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DEVELOPMENT OF HYDROCONVERSION OF BIOMASS TO SYNTHETIC FUELS

**Project 61042 Technical Progress Report
For the Period October 1 Through December 31, 1980**

**Prepared by
Institute of Gas Technology
IIT Center, 3424 S. State Street
Chicago, Illinois 60616**

Date Published — April 1981

**Prepared for the
UNITED STATES DEPARTMENT OF ENERGY
BIOMASS ENERGY SYSTEMS**

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EXECUTIVE SUMMARY

The program to develop the hydroconversion of biomass into synthetic fuels is divided into the following six tasks:

- I. Characterization of Biomass
- II. Biomass Handling Characteristics
- III. Bench-Scale Experiments
- IV. Process Development Unit (PDU) Tests
- V. Data Review for Pilot Plant Tests
- VI. Technoeconomic Evaluation

The work during this quarter proceeded on Tasks I, II, III, and IV.

In Task I, the physical and chemical characterization tests with maple hardwood were completed. Corn stover tests are in progress. The maple hardwood had uniform properties for various size fractions unlike the Douglas fir hog fuel. The ash fusion temperatures for maple hardwood were measured up to 2700°F, which is significantly higher than those for coal ash.

In Task II, fluidized-bed parameters were measured for various sand-char mixtures, and the drying characteristics of maple hardwood were examined.

Studies were conducted to determine the fluidization behavior of mixtures of sand and 5 to 67 vol % of char. Measurements of the bed pressure drop and fluidizing gas velocity were made at several bed heights. At fluidization gas velocities below that of pure sand, the sand provided smooth fluidization and good mixing with the larger, lower density char particles. Fluidization velocities were fairly constant over a wide range of sand-char bed compositions. This fact expands the bed composition design choices and also permits the bed composition to vary during operation without affecting the fluidization.

Drying aspects were examined in terms of front-end drying that will use recovered waste heat. This is important because a constant-moisture feedstock is preferred. There are two reasons for this. First, operation of biomass handling systems is related to moisture content. Second, the feed moisture imposes a heat load on the gasifier. Initial thermobalance tests of low-temperature drying typical of front-end, recovered-heat systems were

conducted. Fairly linear, well-defined behavior was found for moisture loss in time. More tests are planned to define the moisture loss characteristics with temperature in the range of 100° to 400°F and various initial moisture contents.

In Task III, bench-scale tests were conducted in three areas. Nonisothermal thermobalance runs were made to define temperatures where significant reactions occur and to establish if there is any effect of particle size.

Rapid heat-up rate devolatilization of maple hardwood was studied in a free-fall apparatus able to feed and collect large quantities (g/min) of material. Greater than 75% conversion was obtained in less than 0.3 second, and higher hydrogen pressure increased the light hydrocarbon product yield.

Isothermal thermobalance experiments were conducted to establish the kinetics of the steam-char reaction. A first-order kinetic model was developed which represented the data well from 1350° to 1700°F, showing sufficient conversion of char for the process in 3 to 5 minutes.

Task IV work involved a confirmation of the PDU design values in terms of the information developed in Tasks II and III. The fluidization gas velocities for the sand-char mixtures were at or below the PDU design values. In addition, the design choices of the bed composition range were found to be expanded by the constant fluidization behavior. Task III work showed that devolatilization is rapid and that the slower steam-char reaction would control the residence time. The kinetic expression for the steam-char reaction indicates 3 to 5 minutes for process conversion levels.

Additional PDU design details were completed. Nine additional drawings were made defining the necessary gasifier internal construction, the nozzles, and the pressure head details. A PDU system process and control instrumentation index and specification sheet were prepared for vendor bids. Modifications to the existing building's structural steel columns and decks necessary to rig the PDU vessels in place were reviewed. All other existing equipment that could be modified for use in the PDU program was analyzed for modification.

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PROGRAM OBJECTIVE

The objective of this program is to develop the hydroconversion (in-situ production and addition of hydrogen to carbonaceous species) of biomass (forest and crop residues) to produce synthetic fuels. The program will also include experiments to investigate the production of hydrocarbon liquids from biomass. Bench-scale experiments and process development unit (PDU) tests will provide the experimental data base for technoeconomic evaluation of the hydroconversion technology.

INTRODUCTION

The program is divided into the following six tasks:

- Task I. Characterization of Biomass
- Task II. Biomass Handling Characteristics
- Task III. Bench-Scale Experiments
- Task IV. Process Development Unit Tests
- Task V. Data Review for Pilot Plant Tests
- Task VI. Technoeconomic Evaluation.

The scope of each task and the planned approach is presented in the following discussion.

Task I. Characterization of Biomass

Potential resources appropriate for commercial energy conversion will be surveyed, and representative samples of selected large resource materials will be obtained for characterization purposes. These will include forest residues (from both hardwood and softwood trees) and agricultural residues (e.g., corn stalks or pelletized crop residues).

Each selected biomass material will be characterized by standard tests of physical and chemical properties because of the interrelationships between these properties and gasification reactivity. The physical properties of interest include density, hardness, and particle size; significant chemical properties include proximate and ultimate analysis, calorific value, ash constituents, and ash fusion characteristics. The tests will also be used to characterize the chars formed from the biomass materials, which have a direct relation to gasifier design and operation.

Task II. Biomass Handling Characteristics

Experiments will be devised and conducted to obtain engineering design data on the following handling characteristics of selected biomass materials:

- Size reduction
- Drying
- Fluidization and solids transport.

These characteristics are most significant because —

- A synthetic fuel production process operating under pressure and closely regulated conditions may require a continuous feed of controlled size distribution and moisture content.
- Freshly harvested biomass could contain up to 50% moisture by weight, with a possible reduction in moisture content during size reduction.

Means of obtaining controlled product size will be investigated with a hammer mill in a standard single-step shredding operation. The effect of feed size and screen size on reduction ratio and throughput rate will be investigated, along with moisture content of the feed material.

The moisture content can be reduced in several ways, including air drying and heat exchange with flue gases or any waste process energy available in a commercial-size plant. Drying tests will therefore be devised with special equipment to determine the drying characteristics of selected biomass materials.

The hydroconversion program will use a fluidized-bed gasifier. The bed will consist of inert solids and biomass, mostly in the form of char. It is essential to obtain fundamental fluidization and solids transport data for design, operation, and scale-up purposes. Selected and sized biomass materials and wood charcoal will be used in combination with inert solids such as sand and alumina to determine fluidization and solids transport characteristics. These experiments will be conducted in equipment of up to 12 inches in diameter. The fluidization tests are designed to determine the minimum fluidization velocity, bed expansion, pressure drop, solids mixing, segregation, and attrition characteristics. The results from tests with mixed solids will also be used as a basis to select appropriate inert solids, based on their fluidization characteristics relative to the low-density biomass char.

Use of a nonmechanical L-valve for feeding solids to the gasifier will be investigated as an alternative to screw/auger feeding. Data will be collected on rates of transport and aeration. The investigation will also characterize saltation velocity, choking velocity, and pressure drop, for use in the design of a nonmechanical L-valve feeder.

Task III. Bench-Scale Experiments

The devolatilization and gasification characteristics of selected biomass materials will be studied at IGT in existing bench-scale units: the devola-

tilization test units (e.g., autoclave, coil-tube, laminar flow reactors) and the char gasification thermobalance test units. The data obtained from these studies will provide quantitative estimates for product distribution, limiting yields of significant products, and rates of gasification reactions. The data will also help determine process conditions for maximum desirable product yields and help develop kinetic models of significant reaction steps in the hydroconversion process. Procedures and methodology developed under the various IGT carbonaceous fuels conversion programs will be applied with appropriate changes to biomass conversion.

Task IV. PDU Tests

The primary goal of this task is to design, construct, and operate an adiabatic 12-inch-ID PDU steam- and oxygen-blown fluidized bed gasifier. The unit will be designed to operate at up to 1600°F and 300 psig with a maximum capacity of 1000 lb/hr of raw biomass. A pressurized lockhopper system will provide feeding for test runs of up to 8 hours.

This gasifier will vary the bed height feed positions and other operating conditions to help determine optimum conditions for maximizing products yield. The test data on biomass composition and feed rate will form the basis for calculating elemental, material, and energy balances. The data will include —

- Calibrated feed rates as verified by the continuously weighing surge hopper
- Steam and oxygen feed rates
- Product gas, metered and sampled twice
- Collected and analyzed weight and composition data on ash and char trapped in the solids receiver
- Standard temperature, pressure, and flow data.

The results from the PDU tests will be combined with data from Task III to develop kinetic models suitable for reactor design and scale-up purposes.

Task V. Data Review for Pilot Plant Tests

The results from the bench-scale experiments (Task III) and PDU tests (Task IV) will provide basic information for developing process schemes for production of low-Btu gas, synthesis gas, SNG, hydrocarbon liquids, or special chemicals from biomass. Using these results, the conversions and yields in conceptual processes will be estimated. Possible modification and operation

of one of the pilot plants available at IGT (as a cost-effective option) will be explored. The available pilot plant reactors vary in size from 2.5 to 4 feet ID and could possibly handle an estimated 6 to 15 tons/hour of biomass. In terms of feed rate, this reflects a scale-up factor of 10 to 30 compared with the PDU design capacity. Results from Tasks I through IV will form the basis for designing modifications to the selected pilot plant in order to conduct confirming hydrogasification tests over periods of up to several days.

Task VI. Technoeconomic Evaluation

The availability of selected biomass materials will be assessed in view of the conceptual requirements of a high-Btu biomass gasification plant. A reasonable commercial plant capacity at present appears to be in the range of 500 to 1000 tons/day of dry biomass feedstock. A plant of this size could produce 5 to 10 million SCF/day of SNG.

After a commercial plant concept is selected with the consent of the DOE project manager, the results from the bench-scale and PDU tests will be used to prepare material and energy balance flow sheets, which are prerequisites for systematic cost estimation. The parametric results obtained from Task IV, combined with the technoeconomic evaluation, should also aid in estimating the optimum factors for converting biomass to synthetic fuels. The actual cost estimation will be subcontracted to an engineering company, preferably one that has conducted cost estimates on similar DOE contracts.

DISCUSSION

Task I. Characterization of BiomassWork During Period

During this reporting period, the series of characterization tests with maple hardwood chips was completed using the standard methods of analysis described in the Technical Progress Report for the period May 16 through September 30, 1980.

Table 1 shows the ultimate, proximate, and heating value data for maple hardwood as a function of particle size. A precaution was taken to ensure that the analyses were not affected by extraneous material in the wood chip sample. The chips, which were approximately 1 inch square and 1/8 to 1/4 inch thick, were washed and air-dried before grinding and screening. The data in Table 1 show no significant compositional differences between different sample sizes.

Table 1. PROPERTIES OF MAPLE HARDWOOD

	Sample Size		
	-12+16*	-40+50*	-80+100*
----- Proximate Analysis, wt % -----			
Moisture	5.5	5.2	5.8
Volatile Matter	81.2	81.1	79.4
Ash	0.2	0.3	0.4
Fixed Carbon	13.1	13.4	14.4
Total	100.0	100.0	100.0
--- Ultimate Analysis, wt % (dry) ---			
Ash	0.21	0.28	0.38
Carbon	49.8	50.2	50.3
Hydrogen	6.05	6.27	6.18
Sulfur	0.00	0.00	0.02
Oxygen (by difference)	43.79	43.04	42.91
Nitrogen	0.15	0.21	0.21
Total	100.0	100.0	100.0
Gross Heating Value, Btu/lb	8399	8360	8382

* USS Mesh.

Mercury particle density and bulk density measurements as a function of particle size for the raw material and its char are listed in Table 2. The carbonizations of the raw wood samples to produce the char were done in an N₂ atmosphere at 1500°F for 30 minutes.

An ash fusion analysis was performed on samples of maple hardwood ash. The results presented in Table 3 show that the ash is highly refractory and temperatures in excess of 2700°F did not fuse the ash. This is true for both oxidizing and reducing atmosphere tests.

The low-temperature ash minerals analysis by atomic absorption was not successful because of the low wood ash content and the long low-temperature ashing times. A larger representative sample of ash material is now being collected from the wood material.

Table 2. MAPLE HARDWOOD CHIPS DENSITY MEASUREMENTS

		<u>Particle</u>	<u>Bulk</u>
		---- Density, lb/ft ³ ----	
Raw Wood (air dried)	--4+16 mesh	38.0	10.0
	--60+80 mesh	51.8	11.1
Char	--4+16 mesh	38.7	7.9
	--60+80 mesh	41.8	9.2

Table 3. ASH FUSION CHARACTERISTICS

	<u>Maple Hardwood Chips</u>	
	<u>Reducing</u>	<u>Oxidizing</u>
	--- Temperature, °F ---	
Initial Deformation, IT	2700 + °F	2700 + °F
Softening, ST	2700 + °F	2700 + °F
Softening, HT	2700 + °F	2700 + °F
Fluid, FT	2700 + °F	2700 + °F

Characterization of a sample of corn stover obtained from the University of Illinois College of Agriculture (1980 harvest) has not been completed. Table 4 shows the effect of particle size on the ultimate and proximate analyses. The ash content increases as particle size decreases, possibly because of the extraneous material that is picked up during harvesting and collection.

Table 4. PROPERTIES OF CORN STOVER

Properties	Sample Size		
	-12+16*	-40+60*	-80+100*
	----- Proximate Analysis, wt % -----		
Moisture	5.0	3.8	2.9
Volatile Matter	74.2	38.9	30.9
Fixed Carbon	13.8	9.0	6.1
Ash	<u>7.0</u>	<u>48.3</u>	<u>60.1</u>
Total	100.0	100.0	100.0
Composition	--- Ultimate Analysis, wt % (dry) ---		
Carbon	46.50	24.10	18.10
Hydrogen	5.81	3.06	2.37
Nitrogen	0.56	0.54	0.63
Sulfur	0.11	0.09	0.10
Oxygen (by difference)	39.67	21.97	16.97
Ash	<u>7.35</u>	<u>50.24</u>	<u>61.83</u>
Total	100.00	100.00	100.00
Heating Value, Btu/lb	7567	3953	2941

* USS Mesh.

Future Work

The characterization of corn stover and atomic absorption analysis of the low- and high-temperature ash samples will be completed.

Characterization tests will be performed during the course of the program whenever other candidate materials become available for PDU tests.

Task II. Biomass Handling Characteristics

Work During Period

Work proceeded on obtaining fundamental fluidization data on char and sand mixtures, investigating wood drying characteristics, and preparing size reduction test equipment to study size reduction characteristics.

Fluidization Testing

Preliminary fluidization tests were conducted in a 5.5-inch-diameter Plexiglas fluidization column. Tests were made using sand alone ($-20+40$ mesh), char alone ($-12+20$ mesh), and a mixture of sand and char in a volume ratio of 1.3:1.0. This test ratio was selected because it is near the anticipated bed composition in the PDU. The bed height was varied between 6.5 and 16.5 inches to give bed height to column diameter (L/D) ratios between 1.2 and 3.0.

Subsequently, a large number of experiments were conducted in an 8-inch column which was capable of higher gas-flow rates, better dust control, and more accurate bed pressure measurements. The data from the two columns provide some information on the effect of column diameter on fluidization characteristics that is useful for scale-up. Table 5 compares the results of the 5.5-inch column tests with some of the 8-inch column results.

Table 5. EFFECT OF COLUMN DIAMETER ON FLUIDIZATION PARAMETERS
AT BED HEIGHT TO DIAMETER RATIO OF 1.75

Bed Composition	5-1/2-inch column		8-inch column	
	$\Delta P/L$, psi/ft	U_{MF} , ft/s	$\Delta P/L$, psi/ft	U_{MF} , ft/s
Char	0.056	1.55	0.095	1.25
Sand ($-20+40$ mesh)	0.486	0.85	0.670	0.82
Char + Sand*	0.275	0.76	0.570	0.71

* Char-sand mixture was 43% char by volume in the 5-1/2-inch column and 50% char by volume in the 8-inch column.

The minimum fluidization velocities compare well, but bed pressure drop could be affected by wall effects in the smaller column. Fluidization velocity is the more critical design parameter for the PDU, and the 8-inch column size information appears adequate.

The fluidization apparatus is made from an 8-inch diameter Plexiglas column fitted with a sintered metal gas distributor plate. A schematic diagram of the apparatus is shown in Figure 1. Compressed air is supplied to the unit at 50 psig. Seven pressure taps are installed through the column wall to provide pressure drop information. These pressure taps are located as follows: one above the distributor plate, the next five spaced four inches apart (to a height of 20 inches), and the seventh tap 60 inches above the distributor plate. Two pressure differential transducer cells can be connected between any two of the various pressure taps.

Figure 1. SCHEMATIC OF 8-INCH DIAMETER FLUIDIZATION APPARATUS

For these experiments, the pressure drop was measured between 0 and 8 inches and between 0 and 20 inches. The pressure difference at the 8-inch tap was used to determine bed density and the 20-inch tap was used to determine actual bed height during a run. The two pressure differential cells were connected to strip chart recorders.

Three different size fractions of sand were studied (-20+40, -40+80, and -80+170 USS mesh). The sand was mixed with ground hardwood char that was sized to -1/4 in. x 0. The char-sand mixture compositions studied ranged from 5% to 67% char by volume. Fresh char was used for each test because of char attrition during a test run.

A standard experimental procedure was followed to obtain fluidization data on a consistent basis. The various mixtures were all measured for a constant bed height of 14 inches. After charging the column with a mixture, the bed was mixed with fluidizing air for 20 to 30 seconds. The air was turned off and the bed given 1 to 2 minutes to settle. Next, the pressure recorders were activated and the air was turned on (this time to an initial value of 0.1 to 0.2 ft/s — far below the fluidizing velocity). The bed was given 2 to 3 minutes to reach pressure equilibrium; then the gas velocity was increased for the next data point. This procedure was continued until two or three data points had been established beyond the point of complete fluidization (complete fluidization velocity was determined visually). The gas velocity was then decreased incrementally back to zero with measurements repeated.

A summary of the fluidization test information is presented in Table 6 showing the char-to-sand ratios, gas velocities, and pressure differentials. Plots of pressure drop per unit length ($\Delta P/L$) versus the superficial gas velocity (volumetric gas flow rate divided by the column cross-sectional area) are given in Figures 2 to 4. Also shown in Table 6 are values of minimum fluidization velocity (U_{mf}) and pressure drop calculated from the physical properties of the bed. Minimum fluidization velocity was calculated using Equation 1.¹

$$U_{mf} = \left(\frac{\mu}{\rho_g D_p} \right) \{ [(25.25)^2 + 0.0651 Ar]^{1/2} - 25.25 \} \quad (1)$$

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Figure 2. EXPERIMENTAL FLUIDIZATION CURVES FOR -20+40 MESH SAND + CHAR

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Figure 3. EXPERIMENTAL FLUIDIZATION CURVES FOR -40+80 MESH SAND + CHAR

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Figure 4. EXPERIMENTAL FLUIDIZATION CURVES FOR -80+170 MESH SAND + CHAR

Table 6. SUMMARY OF 8-INCH COLUMN FLUIDIZATION TESTS

Material: -20+40 Sand and -1/4 x 0 Char ~14-inch Bed Height

<u>% Char by Volume</u>	<u>U_{MF}, ft/s</u>	<u>U_{CF}, ft/s</u>	<u>U_{CF}-U_{MF}, ft/s</u>	<u>ΔP/L @ U_{MF}, psi/ft</u>	<u>ΔP/L @ U_{CF}, psi/ft</u>
0% (Correlation)	0.97	--	--	--	0.62
0	0.82	1.54	0.72	0.67	0.64
5	0.65	1.04	0.39	0.65	0.58
10	0.67	1.03	0.36	0.64	0.58
20	0.72	1.08	0.35	0.69	0.56
33	0.66	0.99	0.33	0.64	0.51
50	0.71	1.03	0.32	0.57	0.48
67	0.53	0.93	0.40	0.40	0.38
100	1.25	3.75	2.50	0.096	0.088

Material: -40+80 Sand and -1/4 x 0 Char ~14-inch Bed Height

0% (Correlation)	0.153	--	--	--	0.60
0	0.092	0.228	0.430	0.75	0.60
20	0.065	0.223	0.158	0.64	0.53
34	0.072	0.190	0.118	0.55	0.45
50	0.096	0.332	0.236	0.54	0.36
100	1.25	3.75	2.50	0.096	0.088

Material: -80+170 Sand and -1/4 x 0 Char ~14-inch Bed Height

0% (Correlation)	0.080	--	--	--	0.54
0	0.075	0.325	0.250	0.58	0.54
5	0.050	0.113	0.063	0.63	0.55
20	0.034	0.129	0.095	0.61	0.53
33	0.051	0.189	0.138	0.51	0.44
50	0.048	0.197	0.149	0.52	0.50
100	1.25	3.75	2.50	0.096	0.088
100% Char (Correlation)	0.377	--	--	--	0.090

where

$$Ar = \frac{D_p^3 \rho_g (\rho_s - \rho_g) g}{\mu^2} = \text{Archimedes Number}$$

ρ_s = particle density of fluidizing solids, lb/ft³

D_p = average particle diameter, ft = $\frac{1}{\sum (X_i / D_{pi})}$

ρ_g = density of fluidizing gas, lb/ft³

U_{mf} = minimum fluidization velocity, ft/s

μ = viscosity of fluidizing gas, lb/ft-s

g = acceleration of gravity, 32.2 ft/s²

The pressure drop was determined by dividing the completely fluidized weight of the bed by the column cross-sectional area.

The fluidization curves shown in Figures 2 through 4 for the three different sand sizes all show a similar shape. However, as the char concentration increases, the minimum fluidization velocity (determined from the plots) is less well-defined. Instead of an obvious peak, the curves gradually bend over until the pressure drop becomes nearly constant.

A plot of minimum fluidization velocity versus char volume percent is shown in Figure 5 for the three sand size fractions. The U_{MF} rises sharply for char concentrations above 67% and shows the need for an inert material for bed fluidization and control. When one attempts to fluidize a bed of char only, the bed segregates by size very quickly. A very high gas velocity is then required to fluidize the large (1/4-inch) pieces of char. Because of its greater density, some of the sand present in the bed always resides at the bottom of the bed, keeping that portion of the bed in motion. Without the sand present, it is very difficult for the larger char pieces to tumble over each other and fluidize.

For all the tests, the U_{MF} of the sand-char mixtures was less than that of the sand alone. For the coarse sand, the U_{MF} of the mixtures were between 64% and 89% of the U_{MF} for the sand alone; for the fine sand, U_{MF} was between 45% and 65% of that for the sand alone. This indicates the positive effect that a wide range of particle sizes has on lowering the U_{MF} of a mixture. The sand present in the bed "lubricates" the entire bed, causing it to fluidize at a lower gas velocity.

Figure 6 plots the difference between complete fluidization velocity and minimum fluidization velocity versus the char volume percent. This shows the relationship of complete bed fluidization with char concentration and sand size. A plot of $\log U_{MF}$ versus sand particle size at char concentrations of 20%, 33%, and 50% char by volume is shown in Figure 7. Char concentration in the 33% to 50% range appears to provide stable bed behavior and beds of sufficient char inventory for design purposes.

Hollow alumina spheres ($-24+60$ mesh) were ordered and tested with char compositions similar to those used with the sand. The bulk density of the alumina is about 65 pounds per cubic foot compared to the approximate 100 pounds per cubic foot for the sand. The smaller density difference between the char and alumina may promote better mixing and certainly lower fluidization velocities. The data is being processed and will be reported next quarter. The minimum fluidization velocity appears to be about 70% of that for coarse sand, and the spherical shapes of the hollow spheres provide smoother fluidization.

Drying Characteristics

Drying characteristics of biomass are important in the design of the gasifier as well as any front-end dryer using recovered waste heat that may be required to reduce the moisture content of the biomass. Controlled moisture levels in the biomass would help handling systems and would control gasifier heat loads. In the gasifier, heat would be rapidly transferred to the biomass particles primarily by direct contact with hot sand at about 1500°F. A front-end dryer, on the other hand, would probably operate at relatively slow heat-up rates, typically observed in convective heat transfer from hot drying gases at about 150° to 300°F. Work was initiated to investigate biomass drying characteristics in the lower-temperature regime (150° to 300°F) at slow heat-up rates. During this reporting period, one exploratory experiment was

Figure 5. EFFECT OF CHAR CONCENTRATION ON MINIMUM FLUIDIZATION VELOCITY

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Figure 6. EFFECT OF CHAR CONCENTRATION ON COMPLETE MINUS MINIMUM FLUIDIZATION VELOCITY

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Figure 7. EFFECT OF SAND PARTICLE DIAMETER ON MINIMUM FLUIDIZATION VELOCITY FOR VARIOUS CHAR-SAND MIXTURES

conducted with maple hardwood chips that had been sized in a hammer mill to produce a $\frac{1}{4}$ -inch x 0 material. A sample of these chips was placed in a constant-temperature, constant-humidity chamber for about 24 hours prior to the experiment. The conditions of temperature and humidity can be controlled during this period to obtain samples of desired moisture content for the drying experiment.

The drying experiment was conducted in a thermobalance apparatus capable of continuously monitoring the weight of the sample as it is dried. Details of the equipment and experimental procedure were given in the first quarterly report. The data on weight of the sample at any time during the experiment could be translated into moisture content by recalling the weight of the initial sample and its moisture content.

Figure 8 shows the moisture content of the maple hardwood chips as their temperature was raised to 280°F at approximately 8.5°F per minute. Except for the small, almost instantaneous moisture loss at the start of the experiment, the decrease in moisture content (to as low as about 6%) was found to be almost linear with the rise in temperature.

Data from similar experiments at different heat-up rates will be obtained from further experiments to characterize the effect of heat-up rate on drying characteristics of materials that have the same initial moisture content. Other experiments planned will use materials of different initial moisture contents to study the effect of the heat-up rate parameters on drying. The experiments are to be continued up to about 400° to 500°F, which is the temperature at which the effect of chemical reactions (that is, devolatilization) is expected to appear in the weight-loss curves.

Size Reduction Testing

A small laboratory hammermill mill (Weber Bros. Co.) was obtained to study size reduction parameters on a small scale. The small scale permits a large number of tests to be made with small-volume wood samples. New sizing screens were ordered for the unit to vary the size reduction ratio and measure the throughput rate and overall mill power consumption. Different wood types and moisture levels will be tested.

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Figure 8. DRYING CHARACTERISTICS OF MAPLE HARDWOOD CHIPS (8.5°F/min)

Future Work

During the next quarter, construction of a 12-inch Plexiglas fluidization column will be completed to study bed mixing, pressure drop, and gas distributor design. Mixing patterns will be observed for various distributor arrangements. Attrition rates of the char particles will also be examined in this system.

The size reduction tests will begin with the laboratory hammermill will begin and additional drying tests will be conducted.

Task III. Bench-Scale Experiments

Work During Period

The hydroconversion of biomass to produce a medium-Btu gas can be divided into the following reaction steps:

1. **Hydrodevolatilization.** Nearly instantaneous thermal decomposition of biomass in a hydrogen atmosphere, followed by a gas-phase hydrogenation of volatile products into hydrocarbon gases, hydrogen, carbon monoxide, carbon dioxide, and water.
2. **Rapid-Rate Methane Formation.** Rapid conversion of a part of the devolatilized biomass char into methane at appropriate gasification conditions.
3. **Char Gasification.** Slow residual biomass char gasification with hydrogen and steam to produce methane, carbon monoxide, hydrogen, and carbon dioxide.
4. **Char Combustion.** Combustion of residual biomass char, which supplies the energy required for the endothermic char gasification reactions.

The bench-scale experimentation continued during the quarter to investigate these reaction steps with maple hardwood. Three types of bench-scale experiments were conducted: nonisothermal thermobalance gasification experiments to determine the temperature regimes in which the above reaction steps occur; hydrodevolatilization experiments in a free fall reactor; and isothermal char gasification experiments in a thermobalance using a mixture of hydrogen, steam, and helium. Results from the nonisothermal thermobalance gasification experiments provided hydrodevolatilization temperatures as well as information for the choice of operating parameters for the free fall hydrodevolatilization studies. The hydrodevolatilization experiments produced pertinent data on char, liquid, and gaseous product mixture yields, and the makeup of the respective mixtures. The isothermal char gasification

experiments contributed kinetic data on the slower steam-char reactions in gaseous atmospheres containing typical percentages of hydrogen and steam.

All experiments during the reporting period were conducted with maple hardwood chips. The air-dried samples were sized in a disc attrition mill to produce a -12+16 mesh material and stored under nitrogen for subsequent experiments. The properties of this biomass material as analyzed are given in Table 7.

Table 7. PROPERTIES OF SIZED MAPLE HARDWOOD CHIPS

Properties	<u>Proximate Analysis, wt %</u>
Moisture	5.5
Volatile Matter	81.2
Ash	0.2
Fixed Carbon	<u>13.1</u>
Total	100.0
Composition	<u>Ultimate Analysis, wt %</u>
Ash	0.21
Carbon	49.80
Hydrogen	6.05
Sulfur	0.00
Nitrogen	0.15
Oxygen (by difference)	<u>43.79</u>
Total	100.00

Heating Value: 8399 Btu/lb dry wood

Nonisothermal Thermobalance Gasification Experiments and Test Results

The gasification characteristics of the raw biomass were investigated by nonisothermal experiments using a thermobalance apparatus. The apparatus is capable of continuously monitoring the weight of a sample reacting under simulated process conditions. The apparatus was described in the first quarterly report. However, the experimental procedure in review is as follows: A representative sample of about a half gram of the sized test material is suspended in a wire mesh screen basket from a transducer and brought in contact with the gasification medium at predetermined reaction conditions. These nonisothermal experiments provide data on the relationship of biomass weight

loss to temperature by gradually raising the temperature (about 10°F/min) to determine the ranges over which significant conversions occur.

Figure 10 shows the weight fraction of dry maple hardwood remaining in the basket as the temperature of the samples was raised to about 1800°F in pure hydrogen at 300 psig. Results from three experiments are shown in this figure. Two of these experiments used a -16+60 mesh sample, and the third used a -12+16 mesh sample. Figure 9 shows that, within the limits of conditions investigated in this work, particle size has negligible effect on overall conversion for various temperatures at these slow heat-up rates (about 10°F/min). The data also show that overall conversions of about 80% to 84% are expected if the material is devolatilized at 1200°F to 1500°F.

The difference between the devolatilization characteristics of maple hardwood in hydrogen and in inert nitrogen is shown in Figure 10. The nitrogen data points are shown as the open circles. This is compared to a curve representing the hydrogen data of Figure 9. Over the entire range of temperature investigated, overall conversion levels are higher in hydrogen than in nitrogen. In the temperature range of 1200° to 1500°F and for the slow heat-up rates (about 10°F/min) employed in these experiments, the residual char is 5% to 8% less in hydrogen than in helium.

Hydrodevolatilization Experiments and Test Results

On the basis of the results from the nonisothermal thermobalance gasification experiment, the hydrodevolatilization experiments were performed in an apparatus devised to study the devolatilization rate under rapid heat-up conditions (about 5000°F per second). The raw biomass entering a gasifier may encounter similar heat-up rates.

The bench-scale equipment used to conduct the biomass devolatilization experiments is illustrated in Figure 11. It is comprised of the feed gas handling system, the reactor and furnace system, and the product gas and liquids handling system.

The feed gas handling system is designed to supply the devolatilization gaseous medium at the temperature, pressure, composition, and flow rate specified for each experiment. During the course of an experiment, the devolatilization gas flow rate is monitored by measuring the calibrated pressure drop

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Figure 9. THERMOBALANCE GASIFICATION CHARACTERISTICS OF MAPLE HARDWOOD CHIPS IN H_2 AT 300 psig

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Figure 10. THERMOBALANCE GASIFICATION CHARACTERISTICS OF MAPLE HARDWOOD CHIPS IN N_2 AND H_2 AT 300 psig

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Figure 11. SCHEMATIC OF FREE-FALL DEVOLATILIZATION APPARATUS

across a "pig-tail" coil of 1/16-inch diameter tubing. The reactor pressure is maintained with a dome-loaded back pressure regulator installed in the product gas exhaust line. A pressurized, stirred feed hopper with a screw auger to feed the solids is installed on top of the reactor. A screw auger at the bottom of the reactor discharges the char into a dump hopper. The reactor sections are coupled with 4-inch "Graylok" connectors. The reactor can be heated by a clamshell electric furnace to 1400°F (760°C).

The feed solids enter at the top of the reactor. The preheated feed gases are delivered to the reactor approximately 3 inches below the solid feed position in cocurrent flow through the four-foot reactor section. The temperature in the reactor is monitored by four centerline thermocouples. The devolatilization gaseous and liquid products pass through a 200 mesh filter inside the reactor above the bottom char discharge section. The char is rapidly discharged from the bottom of the reactor by the screw auger to a cold dump hopper to quench any further reaction. The solids fall by gravity through the heated reaction zone, hence the term "free-fall" devolatilization apparatus.

The product gas handling system is comprised of a dry-ice liquid trap, back pressure regulator, dry test meter, and on-line gas analysis and sampling systems. The liquid trap is constructed from a 3.5-foot-long by 3.5-inch-diameter pipe with a 1/2-inch diameter dip tube extending to within 6 inches of the bottom of the sealed pipe. The trap houses a glass liner bottle to collect the condensing liquids. This liner is weighed before and after each experiment to obtain the total weight of liquids produced. A back pressure regulator is used after the dry-ice trap to maintain the reactor pressure during the course of an experiment. The volumetric flow rate of the gases free of the condensed liquids is measured with a dry test meter. A part of the metered gases are passed through continuous on-line infrared CO and CO₂ analyzers. The on-line infrared analyzers are used for partial product gas analysis as well as to determine the steady state experimental period. Exhaust from the IR analyzers passes through a gas sampling manifold where periodic product gas samples are taken for mass spectral analysis.

Shakedown operations with this equipment have shown material balances in excess of 85%. Char discharge into the cold dump hopper is complete except for a holdup of about 1% to 2% in the transition sections.

The experiments conducted this quarter were designed to investigate the effect of operating conditions on devolatilization characteristics with maple hardwood chips, which had been ground in hammer and disc mills and screened to -12+16 USS mesh. Riffled representative samples were dried overnight at 130°F (54°C) before the experiment. The moisture content of these samples was about 5.5% by weight as shown in Table 7.

At the beginning of each experiment, the feed hopper was charged with 400 to 600 g of prepared feed. The reactor was then purged with nitrogen and checked for pressure leaks. After the temperature was steady, the reactor was flushed with the devolatilization gas, either H₂ or He. The feed and discharge screws were turned on to start the experiment. The wood sample was fed at rates of 1 to 3 grams per minute to undergo devolatilization in the free-fall region. The experimentally measured free-fall time, in the reactor, for the -12+16 mesh particles was about 0.3 seconds. It was observed that, in all the experiments, the steady-state operation was attained within 5 to 10 minutes after starting the feed. Usually, feeding was continued for another 50 minutes or more, and then the experiment would be terminated by shutting off the screw feeders, electric heaters, and finally the devolatilization gas flow. After the reactor had cooled and was depressurized, the devolatilized char was weighed and analyzed. Quantitative analysis of the oils was achieved by extracting the liquid products with methylene chloride and making a GC-MS analysis of the extract.

The experiments designed to investigate the effect of operating conditions on biomass devolatilization characteristics were conducted at pressures of up to 250 psig and at about 1200° to 1300°F with H₂ and He as devolatilization media. A summary of the experimental conditions and the experimental data is provided in Table 8. During the initial experiments, some material (about 3% to 5% by weight of char) attributed to scaling of the newly built gas preheater and reactor system was collected along with the devolatilized char. In Table 8, this amount was subtracted from the measured char yields. Because of the excess hydrogen employed in these experiments, the dry gas compositions, in Table 8, are expressed on a hydrogen-free basis. The duration of the experiments varied because of mechanical and exit gas line freeze-up problems in the cold trap. The duration of the experiments varied from 50 minutes to 1.4 hours. The steady-state portion of the experimental

data is reported in Table 8. Runs F-1, F-2, and F-3 were aborted in the shakedown experience. A typical analysis of the liquids collected is shown in Table 9 for Run F-7.

The analysis of the experimental data given in Table 8 is proceeding and will be reported next quarter. Product yields and elemental balances will be completed and examined for trends with operating conditions.

Isothermal Gasification Experiments and Test Results

The kinetics of steam-char reactions were investigated by isothermal thermobalance experiments at 300 psig total pressure in the temperature range of 1200° to 1700°F. All experiments during this reporting period employed a gas medium consisting of about 50% H₂O, 5% H₂, and 45% inert gases (He). This composition was selected because the raw product gases from adiabatic steam-oxygen gasifiers operating at about 1500°F and 300 psig could possibly have a similar composition. Table 10 is a summary of the isothermal experiments conducted with the maple hardwood chars. All chars for these tests were prepared in N₂ at the maximum temperatures given in Table 10.

All the isothermal char gasification data were translated into the amount of base carbon converted by using Johnson's kinetic model.² Base carbon is defined as the carbon that remains in the char after devolatilization is complete. These data are presented in Figure 12 to show the effect of gasification temperature on the rates of char gasification at 300 psig.

Analysis of the char gasification results showed that the following first-order kinetic expression was adequate in representing the experimental data:

$$\frac{dx}{dt} = k (1 - x) \quad (2)$$

where

x = base carbon conversion

t = time

and

k = reaction rate constant.

Table 8. EXPERIMENTAL DATA ON FREE-FALL DEVOLATILIZATION OF MAPLE HARDWOOD CHIPS

	Experiment No.				
	F-4	F-5	F-6	F-7	F-8
Operating Conditions					
Devolatilization Medium	He	H ₂	H ₂	H ₂	H ₂
Pressure, psig	250	55	55	150	150
Temperature, °F	1240	1160	1250	1240	1280
Duration of Experiment, min	51	51	74	54	80
Amount of Wood Fed, g (5.5% moisture)	81.00	128.44	107.99	174.46	198.03
Devolatilization Yields					
Char (% feed)	37.05	19.46	17.94	12.25	13.25
Liquids (% feed)	9.26	11.68	11.75	17.24	10.10
Gases (% feed)	73.28	65.40	76.30	54.00	83.32
Char Composition, wt %					
C	65.88	60.19	60.63	83.56	79.30
H	4.49	5.33	5.04	3.86	3.81
N	--	0.30	0.31	0.34	0.44
S	--	0.08	0.05	0.21	0.09
O	29.04	33.01	31.09	9.66	14.63
Ash	0.60	1.10	1.08	1.83	1.73
Gas Composition, mol% (H ₂ -free)					
CO	68.45	51.72	51.46	48.08	47.67
CH ₄	12.35	27.38	26.11	29.34	30.04
CO ₂	14.88	9.13	9.22	11.41	10.27
C ₂ H ₆	1.19	9.13	10.75	10.54	10.08
C ₃ H ₈	0.15	0.60	0.16	0.24	0.39
C ₂ H ₄	2.08	0.71	0.76	0.33	0.58
C ₄ H ₈	0.15	0.10	--	--	--
C ₃ H ₆	0.04	0.40	0.16	--	0.19
C ₆ H ₆	0.01	0.71	1.08	--	0.78
C ₇ H ₈	--	0.10	0.30	--	--

Table 9. ANALYSIS OF LIQUID PRODUCTS FROM EXPERIMENT No. F-7

Devolatilization Medium	H ₂
Feed, g (dry)	165.04
Total Weight of Liquids, g	20.66
Oil Fraction, % by wt	7.7
Products, % by wt	
One-Ring Compounds	
Benzenes	34.0*
Styrenes	0.2
Indans	1.4
Indenes	3.0
Two-Ring Compounds	
Naphtalenes	20.8*
Biphenyl	0.7
Acenaphthene	1.3
Acenaphthylene	0.5
Three-Ring Compounds	
Fluorene	2.1
Phenanthrene and Anthracene	2.5
Phenylnaphthalenes	0.2
Others	0.5
Four-Ring Compounds	2.2
Five-Ring Compounds	0.4
N-Containing Compounds	0.8
O-Containing Compounds	
Phenol	26.3*
Benzofuran	1.3
Others	0.7
Unidentified	1.5
Total	100.4
Water Fraction, % by wt	92.3
Products, % by wt	
Water	99.23
Phenol + O-Cresol	0.38
M- + P-Cresol	0.02
Acetic Acid	0.21
Unidentified	0.16
Total	100.00

* 81% as benzene, naphtalene, and phenol; this is 8% to 10% of the liquids.

Table 10. SUMMARY OF ISOTHERMAL THERMOBALANCE EXPERIMENTS WITH
MAPLE HARDWOOD CHARs

Experiment No.	Maximum Temperature, °F	Pressure, psig	Gasification Medium		
			H ₂ -----	He mol %	H ₂ O -----
MHW-1	1350	100	5.6	52.4	42.0
MHW-2	1500	100	4.9	45.1	50.0
MHW-3	1500	300	4.9	45.3	49.8
MHW-5	1700	300	5.0	46.3	48.7
MHW-6	1700	100	4.8	45.0	50.2
MHW-7	1700	200	4.8	45.1	50.1
MHW-8	1200	300	4.9	45.2	49.9
MHW-9	1350	300	4.9	45.5	49.6
MHW-15	1425	300	4.9	45.1	50.0
MHW-16	1425	100	4.9	45.1	50.0

Integrating Equation (2) and plotting the term $-\ln(1-x)$ versus the time t produces a straight line with the slope equal to k . Alternatively, a characteristic time, τ , could be defined so that plots of $-\ln(1-x)$ versus the reduced time, t/τ , would be a universal straight line for all data. One such characteristic parameter could be defined as the time required to achieve 50% base carbon conversion. Values of this characteristic time τ computed from the experimental char gasification data are given in Table 11. The characteristic time τ has a simple and direct relationship with the first-order rate constant; namely,

$$\tau = \frac{\ln 2}{k} \quad (3)$$

The values of k , the first-order reaction rate constant, are computed from the values of τ and are given in Table 11.

The table also includes a parameter that qualitatively represents the reliability of data obtained from the various experiments. This parameter is Q , defined as the change in weight of the metal basket holding the sample during the experiments. It is presented as a percentage of the weight of the wood sample. Under ideal conditions only the sample in the basket undergoes chemical reactions, and the weight of the basket should remain constant during the experiment. The value of Q under these ideal conditions would be zero. In most experiments, however, the sensitive weighing system also detects that

Table 11. REACTION RATE CONSTANTS DETERMINED FROM ISOTHERMAL THERMOBALANCE
EXPERIMENTAL DATA ON MAPLE HARDWOOD CHAR GASIFICATION IN
5% H₂ + 50% H₂O + 45% He

Experiment No.	Temperature, °F	Pressure, psig	Characteristic Time τ , min	First Order Reaction Rate Constant k , sec ⁻¹ X 10 ⁴	Weight Loss Q of Basket During the Experiment, % of Initial Charge
MHW-1	1350	100	53.7	2.15	5.2
MHW-9	1350	300	52.7	2.19	0.5
MHW-16	1425	100	18.7	6.18	-0.2
MHW-15	1425	300	19.8	5.84	0.7
MHW-2	1500	100	7.1	16.38	10.3
MHW-3	1500	300	7.5	15.42	2.7
MHW-6	1700	100	2.0	57.45	3.7
MHW-7	1700	200	2.0	56.55	3.6
MHW-5	1700	300	2.4	47.68	4.5

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Figure 12. BASE CARBON CONVERSION AS A FUNCTION OF TIME FOR MAPLE HARDWOOD CHARs IN 5% H₂ + 50% H₂O + 45% He AT 300 psig

the basket undergoes a slight loss in weight and the value of Q is a small positive number. The larger this value the less reliable the data from the particular experiment. A negative value of Q indicates a weight gain for the basket that is rarely observed.

The data from the experiments at 1500°F are plotted in Figure 13. The fit to the kinetic model

$$-\ln(1 - x) = \ln 2 (t/\tau) \quad (4)$$

is quite good for the 300-psig data, which had a low basket weight change (i.e., $Q = 2.7$), but it is somewhat poorer for the 100-psig data, which had a higher basket weight change ($Q = 10.3$).

Experiments at 1425°F provided the most reliable data (that is, the lowest values of Q) and consequently showed an excellent fit to the model

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Figure 13. FIRST-ORDER KINETIC FIT OF MAPLE HARDWOOD CHAR GASIFICATION DATA AT 1500°F

as shown in Figure 14. The data from the remaining experiments at 1350° and 1700°F also showed a reasonable fit to the kinetic model as shown in Figures 15 and 16.

An Arrhenius plot for the maple hardwood char gasification rate constants is shown in Figure 17. Up to 1500°F, the values of $\ln k$ are correlated linearly with $1/T$ and yield an activation energy of 52.3 kcal/g mole. The data at 1700°F deviate from the linear correlation, indicating a chemical reaction rate masking effect due to mass transfer. Similar behavior has been reported earlier by Walker, *et al.*,³ for steam-carbon reactions.

Future Work

Analysis of the devolatilization data with maple hardwood will be completed. Trends in product yields with operating conditions will be examined.

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Figure 14. FIRST-ORDER KINETIC FIT OF MAPLE HARDWOOD CHAR GASIFICATION DATA AT 1425°F

Task IV. PDU Tests

Work During Period

The PDU design package was submitted to DOE at the end of September 1980 for review and authorization to proceed with procurement and construction of the PDU. The review process has been in progress at DOE to date.

Work on this task continued with design and specification of systems or support items that are auxiliary to the PDU design. Engineering proceeded with the detailed design and specifications of the internal components for the gasifier involving insulation purging, internal metal sleeve and inlet nozzle supports and provisions for thermal expansion, pressure head details for piping, and prevention of steam condensation in the thermal insulation. Nine detailed drawings were produced along with material and fabricator specification sheets

Figure 15. FIRST-ORDER KINETIC FIT OF MAPLE HARDWOOD CHAR GASIFICATION DATA AT 1350°F

Figure 16. FIRST-ORDER KINETIC FIT OF MAPLE HARDWOOD CHAR GASIFICATION DATA AT 1700°F

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Figure 17. ARRHENIUS PLOT FOR MAPLE HARDWOOD CHAR GASIFICATION
IN 5% H₂ + 50% H₂O + 45% He

to complete the vendor bid package. The design of the internal arrangement is completed in terms of principles. Physical modifications can be made if necessary.

A complete list of process control instrumentation with duty specifications has been prepared according to the three sections of the Process and Instrumentation Diagram submitted with the PDU design package. The index of instruments and requirements is sufficient for obtaining vendor quotes.

The structural steel decks and columns in the existing process building of the Steam-Iron process were reviewed for design loads.

The maximum PDU vessel weights that have to be supported were taken as the weight of the vessel filled with water. Installing and rigging the vessels to the second and third decks of the building is the best possible arrangement. This would not require any clearance cuts in the building walls, and no major existing equipment would have to be moved.

Two of the three decks proposed for use will require major structural steel work to support the vessels according to safe engineering structural design. This cost is still far below the cost of constructing a new structure from a concrete pad to the roof.

A preliminary search was made for suppliers of the special valves needed for the lockhopper feed system. Several manufacturing companies were contacted but only one, to date, has indicated that it could supply a suitable valve. Fabrivalve Co. of Oregon can supply, on special order, an 18 and a 24-inch knife gate valve able to operate at 300 psig. The company has made similar valves but only for use up to a pressure of 150 psig.

An existing piece of mechanical equipment previously used as a slurry heater was reviewed for possible retrofitting and use as a steam superheater and an air heater for startup. A replacement heat exchange coil may be the most significant modification cost item. A detailed analysis of the retrofit will be made and will be compared to quotes for package heater units available for purchase.

Two major design points in the PDU design package have been confirmed by the results of work in Task II fluidization and Task III bench-scale experiments. The fluidization velocities and bed parameters determined in Task II for inert sand and sand-char mixtures support the values chosen for the

fluidized-bed gasifier in the PDU design. Preliminary sand-char mixing observations also indicate that the fluidization should be smooth and that char distribution will be aided by the inert sand material.

The results in the Task III bench-scale studies of wood devolatilization and char gasification support the residence time chosen for the gasifier reactions. The devolatilization step will be instantaneous relative to the slower char gasification step. The char gasification tests show that the design char residence time of 3 to 5 minutes will be sufficient for the process conversion.

Future Work

The next phase of work on this task involves procurement and construction. The results of support task work to date on bench-scale experiments and fluidization parameters appear to confirm and support the design values chosen for the PDU design. A critical path analysis of the project will be completed upon receipt of vendor quotes of cost and delivery for each major component of the PDU.

Task V. Data Review for Pilot Plant Tests

No work is scheduled on this task until the second year.

Task VI. Technoeconomic Evaluation

No work is scheduled on this task until the second year.

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