PNL-SA-7939

INVESTIGATION OF GASIFICATION OF BIOMASS IN THE PRESENCE OF CATALYSTS

Presented at the Eighth Biomass Thermoconversion
Contractors Meeting

Seattle, Washington

31 July - 1 August 1979

by
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PREPARED FOR THE U.S. DEPARTMENT OF ENERGY
UNDER CONTRACT EY-76-C-06-1830

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INTRODUCTION

The overall objective of this study is to determine the technical and economic feasibility of catalyzed biomass gasification to produce specific products: (a) methane, (b) hydrogen, (c) carbon monoxide, and (d) synthesis gases for generation of ammonia, methanol, or hydrocarbons. Specific objectives are to:

- Determine kinetics and yields from reaction between gasification media (H_2O, O_2 and/or CO_2) and wood waste with and without catalysts as a function of temperature, pressure, and gasification media.
- Identify reaction systems for Objective 1 for production of essentially pure products (CH_4, H_2, CO and H_2/CO mixtures).
- Design and construct a process development unit (PDU) for testing of preferred reaction systems.
- Test preferred reaction systems in the PDU.
- Identify and develop process features required for feasibility such as catalyst recovery and conditioning, use of ash or ash-derived material as a reaction catalyst, feed preparation, and product gas treatment.
- Prepare conceptual design, flowsheets, material balances, and energy balances for processes identified as technically feasible.
- Determine economics of the technically feasible systems.

Studies that have been completed and previously reported (1,2,3,4,5) include 1) determination of relative gasification catalyst activity, 2) determination of reaction kinetics, 3) evaluation of catalyst-wood contacting methods, 4) development of catalyst combinations on a laboratory scale for direct generation of specific products, and 5) design, construction, and operation of a process development unit (PDU) for evaluation of gasification systems. These studies have illustrated the technical feasibility for generating synthesis gases specifically tailored for production of either methanol, hydrocarbons, or ammonia and for generating a methane rich gas.

Work to achieve the objectives of this study was continued in the laboratory and PDU. Laboratory studies further defined the effect of primary catalyst concentration on gasification rate. Systems for direct generation of ammonia synthesis gas and hydrogen were defined at the laboratory scale. No promising system for direct carbon monoxide production was found. A new wood feed system was installed in the PDU and has proved to be reliable and effective for metering wood into the gasifier. New heaters installed in the PDU reactor have greatly improved temperature control in the system.

Preliminary calculations on the feasibility of catalyzed gasification of wood to produce methanol are encouraging. Potential methanol yield is about 180 gallons per dry ton of wood. Energy efficiency of the process would be 68%.

Details of the results obtained since the last contractors' meeting are presented in the following discussion. Status of the project is also presented.

PROJECT TASKS

Four tasks were defined to accomplish the objectives of this program. These tasks are the following:

Task 1. Laboratory studies

Task 2. Process development unit (PDU) design, procurement, and installation, now completed

Task 3. PDU operation

Task 4. Technical and economic feasibility studies

Status of activities and milestones in the project tasks for FY-79 are shown in Figure 1. This figure reflects considerable revision of the original milestone completion dates and addition of milestones. These changes are the result of both delays in operations and findings from completed studies.

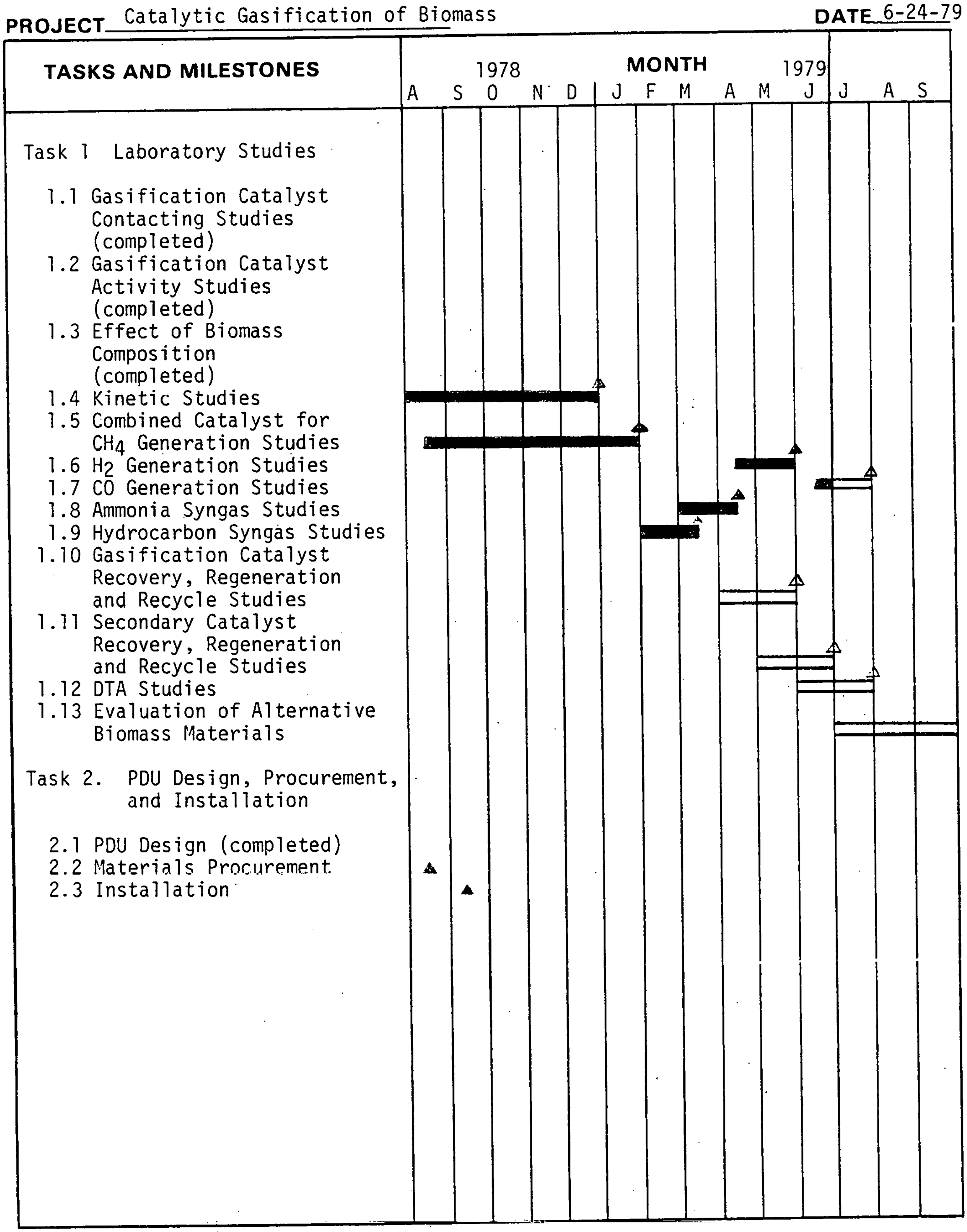


FIGURE 1. PROJECT SCHEDULE

PROJECT Catalytic Gasification of Biomass **DATE** 6-24-79

TASKS AND MILESTONES

Task 3. PDU Operation

3.1 QA and Acceptance Testing
3.2 Prepare Safety Analysis and Operating Procedures
3.3 Equipment Performance Evaluation
3.4 Operation without Catalysts
3.5 Demonstration of CH_4 Generation
3.6 Demonstration of H_2 Generation
3.7 Demonstration of CO Generation
3.8 Demonstration of Ammonia Syngas Generation
3.9 Demonstration of Hydrocarbon Syngas Generation
3.10 Determine Catalyst Durability
3.11 Determine Catalyst Recovery and Recycle Methods
3.12 Catalyst Regeneration Demonstrated
3.13 Alternative Feedstocks Evaluated

Task 4. Feasibility Studies

4.1 Prepare Flowsheets, Estimate Costs
4.2 Prepare Pilot Plant Design

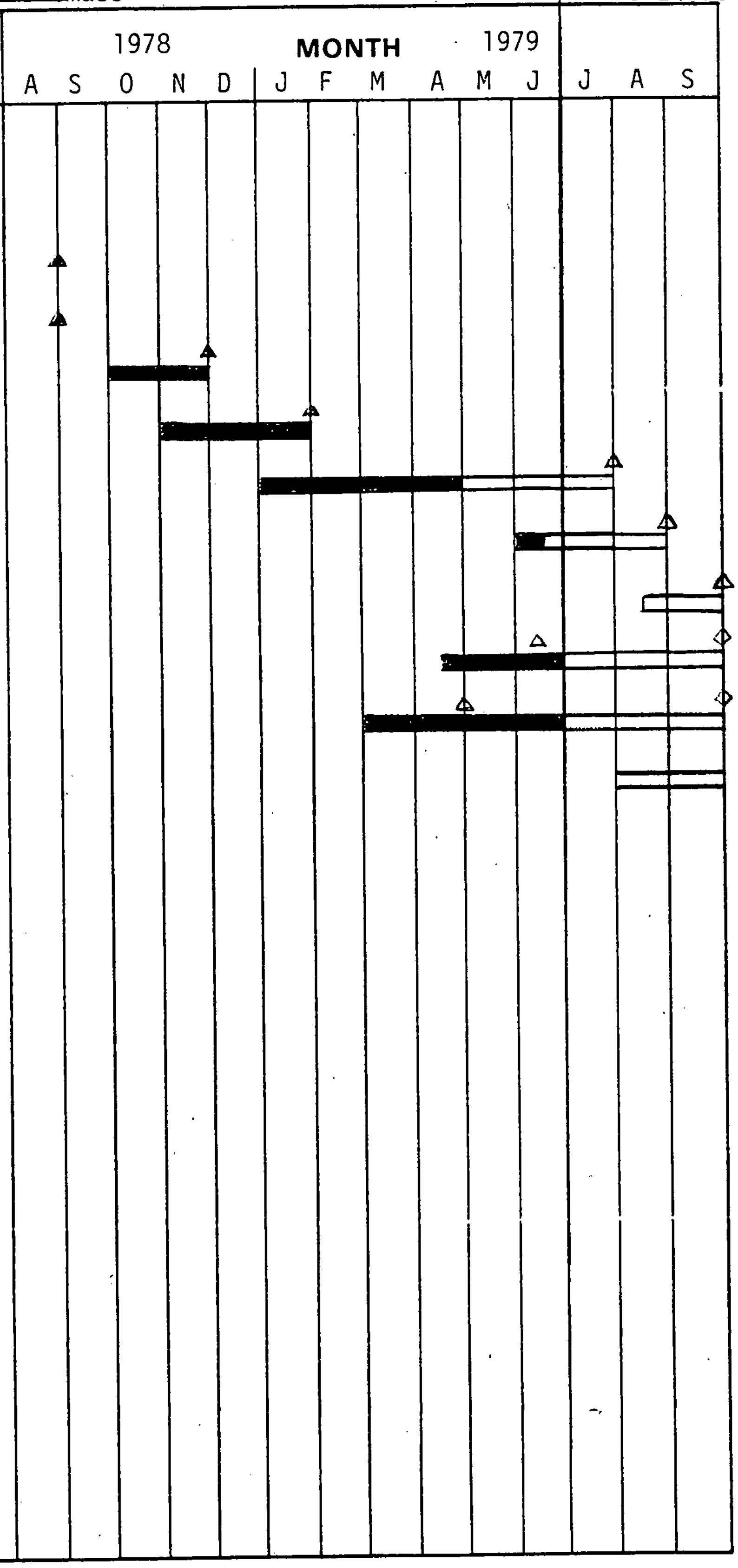


FIGURE 1. (CONTINUED)

MILESTONES (Figure 1, continued)

Task 1.

1.1 Most advantageous method of contacting reference catalyst (Na_2CO_3) and biomass (wood) identified and quantified at laboratory scale, 2/16/78.

1.2 Relative activity of Na_2CO_3, trona and borax as biomass gasification catalysts established with both steam and CO_2, 6/1/78.

1.3 Relative gasification reactivity for varying moisture content and wood components (bark and heart/sap wood) established, 6/18/78.

1.4 Rate expressions determined for preferred catalyst and contacting methods over the temperature range of 400-800°C, 12/31/78.

1.5 The variation of rate of biomass gasification (by steam) and product gas composition established at laboratory scale as functions of temperature, steam space velocity and secondary catalyst concentration to maximize CH_4 production, 1/15/79.

1.6 Variation of rate of biomass gasification (by steam) and product gas composition established at laboratory scale as functions of temperature, steam space velocity and secondary catalyst concentration to maximize H_2 production, 5/31/79.

1.7 Variation of CO production established at laboratory scale with biomass gasification reactant (steam with CO_2 and CO_2-O_2), temperature (650-850°C), space velocity in the presence of the preferred gasification catalyst, 7/31/79.

1.8 Required catalysts, operating conditions, and gasification media established at laboratory scale for production of ammonia syngas, 4/15/79.

1.9 Required catalysts, operating conditions, and gasification media established at laboratory scale for production of CO-H_2 syngas over the range of 1:1 to 4:1 hydrogen:carbon monoxide, 2/28/79.

1.10 Feasibility established and methods defined at laboratory scale for gasification catalysts recovery, regeneration, and recycling, 11/1/79.

1.11 Feasibility established and methods defined at laboratory scale for secondary catalyst recovery, regeneration, and recycle, 1/31/80.

1.12 DTA analyses completed to establish heat release/requirements for each desired product gas at optimal conditions, 3/1/80.

1.13 Feasibility established for use of alternative biomass feedstock to generate the desired products by processes developed for wood, 8/1/80.

MILESTONES (Figure 1, continued)

Task 2.

2.1 PDU design completed, 2/16/78.

2.2 PDU procurement completed, 8/21/78.

2.3 PDU installation completed, 9/15/78.

Task 3.

3.1 PDU functional/acceptance tests completed, 9/8/78.

3.2 Safety approval for operation obtained. Operating procedures prepared, 8/21/78.

3.3 Equipment operability established, equipment calibrated, 10/31/78.

3.4 Performance without catalysts established, 1/31/79.

3.5 Technical feasibility for methane generation established, 3/15/79.

3.6 Technical feasibility for H_2 generation established, 8/1/79.

3.7 Technical feasibility for CO generation established, 9/30/79.

3.8 Technical feasibility for ammonia synthesis gas generation established, 6/15/79.

3.9 Technical feasibility for hydrocarbon synthesis gas generation established, 5/1/79.

3.10 Secondary catalyst durability and active life established in the PDU, 3/1/80.

3.11 Methods for recycle of primary catalyst determined and tested in the PDU, 3/1/80.

3.12 Regeneration of secondary catalyst developed in the PDU, 5/1/80.

3.13 Use of alternative biomass feedstocks evaluated, 9/1/80.

Task 4.

4.1 Preliminary design for full scale systems completed. Cost estimates and economic analysis completed, 8/1/80.

4.2 Pilot plant design completed, 10/1/80.

Task 1. Laboratory Studies

Two experimental systems were employed this quarter: the continuous wood feed reactor shown in Figure 2 and the ball valve batch reactor shown in Figure 3. The continuous wood feed reactor was used for the combined catalyst performance studies. The ball valve reactor was used to study the kinetics and gas production rates for various alkali carbonate catalyst concentrations.

Combined Catalyst Performance

Experiments to investigate the use of secondary catalysts in combination with an alkali carbonate primary catalyst for producing or increasing the yield of specific products continued this quarter. It is postulated that, by using proper catalyst combinations and operating conditions, products formed in the reactor will consist primarily of either CH_4, H_2, CO, H_2-N_2, or H_2-CO in a mixture with CO_2. The primary product areas studied in combined catalyst performance experiments were ammonia synthesis gas, hydrogen, and carbon monoxide. Discussions of the results of each of these follow.

Ammonia Synthesis Gas Studies

Studies on conversion of biomass to an ammonia synthesis gas were completed this quarter. The objective of these studies was to produce a gas having a H_2:N_2 ratio of 3 to 1 which makes gas specifically tailored as a feedstock for an ammonia plant. The tailored gas is produced by reacting air, steam, and wood in the presence of catalysts. A summary of the experimental results and operating parameters employed this quarter are included in Table 1.

Effective catalyst systems for ammonia synthesis gas production consist of 17 wt % K_2CO_3 impregnated in the wood and gasified in the presence of Girdler G-93 cobalt molybdate:silica-alumina (Si-Al) catalyst system at a weight ratio of 3 to 1 respectively or in the presence of a Girdler G-3 chromium promoted iron oxide catalyst and a silica-alumina cracking catalyst at a weight ratio of 3 to 1. Both secondary catalyst systems produced similar results.

The primary role of the silica-alumina catalyst employed in these studies is to crack the small quantities of liquids generated from pyrolysis. This

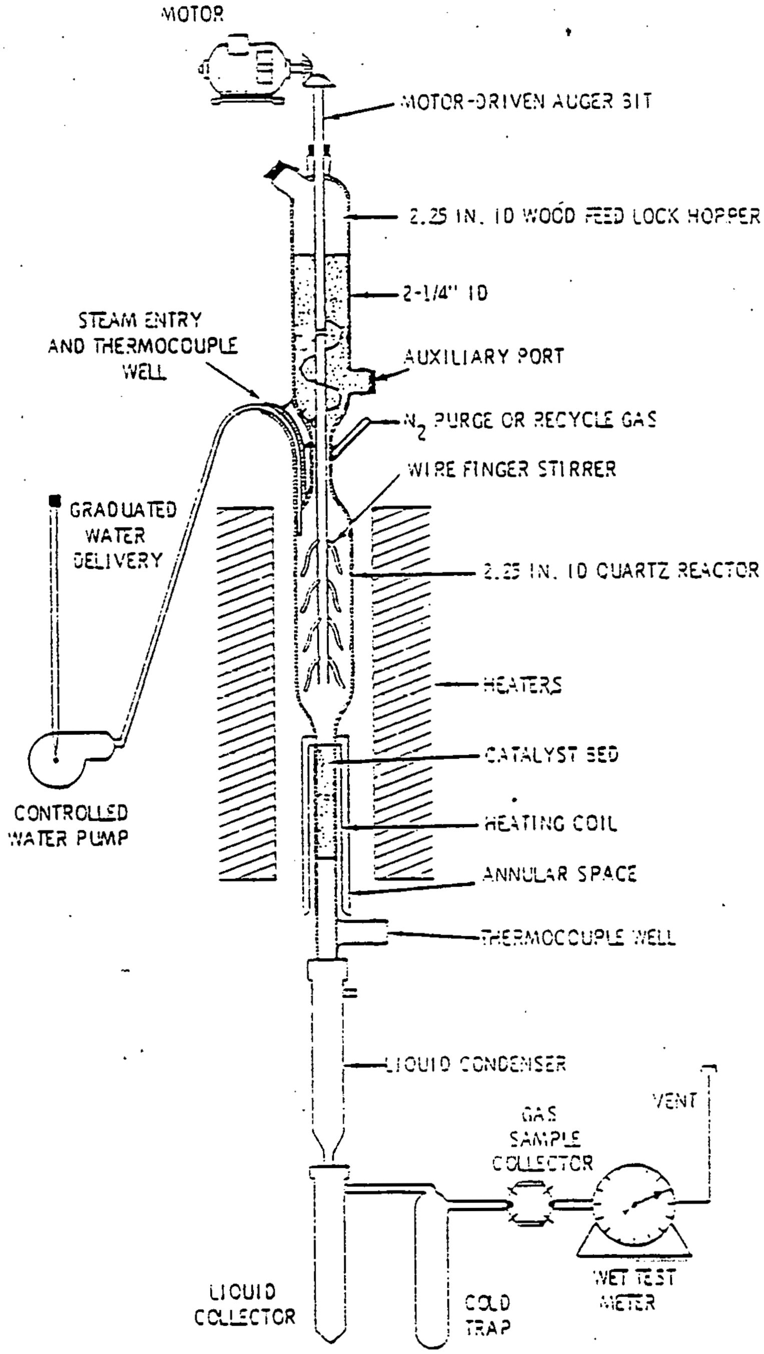


FIGURE 2. Continuous Wood Feed Quartz Reactor

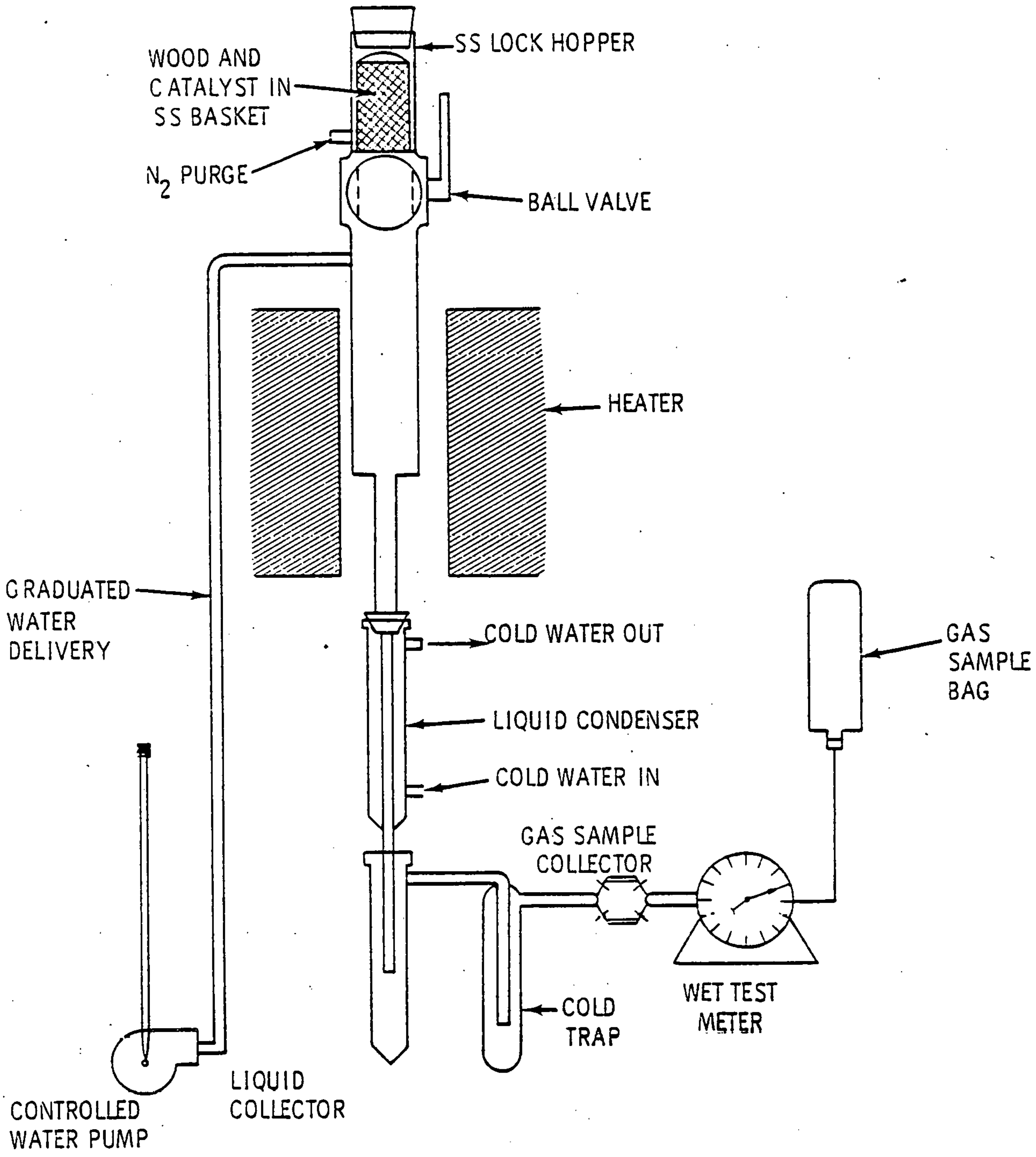


FIGURE 3. BALL VALVE BATCH REACTOR

TABLE 1. CATALYTIC GASIFICATION OF BIOMASS FOR THE PRODUCTION OF AMMONIA SYNTHESIS GAS

Run #	Catalyst	Air Rate ℓ/min	Reactor Temp °C	Cat. Bed Temp °C	% C Con. to Gas	Wood Feed Rate g/min	Steam Rate g/min	Gas Composition - Vol. %							H_2/N_2 Ratio
								H_2	CO_2	C_2H_4	C_2H_6	CH_4	CO	N_2	
6/17	Girdler G-3 Fe-Cr:Strem Si-Al (3:1)	0.15	650	620-675	70	0.4	1.7	55.5	24.9	tr	tr	1.4	3.1	14.2	3.9
6/17	Girdler G-3 Fe-Cr:Strem Si-Al (3:1)	0.17	655	625-680	67	0.4	1.7	53.4	22.9	0.1	0.1	2.4	3.3	17.0	3.1
6/17	Girdler G-3 Fe-Cr:Strem Si-Al (3:1)	0.18	655	630-680	66	0.4	1.2	51.3	22.3	tr	tr	1.2	5.4	18.4	2.8
6/17	Girdler G-3 Fe-Cr:Strem Si-Al (3:1)	0.2	657	630-680	61	0.4	1.2	59.0	23.1	tr	tr	1.0	0.4	15.4	3.8
6/19	Girdler G-3 Fe-Cr:Strem Si-Al (3:1)	0.17	750	700-765	82	0.3	1.6	48.0	22.8	tr	tr	1.9	2.2	24.3	2.0

in turn increases the amount of carbon converted to gas. At a steam rate of 4 times the wood feed rate the carbon conversions to the gaseous state for the Fe-Cr catalyst were between 61 and 66%. Carbon conversions to the gas phase for the Fe-Cr: Si-Al (3:1) catalyst were 67 to 73% at the same 4 to 1 steam to wood feed rate, an average increase in carbon conversion to gas of approximately 10%.

Major conclusions for the ammonia synthesis gas studies were presented last quarter. In addition to those conclusions use of the silica-alumina cracking catalyst to increase the overall carbon conversion to gas is recommended.

Hydrogen Production Studies

Hydrogen production studies were initiated and 97% completed this quarter. The objective of these studies was to optimize the selective production of hydrogen. A total of twenty-two experimental runs were completed. The experimental results are presented in Table 2. Various operating parameters and catalyst systems were investigated. Twelve specific catalyst systems were evaluated, and three temperature ranges (550°, 650°, and 750°C) were studied.

Two catalyst systems were found to be effective for hydrogen production: (1) Girdler Fe-Cr CO shift catalyst and a Harshaw Ni 1404 catalyst in a weight ratio of 3:1 respectively and (2) Girdler G-93 CO-Mo CO shift catalyst and Ni 1404 with the same 3:1 ratio. In all cases the wood feed was impregnated with 17 wt % K_2CO_3. Table 3 presents typical results employing preferred catalysts at each temperature range. Data presented in Table 3 show that 64 vol % hydrogen is obtained with a carbon conversion to gas of 78%.

Conclusions that can be drawn from experimental results for the hydrogen production case are:

- 750°C is the preferred operating temperature of the three temperatures investigated.
- Hydrogen production is extremely poor at 550°C.
- Approximately 80% of the carbon in the wood was converted to gas in runs at 750°C.
- The two catalyst systems previously described are suitable for hydrogen production.

TABLE 2. CATALYTIC GASIFICATION OF BIOMASS FOR THE PRODUCTION OF HYDROGEN

Run #	Catalyst	Reactor Temp °C	Cat. Bed Temp °C	C Con. To Gas $\frac{\text{(Wt. in Gas)}}{\text{(Wt. in Wood)}} \times 100$	Wood Feed Rate g/min	Steam Rate g/min	Gas Composition Vol. %					
							H_2	CO_2	C_2H_4	C_2H_6	CH_4	CO
7-1	Girdler G-3 Fe-Cr	650	580-650	58	0.6	0.7	61.5	24.1	0.2	0.2	3.0	11.0
7-1	Girdler G-3 Fe-Cr	650	580-650	69	0.3	1.7	67.1	25.7	0.2	0.1	2.3	4.6
7-2	Girdler G-93 Co-Mo	650	570-620	52	0.3	0.7	61.3	27.9	0.2	0.3	4.4	5.9
7-2	Girdler G-93 Co-Mo	650	570-620	60	0.3	1.0	57	30.5	0.3	0.6	5.8	5.8
7-4	Girdler G-64 Fe_2O_3	650	600-645	51	0.3	1.0	56.5	35.3	0.4	0.4	4.1	3.2
7-4	Girdler G-64 Fe_2O_3	650	575-620	51	0.3	1.1	59.7	35.1	0.2	0.3	2.9	1.7
7-5	Girdler G-64 Fe_2O_3 G-72D ZnO (1:1)	650	550-580	45	0.3	1.0	60.8	32.5	0.3	0.3	3.5	2.6
7-5	Girdler G-64 Fe_2O_3 G-72D ZnO (1:1)	650	560-580	54	0.3	1.5	60.9	33.4	0.2	0.2	2.8	2.5
7-6	Strem Si-Al	650	>590	42	0.4	1.0	58.3	32.5	0.4	0.3	3.6	5.0

TABLE 2. CATALYTIC GASIFICATION OF BIOMASS FOR THE PRODUCTION OF HYDROGEN (CONTINUED)

Run #	Catalyst	Reactor Temp °C	Cat. Bed Temp °C	C Con. To Gas $\frac{\text{(Wt. in Gas)}}{\text{(Wt. in Wood)}} \times 100$	Wood Feed Rate g/min	Steam Rate g/min	Gas Composition Vol. %					
							H_2	CO_2	C_2H_4	C_2H_6	CH_4	CO
7-6	Strem Si-Al	650	580	47	0.4	1.5	60.1	33.3	0.3	0.3	3.1	3.0
7-8	(1:1) Strem Si-Al: Girdler G-3 Fe-Cr	650	580-620	57	0.5	1.1	55.3	37.1	0.3	0.3	3.1	3.9
7-8	(1:1) Strem Si-Al: Girdler G-3 Fe-Cr	650	580-620	60	0.4	1.5	58.4	36.6	0.3	0.3	2.0	2.4
7-9	Girdler G-66 Cu-Zn	650	580-600	63	0.3	1.4	58.7	33.9	0.2	0.3	3.9	3.0
7-11	Girdler G-3 Fe-Cr	650	570-635	60	0.4	1.6	60.1	34.2	0.3	0.3	3.0	2.1
7-12	Girdler G-3 Fe-Cr + Grace Si-Al (2:1)	660	580-640	68	0.3	1.7	64	30.4	0.2	0.3	2.9	2.0
7-13	Girdler G-3 Fe-Cr + Harshaw Ni-1404 (3:1)	660	580-620	67	0.4	1.7	65.4	30.9	-	-	0.4	3.3
7-15	Girdler G-3 Fe-Cr + Harshaw Ni-1404 (3:1)	760	670-730	71	0.6	1.2	61.5	27.8	-	-	0.4	10.3

TABLE 2. CATALYTIC GASIFICATION OF BIOMASS FOR THE PRODUCTION OF HYDROGEN (CONTINUED)

Run #	Catalyst	Reactor Temp °C	Cat. Bed Temp °C	C Con. To Gas $\frac{\text{(Wt. in Gas)}}{\text{(Wt. in Wood)}}$ x 100	Wood Feed Rate g/min	Steam Rate g/min	Gas Composition Vol. %					
							H_2	CO_2	C_2H_4	C_2H_6	CH_4	CO
7-15	Girdler G-3 Fe-Cr + Harshaw Ni-1404 (3:1)	750	670-730	77	0.5	2.1	65.6	28.5	-	-	0.2	5.7
7-18	Girdler G-93 Fe-Cr + Grace Si-Al (2:1)	650	570-620	52	0.5	1.7	57.4	36.2	0.2	0.4	3.6	2.1
7-19	Girdler G-3 Fe-Cr + Harshaw Ni 1404 (3:1)	750	670-715	78	0.3	1.7	64.0	29.9	-	-	0.2	5.8
7-20	Girdler G-3 Fe-Cr	550	450-520	33	0.5	0.7	45.3	45.0	0.3	1.0	7.2	1.2
7-20	Girdler G-3 Fe-Cr	550	450-520	35	0.4	1.0	42.6	45.2	0.2	1.1	6.8	4.0
7-20	Girdler G-3 Fe-Cr	550	450-520	34	0.4	1.2	49.6	41.0	0.3	1.1	7.0	1.0
7-21	Girdler G-3 Fe-Cr + Grace Si-Al (3:1)	550	440-480	34	0.5	0.4	38.2	49.8	0.7	1.2	8.5	1.4
7-21	Girdler G-3 Fe-Cr + Grace Si-Al (3:1)	550	440-480	30	0.5	0.7	38.4	49.9	0.6	1.0	6.7	1.0
7-22	Girdler G-3 Fe-Cr + Grace Si-Al + 5g Harshaw Ni-1404 (2:1)	600	460-500	42	0.5	0.4	54.3	35.7	-	-	6.3	3.7

TABLE 2. CATALYTIC GASIFICATION OF BIOMASS FOR THE PRODUCTION OF HYDROGEN (CONTINUED)

Run #	Catalyst	Reactor Temp °C	Cat. Bed Temp °C	C Con. To Gas $\frac{\text{(Wt. in Gas)} \times 100}{\text{(Wt. in Wood)}}$	Wood Feed Rate g/min	Steam Rate g/min	Gas Composition Vol. %					
							H_2	CO_2	C_2H_4	C_2H_6	CH_4	CO
7-22	Girdler G-3 Fe-Cr + Grace Si-Al + 5g Harshaw Ni-1404	600	460-500	39	0.3	0.7	61.3	34.4	-	-	2.5	1.8
7-17	Girdler G-93 Co-Mo + Harshaw Ni-1404	650	580-630	65	0.4	1.7	65.8	29.2	-	-	0.5	4.5

TABLE 3. TYPICAL RESULTS OF LODGEPOLE WOOD IMPREGNATED WITH 17 WT % K_2CO_3 IN THE PRESENCE OF STEAM AND CATALYSTS.

	550°C	650°C	750°C
Catalyst	Fe-Cr:Si-Al (3:1)	Fe-Cr:Ni-1404 (3:1)	Fe-Cr:Ni-1404 (3:1)
Steam Rate (g/min)	0.4	1.7	1.7
Wood Feed Rate (g/min)	0.5	0.4	0.3
% Carbon Conversion to Gases	34	67	78
Gas Composition (Vol. %)			
H_2	38.2	65.4	64.1
CO_2	49.8	30.9	29.9
C_2H_4	0.7	--	--
C_2H_6	1.2	--	--
CH_4	8.5	0.4	0.2
CO	1.4	3.3	5.8

- High steam-to-wood feed rates (order of 4:1) are required to obtain the desired CO shift reaction needed for hydrogen production.
- The high steam-to-wood feed rate does not look favorable from an energy balance standpoint.

A small number of experiments remain to be completed next quarter in an attempt to reduce the steam requirement.

CO Production Studies

The objective of the CO studies is to optimize the selective production of CO by employing steam, oxygen, and CO_2 as reactants to gasify wood. Preliminary runs have been completed and are presented in Table 4. Maximum results for CO production obtained up to this point are presented in Table 5. Results to date appear unfavorable and it is expected that the production of CO from biomass will not be recommended. CO production studies will be completed next quarter.

Alkali Carbonate Concentration Studies

Experiments were conducted this quarter to study gasification rates using wood impregnated with various concentrations of K_2CO_3 catalysts. The objective of these studies is to determine if the concentration of alkali carbonate required to obtain desired gasification rates and compositions can be lowered. The ball valve batch reactor shown in Figure 3 was used for these studies.

Six concentrations of impregnated K_2CO_3 are being studied: 0,2,4,8,12 and 17 wt %. Temperatures being studied include 550, 650, 750 and 850°C. Gas production rates, rate constants, and activation energies will be determined from these studies. The following is a discussion of the results obtained up to this point.

Data generated from initial studies completed at 550°C indicate that the presence of alkali carbonate has essentially no effect on the carbon-steam reaction. However, the presence of alkali carbonate does have a significant effect on the pyrolysis reaction of the wood, as shown in Figure 4. The rapid gas production in the first 440 seconds occurs during the pyrolysis of the wood. The rate-controlling carbon-steam reaction follows pyrolysis. The unchanging carbon-steam reaction slopes of the four alkali carbonate concentrations studied at 550°C demonstrate that the alkali carbonate has no

TABLE 4. BIOMASS GASIFICATION FOR THE PRODUCTION OF CARBON MONOXIDE

Run #	Primary Catalyst	Secondary Catalyst	Reactor Temp °C	Cat. Bed Temp °C	C. Con To Gas $\left(\frac{\text{Wt. in Gas}}{\text{Wt. in Wood}}\right)\times 100$	Wood Feed Rate g/min	Steam Rate g/min	O_2 Rate g/min	CO_2 Rate g/min	Gas Composition - Vol %					
										H_2	CO_2	C_2H_4	C_2H_6	CH_4	CO
8-1	17% K_2CO_3	Grace Si-Al	650	530-580	67	0.4	0.1	0.1	1.5	2.9	89.9	tr	tr	0.8	6.3
8-1	17% K_2CO_3	Grace Si-Al	650	505-550	49	0.4	0.1	None	1.5	2.8	90.7	0.1	0.1	0.8	5.5
8-2	17% K_2CO_3	Grace Si-Al	750	520-670	79	0.4	0.1	None	1.4	11.2	68.2	0.4	0.2	1.3	18.7
8-3	17% K_2CO_3	Grace Si-Al	850	725-770	93	0.6	0.1	0.08	1.5	15.7	43.8	0.6	0.1	3.1	36.7
8-4	None	Grace Si-Al	750	550-690	82	0.5	0.1	0.07	1.5	4.2	73.8	0.8	0.2	4.6	16.3
8-4	None	Grace Si-Al	750	550-690	71	0.5	0.1	None	1.5	5.3	71.9	0.9	0.3	5.1	15.5

TABLE 5. EXPERIMENTAL RESULTS FOR CO PRODUCTION FROM LODGEPOLE WOOD

Primary Catalyst	17% K_2CO_3
Secondary Catalyst	Grace Si-Al
Reactor Temp °C	850
Catalyst Bed Temp °C	725-770
Wood Feed Rate g/min	0.6
Steam Rate g/min	0.1
O_2 Rate g/min	0.08
CO_2 Rate g/min	1.5
Carbon Conversion to Gas %	93

Gas Composition - Vol %

H_2	15.7
CO_2	43.8
C_2H_4	0.6
C_2H_6	0.1
CH_4	3.1
CO	36.7

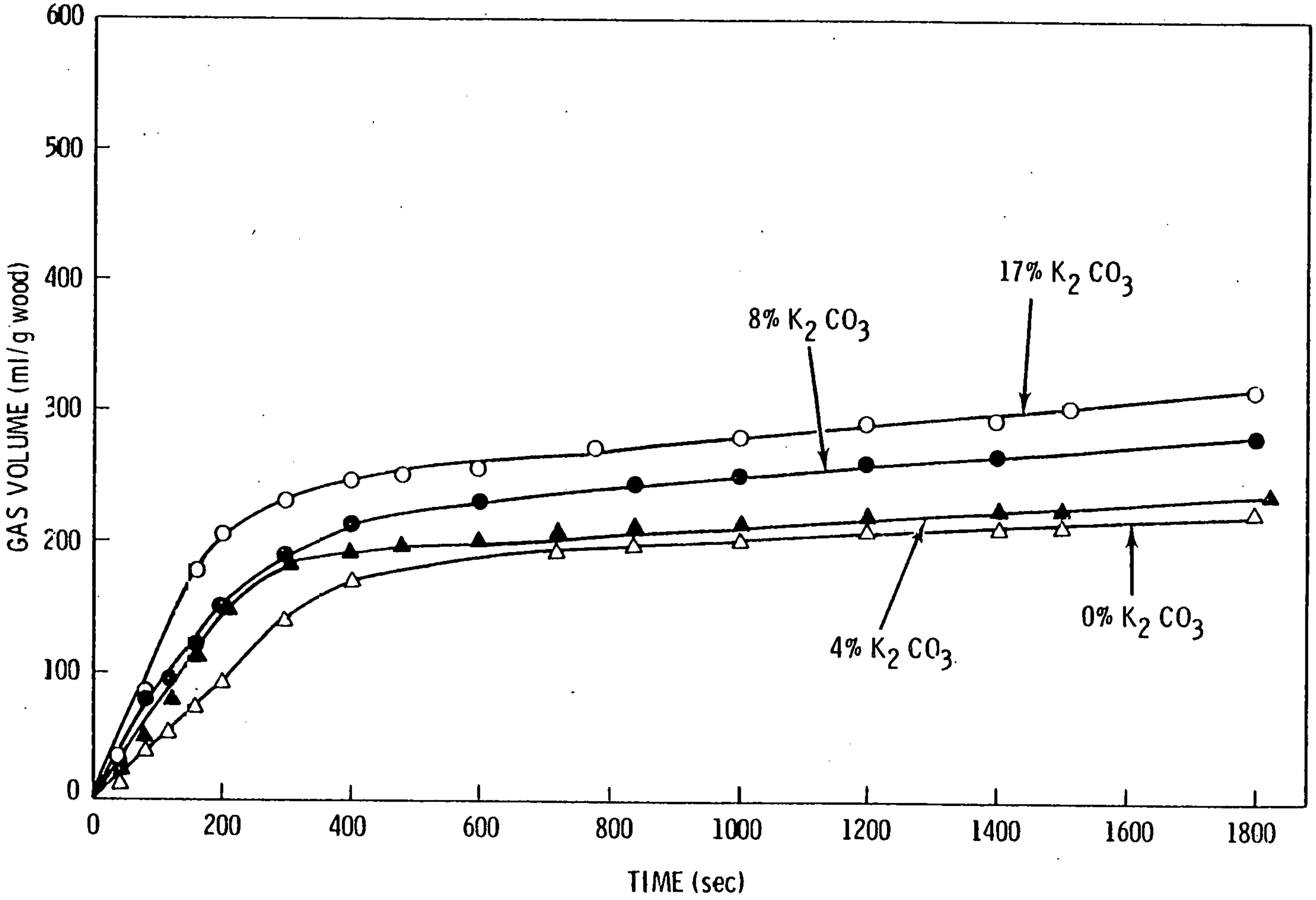


FIGURE 4. RATE OF GAS PRODUCTION FOR VARIOUS IMPREGNATED CONCENTRATIONS OF K_2CO_3 AT 550°C.

effect on the carbon-steam reaction at 550°C. This is supported by the graphs constructed to determine rate constants for the carbon-steam reaction. The rate constants are determined by a semi-log plot of the carbon remaining versus time. A pseudo-first order reaction is assumed to calculate the rate constant. A detailed discussion of the method employed for determining the carbon-steam reaction rate constant is included in an earlier report.(5) Figure 5 presents a plot of percent carbon unconverted-to-gas versus time at 550°C. Initial rate constants obtained from the 550°C and 650°C studies are presented in Table 6. Note the consistency of the rate constant values at 550°C and the change in rate constants for different alkali carbonate concentrations at 650°C. Unlike the 550°C results, data generated from initial studies completed at 650°C indicate a significant contribution of the alkali carbonate to the carbon-steam reaction but a significantly smaller contribution to the pyrolysis reaction. Figure 6 presents the gas production rate per gram of wood versus time at 650°C. Figure 7 presents the percent carbon unconverted-to-gas versus time at 650°C for the rate constant determination.

Alkali concentration studies will continue next quarter. The effect of altering the steam feed rates on various catalyst concentrations will also be evaluated next quarter.

Task 2. PDU Design, Procurement and Installation

This task was completed in September 1978.

Task 3. PDU Operations

Progress in Task 3 is presented in Figure 1. Failure of reactor heaters has forced some deviation from the original schedule. Conditions that can be tested without auxiliary heaters have been studied. Flowsheets for production of synthesis gases are currently being tested. Now that new heaters have been installed, flowsheets for methane production can be tested.

Early in the quarter a new wood feeder was installed. This unit -- designed and built by Tom Miles, a Consulting Engineer from Beaverton, OR, -- has separate variable speed metering (2 each) and injection (1 each) screws. Hence, wood can be metered at low flow rates to the injection screw, but is always transported rapidly into the bed. This new feeder is a significant improvement over the previous single screw system. Wood feeds now require only coarse screening to remove twigs and large chunks which might bridge in the lock hopper or bind the screws.

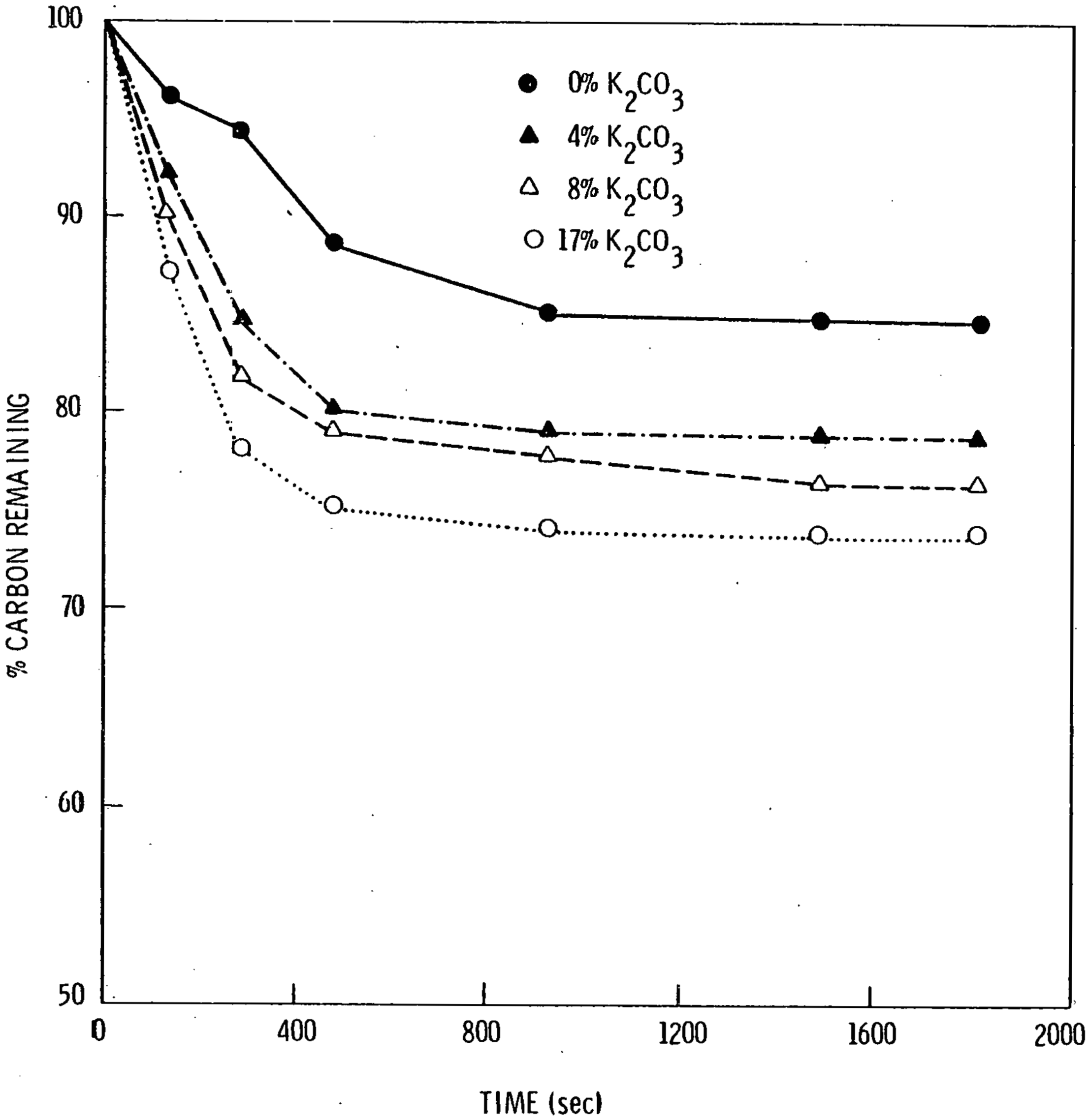


FIGURE 5. UNREACTED CARBON TO GAS VERSUS TIME AT 550°C

TABLE 6. KINETIC STUDIES ON LODGEPOLE WOOD IN THE PRESENCE OF STEAM

Reaction Temp °C	Steam Rate g/min	Wt. % Impregnated K_2CO_3	Rate Constant (sec^{-1})
550	0.4	17	2.6×10^{-5}
550	0.4	8	2.5×10^{-5}
550	0.4	4	2.2×10^{-5}
550	0.4	0	2.6×10^{-5}
650	0.4	17	9.7×10^{-5}
650	0.4	8	8.6×10^{-5}
650	0.4	4	8.0×10^{-5}
650	0.4	0	4.0×10^{-5}

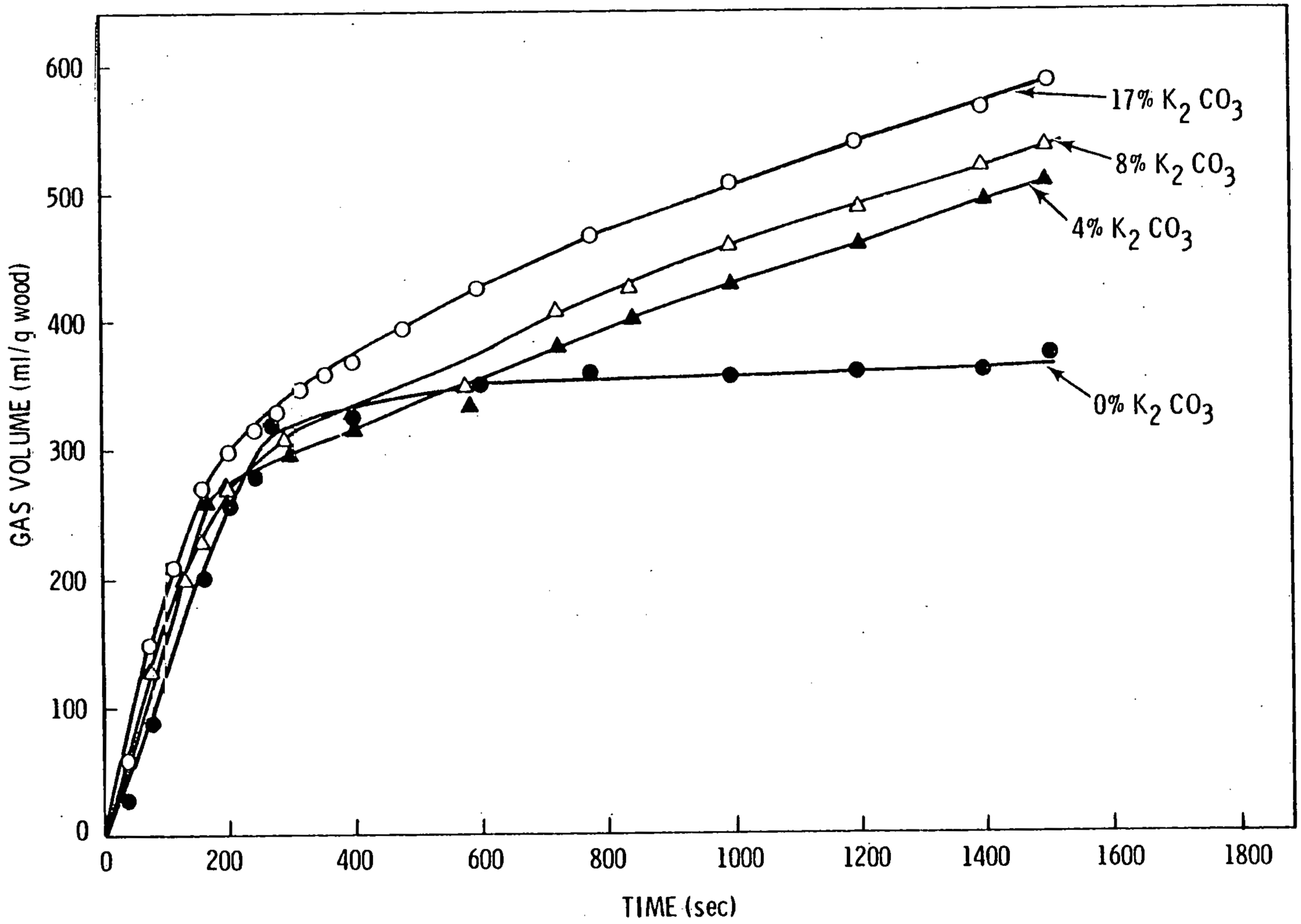


FIGURE 6. RATE OF GAS PRODUCTION FOR VARIOUS IMPREGNATED CONCENTRATIONS OF K_2CO_3 AT 650°C.

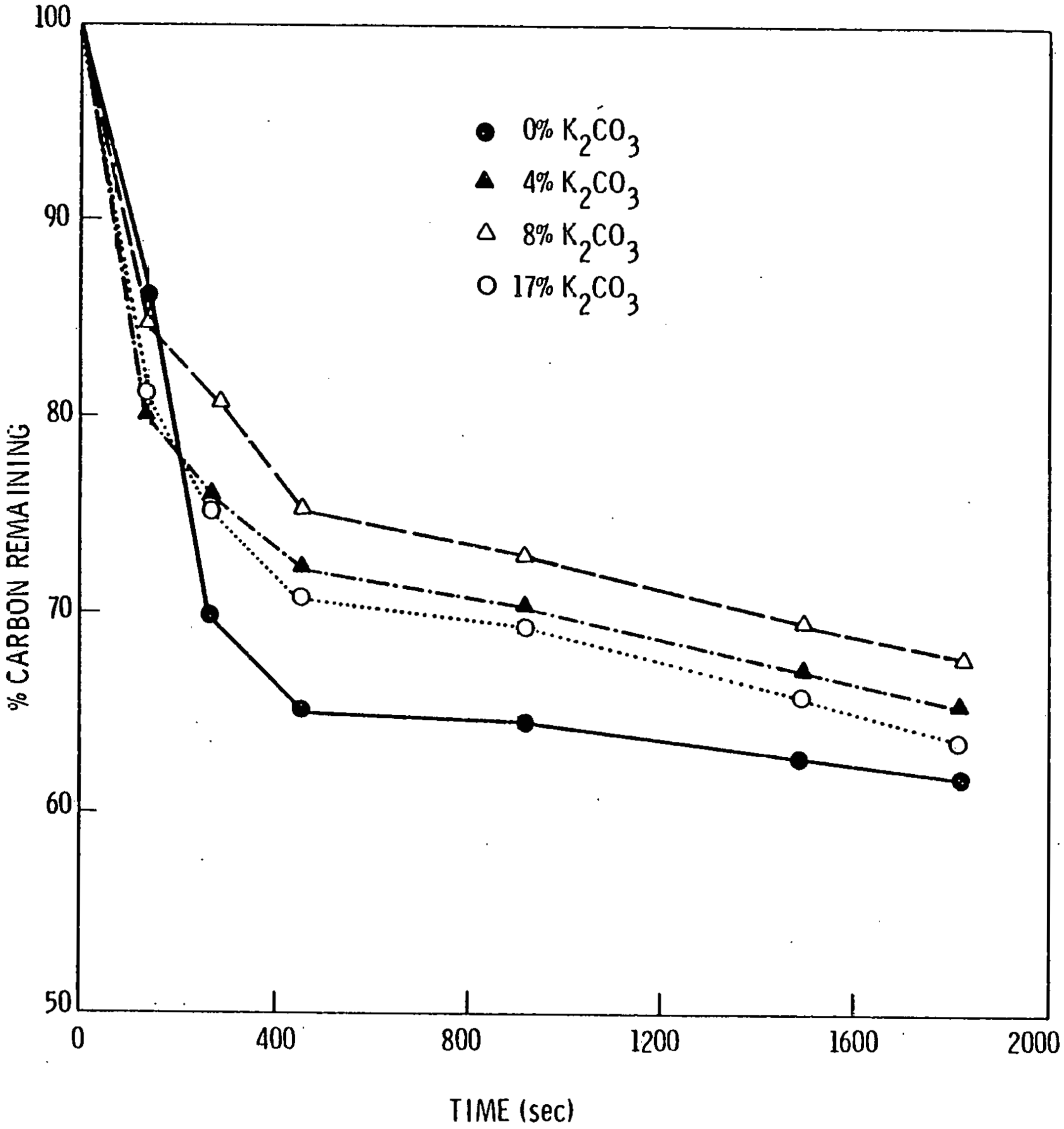


FIGURE 7. UNREACTED CARBON TO GAS VERSUS TIME AT 650°C.

Tests during the quarter examined ammonia synthesis gas production and hydrocarbon synthesis gas production. New heating elements for the reactor interior arrived early in June. These have been installed and will allow additional synthesis gas methane production studies.

The ammonia synthesis gas studies were conducted to determine the effects of temperature and gasification catalyst on product gas flows and compositions, as well as wood conversions. All runs used a silica-alumina cracking catalyst plus a cobalt molybdenum shift catalyst. Prior laboratory studies recommended a 4 to 1 steam/wood ratio to minimize CO in the product gases. The PDU studies used ratios close to this. We recognize the high steam flows represent a significant energy penalty for any commercial operation. Future work will study effects of reduced steam flows.

In order to maintain desired bed temperatures, pure oxygen was added to the air stream to burn a portion of the wood feed. From an operational standpoint our procedure was 1) first get to the desired operating temperature using precalculated oxygen/air ratios, 2) note hydrogen concentrations and product flows at steady state, 3) readjust oxygen and air flows to give desired 3:1 H_2/N_2 ratio.

A detail is important here when examining the gas compositions in Table 7. Nitrogen compositions depend solely on the air flow rates. With addition of pure O_2 and air, the two sources of oxygen can be traded to get whatever nitrogen concentration is desired. Only operator inexperience and imprecise flow control prevented our getting exactly the 3:1 $H_2:N_2$ ratio in the product gas. The important numbers are residual CO and gas yields as temperatures change and/or gasification catalyst is added.

Some observations from these tests are:

- The gasification catalyst (10 wt % dry mix K_2CO_3) markedly shifts the CO to H_2 at both 650 and 750°C.
- Addition of the gasification catalyst had little effect on gas yield.

Although it is not shown in Table 7 the water content of the exit gases is of interest. In all cases it exceeded 70 mole % of the product stream. This suggests a huge excess of steam was present and supports our earlier contention that more work is needed at lower steam flow rates. Effect of the decreased steam flow on CO concentration will be of prime interest.

TABLE 7. AMMONIA SYNTHESIS GAS STUDIES

Bed Temperature (°C)	615	660	750	750
Wt % K_2CO_3[(a)]	0	10	0	10
lb steam/lb dry wood	5.2	4.0	4.7	3.8
lb air/lb dry wood	.32	.19	.29	.25
lb O_2/lb dry wood	.19	.15	.23	.17
Dry Gas Comp (Vol %)				
N_2	5	10	12	15
CH_4	5	3	6	4
H_2	26	39	23	32
CO_2	51	40	39	40
CO	11	7	18	7
Carbon Conversion (%)	92	98	91	99
Ft^3 Dry Gas/lb Dry wood	22	36	36	35
Btu Gas/lb Wood (HHV)	0.47	0.78	0.86	0.71

(a) Dry mixed with wood

Seven tests addressed hydrocarbon synthesis gas production all at a nominal 750°C bed temperature. The tests were set up to study gasification with no catalysts and with silica-alumina plus potassium carbonate. Frequent intermittent loss of wood feed prevented our reaching steady-state in five of the tests. The wood feed problem was eventually traced to twigs wrapping around the metering screws. The solution to this problem is coarse screening of the wood prior to addition to the lock hopper.

Table 8 gives results of five of the seven tests which approached a steady state condition. For varied reasons not all of the tests reached the desired 750°C. Reported temperatures are averaged values for the middle of the bed of solids. Some trends do appear even though most tests were not ideal in terms of smooth steady operations:

- Addition of either 4 wt % or 10 wt % gasification catalyst increases gas yields and shifts CO to H_2. Addition of 10 wt % K_2CO_3 seemed to be better than 4 wt %.
- Effect of the cracking catalyst (silica-alumina) alone is hard to detect because temperature levels with and without it were quite different. Analysis of liquid samples is not complete, but visual inspection indicated less oil in the scrubber liquid when the cracking catalyst is used.

The carbon conversions are based on solids inventory, i.e.,

$$\text{Carbon Conversion} = \frac{C_{\text{wood}} - C_{\text{Solid Residues}}}{C_{\text{wood}}} .$$

The seemingly low value at 710°C could be misleading. The reactor is left with a carbon bed in it over weekends. It is difficult to measure accurately the amount of carbon which disappears during the cooling off and reheating after a weekend. The 710°C case was conducted on Monday.

The preferred method for generation of hydrocarbon synthesis gas is by steam gasification without the addition of oxygen. Unfortunately, the system heaters have not been adequate for obtaining the desired temperatures of 700°C or higher. The new heaters should improve this situation, although it may be necessary to heat with internal tube banks similar to the method used for heating catalytic natural gas reformers.

TABLE 8. HYDROCARBON SYNTHESIS GAS STUDIES

Bed Temperature (°C)	690	630	710	650	670
Wt % K_2CO_3 (a)	0	0	0	4	10
Silica-Alumina Catalyst	No	No	Yes	Yes	Yes
lb steam/lb dry wood	.88	.64	.67	.91	1.2
lb O_2/lb dry wood	.14	.07	.22	.13	.15
Dry Gas Comp (Vol %)					
N_2	2	5	1	1	2
CH_4	5	4	5	7	4
H_2	33	27	32	32	40
CO_2	35	38	44	42	41
CO	23	19	16	14	11
Carbon Conversion (%)	99	99	81	96	94
Ft^3 dry gas/lb dry wood	25	27	20	31	35
Btu Gas/Btu Wood (HHV)	0.72	0.64	0.51	0.68	0.68

(a) Dry mixed with wood

Task 4. Feasibility Studies

Feasibility studies are scheduled to begin in FY-1980. Preliminary mass and energy balance calculations have been made to estimate potential methanol yields from wood based on laboratory results on synthesis gas production.

Synthesis gas is generated by steam gasification of wood in a fluidized bed of catalysts operating at atmospheric pressure. A carbon conversion of 90% is used in the calculation of synthesis gas yields. This is a slightly lower conversion than has been obtained in our studies (up to 98%). Heat requirements for compression, endothermic reactions, etc., is provided by combustion of char and wood.

Generation of synthesis gas is represented by the reaction which takes place in the presence of catalysts at 760°C:

Wood + Steam → Gas Mixture + Char

Yields from this reaction are based on results obtained in the laboratory and are illustrated in the flow diagram shown in Figure 8.

The preliminary calculations show that 0.56 lb of methanol/lb of dry wood can be obtained (170 gal methanol/ton dry wood). The energy content of the methanol is 63% of the energy in the wood to the gasification plant. The overall energy conversion efficiency is 62% based on higher heating values. Operation of the gasifier at 15 atm pressure would increase the yield to 0.61 lb methanol/lb dry wood (180 gal methanol/ton dry wood). The energy conversion efficiency would increase to 68% based on higher heating values.

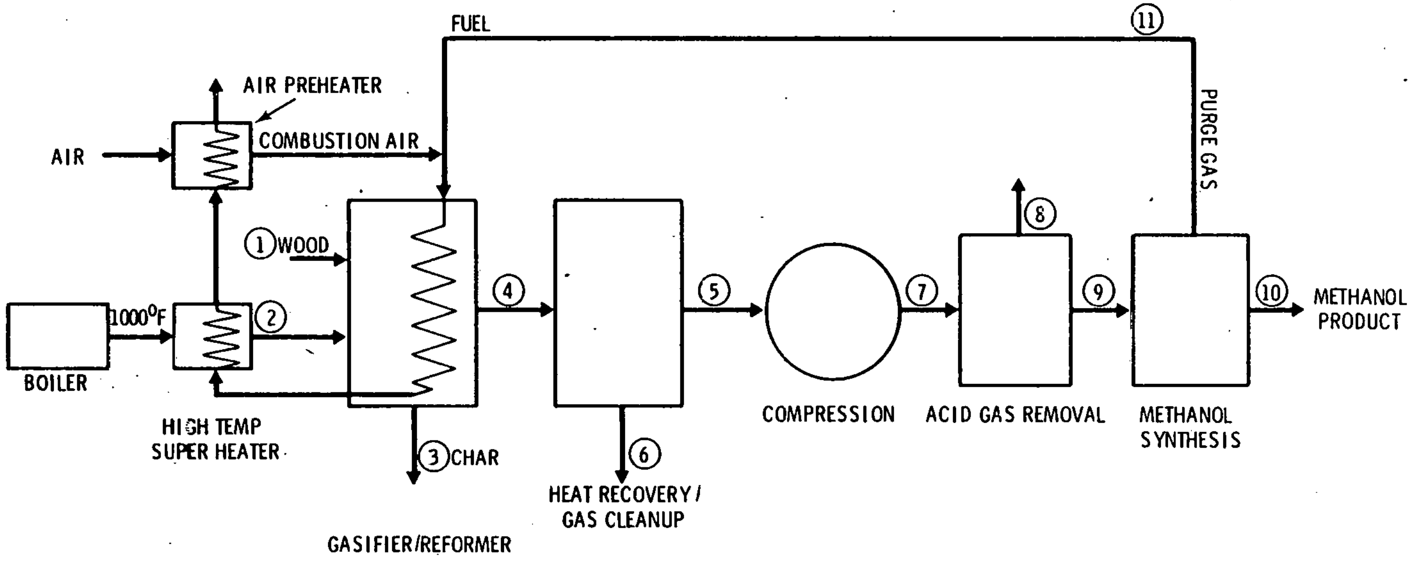
These calculations are preliminary to development of detailed flowsheets for generation of different products from wood. Process costs will be estimated after development of detailed flowsheets.

FINANCIAL STATUS

Actual and projected spending and manpower status for FY 1979 are shown in Figure 9.

FUTURE PLANS

Studies on recovery, regeneration and recycle of primary and secondary catalysts will begin during the next quarter. Laboratory studies will continue



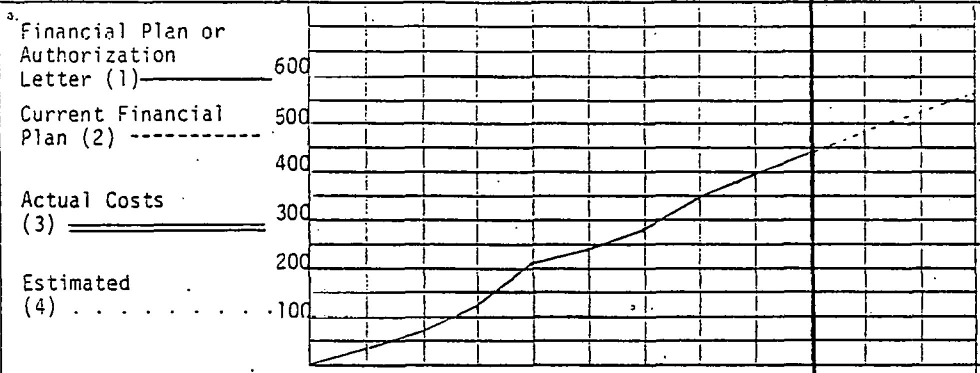
STREAM	① WOOD		② STEAM	③ CHAR		④ RAW GAS		⑤ CLEAN GAS		⑥ SLURRY		⑦	⑧	⑨ SYN GAS		⑩ METHANOL	⑪ PURGE GAS
	Wt%	t/d	t/d	Wt%	t/d	Wt%	t/d	Wt%	t/d	Wt%	t/d	t/d	t/d	Wt%	t/d	t/d	t/d
TOTAL		500	500		30		970		694.7		275.3	694.7	338.5		356.2	301.6	54.6
C	50.5	252.5		74.0	22.2												
H	6.3	31.5		2.8	0.8												
O	42.9	214.5		18.7	5.6												
ASH	0.3	1.5		4.4	1.3												
H_2						5.2	50.4	7.3	50.4			50.4		14.1	50.4		
CO						28.8	279.4	40.2	279.4			279.4		78.4	279.4		
CO_2						34.8	337.5	48.6	337.5			337.5	331.5	1.7	6.0		
CH_4						2.1	20.4	2.9	20.4			20.4		5.7	20.4		
H_2O						28.7	278.4	1.0	7.0	98.6	271.4	7.0	7.0	TRACE			
CHAR						0.4	3.9	—	—	1.4	3.9	—	—	—	—		
TEMP, °F	400		1400	1400		1400		110		110				100			
P, ATM	1		10	1		7		6		1		50	1	50			
TOTAL FLOW, SCFD	—		19.9×10^6	—		42.8×10^6		32.0×10^6		—		32×10^6	5.7×10^6	26.3×10^6		—	5.91×10^6
LHV, BTU/DAY	8130×10^6		—	732×10^6		8500×10^6		8500×10^6		95×10^6		8500×10^6	—	8500×10^6		5165×10^6	2359×10^6
SENSIBLE HEAT, BTU/DAY	100×10^6		655×10^6	27×10^6		1320×10^6											

FIGURE 8. PROCESS SCHEMATIC FOR METHANOL PRODUCTION

1. Contract Identification Catalytic Gasification of Biomass AJ-01-03/80012	2. Reporting Period 2-25-79 through 6-24-79	3. Contract Number EY-76-C-06-1830
4. Contractor (name and address) Battelle Memorial Institute Pacific Northwest Laboratory P.O. Box 999, Richland, WA 99352		5. Contract Start Date November 1977 6. Contract Completion Date Continuing

7. Months	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	8. FY

9. Cost Status ($ in Thousands) (1)



e. Actual Costs Prior FYs
$480

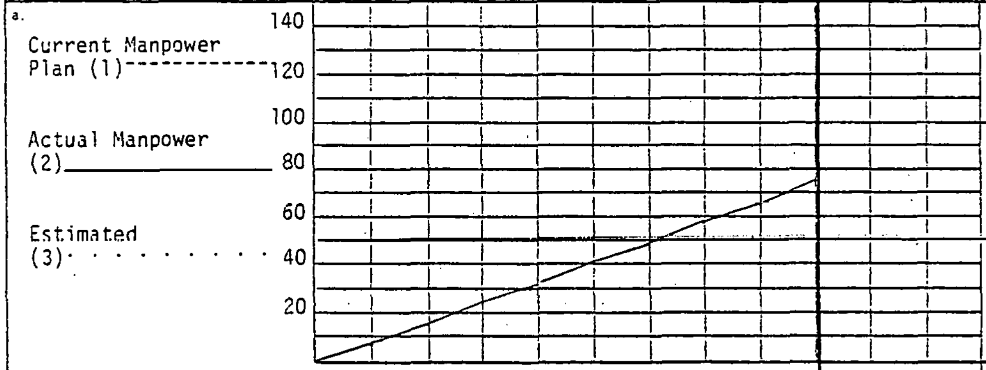
f. Planned Costs Prior FYs
$490

g. Total Estimated Costs for Contract
(4) $560

h. Total Contract Value
(2) $560

		Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
Costs	b. Planned (2)	33	36	50	87	38	37	69	47	39	46	37	41
	c. Actual (3)	33	36	50	73	52	34	68	48	45			
	d. Variance	0	0	0	(14)	14	(3)	(1)	1	6			

10. Manpower Status (Man Months)



e. Actual Manpower Prior FYs
71.9

f. Planned Manpower Prior FYs
73

g. Total Estimated Manpower for Contract
(3)

h. Total Contract Manpower
(1)

		Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
Manpower	b. Planned (1)	7.09	7.96	9.27	7.24	9.11	7.89	8.43	8.52	9.08			
	c. Actual	7.09	7.96	9.27	7.24	9.11	7.89	8.43	8.52	9.09			
	d. Variance	0	0	0	0	0	0	0	0	0			

FIGURE 9. SPENDING AND MANPOWER STATUS

on development of catalyst systems for evaluation in the PDU. Feasibility studies will concentrate on development of flowsheets for methane and synthesis gas production.

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4. L.K. Mudge, et al., "Catalytic Gasification of Biomass" PNL-SA-7766, Third Annual Biomass Energy Systems Conference, Golden, CO., 5-7 June 1979.
5. L.K. Mudge, L.J. Sealock, Jr., and S.L. Weber, "Catalyzed Steam Gasification of Biomass", PNL-SA-7678, to be published in Journal of Analytical and Applied Pyrolysis, Elsevier Scientific Publishing Co., 1979.