METHANE OR METHANOL VIA CATALYTIC GASIFICATION OF BIOMASS

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METHANE OR METHANOL VIA CATALYTIC WOOD GASIFICATION

SUMMARY

Methane and methanol synthesis gas can be produced by steam gasification of biomass in the presence of appropriate catalysts. A 5 cm diameter reactor has been used to determine the desired catalysts and operating temperature. A process development unit (PDU) has demonstrated steam gasification of biomass with catalysts at rates up to 35 kg per hour.

Methane yields of 0.28 nm^3 per kg of dry wood were produced in the small laboratory reactor. Further methanation of the product gas mixture can increase methane yields to 0.33 nm^3/kg. The catalyst system is nickel and silica-alumina. The preferred reactor operating temperature is 500 to 550^oC. Tests have been at atmospheric pressure. The PDU performance has confirmed results obtained in the laboratory.

Methanol synthesis gas can be produced in a single stage reactor at 750^o to 850^oC by steam gasification of wood with silica-alumina and nickel catalysts present. From this gas, up to 0.6 kg of methanol can be produced per kg of wood. Gasification of the wood to produce synthesis gas has been demonstrated in the laboratory scale reactor, but remains to be successfully done using the PDU.

Catalyst deactivation rates and regeneration schemes must be determined in order to determine the economic feasibility of wood to methane or methanol processes.

Some advantages of catalytic steam gasification of biomass over steam-oxygen gasification are:

- no oxygen is required for methane or methanol synthesis gas, therefore, no oxygen plant is needed
- little or no tar is produced resulting in simpler gas cleaning equipment
- no shift reactor is required for methanol synthesis
- methanation requirements are low resulting in high conversion efficiency
- yields and efficiencies are greater than obtained by conventional gasification.

These advantages significantly reduce the capital expenditures for a commercial scale plant.

INTRODUCTION

The traditional method for gasification of biomass to produce methane or methanol uses pure oxygen or steam-oxygen mixtures to produce a synthesis gas. The synthesis gas is subsequently cleaned and processed for methane or methanol generation. By-products of the gasification are significant quantities tars and water soluble organic materials, particularly with counterflow, fixed bed operation.

By gasfication of biomass using only steam and appropriate catalysts in the gasifier, the product gas will require less cleanup and processing equipment to prepare the gas for the methanator or methanol converter. By-products of this gasification scheme are mainly char. Production of tar and water-soluble organics is minimized.

Extensive gasification tests in a 5 cm diameter reactor have determined catalyst systems and desired operating temperatures for methane production and methanol synthesis gas production.

A process development unit (PDU) has tested these catalysts with wood chips (1 cm nominal size) at rates up to 35 kg/hr of dry wood. Results from these tests and future operation will be used to estimate the economics of catalytic steam gasification of wood to produce methane and methanol.

EXPERIMENTAL EQUIPMENT

Laboratory scale experiments have employed the quartz reactor depicted in Figure 1. This reactor continuously feeds wood at the rate of 0.3 grams per minute. A fixed catalyst bed is located below the gasification zone. Product gas volume is measured in a wet test meter.

The PDU reactor shown in Figure 2 does not have separate gasification and catalyst zones as does the lab scale reactor. Instead the catalyst and wood char are continuously mixed together. Wood is injected at the bottom of the

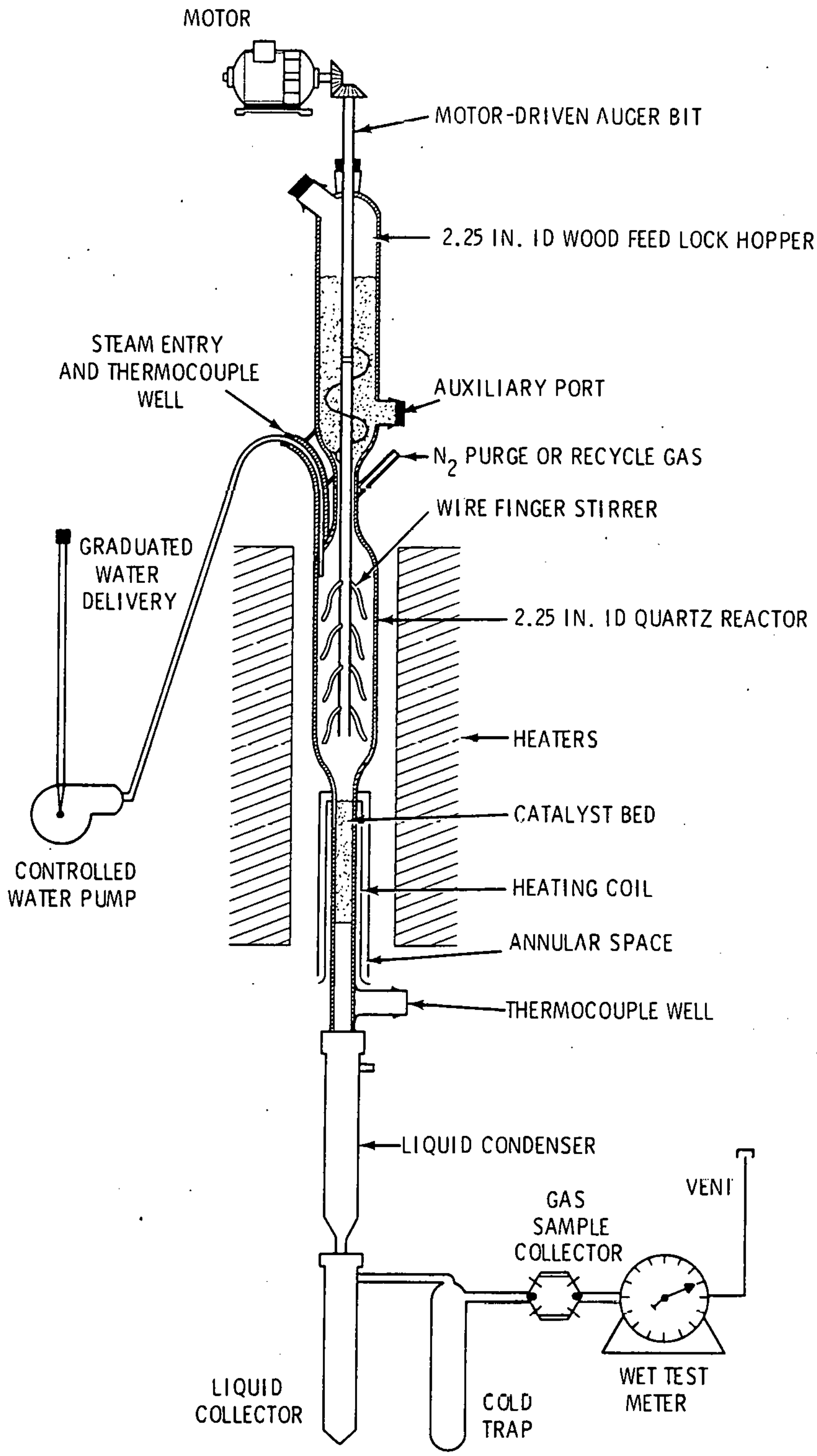

FIGURE 1. Laboratory Biomass Gasifier

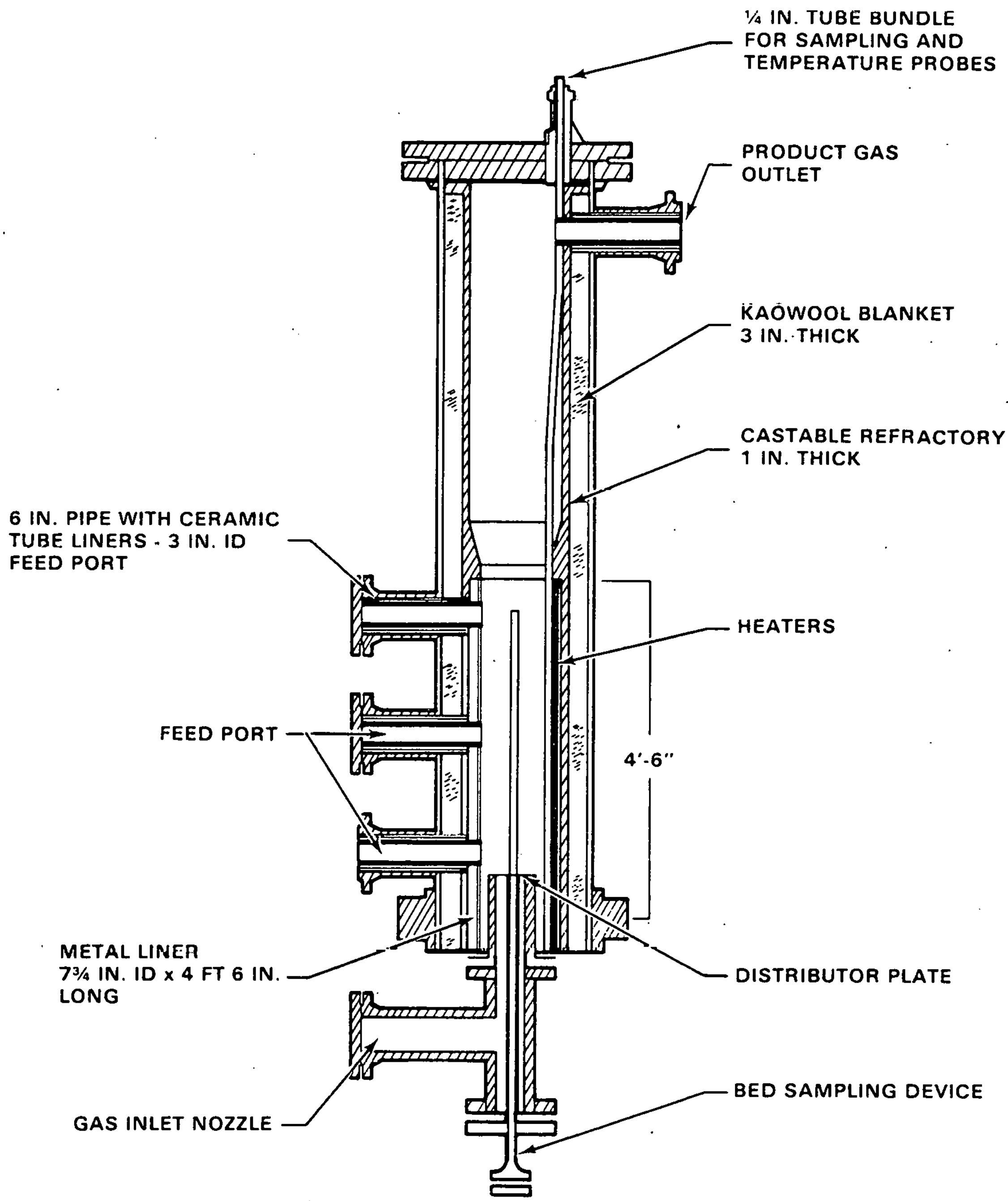

FIGURE 2. Schematic of PDU Biomass Gasifier

bed. Originally, the wood and catalyst were mixed with an agitator extending into the bed. The agitator was believed to be responsible for catalyst attrition and losses. The agitator was also considered to be impractical on a larger scale. For these reasons it was removed and the reactor now operates in a fluidized bed mode allowing intimate mixing of char, gas, and catalyst, increased heat transfer, and less catalyst attrition.

Heat for the endothermic reaction in the reactor is supplied by electrical heaters. To date, many difficulties have been encountered with heater operation. Of course on a large scale, heat will be provided by other means, either gas fired high temperature heat exchangers or circulating solids.

The peripheral equipment to the gasifier is shown in Figure 3. Originally the gas was cooled and cleaned by a venturi scrubber. Tar and char often collected in the water circulation lines making steady operation very difficult. A heat exchanger followed by an electrostatic precipitator is now used in place of the venturi scrubber.

METHANE PRODUCTION

Catalyst systems developed in the laboratory for methane production include combinations of alkali carbonates, nickel or nickel oxide on alumina supports, and silica-alumina. The most promising catalyst system at this time is nickel and silica-alumina in a 3:1 weight ratio. The nickel serves as a methanation and hydrogenation catalyst. The silica-alumina catalyst function is to crack condensible organic compounds.

Table 1 shows the results of a methane test in the laboratory with the nickel-silica-alumina catalyst system. The standard heat of reaction is determined from heat of combustion data at 25^{o}C. Assuming a steam temperature of 650^{o}C, a wood temperature of 100^{o}C, and a wood moisture content at 20% (dry basis), the theoretical heat requirement of the reactor is about 998,000 J/kg dry wood. Additional energy will be required to counteract heat losses.

Studies on catalyst deactivation and regeneration are in progress. No results are available at this time.

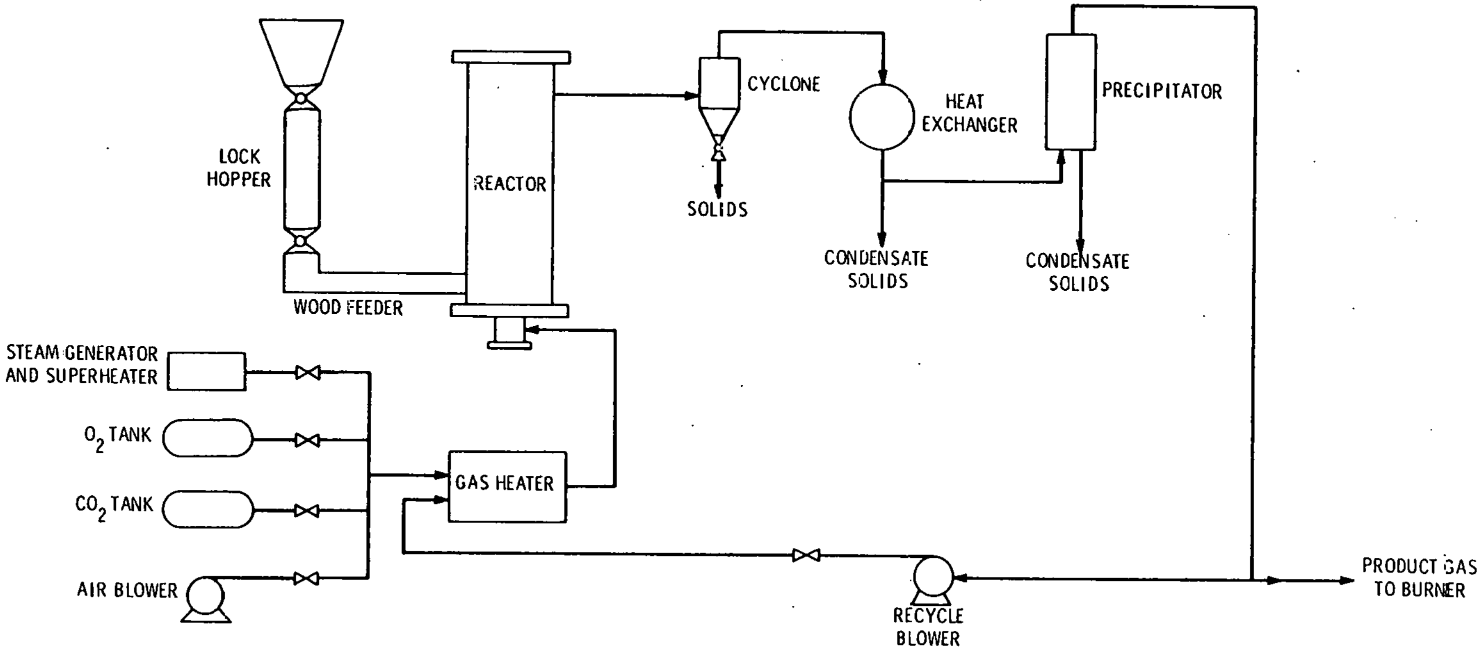

FIGURE 3. Process Flow Diagram for PDU

TABLE 1. Laboratory Results on Methanation of Lodgepole Wood Catalyst Nickel + Silica-Alumina (3:1)

Catalyst		Nickel+Silica-Alumina (3:1)
Temperature		550°C
Steam:wood wt. ratio		0.33
Carbon conversion to gas (%)		70
Carbon conversion to liquid (%)		0
J gas/J wood x 100		68
nm^3 CH_4/kg dry wood[a]		0.33
Composition		
CH_4	20.7	
H_2	32.3	
CO_2	33.6	
CO	13.4	
Standard heat reaction (J/kg wood)		64800

(a) Includes methanation of H_2 + CO

Results from a PDU test for methane production using the same catalyst system are given in Table 2. A promising aspect of the laboratory scale studies has been the absence of tar as a product. The PDU has produced tars in small amounts. The reason tars are not completely destroyed in the PDU reactor may be explained differences in the laboratory and PDU operations. The gas residence time in the laboratory scale reactor bed is about 5 seconds whereas the residence time in the PDU bed is about 0.8 seconds. The gradual loss of catalyst from the reactor and catalyst poisoning appear to be additional factors responsible for incomplete cracking of tar products in the PDU.

A conceptual flow diagram of wood to methane process is shown in Figure 4. Each of the areas are discussed briefly.

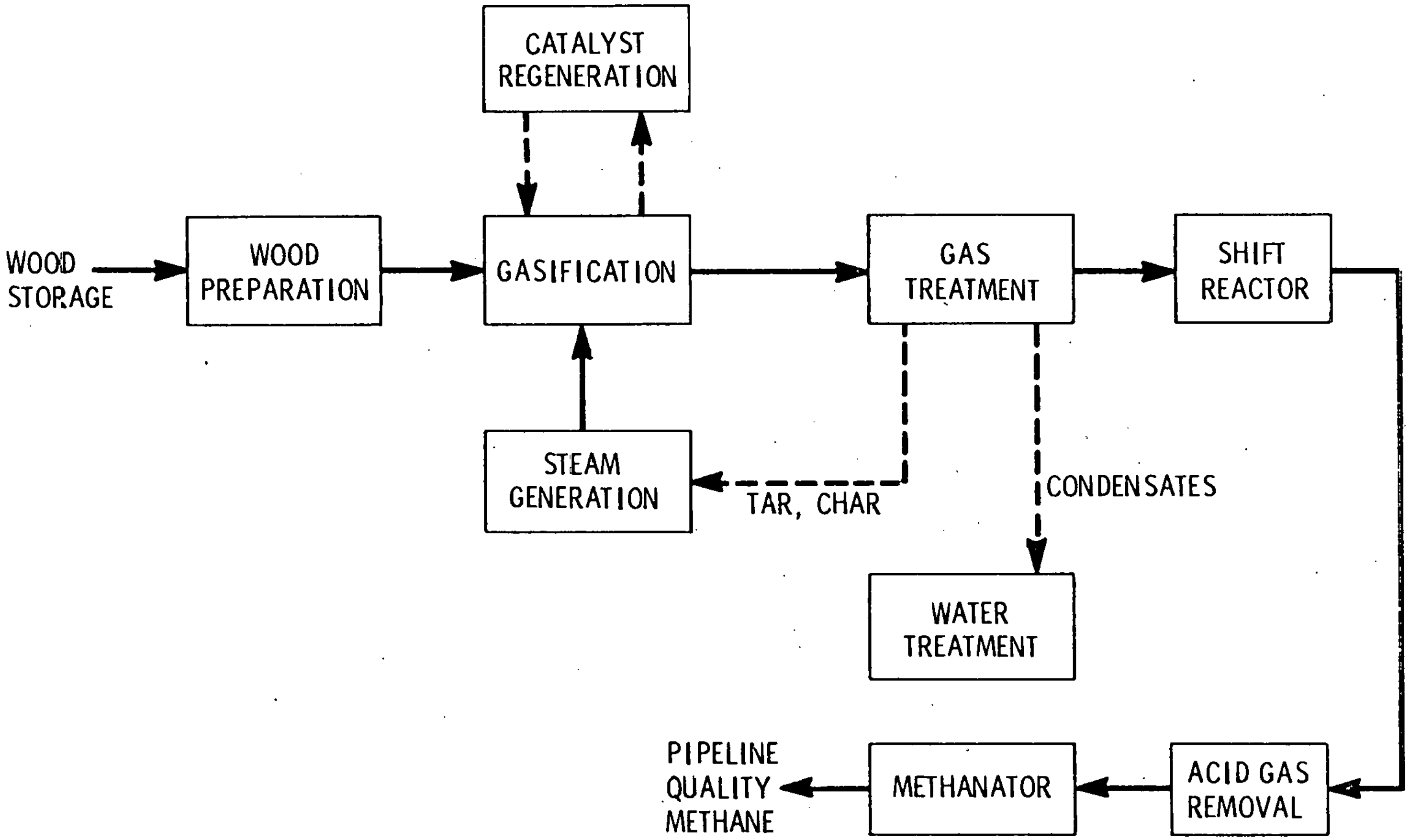

FIGURE 4. Block Flow Diagram for Wood to Methane Plant

TABLE 2. PDU Results for a Methanation Run

Catalyst		Nickel+Silica-Alumina (3:1)
Temperature °C		520
Steam/wood wt. ratio		0.9
Carbon conversion to gas (%)		66
Carbon conversion to liquid (%)		6
J gas/J wood x 100		61
nm^3 CH_4/kg dry wood[a]		0.29
Composition		
CH_4	0.233	
H_2	0.255	
CO_2	0.328	
CO	0.166	

(a) Includes methanation of H_2 + CO

Wood preparation. This module consists of equipment for removal of metallic scrap and sand, size reduction, storage, and drying. The type of wood which is anticipated as the feedstock is forest residue with 65 and 100 kg moisture per 100 kg of dry wood.

Gasifier. The gasifier will be designed baseds on PDU results and experience. Wood will be fed into the reactor at the bottom of the bed.

Gas Cleaning. The gas cleaning system proposed in based on commercially available units and will consist of cyclone separator, a heat exchanger, and electrostatic precipitator

Steam Generation. Char and tar will provide the energy for steam generation.

Catalyst Regeneration. Requirement for this area are being developed.

Water Treatment. Water from the process will be contaminated with organic materials. Treatment of gasification wastewater by aerobic digestion has been demonstrated.[a]

Water-Gas Shift. The hydrogen:carbon monoxide ratio from the gasifier will need to be increased to at least 3:1 to successfully methanate the remaining carbon monoxide.

Compression. Depending on the gasification pressure, compression may be required for CO_2 removal and subsequent methanation.

Acid Gas Removal. H_2S removal is required to preserve the methanation catalyst. H_2S in product gas from the PDU studies has been less than 10 ppm. A zinc reactor may be all that is required. CO_2 must be removed to make a high purity methane product.

Methanation. This unit will convert the H_2 and CO from the shift reactor to CH_4 by conventional methanation. After dehydration, the gas can be added to an existing natural gas pipeline.

METHANOL PRODUCTION

Methanol is produced from a synthesis gas of hydrogen and carbon monoxide in a 2:1 ratio. By steam gasification of biomass in the presence of appropriate catalysts, a gas of this ratio can be obtained in one vessel, thus eliminating the need for a shift reactor. Of course, some CO_2 removal may be required before methanol synthesis.

Laboratory scale experiments have determined two promising catalyst systems. They both contain nickel and silica-alumina. One system has the nickel precipitated on silica-alumina; the second system is a mixture of silica-alumina and nickel on alumina. The silica-alumina function is to crack the hydrocarbons. The nickel reforms methane and hydrogenates higher molecular

(a) Wakamiya, Will and J. V. Maxham 1980. "Treatability of Biomass Gasification Wastewater." Paper presented at the 10th Biomass Thermochemical Conversion Contractors Meeting, February 12-13, 1980, Berkeley, California.

weight hydrocarbons. Gas production increases with temperature. The maximum temperature tested has been 850°C. All tests have been at atmospheric pressure.

Table 3 lists the results of four laboratory reactor experiments. The first three tests were catalyst life studies. These tests were continued until traces of tar appeared in the product condensate. At 850°C virtually all the wood is converted to gas, and no catalyst deactivation was observed. All the char was converted to gas at these conditions.

TABLE 3. Laboratory Scale Reactor Results for Methanol Synthesis Gas

Case Number	1	2	3	4
Catalyst	Ni:SiAl 1:1	Ni:SiAl 1:1	Ni on SiAl	Ni on SiAl
Temperature°C	750	850	750	850
Wood/Catalyst Weight Ratio at Deactivation	16.1	100 (no deactivation)	52.5	Not tested
Carbon Conversion (%) to				
Gas	73	99.6	77	95
Liquid	Trace	0	Trace	0
Char	27	0.4	23	5
J gas/J wood x 100	82	115	87	110
Steam:Wood wt Ratio	0.63	1.25	0.71	1.25
Composition				
H_2	53.4	56.7	55.9	58.2
CO	28.1	27.9	27.8	28.5
CH_4	2.8	0.5	1.3	0.1
CO_2	15.6	14.9	15.2	13.2
Standard Heat of Reaction kg wood	5.258E+6	3.17E+6	4.952E+6	3.679E+6
kg Potential Methanol/kg Wood	0.59	0.86	0.64	0.86

Case 4 was only an 8 hour test. Catalyst deactivation and regeneration is now being studied. The potential methanol production from the gases in Table 3 is as high as 0.86 kg of methanol per kg of dry wood. However, energy is required for gasification. Some of the energy will come from combustion of char. In cases where the char production is low, the additional energy will be supplied by wood combustion. Therefore the actual yield of methanol will be reduced to about 0.6 kg per kg of dry wood.

The calculated standard heat of reaction is very endothermic. Using data from Case 3 and assuming wood feed at 20% moisture and 100^{o}C and steam feed at 850^{o}C, the net reactor heat requirement is approximately 6,706,000 J/kg dry wood. Additional energy is required to compensate for heat losses.

Electric heaters in the PDU reactor have not been able to maintain reactor temperatures above 600^{o}C. In order to reach 700^{o}C in the reactor, pure oxygen was added. The oxygen deactivates and sinters the catalyst. The thermal efficiency and synthesis gas yield with oxygen are much lower than obtained in the laboratory experiments. Table 4 gives results from a PDU test using oxygen for comparison with the laboratory tests. Modifications to the PDU will allow operation of the reactor at higher temperatures without oxygen addition.

A block flow diagram in Figure 5 shows the major process units for a wood-to-methanol plant using steam gasification of biomass with catalysts. Most modules are similar to the wood-to-methane flowsheet discussed earlier. Notably absent from schemes using steam-oxygen gasification are the shift reactor and oxygen plant. These absences significantly affect the cost of producing methanol by this method. The reduced production of tar will also require less sophisticated tar handling equipment and water treatment systems.

TABLE 4. Results From a Synthesis Gas Test on the PDU Using Steam Oxygen Gasification

Catalyst		Nickel+Silica-Alumina
Temperature		690^{o}
Steam:wood ratio		1.2
Oxygen:wood ratio		0.1
Carbon conversion to gas (%)		7
Carbon conversion to liquid (%)		3
J gas/J wood x 100		61
Composition		
CH_4	9.9	
H_2	28.9	
CO_2	33.2	
CO	24.6	
Potential kg methanol/kg wood		0.31

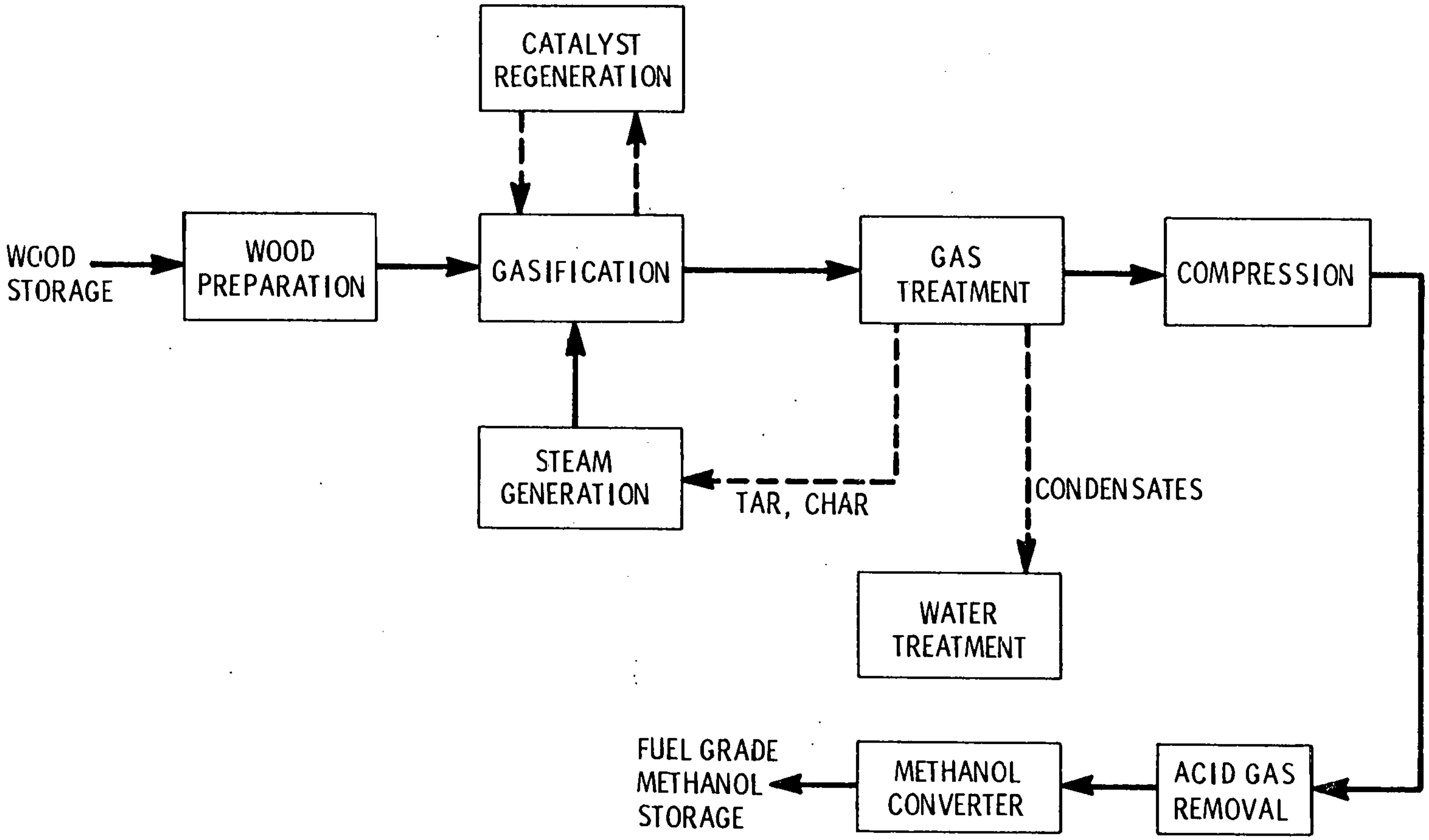

FIGURE 5. Block Flow Diagram for Wood to Methanol Plant