figure 9 also indicates that significant tar cracking takes place in the first temperature regime. The major fraction of the tar cracked between 850 and 940 K originates from cellulose. The increase in carbon conversion with increasing temperature for wood is notably lower than for alpha-cellulose as shown in Fig. 7. This is due to the fact that cellulose is not the sole component of wood and that lignin tar cracking is only weakly affected by temperature in comparison to cellulose tar cracking. Cellulose tar cracking is essentially complete at 940 K as indicated by Fig. 9, whereas lignin tar continues to crack slowly over the entire temperature range. Consequently, the estimates of tar yields presented in Fig. 9 offer an explanation for the differences in carbon conversion for cottonwood and cellulose. Visual observations of the change in color of the condensate in the first regime provide additional evidence to support the proposition that the amount of tar decreases with increasing temperature. The condensate color progressively changed from dark brown to a pale yellow.

A comparison of the gas compositions for wood and cellulose in the first regime as shown in Fig. 3, reveals that the trends for CO and CO_2 are similar, while the trend for H_2 is significantly different. Antal (1985) showed that hardwood (cherry) produced less H_2 than cellulose while lignin produced a significantly larger amount. Cellulose produced the most CO, followed by wood and lignin. Wood gave slightly higher CO_2 compared to cellulose, while lignin gave the least. The relative results for wood and cellulose observed by Antal (1985) correspond broadly to those in

TABLE 5. *Comparison of gasification results.*

	Cellulose ($\tau \sim 1.5$ sec)				Wood ($\tau \sim 2.2$ sec)			
	Antal (1985)		Walawender et al. (1985b)		Antal (1985)		This work	
	873 K	973 K	873 K	973 K	873 K	973 K	873 K	973 K
mole % CO	54.0	53.4	25.7	20.0	43.1	46.7	19.6	14.0
mole % CO_2	21.1	10.7	26.7	26.3	28.7	16.7	31.8	29.5
mole % H_2	13.4	14.5	42.0	44.5	9.2	11.1	36.6	46.5
mole % CH_4	7.3	13.3	3.2	4.2	14.3	17.8	8.6	6.5
Carbon conversion (%)	20	60	39	75	15	42	29	74
Mass yield (kg gas/kg feed)	0.23	0.57	0.47	0.88	0.25	0.45	0.43	1.10

the tar cracking regime in this work. It should also be pointed out that the condensate measurements in the first temperature regime did not indicate any water consumption. Consequently cracking of tar, generated primarily from cellulose, dominated the first temperature regime.

A comparison is presented in Table 5 of Antal's cellulose and wood gasification results (Antal 1985) and those for cellulose from Walawender et al. (1985b) and for wood from this study. It can be noted that the produced gas in Antal's experiments always had higher levels of CO and lower levels of CO_2 and H_2 than observed in our experiments at the corresponding temperatures. The steam to DAF feed ratio used by Antal was about 1.4:1, while those used in our experiments ranged from 6 to 10:1. In light of the differences in these ratios, Antal's gas compositions are to be expected. The shift reaction was not significant in his experiments; thus higher CO, and lower CO_2 and H_2 resulted. Results from a separate set of experiments, conducted on the gasification of cottonwood in a pilot-scale fluidized bed reactor (Walawender et al. 1983), correspond closely to the observations of Antal (1985) for wood. The conditions of gasification in their experiments were similar to those used by Antal; the steam to DAF feed ratio was less than 1:1. The mass yield of gas was found to be less than 1 kg gas/kg DAF feed at 1,010 K.

Antal (1979) has concluded that steam ratios higher than 1.4 g steam per g feed have little effect on gasification results for temperatures below 1,023 K. On the other hand, Schoeters et al. (1981), working on a system similar to the one reported here, and Rensfelt et al. (1978) have indicated that steam takes part in gasification. The observations reported here show that steam, when present in large amounts is a major factor in determining the gas composition and yield in the second temperature regime.

CONCLUSIONS

Steam gasification experiments were conducted with cottonwood (branches) in a bench-scale fluidized bed reactor, over a temperature range of 850 K to 1,075 K. The volumetric yield of the produced gas increased with increasing temperature, and the HHV of the gas averaged 11.8 MJ/m³. The major components of the produced gas were CO, CO_2, H_2, and CH_4, which comprised over 90% of the

gas. Both the carbon conversion and energy recovery increased with increasing temperature.

The gas composition data suggests the existence of two temperature regimes for the secondary gas phase reactions as postulated by Walawender et al. (1985b). The first regime (low temperature) is dominated by tar cracking and the second, by the water gas shift reaction, with the transition occurring at 930–950 K. Unlike alpha-cellulose, there is no sharp transition point. The tar cracking reactions for volatiles generated from wood occur above 950 K also, but their extent is small relative to the water gas shift reaction; hence the shift reaction dominates the second temperature regime. Steam was found to be an important gasification agent in the second regime when present in large quantities. It is transferred in significant amounts, to the product gas through the shift reaction.

ACKNOWLEDGMENT

REFERENCES

ANTAL, M. J. 1979. The effects of residence time, temperature, and pressure on the steam gasification of biomass. Presented at Symposium on Biomass as a Non-Fossil Fuel Source, Div. of Fuel Chem. ACS meeting, Honolulu, Apr. 1–6.

———. 1983. Effects of reactor severity on the gas phase pyrolysis of cellulose and kraft lignin derived volatile matter. Ind. Eng. Chem. Prod. Res. Dev. 22:366–375.

———. 1985. A review of the vapor phase pyrolysis of biomass derived volatile matter. Pages 511–537 *in* R. P. Overend, T. A. Milne, and L. K. Mudge, eds. Fundamentals of thermochemical biomass conversion. Elsevier Applied Science Publishers, London.

———, ET AL. 1978. A study of the steam gasification of organic wastes. Project Report to EPA, Princeton University Grant No. R804836010, W. W. Liberick, Project Officer, Industrial Environmental Research Laboratory, Cincinnati, Ohio.

BARIN, I., AND O. KNACKE. 1973. Thermochemical properties of inorganic substances. Springer-Verlag, Berlin, supplement 1977.

FELDMANN, H. F., ET AL. 1981. Steam gasification of wood in a multi-solid fluidized-bed (MSFB) gasifier. Pages 529–547 *in* Symposium papers, Energy from Biomass and Wastes V, sponsored by IGT, Lake Buena Vista, FL, Jan. 26–30.

GOERING, H. K., AND P. J. VAN SOEST. 1970. Forage fiber analysis. Agricultural Handbook no. 379, Agricultural Research Serv. U.S.D.A.

GOLDSTEIN, I. S. 1978. Wood as a source of chemical feedstocks. *In* Energy and Environmental Concerns in the Forest Products Industry, AIChE Symposium Series 177; 74:111–114.

HUDSON, D. J. 1966. Fitting segmented curves whose join points have to be estimated. Amer. Stat. Ass. J. 61:1097–1129.

KILBURN, D. G., AND B. H. LEVELTON. 1963. Charcoal production by a fluid-bed process. Forest Prod. J. 13:427–432.

LIAN, C. K., M. E. FINDLEY, AND V. J. FLANIGAN. 1982. Air-blown wood gasification in a large fluidized bed reactor. Ind. Eng. Chem. Proc. Des. Dev. 21:699–705.

MAA, P. S., AND R. C. BAILIE. 1973. Influence of particle sizes and environmental conditions on high temperature pyrolysis of cellulosic material—I. Theoretical. Comb. Sci. Tech. 6:1–13.

MILNE, T. 1979. Pyrolysis—The thermal behavior of biomass below 600°C. Pages 95–131 *in* A survey of biomass gasification. Vol. II—Principles of gasification. SERI/TR-33-239.

MORGAN, L. W., G. M. ARMSTRONG, AND H. C. LEWIS. 1953. Distillation of hardwood in a fluidized bed. Chem. Eng. Prog. 49:98–101.

MUDGE, L. K., ET AL. 1981. Economics of methanol and SNG production from biomss via catalytic

gasification. Pages 687–719 *in* Symposium papers, Energy from Biomass and Wastes V, sponsored by IGT, Lake Buena Vista, FL, Jan. 26–30.

RAMAN, K. P., ET AL. 1981a. Thermogravimetric analysis of biomass devolatilization studies on feedlot manure. Ind. Eng. Chem. Proc. Des. Dev. 20:630–636.

———. 1981b. Mathematical model for fluid-bed gasification of biomass materials. Application to feedlot manure. Ind. Eng. Chem. Proc. Des. Dev. 20:686–692.

RENSFELT, E., ET AL. 1978. Basic gasification studies for development of biomass medium BTU gasification processes. Pages 465–494 *in* Symposium papers, Energy from Biomass and Wastes, sponsored by IGT, Washington D.C., August 14–18.

SCHOETERS, J., K. MANIATIS, AND A. BUEKENS. 1981. Fuel gas from agricultural residues in a fluidized bed reactor. Pages 313–317 *in* Proceedings of the 2nd World Congress of Chemical Engineering, vol. I, Montreal, Canada, Oct. 4–9.

SHAFIZADEH, F., AND G. D. McGINNIS. 1971. Chemical composition and thermal analysis of cottonwood. Carbohyd. Res. 16:273–277.

UNITED CATALYSTS INC. 1969. Physical and thermodynamic properties of elements and compounds. Girdler and CCI Catalysts, Louisville, Kentucky.

VAN DEN AARSEN, F. G., A. A. C. M. BEENACKERS, AND W. P. M. VAN SWAAIJ. 1985. Wood pyrolysis and carbon dioxide char gasification kinetics in a fluidized bed. Pages 691–715 *in* R. P. Overend, T. A. Milne, and L. K. Mudge, eds. Fundamentals of thermochemical biomass conversion. Elsevier Applied Science Publishers, London.

WALAWENDER, W. P., ET AL. 1983. Fluid-bed gasification of cottonwood. Presented at Seventh Annual FPRS Industrial Wood Energy Forum '83, Nashville, Tennessee, Sept. 19–21.

———, D. A. HOVELAND, AND L. T. FAN. 1985a. Steam gasification of alpha cellulose in a fluid bed reactor. Pages 897–910 *in* R. P. Overend, T. A. Milne, and L. K. Mudge, eds. Fundamentals of thermochemical biomass conversion. Elsevier Applied Science Publishers, London.

———, ———, AND ———. 1985b. Steam gasification of pure cellulose. Part I. Uniform temperature profile. Ind. Eng. Chem. Proc. Des. Dev. 24:813–817.

ZERBE, J. J. 1981. The contribution of wood to the energy picture. Presented at Conference on Wood—An Alternate Energy Resource for Appalachian Industry and Institutions, Proceedings published by School of Engineering, North Carolina State University.