Biomass Reactivity in Gasification by the Hynol Process

Yuanji Dong

ARCADIS, Geraghty & Miller, 4915 Prospectus Drive, Durham,
North Carolina 27709

Robert H. Borgwardt

Air Pollution Prevention and Control Division, National Risk
Management Research Laboratory, U.S. Environmental Protection
Agency, Research Triangle Park, North Carolina 27711

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A thermobalance reactor was used to evaluate the reactivity of poplar wood during gasification under operating conditions specific for the Hynol process where biomass is gasified at 30 atm and 800 °C with a hydrogen-rich gas recycled from methanol synthesis. The gasification involved a rapid devolatilization and pyrolysis reaction of the volatile matter in biomass and a slow reaction of residual carbon with the process gas. Nearly 86% of $1/8$-in. poplar particles and 90% of sawdust were converted into gas products by a feed gas corresponding to the Hynol process (66% H_2) in 60 min. About 4% additional conversion of the $1/8$-in. particles was obtained when gasification time was extended from 60 to 150 min. Gasification rate and biomass conversion were strongly affected by reaction temperature and particle size. The conversion was proportional to the partial pressures of H_2 and steam in the feed gas. A kinetic model was developed to correlate the experimental data and quantitatively express gasification rates and biomass conversion as functions of reaction time. The activation energies for the rapid and slow reactions were estimated to be 3.8 and 34 kcal/g-mol, respectively.

Introduction

Methanol has many advantages as a potential alternative fuel for road transport. It is a chemically simple liquid fuel and compatible with the existing automotive refueling infrastructure. It can be made from a variety of domestic feedstocks and is relatively inexpensive to produce. The combustion of methanol in internal-combustion engines is very efficient and produces less toxic emissions than gasoline. In addition, methanol is a viable on-board hydrogen source for fuel-cell vehicles (FCVs) which will soon enter the commercial market. FCVs will be much more efficient than the vehicles using petroleum fuels that currently dominate U.S. transportation needs and will emit virtually no pollution. Future prospects for compliance with air quality standards, currently unmet in more than 100 U.S. cities, should be greatly enhanced by FCVs using clean fuels such as methanol.

Most methanol is produced from natural gas. Use of biomass as feedstock to produce methanol is of current interest because it offers substantial benefits for reduction of greenhouse gas emissions, especially when used in FCVs. Research and development of biomass-to-methanol processes are now in progress. One of those processes is called Hynol,[1] which was proposed to utilize biomass as a feedstock and natural gas as a cofeedstock to increase methanol yield and reduce costs. The process consists of three reaction steps: (1) gasification of biomass with the H_2-rich gas recycled from methanol
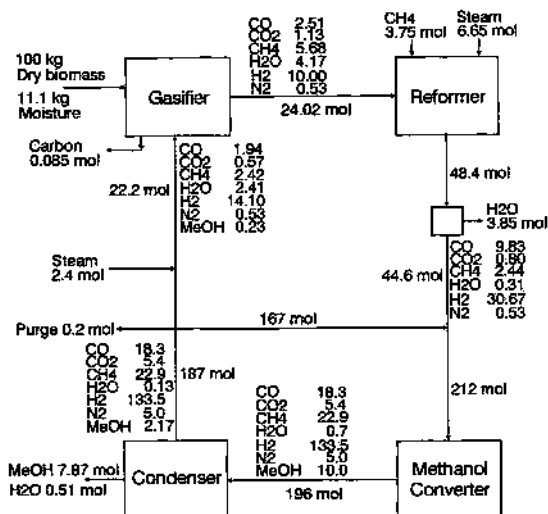
Figure 1. Schematic flow diagram of the Hynol process.

synthesis, (2) steam reforming of the produced gas with an addition of natural gas feedstock, and (3) methanol synthesis from the H_2 and CO produced by the reformer. A schematic flow diagram of the process is shown in Figure 1. Since the reaction of biomass with the hydrogen in the recycle gas to form methane is exothermic, the heat so generated, together with the sensible heat recovered from the reforming step, is able to offset the energy required for other endothermic reactions in a Hynol gasifier. As a result, no expensive oxygen plant or external heat source is needed for gasification. The use of natural gas as cofeedstock eases the requirement

(1) Steinberg, M.; Dong, Y. U.S. Patent 5,344,848, 1994.

for a consistent composition of biomass feedstock. The integrated cyclical process configuration helps ensure the completion of overall conversion and increases thermal efficiency. CO shifting is not necessary and the requirement for acid gas removal is reduced, which lowers capital and operating costs.

The Air Pollution Prevention and Control Division (APPCD) of the National Risk Management Research Laboratory, U.S. Environmental Protection Agency (EPA), has conducted a theoretical evaluation of process options for production of transportation fuel from biomass and concluded that the Hynol process represents a promising technology for maximizing fuel production inexpensively and with minimum greenhouse gas emissions.[2,3] Consequently, the APPCD established a laboratory to further assess the process feasibility. In the first phase of the study, a thermobalance reactor (TBR) was installed and used to evaluate biomass reactivity in gasification at the operating pressure, temperature, and feed gas composition specific for the Hynol process. The experimental work also attempted to improve understanding of the variables affecting Hynol gasification and identify needs for process development. This article summarizes the TBR results.

Previous Work

Much research has been carried out on biomass gasification; most of which, however, was concerned with pyrolysis and steam gasification. High reactivity of biomass in steam gasification has been reported.[4,5] The gasification rate was found to be 4–10 times greater than those for lignite chars and was strongly dependent on weight loss fraction of biomass. Steam gasification is highly endothermic. The heat required for gasification is usually supplied by combusting a portion of the biomass with air or oxygen within the gasifier or by supplying heat to the reactor indirectly.

In contrast, little information is available on hydrogasification of biomass although it is exothermic and more energy efficient than steam gasification. Early investigators of biomass hydrogasification were conducted on peat[6,7] which showed a 40% increase in carbon conversion at 60 atm pressure in comparison with pyrolysis in an inert atmosphere. Hydrogasification of wood was studied at atmospheric pressure using nickel catalysts[8] in an externally heated fluidized bed in which 70% conversion of the carbon feed was converted to gaseous products. Recently, biomass hydrogasification study with a tubular reactor[9] reported 90% conversion of poplar wood at 50 atm and 800 °C with an initial gasification rate of 0.31 min^{-1}.

(2) Borgwardt, R. *Proc. Symp. Greenhouse Gas Emissions Mitigation Res.* **1996**, EPA-600/R-98-072, Section 4, 128–135.

(3) Borgwardt, R. *Biomass Bioenergy* **1997**, *12*, 333–345.

(4) Rensfelt, E.; Blomkvist, G.; Eastrom, C.; Engstrom, S.; Esperas, B. G.; Liinaki, L. *Proc. Symp. Energy Biomass Wastes, Washington, D.C.* **1978**, 465–494.

(5) Graboski, M. In *Biomass Gasification*; Reed, T. B., Ed.; Noyes Data Corp.: Park Ridge, NJ, 1981; p 154.

(6) Punwani, P. V.; Nandi, S. P.; Gavin, L. W.; Johnson, J. L. Presented at the 85th AIChE Meeting, Philadelphia, PA, June 1978.

(7) Wiel, S.; Nandi, S.; Punwani, D. I.; Kopstein, M. Presented at the 176th Meeting, American Chemical Society, Miami, FL, September 1978.

(8) Garg, M.; Piskorz, J.; Scott, D. S.; Radllein, D. *Ind. Eng. Chem. Res.* **1988**, *27*, 256–264.

(9) Kobayashi, A.; Steinberg, M. Brookhaven National Laboratory Report, BNL-47158, January 1992.
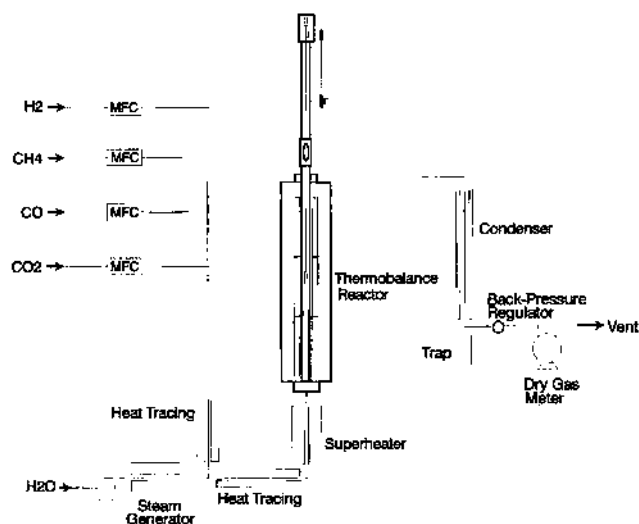
Since similarities can be expected between coal hydrogasification and biomass hydrogasification, a brief review of previous studies on coal hydrogasification at elevated pressures and temperatures is useful. Despite discrepancies in experimental data reported by different investigators, most authors agree that the initial gasification is very rapid, followed by a slow rate of conversion of residual char. Thermal decomposition of the volatile matter in coal occurs at elevated temperatures, resulting in devolatilization of certain coal components. The distribution of the evolved products is generally a function of temperature, pressure, and gas composition existing during devolatilization. When coal is heated in an environment containing hydrogen at elevated pressures, methane would be rapidly formed in addition to thermal pyrolysis reactions. This rapid-rate stage lasts only for seconds and is followed by a much slower period in which the residual char reacts with hydrogen. The amount of carbon gasified to methane increases significantly with hydrogen partial pressure. At sufficiently high hydrogen partial pressures, almost all of the carbon not evolved during devolatilization can be gasified to methane. With a reasonable degree of accuracy, the kinetics of both coal devolatilization and char–hydrogen reaction can be assumed to be first order.

Biomass is much more reactive than coal in pyrolysis and gasification. Higher reactivities of biomass, typically woods, result from its specific physical and chemical properties. Wood contains 80–90% of volatile content, which is almost twice that in coal. The mole ratios of hydrogen/carbon and oxygen/carbon in wood are higher, ranging from 1.3 to 1.5 and 0.5 to 0.6, respectively, in comparison with the corresponding values of 0.8–0.9 and 0.1–0.3 in coals. Wood is more porous, with a porosity as high as 40–50% and typical pore size between 20 and 30 μm. In contrast, the porosity of coal is 2–18% and a pore size of 5 Å.

In the Hynol process, as shown in Figure 1, biomass is gasified at 30 atm and 800 °C with a gas recycled from the methanol synthesis reactor. This stream consists mainly of hydrogen with lesser amount of CH_4, CO, CO_2, and steam. Information on biomass gasification under these specific operating conditions was not available from the literature.

Experimental Section

The TBR used in this study is electrically heated and consists of a 1.38 in. i.d. stainless steel reactor pipe, a 12 in. o.d. pressure vessel, and a topwork which houses a weight transducer for measurement of sample weight during reaction. A pulley assembly is used to raise and lower a sample basket between the topwork and the reaction zone. The TBR provides automatic recording of weight loss of a solid sample as a function of reaction time.

A flow diagram of the TBR system is detailed in Figure 2. To initiate an experimental run, a basket with known weight of biomass sample was placed into the topwork through the removable window. A constant helium flow was introduced to the topwork to protect the wood sample from contact with process gas prior to entry in the reaction zone. Mass flow controllers were used to control the flow rates of hydrogen, methane, carbon monoxide, and carbon dioxide from individual gas cylinders to obtain the desired feed gas composition. Steam was added to the feed gas from a steam generator fed

Figure 2. Experimental reactor system.

Table 1. Composition of Poplar Wood Used

carbon (wt %)	51.52
hydrogen (wt %)	6.20
oxygen (wt %)	41.37
ash (wt %)	0.47
sulfur (wt %)	0.02
nitrogen (wt %)	0.42
volatile (wt %)	91.38
fixed carbon (wt %)	8.15
HHV (Btu/lb dry wood)	8768

with distilled water by a metering pump. The gas mixture was further heated by a superheater and then entered the reactor. The reactor exit gas was cooled in a condenser to remove moisture, and then depressurized through a back-pressure regulator before it was vented to atmosphere. When pressure and temperature in the reactor system were stabilized at the desired levels, the sample basket was lowered into the reaction zone and the change in sample weight was automatically recorded by the transducer as a function of reaction time. A computer was used to control the TBR system and log experimental data. After gasification, the basket was raised back into the topwork and the reactor was depressurized and cooled. The discharged char was then weighed to determine the final sample weight. Because changes in gas composition across the sample are negligible, the reaction can be considered to take place at constant operating conditions.

Poplar wood, which is considered a primary candidate for large scale production as an energy crop for fossil fuel displacement,[10] was used as a representative biomass sample. It was grown in North Carolina and cut to desired sizes and dried before its use. Composition of this wood is shown in Table 1.

The TBR feed gas used for this study simulated the recycle stream of the Hynol process and had the following composition: $H_2 = 65.83\%$; $CH_4 = 11.63\%$; $CO = 8.95\%$; $CO_2 = 2.32\%$; and steam = 11.27%.

Kinetic Model and Data Treatment

The weight transducer output was recorded as a function of reaction time during a test. The output was converted to biomass conversion, X, on an ash-free basis by

$$X = \frac{W_0 - W}{W_0 - W_0 C_A} \tag{1}$$

(10) Wright, L. *Proceedings of the Second Biomass Conf. Americas*; National Renewable Energy Laboratory: Golden, CO, 1995; NREL/CP-200-8098, pp 1−10.
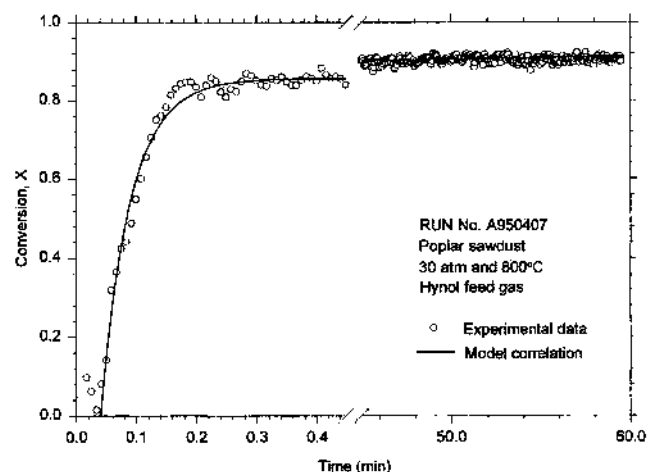

Figure 3. Example of TBR experimental results and data fitting by the model.

where W_0 is the initial sample weight, W is the sample weight at any reaction time, C_A is the weight fraction of ash obtained from the ultimate analysis of the original sample, and X is thus also a function of reaction time.

Similar to that observed in coal hydrogasification, biomass gasification by the Hynol process involves a rapid devolatilization and pyrolysis reaction of the volatile matter in biomass with hydrogen and steam, and a very slow reaction of residual carbon with the process gas. These two reactions are considered to initiate simultaneously and are first order with respect to the remaining solid reactants. The rate of the rapid reaction can be expressed as

$$dX_1/dt = k_1(X_C - X_1) \tag{2}$$

and the rate expression for the slow reaction is

$$dX_2/dt = k_2(1 - X_C - X_2) \tag{3}$$

where X_1 and X_2 are the biomass conversions by the rapid and slow reactions at time t, X_C is the maximum attainable conversion by the rapid reaction, and k_1 and k_2 are the reaction rate constants for the rapid reaction and the slow reaction, respectively.

Equations 2 and 3 can be integrated to obtain the total biomass conversion as

$$X = X_1 + X_2$$

$$X = 1 - X_C \exp(-k_1 t) - (1 - X_C) \exp(-k_2 t) \tag{4}$$

From eq 4, the conversion is zero at $t = 0$ and would approach 1 as t approaches infinity. The model involves three parameters: X_C, k_1, and k_2, which are functions of operating conditions such as biomass properties, reaction temperature, pressure, and feed gas composition. They can be determined by fitting eq 4 to the experimental conversion data obtained from TBR tests. Marquardt−Levenberg algorithm was used to find the parameters that give the best fit.

Results and Discussion

Figure 3 illustrates a typical result of curve fitting by the model. Good agreement between experimental

Table 2. Estimate of Data Repeatability

run no.	conversion (%)
B941215	85.17
B941216	85.35
A941220	85.02
A941222	85.35
B950123	86.18
A950201	84.62
mean	85.28
s	0.5167

data and model regression over the entire reaction period indicates that the model developed above is suitable for TBR experimental data correlation and gasification behavior can be characterized with three model parameters.

Since the heating rate of the TBR is low, a temperature drop was observed immediately after the basket reached the reaction zone. The initial temperature drop can be improved by reducing the amount of sample initially charged into the reactor. This is consistent with the observed experimental results. However, the reduction in the amount of sample may increase the error in weight transducer readings. As a best compromise, the amounts of samples used in most of the tests were less than 3 g. The initial temperature drop with this amount of sample usually took about 10 s to get back to the original temperature. As a result, this initial temperature deviation strongly influenced the measurements of the rapid reaction rate.

In most cases, three experimental runs were repeated for each test condition. Only the 20 min gasification tests for $^{1}/_{8}$ in. poplar particles at 30 atm and 800 °C were repeated six times, allowing to perform a statistical calculation for evaluation of the repeatability of the biomass conversion measurements. The statistical results are presented in Table 2. As shown in the table, the standard deviation of the measurements is 0.5167. If a 95% confidence interval is desired, the value of Student's t for 5 degrees of freedom is 2.571 and the confidence interval for the mean conversion under these operating conditions can be expressed as

$$84.74 < \bar{X} < 85.82 \qquad (5)$$

Four different sizes of poplar particles were used to investigate the effects on gasification: $^{7}/_{16}$ in. diameter cylinders, $^{1}/_{4}$ in. diameter cylinders, $^{1}/_{8}$ in. cubes, and 20–30 mesh sawdust. Figure 4 shows that the rate of the rapid reaction increased significantly when particle size was reduced from $^{7}/_{16}$ to $^{1}/_{8}$ in. The lower reaction rate in the rapid reaction stage observed for larger particles in the TBR tests is attributable to the relatively slower heating rate, evidenced by the initial temperature drop discussed previously. The heat transfer dictated the rapid reaction rate in this case. Agglomeration during gasification was also observed for the particles larger than $^{1}/_{8}$ in. which reduced surface area for reaction and inhibited gas diffusion within the particles. Sawdust showed the highest conversion among the four sizes of particles. It heated more quickly, and no agglomeration was observed. At 30 atm and 800 °C, 87% of the $^{1}/_{8}$ in. poplar particles and 90% of the sawdust were gasified by the Hynol feed gas in 60 min.

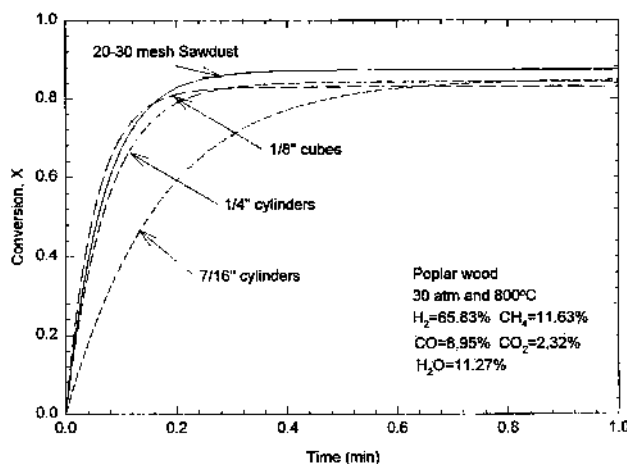The agglomerates of residual chars formed in the TBR were fragile and easily crushed to fines. Therefore,

Figure 4. Effects of poplar particle size on the rapid reaction.

Table 3. Chars Obtained from Different Sizes of Poplar (30 atm and 800 °C)

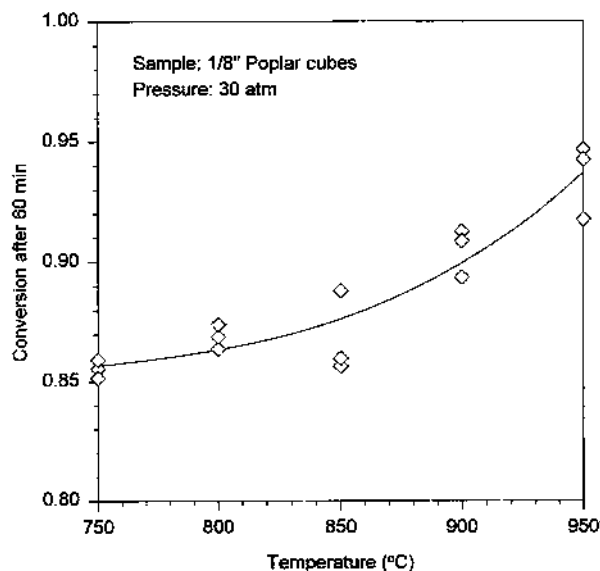| particles	7/16-in	1/8-in	sawdust
reaction time (min)	30	20	20
initial weight (g)	2.3477	3.9749	2.0681
final weight (g)	0.4035	0.6019	0.2401
conversion (%)	83.20	85.26	88.81
in char			
C (wt %)	89.93	95.32	90.60
H (wt %)	2.32	0.64	1.13
O (wt %)	5.57	0.35	0.38
N (wt %)	0.21	0.85	0.69
ash (wt %)	1.97	2.84	7.20
conversion			
C (%)	70.00	71.98	79.58
H (%)	93.57	98.44	97.88
O (%)	97.69	99.87	99.89

agglomeration is unlikely to occur in a fluidized bed gasifier where strong particle attrition exists, and higher reaction rate and conversion than observed in TBR may be expected in such systems.

The compositions of charred samples obtained from gasification of poplar particles of $^{7}/_{16}$ in. $^{1}/_{8}$ in. and sawdust are compared in Table 3. The carbon, hydrogen, and oxygen in the char remaining after gasification were calculated by subtracting the elements in the char from the elements in the original wood sample. It can be seen that the char from $^{7}/_{16}$ in. poplar particles has the lowest carbon conversion and highest hydrogen and oxygen contents, indicating that some of the volatile matter remains after gasification. However, for $^{1}/_{8}$ in. poplar particles or sawdust, nearly all of the hydrogen and oxygen were converted into product gas in 20 min.

The rapid-reaction stage of poplar gasification was found to be essentially completed in less than 0.2–0.3 min, contributing most of the biomass conversion. A small additional conversion is provided by the slow reaction. To achieve high biomass conversion, sufficient gasification time must be provided. Experiments showed that biomass conversion increased from 85 to 90% when gasification time extended from 20 to 150 min. The composition comparison between the chars after 20 and 150 min gasification, given in Table 4, showed that there was virtually no further conversion of hydrogen and oxygen in the char after 20 min. The additional biomass conversion resulted from the reaction of carbon in the residual char with the process gas as indicated by a significant increase in carbon conversion from 72 to 81.3%.

Table 4. Chars Obtained with Different Reaction Times (30 atm and 800 °C)

particles	1/8-in	1/8-in
reaction time (min)	20	150
initial weight (g)	3.9749	1.0012
final weight (g)	0.6019	0.1051
conversion (%)	85.26	89.93
in char		
C (wt %)	95.32	91.64
H (wt %)	0.64	0.88
O (wt %)	0.35	2.56
N (wt %)	0.85	1.11
ash (wt %)	2.84	3.81
conversion		
C (%)	71.98	81.33
H (%)	98.44	98.51
O (%)	99.87	99.35

Figure 5. Effect of reaction temperature.

Figure 6. Arrenius plots of the rate constants.

Figure 7. Comparison of the model prediction with experimental conversion data.

Experimental results of 60 min gasification with $1/8$ in. poplar particles at different reaction temperatures showed great increase in biomass conversion and gasification rates when temperature increased from 750 to 950 °C as shown in Figure 5. The rate constants for the rapid and slow reactions, k_1 and k_2, at different reaction temperatures were determined by fitting the experimental data for gasification of $1/8$ in. poplar particles. The rate constants thus obtained were plotted against the reciprocal of the absolute temperature, as shown in Figure 6, and expressed as functions of reaction temperature by the Arrhenius equation:
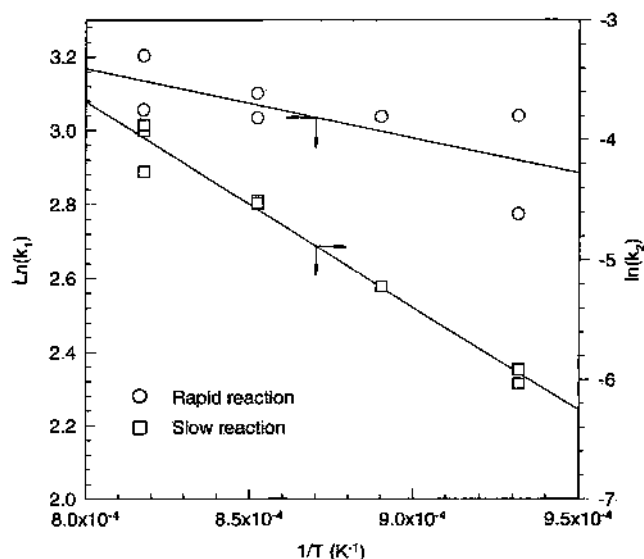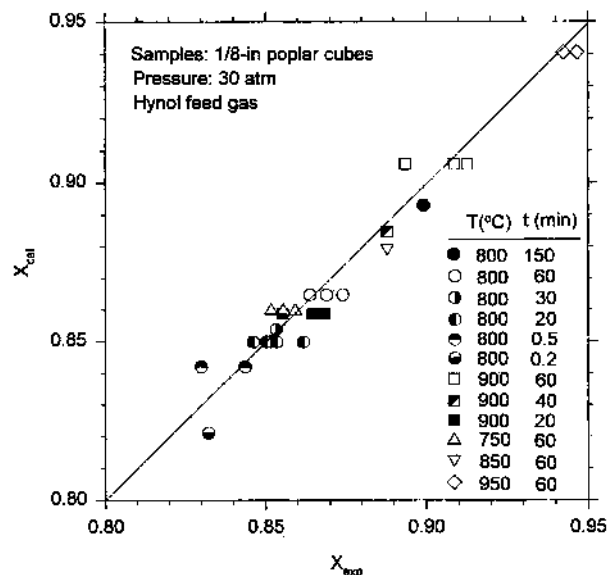
$$k_i = k_{i0} \exp(-E_i/RT) \qquad (6)$$

where subscript i is 1 for the rapid reaction and 2 for the slow reaction. E_i is the activation energy. k_{i0} is the frequency factor. The results obtained were $k_{10} = 108.85$ min^{-1}, $k_{20} = 22925$ min^{-1}, $E_1 = 3.78$ kcal/mol, and $E_2 = 34.1$ kcal/mol.

The maximum attainable conversion by the rapid reaction, X_C, was also correlated as a function of temperature for gasification of $1/8$ in. poplar particles at 750 to 950 °C by

$$X_C = 0.9611 - 0.000149T \qquad (7)$$

where T is the reaction temperature in °C. It should

be noted that eq 7 is valid only within the range of the experimental conditions under which the data were obtained and used for the correlation. The equation shows a slight decrease in the value of X_C with reaction temperature. This is because the rapid and slow reactions are competitive and the higher activation energy of the slow reaction results in an increase in its contribution to the overall biomass conversion as the reaction temperature increases. With eqs 4, 6, and 7 and the values of k_{10}, E_1, k_{20}, and E_2, the conversions of $1/8$ in. poplar particles at different temperatures and gasification times were predicted. Figure 7 compares the prediction with the conversion data obtained from the separate experimental tests at different temperatures and gasification times. The comparison covers a temperature range of 750–950 °C and gasification times ranging from 0.2 to 150 min for $1/8$ in. poplar particles exposed to the Hynol feed gas at 30 atm. The activation energy obtained for the rapid reaction was low, implying that heat transfer dominates the rates of devolatilization and pyrolysis of biomass in the TBR.
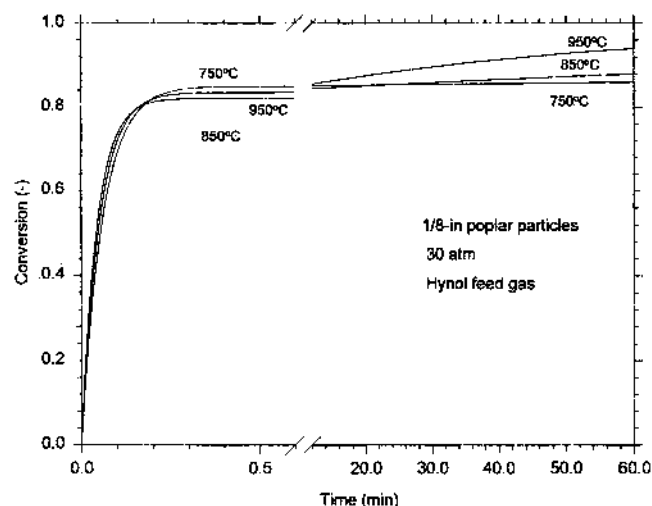
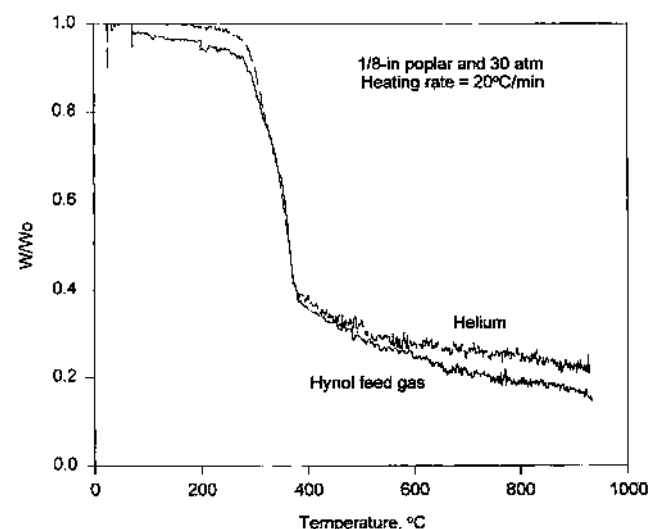**Figure 8.** Temperature effects on the rates of the rapid and slow reactions.

Figure 9. Weight loss as a function of reaction temperature under different feed gases.

Figure 10. Effect of hydrogen partial pressure on conversion.
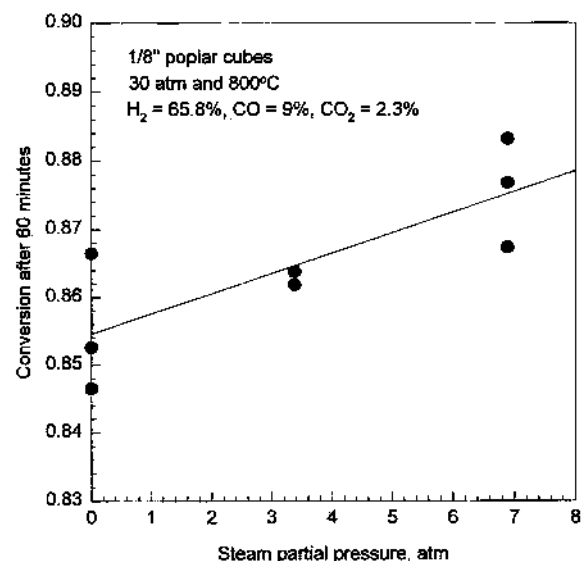
Figure 11. Effect of steam partial pressure on conversion.

The gasification conversion curves of $^1/_8$ in. poplar particles at different temperatures, reproduced by substituting these parameters into the model, are compared in Figure 8. It is seen that the higher biomass conversion obtained at higher reaction temperatures results from the carbon—gas reaction in the slow reaction stage. The contribution of the carbon—gas reaction at high temperatures was further illustrated by two specially designed experiments. One test used helium as feed gas and the other used the Hynol feed gas. In both tests, the heating rate was controlled at about 20 °C/min. The loss of sample weight was monitored as temperature increased from room temperature. The recorded sample weight changes are compared in Figure 9, which indicates that the hydrogen and steam in the feed gas react with carbon resulting in an additional weight loss at high temperatures.

The effect of feed gas composition on poplar gasification was investigated by varying the flow rates of individual gas components under constant system pressure. Helium was used as an inert "make-up" gas for this purpose. At 30 atm and 800 °C, the final conversion of $^1/_8$ in. poplar particles gasified by pure helium after
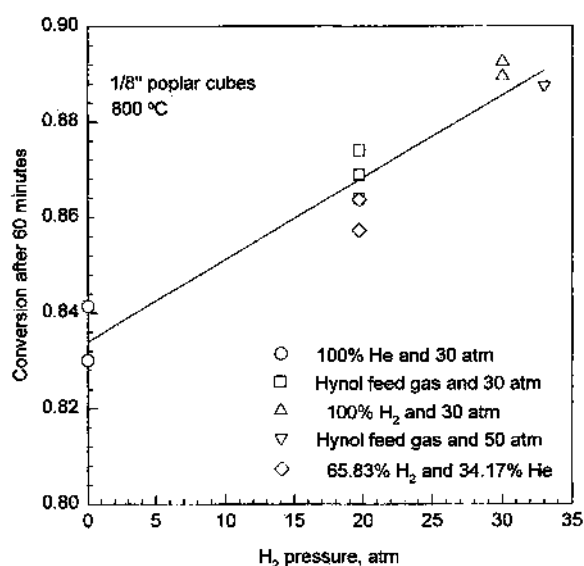
60 min was about 6% lower than that obtained under pure H_2. If the conversion obtained after 60 min of gasification was plotted against H_2 partial pressure (P_{H_2}), a linear relationship was obtained as shown in Figure 10. The conversion is proportional to hydrogen partial pressure by a factor of $0.0017P_{H_2}$. When steam partial pressure in the feed gas was varied from 7 atm to zero while the partial pressures of other gas components remained constant, the conversion of $^1/_8$ in. poplar particles gasified at 30 atm and 800 °C for 60 min was proportional to $0.003P_{H_2O}$, as shown in Figure 11. Negligible effects on the gasification conversion and reaction rate of $^1/_8$ in. poplar particles were observed as the CH_4 in the feed gas was reduced from the simulated Hynol composition, 11.63%, to zero. Replacing CO and CO_2 in the feed gas with helium did not affect the gasification rate. The conversion and reaction rates of $^1/_8$ in. poplar particles gasified by the Hynol feed gas were nearly the same as those observed by the feed gas containing no CO and CO_2.