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July 1983

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
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SUMMARY

The Pacific Northwest Laboratory (PNL) is conducting an ongoing project, sponsored by the Biomass Energy Technology Division of the U.S. Department of Energy, on the gasification of biomass in the presence of catalysts. The purpose of the project is to evaluate the technical and economic feasibility of producing specific gas products via the catalytic gasification of biomass. This report presents the results of research conducted from October 1980 to November 1982.

The project was comprised of laboratory studies, process development, and economic analyses. The laboratory studies were conducted to develop operating conditions and catalyst systems for generating methane-rich gas, synthesis gases, hydrogen, and carbon monoxide. The process development unit (PDU), previously used for tests at atmospheric pressure, was modified for operation at absolute pressures of up to 10 atm (1000 kPa). A program for use on a microcomputer was written to determine the effect of yield changes at elevated pressures on process economics.

In the laboratory scale studies, active catalysts were developed for generation of synthesis gases from wood by steam gasification. A trimetallic catalyst, Ni-Co-Mo on silica-alumina doped with 2 wt% Na, was found to retain activity indefinitely for generation of a methanol synthesis gas from wood at 1380°F (750°C) and 1 atm (100 kPa) absolute pressure. Catalysts for generation of a methane-rich gas were deactivated rapidly and could not be regenerated as required for economic application. Sodium carbonate and potassium carbonate were effective as catalysts for conversion of wood to synthesis gases and methane-rich gas and should be economically viable. Catalytic gasification conditions were found to be suitable for processing of alternative feedstocks: bagasse, alfalfa, rice hulls, and almond hulls.

The PDU was operated successfully at absolute pressures of up to 10 atm (1000 kPa) and temperatures of up to 1380°F (750°C). Yields of synthesis gases at elevated pressure were greater than those used for previous economic evaluations (Mudge et al. 1981). A trimetallic catalyst, Ni-Cu-Mo on silica-alumina, did not display a long life as did the doped trimetallic catalyst used in

laboratory studies. The catalyst was active for a weight ratio of wood-to-catalyst of about 6 compared to over 1400 in the laboratory. Initial results on the effects of various process variables (pressure, temperature, wood particle size) are inconclusive because of the limited number of tests that were completed with active catalysts. No attempt was made to regenerate the catalyst.

A computer program for a Radio Shack TRS-80 Model I microcomputer was developed to evaluate rapidly the economics of producing either methane or methanol from wood. The program is based on economic evaluations reported in previous studies (Mudge et al 1981). Improved yields from the PDU studies were found to result in a reduction of about 9 cents/gal in methanol cost.

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INTRODUCTION

The Pacific Northwest Laboratory (PNL) is conducting studies on steam gasification of biomass in the presence of catalysts. These studies are sponsored by the Biomass Energy Technology Division of the U.S. Department of Energy (DOE).

Gasification processes are commonly used to convert carbonaceous matter, including biomass, into gases and some condensible liquids (Von Fredersdorff et al. 1963, Fritz et al. 1979). Although there are exceptions with some refractory carbonaceous materials, the residues from such gasification processes comprise principally the inert mineral constituents of the feed material. These residues are essentially devoid of significant quantities of carbon or char. In contrast, the residues from many so-called pyrolysis processes are classified as chars because they contain a substantial fraction of the carbon from the original carbonaceous feed material.

Both gasification and pyrolysis of carboneous materials produce a mixture of gaseous products as a result of the complex parallel, competitive, and sequential chemical reactions. The preferred reactions, those that produce the most desirable products, are limited and slow at conventional processing temperatures. However, the rates can be enhanced by inclusion of certain catalysts. Furthermore, a variety of catalysts are used industrially to promote certain reactions to emphasize formation of desired products from other gas mixtures. For example, methanation catalysts promote the formation of hydrogen from water and carbon monoxide, and gasification catalysts promote the breakdown of carbonaceous matter to gases.

The state-of-the-art procedure for conversion of a carbonaceous material to a synthesis gas involves several steps:

1. gasification with pure oxygen and steam to form a mixture of gases (CO, H_2, CO_2, CH_4, H_2S)
2. shift conversion to yield the required H_2-to-CO ratio in the gas mixture
3. acid gas removal

4. reforming hydrocarbons
5. moisture removal
6. further gas cleanup to remove traces of sulfur compounds that would otherwise poison catalysts.

Partial combustion of the carbonaceous feed material with pure oxygen to provide heat for the endothermic steam-carbon reaction is currently used to produce the gas mixture. Such practice results in a relatively simple gasifier design but requires an oxygen plant. Processes such as the CO_2 Acceptor (Fink 1973), Ash Agglomeration (Goodridge 1973), and Electrothermal (Oliveira 1980) offer schemes that avoid use of an oxygen plant.

Use of catalysts for reaction of steam with wood to produce a synthesis gas mixture allows operation at temperatures under 750°C with good carbon conversion (Mudge et al. 1979, Mitchell et al. 1980, Mudge et al. 1981). The required heat is provided indirectly with heat exchanger bundles in a fluid-bed system. No pure oxygen is used.

The overall objective of the PNL studies is to evaluate the technical and economic feasibility of producing specific gas products via the catalytic gasification of biomass. Specific products that are being studied include: 1) methane, 2) synthesis gases for production of ammonia, methanol, and hydrocarbons, 3) hydrogen, and 4) carbon monoxide. In the studies, yields of high-value, gaseous products from a single-reaction stage are enhanced by the proper choice of reactants, operating conditions, and catalyst combinations. Gaseous products, successfully produced by the various steam gasification systems employed to date, include synthesis gases for hydrocarbon, methanol, and ammonia generation and a methane-rich gas.

Results of earlier studies (Mudge et al. 1981) show that catalytic processes for conversion of wood to valuable products are technically and economically feasible. Economic feasibility depends on favorable yields at a pressure of 10 atm (1000 kPa). This report presents results of process development unit (PDU) operations at 10 atm (1000 kPa) pressure and their effect on economic feasibility. Also included are results of recent laboratory studies on catalyst development.

CONCLUSIONS

PDU operations were completed at 10 atm (1000 kPa) absolute pressure, and economic evaluations are based on yields at this pressure. The following conclusions are based on results of laboratory, PDU, and feasibility studies.

- A trimetallic catalyst (Ni-Co-Mo on silica-alumina doped with 2% sodium) retained activity indefinitely in laboratory tests for generation of a methanol synthesis gas.
- Bagasse, alfalfa, rice straw, and almond hulls are potentially suitable alternative feedstocks for gasification in the presence of catalysts. Laboratory tests conducted in the continuous flow reactor with these feedstocks showed that yields increased with increasing bulk density.
- Catalysts tested in the laboratory for generation of a methane-rich gas were active but short-lived and could not be regenerated. Loss of metal surface area (sintering) appeared to be a major cause of deactivation.
- Gasification of wood with steam in a fluid bed at 10 atm (1000 kPa) absolute pressure and 1380°F (750°C) was demonstrated. These conditions with an active catalyst are suitable for generation of a methanol synthesis gas.
- Gas cleaning at high temperature with a cyclone and a porous metal filter was effective and reliable in PDU operations. This cleanup system is recommended for any future PDU, or pilot scale, operations since material accountability is good.
- An absolute pressure of 10 atm (1000 kPa) for wood gasification was found to increase the methane concentration (6 vol% was the lowest concentration with active catalyst) in the product gas and to reduce the yield of condensible organics relative to operation at atmospheric pressure.
- Potassium carbonate was an active primary catalyst for generation of a methanol synthesis gas from wood in PDU tests. Sodium carbonate

did not show significant activity in PDU tests but was active in laboratory-scale tests. Agglomeration was a problem when alkali carbonates were used in the PDU but could perhaps be avoided with cool down of the bed before gas flow is shut off.

- A trimetallic catalyst (Ni-Co-Mo on silica-alumina) was active in PDU tests for an exposure of 6 lb wood/lb catalyst, far below the life of the catalyst in laboratory tests (1400 lb wood/lb catalyst). Catalyst activity was depleted during the third test. Repeated temperature cycles and exposure to air may have contributed to catalyst deactivation. Doping the catalyst with alkali carbonate may help extend the exposure time before deactivation. Carbon deposition appeared to be a major cause of loss in catalyst activity. No attempt was made to regenerate the catalyst.
- Synthesis gas yields at 10 atm (1000 kPa) absolute pressure and 1380°F (750°C) were greater than projected yields from operations at atmospheric pressure. The methanol yield will, therefore, be greater than previously reported (Mudge et al. 1981).
- PDU operations at 10 atm (1000 kPa) absolute pressure showed increased yields with increased wood particle size from 1/16 in. (1.5 mm) to 1/4 in. (8 mm) average size. The increased yields probably result from an increase in char residence time since the finer particle size was partially entrained in the product gas.
- The superficial linear velocity required for fluidization was above 1 ft/sec (0.3 m/sec) at all process conditions up to 10 atm (1000 kPa).
- Operations at 10 atm (1000 kPa) showed yields that could reduce earlier reported methanol costs (Mudge et al. 1981) by about 9 cents/gal with operations adjusted to give the proper H_2:CO ratio in the product gas.

RECOMMENDATIONS

Conversion of wood to valuable chemical products by steam gasification in the presence of catalysts appears to be technically and economically feasible. Yields from gasification at 10 atm (1000 kPa) absolute pressure and 1380°F (750°C) exceed the yields that were projected from atmospheric studies. These results enhance the technical and economic feasibility of catalytic gasification; however, further studies are recommended to reduce the risk for large-scale, commercial use. Development of catalyst systems to define techniques for catalyst handling to avoid losses in large-scale systems is needed. We recommend studies to determine catalyst mechanisms, develop catalyst systems, and evaluate the effect of variables on yields at elevated pressure. Updating of process economics is also recommended.

Laboratory studies on development of catalyst systems for generation of different gas products is needed. Catalytic mechanisms involved in conversion of wood to specific products should be investigated. Understanding these mechanisms would help develop secondary catalysts that are active and resistant to deactivation. Development of methods for regeneration of secondary catalysts would be aided with knowledge of catalytic mechanisms. Primary catalysts, such as the alkali carbonates, should be studied to determine reaction mechanisms. Required concentrations for use of primary catalysts and application methods should be defined. Methods for separation and recovery of catalysts from char should be developed.

Many problems were solved in completion of pressure operations in the PDU. Operation at absolute pressures of up to 10 atm (1000 kPa) are now trouble-free. The PDU should be operated to define fully the effect of variables such as wood particle size, wood moisture content, and operating temperature on gas yields. Conditions that use air or oxygen in the blast should be studied to compare yields to steam-only operation and to develop conditions for generation of ammonia synthesis gas. Energy requirements should be determined by conducting long-term (5-day) tests. The effects of temperature cycling and exposure to air on catalyst life should be determined in long-term tests. A trimetallic catalyst doped with alkali should be prepared for testing in the PDU. An active catalyst resistant to poisoning is the major need for continued process development. Alkali carbonates, a promising alternative to trimetallic catalysts, should be tested to determine if fusion in the fluid bed can be prevented.

Catalysts are effective for reforming and cracking volatile products from biomass gasification. Schemes that employ catalysts in separate vessels should be investigated. Bench-scale studies should be conducted to develop economic systems for generation of valuable gas products. The studies should employ fluid-bed reactors for simulation of single-vessel and dual-vessel operation. These studies would effectively evaluate conditions and catalysts for gasification of biomass to produce valuable gas products. Promising systems developed in the bench-scale studies could be tested in the PDU.

A program to evaluate the effect of yield changes on process economics and to update economics is available. New results should be used as they become available to assess their impact on process economics. Methods for evaluation of the economics of new plant configurations should be developed.

LABORATORY STUDIES

The primary objectives of the laboratory studies were to obtain a fundamental understanding of the catalytic gasification of biomass and develop long-lived catalyst systems for use in the fluid-bed PDU and eventually in a full-scale plant. Results of these studies, presented in the following sections, serve as a basis for PDU operation and provide key technical inputs for process economic evaluations.

EXPERIMENTAL EQUIPMENT AND FEED MATERIALS

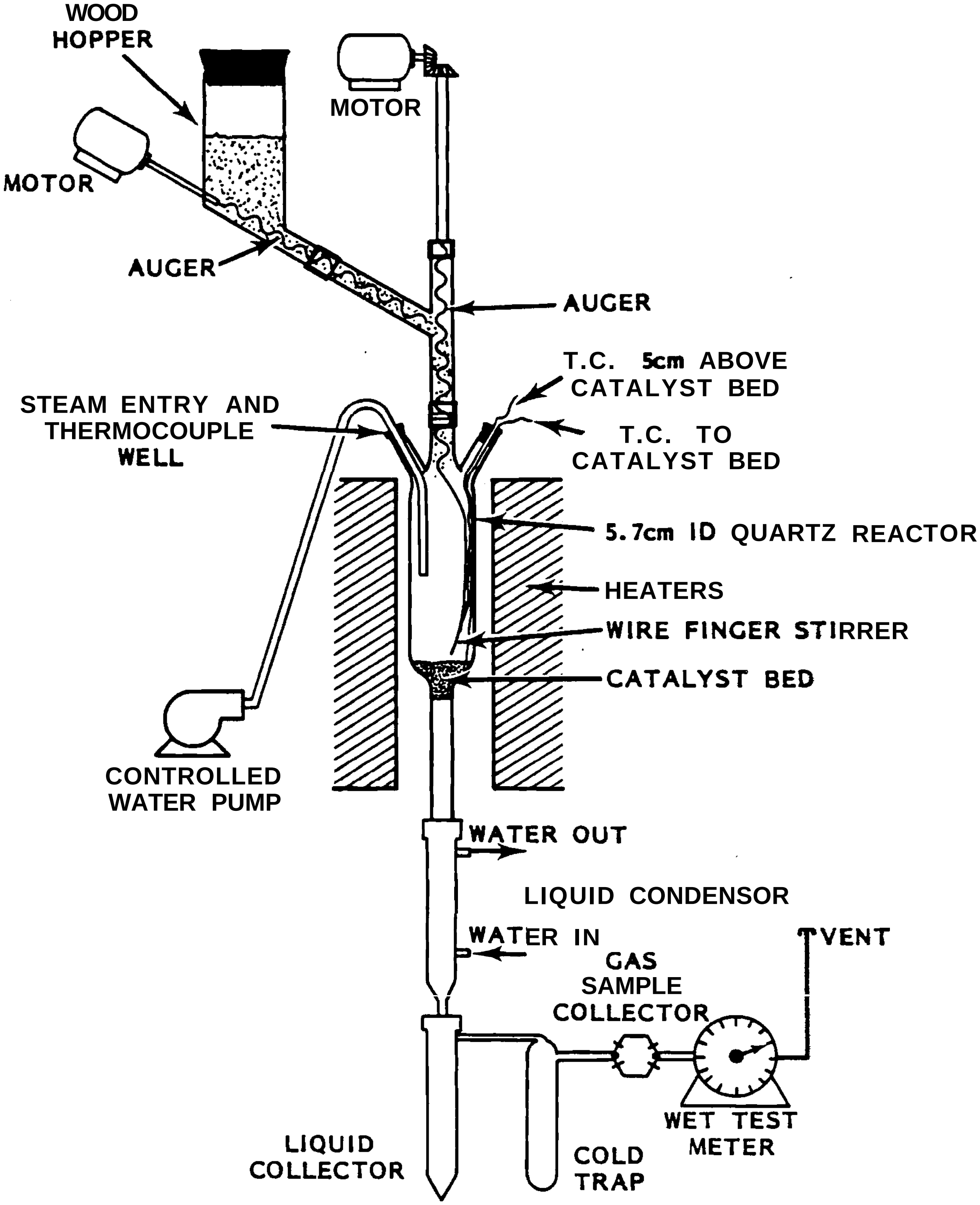
Experimental equipment used in the laboratory studies include the laboratory-scale gasifiers and analytical systems for product and catalyst analysis. Wood was the primary feed material used, although several agricultural residues were also tested.

Laboratory Gasifiers

Laboratory studies were conducted primarily in two continuous-wood-feed reactors. These reactors, constructed of quartz glass and operated at atmospheric pressure, are shown in Figure 1. Wood is fed into the top of the reactor and gasified in the presence of various reactants. Water, tars, and water-soluble organics are condensed and collected before the gas is metered and analyzed. Char and ash accumulate on a support just above the catalyst bed and are vacuumed out periodically.

The reactor system is flexible with respect to experimental variables including: 1) wood feed rate, 8-12 g/hr; 2) steam rates, 3-60 g/hr; 3) catalyst weight, 10-30 g/hr; 4) temperature, 500-850°C, and 5) addition of reactant gases (air, oxygen, CO_2, recycle gas).

Despite the differences in gas/solid contacting between the laboratory-scale reactors and fluid-bed PDU, similar results are obtained. The space velocity of the hot gases over the catalyst in the laboratory reactors is typically 1000-2000 cm^3/g catalyst/hr with corresponding residence time of 1.5-3.0 sec. These are similar to the gas/catalyst contact times achieved in the PDU and the composition of gases produced in both systems under similar



<u>FIGURE 1</u> Continuous Wood-Feed Reactor

conditions is nearly identical. Char residence time is significantly longer in the laboratory gasifiers and total carbon conversion is correspondingly higher than that achieved in the PDU.

Feed Materials

Three different types of wood were used in the laboratory studies. The primary feedstock was a maple/alder headrig sawdust which has been the primary feedstock for the PDU. Laboratory samples were obtained by screening the PDU feedstock material and separating the -7 + 40 mesh fraction, Other wood species that were used were maple and Douglas Fir. Wood was the feedstock for all tests discussed unless otherwise indicated.

Tests were also performed on four agriculture residues. Bagasse pellets were obtained from Davies Hamakau, Inc. in Hawaii and ground to the appropriate size. Rice straw, alfalfa, and almond hulls were obtained as cubes from Warren & Baerg, Inc., Dinuba, California. They were also ground to the appropriate size. With the feed system on the laboratory gasifier we were unable to feed agricultural residues that had not been densified.

The chemical and physical characteristics of these materials are shown in Table 1, The elemental composition is determined with a Perkin-Elmer 240 elemental analyzer. Ultimate analysis is based on ASTM D3175. The primary differences between the materials are the ash content and the density. On a moisture and ash-free basis the materials have nearly identical elemental composition.

Product Analysis

Gases from the laboratory gasifiers are collected in plastic (Tedlar)(a) bags and analyzed with a Carle AGC-S gas chromatograph. Char is vacuumed from the gasifiers, weighed, and then analyzed with the Perkin-Elmer 240. Tar is separated from the water, weighed, and analyzed with the Perkin-Elmer 240. A Dohrmann DC80 carbon analyzer is used to determine the carbon content of the product water.

(a) Trademark of DuPont.

TABLE 1. Composition of Feedstocks

Analysis[a]	Maple/Alder Headrig Sawdust	Maple	Douglas Fir	Bagasse	Rice Straw	Alfalfa	Almond Hulls
Proximate Analysis							
Volatile Matter	82.5	--	85.7	64.6	59.5	67.3	68.5
Fixed Carbon	16.2	--	14.2	22.1	20.6	21.7	24.9
Ash	1.3	--	0.1	13.3	19.9	11.0	6.6
Ultimate Analysis							
Carbon	46.5	48.7	48.6	43.0	39.0	45.0	43.6
Hydrogen	6.1	6.0	6.2	5.0	4.8	5.1	5.5
Oxygen	45.5	43.6	42.7	37.6	34.0	37.0	42.0
Nitrogen	0.1	0.1	0.1	0.3	0.1	2.8	0.8
Ash	1.3	0.2	0.1	13.3	19.9	11.0	6.6
Heating Value							
kJ/kg	19,300	19,900	19,800	18,100	16,900	20,600	19,700
Btu/lb	8,300	8,570	8,530	7,780	7,280	8,860	8,470
Physical Properties as Processed							
Moisture content, wt%	0-5	0-5	0-5	8.3	9.1	11.9	10.3
U.S. Screen size	-7 + 40	-7 + 40	-7 + 20	-14	-14	-14	-7 + 20
Bulk Density g/cm^3	0.15	0.12	--	0.20	0.14	0.25	0.61

(a) All analyses wt% on a dry basis except where indicated.

Catalyst Preparation and Analysis

Early studies primarily used commercial catalysts. It became apparent that use of these catalysts was not ideal, particularly in the fluid-bed PDU. W. R. Grace, Inc. supplied several catalysts prepared to our specifications and many other catalysts were prepared at PNL.

Catalysts were prepared at PNL using two techniques: 1) metal impregnation by the incipient wetness method on commercial support materials, and 2) coprecipitation of high-surface-area, highly-dispersed metal catalysts. All supported metal catalysts were reduced for 18 hr at 450°C in hydrogen prior to start-up of testing.

An Aminco-Dietz Sor-BET surface area meter was used to determine total surface area. Metal surface area based on hydrogen chemisorption was determined using the apparatus shown in Figure 2. Surface area measurements were made on both fresh and used catalysts. Used catalysts were also analyzed with a Perkin-Elmer 240 to determine carbon deposition.

PRELIMINARY CATALYST SCREENING RESULTS

Early laboratory studies were'directed at gaining a basic understanding of biomass gasification and selecting appropriate catalysts and operating conditions for the production of specific gas products by steam gasification. Results of these studies are included in the interim report "Investigations on Catalyzed Steam Gasification of Biomass," PNL-3695 (Mudge et al. 1981) and will only be summarized here.

Gasification of biomass with steam involves a combination of three types of reactions:

1. Pyrolysis to produce gaseous products (H_2, CO, CO_2, CH_4 and some heavier hydrocarbons), tar, water soluble organics (acetic acid, methanol, acetone, esters, and aldehydes), and char
2. Reaction of char from 1 with H_2O, CO_2, and H_2 to produce H_2, CO, CH_4, and CO_2

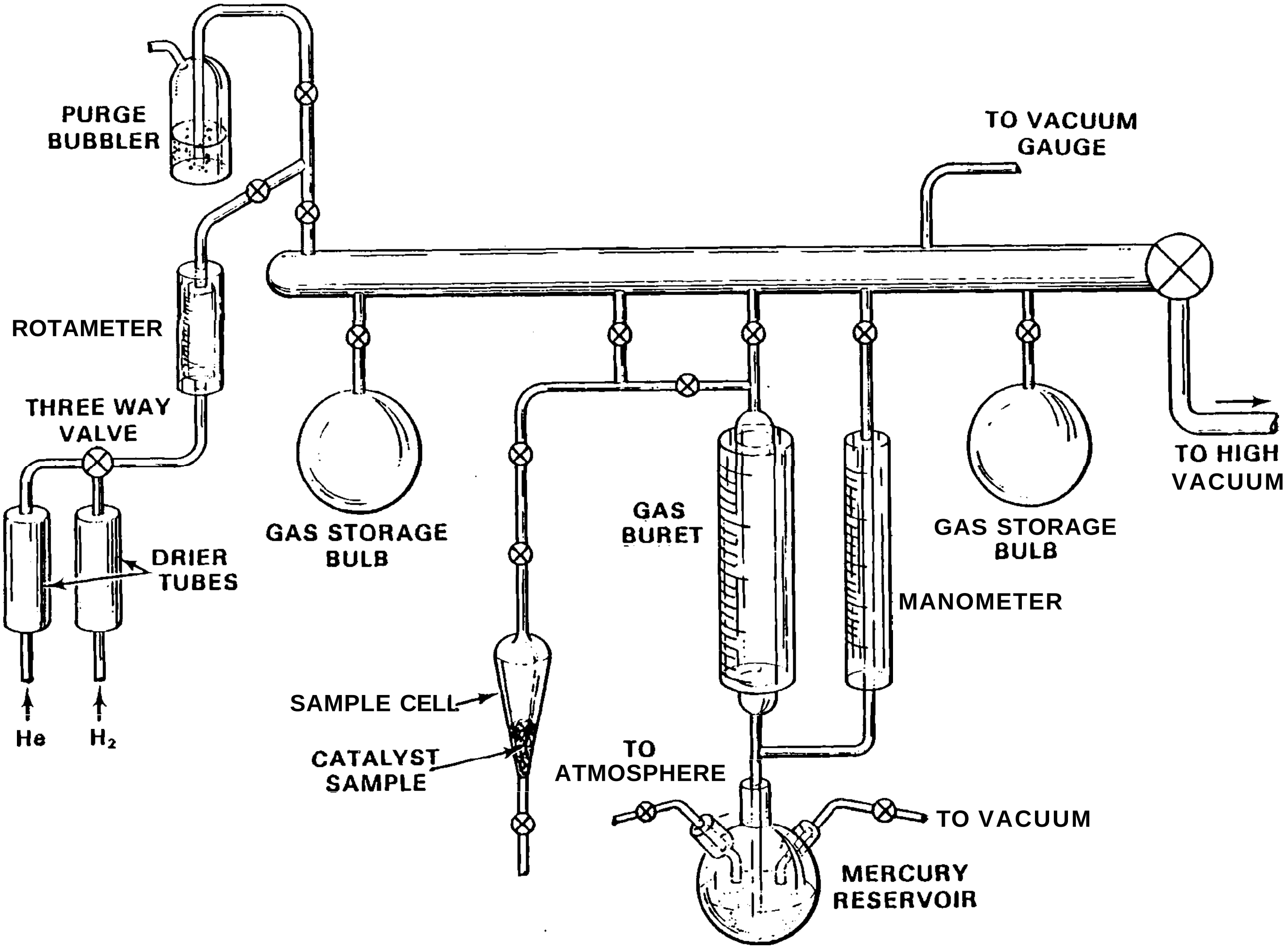


FIGURE 2. Chemisorption Apparatus

3. Reforming and condensation of the products of 1 and 2 to produce additional gas products, tars, and char.

In studying catalytic steam gasification we have used alkali carbonates impregnated or mixed with the wood to enhance the steam char reaction. These were referred to as primary catalysts. Supported metal catalysts were used to catalyze the gas phase reactions and were referred to as secondary catalysts.

Primary Catalysts

The effectiveness of four different catalysts (potassium carbonate, sodium carbonate, trona, and borax) was evaluated (Mudge et al. 1981). These catalysts were chosen because: 1) experimental investigations showed them to be effective catalysts for other materials (coal char), and 2) they are relatively inexpensive. Two different catalyst concentrations, 3×10^{-3} and 3×10^{-4} g-moles/g wood, were studied at 550°C, 650°C, and 750°C. These concentrations correspond to 0.159 to 0.0159 g Na_2CO_3/g wood and 0.207 to 0.0207 g K_2CO_3/g wood. The main conclusions of these studies on primary catalysts were:

- Alkali catalysts significantly increase the yield of gases from pyrolysis of biomass primarily at the expense of liquid yield.
- The order of catalyst effectiveness is K_2CO_3, Na_2CO_3, trona, borax.
- The char remaining after pyrolysis is more reactive with respect to steam gasification at temperatures greater than 550°C.
- The steam-char reaction rate increases with increasing alkali concentration.
- The catalyst appears to increase the steam-char reaction rate by increasing the carbon surface area available for reaction.

Secondary Catalysts

The main gas phase reactions that occur during steam gasification are shown in Table 2. The conditions and catalysts used for these reactions in the hydrocarbon processing industries are also included. Using this and equilibrium data on the C-H-O system as a basis we selected operating conditions and catalysts for production of methane, methanol synthesis gas ($2H_2/CO$), ammonia synthesis gas ($3H_2/N_2$), and hydrogen.

Gasification of biomass with steam is endothermic. At temperatures above about 500°C, heat must be added to the gasifier to maintain the reaction temperature. While this is not a problem in laboratory studies, in a commercial-scale unit the amount of heat that can be added economically is limited. Experience with the PDU and economic evaluations of large gasifiers indicated that 750°C is the maximum practical upper limit. We also set 550°C as the minimum gasification temperature. Production of methane is thermodynamically more favorable at lower temperatures; however, carbon conversion and the rate of gas production are too low to be economically feasible.

TABLE 2. Gas Phase Reactions in Steam Gasification of Biomass (Thomas 1970; Venuto 1979; Rostrup-Nielson 1975)

	Temp (°C)	Press (atm)	Catalysts
1. Shift Reaction ($CO + H_2O \rightleftarrows CO_2 + H_2$)	315-485	1-20	Metal oxides: Fe, Cr, Cu, Zn
2. Methanation ($CO + 3H_2 \rightleftarrows CH_4 + H_2O$)	230-450	1-300	Ni on a support (silica, alumina, refractory)
3. Hydrocarbon Reforming ($C_nH_m + n\ H_2O \rightleftarrows n\ CO + (n + m/2)H_2$)	550-1000	1-40	Ni on oxides (alumina, magnesia)
4. Cracking	250-500	2-200	Silica-alumina, Ni and W on silica-alumina

Table 3 shows typical results obtained for each case at the optimum conditions determined by our studies. The gasification temperature was constrained to 550-750°C as previously indicated, and all tests were run at atmospheric pressure. No tar or condensible organics were produced in any of the cases as long as the catalyst was active; char was the only byproduct.

Gasification tests made using a combination of primary and secondary catalysts showed little improvement over using secondary catalysts alone, so primay catalysts were dropped from consideration. Subsequently, it was found that alkali carbonates were as effective as secondary catalysts for production of methanol synthesis gas, and they were used in this manner.

CATALYST LIFETIME STUDIES

An effective catalyst for the production of specific gases by catalytic steam gasification of biomass will:

- have the right chemical and physical properties to promote the desired reactions

TABLE 3. Production of Specific Gases from Biomass by Steam Gasification

	Product Gas			
	Methane-Rich Gas	Methanol Synthesis Gas	Ammonia Synthesis Gas	Hydrogen
Secondary Catalyst	Harshaw 3266 Ni/support	Harshaw 3266 Ni/support	Girdler G-93 Co-Mo Co-Mo/Al_2O_3	Girdler G-3, Harshaw 1404 Fe-Cr, Ni/support
Gasification Temperature, °C	540-560	740-770	640-660	740-770
Catalyst Temperature, °C	550-560	740-760	650-670	720-750
Steam/wood, g/g	0.33	0.70	1.60	5.7
Air/wood, g/g	--	--	0.65	--
Carbon Conversion to Gas, %(a)	68	90	65	78
Gas Composition, vol%				
H_2	29.5	53.1	50.7	64.1
CO_2	34.3	15.5	21.2	29.9
CO	10.8	28.3	7.3	5.8
CH_4	25.4	3.1	2.7	0.2
C_2^+	tr	0.1	0.3	--
N_2	--	--	17.8	--

(a) No liquid products were formed when the catalysts were active. Char is the only other product.

- be resistant to deactivation or be easily regenerated
- be physically durable in fluid bed operations.

Preliminary catalyst screening studies identified numerous active catalyst systems for the production of methanol synthesis gas, methane-rich gas, ammonia synthesis gas, and a hydrogen-rich gas. For the past 18 months laboratory studies have concentrated on evaluating deactivation and regeneration of prospective catalysts and studying their durability in fluid-bed systems. Catalysts for a methanol synthesis gas and a methane-rich gas have been emphasized. Because production of ammonia synthesis gas and a hydrogen-rich gas is similar to production of methanol synthesis gas, catalyst lifetime information for these systems can be extrapolated from the methanol synthesis gas case.

In all of the cases no tar was formed as long as the catalyst was active. Appearance of tars in the reactor condenser (see Figure 1) was one of the first signs of loss of catalyst activity. Some deterioration in the gas quality was usually noted prior to the appearance of tars; however, once tars began appearing in the product gas, gas quality deteriorated quite rapidly. We defined catalyst lifetime as the weight of wood processed per unit weight of catalyst prior to the appearance of tar in the product gas.

Early in the lifetime studies it became apparent that carbon deposition was a serious problem with respect to catalyst deactivation. Reactions which deposit carbon include:

1. $2CO \rightleftarrows C + CO_2$
2. $CH_4 \rightleftarrows C + 2H_2$
3. $C_nH_m \longrightarrow$ polymers $\longrightarrow$ coke + XH_2
4. Phenols $\longrightarrow$ coke + gases

Carbon is removed from the catalysts by the carbon-steam reaction:

5. $C + H_2O \rightleftarrows H_2 + CO$

and by the reverse of reaction 1.

Even though the equilibrated gas may show no affinity for carbon formation, in an open thermodynamic system carbon may be stable in a steady state, and the accumulation of carbon may continue. The question of whether there is a net buildup of carbon, and subsequent catalyst deactivation, is thus a kinetic one and is influenced by the choice of catalysts (Rostrup-Nielsen 1974, Wang 1982).

Another cause of loss of activity is thermal sintering. Sintering is the loss of metal surface area due to growth in nickel particle size on the catalyst. This is particularly troublesome with high-surface-area, dispersed-metal catalysts such as those used for methanation (Reucroft 1980). Support materials can also lose their porosity and surface area when subjected to high temperatures, particularly in the presence of steam. In general, support stability increases in the following series: silica, alumina, silica-alumina, ceramic supports.

Sulfur compounds are notorious for deactivation of Ni catalysts by formation by sulfides (Rostrup-Nielsen 1975). With wood as the feedstock, sulfur was not a cause of catalyst deactivation as determined from analysis of the catalyst for sulfur after exposure. With bagasse as a feedstock, poisoning of the catalyst by sulfidation was noted.

Catalyst for Methanol Synthesis Gas (MSG)

Preliminary screening studies showed supported nickel catalysts to be the most effective for production of methanol synthesis gas (MSG). During the course of the lifetime studies we discovered that alkali carbonates are effective catalysts for the production of MSG. Table 4 shows typical results obtained with several types of catalysts at 750°C and atmospheric pressure. We determined the catalyst lifetime for many different catalyst systems and tried to define the mechanism of catalyst deactivation. The catalysts listed in Table 4 all show the potential for a long lifetime in laboratory studies.

The lifetimes of catalysts tested for methanol synthesis gas are shown in Table 5. Catalysts with a high nickel loading and a high metal surface area generally had lifetimes of less than 100. Examples are Harshaw Ni-3266,

TABLE 4. Methanol Synthesis Gas Production from Wood with Various Catalysts at 750°C, 1 atm

	United, G-90C Ni/Ceramic	Ni-Co-Mo/ SiO_2-Al_2O_3	17 wt% K_2CO_3 Impregnated on Wood	Ni, Na_2CO_3/ Al_2O_3	Na_2CO_3/ Al_2O_3	None(a)
Steamlwood, glg	1.2	0.9	1.0	0.9	1.0	1.0
Gas Composition, vol%						
H_2	53.0	50.0	52.4	47.9	46.7	42.7
CO_2	21.3	19.2	21.8	21.6	24.2	24.6
CH_4	5.5	5.8	3.2	6.4	7.9	8.7
CO	19.7	24.7	21.4	22.9	10.7	21.8
C_2^+	0.6	0.3	1.2	1.1	1.5	2.4
Carbon Conversion, wt%						
To gas	93	93	90	98	97	87
To char	7	7	10	2	3	4
To liquids	--	--	--	tr	tr	tr
Synthesis Gas Yield, nm^3 (H_2 + CO)/kg feed	1.27	1.26	1.23	1.17	1.05	0.84

(a) Average of four tests.

TABLE 5. Lifetime of Catalysts Tested for the Production of Methanol Synthesis Gas at 750°C, 1 atm

Nickel Catalysts		Catalyst Lifetime g wood/g catalyst
Harshaw	Ni/Support, Ni-1404	52, 100(a)
	Ni/Support, Ni-3266	74, 23
Girdler(c)	Ni/Refractory, C-13-3	17
United Catalysts	Ni/Refractory, G-90C	60(a)
PNL	Ni/Al_2O_3	17, 50
Grace	Ni/Al_2O_3	70
Combination Nickel Catalysts and Cracking Catalysts		
Harshaw Ni-1404 and Grace SiO_2-Al_2O_3		16
Nickel Alloy Catalysts		
Harshaw	Ni-Cu-Mo/Al_2O_3, Ni-XL-664A	188(a)
Grace	Ni-Cu-Mo/Al_2O_3, SMR-1	52
	Ni-Cu-Mo/SiO_2-Al_2O_3, SMR-2	100(a,b)
	Ni-Co-Mo/Al_2O_3, SMR-3	80,(a) 84(b)
	Ni-Co-Mo/SiO_2-Al_2O_3, SMR-4	1470(a,b)
PNL	Ni-Cu-Mo/Al_2O_3	30, 30(a)
Alkali Carbonate Catalyst		
PNL	Ni/Na_2CO_3/Al_2O_3	90(a)
PNL	K_2CO_3/Al_2O_3	90(a)
Others		
Girdler(c)	Cu-Zn	NA
	Fe_2O_3	NA
Harshaw	CoMo/Al_2O_3 MT-40	NA
Strem	mordenite molecular sieve	NA
	type y molecular sieve	NA
Grace	SiO_2-Al_2O_3	NA

(a) Still active when test was terminated.
(b) Impregnated with 2% Na at PNL.
(c) Now part of United Catalysts.
NA Not active.

Ni-1404, and Girdler C-13-3. These catalysts are hydrogenation and methanation catalysts and are generally not to be used above 500°C.

A series of trimetallic nickel alloy catalysts developed by PNL with the aid of W. R. Grace had significantly longer lifetimes as shown in Table 5. One of these catalysts, Ni-Co-Mo on a silica-alumina support. doped with 2 wt% Na, ran for over a year in a laboratory reactor without deactivation. A lifetime of 1470 g wood/g catalyst was achieved before the test was terminated with the catalyst still active. Table 6 shows the progress of this test.

At the start of a test the trimetallic catalysts are not quite as active as the high metal surface area catalysts in terms of the yield of synthesis gas per gram of wood. The trimetallic alloy catalysts maintain their activity for a much longer period of time, as shown in Figure 3.

Several other supported catalysts which show potential for long life times include: 1) United G-90C, a steam reforming catalyst for severe coking conditions, 2) alkali carbonates supported on alumina or silica alumina, and 3) supported alkali carbonates doped with small quantities of nickel.

Another option for production of MSG is the use of alkali carbonates impregnated or dry mixed with the biomass. These catalysts were originally tested for their catalytic effect on the carbon-steam reaction, but studies in this and other projects at PNL indicate that they also catalyze gas phase reactions (Hallen et al. 1982). Laboratory studies indicate these catalysts are as effective as nickel catalysts for the production of methanol synthesis gas (see Table 4). Recovery of these catalysts from the char has been demonstrated (Mudge et al. 1981).

All supported metal catalysts tested were deactivated to some degree compared to their activity at startup. Table 7 shows the BET and metal surface areas of several catalysts tested. The metal surface area of the Harshaw Ni-3266 was reduced from about 50 m^2/g to 0.3 m^2/g after a lifetime of 74. The Grace SMR-4 had only 4 m^2/g of metal surface area originally, but still had 1.1 m^2/g after a lifetime of 670 and 0.4 m^2/g after a lifetime of 1470.

This loss of surface area is probably due to both thermal sintering and carbon deposition. Both the Harshaw Ni-3266 and the Grace SMR-4 lost over 50%

TABLE 6. Lifetime Study with $Ni\text{-}Co\text{-}Mo/SiO_2\text{-}Al_2O_3$ Catalyst(c)

	Date						
	4/2/81	5/8/81	8/13/81	11/17/81	2/22/82	3/17/82	4/8/82
Lifetime, g wood/ g catalyst	Start	100	580	816(b)	1197	1358	1469
Steam Rate, g/g wood	0.8	0.9	1.6	1.1	0.9	0.9	0.9
Gas Composition, vol%							
H_2	51.5	49.6	47.1	43.6	45.9	51.7	50.9
CO_2	16.3	19.4	25.9	23.6	22.2	18.8	19.4
CH_4	4.0	6.8	7.6	8.2	8.0	5.3	5.0
CO	28.0	24.0	18.1	23.6	23.1	24.1	24.4
C_2H_4	0.0	0.2	0.3	0.5	0.5	0.1	0.2
C_2H_6	0.0	0.04	0.5	0.5	0.4	0.1	0.1
Carbon Conversion to Gas, %(a)	91	90	95	98	98	95	90
Synthesis Gas Yield, m^3/kg wood	1.41	1.24	1.09	1.08	1.10	1.33	1.21

(a) Conversion to liquid is very small, less than 0.1%. The rest of the carbon is converted to char.

(b) At a lifetime of 802 the reactor plugged and the catalyst had to be removed from the reactor. After being replaced in the reactor and reduced the catalyst had lost activity and a significant quantity of tar was formed. The catalyst was regenerated with steam at 800°C and then reduced. Activity was restored to the level prior to shutdown.

(c) Doped with 2 wt% Na as Na_2CO_3.

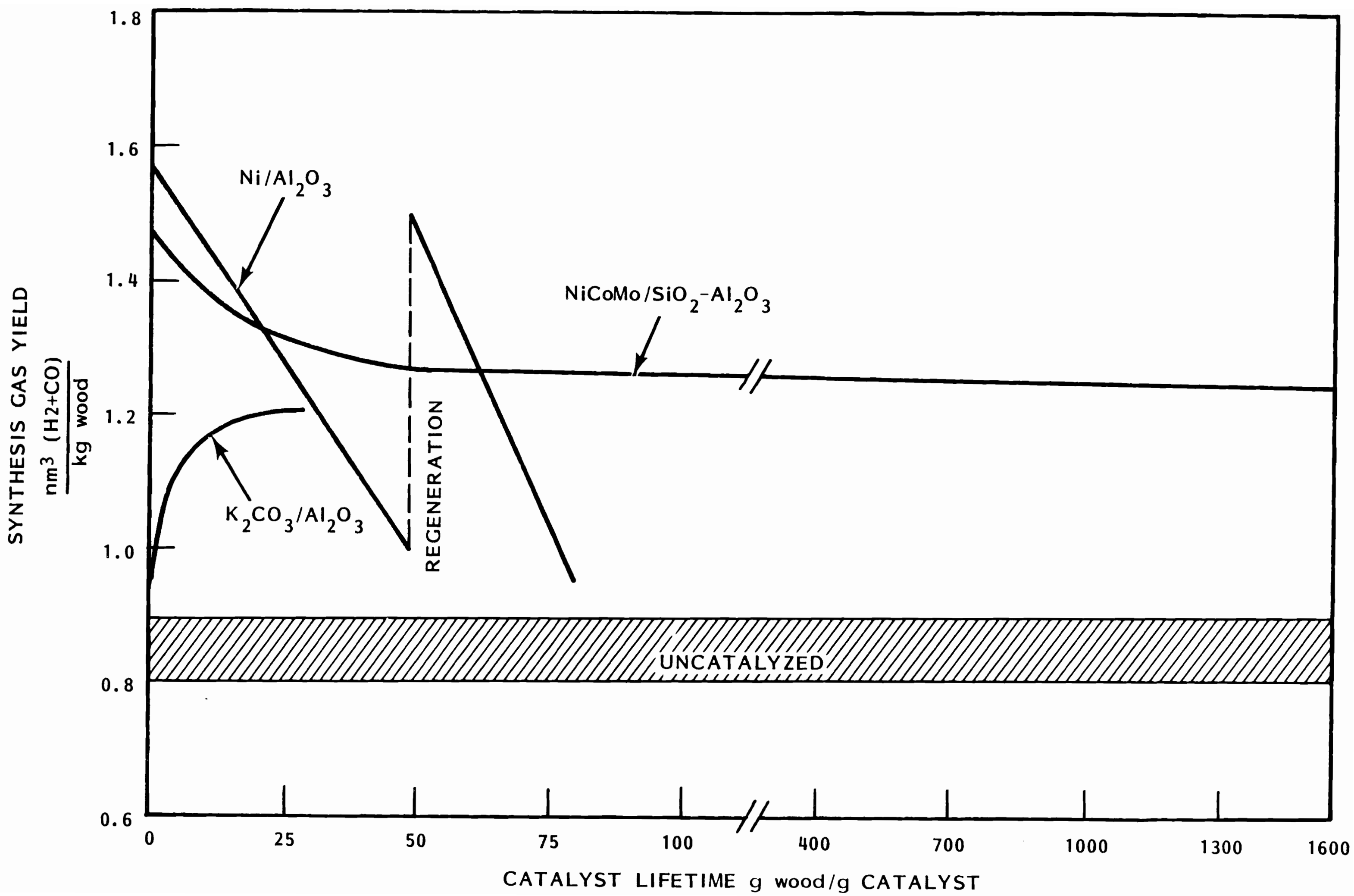


FIGURE 3. Effect of Catalyst Age on Yield

TABLE 7. Typical Surface Areas of Catalysts Used for Methanol Synthesis Gas

Catalyst	Fresh		Used	
	BET Surface Area, m2/g	Metal Surface[a] Area, m2/g	BET Surface Area, m2/g	Metal Surface Area, m2/g
Harshaw Ni-3266	150	58,48	75,47	0,0.3
United C-13-3	64	32	--	--
Harshaw Ni-XL-6644	129	6	32	0.4
Harshaw Ni-1401	125	--	--	--
Grace Ni-Co-Mo/SiO_2-Al_2O_3	204,209	4	72,51	1.1,0.4
Grace Ni-Cu-Mo/Al_2O_3	109,117	6	41	--

(a) For alloy catalysts, this is the equivalent Ni surface area.

of their metal surface area after steaming at 550°C for 48 hr. Both catalysts also had carbon on them after their lifetime tests, as shown in Table 8. The Harshaw Ni-3266 had 20 wt% carbon on the catalyst after a lifetime of 74. The Grace SMR-4 had 7 wt% after a lifetime of 100, 5 wt% after a lifetime of 670, and 4 wt% after a lifetime of 1470. Interim report PNL-3695 (Mudge et al. 1981) represents scanning electron microscope micrographs, which show a gradual buildup of carbon on the surface of the Ni-3266 catalyst during a lifetime test.

We attempted to regenerate the Ni-3266 catalyst by passing steam over the catalyst at 750-800° for 64 hr. Steam was continued until no more carbon oxides were present in the off gas. The catalyst surface area after regeneration was basically the same as the "coked" catalyst. This indicates that the catalyst was sintered. The catalyst had a lifetime of only 4 g wood/g catalyst after regeneration.

TABLE 8. Carbon Deposition on Catalysts Used for Methanol Synthesis Gas at 750°C, 1 atm

Catalyst	Carbon on Used Catalyst, wt%
Harshaw Ni-3266	20
United C-13-3	21
Grace Ni-Co-Mo/Si02-A13, 2% Na	7,5,4
Ni-Cu-Mo/Al_2O_3, 2% Na	7
Ni-Co-Mo/Al_2O_3	3
Ni-Co-Mo/Al_2O_3, 2% Na	4
Ni-Cu-Mo/Si02-Al_2O_3	2
Ni-Cu-Mo/SiO_2-Al_2O_3(a)	13
United G-90C	0.1
PNL K_2CO_3/SiO_2-Al_2O_3	0.4
PNL Ni/Na_2CO_3/Al_2O_3	0.4

(a) Tested at 650°C.

The Grace SMR-4 catalyst had to be removed from the reactor after a lifetime of 800 due to a plug in the reactor. When the catalyst was replaced and reduced, it was not active. We then passed steam over the catalyst at 750-800°C for 72 hr until there were only small quantities of carbon oxides in the off gas. After being reduced, the catalyst regained its original activity prior to the shutdown and remained active until the test was terminated after a lifetime of 1470 g wood/g catalyst.

This indicates that sintering is a severe problem for the highly loaded, high metal surface area catalysts, but not as serious for the lower metal surface area catalysts. Carbon deposition occurs on both catalysts but appears to stabilize at 3-6 wt% on the SMR-4. Bimetallic and trimetallic catalysts are known to be more stable than nickel catalyst with respect to both sintering (Cusumano 1978) and carbon deposition (Van Hook 1980, Araki 1976).

Two types of catalysts had little or no carbon deposited on them at the end of a test. United Catalysts G-90C is a catalyst developed specifically for difficult reforming conditions. It contains nickel on a ceramic support. Catalysts containing 25 wt% alkali carbonate (K_2CO_3 or Na_2CO_3) impregnated on alumina also have little or no carbon on them at the end of a test. This is probably due to the catalytic effect of the alkali on the carbon-steam reaction. These catalysts are not as active as Ni catalysts with respect to the yield of synthesis gas per gram of wood. We doped one of these catalysts with 10 wt% Ni to increase its activity as shown in Table 4. The activity was improved, but a longer test is needed to see if the activity is maintained.

The temperature in the reactor is significant with respect to deactivation of supported catalysts. At 650°C the SMR-2 catalyst only had a lifetime of 59 g wood/g catalyst and had 15 wt% carbon on it at the end of the test. At 550°C the lifetime of the catalyst is only about 5 g wood/g catalyst.

Conclusions derived from studies on catalysts for production of methanol synthesis gas are:

- Highly loaded, high metal surface area nickel catalysts, such as those used for hydrogenation and methanation, have short active lifetimes. Loss of activity appears to be due to both sintering and carbon deposition.
- Trimetallic nickel catalysts are more stable with respect to sintering and carbon deposition and have long active lifetimes in the laboratory.
- Catalysts developed for severe steam applications such as United G-90C also have the potential for long lifetimes.
- Catalyst lifetime is sensitive to gasifier operating temperature.
- Supported alkali carbonate catalysts have the potential for long lifetimes but must be doped with Ni to increase their activity.
- Alkali carbonates impregnated on the biomass feedstock are nearly as effective as nickel catalysts.

Catalysts for Methane-Rich Gas (MRG)

Results of the early catalyst screening studies indicated that the most effective catalysts for production of a methane-rich gas (MRG) have the following properties:

- a nickel loading of 25 wt% or greater
- a BET surface area of 100 m^2/g catalyst or greater
- a nickel surface area of 30 m^2/g catalyst or greater.

The results obtained with these catalysts at 550°C and atmospheric pressure are quite similar to those shown for Harshaw Ni-3266 in Table 3.

The lifetime of catalysts tested for production of MRG ranged from 1 to 78 g wood/g catalyst. Most of the commercial catalysts tested had lifetimes under 10 g wood/g catalyst, as shown in Table 9. Catalysts with the longest lifetimes were catalysts prepared at PNL by coprecipitation (see Table 10). These generally contained 40-50 wt% nickel. This is the type of catalyst that is being developed for methanation for production of SNG. Addition of about 10 wt% Fe to the catalyst increased the catalyst lifetime somewhat. Other

TABLE 9. Lifetime of Commercial Catalysts Tested for Production of a Methane-Rich Gas at 550°, 1 atm

		Catalyst Lifetime g wood/g catalyst
Nickel Catalysts		
Harshaw	Ni/Support, Ni-3266	10, 52,(e) 2(a) 2,(b) 1(c)
Harshaw	Ni/Support, Ni-1404	1
Harshaw	Ni/Support, Ni-3210	1
Harshaw	Ni/Support, Ni-5124	1
Harshaw	Ni/Kieselguhr, Ni-0101	NA
Grace	Ni/Al_2O_3	13
Girdler(d)	Ni/Refractory, G-56B	2
United Catalyst	Ni/Refractory + Ni/Al_2O_3, G-90C + C150-4-03	29
United Catalyst	Ni/Refractory, G-90C	NA
Nickel Alloy Catalysts		
Grace	Ni-Cu-Mo/Al_2O_3	4
Grace	Ni-Cu-Mo/SiO_3-Al_2O_3	6
Grace	Ni-Co-Mo/Al_2O_3	8
Harshaw	Ni-Cu-Mo/Al_2O_3, Ni-XL-664A	NA
Harshaw	Ni-Mo/Al_2O_3, HT-500	NA
Harshaw	Ni-W/Al_2O_3, Ni-4301	NA
Girdler(d)	Ni-Co/Refractory, 6-87	NA
Others		
Strem	Ru/Al_2O_3	NA
Strem	Rh/Al_2O_3	2
Strem	Pd/Al_2O_3	NA
Harshaw	Co-Mo/Al_2O_3, HT-400	NA
Grace	SiO_2-Al_2O_3, 980-13	2
Harshaw	SiO2-Al_2O_3	2
Union Carbide	SiO_2-Al_2O_3, Zeolite, LZY-82	3

(a) Impregnated with 2% Na.
(b) Impregnated with 2% K.
(c) Impregnated with 2% Fe.
(d) Now part of United Catalyst.
(e) After regeneration.
NA Not active.

TABLE 10. Lifetime of Catalysts Prepared at PNL and Tested for Production of a Methane-Rich Gas at 550°C, 1 atm

Prepared by Impregnation on a Commercial Support	Catalyst Lifetime g wood/g catalyst
Ni/SiO_2-Al_2O_3	5,3
Ni-Cu/SiO_2-Al_2O_3	2,4
Ni-Co/SiO_2-Al_2O_3	2
Ni-Mo/Al_2O_3	1
Ni-Fe/SiO_2-Al_2O_3	5
Ni-Fe/Al_2O_3	3,3
Ni/SiO_2	4,5
Prepared by Coprecipitation	
Ni-Fe/Al_2O_3	73,41,50,78
Ni-Fe-Mg/Al_2O_3	44,56
Ni-Co/Al_2O_3	49
Ni-Cu-Fe/Al_2O_3	20
Ni-Fe-Ca/Al_2O_3 (impregnated with 2% K)	13
Ni-Fe/Al_2O_3 (impregnated with 2% Pb)	60
Ni-Cu/Al_2O_3	8,10
Ni/Al_2O_3 (impregnated with 1% Pt)	20,51
Ni/SiO_2	53
Ni-Fe/Si[illegible]	8
Ni-Fe/Al_2O_3 (impregnated with 2% Na)	58
Ni-/Al_2O_3 (impregnated with 0.5% Ru)	23
Ni/SiO_2 (impregnated with 1% Pt)	1

additives such as Co, Cu, Mg, Na, K, Pt, Ru, and Pb had little or no effect. The properties of the Ni-Fe/Al_2O_3 catalyst which had the longest lifetime are shown in Table 11.

The active lifetime of the catalyst seems to be related primarily to the amount of active metal surface area on the catalyst as shown in Figure 4. Work at the University of Louisville indicates the maximum metal surface area that

TABLE 11. Properties of Ni-Fe/Al_2O_3 Catalyst Used for Production of Methane-Rich Gas

Composition	BET Surface Area	Metal Surface Area
52 wt% Ni	150 m^2/g catalyst	59 m^2/g catalyst
13 wt% Fe		
35 wt% Al_2O_3		

can be achieved with coprecipitated nickel catalysts is in the range of 40-60 m^2/g (Reucroft 1980). Other methods of catalyst preparation result in even less surface area.

Deactivation of high surface area, dispersed metal catalysts is a complicated phenomenon in which chemical poisoning (carbon deposition in our case) and thermal sintering may both be involved (Reucroft 1980). At temperatures over 500°C, sintering (the loss of metal surface area due to growth in nickel particle size on the catalyst) may be a significant cause of deactivation. Two coprecipitated catalysts were steamed at 550°C for 48 hr and their surface area was reduced by 50-70%. This rate of surface area loss corresponds approximately to the rate of loss of activity.

Deactivated catalysts generally had 15-30 wt% carbon on them, indicating carbon deposition may also be a problem. Some catalysts were tested in both the methane case and the methanol synthesis gas case at 750°C, and in all instances had longer active lifetimes at 750°C where sintering should be more severe than at 550°C. It is likely that both sintering and carbon deposition contribute to catalyst deactivation at 550°C.

An attempt was made to regenerate the Ni-Fe/Al_2O_3 catalyst by passing steam over it at 550-600°C. It took over 240 hours before the amount of carbon oxides in the off gas began to drop significantly indicating most of the carbon had been removed. The regenerated catalyst only had a lifetime of 4 g wood/g catalyst. Attempts were made to regenerate several other catalysts. The best results were achieved with Ni-3266 which had a lifetime of 52 g wood/g catalyst after regeneration compared to 10 g wood/g catalyst as a fresh catalyst.

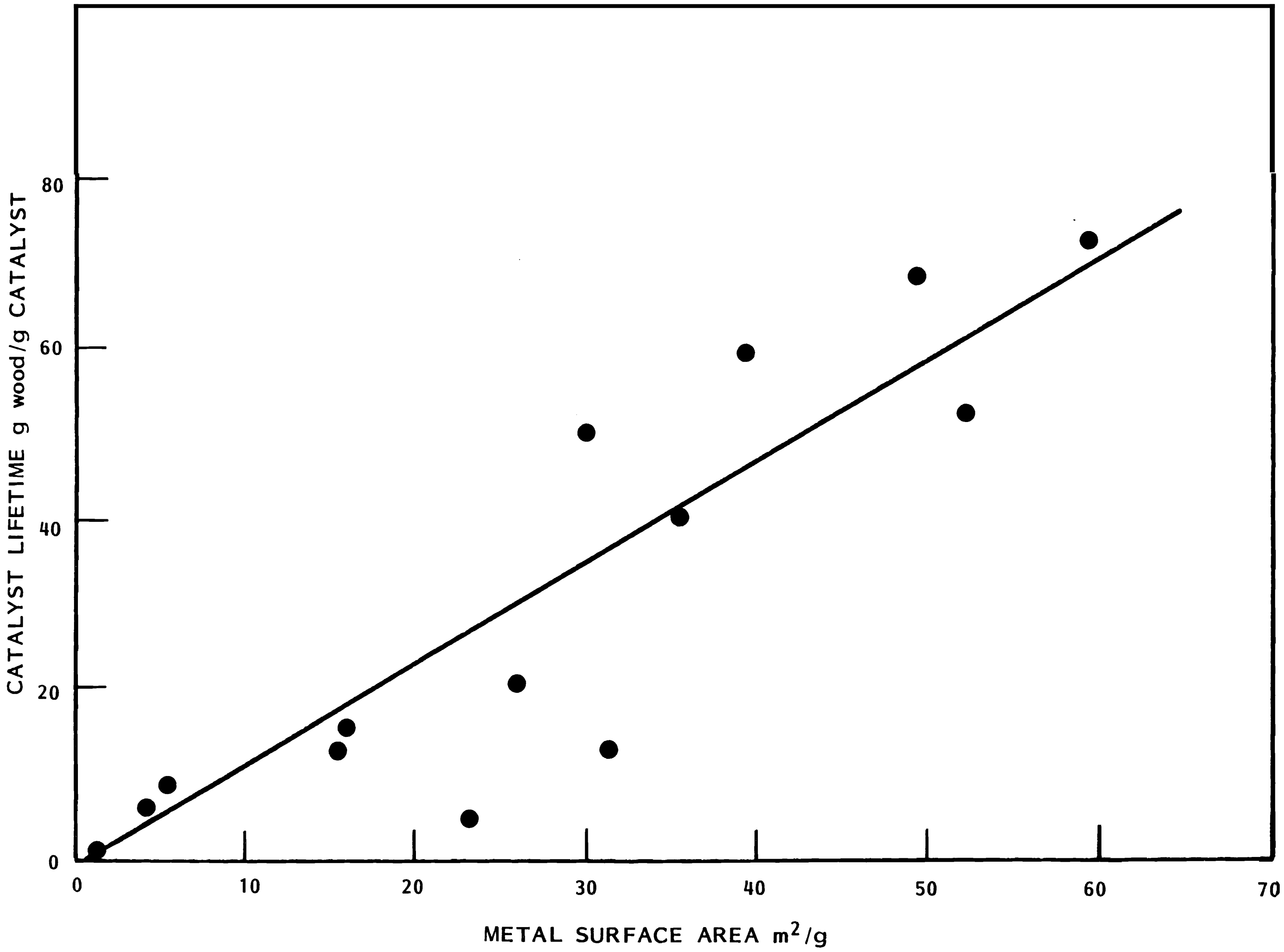


FIGURE 4. Effect of Metal Surface Area on Catalyst Lifetime

The lifetimes achieved with even the best catalysts for production of MRG are not economically attractive. In addition, regeneration is not very effective and takes a long time. Development of a long-lived catalyst system for production of MRG directly from biomass will require a better understanding of the mechanism of deactivation, and probably a novel catalytic system.

Catalysts for Hydrogen-Rich Gas and Ammonia Synthesis Gas

Screening studies were conducted to identify catalysts to produce a hydrogen-rich gas and ammonia synthesis gas (Table 3). No lifetime studies were performed; however, based on the results of lifetime studies for methanol synthesis gas it is unlikely that any of the catalyst systems suggested for these cases (see Table 5) will have long lifetimes.

The trimetallic catalysts developed for methanol synthesis gas can be used for production of hydrogen-rich gas and ammonia synthesis gas at 750°C and 1 atm, as shown in Table 12. Based on the methanol synthesis gas studies the catalysts should have good lifetimes; however, the effect of oxygen on catalyst lifetime in the ammonia case and the lifetime of the shift catalyst in the hydrogen case are unknown. In the fixed-bed laboratory gasifier, little oxygen reached the catalyst bed in the ammonia case. But in a fluidized bed unit the catalyst would be exposed to some oxygen from air in the fluidizing gas.

Alkali carbonates impregnated on the wood are also effective catalysts for production of hydrogen and ammonia synthesis gas, as shown in Table 12. Other catalyst possibilities include supported alkali carbonates and steam reforming catalysts such as United G-90C.

Catalyst Attrition

One problem encountered in operation of the fluidized bed PDU is catalyst attrition. Most commercial catalytic fluid-bed reactors use a finer mesh catalyst than is used in the PDU gasifier. With small catalyst particles, circulation, flow and mixing are good and attrition is low. Although data are limited, it appears that fluidization is not as good and attrition is appreciably higher with large particles (Kono 1980, Wen 1977).

TABLE 12. Production of Hydrogen-Rich Gas and Ammonia Synthesis Gas at 750°C, 1 atm

Catalyst	Ni-Cu-Mo/SiO_2-Al_2O_3		17 wt% K_2CO_3 Impregnated on Wood	
Product	NH_3 SynGas	H_2	NH_3 SynGas	H_2
Steam Rate, g/g wood	2.1	2.9	1.2	2.6
Air Rate, g/g wood	0.7	--	0.6	--
Carbon Conversion(a) to Gas, wt%	97	91	87	91
Gas Composition, vol %				
H_2	44.5	55.2	40.2	55.1
CO_2	24.9	28.4	22.1	28.6
CH_4	3.7	4.8	2.6	4.1
CO	9.0	11.2	14.4	10.9
C_2^+	0.7	0.5	0.7	1.3
N_2	17.5	--	19.3	--
Potential NH_3 Yield(b) kg/kg wood	0.60	--	0.53	--
Hydrogen Yield(c/b) nm^3/kg	--	1.00/1.20	--	0.97/1.16

(a) The remainder is converted to char, no liquids were formed.
(b) Includes shifting CO to make additional H_2, no reforming.
(c) Without shifting.

Two different laboratory fluidized beds were used to screen catalysts for their resistance to attrition: 1) a 5-cm I.D. model in which the catalyst was fluidized with air at ambient temperature, and 2) a heated 2-cm I.D. model which was fluidized with steam and hydrogen at 750°C. Three different catalysts, shown in Table 13, were used for the tests. In the final evaluation catalysts are tested in the PDU at expected process conditions.

In most of the tests, attrition was high at first and then leveled off to a lower steady-state rate within the first 24 hours. The rate of attrition for all of the catalysts was low at the lowest fluidization velocity tested, but

TABLE 13. Results of Laboratory-Scale Catalyst Attrition Tests

Catalyst	Grace Ni/Al_2O_3			Alcoa F-100 Alumina		Grace Ni-Cu-Mo/Al_2O_3 (SMR-2)					
Reactor I.D., cm	5.1	5.1	5.1	5.1	5.1	5.1	5.1	5.1	2.1	2.1	2.4(a)
Fluidizing Gas	Air	Air	Air	Air	Air	Air	Air	Air	(b)	(b)	([illegible])
Temperature, °C	20	20	20	20	20	20	20	20	750	750	750
Velocity, cm/sec	23	31	52	16	31	12	23	34	14	12	13
Velocity, ft/sec	0.75	1.0	1.7	0.53	1.0	0.40	0.75	1.1	0.47	0.41	0.43
Duration of Test, hr	120	132	168	144	96	216	144	90	168	408	153
Steady-State Attrition, %/hr	0.007	0.012	0.033	0.004	0.009	0.006	0.025	0.12	0.008	0.007	0.020

(a) Used catalyst with 6 wt% carbon.
(b) 90% steam, 10% hydrogen.

increased quite rapidly as the velocity was increased. The steady-state rate of attrition was found to be a function of velocity in the following manner:

$$K = 0.10\ V^3 \text{ for Grace SMR-2}$$

$$K = 0.0076\ V^{2.1} \text{ for Grace } Ni/Al_2O_3$$

where K is the rate of attrition (percent of original catalyst charge reduced to fines in one hour) and V is the gas velocity (ft/sec). Fines were defined as catalyst particles smaller than 100 mesh.

The rate of attrition for the SMR-2 catalyst was higher than the rate of attrition for a Ni/Al_2O_3 catalyst and a plain alumina catalyst tested at similar velocities, and was much more sensitive to changes in velocity. However, the SMR-2 catalyst has a lower bulk density than the other two catalysts (see Table 14) so it can be fluidized at lower velocities where the rate of attrition is similar to the other two catalysts.

An actual measurement of catalyst attrition in the PDU has not been made, but it appears to be somewhat higher than that observed in the 5-cm model. A review of the literature suggested two possible reasons for the increased attrition in the PDU: 1) steam may reduce the strength of the catalyst support, and 2) formation of elemental carbon within the catalyst particle may weaken it (Zenz 1960). To test these possibilities, tests were made in the 2-cm I.D. heated model fluidized with steam and hydrogen. Tests used fresh SMR-2 and "coked" SMR-2 (6% carbon on the catalyst) obtained from a laboratory gasifier. The fresh catalyst showed no increase in attrition compared to tests using air at ambient temperature. The rate of attrition increased somewhat

TABLE 14. Characteristics of Catalysts Used for Attrition Tests

Catalyst	Grace Ni/Al_2O_3	Alcoa F-100 Alumina	Grace SMR-2 $Ni\text{-}Cu\text{-}Mo/SiO_2\text{-}Al_2O_3$
Bulk Density, g/cm^3	1.3	0.72	0.62
Particle Size, U.S. Screen	-36 + 70	-48 + 80	-40 + 80
Minimum Fluidization Velocity, cm/sec	18	14	11

with the "coked" catalyst, but part of this was due to removal of carbon from the catalyst. We now believe that the feed screw causes most of the attrition in the PDU by crushing the catalyst that falls back into it.

EVALUATION OF ALTERNATIVE FEEDSTOCKS

Bagasse, rice straw, alfalfa, and almond hulls were gasified in a continuous laboratory reactor to evaluate the potential of alternative feedstocks for production of synthesis gas. All samples used were obtained in pelleted or cubed form and ground to about 14 mesh for use in the laboratory reactors. Other materials that had not been densified could not be fed into the reactor.

Table 1 shows the composition of all four materials. The samples all contained considerable ash (from 6-20%) and about 10% moisture. On a moisture and ash-free basis the chemical composition of the alternative feedstocks is quite similar to wood. The biggest difference between the feedstocks is their bulk density, which ranges from 0.14 to 0.65 g/cc.

Table 15 shows the results obtained with the four feedstocks at about 750°C with 1 gram of steam per gram of feedstock, using a Ni-Cu-Mo/SiO_2-Al_2O_3 (SMR-2) catalyst. Almond hulls were the best feedstock with respect to both carbon conversion and gas composition, followed by alfalfa. Carbon conversion and gas quality appear to be related more to the bulk density of the material than to any other property. This appears to be due to the design of the laboratory reactor and would not necessarily be the case in a fluidized bed. The materials with the lowest bulk densities have more stringy, fibrous pieces, which cause channeling and bridging in the laboratory reactor. When this occurs, carbon conversion and gas quality are adversely affected.

Overall, the results with the alternative feedstocks were quite similar to those obtained with wood. The yield data shown in Table 15 are based on the weight of the feed material as processed. When converted to a moisture and ash-free basis, results are about the same as those achieved with wood. Results in the case of almond hulls are greater than those with wood. With

TABLE 15. Gasification of Alternative Feedstocks for the Production of Methanol Synthesis Gas with Ni-Cu-Mo/SiO_2-Al_2O_3 Catalyst

	Bagasse	Rice Straw	Alfalfa	Almond Hulls
Reactor Temp., °C	760	780	760	760
Catalyst Temp., °C	750	730	740	740
Feed rate, g/min	0.20	0.17	0.18	0.22
Steam rate, g/g feed	1.3	0.8	0.8	0.7
Gas Composition, vol%				
H_2	51.8	50.4	50.4	52.9
CO_2	24.3	23.9	20.8	18.8
CH_4	5.5	6.7	5.5	3.8
CO	17.8	18.3	22.2	24.2
C_2^+	0.7	0.7	1.1	0.3
Carbon Conversion, wt%				
To gas	81	78	91	95
To char	18	23	--(c)	2
Carbon Balance, %(a)	99	101	91	97
Synthesis Gas Yield, nm^3 (H_2 + CO)/kg feed	0.85	0.73	0.96	1.2
Potential Methanol Yield,(b) wt/wt of feed	0.40	0.34	0.45	0.55
Bulk Density, g/cm^3	0.20	0.14	0.25	0.65

(a) The quantity of tar and oils produced was negligible for all tests.

(b) Without reforming CH_4 and C_2^+.

(c) The char yield is determined by subtracting the weight of ash in the feed material from the weight of the residue remaining after the test; for alfalfa this resulted in a negative number.

both alfalfa and bagasse, a slight sulfur odor was noticed. No H_2S was detected in the gas; however, the gas chromatograph used for analysis was not sensitive to less than 100 ppm of H_2S.

PROCESS DEVELOPMENT UNIT STUDIES

The main objectives of the process development unit (PDU) studies are to determine the yields from gasification of wood with steam in the presence of catalysts at 10 atm (1000 kPa) absolute pressure and to provide information on equipment performance for scaling to pilot plant size. Previous studies (Mudge et al. PNL-3695 1981) determined yields at atmospheric pressure which were extrapolated to 10 atm (1000 kPa) absolute pressure for economic evaluations.

Equipment in the PDU was modified to allow operation at pressure conditions. Equipment design and operating results are presented in the following sections along with considerations necessary to allow operation.

DESIGN CONSIDERATIONS FOR PRESSURE OPERATION

Operation at 10 atm (1000 kPa) absolute pressure involves special procedures to assure continued safety. Equipment must be designed to established codes. Process gas flows change significantly with pressure. The resulting reduction in equipment size is a prime incentive for pressure operation. The following sections summarize considerations for pressure operation.

Equipment Design

Many PDU components that were used for atmospheric pressure operations needed to be redesigned and replaced. The gasifier and the gas-fired heater did not require replacement. The gas-fired heater had not been used previously. Design criterion for the pressurized PDU equipment were based on ANSI B31.1 for the process piping and the ASME unfired pressure vessel code for process vessels.

The gas-fired heater did not qualify under any of the standard codes. An analysis of this heater was prepared and presented to the Washington State Boiler Board. A special license allowing 3000 hr of operation at up to 170 psig (1170 kPa) was obtained for the heater.

Flow Requirements

The most critical design criterion is the flow in the gasifier. The wood/steam mixture must fluidize in order to allow feed addition, catalyst gas mixing, and heat transfer from the cartridge heaters. Constraints in the design were (1) gasifier configuration, (2) cartridge heater capacity, and (3) gas heater capacity. Specifically, the inside diameter of the gasifier is 7.75 in. (19.7 cm). The maximum capacity of the cartridge heaters is 119,000 Btu/hr (35 kW); however, heat transfer limits the design capacity for a 750°C bed temperature to 48,000 Btu/hr (14 kW). The gas heater has a 48,000 Btu/hr (14 kW) rating. Conversations with the manufacturer indicated the gas heater duty could be increased by using a larger burner orifice.

Estimations of gasifier heat requirements were made from equilibrium calculations. At 1380°F (750°C) bed temperature and 10 atm (1000 kPa) absolute pressure with 0.75 lb steam/lb wood and 100% carbon conversion, the standard heat of reaction is 400 to 600 Btu/lb (930 to 1400 kJ/kg) of wood. At 75% conversion the reaction should be close to autothermal. Therefore, based on 5% wood moisture and 0.75 weight ratio of steam to wood, 150 to 200 1b/hr (70 to 90 kg/hr) of wood is the maximum processing rate, and 50 lb/hr (23 kg/hr) would be a reasonable design rate.

From atmospheric testing, a 0.7 weight ratio of steam to dry wood was determined for methanol synthesis gas production. This value was reasonable for the pressure design case, as higher steam rates would be less economical. For the design basis, 38 lb/hr of steam would be used. This equals a bed velocity of only 0.24 ft/sec (7 cm/sec) which is not high enough to fluidize a wood/catalyst mixture. Unfortunately, the constraint of the existing gasifier-cartridge combination could not be resolved. Therefore, we had to consider higher steam rates, smaller catalyst particle size, and recycle of product gas.

A catalyst of about 250 microns (-40 + 80 U.S. Screen) in size was ordered for use in the PDU. This size should allow fluidization at about 0.5 ft/sec (15 cm/sec) as compared to a velocity of 1.5 ft/sec (46 cm/sec) in the atmospheric cases. Potential advantages would be less catalyst attrition and high gas and char residence times. From fluidization tests in a cold model, a gas velocity of 0.5 ft/sec (15 cm/sec) appeared to fluidize a bed of catalyst and headrig sawdust.

A compressor was procured for recycle of product gas. Gas was recycled for startups, catalyst reduction, and increasing velocities in the gasifier.

The gas heater was estimated to be overdesigned. It appeared that it would handle the extra heat load for increased steam flow and product gas recycle flow.

The rest of the equipment was designed based on a velocity of 0.5 ft/sec (15 cm/sec) in the bed, a bed temperature of 1380°F (750°C), and a maximum wood rate of 150 lb/hr (68 kg/hr).

Safety Systems

Pressure operation posed a number of different potential hazards compared to atmospheric operation. Of primary concern were increased leak potential and failure of pressure containment pipes and vessels.

An Operational Readiness Plan (ORP) was developed which called for an Operational Safety Analysis Review (OSAR) discussing potential hazards, and Safe Operating Procedures (SOP) for startup, shutdown, normal operation, and emergencies. An Operational Readiness Review board was appointed to scrutinize the ORP, OSAR, and SOP. When the board recommendations and the ORP were completed, approval was granted to operate.

Safety features in the plant include rupture discs, relief valves, fixed and portable carbon monoxide alarms, over-temperature controllers on critical pieces of equipment, interlocks on lockhopper systems, backflow prevention devices, interlocks between certain pieces of equipment, and continuous gas monitors.

A reliable datalogging system was used to shut down the plant if programmed temperature limits on critical pieces of equipment were exceeded or pressures exceed programmed limits. The plant was designed so operators are not required to be on the structure during routine operation.

Quality Assurance

A quality assurance program was developed for the PDU that scheduled periodic instrument calibration and machinery maintenance.

Description of the Pressurized PDU

The process flow diagram for the PDU is shown in Figure 5. Steam is superheated in the gas heater and contacts wood in the gasifier. Product gas and char exiting the gasifier are separated by a cyclone and filter. A heat exchanger condenses steam and organic compounds which are then separated from the gas in the demister. The gas can be recycled to the gas heater via the recycle compressor. Product gas is released through a letdown valve. A parallel off-gas system employs a venturi scrubber; however, it was never required and will not be discussed. All other components are discussed in detail.

Gasifier

The gasifier is the same vessel used for previous atmospheric tests, with a modified gas inlet, distributor plate, and cover. The gasifier is a 24-in. (0.61 m) carbon steel pipe, 10 ft (3 m) long, with blind flanges at each end and a flanged connection near the middle of the vessel. A schematic is shown in Figure 6. The gasifier has ceramic fiber insulation [approximately 2 in. (5 cm) thick] and a cast refractory lining 1.5 in. (4.25 cm) thick. The reaction zone (bed) is in an 8 in. (20 cm) diameter tube of stainless steel. The bed is 3 ft (0.91 m) deep when stagnant and 4 ft (1.21 m) deep when fluidized.

The reaction-zone liner has heaters strapped on its exterior. These elements provide energy to maintain the bed temperature during idle periods. However, these elements failed before tests were complete. Failure was probably due to moisture accumulation where terminals are connected to the electrical glands on the gasifier vessel. Carbon accumulation is another possible explanation. Although these heaters are a desirable feature needed to maintain temperatures between tests, they are not essential for successful operation of the PDU. Six cartridge elements [0.75 in. (1.9 cm) diameter] are inserted into the reaction zone. Their heated length is 4 ft (1.21 m) and they are capable of maintaining 1600°F (870°C) skin temperature. Total capacity was 100,000 Btu/hr (30 kW). These elements provide energy to heat reactants (wood) to the bed temperature and energy for the heat of reaction. Energy consumption by these elements is measured by a watt-hour meter. A seventh cartridge heater element was added during the testing period, which increased the capacity to 120,000 Btu/hr (35 kW) total. Our experience showed that the heat transfer

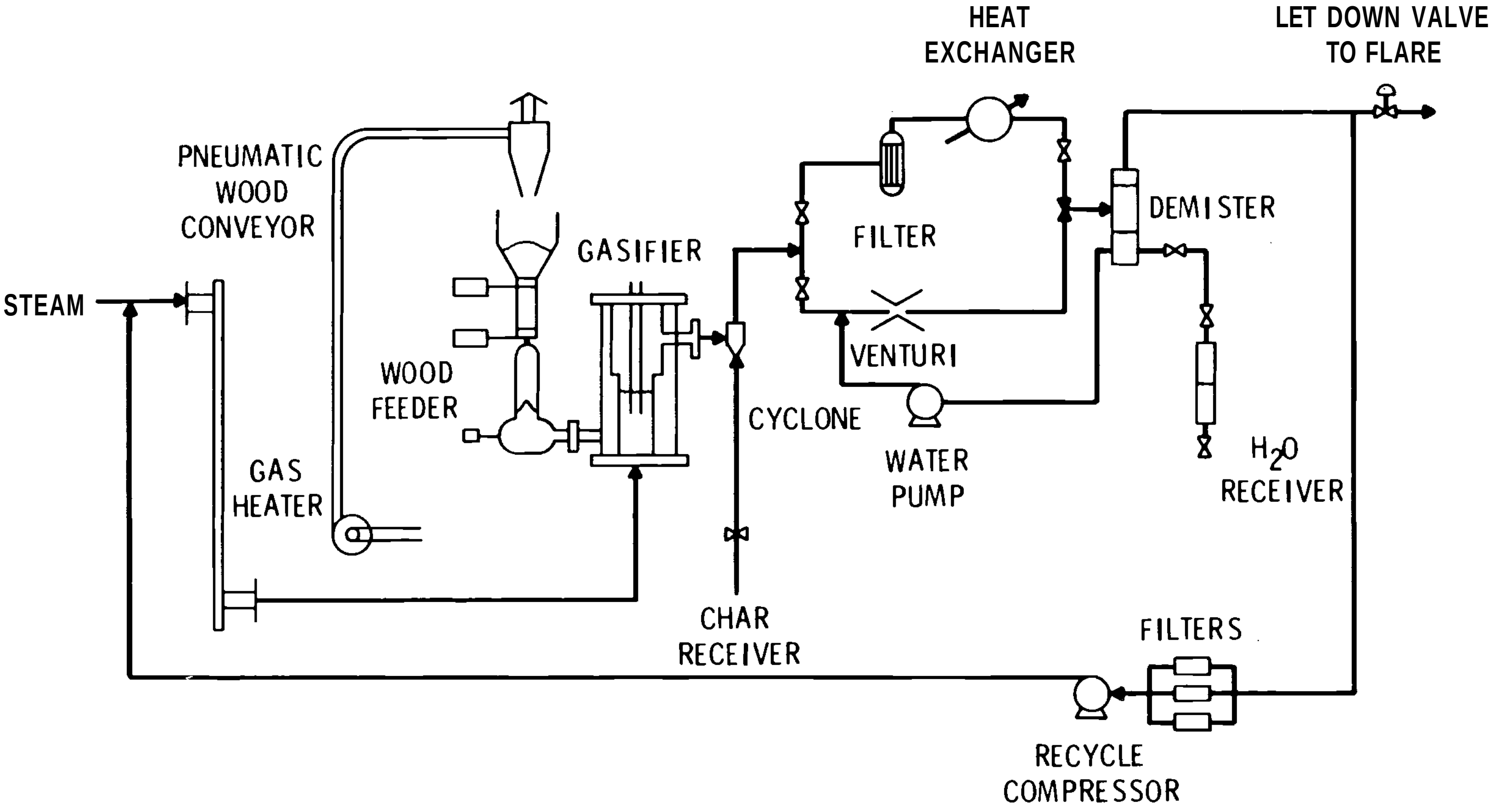


FIGURE 5. PDU Schematic

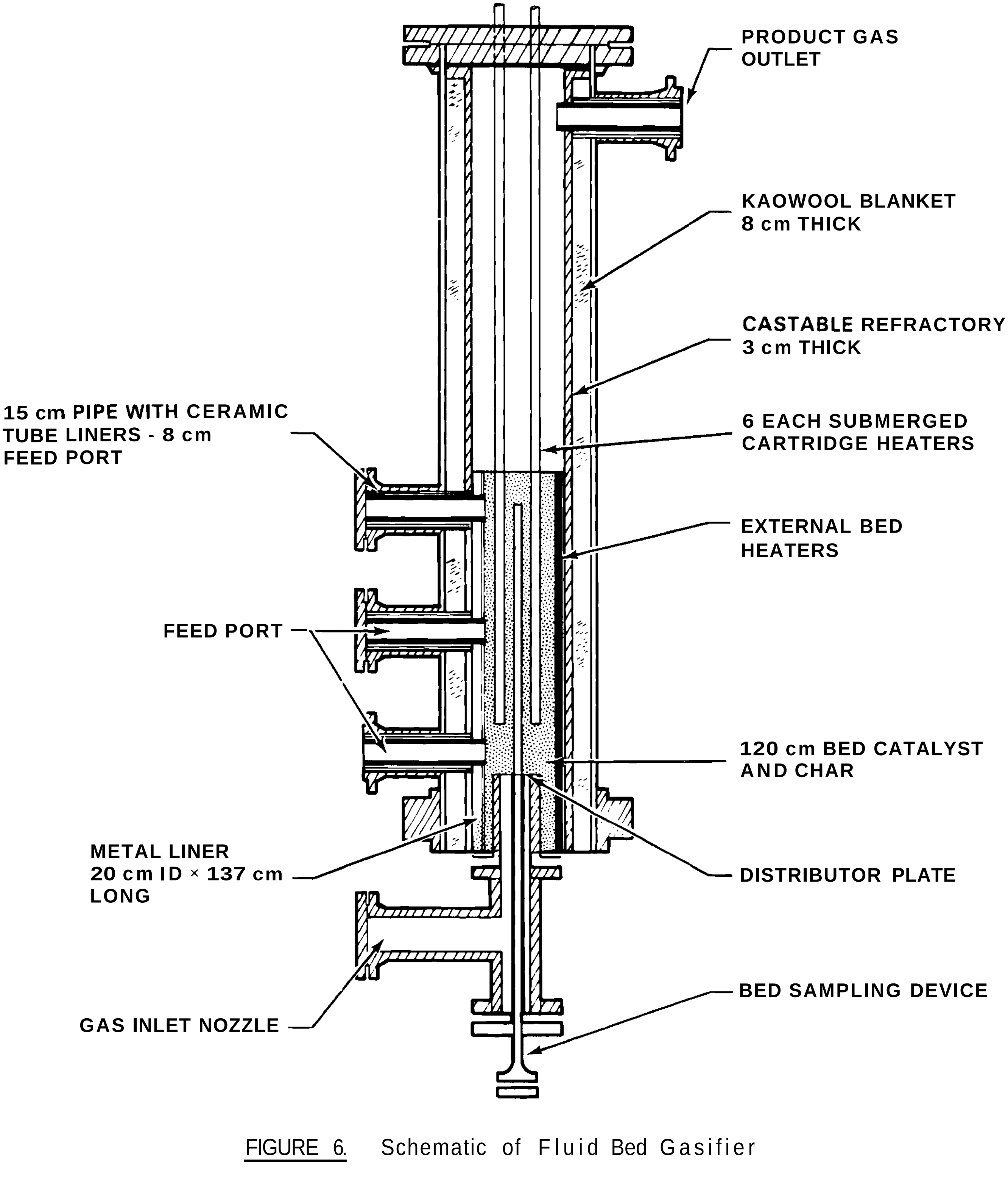


FIGURE 6. Schematic of Fluid Bed Gasifier

from the elements to the bed limited the output from the cartridge heater elements to about 75,000 Btu/hr (22 kW) output. The effective heat transfer coefficient is about 80 Btu/hr-ft^2°F (1600 kJ/hr-m^2-°C).

Gas enters the gasifier through a refractory lined pipe tee. A distributor plate made of Incoloy 800H (trade name of Huntington Steel Corp.) is placed just below the wood feed inlet. The distributor plate has 144 holes of 0.05 in. (1.3 mm) diameter.

A freeboard disentraining area 6 ft (1.3 m) long is above the fluid bed. The diameter was 14 in. (36 cm); however, during testing a 12 in. (30 cm) diameter stainless steel liner was added to (1) prevent spalling refractory from falling into the bed and destroying the fluidization and (2) to inhibit steam diffusion to the gasifier wall.

Thermocouples and pressure probes are inserted via a 0.25 in. (6.4 mm) tubing from the reactor top to the desired level in the gasifier.

Biomass Lockhopper and Feeder

The fuel feeding system is shown in Figure 7. The design is basically the same as the design used for atmospheric tests; however, the feeder is enlarged to handle a variety of feedstocks and is designed for high pressure. The lockhopper valves are self-cleaning-knife gate valves. The lockhopper is a 12 in. (0.3 m) diameter pipe, 4 ft (1.22 m) long.

The live bin is 2 ft (0.61 m) in diameter and about 6 ft (1.8 m) tall. It contains three metering screws of 6 in. (15 cm) diameter. These metering screws push biomass into an injector screw 3.5 in. (8.9 cm) diameter which rapidly conveys the fuel into the fluid bed. The injector screw typically operates at 150 rpm.

Levels of wood in the live bin are indicated by two types of sensors: a vibrating plate device and an energy transmission device. The antenna for the energy transmission devices needed to be vertically oriented in the wood bin before satisfactory calibration and operation were attained.

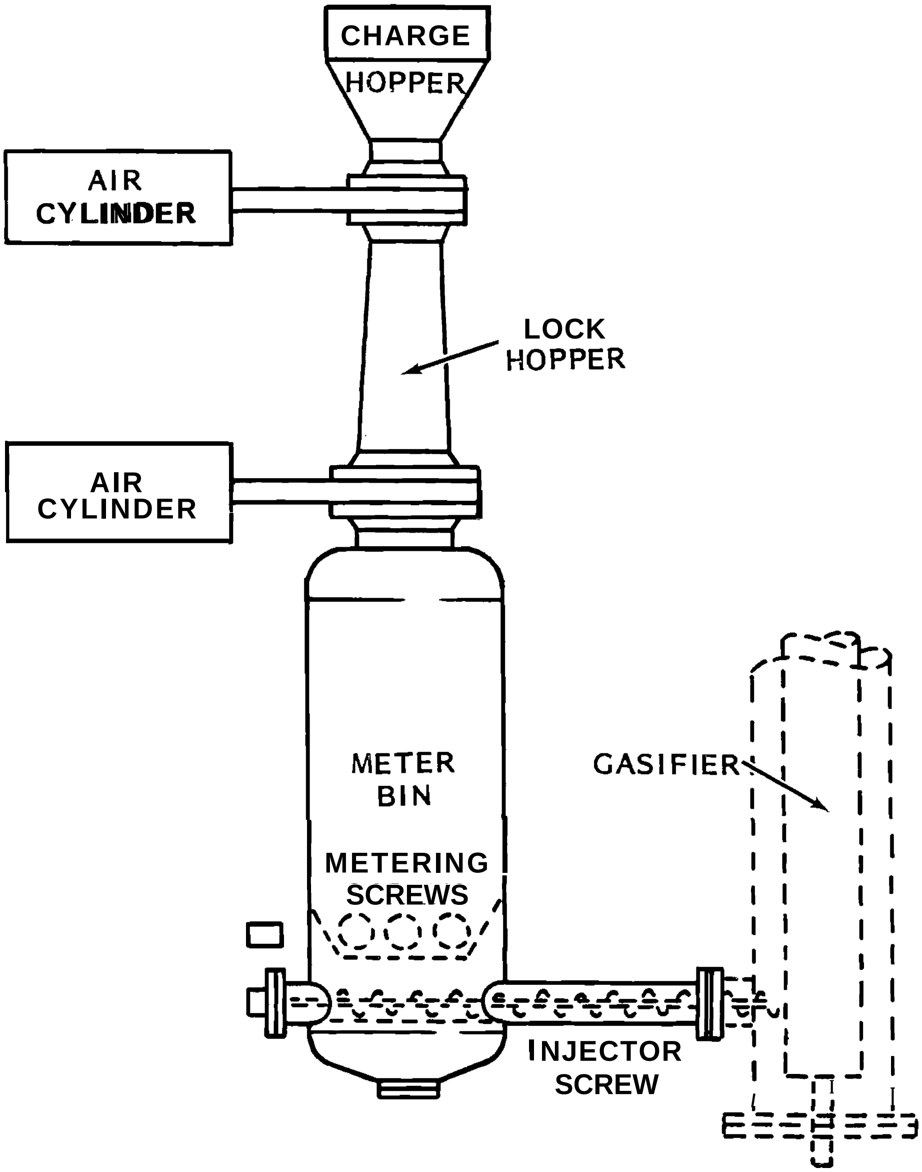


FIGURE 7. Wood Feeder and Lockhopper

A nitrogen purge in the feeder is used during all tests to attempt to prevent any flow of steam from the gasifier into the live bin. This technique apparently was successful because wood removed from the live bin at the end of tests was never moist.

Calibration of the feeder with headrig sawdust showed that dry headrig sawdust bypassed the metering screws and fell onto the injector screw. This resulted in intermittently high wood feed rates which were responsible for many of the difficulties observed in the shakedown tests. Addition of a baffle to the live bin area eliminated this feeder problem when using headrig sawdust. When dense wood flakes were used, the bypassing problem appeared again and the baffle was extended to remedy the problem.

The feeder is driven hydraulically with manual controls for injector and metering screw speeds. The injector screw can be moved in and out while in operation. The 6 in. (15 cm) travel on the injector is useful during startup when stagnant catalyst has settled on the screw and in the injector shaft.

The metering screws are electrically interlocked with the injector so they cannot operate without the injector. The feeder is interlocked with the data-logger to stop feeding in alarm conditions.

The lockhopper is manually operated with elecrical interlocks which prevent both hopper valves from opening at the same time. Interlocks also prevent the top valve from opening without the pressure vent line open. A differential pressure switch prevents opening the bottom hopper valve until pressures in the live bin and the hopper are equalized.

Wood is conveyed from ground level to the lockhopper charge bin with a pneumatic conveying system. Besides easing the operator work load, this system is essential in minimizing operator time on the PDU structure.

Gas Preheater

The gas preheater function is to heat steam and/or recycle gas to the desired bed temperature (or higher if possible). The preheater was designed to heat steam (60 lb per hr) at 2 psig from 212°F (100°C) to 1800°F (980°C). This is a duty of 48,000 Btu/hr (50,000 kJ/hr). The heater is a propane fired, annular finned tube made of stainless steel and a cast chrome-nickel alloy.

After a thorough stress analysis, a permit was issued by the Washington State Boiler Board allowing operation at 170 psig (1200 kPa) for 3000 hr. Heat transfer calculations showed that the convective heat transfer coefficient remains nearly constant for equal mass flow rates at different pressures. The needed maximum steam temperature is only 1380°F (750°C), so the duty is decreased for the design mass flow rate, or the steam/recycle rate can be increased. The steam/recycle rates needed to be increased at 10 atm (1000 kPa) to provide sufficient fluidization velocity in the bed. In actual operation the gas heater never performed to design conditions during atmospheric or pressure operation,

The gas heater and the line between the heater and the reactor [3 in. (7.5 cm) 316 stainless steel] were both heavily insulated and waterproofed. Heat loss in the line causes extremely slow heatups, so high temperature heat tapes were eventually installed, effectively eliminating heat losses in the line,

Controls on the gas heater include a three-mode temperature controller which activates a propane valve positioner. A high-temperature controller shuts down the heater if the finned tube temperature exceeds 1490°F (810°C). High and low pressure switches on the propane supply are additional safety features.

Product Gas Cleaning

Gas scrubbing was always a problem in atmospheric tests. Poor scrubbing caused some uncertainty in the mass and energy balances and also caused operational problems. Scrubbing systems used in atmospheric tests included a cyclone followed by either a venturi scrubber or electrostatic precipitator. The problems with these systems centered around char contacting water and condensed organic liquids. When this happened, a sticky mass developed and grew, eventually plugging lines and decreasing scrubber efficiency even further.

The problem was successfully eliminated in the design of the pressurized PDU. Most of the char is separated from the gas in an efficient 3 in. (7.5 cm) diameter high temperature cyclone. The char which passes through the cyclone is separated using seven high-temperature sintered stainless steel filters 2.6 in. [6.5 cm) outside diameter by 3.3 ft (1 m) long. Filter pore size is 10 microns. The filter vessel houses the filters and is equipped with a differential pressure gauge to measure pressure drop across the filter elements. A nitrogen pulse backflush system is used to remove the char cake from the elements. The cyclone and filter vessel are insulated and are operable at 1000°F (540°C). Gas leaving the filters passes through a heat exchanger where steam and any organic compounds condense. The condensate is collected in a demister column with a 4 in. (10 cm) diameter teflon packed demister. Clean gas passing through the demister screen is either recycled or released to a flare via a pneumatically controlled letdown valve.

The cyclone hopper system is the biggest operational problem in the off-gas system. The bottom hopper valve had a tendency to leak, thereby allowing steam to condense in the hopper forming a muddy mixture of char or inhibiting the flow of the char during hopper draining activities. This was eliminated to some extent by purging the hopper with nitrogen. Pressure sensing and vent lines also had a tendency to plug with char. It is recommended that future vent systems be carefully sized to prevent entrainment of char when depressurizing the hopper and sensing lines be equipped with filters to prevent char from entering. Another potential improvement would be self-cleaning knife gate valves instead of ball valves on both ends of the hopper. Heat tracing may be required to prevent moisture condensation.

The cyclone hopper was drained, and the discharge weighed, at hourly intervals during tests. Samples were taken and analyzed for moisture, ash, carbon, hydrogen, nitrogen, heat of combustion, and potassium or sodium when carbonate catalysts were used. The filter vessel was emptied only after completion of a test. Similar sample analyses were performed on filter vessel samples.

The demister was equipped with two thermal conductivity type level indicators which activated a drain valve leading to a condensate receiver. The liquid in the receiver was drained and weighed at 20 minute intervals. Samples were taken and analyzed for organic carbon. The condensates were saved in steel drums and decanted after settling overnight. The tar (if any) at the bottom of the drum was weighed and sampled, and analyzed for carbon, hydrogen, and nitrogen.

Product Gas Recycle System

Gas is recycled during startup, catalyst reduction, and operation by a piston type recycle compressor. Initially a 120 gal (450 a) surge tank was used to dampen piston pulses; however, this tank was removed to eliminate the large amount of gas needed to pressurize the plant and to decrease time required to reach steady state gas compositions when recycling product gas during operation. The recycle flow is measured with an orifice meter and is manually controlled by a variable speed drive. When required recycle flow rates are below the compressor's minimum capacity, a valve in a bypass loop is manually opened and adjusted.

Control Instrumentation

System pressure is controlled with a proportional pneumatic controller. A stainless steel diaphragm transmits pressure to a Bourdon tube via a glycerin filled line. A remote set point for the controller is located in the laboratory. The controller drives a pneumatically-operated 2 in. (5 cm) pressure letdown valve with stainless steel trim and a maximum orifice of 0.38 in. (0.96 cm). On loss of air, the valve fails to the open position.

Steam flow is measured by differential pressure across an orifice meter. The differential pressure is converted to a signal by a pneumatic differential pressure cell. The signal feeds a pneumatic, three-mode controller inside the laboratory. The controller operates a 1 in. (2.5 cm) pneumatic control valve which fails to a closed position on loss of signal.

Temperature controllers are used on the in-bed, cartridge heaters. The heater elements contain internal thermocouples which measure the skin temperature. A high-temperature limit control is used on this circuitry. To maximize heater life and to provide steady energy input, silicon control rectifiers are used.

Other heating circuitry (heat tapes) are controlled manually with rheostats.

Steam Generation

Packaged electric boilers are used for steam supply. Originally, two parallel generators, each with 50 lb/hr (23 kg/hr) capacity, were used. However, they could not generate a steady 100 lb/hr (45 kg/hr) steam flow. A 300 1b/hr generator was procured, and steady steam flow was attained.

Gas Sampling

Gas samples can be drawn from the filter vessel outlet or from the demister (see Figure 5). The gas is cooled in a small heat exchanger and filtered. Gas pressure is reduced to 2 psig (14 kPa). The low pressure lines convey gas to the laboratory gas analysis equipment.

The gas sample flow is continuous (about 0.1% of product flow) during PDU operation. Readings from continuous CO, CO_2, H_2, O_2, and CH_4 analyzers are recorded by operators every 20 minutes. A gas chromatograph with a thermal conductivity detector is used for gas analysis. This unit determines concentrations of N_2, C_2H_4, C_2H_6, C_3H_8, acetylene and normal-butane as well as the gases monitored by the continuous analyzers. Samples are automatically injected into the gas chromatograph for analysis on 20 minute intervals.

Product gas flow rate is measured with a differential pressure gauge and an electronic differential pressure transducer connected with an orifice meter.

Data Acquisition

On 30 minute intervals operators take readings of controller indicators, meters, pressure gauges and differential pressure gauges. In addition, the datalogger continuously monitors 32 thermocouples, 4 pressure transducers, and the product gas differential pressure transducer. The datalogger prints on 15 minute intervals and plots important points on 2 minute intervals. Important data points are recorded on magnetic tape on 2 minute intervals.

Data Analysis

After a PDU test, preliminary results are determined using estimated compositions (moisture, ash, C, H, 0, and total organic content). Then, when chemical analyses are complete, a final analysis of the test is made using measured values. This analysis is programmed on a microcomputer. The calculated results include elemental mass balances, energy balances, conversions, and efficiencies. Summaries of data from all tests except shakedowns are included in the appendix.

OPERATION OF THE PRESSURIZED PDU

Operation at elevated pressures is described in the following sections. Many shakedown tests were made before usable data were obtained. The PDU is now operable at 10 atm (1000 kPa) absolute pressure and 1380°F (750°C) temperature on a routine basis. Time and funds for operation and preparation of this report expired before all variables could be investigated thoroughly.

Safe Operating Procedure

A Safe Operating Procedure (SOP) covering startup, normal operation, shutdown, and maintenance was developed. The startup and shutdown procedures were placed in each test data book in checklist form to assure that they were followed.

Operations typically consisted of about 5 hr of heatup, followed by 3 to 5 hr of operation and 1 hr for plant shutdown. Three operators were used to conduct the tests.

Nickel catalysts required about 12 hr of reduction in a hydrogen-nitrogen atmosphere at 750°F (400°C). This was performed with a two-man crew.

Feedstock Description

Two types of feedstock were used in the pressurized PDU testing program: alder headrig sawdust and softwood densified flakes. These feedstocks are shown in Figure 8 along with whole tree chips which were to be tested. The densified flakes are made with broken pellets from a wood pelleting operation. These rejects are attrited on a disk mill.

Average wood compositions are shown in Table 16 along with results of screen tests. For PDU tests wood is dried to less than 5% moisture on a dry basis.

Corrosion

Although the PDU has only limited hours of operation, it is worthwhile noting that during maintenance on the plant, no corrosion has been observed. The places with the most severe conditions are the gas heater (Duralloy HP-40), the hot feed line (316 stainless steel), the distributor plate (Incoloy 800H), the reactor liner (310 stainless steel), and Incoloy sheathed cartridge

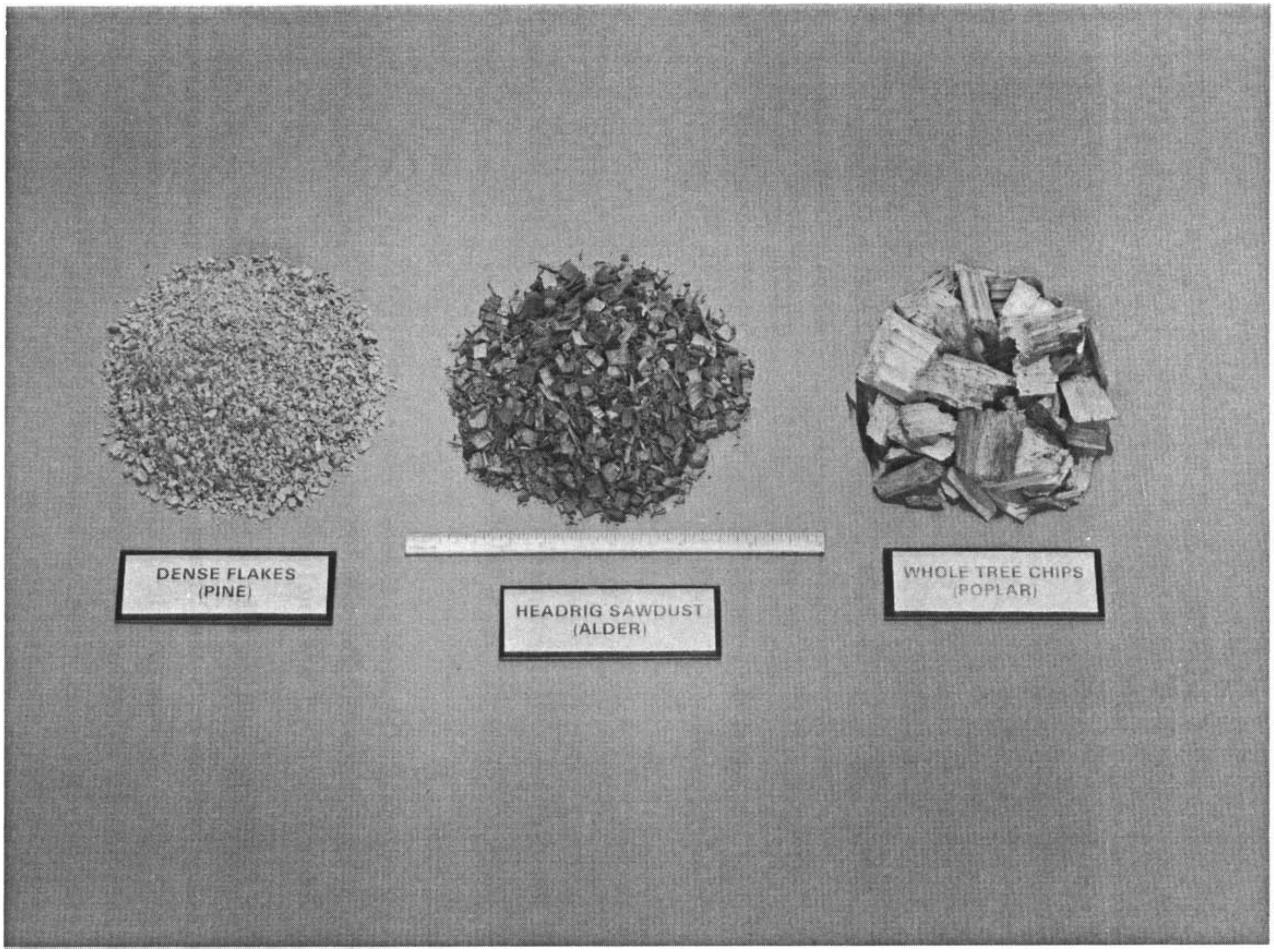


FIGURE 8. Feedstock for PDU

TABLE 16. Typical Wood Compositions and Size Distributions

	Dense Flakes (Pine)	Headrig Sawdust (Alder)	Whole Tree Chips (Poplar)
Wt fraction C	0.503	0.450	0.469
Wt fraction H	0.064	0.058	0.063
Wt fraction O[a]	0.427	0.492	0.458
Wt fraction Ash	0.006	0.009	0.010
HHV, Btu/lb	8770	8235	--

U.S. Screen	wt%	U.S. Screen	wt%	U.S. Screen	wt%
+8	8.29	+4	27.41	+3/4	32.4
-8+16	37.85	-4+8	41.64	-3/4+.53	30.37
-16+40	42.74	-8+16	19.39	--	--
-40+100	10.50	-16+40	10.01	-.53+8	37.06
-100	0.63	-40	1.55	-8	0.17

(a) By difference.

heaters. The cyclone (304 stainless steel) operating at up to 1000°F (540°C) showed no signs of corrosion or erosion.

Operating Results

Tests P1 through P11 were shakedown tests and little information can be drawn from them. Tests P12 through P21 generated useful data. Summaries of data from Tests P12 to P21 are included in the appendix.

Effect of Pressure on Yields

Operating Results at 5 and 10 atm (500 and 1000 kPa) absolute pressure are compared with those at atmospheric pressure in Table 17. When comparing these data, differences in operation need to be considered. Tests at atmospheric pressure used only steam as a feed gas whereas at elevated pressure, tests used steam and recycle gas. Kinetic data show that steam is more reactive than hydrogen and carbon dioxide for conversion of carbonaceous solids and vapors. Methane and carbon monoxide are non-reacting species with negative effects on

TABLE 17. Effect of Pressure in Tests with Spent Catalyst

	Test No.						
	P14A	P14B	P15	P19	P12	P13	P18
Pressure, atm absolute	1	1	5.1	5.8	10	10	10
Wood	headrig	headrig	headrig	headrig	headrig	headrig	headrig
T, °C	745	743	740	740	735	730	740
Steam-to-Wood Wt. Ratio	1.1	0.53	1.5	1.2	3.5	1.6	1.4
Normalized Carbon Conversion, wt%							
To Gas	76	75	73	76	72	71	65
To Solid	17	18	18	21	26	22	33
To Liquid	7	6	9	3	2	7	2
Gas Composition, vol%							
H_2	35.6	27.2	44.2	32.3	26.5	33.2	42.3
CO_2	23.0	23.0	28.6	28.6	38.8	32.7	21.2
CH_4	12.7	14.8	13.5	18.1	21.7	20.6	17.2
CO	25.9	31.0	11.9	18.4	11.2	11.9	18.2
$C_2+C_3+C_4$	0.7	4.0	1.9	2.5	1.7	1.6	1.1

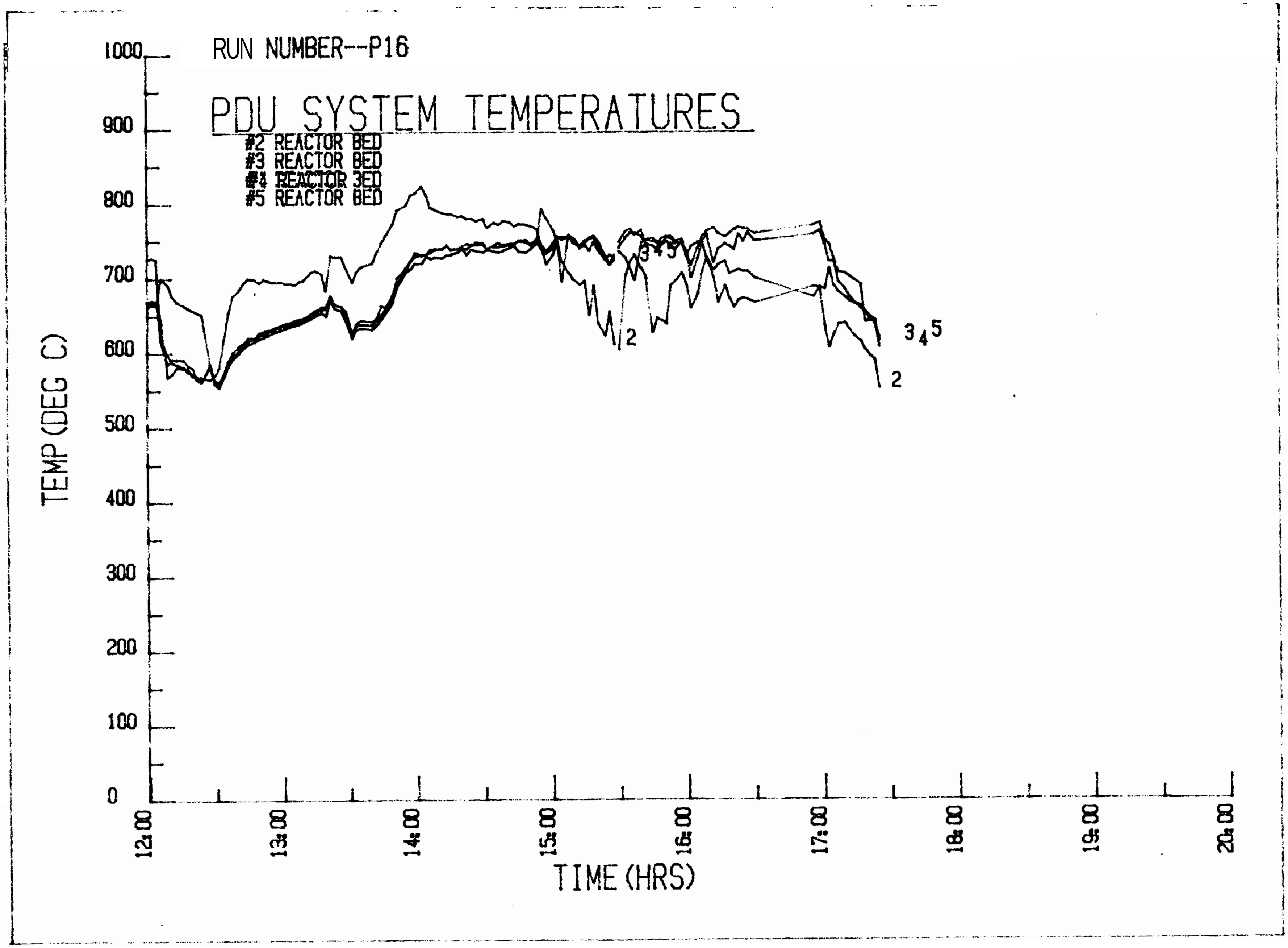


FIGURE 9. Gasifier Temperature Profiles carbon conversion as a result of equilibrium and kinetics. Because the steam was diluted with recycle gas at elevated pressure, one might expect the atmospheric pressure results to be more favorable for carbon conversion to gas. We measure more carbon conversion to gas and less tar at pressure conditions.

The explanation is that the gasification rate is proportional to steam partial pressure to some power. Even though the steam is diluted with recycle gas in the high pressure tests, the partial pressure usually is about 2 to 3 atm (200 to 300 kPa) compared to 1 atm (100 kPa) during atmospheric tests.

From the data, we can conclude that pressure operation:

- decreases conversion of carbon to liquids
- increases carbon conversion to gas to as high as 86%
- causes an increase in methane concentration to 7% in catalyzed tests and to 20% in uncatalyzed tests
- decreases the standard heat of reaction and decreases reactor energy requirements.

It is expected that carbon conversion will be further increased if the use of recycle gas is eliminated.

Feedstock Size Versus Yield

Yields from dense flakes and headrig sawdust in the presence of sodium carbonate catalyst are shown in Table 18, Tests P20 and P21. Gas Yield decreases and char yield increases with the smaller, dense flakes. The char residence time for the large headrig sawdust was about 16 min. The char residence time for dense flakes was lower than 16 min since the char inventory in the fluid bed decreased. Data were insufficient to calculate a char residence time for dense flakes. A time of less than 1 min is probable.

The gas yield increases with the larger feedstock probably because of increased char residence time. More testing of the effect of feedstock size is needed before a definite conclusion can be made.

Effect of Primary Catalysts

Primary catalyst refers to an alkali carbonate fed with the wood, either dry mixed or impregnated into the wood. Tests have been performed with sodium and potassium carbonates at 13 and 16 wt% concentrations respectively.

Wet wood can be mixed with anhydrous potassium carbonate. If the wood is moist enough (>20 wt%), the wood particles will absorb the carbonate. We did not see this effect with sodium carbonate. This salt was dry mixed with wood and then water was added to enhance its absorption into wood particles. The wood-carbonate mixtures were dried before use in a test.

Results are summarized in Table 18. The potassium carbonate promotes the water-gas shift reaction and reduces methane formation (Sealock et al. 1982);

TABLE 18. Comparison of Alkali Carbonate Catalysts With No Catalysts

	Test Number				
	P16	P20	P21	P12	P13
Pressure, atm absolute	10	10	10	10	10
Wood	dense flakes	headrig	dense flakes	headrig	headrig
Catalyst	K_2CO_3	Na_2CO_3	Na_2CO_3	None	None
T, °C	745	730	750	735	730
Steam-to-Wood Wt Ratio	1.2	0.8	1.2	3.4	1.6
Normalized Carbon Conversion, wt%:					
To Gas	74	74	64	72	71
To Solid	26	20	33	26	22
To Liquid	0.5	6	3	2	7
Gas Composition, vol%					
H_2	52.6	33.0	34.3	26.5	33.2
CO_2	24.9	33.1	30.6	38.8	32.7
CH_4	7.8	18.3	18.7	21.7	20.6
CO	14.2	13.3	14.3	11.2	11.9
$C_2+C_3+C_4$	0.5	2.2	2.1	1.7	1.6

however, sodium carbonate had only a small effect on methane content. Increased yields of tars and water-soluble organics occurs when sodium carbonate is used in place of potassium carbonate. The ineffectiveness of the sodium carbonate may be due to the fact that it did not absorb into the wood particles completely. Sodium carbonate forms hydrated solids ($Na_2CO_3 \cdot 10\ H_2O$) requiring much more water to get them into a solution that could permeate the wood particles.

During the first potassium carbonate test, a superficial gas velocity at conditions of less than 1 ft/sec (30 cm/sec) was used, resulting in appreciable accumulation of the salt in the bed in the form of fritted chunks, which began to interfere with fluidization as can be seen in the temperature profile shown in Figure 9. A loss of isothermal conditions was evident as the test proceeded. Some agglomeration of char was noted at the end of these tests. More testing is needed to see if operation without agglomeration can be sustained.

Secondary Catalyst Tests

Secondary catalysts are those catalysts supported on porous ceramic spheres in the fluid bed. The laboratory catalyst development studies showed that nickel alloy catalysts on silica-alumina supports potentially have an active lifetime sufficient to be economically feasible in a commercial process. A nickel-copper-molybdenum alloy (12% NiO, 4.5% CuO, 9% MoO_3) on a proprietary silica-alumina substrate was used in PDU tests.

Two potential problems arise when using secondary catalysts: attrition and deactivation. Laboratory-scale tests at PNL confirmed that attrition was a function of superficial gas velocity to the third power and that attrition was minimal at the minimum fluidization velocity. Zenz (1982) states that fluid catalytic cracking (FCC) catalysts' physical strength decreases as the carbon content increases. In the PDU, secondary catalyst losses are large; however, this may be due to the catalyst continually grinding at the tip of the wood-feed auger.

Catalyst deactivation may occur by carbon buildup, thermal cycling, metal migration, and loss of surface area. Catalysts in the PDU showed relatively rapid deactivation compared to the laboratory-scale tests. The catalyst is exposed to much more thermal cycling in the PDU than the small scale systems. We have seen a large buildup of carbon (about 20 wt%) on deactivated catalyst samples.

Results from one test using the alloy catalyst are tabulated in Table 19. The alloy catalyst has similar effects as the potassium carbonate. Gas yields are essentially the same. Slightly lower methane concentrations are seen with the alloy catalyst. Note that both catalysts decrease the conversion of carbon to liquids.

One potential improvement on the alloy catalyst may be a solution to the deactivation problem. This is to impregnate the catalyst with an alkali carbonate to help reduce carbon deposition.

TABLE 19. Comparison of an Alloy Catalyst Test with an Alkali Carbonate Test and an Uncatalyzed Test

	P17	P16	P18
Catalyst	NiCuMo	16% K_2CO_3	None
Pressure, atm absolute	10	10	10
T, °C	730	745	740
Steam-to-Wood Wt. Ratio	2.2	1.2	1.4
Wood	dense flakes	dense flakes	headrig
Normalized Carbon Conversion, wt%:			
Gas	80	74	65
Solid	20	26	33
Liquid	0.1	<0.5	2
Gas Composition, vol%:			
H_2	56.9	52.6	42.3
CO_2	24.2	24.9	21.2
CH_4	5.7	7.8	17.2
CO	13.1	14.2	18.2
$C_2+C_3+C_4$	0.1	0.5	1.1

Temperature Effect

The tests were restricted to 1380°F (750°C) primarily because carbon conversion to gas decreases with temperature. Higher temperatures are difficult to achieve by indirect heating. High carbon conversion is an important economic factor. Also, alloy catalyst deactivation is more rapid at lower temperatures, as illustrated in some shakedown tests. Methane content increases with lower temperatures, which is undesirable for a methanol synthesis gas.

Steam-to-Wood Ratio

Increasing the steam-to-wood ratio should promote the carbon-steam reaction, the shift reaction, and the steam reforming and cracking reactions. The desired hydrogen to carbon-monoxide ratio is slightly greater than two for methanol synthesis gas. If methane is steam reformed, this stream will provide a H_2:CO ratio of three, so an even smaller ratio would be acceptable from the gasifier.

Atmospheric PDU tests showed that a 0.7 steam-to-wood ratio produced proper product gas compositions. At 10 atm (1000 kPa) absolute pressure the PDU requires excessively high steam rates to fluidize the bed. Therefore, steam-to-wood ratios are usually greater than one and the steam is still diluted with recycle gas. Predictably high H_2:CO ratios are observed. Figure 10 shows the effect of the steam-to-wood ratios in uncatalyzed tests. The effect is probably even greater in catalyzed cases.

Gasifier Energy Requirements

In a physical sense, energy must be supplied to the gasifier to heat the reactants (wood and steam) to the reaction temperature, compensate for heat losses, and sustain the endothermic reactions. Thermodynamically, the process is a state function. Therefore, the heat requirement can be calculated from the standard heat of reaction at 77°F (25°C) and the mass and specific heat of the reaction products. The calculation procedure theoretically involves taking credit for the sensible heat above 77°F (25°C) in the reactants and adding the standard heat of reaction at 77°F (25°C), the heat losses, and the sensible heat needed to heat the products to the gasifier operating temperature.

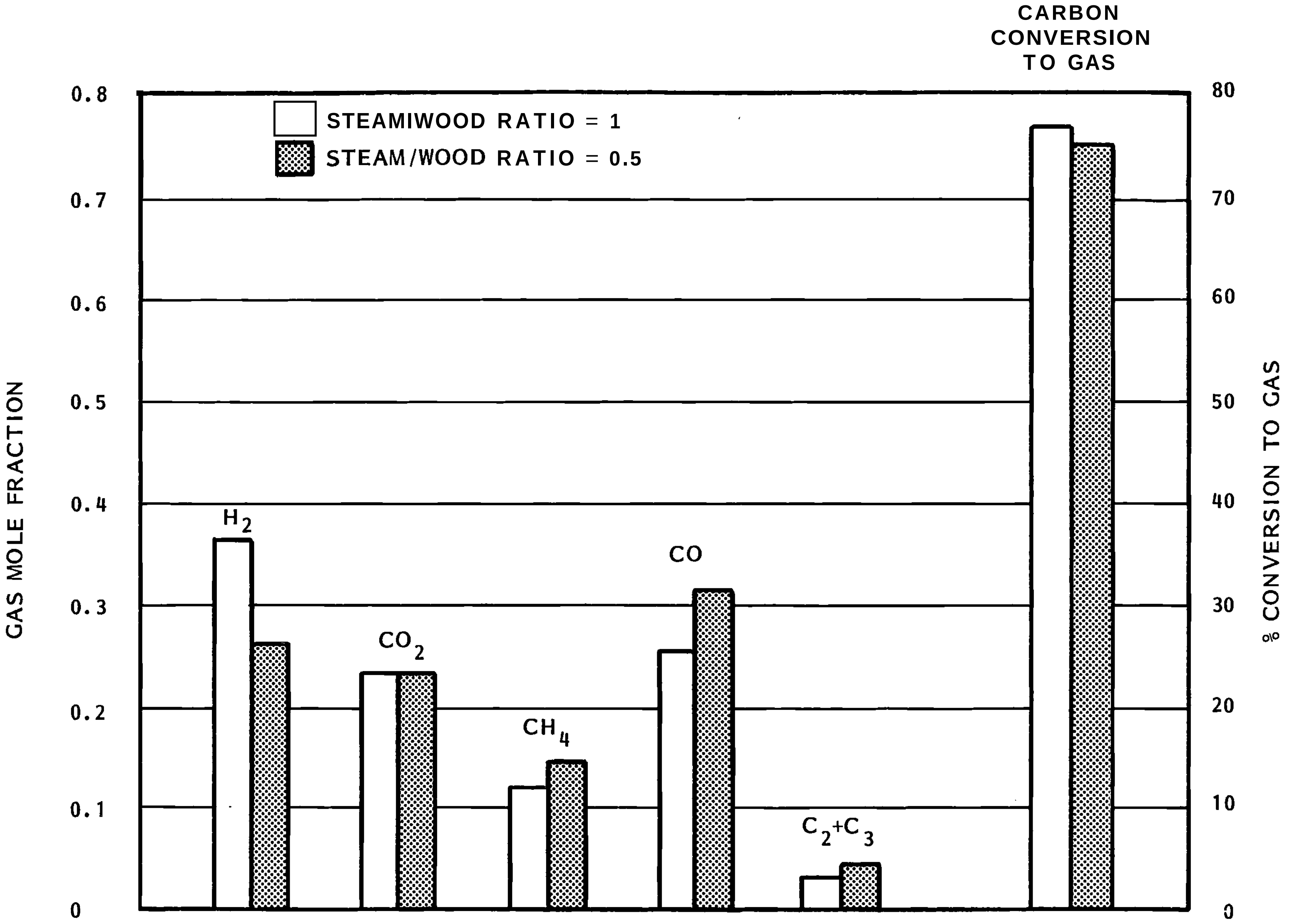


FIGURE 10. Effect of Steam-to-Wood Ratio

The standard heat of reaction at 77°F (25°C) is the difference between the heats of combustion of reactants and products. The higher the potential energy in the products, the more endothermic the reaction. High carbon conversion, high gas yield, and low hydrocarbon yield give a highly endothermic reaction. The reaction is usually endothermic for generation of synthesis gas but can be exothermic for generation of a methane-rich gas. The standard heat of reaction at 77°F (25°C) is positive for an endothermic reaction and negative for an exothermic reaction.

The energy flow for the gasifier is shown schematically in Figure 11. The direction of energy flow for the standard heat of reaction, ΔH°, is from the gasifier for an endothermic reaction and into the gasifier for an exothermic reaction. The required heat input, Q_i (provided by electrical cartridge heaters in the PDU gasifier), is calculated from the following equation:

$$\begin{aligned} Q_i = {} & m_s C_{p_s} (77^{0}F - T_s) + m_f C_{p_f} (77^{0}F - T_f) + m_f \Delta H^{0} \\ & + Q_l + m_p C_{p_p} (T_g - 77^{0}F) + m_c C_{p_c} (T_g - 77^{0}F) \end{aligned} \qquad (1)$$

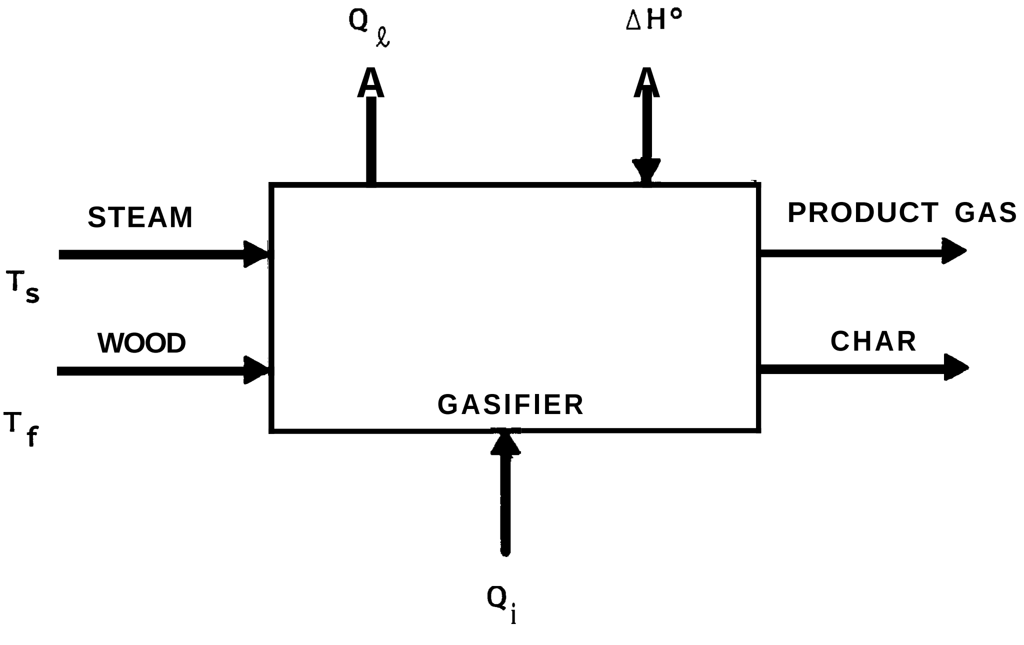


FIGURE 11. Gasifier Energy Flow

where m_s = mass flow rate of steam, lb/hr
m_f = mass flow rate of dry wood, lb/hr
m_p = mass flow rate of product gas, lb/hr
m_c = mass flow rate of char, lb/hr
C_{p_s} = specific heat of steam, Btu/lb °F
C_{p_f} = specific heat of wood, Btu/lb °F
C_{p_p} = average specific heat of product gas, Btu/lb °F
C_{p_c} = specific heat of char, Btu/lb °F
T_s = inlet steam temperature, °F
T_f = inlet wood temperature, °F
T_g = gasifier operating temperature, °F
ΔH° = standard heat of reaction at 77°F (25°C) per unit mass of wood, Btu/lb
Q_l = heat loss from gasifier surface, Btu/hr.

Recycle gas is used to increase bed velocity. The amount of steam that reacts varies from test to test. We assume no steam reacts, wood enters the gasifier at 77°F (25°C), and wood moisture must be heated to the gasifier operating temperature. Although steam does react in the gasifier, we assume no reaction to get a high estimate of the heat requirement. The equation becomes:

$$\begin{aligned} Q_i = {} & m_s C_{p_s} (T_g - T_s) + m_r C_{p_r} (T_g - T_r) + m_f \Delta H^0 \\ & + Q_l + m_p C_{p_p} (T_g - 77^0F) + m_m \Delta H_v \end{aligned} \tag{2}$$

where m_m = mass flow rate of wood moisture into the gasifier, lb/hr
ΔH_v = enthalpy change for water between inlet and outlet conditions, Btu/lb
C_{p_r} = heat capacity of recycle gas, Btu/lb °F
T_r = recycle gas temperature, °F.

The heat loss, Q_l, is calculated from gasifier surface and ambient temperatures using standard heat loss correlations.

Examination of the above equation shows that the gasifier energy requirement, Q_i, can be reduced by several methods. Increasing the inlet steam temperature, T_s, above the gasifier operating temperature, T_g, will produce a net heat input. We were unable to do this with the gas-fired preheater. Also, the wood moisture content should be as low as possible. In a commercial system some energy could be saved by using hot wood at 210°F (100°C) from the wood dryer to feed the gasifier.

The equation is used to find ΔH° for tests P12 to P17. Results are compared with ΔH° calculated by the difference in heats of combustion of reactants and products in Table 20. There is relatively poor correlation in the heat of reaction by the two methods due to the sensitivity of the heat of reaction to heat losses by the first method and to the carbon conversion by the second method. The relative magnitude of the terms in Equation 2 for two catalyzed tests is shown in Table 21. Energy balance results are important design considerations. The required heat input for large gasifier will decrease as a result of lower heat loss per unit weight of wood.

TABLE 20. Standard Heat of Reaction

Test No.	Catalyst	Pressure	ΔH°, Btu/lb Wood Method 1	Method 2
P12	None	10	418	-944
P13	None	10	340	687
P14A	None	1	1305	-444
P14B	None	1	-411	-751
P15	None	5	621	-246
P16	K_2CO_3	10	1039	294
P17	Trimetallic	10	1294	451

Method 1 - calculated from Equation 2.
Method 2 - difference between heat of combustion of reactants and products.

TABLE 21. Value of Terms in Energy Balance Equation

Term	Btu/lb P16	Btu/lb P17
Q_i/m_f	2539	2470
$[m_s C_{p_s}(T_g-T_s) + m_r C_{p_r}(T_g-T_r)]/m_f$	33	0
Q_l/m_f	610	458
$m_p C_{p_p}(T_g-77)/m_f$	702	1039
$m_m \Delta H_v/m_f$	52	21

Heat Transfer Considerations

Electrical cartridge heaters (7 cartridges) are immersed in the fluid bed to provide energy for the PDU gasifier (see Figure 6). A watt-hour meter is used to measure the energy input to the gasifier during a test. Each cartridge heater is 0.75 in. (1.9 cm) in diameter by 11 ft (3.4 m) long with the lower 4 ft (1.2 m) heated by resistance elements.

Overall heat transfer coefficients from the surface of the cartridge heaters to the fluid bed are calculated by the following equation:

$$U_{oa} = \frac{Q_i}{A_e\ (T_e-T_b)}$$

where U_{oa} = overall heat transfer coefficient, Btu/hr-ft^2-°F
Q_i = energy input to the gasifier, Btu/hr (3413 times the kilowatt input)
A_e = heated surface area of seven elements (5.5 ft^2)
T_e = average surface temperature of the elements, °F
T_b = solids temperature in the fluid bed, °F.

All data needed to calculate U_{oa} are recorded for each test. Values obtained for Tests P12 through P22 are plotted against the superficial linear velocity of gases in Figure 12.

The coefficient includes convective, conductive, and radiant heat transfer from the interior element metal surface to the bed solids and gases. These data indicate that a coefficient of 80 Btu/hr-ft^2-°F (1600 kJ/hr-m^2-°K) may be a reasonable, conservative design value for a gasifier operating at similar velocities and temperatures with vertical heater orientation.

ECONOMIC EVALUATIONS

The economics of producing either methane or methanol can be evaluated rapidly for small or large plants. A computer program to do the evaluations was developed for a Radio Shack TRS-80 Model I microcomputer, using a commercially-available software package, VisiCalc.(a) VisiCalc basically generates an electronic sheet of paper containing a grid of columns and rows. The intersecting lines of the columns and rows define position addresses. At each position one can enter an alphabetic title, a number, or a formula to be calculated. The power of VisiCalc is that the computer remembers formulas and calculations used as a problem is solved. If one number on the sheet is changed, VisiCalc automatically recalculates all related numbers from specified formulas. This recalculation feature makes VisiCalc a powerful forecasting tool.

The programs for methane production and methanol production are based on data from the Davy McKee studies for 2000 ton-per-day dry wood plants. Reference data for construction costs of the methane and methanol plants are shown in Tables 22 and 23, respectively. These tables remain as fixed constants for each analysis. The scale factors for each plant segment are those recommended by Davy McKee in their analysis of 200 ton-per-day facilities (Mudge et al. 1981). They are the exponents used in the cost/capacity relationships.

Another set of fixed constants also exists for each program. These are the base case annual raw material and utility requirements for the 2000 ton-per-day facilities. The $/unit values are input items which should be changed with each run to reflect true costs at the time of the analysis.

(a) VisiCalc is a registered trademark of Visicorp Software, Inc. It is available for other microcomputers, also.

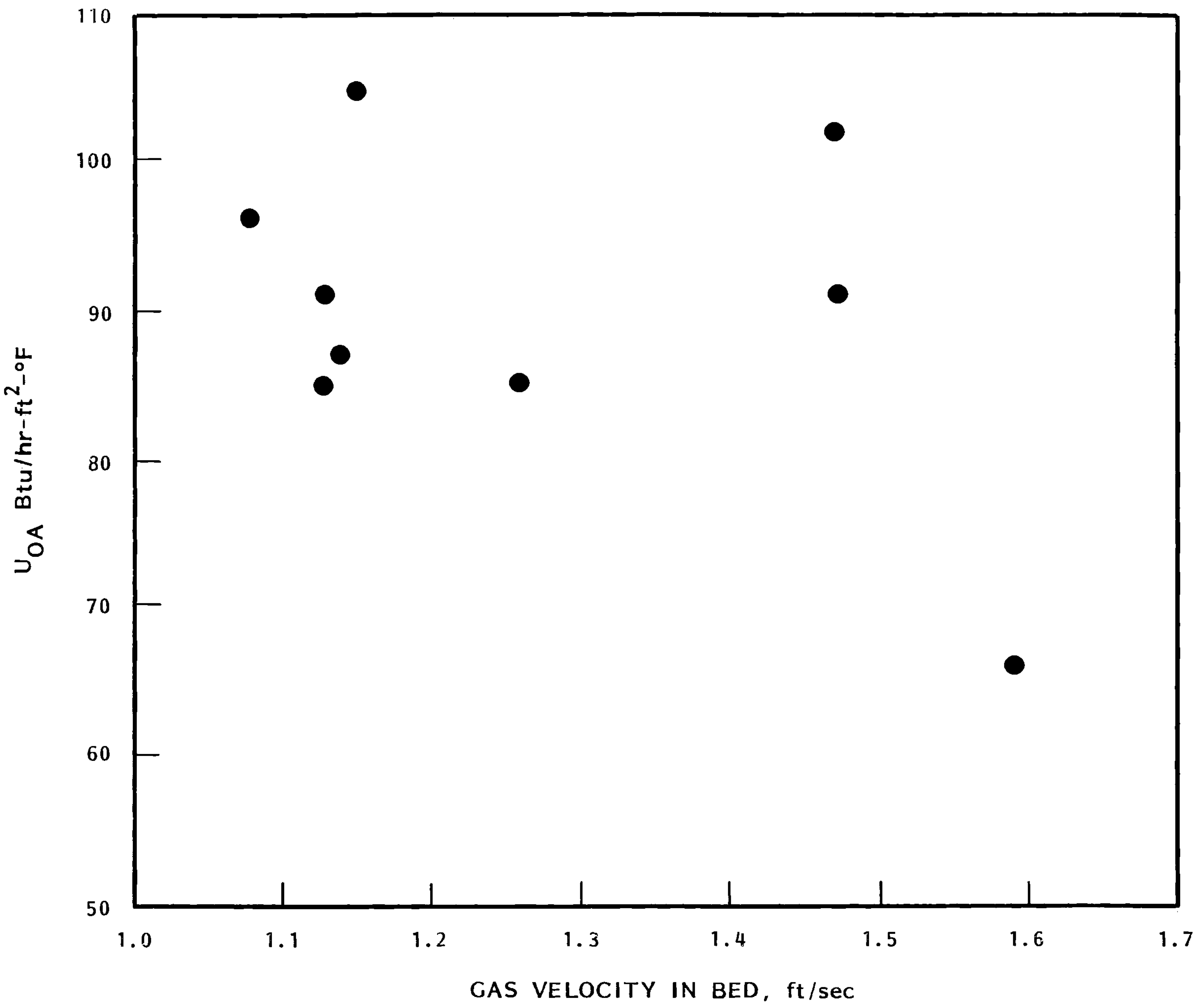


FIGURE 12. Overall Heat Transfer Coefficients

TABLE 22. Reference Case for Methane Production

Capacity (Daily) = 2,000 dry tons
CE Plant CST Index = 266 (Sept. 1980)

Gas **Btu** Yield = 6,810,000 **MMBtu/yr**
Labor Index = 208.7

2,000 TPD Wood to Methane **Newport,** Oregon		Direct PO Material	Subcontract					Direct Hire Labor			Grand	Exp. Scale
			Material,	Labor			Grand					
Code	Description	Total, $	$	Man-hours	Rate	Total $	Total, $	Man-hours	Rate	Total $	Total, $	Factors
					26.96				12.84			
201	Wood Storage & Sizing	1,239	9,598	156.4		4,217	13,815	206.5		2,651	17,705	0.9
202	Wood Drying	0.001	4,730	77.6		2,092	6,822	0.0001		0	6,822	0.6
203	Gasification	8,606	460	30.1		811	1,271	164.2		2,108	11,986	0.75
204	Compression	1,610	22	1.5		40	62	19.8		254	1,927	0.7
205	Shift Conversion	2,309	52	4.1		111	163	41.2		529	3,001	0.65
206	Primary Methanation	1,749	26	1.9		51	77	28.5		366	2,192	0.65
207	Acid Gas Removal	0.0001	1,322	30.5		822	2,144	0.0001		0	2,144	0.5
208	Final Mthn & Gas Drying	2,198	114	3.6		97	211	43.2		555	2,964	0.65
209	Catalyst Regeneration	1,220	17	1.2		32	49	19		244	1,513	0.5
210	Waste Water Treating	463	649	17.3		466	1,115	17.3		222	1,801	0.6
211	Raw Water & Cooling Wtr.	941	727	16.1		434	1,161	29.7		381	2,483	0.6
212	Boilers & BFW System	2,049	3,222	42.3		1,140	4,362	68.2		876	7,287	0.6
213	**Misc.** Utility Systems	1,219	52	2		54	106	46.9		602	1,927	0.65
	TOTAL	23,603	20.991	384.6		10,369	31,360	684.50		8,789	63,752	

TABLE 23. Reference Case for Methanol Production

Capacity (Daily) = 2.000 dry tons
CE Plant CST Index = 266 (Sept. 1980)

MeOH Yield = 98,810,000 gal/yr
Labor Index = 208.7

2.000 TPD Wood to Methanol Newport, Oregon		Direct PO Material Total, $	Subcontract					Direct Hire Labor			Grand Total, $	Exp. Scale Factors
			Material, $	Labor			Grand Total, $					
Code	Description			Man-hours	Rate	Total $		Man-hours	Rate	Total $		
					26.96				12.84			
101	Wood Storage & Sizing	1,239	9,598	156.4		4,216	13,814	206.5		2,651	17,704	0.9
102	Wood Drying	0.001	4,730	77.6		2,091	6,821	0.0001		0	6,821	0.99
103	Gasification	12,090	1,322	56		1.509	2.831	231.2		2.968	17,889	0.85
104	Shift Conversion	651	15	1.3		34	49	11.7		150	850	0.65
105	Acid Gas Removal	0.001	2,914	60.3		1,625	4,539	0.0001		0	4,539	0.6
106	Compression	4,459	58	3.8		102	160	61.8		793	5,412	0.7
107	MeOH Syn. & Distillation	15,038	0.0001	0.0001		0	0				15,038	0.42
108	Purge Gas Reforming	766	25	2.2		59	84	8.6		109	959	0.6
109	Waste Water Treating	642	1,255	17.6		475	1,730	28.1		361	2,733	0.6
110	Raw Water Treatment & Cooling Water	1,072	587	10.9		293	880	28.4		364	2,316	0.6
111	Boilers & BFW System	1,154	2,275	30.8		830	3,105	44.3		569	4,828	0.6
112	Misc. Utility Systems	891	29	1.4		38	67	34.7		447	1,405	0.65
113	Storing and Loading-Product & Utilities	175	935	12		323	1,258	9.2		118	1,551	0.6
	TOTAL	38,177	23,743	430.3001		11,595	35,338	664.5		8,530	82,045	

Several kinds of analyses can be done with these programs:

- Simple scaling to another plant capacity
- Scaling to another plant capacity and updated dollars
- Scaling, but changing base-case constants also
- Estimating capital for different plant configurations (standalone versus coupled to existing facilities).

The base-case data (2000 ton/day) are considered accurate to ±25%. Additional uncertainties in some of the scaling factors would reduce the accuracy of estimates from these programs to ±30-40%.

An explanation of typical input requirements and examples of selected outputs follows.

Simple Scaling to Another Plant Capacity

Only one data item needs to be changed. A new plant capacity is entered, then all costs are scaled accordingly and a price for methanol (or methane) is computed. The costs remain in September 1980 dollars, which is the base case month and year. This provides a rapid way of seeing relative trends in price of product as a function of plant capacity. Actual costs for any given capacity will, of course, be low.

Scaling to Another Plant Capacity and Update Dollars

Input data required here are: (a) new plant capacity, (b) *Chemical Engineering* plant cost index for month of interest, (c) *Chemical Engineering* labor cost index for month of interest, and (d) current utility and raw material unit costs. The program then scales costs based on size, but also escalates equipment and labor costs using plant and labor index ratios from *Chemical Engineering* magazine. The index values for September 1980 are part of the fixed constants tables.

For this option, the dollar figures generated are realistic and should provide a basis for decision making. The first time this option is selected, items (a) through (d) must be entered. After that, only item (a) need be changed to calculate and observe the effect of plant capacity on product cost in today's dollars.

Scaling, But Changing Base Constants Also

This option allows a great deal of flexibility in analysis of the plants. Normally, all the data inputs shown in Option 2 are also required here. Other input changes provide additional economic information. The approximate effect of high yields is estimated by simply changing the base yield figure. [If the yield (or gas composition change) affects equipment sizing significantly, new base cost figures in appropriate plant sections are required.] If only one section of the plant is to take on a new configuration, its cost is estimated for the size plant of interest and inserted in the Grand Total column of the worksheet.

Default values for rate of return and interest on debt are 15% and 10% for utility financing. These can be changed easily to reflect current money values.

Estimating Capital for Different Plant Configurations

When a biomass gasification facility is to be built as an addition to another wood processing facility, savings will result in both capital and operating expenses. Actual amounts are very site-specific. The programs developed here are useful in comparing relative merits of several options. As the plant configuration deviates more and more from the base-case, the absolute numbers generated become less and less reliable. Still, the program quickly shows sensitivity of product costs to changes either in capital, operating costs, or both.

Additional (beyond that required for Option 2) input data for this option could be as little as changing one figure in the base constants. It could also be as complicated as changing nearly all the direct cost entries for the various plant sections. Getting the new cost figures for completely new plant configurations is beyond the capability of these programs. The totally revised figures would have to come from other cost estimating sources. If that amount of effort is required, the real utility of these programs is questionable.

Effect of Yield Changes

The justification for writing this program was to be able to compare real experimental data taken at 10 atm (1000 kPa) absolute pressure with that used by Davy McKee in their economic studies. The data used by Davy McKee were really extrapolated from atmospheric tests using equilibrium data to predict the high pressure yields. Now real experimental data exist, and yields look better than those predicted earlier.

Using the VisiCalc program and experimental data from Test P17 (shown in Table 24 with data used by Davy McKee), we projected new methanol costs for three different assumptions:

1. Methanol yields were 20% higher than those used by Davy McKee but capital requirements remained the same. (This figure was chosen because dry gas yields really were about 20% higher than those given to Davy McKee. Compositions differed some, as shown in Table 24.)
2. Methanol yields were 50% higher than those used by Davy McKee but equipment costs were significantly higher.
3. Methanol yields were 50% higher than those used by Davy McKee but equipment costs remained the same.

The primary change in the economic picture for all the cases is due to increased revenue from the additional methanol. The 50% figure for Cases 2 and 3 was arrived at by assuming all the carbon in the gases could be converted to methanol by suitable shifting and reforming. As a practical matter this is unrealistic, but does place a lower bound on the methanol price. Case 3 was simple to run but is the least realistic of the three. In Case 2 new equipment costs were estimated because of the additional shifting and reforming required. Appropriate operating costs were also adjusted. The total capital required increased by 25% and total gross operating costs increased by 15%. All three

TABLE 24. Plant Design Bases

	Davy McKee	PDU Data (Test P17)
Temperature, °C	750	730
Pressure, atm absolute	10	10
Steam Rate, wt/wt Dry Wood	0.75	2.2(a)
Char Yield, wt/wt MAF Wood	0.15(b)	0.1
Char Heating Value, Btu/lb	14,000	13,200
Wet Gas Yield, wt/wt MAF Wood	1.6	3.1
Cold Gas Efficiency, %(c)	88	95
Gas Composition, vol%		
	28.7	56.4
H_2	36.6	24.8
CH_4	4.0	2.5
CO_2	12.4	10.6
CO	18.3	5.7
Lb moles (H_2+CO)/ton MAF Wood	103(d)	109(d)
Wood Composition, wt%		
C	46.50	50.3
H	5.87	6.6
O	41.99	42.5
Ash	5.64	0.6
Btu/lb	8,710	8,770

(a) Extra steam needed to maintain fluidization.
(b) Includes ash from high ash feed.
(c) Combustible energy in a unit of product gas divided by the energy in the wood needed to generate that unit of gas times 100.
(d) Does not include CH_4, which is slightly higher in PDU data.

cases still used September 1980 dollars and assumed a $20/dry ton cost for wood, as did Davy McKee. For comparison, the methanol costs ($/gal) were:

	Utility Financing	Equity Financing
Davy McKee Base Case	0.55	0.69
Case 1	0.47	0.60
Case 2	0.42	0.54
Case 3	0.37	0.46

All comparisons used the same assumptions for cost of borrowed capital and required rate of return (Mudge et al. 1981).

A similar comparison was to be completed for methane production. Unfortunately, none of the high pressure tests were completed with the goal of producing high methane. Some uncatalyzed tests gave high methane product gases, but potential methane yields were slightly lower than those used by Davy McKee. A good methane-forming catalyst with long life was not found, so it could not be tested.

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APPENDIX

TEST SUMMARIES

Following are summaries of Tests P12 through P21. Three sheets of information and one page of temperature profiles are generated for each test. Most of the terms from the computer output need no further explanation. The following list is a key to terms that may need further definition.

BED - solids from the reactor

BED GAS VELOCITY - superficial linear velocity in ft/sec at reactor conditions

BURNER TRAP - condensate liquid collected from the product gas downstream from the demister

CART HEAT COEFF - overall heat transfer coefficient from heaters in Btu/hr-ft^2-°F

CCHAR - char from the cyclone, also called CYCLONE SOLIDS

DRY MOL WT - molecular weight of the dry product gas

FCHAR - char from the filter; also called FILTER SOLIDS

METHANOL #/# WOOD - total possible yield in lb methanol/lb dry wood if (1) all H_2+CO were converted and (2) if all H_2+CO+CH_4 were converted

N2-02 FREE MW - molecular weight of dry, O_2-N_2 free product gas

RECYCLE - refers to the recycle gas stream

STANDARD HT OF RX - standard heat of reaction in Btu/lb dry wood

STEAM - refers to steam from generator; heated to reactor inlet temperature in the gas preheater

TAR - tars from the demister

TOC-DEMISTER (PPM) - total organic carbon in the demister liquid (aqueous) in ppm by weight

WET MOL WT - molecular weight of product gas saturated with water (used to calculate flow rate)

WT FRAC CAT-CCHAR - weight fraction of catalyst in the cyclone char

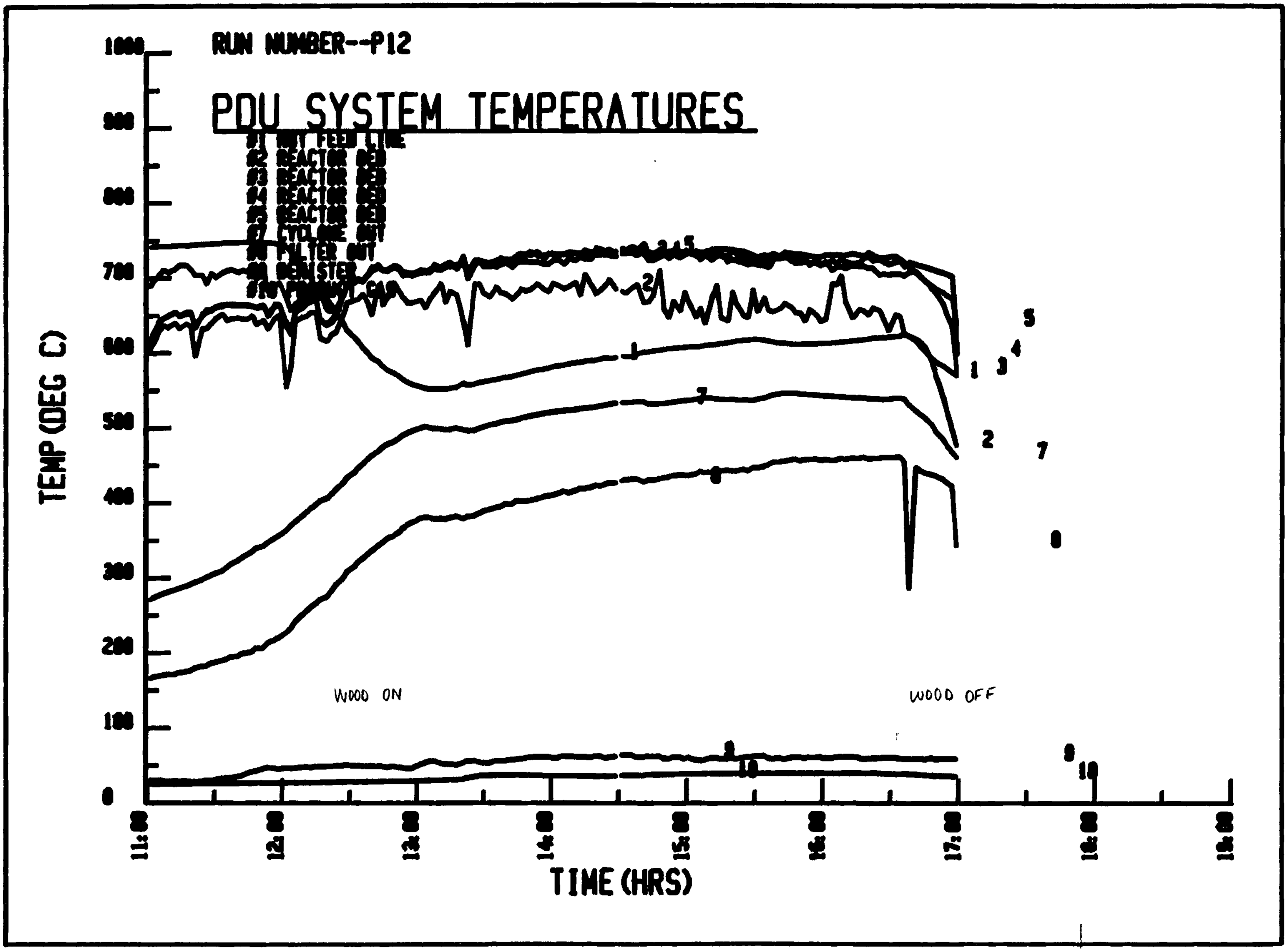
WT FRAC CAT-FCHAR - weight fraction of catalyst in the filter char

YH20 - mole fraction of water determined by assuming saturation in the gas stream

```
RUN#:  P12                          TIME: 1500
DATE: 090182                       TOTAL RUN TIME(HRS) :4.2
WOOD TYPE: HEADRIG                 CATALYST: DEACTIVATED NICUMO

**PRODUCT GAS COMPOSITIONS**
       (MOLE FRACS)
                        N2,O2 FREE
H2                       .262
CO2        .349          .388
C2H4       .003          .003
C2H6       .013          .014
O2         .004         0.000
N2         .095         0.000
CH4        .195          .217
CO         .101          .112
C3H6       .000          .000
C3H8       .000          .000
YH2O       .069          .069


**TEMPERATURES**
     (DEG C)

REACTOR INLET   h08
CATALYST BED    735
REACTOR OUTLET  690
STEAM           183
CARTRIDGE HTRS  815
PRODUCT METER   39
DEMISTER        59


**DIFFERENTIAL PRESSURES**

PRODUCT 4.8 IN H2O
STEAM   55 IN H2O
RECYCLE 5 IN H2O


**ORIFICE SIZES AND CONSTANTS**

ORIFICE     K     SIZE
....................
PRODUCT   1[illegible]    .50
STEAM      32.0     .30
RECYCLE   116.0     .50


**PRESSURES**
   (PSIG)

STEAM      145
DEMISTER   145
REACTOR    135
PRODUCT    0

#/HR CYCLONE    1.9
#/HR FILTER     1.2
#/HR TAR        .1
```

```
**     SOLIDS     **
IS  COMPOSITIONS  **

.............................................................
              CARBON     HYDROGEN     OXYGEN        ASH      MOISTURE
-------------------------------------------------------------------------


WOOD          .472        .059        .456        .013        .042
CCHAR         .805        .016        .149        .030        .059
FCHAR         .910        .016        .044        .030        .010
BED           .820        .030        .130        .020       0.000
'TAR          .840        .030        .130       0.000       0.000


**HEATS OF COMBUSTION**

WOOD               8300
SYCLONE CHAR      12630
FILTER CHAR       13460
BED               10000
TAR               15000

                       *******************************
                       ***      INPUT STREAMS      ***
                       *******************************


                                  TOTAL        CARBON       HYDROGEN      OXYGEN          ASH
..........................................................................
WOOD (DRY)                        30.36        14.33          1.79        13.84           .39
WOOD MOISTURE                      1.54         0.00           .15         1.19          0.00
STEAM                            104.64         0.00         11.65        93.02          0.00
..........................................................................
TOTAL  INPUTS                    136.34        14.33         13.57       108.05           .39


                       *******************************
                       ***     OUTPUT  STREAMS     ***
                       *******************************


                                  TOTAL        CARBON       HYDROGEN      OXYGEN          ASH
-------------------------------------------------------------------------------------

DRYGASES                          26. 04        9.52          1.59        15.09          0.00
MOISTURE  I N  PRODUCT             1.56         0.00           .17         1.39          0.00
CYCLONE  SOLIDS                    1.90         1.34           .03          .25           .05
FILTER  SOLIDS                     1.30         1.02           .02          .05           .03
BED  BUILDUP                       1.41         1.04           .04          .17           .17
DEMISTER  LIQUIDS                 95.00          .23         10.56        84.44          0.00
DEMISTER  TAR                       .10          .08           .00          .01          0.00
BURNER  TRAP                       4.29          .01           .49         3.81          0.00
..........................................................................
TOTAL  UUTPUTS                   131.50        13.25         12. 87       105.21           .25
```

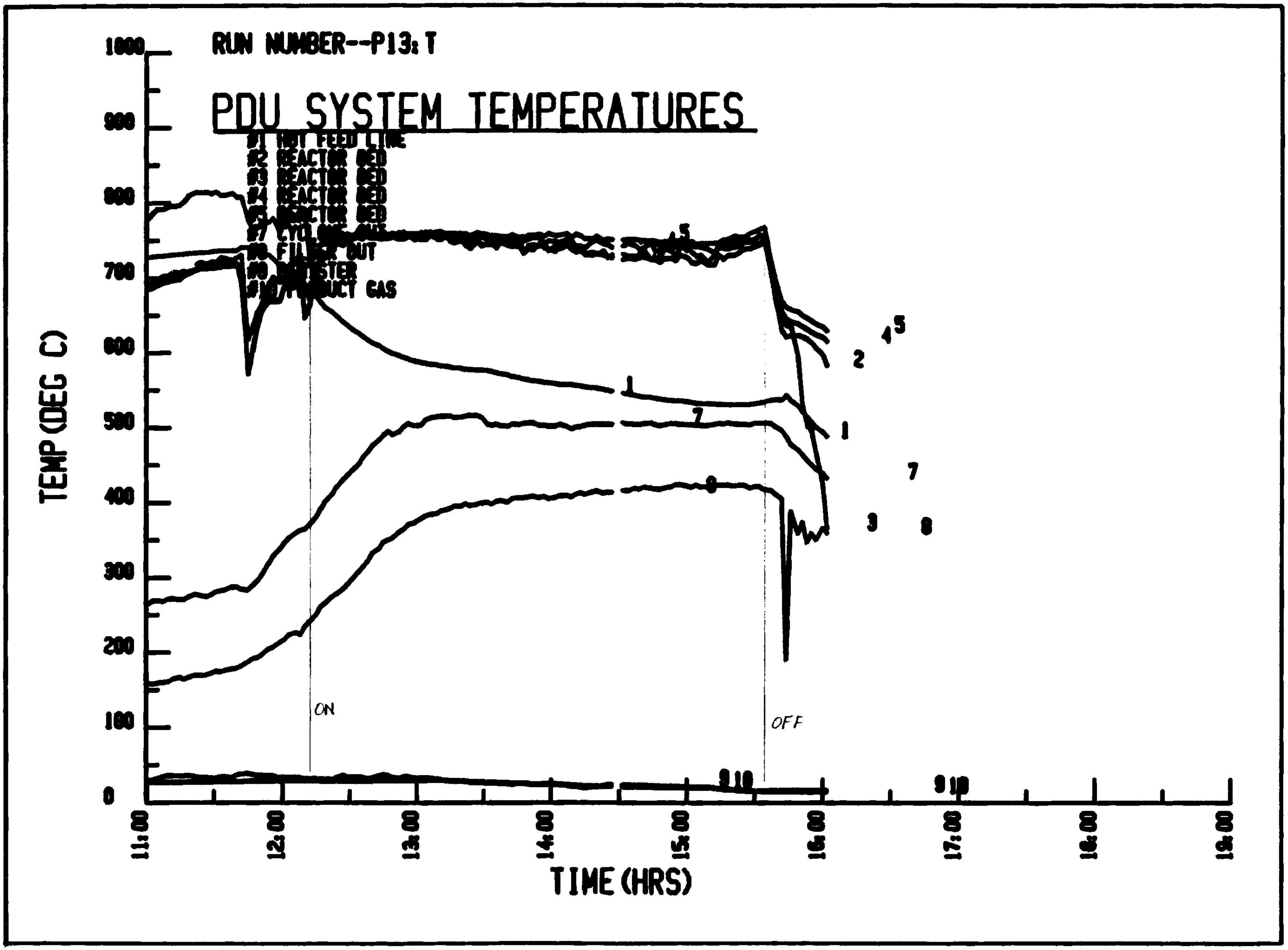
```
******************************
** PRODUCT GAS (N2-02 FREE) **
******************************

SCFM(DRY)               7.27
LB GAS/LB DRY WOOD       .86
INST SCF/# DRY WOOD    13.12
AVG SCF/# DRY WOOD     13.44

TOTAL FLOW(SCF)      1711.64

TOTAL WOOD FED        127.37
YH20 AT PRODUCT          .07
YH20 AT REACTOR OUT      .84
BTU/SCF               371.96


*************************
**MISCELLANEOUS TIDBITS**
*************************

WT FRAC CAT-CCHAR        .13
WT FRAC CAT-FCHAR        .07
#CAT LOSS THIS RUN       .32

TOC-DEMISTER(PPM)    2466.00

STEAM/WOOD RATIO        3.45

DRY MOL WT             25.10
WET MOL WT             24.61
N2-02 FREE MW          24.77

ELEC INPUT(KW)         21.86
(based on 7 elements)
KWHR/LB DRY WOOD         .62
ELECTRIC BTU/LB DRY  2106.87


**CONVERSIONS & BALANCES**
HEAT GAS/HEAT WOOD       .59
GAS BTUS/LE WOOD    4882

CARBON CONVERSION
-----------------
TO GAS(%)              66.45
TO SOLID(%)            23.73
TO LIQUID(%)            2.30
SUM CONVERSIONS        92.47

METHANOL #/#WOOD .14251813243 TO .327434200192


**DESIGN INFORMATION**

BED GAS VELOCITY        1.13
CART HEAT COEFF        94.31
STANDARD HT OF <X    -944.70
```


RUN NUMBER--P12
PDU SYSTEM TEMPERATURES
#1 HOT FEED LINE
#2 REACTOR BED
#3 REACTOR BED
#4 REACTOR BED
#5 REACTOR BED
#7 CYCLONE OUT
#8 FILTER OUT
#9 DEMISTER
#10 PRODUCT GAS
TEMP (DEG C)
1000
900
800
700
600
500
400
300
200
100
0
TIME (HRS)
11:00
12:00
13:00
14:00
15:00
16:00
17:00
18:00
19:00
WOOD ON
WOOD OFF
1
2
3
4
5
7
8
9
10

```
RUN#: P13                         TIME: 13:00
DATE:  090982                    TOTAL RUN TIME(HRS) :3.5
WOOD TYPE:  HEADRIG              CATALYST:  Deactivated NICUMO

**PRODUCT GAS UOMPOSITIONSYX
       (MOLE FRACS)
                         N2,02 FREE
H2        .319        .[illegible]
CO2       .314        .327
C2H4      .003        .003
C2H6      .013        .013
O2        .004       0.000
N2        .035       0.000
CH4       .198        .206
CO        .114        .119
C3H6      .000        .000
C3H8     0.000       0.000
YH2O      .017        .017


**TEMPERATURES**
     (DEG C)

REACTOR INLET   531
CATALYST BED    730
KEACTOR OUTLET  700
STEAM           182
CARTRIDGE HTRS  850
PEODUCT METER   15
DEMLSTER        17


**DIFFERENTIAL PRESSURES**

PRODUCT 5 IN H2O
STEAM   15 IN H2O
EECYCLE 10 IN H2O


**ORIFICE SIZES AND CONSTANTS**

ORIFICE     K     SIZE
.....................
PRODUCT    11[illegible]9.    .50
STEAM       32.0     .30
FECYCLE    116.0     .50


**PRESSURES**
   iPSIG)

STEAM      140
DEMISTER   140
REACTOR    135
PRODUCT    0

#/HR CYCLONE    2.5
#/HR FILTER     .5
#/HR TAR        .14
```

```
**      SOLIDS      **
** COMPOSITIONS **

.....................................................
            CARBON     HYDROGEN     OXYGEN        ASH      MOISTURE
.....................................................

WOOD          .450        .060        .480        ,010        .100
CCHAR         .820        .030        .048        .030       0.000
FCHAR         .820        .030        .075        .030       0.000
BED           .820        .030        .130        .020       0.000
TAR           .840        .030        .130       0.000       0.000

**HEATS OF COMBUSTION**

WOOD              8300
CYCLONE CHAR     12500
FILTER CHAR      13500
BED              10000
TAR              15000

                        ******************************
                        ***      INPUT STREAMS      ***
                        ******************************

                               TOTAL       CARBON     HYDROGEN      OXYGEN         ASH
..............................................................
WOOD(DRY)                      34.65        15.59        2.08        16.63         .35
WOOD MOISTURE                   3.85         0.00         .43         3.42        0,00
STEAM                          53.84         0.00        5.98        47.86        0.00
--------------------------------------------------------------------------------------
TOTAL INPUTS                   92.34        15.59        8.49        67.92         .35

                        ******************************
                        ***      OUTPUT STREAMS     ***
                        ******************************

                               TOTAL       CARBON     HYDROGEN      OXYGEN         ASH
--------------------------------------------------------------------------------------
DRYGASES                       29.29        10.86        2.09        16.50        0.00
MOISTURE IN PRODUCT              .42         0.00         .05          .38        0.00
CYCLONE SOLIDS                  2.50         1.95         .07          .11         .07
FILTER SOLIDS                    .50          .41         .01          .04         .01
EED BUILDUP                     1.25          .93         .03          .15         .15
DEMISTER LIQUIDS               60.00          .15        6.67        53.33        0.00
DEMISTER TAR                     .14          .12         .00          .02        0.00
BURNER TRAP                     0.00         0.00        0.00         0.00        0.00
..............................................................
TOTAL OUTPUTS                  04.11        14.41        8.93        70.53         .93
```

```
******************************
** PRODUCT GAS (N2-O2 FREE) **
******************************

SCFM(DRY)                a. 65
LB GAS/LB DRY WOOD         .85
INST SCF/# DRY WOOD     14.46
AVG SCF/# DRY WOOD      12.97

'TOTAL FLOW(SCF)      1634.37

TOTAL WOOD FED         126.00
YH2O AT PRODUCT           .02
YH2O AT REACTOR OUT      .72
BTU/SCF                380.95


*************************
**MISCELLANEOUS TIDBITS**
*************************

WT FRAC CAT-CCHAR         .05
WT FRAC CAT-FCHAR         .01
#CAT LOSS THIS RUN        .13

TOC-DEMISTER(PPM)     2500.00

STEAM/WOOD RATIO         1.55

DRY MOL WT              22.40
WET NOL WT              22.33
N2-O2 FREE MW           22.16

ELEC INPUT(KW)          26.02
(based on 7 elements)
KWHR/LB DRY WOOD         .64
ELECTRIC BTU/LB DRY  2197.18


**CONVERSIONS & BALANCES**
HEAT GAS/HEAT WOOD        .66
GAS BTUS/LB WOOD     5507

CARBON CONVERSION
-----------------

TO GAS)                 67.64
TO SOLID(%)             21.03
TO LIQUID(%)             1.72
SUM CONVERSIONS         92.39

METHANOL #/#WOOD .164517764576 TO .334130772439


**DESIGN INFORMATION**

BED GAS VELOCITY         1.08
CART HEAT COEFF         74.83
STANDARD HT OF RX     -686.74
```


RUN NUMBER--P13:T
PDU SYSTEM TEMPERATURES
#1 HOT FEED LINE
#2 REACTOR BED
#3 REACTOR BED
#4 REACTOR BED
#5 REACTOR BED
#7 CYCLONE OUT
#8 FILTER OUT
#9 CANISTER
#10 PRODUCT GAS
TEMP (DEG C)
1000
900
800
700
600
500
400
300
200
100
0
TIME (HRS)
11:00
12:00
13:00
14:00
15:00
16:00
17:00
18:00
19:00
ON
OFF
1
2
3
4
5
7
8
9
10

```
RUN#:  P14A                        TIME: 13:00
DATE:  09168A                   TOTAL RUN TIME(HRS) :2.5
WOOD TYPE:  HEADRIG             CATALYST:  DEACT NICUMO

**PRODUCT GAS COMPOSITIONS**
       (MOLE FRACS)
                          N2,02 FREE
H2          .344        .356
            .333        .230
C2H4        .021        .022
C2H6        .004        .004
02          .004       0.000
N2          .028       0.000
CH4         .123        .127
CO          .250        .259
C3H6       0.000       0.000
C3H8        .003        .003
YHZO        .020        .020


**TEMPERATURES**
     (DEG C)

REACTOR INLET   713
CATALYST BED    745
KEACTOR OUTLET  652
STEAM           111
CARTRIDGE HTRS  810
PRODUCT METER   18
DEM[illegible]STER        38


**DIFFERENTIAL PRESSURES**

PRODUCT 2.8  IN H20
STEAM   26 IN H20
RECYCLE 0 IN H20


**ORIFICE SIZES AND CONSTANTS**

ORIFICE    K     SIZE
..................
PRODUCT   110.9    .50
STEAM      32.0    .30
RECYCLE   116.0    .50


**PRESSURES**
   (PSIG)

STEAM      1
DEMISTER   1
REACTOR    1
PRODUCT    0

#/HR CYCLONE    1.59
#/HR FILTER     .56
#/HR TAR        .61
```

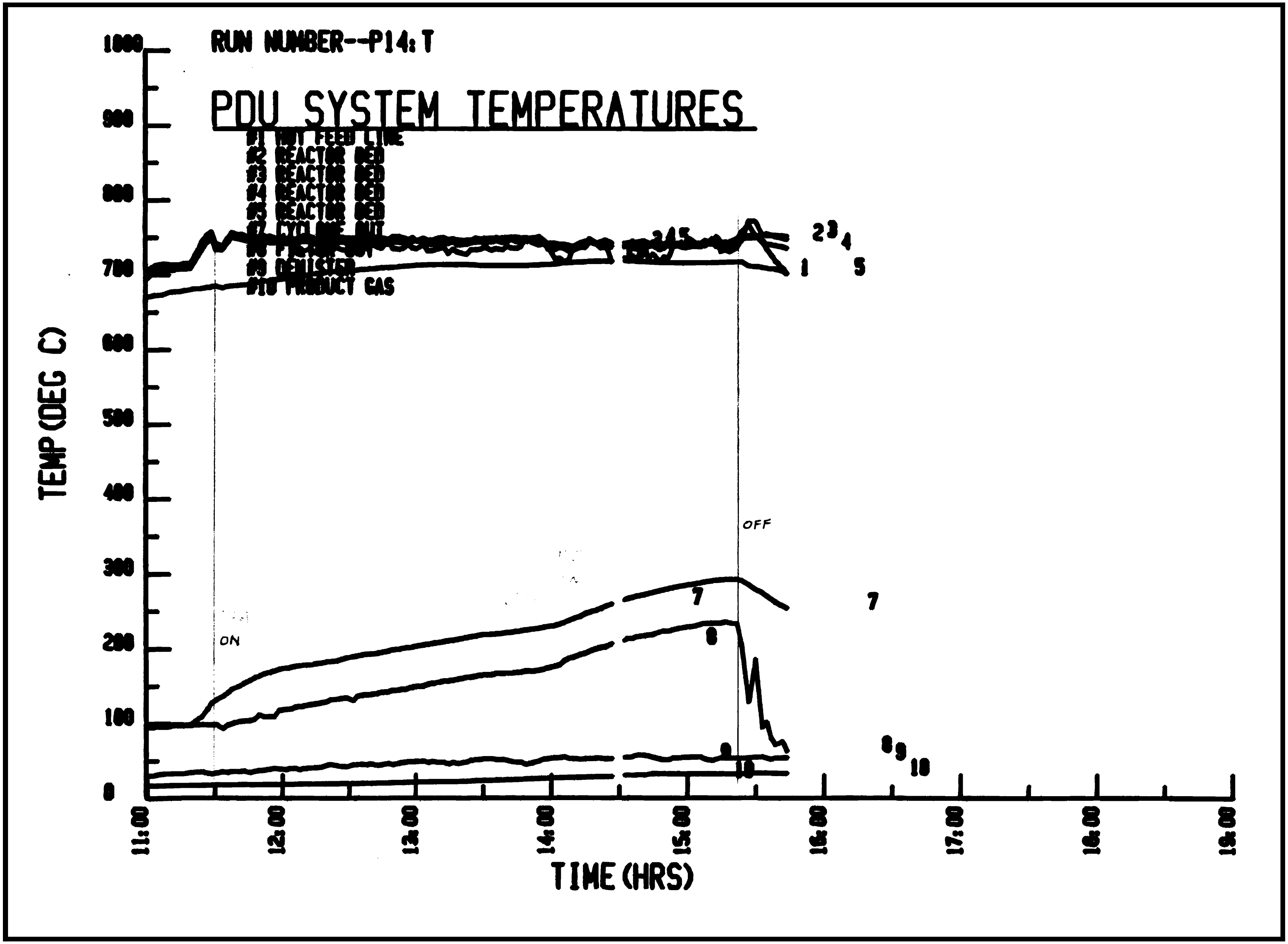
```
**    SOLIDS    **
** COMPOSITIONS **

.....................................................
          CARFON   HYDROGEN   OXYGEN     ASH    MOISTURE
.....................................................

WOOD        .470      .062      .462      .006      .048
CCHAR       .876      .012      .082      .030     0.000
FCHAR       .887      .016      .062      .035      .021
BED         .820      .030      .130      .020     0.000
TAR         .840      .030      .130      .001     0.000

**HEATS OF COMBUSTION**

WOOD            8425
CYCLONE CHAR   13914
FILTER CHAR    14100
BED            10000
TAR            15000

                   ********************************
                   ***     INPUT STREAMS        ***
                   ********************************

                          TOTAL     CARBON    HYDROGEN    OXYGEN      ASH
.......................................................................
WOOD!DRY )                23.14     10.87       1.44       10.69       .14
WOOD MOISTURE              1.16      0.00        .13        1.03      0.00
STEAM                     24.58      0.00       2.73       21.85      0.00
.......................................................................
TOTAL INPUTS              48.88     10.87       4.30       33.58       .14

                   ********************************
                   ***     OUTPUT STREAMS       ***
                   ********************************

                          TOTAL     CARBON    HYDROGEN    OXYGEN      ASH
-----------------------------------------------------------------------------
DRYGASES                  21.26      8.23       1.38       11.78      0.00
MOISTURE IN PRODUCT         .39      0.00        .04         .35      0.00
CYCLONE SOLIDS             1.59      1.32        .02         .12       .05
FILTER SOLIDS               .56       .50        .01         .03       .02
EED BUILDUP                0.00      0.00       0.00        0.00      0.00
DEMISTER LIQUIDS          31.60       .21       3.51       28.09      0.00
DEMISTEH TAR                .61       .51        .02         .08      0.00
BURNER TRAP                1.00       .01        .11         .89      0.00
.......................................................................
TOTAL OUTPUTS             57.01     10.79       5.09       41.35       .06
```

```
******************************
** PRODUCT GAS (N2-O2 FREE) **
******************************

SCFM(DRY)                  6.59
LE GAS/LB DRY WOOD          .92
INST SCF/# DRY WOOD       16.62
AVG SCF/# DRY WOOD        16.42

TOTAL FLOW(SCF)         1016.37

TOTAL WOOD FED            61.89
YH2O AT PRODUCT             .02
YH2O AT REACTOR OUT         .65
BTU/SCF                  375.40


*************************
**MISCELLANEOUS TIDBITS**
*************************

WT FRAC CAT-CCHAR           .05
WT FRAC CAT-FCHAR          0.00
#CAT LOSS THIS RUN          .08

TOC-DEMISTER(PPM)       6800.00

STEAM/WOOD RATIO           1.06

DRY MOL WT                21.20
WET MOL WT                21.13
N2-O2 FREE MW             20.96

ELEC INPUT(KW)            17.50
(based on 7 elements)
KWHR/LB DRY WOOD            .65
ELECTRIC BTU/LB DRY     2213.20


**CONVERSIONS & BALANCES**
HEAT GAS/HEAT WOOD          .74
GAS BTUS/LB WOOD      6239

CARBON CONVERSION
-----------------

TO GAS(%)                 75.78
TO SOLID(%)               16.75
TO LIQUID(%)               6.76
SUM CONVERSIONS           99.29

METHANOL #/#WOOD .283895321577 TO .416496235051


**DESIGN INFORMATION**

BED GAS VELOCITY           1.47
CART HEAT COEFF           92.93
STANDARD HT' OF RX      -444.38
```

```
RUN#: P14B                        TIME:  15:00
DATE: 09168B                    TOTAL RUN TIME(HRS) :1.42
WOOD TYPE:  HEADRIG             CATALYST:  DEAC NICUMO

**PRODUCT GAS COMPOSITIONSSS
       (MOLE FRACS)
                      N2,O2 FREE
HZ         .270        .272
CO2        .228        .230
C2H4       .025        .025
C2H6       .006        .006
O2         .001       0.000
N2         .006       0.000
CH4        .147        .148
CO         .308        .310
C3H6       .004        .004
C3H8       .005        .005
YHZO       .020        .020


**TEMPERATURES**
     (DEG C)

REACTOR INLET   716
CATALYST BED    743
REACTOR OUTLET  652
STEAM           111
CARTRIDGE HTRS  810
PRODUCT METER   18
DEMISTER        38


**DIFFERENTIAL PRESSURES**

PRODUCT 7.2  IN H2O
STEAM   26  IN H2O
RECYCLE 0  IN H2O


**ORIFICE SIZES AND CONSTANTS**

ORIFICE     K     SIZE
--------------------
PRODUCT   110.9     .50
STEAM      32.0     .30
RECYCLE   116.0     .50


**PRESSURES**
   (PSIG)

STEAM      1
DEMISTER   1
REACTOR    1
PRODUCT    0

#/HR CYCLONE    3.18
#/HR FILTER     1.12
#/HR TAR        1.22
```

```
**     SOLIDS      **
** COMPOSITIONS **

..........................................................
             CARBON    HYDROGEN    OXYGEN      ASH     MOISTURE
----------------------------------------------------------------------

WOOD          .470       .062       .462       .006       .048
CCHAR         .876       .012       .082       .030       .050
FCHAR         .887       .015       .063       .035       .021
BED           .820       .030       .130       .020      0.000
TAR           .840       .030       .130       .001      0.000


**HEATS OF COMBUSTION**

WOOD               8425
CYCLONE CHAR      13914
FILTER CHAR       14100
BED               10000
TAR               15000


                          ********************************
                          ***     INPUT STREAMS        ***
                          ********************************

                                  TOTAL      CARBON     HYDROGEN     OXYGEN       ASH
...............................................................................
WOOD (DRY)                        46.37      21.78        2.88       21.43        .28
WOOD MOISTURE                      2.33       0.00         .26        2.07       0.00
STEAM                             24.58       0.00        2.73       21.85       0.00
...............................................................................
TOTAL INPUTS                      73.28      21.78        5.87       45.35        .28


                          ********************************
                          ***     OUTPUT STREAMS       ***
                          ********************************

                                  TOTAL      CARBON     HYDROGEN     OXYGEN       ASH
------------------------------------------------------------------------------------
DRYGASES                          36.81      14.93        2.14       19.81       0.00
MOISTURE IN PRODUCT                 .61       0.00         .07         .54       0.00
CYCLONE SOLIDS                     3.18       2.65         .04         .25        .09
FILTER SOLIDS                      1.12        .99         .02         .07        .04
BED BUILDUP                        0.00       0.00        0.00        0.00       0.00
DEMISTER LIQUIDS                  31.60        .24        3.51       28.09       0.00
DEMISTER TAR                       1.22       1.02         .04         .16       0.00
BURNER TRAP                        1.00        .01         .11         .89       0.00
............................................       ------------------------------
TOTAL OUTPUTS                     75.54      19.84        5.92       49.80        .13
```

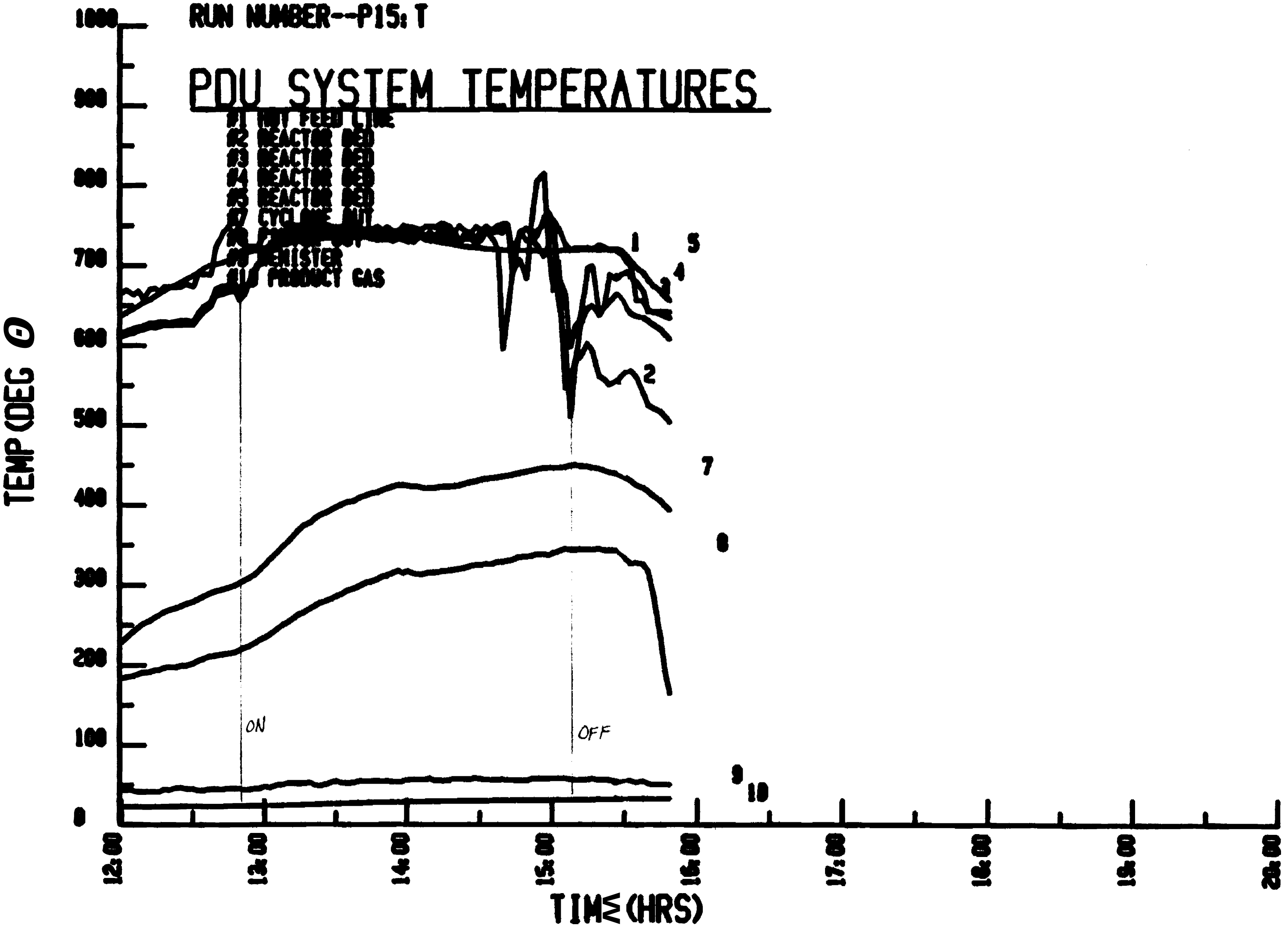
```
******************************
** PRODUCT GAS (N2-O2 FREE) **
******************************

SCFM!DRY )                10.19
LB GAS/LB DRY WOOD          .79
INST SCF/# DRY WOOD       13.10
AVG SCF/# DRY WOOD        13.62

TOTAL FLOW(SCF)          972.92

TOTAL WOOD FED            71.42
YH2O AT PRODUCT             .02
YH2O AT REACTOR OUT         .54
BTU/SCF                  408.22


*************************
**MISCELLANEOUS TIDBITS**
*************************

WT FRAC CAT-CCHAR           .05
WT FRAC CAT-FCHAR          0.00
#CAT LOSS THIS RUN          .16

TOC-DEM▮STER(FFM)       7577.00

STEAM/WOOD RATIO            .53

DRY MOL WT                23.01
WET MOL WT                22.91
N2-O2 FREE MW             22.97

ELEC INPUT(KW)            21.00
(based on 7 elements)
KWHR/LB DRY WOOD            .39
ELECTRIC BTU/LB DRY     1325.19


**CONVERSIONS & BALANCES**
HEAT GAS/HEAT WOOD          .63
GAS BTUS/LB WOOD      5347

CARBON CONVERS▮ON
-----------------
TO GAS(%)                 68.57
TO SOLID(%)               16.71
TO LIQUID(%)               5.84
SUM CONVERSIONS           91.13

METHANOL #/#WOOD .223270922747 TO .351353859671


**DESIGN INFORMATION**

BED GAS VELOCITY           1.47
CART HEAT COEFF          108.19
STANDARD HT OF RX       -757.40
```


RUN NUMBER--P14:T
PDU SYSTEM TEMPERATURES
#1 HOT FEED LINE
#2 REACTOR BED
#3 REACTOR BED
#4 REACTOR BED
#5 REACTOR BED
#7 CYCLONE OUT
#8 FILTER OUT
#9 DEMISTER
#10 PRODUCT GAS
TEMP (DEG C)
1000
900
800
700
600
500
400
300
200
100
0
TIME (HRS)
11:00
12:00
13:00
14:00
15:00
16:00
17:00
18:00
19:00
ON
OFF
2
3
4
1
5
7
7
8
8
9
9
10
10

```
RUN#: P15                           TIME: 14:00
DATE: 091762                      TOTAL RUN TIME(HRS) :2.3
WOOD TYPE: HEADRIG SAWDUST              CATALYST: DEACTIVATED GRACE

**PRODUCT GAS COMPOSITIONS**
       (MOLE FRACS)
                        N2,O2 FREE
H2         .426       .442
CO2        .276       .286
C2H4       .007       .008
C2H6       .009       .010
O2         .003      0.000
N2         .033      0.000
CH4        .130       .135
CO         .114       .119
C3H6       .001       .001
C3H8       .000       .000
YH2O       .035       .035


**TEMPERATURES**
      (DEG C)

REACTOR INLET  740
CATALYST BED   740
REACTOR OUTLET 670
STEAM          156
CARTRIDGE HTRS 820
PRODUCT METER  28
DEMISTER       55


**DIFFERENTIAL PRESSURES**

PRODUCT 8 IN H2O
STEAM   26 IN H2O
RECYCLE 4 IN H2O


**ORIFICE SIZES AND CONSTANTS**

ORIFICE     K    SIZE
....................
PRODUCT   110 9    .50
STEAM      32.0    .30
RECYCLE   116.0    .50


**PRESSURES**
   (PSIG)

STEAM     65
DEMISTER  63
REACTOR   60
PRODUCT   1

#/HR CYCLONE   2.17
#/HR FILTER    .65
#/HR TAR        1.52
```

```
**     SOLIDS     **
** COMPOSITIONS **

.................................................................
               CARBON    HYDROGEN    OXYGEN      ASH     MOISTURE
.................................................................

WOOD           .470       .060       .470       .001       .083
CCHAR          .920       .017       .043       .020       .161
FCHAR          .920       .017       .043       .020      0.000
BED            .820       .030       .130       .020      0.000
TAR            .840       .030       .130       .001      0.000


**HEATS OF COMBUSTION**

WOOD              8379
CYCLONE CHAR     12500
FILTER CHAR      12500
BED              10000
TAR              15000

                             ******************************
                             ***      INPUT STREAMS     ***
                             ******************************

                                TOTAL      CARBON     HYDROGEN     OXYGEN        ASH
..............................................................................
WOOD (DRY)                      35.89      16.87        2.15        16.87        .04
WOOD MOISTURE                    3.24       0.00         .36         2.88       0.00
STEAM                           52.40       0.00        5.82        46.58       0.00
--------------------------------------------------------------------------------------
TOTAL INPUTS                    91.53      16.87        8.34        66.32        .04

                             ******************************
                             ***     OUTPUT STREAMS     ***
                             ******************************

                                TOTAL      CARBON     HYDROGEN     OXYGEN        ASH
--------------------------------------------------------------------------------------
DRYGASES                        34.49      12.24        2.68        19.75       0.00
MOISTURE IN PRODUCT              1.20       0.00         .13         1.06       0.00
CYCLONE SOLIDS                   2.17       1.88         .03          .09        .04
FILTER SOLIDS                     .65        .56         .01          .03        .01
BED BUILDUP                       .67        .50         .02          .08        .08
DEMISTER LIQUIDS                47.60        .19        5.29        42.31       0.00
DEMISTER TAR                     1.52       1.28         .05          .20       0.00
FURNER TRAP                      3.91        .02         .43         3.48       0.00
..............................................................................
TOTAL OUTPUTS                   92.22      16.65        8.65        66.99        .13
```

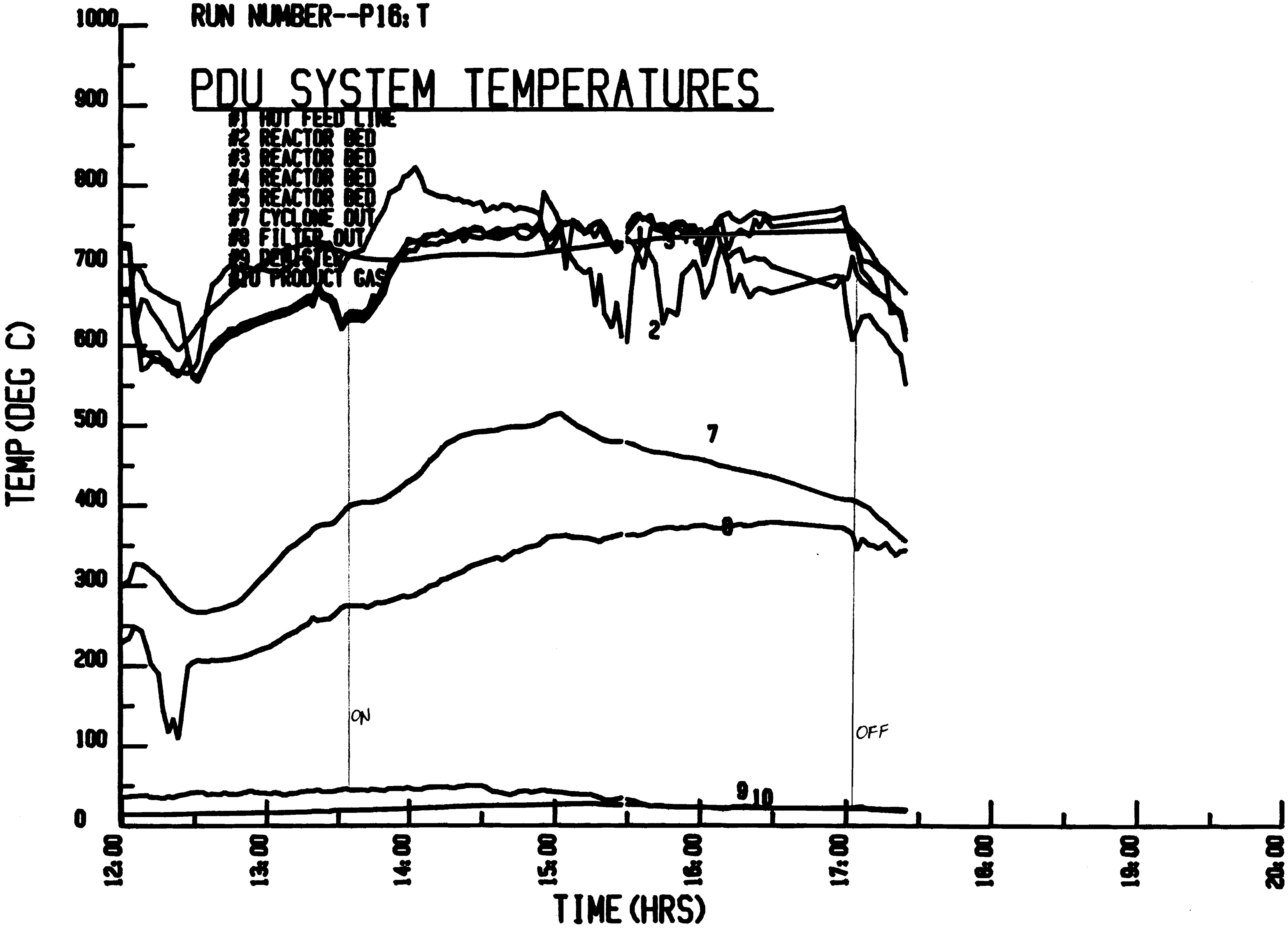
```
******************************
** PRODUCT GAS (N2-02 FREE) **
******************************

SCFM(DRY)                  11.55
LE GAS/LB DRY WOOD           .96
INST SCF/# DRY WOOD        18.67
AVG SCF/# DRY WOOD         16.82

TOTAL FLOW(SCF)          1388.45

TOTAL WOOD FED             82.56
YH2O AT PRODUCT              .04
YH2O AT REACTOR OUT          .63
BTU/SCF                   347.23


*************************
**MISCELLANEOUS TIDBITS**
*************************

WT FRAC CAT-CCHAR            .06
WT FRAC CAT-FCHAR            .06
#CAT LOSS THIS RUN           .17

TOC-DEM▮STER(PPM)        3899.00

STEAM/WOOD RATIO            1.46

DRY MOL WT                 19.82
WET MOL WT                 19.76
N2-02 FREE MW              19.50

ELEC INPUT(KW)             12.45
!based on 7 elements)
KWHR/LB DRY WOOD             .30
ELECTRIC BTU/LB DRY      1014.86


**CONVERSIONS & BALANCES**
HEAT GAS/HEAT WOOD           .77
GAS BTUS/LB WOOD        6484

CARBON CONVERSION
-----------------
TO GAS(%)                  72.56
TO SOLID(%)                17. 40
TO LIQUID(%)               €3.76
SUM CONVERS▮ONS            98.72

METHANOL #/#WOOD .265454039107 TO .409189511347


**DESIGN INFORMATION**

BED GAS VELOCITY            1.33
CART HEAT COEFF            53.71
STANDARD HT OF RX        -246.08
```


RUN NUMBER--P15:T
PDU SYSTEM TEMPERATURES
#1 HOT FEED LINE
#2 REACTOR BED
#3 REACTOR BED
#4 REACTOR BED
#5 REACTOR BED
#7 CYCLONE OUT
#8
#9 DEMISTER
#10 PRODUCT GAS
TEMP (DEG C)
1000
900
800
700
600
500
400
300
200
100
0
12:00
13:00
14:00
15:00
16:00
17:00
18:00
19:00
20:00
TIME (HRS)
ON
OFF
1
2
3
4
5
7
8
9
10

```
HUN#:  F16                         TIME:  16: 18
DGTE:  100582                    TOTAL RUN TIME(HRS) :3.45
WOOD TYPE:  DENSE FLAKES-K2C03              CATALYST:  DEACT NICUMO

**PRODUCT GAS COMPOSITIONS**
        (MOLE FRACS)
                           N2,02 FREE
HZ          .508        .526
C02         .240        .249
C2H4        .000        .000
C2H6        .005        .005
02          .004       0.000
N2          .029       0.000
CH4         .075        .078
CO          .138        .142
C3H6       0.000       0.000
C3H8       0.000       0.000
YH20        .028        .028


**TEMPERATURES**
      (DEG C)

AEACTOR INLET   737
CATALYST BED    745
KEACTOR OUTLET  687
STEAM           183
CARTRIDGE HTRS  825
PRODUCT METER   23
DEM▮STER        23


**DIFFERENTIAL PRESSURES**

PRODUCT 7 IN H20
STEAM    10 IN H20
RECYCLE  10 IN H20


**ORIFICE SIZES AND CONSTANTS**

ORIFICE    K    SIZE
...................
PRODUCT    1I!:). 9    .50
STEAM        32.0      .30
RECYCLE    116.0       .50


**PRESSURES**
   (PSIG)

STEAM       135
OEMISTER    135
REACTOR     130
F'RODUCT    0

#/HR CYCLONE     1.13
#/HR FILTER      1.45
#/HR TAR         0
```

```
**     SOLIDS     **
** COMPOSITIONS **

-----------------------------------------------------------------------------
               CARBON      HYDROGEN     OXYGEN        ASH      MOISTURE
-----------------------------------------------------------------------------

WOOD            .422         .056         .365        .157        .026
CCHAR           .667         .001         .089        .233        .106
FCHAR           .565         .011         .076        .350       0.000
EED             .430         .009         .130        .423       0.000
TAR             .840         .030         .130        .001       0,000

**HEATS OF COMBUSTION**

WOOD                 7550
CYCLONE CHAR         9526
FILTER CHAR          9526
BED                  1400
TAR                 15000

                              *******************************
                              ***      INPUT STREAMS      ***
                              *******************************

                                 TOTAL       CARBON      HYDROGEN      OXYGEN        ASH
......................................................................
WOOD (DRY)                       35.01       14.77         1.96        12.78         5.50
WOOD MOISTURE                      .93        0.00          .10          .83         0.00
STEAM                          , 43.20        0.00         4.80        38.40         0.00
......................................................................
TOTAL INPUTS                     7?.14       14.77         6.86        52.01         5.50

                              *******************************
                              ***      OUTPUT STREAMS     ***
                              *******************************

                                 TOTAL       CARBON      HYDROGEN      OXYGEN        ASH
--------------------------------------------------------------------------------------------
DRYGASES                         29.89        9.89         2.40        17.82         0.00
MOISTURE IN PRODUCT                .92        0.00          .10          .81         0.00
CYCLONE SOLIDS                   1. 13         .75          .00          .10          .26
FILTER SOLIDS                     1.45         .82          .02          .ll          .51
BED BUILDUP                       6.29        2.43          .05          .74         3.02
DEMISTER LIQUIDS                 30.00         .02         3.33        26.67         0.00
DEMISTER TAR                      0.00        0.00         0.00         0.00         0.00
BURNER TRAP                       2.70         .00          .30         2.40         0.00
......................................................................
TOTAL OUTPUTS                    72.58       13.92         6.20        48.65         3.79
```

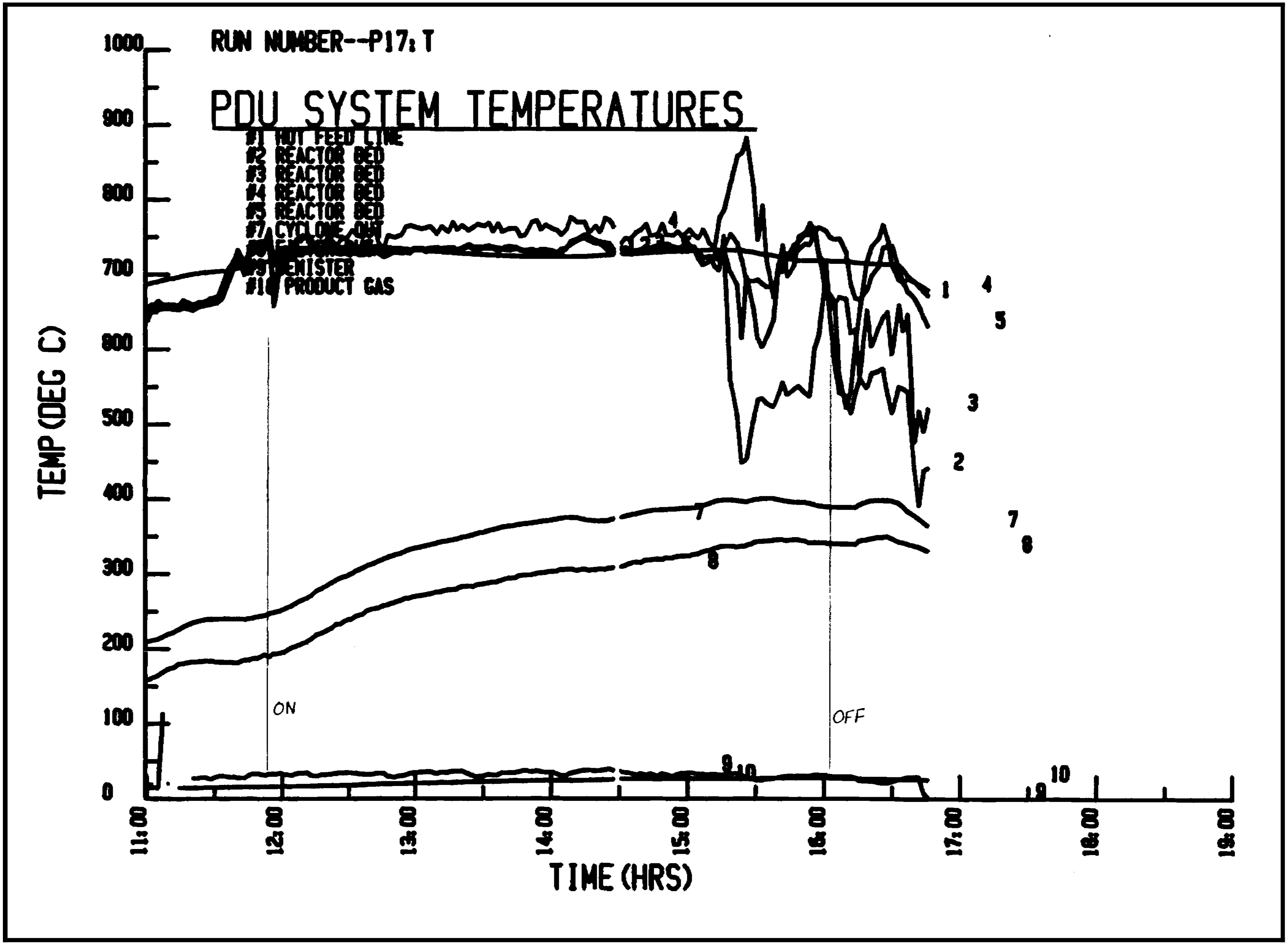
```
******************************
** PRODUCT GAS (N2-O2 FREE) **
******************************

SCFM(DRY)                  11.20
LB GAS/LB DRY WOOD           .85
INST SCF/# DRY WOOD        16.62
AVG SCF/# DRY WOOD         18.98

TUTAL FLOW(SCF)          1933.36

TOTAL WOOD FED            101.88
YH20 AT PRODUCT              .03
YH20 AT REACTOR OUT          .53
BTU/SCF                   302.52


*************************
**MISCELLANEOUS TIDBITS**
*************************

WT FRAC CAT-CCHAR           0.00
WT FRAC CAT-FCHAR           0.00
#CAT LOSS THIS RUN          0.00

TOC-DEMISTER(PPM)         720.00

STEAM/WOOD RATIO            1.23

DRY NOL WT                 17.75
WET MOL WT                 17.76
N2-O2 FREE MW              17.38

ELEC ▮NPUT(KW)             25.28
!based on 7 elements)
KWHR/LB DRY WOOD             .62
ELECTRIC BTU/LB DRY  2113.42


**CONVERSIONS & BALANCES**
HEAT GAS/HEAT WOOD           .75
GAS BTUS/LB WOOD     5633

CARBON CONVERSION
-----------------

TO GAS(%)                  66.96
TO SOLID!%)                27.13
TO LIQUID(%)                 .16
SUM CONVERSIONS            94.25

METHANOL #/#WOOD .356974582963 TO .45051853795


**DESIGN INFORMATION**

BED GAS VELOCITY            1.14
CART HEAT COEFF           109.08
STANDARD HT OF RX        -712.66
```


RUN NUMBER--P16:T
PDU SYSTEM TEMPERATURES
#1 HOT FEED LINE
#2 REACTOR BED
#3 REACTOR BED
#4 REACTOR BED
#5 REACTOR BED
#7 CYCLONE OUT
#8 FILTER OUT
#9 DEMISTER
#10 PRODUCT GAS
1000
900
800
700
600
500
400
300
200
100
0
TEMP (DEG C)
12:00
13:00
14:00
15:00
16:00
17:00
18:00
19:00
20:00
TIME (HRS)
1
3
5
2
7
8
9
10
ON
OFF

```
RUN#: P17                          TIME:  15:00
DGTE: 101482                     TOTAL RUN TIME(HRS) :2.95
WOOD TYPE:  DENSE FLAKES               CATALYST:  GOOD NICUMO

**PRODUCT GAS COMPOSITIONS**
       (MOLE FRACS)
                        N2,02 FREE
H2        .528        .569
CO2       .224        .242
C2H4     0.000       0.000
C2H6      .001        .001
O2        .004       0.000
N2        .068       0,000
CH4       .053        .057
CO                    .131
C3H6     0,000       0.000
C3H8     0.000       0.000
YH2O      .023        .023


**TEMPERATURES**
     (DEG C)

REACTOR INLET   730
CATALYST BED    730
REACTOR OUTLET 680
STEAM           183
CARTRIDGE HTRS 825
PRODUCT METER   20
DEMISTER        30


%#DIFFERENTIAL PRESSURESXI

PRODUCT 6 IN H2O
STEAM    16 IN H2O
RECYCLE 8 IN H2O


**ORIFICE SIZES AND CONSTANTS**

ORIFICE     K     SIZE
--------------------
PRODUCT    110.9     .50
STEAM       32.0     .30
RECYCLE    116.0     .50


**PRESSURES**
   (PSIG)

STEAM      138
DEMISTER   136
REACTOR    132
PRODUCT    0

#/HR CYCLONE     1
#/HR FILTER       30
```

```
#/HR FILTER     .38
#/HR TAR        0


**     SOLIDS    **
** COMPOSITIONS **

.............................................................
            CARBON    HYDROGEN    OXYGEN       ASH      NOISTURE
.............................................................

WOOD         .503       .066        .425       .006       .013
CCHAR        .850       .013       0.000       .140       .030
FCHAR        .650       .013       0.000       .350       .088
BED          .920       .019        .030       .030      0.000
TAR          .840       .030        .130       .001      0.000

**HEATS OF COMBUSTION**

WOOD             8774
CYCLONE CHAR    13240
FILTER CHAR      8854
BED             10000
TAR             15000

                       ******************************
                       ***      INPUT STREAMS     ***
                       ******************************

                               TOTAL      CARBON     HYDROGEN     OXYGEN       ASH
.............................................................................
WOOD(DRY)                      24.87      12.51        1.64       10.57        .15
WOOD MOISTURE                    .33       0.00         .04         .29       0.00
STEAM                          55.19       0.00        6.13       43.06       0.00
.............................................................................
TOTAL INPUTS                   80.39      12.51        7.81       59.92        .15

                       ******************************
                       ***     OUTPUT STREAMS     ***
                       ******************************

                               TOTAL      CARBON     HYDROGEN     OXYGEN       ASH
.............................................................................
DRYGASES                       25.65       6.11        2.15       15.61       0.00
MOISTURE IN PRODUCT              .72       0.00         .08         .64       0.00
CYCLONE SOLIDS                  1.00        .85         .01        0.00        .14
FILTER SOLIDS                    .38        .25         .00        0.00        .13
BED BUILDUP                     1.40       1.16         .02         .04        .16
DEMISTER LIQUIDS               48.20        .01        5.36       42.64       0.00
DENISTER TAR                    0.00       0.00        0.00        0.00       0.00
BURNER TRAP                     3.15        .00         .35        2.80       0.00
-----------------------------------------------------------------------------------
TOTAL OUTPUTS                  80.50      10.38        7.98       61.94        .45
```

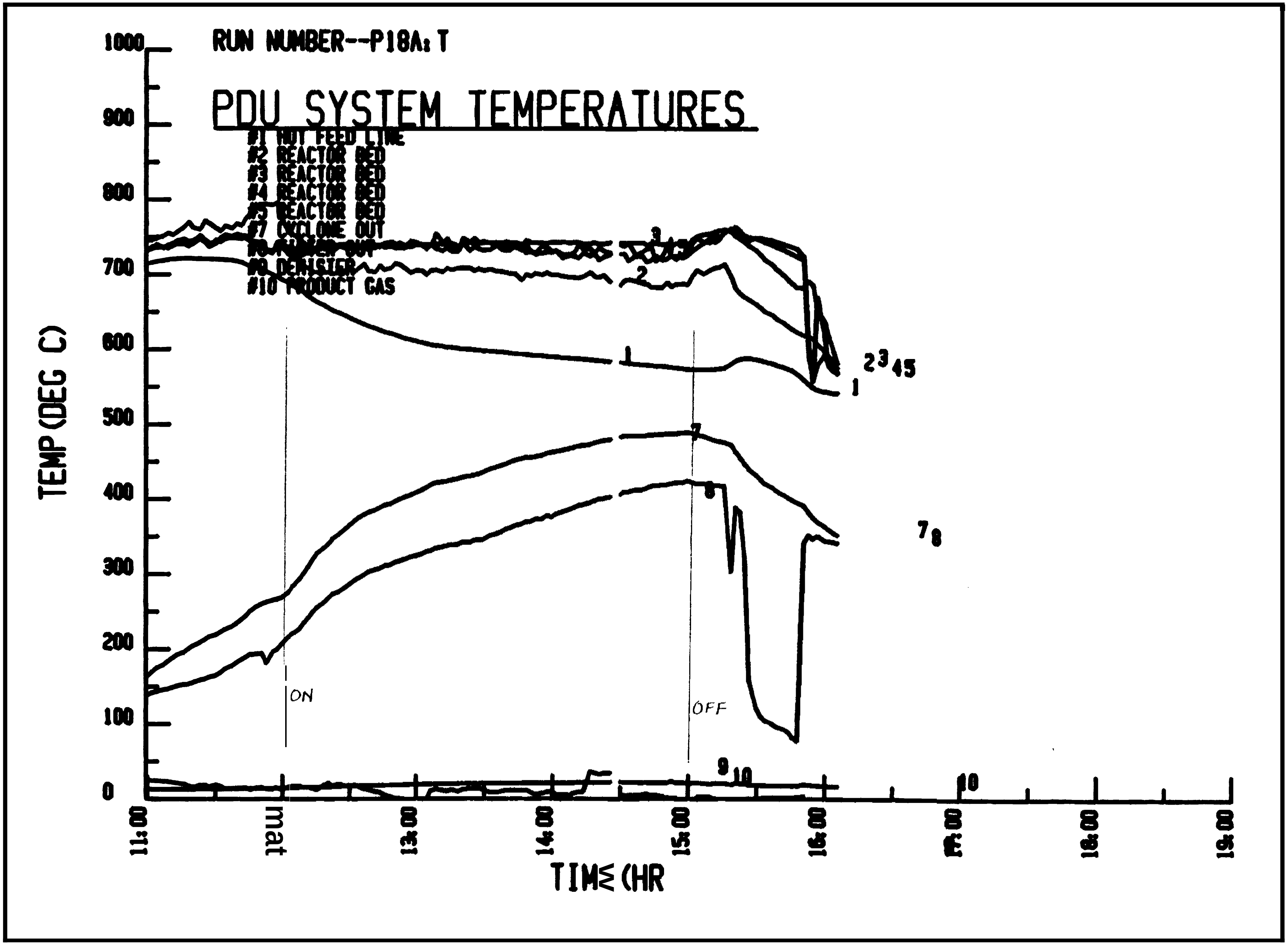
```
******************************
** PRODUCT GAS (N2-O2 FREE) **
******************************

SCFM(DRY)                   10.59
LB GAS/LB DRY WOOD           1.03
INST SCF/# DRY WOOD         23.86
AVG SCF/# DRY WOOD          22.41

TOTAL FLOW(SCF)           1670.01

TOTAL WOOD FED              74.52
YH2O AT PRODUCT               .02
YH2O AT REACTOR OUT           .66
BTU/SCF                    284.56


*************************
**MISCELLANEOUS TIDBITS**
*************************

WT FRAC CAT-CCHAR            0.00
WT FRAC CAT-FCHAR            0.00
#CAT LOSS THIS RUN           0.00

TOC-DEMISTER(PPM)          289.00

STEAM/WOOD RATIO             2.22

DRY MOL WT                  17.24
WET MOL WT                  17.26
N2-O2 FREE MW               lt.38

ELEC INPUT(KW)              21.00
(based on 7 elements)
KWHR/LB DRY WOOD              .72
ELECTRIC BTU/LB DRY       2470.69


**CONVERSIONS & BALANCES**
HEAT GAS/HEAT WOOD            .77
GAS BTUS/LB WOOD       6789

CARHON CONVERSION
-----------------

70 GAS(%)                   64.83
TO SOLID(%)                 18.04
TO LIQUID(%)                  .12
SUM CONVERSIONS             82.99

METHANOL #/#WOOD .441648712858 TO .523246627474


**DESIGN INFORMATION**

BED GAS VELOCITY             1.10
CART HEAT COEFF             76.30
STANDARD HT OF RX          451.43
```


RUN NUMBER--P17:T
PDU SYSTEM TEMPERATURES
#1 HOT FEED LINE
#2 REACTOR BED
#3 REACTOR BED
#4 REACTOR BED
#5 REACTOR BED
#7 CYCLONE OUT
#9 DEMISTER
#10 PRODUCT GAS
TEMP (DEG C)
1000
900
800
700
600
500
400
300
200
100
0
ON
OFF
1
2
3
4
5
7
8
9
10
11:00
12:00
13:00
14:00
15:00
16:00
17:00
18:00
19:00
TIME (HRS)

```
RUN#: P18                        TIME:  15:00
DATE:  110182                   TOTAL RUN TIME(HRS) :3.0
WOOD TYF'E:  HEADRIG            CATALYST:  NICUMO-DEAD

**PRODUCT GAS COMPOSITIONS**
        (MOLE FRACS)
                     N2,02 FREE
          .391       .423
CO2       .196       .212
C2H4      .001       .001
C2H6      .009       .010
O2        .010      0.000
N2        .067      0.000
CH4       .158       .172
CO        .168       .182
C3H6     0.000      0.000
C3H8     0.000      0.000
YH2O      .023       .023


**TEMPERATURES**
      (DEG C)

REACTOR INLET   600
CATALYST BED    740
REACTOR OUTLET  720
STEAM           183
CARTRIDGE HTRS  840
F'RODUCT METER  21
DEMISTER        30


**DIFFERENTIAL PRESSURES**

PRODUCT 5 IN H2O
STEAM   10 IN H2O
RECYCLE 16 IN H2O


**ORIFICE SIZES AND CONSTANTS**

ORIFICE     K     SIZE
------------------
PRODUCT    110.9    .50
STEAM       32.0    .30
RECYCLE    116.0    .50


**PRESSURES**
   (PSIG)

STEAM      135
DEMISTER   135
REACTOR    135
F'RODIJCT  1

#/HR CYCLONE    2.93
#/HR FILTER     1.17
#/HE TAR        .16
```

```
**    SOLIDS    **
** COMPOSITIONS **

.....................................................
          CARBON   HYDROGEN   OXYGEN     ASH    MOISTURE
----------------------------------------------------------------

WOOD       .478      .058      .438     .026      .088
CCHAR      .886      .012     0.000     ,100      .030
FCHAR      .805      .013     0.000     .190      .146
PED        .820      .030      .130     .020     0.000
TAR        .840      .030      ,130     .001     0.000

**HEATS OF COMBUSTION**

WOOD              8342
CYCLONE CHAR     13500
FILTER CHAR      11900
BED              10000
TAR              15000

                   *******************************
                   ***     INPUT STREAMS       ***
                   *******************************

                          TOTAL      CARBON    HYDROGEN    OXYGEN      ASH
-----------------------------------------------------------------------------
WOOD(DRY)                 30.71      14.68      1.78       13.45        .80
WOOD MOISTURE             "1.96       0.00       .33        2.63       0.00
STEAM                     43.20       0.00      4.80       38.40       0.00
.........................................................................
TOTAL INPUTS              76.87      14.68      6.91       54.48        .80

                   *******************************
                   ***     OUTPUT STREAMS      ***
                   *******************************

                          TOTAL      CARBON    HYDROGEN    OXYGEN      ASH
-----------------------------------------------------------------------------
DRYGGSES                  25.59       9.84      2.23       13.99       0.00
MOISTURE IN PRODUCT         .64       0.00       .07         .57       0.00
CYCLONE SOLIDS             2.93       2.60       .04        0.00        .29
FILTER SOLIDS              1.17        .94       .02        0.00        .22
EED BUILDUP                1.98       1.46       .05         .23        .23
OEMISTER LIQUIDS          52.30        .15      5.81       46.49       0.00
DEMISTER TAR                .16        .13       .00         .02       0.00
BURNER TRAP                3.83        .01       .43        3.40       0.00
.........................................................................
TOTAL OUTPUTS             88.60      15.13      8.64       64.71        .75
```

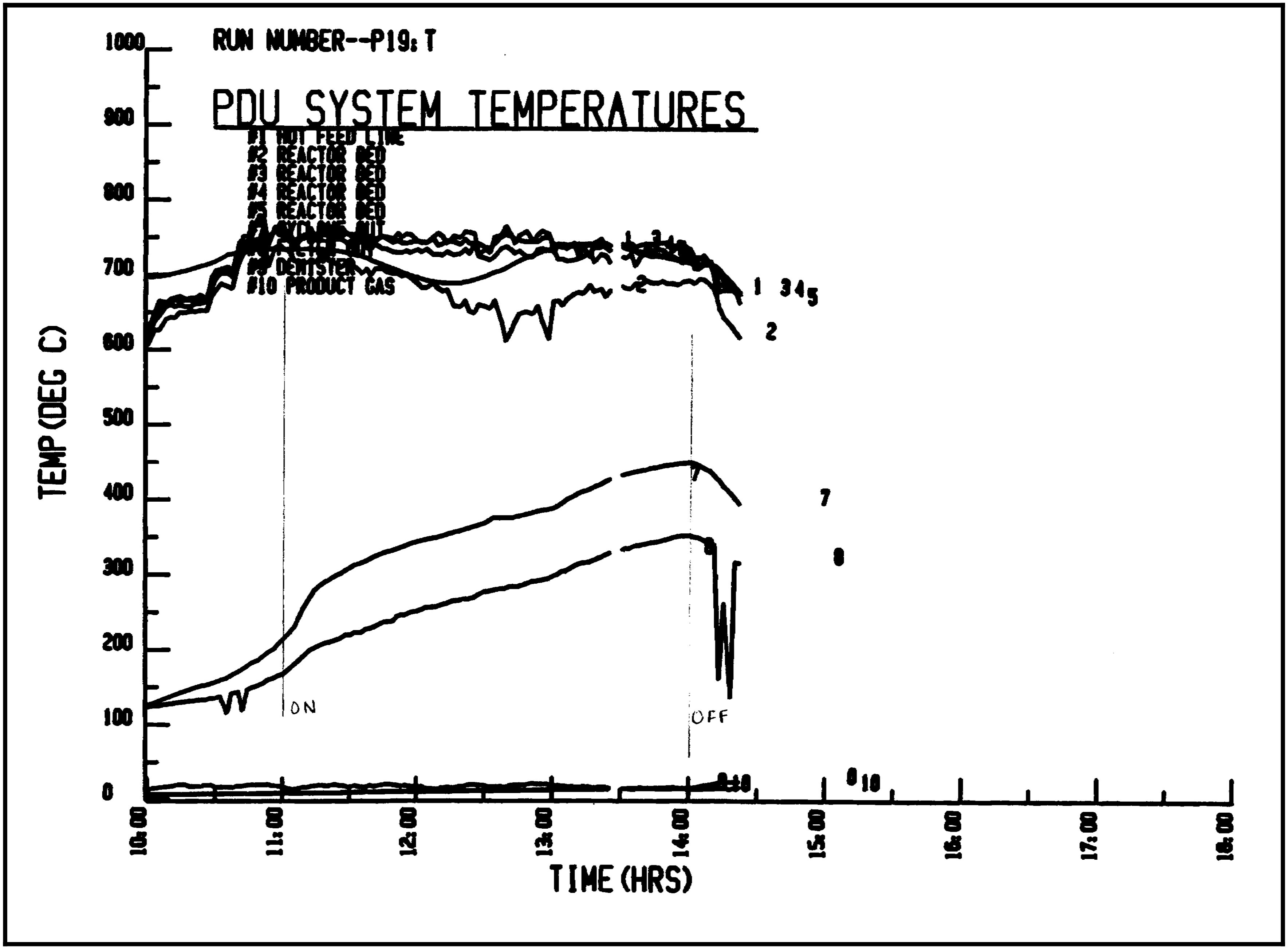
```
******************************
** PRODUCT GAS (N2-O2 FREE) **
******************************

SCFM(DRY)                    9.46
LB GAS/LB DRY WOOD            .83
INST SCF/# DRY WOOD         17.21
AVG SCF/# DRY WOOD          21.79

TOTAL FLOW(SCF)           2007.26

TOTAL WOOD FED              92.11
YH2O AT PRODUCT               .02
YH2O AT REACTOR OUT           .70
BTU/SCF                    387.01


*************************
**MISCELLANEOUS TIDBITS**
*************************

WT FRAC CAT-CCHAR            0.00
WT FRAC CAT-FCHAR            0.00
#CAT LOSS THIS RUN           0.00

TOC-DEMISTER(PPM)         2890.00

STEAM/WOOD RATIO             1.41

DRY MOL WT                  19.13
WET MOL WT                  19.11
N2-O2 FREE MW               18.35

ELEC INPUT(KW)              25.28
!based on 7 elements)
KWHR/LB DRY WOOD              .71
ELECTRIC BTU/LB DRY       2409.26


**CONVERSIONS & BALANCES**
HEAT GAS/HEAT WOOD            .80
GAS BTUS/LB WOOD        6661

CARBON CONVERSION
-----------------

TO GAS(%)                   67.03
TO SOLID(%)                 34.06
TO LIQUID(%)                 2.02
SUM CONVERSIONS            103.11

METHANOL #/#WOOD .370826296851 TO .608784567419


**DESIGN INFORMATION**

BED GAS VELOCITY             1.26
CART HEAT COEFF             87.26
STANDARD HT OF RX          207.72
```


RUN NUMBER--P18A: T
PDU SYSTEM TEMPERATURES
#1 HOT FEED LINE
#2 REACTOR BED
#3 REACTOR BED
#4 REACTOR BED
#5 REACTOR BED
#7 CYCLONE OUT
#8 [illegible] OUT
#9 DEMISTER
#10 PRODUCT GAS
TEMP (DEG C)
1000
900
800
700
600
500
400
300
200
100
0
11:00
mat
13:00
14:00
15:00
16:00
17:00
18:00
19:00
TIME (HR
ON
OFF
1
2
3
2 3 4 5
1
7
8
7 8
9 10
10

```
RUN#: P19                          TIME: 13:35
DATE: 110282                     TOTAL RUN TIME(HRS) :3.0
WOOD TYPE: HEADRIG               CATALYST:  NICUMO-DEAD

**PRODUCT GAS COMPOSITIONS**
       (MOLE FRACS)
                       N2,O2 FREE
H2        .315       .322
CO2       .280       .286
C2H4      .006       .006
C2H6      .018       .019
O2        ,001      0.000
N2        .032      0.000
CH4       .177       .181
CO        .179       .184
C3H6      .000       .000
C3H8      .000       .000
YH2O      .016       .016


**TEMPERATURES**
     (DEG C)

REACTOR INLET   740
CATALYST RED    740
REACTOR OUTLET  680
STEAM           160
CARTRIDGE HTRS  820
PRODUCT METER   15
DEMISTER        20


**DIFFERENTIAL PRESSURES**

F'RODUCT  4  I N  H2O
STEAM     15  I N  H2O
RECYCLE  1.3  I N  H2O


**ORIFICE SIZES AND CONSTANTS**

ORIFICE     K     SIZE
..................
PRODUCT   110.3     .50
STEAM      32.0     .30
RECYCLE   116.0     .50


**PRESSURES**
   (PSIG)

STEAM      75
DEMISTER   70
REACTOR    70
PRODUCT    1

#/HR CYCLONE    2.42
#/HR FILTER     .5
#/HR TAR        .16
```

```
**     SOLIDS      **
** COMPOSITIONS  **

.............................................................
            CARBON    HYDROGEN    OXYGEN       ASH      MOISTURE
.............................................................

WOOD          .473       .060        .455      .012        .027
CCHAR         .863       .011       0.000      .127        .046
FCHAR         .861       .012       0.000      .127        .130
BED           .517       .007       0.000      .480       0.000
TAR           .840       .030        .130      .001       0.000


**HEATS OF COMBUSTION**

WOOD             8500
CYCLONE CHAR    12500
FILTER CHAR     12500
BED             10000
TAR             15000

                               ********************************
                               ***       INPUT STREAMS      ***
                               ********************************

                               TOTAL       CARBON     HYDROGEN      OXYGEN         ASH
...........................................................................
WOOD (DRY)                     36.98        17.49        2.22        16.82         .44
WOOD MOISTURE                   1.02         0.00         .11          .91        0.00
STEAM                          42.03         0.00        4.67        37.36        0.00
...........................................................................
TOTAL INPUTS                   80.03        17.49        7.00        55.09         .44

                               ********************************
                               ***      OUTPUT STREAMS      ***
                               ********************************

                               TOTAL       CARBON     HYDROGEN      OXYGEN         ASH
-------------------------------------------------------------------------------------
DRYGASES                       27.51        10.52        1.89        15.16        0.00
MOISTURE IN PRODUCT              .37         0.00         .04          .33        0.00
CYCLONE SOLIDS                  2.42         1.88         .02         0.00         .28
FILTER SOLIDS                    .50          .41         .01         0.00         .06
BED BUILDUP                     1.46          .68         .01         0.00         .78
DEMISTER LIQUIDS               39.00          [illegible]        4.33        34.67        0.00
DEMISTER TAR                     .16          .13         .00          .02        0.00
BURNER TRAP                     2.67          .02         .30         2.37        0.00
-------------------------------------------------------------------------------------
TOTAL OUTPUTS                  74.09        13.88        6.60        52.55        1.12
```

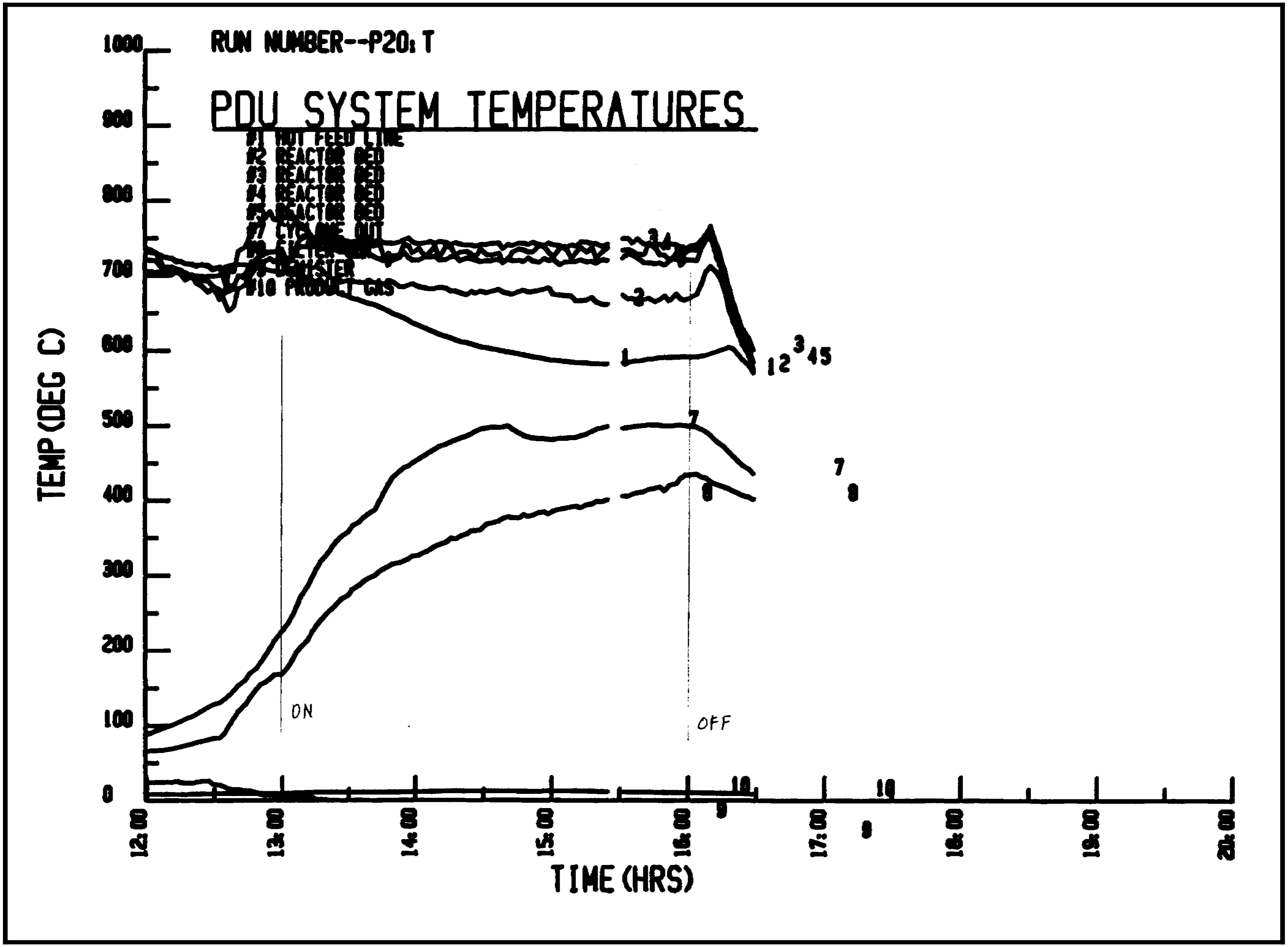
```
*******************************
** PRODUCT GAS (N2-O2 FREE) **
*******************************

SCFM(DRY)                   8.05
LB GAS/LB DRY WOOD           .74
INST SCF/# DRY WOOD        12.78
AVG SCF/# DRY WOOD         12.01

TOTAL FLOW(SCF)          1332.64

TOTAL WOOD FED            110.93
YH2O AT PRODUCT              .02
YH2O AT REACTOR OUT          .65
BTU/SCF                   389.85


*************************
**MISCELLANEOUS TIDBITS**
*************************

WT FRAC CAT-CCHAR            .10
WT FRAC CAT-FCHAR            .05
#CAT LOSS THIS RUN           .27

TOC-DEMISTER(PPM)        6000.00

STEAM/WOOD RATIO            1.14

DRY MOL WT                 22.20
WET MOL WT                 22.13
N2-O2 FREE MW              22.05

ELEC INPUT(KW)             19.83
(based on 7 elements)
KWHR/LB DRY WOOD             .46
ELECTRIC BTU/LB DRY      1569.54


**CONVERSIONS & BALANCES*&
HEAT GAS/HEAT WOOD           .59
BAS BTUS/LB WOOD     4984

CARBON CONVERSION
------------------
TO GAS(%)                  60.18
TO SOLID(%)                16.98
TO LIQUID(%)                2.20
SUM CONVERSIONS            79.36

METHANOL #/#WOOD .171321301932 TO .309558383105


**DESIGN INFORMATION**

BED GAS VELOCITY            1.59
CART HEAT COEFF            85.57
STANDARD H i OF RX       -389.63
```

RUN NUMBER--P19:T
PDU SYSTEM TEMPERATURES
#1 HOT FEED LINE
#2 REACTOR BED
#3 REACTOR BED
#4 REACTOR BED
#5 REACTOR BED
#7 CYCLONE OUT
#8 FILTER OUT
#9 DEMISTER
#10 PRODUCT GAS
TEMP (DEG C)
1000
900
800
700
600
500
400
300
200
100
0
TIME (HRS)
10:00
11:00
12:00
13:00
14:00
15:00
16:00
17:00
18:00
ON
OFF
1
2
3
4
5
7
8
9
10

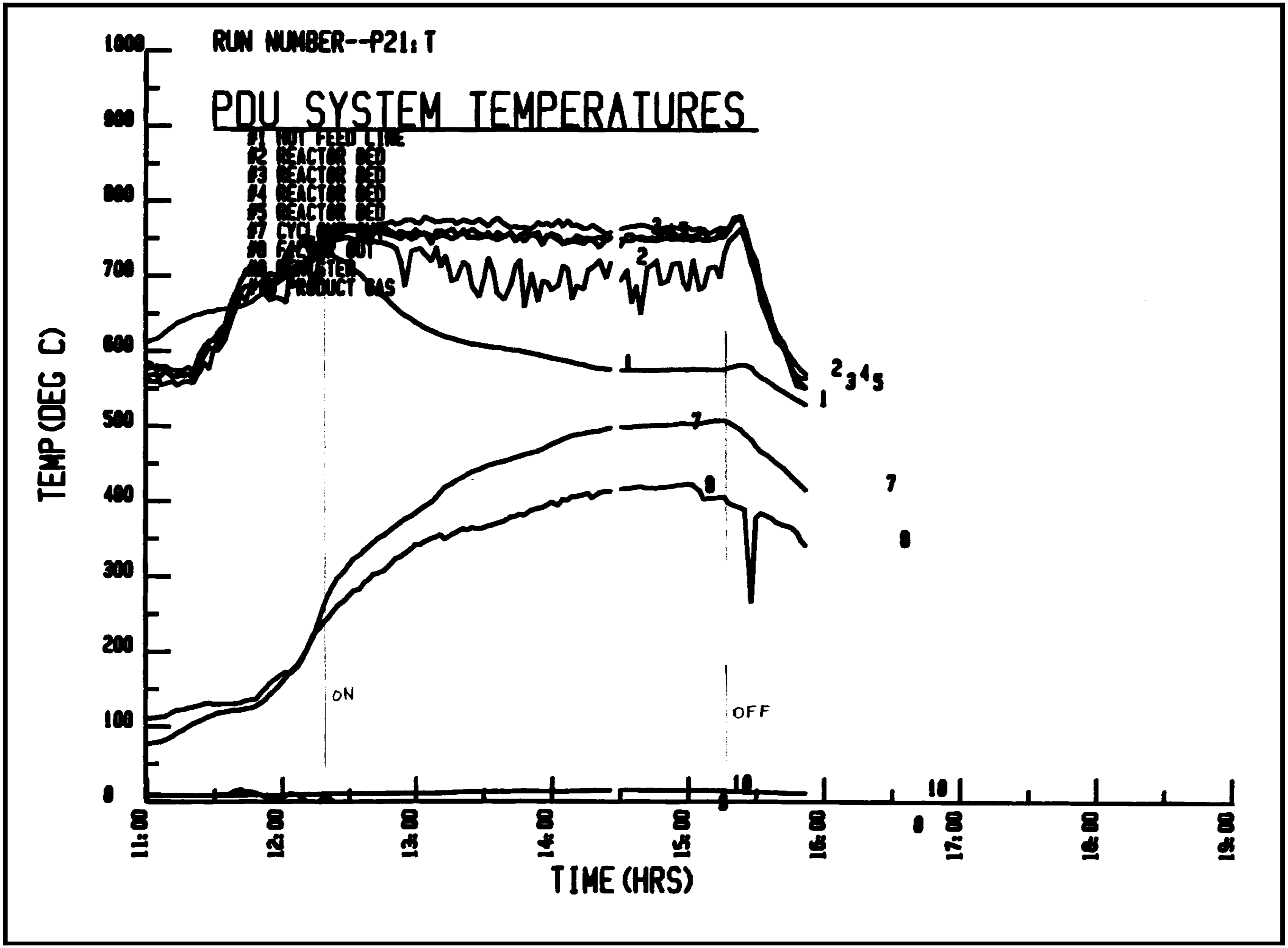
```
RUN#:  P20                          TIME:  14:30
DATE:  110882                     TOTAL RUN TIME(HRS) :3
WOOD TYPE: HEADRIG W/NACO3                CATALYST: DEAD NI-CU-MO

**PRODUCT GAS COMPOSITIONS**
       (MULE FRACS)
                     N2,O2 FREE
H2        .302      .330
CO2       .303      .331
C2H4      ,003      .003
C2H6      .017      .019
O2        .003     0.000
N2        .081     0.000
CH4       .168      .183
CO        .122      .133
C3H6      .000      .000
C3H8      .000      .000
YH2O      .013      .013


**TEMPERATURES**
     (DEG C)

REACTOR INLET   607
CATALYST BED    730
REACTOR OUTLET  700
STEAM           183
CARTRIDGE HTRS  840
PRODUCT METER   12
DEMISTER        25


**DIFFERENTIAL PRESSURES**

PRODUCT 4 IN H2O
STEAM   8 IN H2O
RECYCLE 14 IN H2O


**ORIFICE SIZES AND CONSTANTS**

ORIFICE    K    SIZE
..................
PRODUCT   110.9    .50
STEAM      32.0    .30
RECYCLE   116.0    .50


**PRESSURES**
   (PSIG)

STEAM      140
DEMISTER   135
REACTOR    130
PRODUCT    1

#/HR CYCLONE    3.67
#/HR FILTER     1.6
#/HR TAR        .7
```

```
**     SOLIDS     **
** COMPOSITIONS **

.......................................................
              CARBON    HYDROGEN    OXYGEN       ASH      MOISTURE
------------------------------------------------------------------

WOOD          .340       .042        .505        .114        .084
CCHAR         .615       .010        .032        .344        .089
FCHAR         .633       .011        .024        .333        .006
EED           .820       .030        .130        .020       0.000
TAR           .840       .030        .130        .001       0.000


**HEATS OF COMBUSTION**

WOOD               7550
CYCLONE CHAR      10050
FILTER CHAR       11038
BED               10000
TAR               15000


                            ********************************
                            ***      INPUT STREAMS       ***
                            ********************************


                                     TOTAL        CARBON      HYDROGEN      OXYGEN        ASH
...........................................................................
WOOD IDRY)                           44.90        15.24         1.89        22.67        5.1(I)
WOOD MOISTURE                         4.10         0.00          .46         3.65        0.00
STEAM                                39.28         0.00         4.36        54.91        0.00
------------------------------------------------------------------------------------------
TOTAL INPUTS                         88.25        15.24         6.71        61.23        5,10


                            ********************************
                            ***      OUTPUT STREAMS      ***
                            ********************************


                                     TOTAL        CARBON      HYDROGEN      OXYGEN        ASH
...........................................................................
DRYGASES                             26.12         3.62         1.76        14.86        0.0(
MOISTURE IN PRODUCT                    .30         0.(:)(I)      .03          .27        (I!.0(
CYCLONE SOLIDS                        3.67         2.26          .04          .12        1.26
FILTER SOLIDS                         1.60         1.01          .02          .04         .53
BED EUILDUP                           -.60         -.44        -.02         -.07        -.07
OEMISTER LIQUIDS                     55.00          .18         6.11        48.89        0.00
DEMISTER TAR                           .70          .59          .02          .04        0.00
BURNER TRAP                           5.00          .02          .56         4.44        0.00
...........................................................................
TOTAL OUTPUTS                        $1.78        13.23         a.52        68.64        1.72
```

```
*******************************
** F'RODUCT GAS (N2-02 FREE) **
*******************************

SCFM(DRY)                    7.90
LB GAS'LB  DRY WOOD           .58
INST SCF/# DRY WOOD          3.77
AVG SCF/# DRY WOOD          10.20

TOTAL FLOW(SCF)           1373.56

TOTAL WOOD FED             134.70
YH20 AT PRODUCT               .01
YH20 AT REACTOR OUT           .75
BTU/SCF                    372.76


**************************
**MISCELLANEOUS TIDBITSXI
**************************

WT FRAC CAT-CCHAR            0.00
WT FRAC CAT-FCHAR            0.00
#CAT LOSS THIS RUN           0.00

TOC-DEMISTER(PPM)         3356.00

STEAM/WOOD RATIO              .87

DRY MOL WT                  23.03
WET MOL WT                  22.96
N2-02 FREE MW               22.55

ELEC INPUT(KW)              25.67
(based on 7 elements)
KWHR/LB DRY WOOD              .49
ELECTRIC BTU/LB DRY   1672.83


**CONVERSIQNS & BALANCES**
HEAT GAS/HEAT WOOD            .48
GAS BTUS/LB WOOD      3644

CARBON CONVERSION
-----------------

TO GAS(%)                   63.13
TO SOLID(%)                 18.52
TO LIQUID(%)                 5.18
SUM CONVERSIONS             86.82

METHANOL #/#WOOD .132930228201 TO .251551618564


**DESIGN INFORMATION**

BED GAS VELOCITY             1.13
CART HEAT COEFF             80.54
STANDARD HT OF RX        -1984.23
```


RUN NUMBER--P20: T
PDU SYSTEM TEMPERATURES
#1 HOT FEED LINE
#2 REACTOR BED
#3 REACTOR BED
#4 REACTOR BED
#5 REACTOR BED
#7 CYCLONE OUT
#8 FILTER OUT
#9 DEMISTER
#10 PRODUCT GAS
TEMP (DEG C)
1000
900
800
700
600
500
400
300
200
100
0
TIME (HRS)
12:00
13:00
14:00
15:00
16:00
17:00
18:00
19:00
20:00
ON
OFF
1
2
3
4
12345
7
8
78
9
10
10
9

```
RUN#: 21                          TIME:  14:30
DATE: 110982                      TOTAL RUN TIME(HRS) :3
WOOD TYPE:  DENSE FLAKES                CATALYST:  13% NACO3

**PRODUCT GAS COMPOSITIONS**
       !MOLE  FRACS!
                        N2,O2 FREE
H2        .320       .343
902       .285       .306
C2H4      .003       .003
C2H6      .017       .016
O2        .002      0.000
N2        .066      0.000
CH4       .174       .187
30        .133       .143
C3H6     0.000      0.000
C3H8     0.000      0.000
YH2O      .014       .014


**TEMPERATURES**
     (DEG C)

REACTOR INLET  600
CATALYST BED   750
REACTOR OUTLET 740
STEAM          184
CARTRIDGE HTRS 840
PRODUCT METER  13
DEMISTER       20


**DIFFERENTIAL PRESSURESIX

PRODUCT 2 IN H2O
STEAM   3 IN H2O
RECYCLE 13 IN H2O


**ORIFICE SIZES AND CONSTANTS**

ORIFICE     K     SIZE
--------------------
PRODUCT   110.9    ,50
STEAM      32.0    .30
RECYCLE   116.0    .50


**PRESSURES**
   IPSIG)

STEAM      140
DEMISTER   135
REACTOR    130
PRODUCT    1

#/HR CYCLONE    6.67
#/HR FILTER     1
#/HR TAR        1.17
```


RUN NUMBER--P21:T
PDU SYSTEM TEMPERATURES
#1 HOT FEED LINE
#2 REACTOR BED
#3 REACTOR BED
#4 REACTOR BED
#5 REACTOR BED
#7 CYCLONE OUT
#8 FA[illegible] OUT
#9 DEMISTER
#10 PRODUCT GAS
TEMP (DEG C)
0
100
200
300
400
500
600
700
800
900
1000
TIME (HRS)
11:00
12:00
13:00
14:00
15:00
16:00
17:00
18:00
19:00
ON
OFF
1
2
3
4
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8
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