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Bench-Scale Studies on Gasification of Biomass in the Presence of Catalysts

**L. K. Mudge
E. G. Baker
M. D. Brown
W. A. Wilcox**

November 1987

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

**Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
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PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE MEMORIAL INSTITUTE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

NTIS Price Codes
Microfiche A01

Printed Copy

Pages	Price Codes
001-025	A02
026-050	A03
051-075	A04
076-100	A05
101-125	A06
126-150	A07
151-175	A08
176-200	A09
201-225	A010
226-250	A011
251-275	A012
276-300	A013

PNL--5699

DE88 003860

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EXECUTIVE SUMMARY

This report summarizes the results of bench-scale studies on the development of catalysts for conversion of biomass to specific gas products. The primary objective of these studies was to define operating conditions that allow long lifetimes for secondary catalysts used in biomass gasification. Nickel-based catalysts that were found to be active for conversion of wood to synthesis gases in previous studies were evaluated. These catalysts remained active indefinitely in laboratory studies but lost activity rapidly when evaluated in a process research unit (PRU). Bench-scale equipment was designed and installed to resolve the differences between laboratory and PRU results. Primary catalysts (alkali carbonates) were also evaluated for their effectiveness in improving conversion yields from biomass gasification.

Three different process configurations for testing secondary catalysts were evaluated:

- Configuration 1, with the catalyst as the fluid-bed material in the gasifier
- Configuration 2, with the catalyst in a separate fixed-bed reactor where it contacted products from the gasifier
- Configuration 3, similar to Configuration 2 but with the separate reactor operated as a fluid bed.

In the separate fluid-bed reactor, NiCuMo on silica-alumina and Ni on α -alumina remained active during tests lasting 30 to 40 hours for generation of synthesis gas from wood at 750°C. No sign of catalyst deactivation was noted at the end of these tests. Based on similar previous results obtained in the laboratory where a NiCoMo catalyst was tested for over 1200 hours and remained active, it is believed that the activity of these catalysts can be maintained indefinitely in Configuration 3. Deactivation of these same catalysts occurred within 10 hours when used in Configuration 1, which is similar to results obtained previously in the PRU. Used in Configuration 2, these catalysts were deactivated after about 20 hours.

Carbon deposition on the catalysts was identified as the major cause of deactivation. The carbon content on the catalyst surface leveled off at 2 to 5 wt% after about 10 hours in Configuration 3 but continued to increase with exposure in the other two configurations. Apparently the rate of carbon-forming reactions continues to exceed the rate of carbon-removing reactions in Configurations 1 and 2, and an equilibrium in rates is achieved in Configuration 3. Differences in heat transfer to the catalyst pellets in the fixed-bed and fluid-bed catalytic reactors are postulated to influence the net rate of carbon deposition on the catalyst surface.

As in previous studies, sodium and potassium carbonates were found to catalyze wood pyrolysis and steam/char reaction. Although the gas yield from wood pyrolysis is increased significantly with potassium carbonate as a catalyst, the increased steam/char reaction rate is not sufficient to offset the increased char yield. Therefore, overall gas yields are less with primary catalysts than with secondary catalysts.

Kinetics of the char/steam and char/carbon dioxide reaction were evaluated with and without primary catalyst in the fluid-bed gasifier. Char was produced directly in the fluid bed by wood pyrolysis just prior to the kinetic tests.

Yields and compositions of condensible organics (tars) from steam and carbon dioxide gasification of wood are reported. Tar yields are reduced by both primary and secondary catalysts, and compositions are significantly altered. In the presence of secondary catalysts, tars consist mainly of benzene, toluene, and xylene. Yield and composition of tars are also significantly changed by using carbon dioxide instead of steam for wood pyrolysis.

ACKNOWLEDGMENTS

This report summarizes the technical results of bench-scale studies on catalyzed gasification of biomass conducted by the Pacific Northwest Laboratory (PNL) for the Biofuels and Municipal Waste Technology Division of the U.S. Department of Energy (DOE). The guidance and support provided by Gary F. Schiefelbein and Mark A. Gerber of the Program Office and Simon Freidrich of DOE are greatly appreciated.

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INTRODUCTION

Catalysts are widely used in industry, particularly the petroleum industry, to improve the energy efficiencies of conversion and refining processes. Development of catalysts for petroleum refining has had a major positive impact on the efficiency of that industry.

Catalysts may be used in biomass conversion processes in a variety of applications to enhance conversion efficiency and environmental acceptability. Gasification of biomass in the presence of catalysts has been studied in the laboratory and the process research unit (PRU) at the Pacific Northwest Laboratory (PNL)^(a) since 1978 (Mudge et al. 1981; Mudge et al. 1983; Baker and Mudge 1984a) under a contract with the Biomass Thermochemical Conversion Program of the U.S. Department of Energy (DOE). These studies identified secondary (supported metal) and primary (alkali carbonate) catalysts that were effective for conversion of biomass to specific gas products. Gases that can be produced include synthesis gases for methanol and hydrocarbon production, a methane-rich gas, and a hydrogen-rich gas.

Nickel-based catalysts were the most effective for producing specific gas products. Rapid catalyst deactivation was found to be a problem in some cases. In laboratory tests where the catalyst was placed in a fixed bed downstream from the gasifier, a NiCoMo on silica-alumina catalyst remained active for over 1200 hours of exposure for the production of synthesis gas from wood at 750°C. Catalyst lifetime in PRU tests where the catalyst was added directly to the fluid-bed gasifier was less than 10 hours (Mudge et al. 1983).

The objective of the bench-scale studies was to resolve discrepancies in results of laboratory and PRU studies. Bench-scale equipment included a fluid-bed gasifier and a secondary catalytic reactor for testing catalysts in a variety of configurations under realistic gasification conditions. Different methods for contacting the secondary (supported metal) catalyst and reactants could be readily tested in the bench-scale equipment.

(a) Operated for the U.S. Department of Energy by Battelle Memorial Institute.

The bench-scale studies successfully resolved questions concerning catalyst activity that were unanswered in previous laboratory and PRU studies. Process configurations for the effective use of nickel-based catalysts are presented. Yields of specific gas products from gasification of wood in the presence of supported metal and alkali carbonate catalysts and process requirements are presented in this report. The effects of catalysts on generation of condensible organics (tars) are outlined.

DESCRIPTION OF THE EXPERIMENTS

Equipment, materials, and procedures used in the bench-scale studies are described in this section. The different configurations employed to accomplish the study objectives are outlined.

EQUIPMENT

The bench-scale equipment was designed for evaluation of catalysts for biomass gasification. A schematic of the unit is shown in Figure 1. The equipment simulates steady-state operation in a fluid-bed gasifier. Catalysts can be contacted with the biomass in the primary reactor, as was done in PRU studies (Mudge et al. 1983); or catalysts can be contained in a secondary reactor to contact volatile products from the primary reactor, as was done in previous laboratory studies (Mudge et al. 1981). Catalysts that are active in laboratory tests can be rapidly tested in the bench-scale equipment to verify promising results.

The original equipment design was based on the following criteria:

- atmospheric pressure operation
- temperatures of up to 1470°F (800°C)
- wood feed rates of up to 4 lb (1.8 kg) per hour
- superficial linear velocities of up to 2 ft (60 cm) per second
- control of fluid-bed depth in the primary gasifier
- volumetric processing rates of up to 70 lb/h-ft³ (1100 kg/h-m³)
- single or dual vessel operation
- ability to handle alternate feedstocks.

Discussion during the design stage focused primarily on pressurized versus atmospheric operation and the effects of active fluid-bed depth. Pressurized operation presented several difficult problems during both design and experimentation. Designing a vessel to handle 1470°F (800°C) and 10 atm (1000 kPa) required special materials and fabrication and greatly increased the complexity and cost of the project. Feeding at pressure is not a simple task, as was evident in previous PRU experiments (Mudge et al. 1983). In other studies (Baker and Mudge 1985), a trend toward extended catalyst life with increased

FIGURE 1. Bench-Scale Equipment Design

pressures was observed. In light of potential operational problems at high pressures, an atmospheric pressure unit was built. Results at atmospheric pressure are conservative with respect to expected catalyst life.

Length-to-diameter (L/D) ratio is an important criterion in designing fluid-bed systems (Zenz and Othmer 1960). Ratios of L/D greater than 4 tended to encourage slugging due to bubble growth. To minimize slugging in a 3-in.-diameter (7.6-cm) bed required a bed depth of less than 1 ft (30.5 cm).

Steam was generated, superheated, and used to entrain feedstock in a line to the primary gasifier. From the primary gasifier, hot product gases, tar, and char then entered the filters, where the char was removed. The remaining gases and tar were either sampled or routed to the secondary gasifier. Products leaving the secondary reactor were sampled, then cooled and condensed in a submerged-bed scrubber. Gases were metered, sampled, and finally discharged to the vent.

Gasifier

The gasifier consisted of a section of 3-in. (7.6-cm) Sch 40 304L stainless steel pipe, two welded 304L stainless steel reducers, a length of 5-in. (12.7-cm) Sch 40 pipe, and assorted flanges and couplings (see Figure 2). The entire reactor was enclosed in a 16-kW, SCR-controlled, 4-zone furnace capable of operation at 2190°F (1200°C). The maximum operating temperature of the gasifier catalyst bed was about 1470°F (800°C). The tube wall temperature probably reached 1560 to 1650°F (850 to 900°C).

Steam and wood (plus any other reactant gases) entered the gasifier through the 1/2-in. (1.3-cm) tube in the bottom. The feedstock was entrained in the gas stream. Offgas exited the reactor through 1-in. (2.5-cm) 316 stainless steel tubing for downstream processing.

Char was removed intermittently from the catalyst bed to keep the level somewhat constant. The char was vacuumed off the top of the bed using an inert-gas, vacuum flask arrangement.

FIGURE 2. Feeder/Reactor

Biomass Feeder

Feedstock was fed to the reactor by a variable-speed (0 to 1000 rpm) auger in a 1-in. (2.5-cm) glass tube from a 1-ft³ (28-L) hopper (see Figure 2). With a wood density of 25 lb/ft³ (400 kg/m³), a charge of approximately 25 lb (11 kg) of reserve feedstock was contained in the hopper. This feeder has been

tested over a wide range; and in the present experiments, desired feed rates were controlled over a range of 0 to 30 lb/h (0 to 13 kg/h).

Wood was kept dry and cool while being fed by a nitrogen purge introduced into the top of the hopper. Steam in the feed tube was minimized, and any pyrolysis gases formed in the feed tube were swept into the reactor.

Catalytic Reactor

Both fixed-bed and fluid-bed catalytic reactors were used to determine the effectiveness of secondary catalysts for conversion of condensible organics from the gasifier. The catalysts were physically separated from the wood gasification/pyrolysis to avoid deactivation of the catalysts from excessive carbon deposition and to simplify catalyst recovery.

The fixed-bed catalytic reactor shown in Figure 3 was a 6-ft long (1.8-m) unit consisting of a 2-in.-diameter (5-cm) Sch 40 stainless steel pipe with tees attached to each end. Catalysts were packed as a layer between plain saddles and ceramic balls. Typical catalyst bed depths were up to 1 ft (30 cm). The entire length of the reactor was enclosed in a 4-zone, 18-kW clamshell furnace. Thermocouples were spaced evenly throughout the preheat and active zones. The reactor could be operated in either upflow or downflow, depending on the piping configuration desired. The entire product gas stream from the primary gasifier was treated at temperatures from 1200 to 1380°F (650 to 750°C) to destroy condensible organics.

In external dimensions, the fluid-bed catalytic reactor was a duplicate of the primary gasifier vessel. In the fluid bed, the catalyst was held in place by a single "bubble cap"-type distributor plate, as shown in Figure 4.

The particle size of the catalyst for the fluid bed is typically much smaller than for a fixed bed. Most fluid-bed catalysts used here were in the range of 40 to 100 mesh (100 to 400 μm). Fixed-bed units use particles between 0.125 in. and 1 in. (0.3 cm and 2.5 cm) to reduce the pressure drop at high gas velocities.

FIGURE 3. Fixed-Bed Catalytic Reactor

FIGURE 4. Fluid-Bed Catalytic Reactor

Steam Generator

Steam for the bench-scale gasifier was generated as used. Deionized water, stored in a 5-gal (20-L) polyethylene carboy, was pumped through 40 ft (12 m) of 0.375-in.-diameter (0.95-cm) stainless steel tubing coiled inside two Linberg clamshell furnaces. The furnaces were capable of operation at 2200°F (1200°C). Superheated steam was generated at 0 to 7 lb/h (0 to 3 kg/h) at 1470°F (800°C).

Char Removal System

A constant bed depth was maintained for steady-state operation of the fluid-bed gasifier. Accumulated (unreacted) char was removed from the gasifier by the vacuum system shown in Figure 5. The bed depth was maintained at the level where the removal pipe was located by hourly removal of about 0.25 to 1 lb (100 to 450 g) of bed material. This material was typically 20% to 40% char, with the remainder being inert materials (sand or bauxite) or catalyst. Inert materials were added to the gasifier with feedstock to avoid their depletion.

The char removal device was a 1/2-in. (1.3-cm) stainless steel tube that extended through the top flange into the fluid bed and was connected to a vacuum flask. The valve between the flask and the gasifier was closed and the flask evacuated. The valve to the vacuum pump was then closed and the valve to the gasifier opened to remove a pulse of bed material and gas. This procedure was repeated until very few solids were contained in the pulse of gas.

Product Gas Filters

Product gases leaving the primary reactor contained suspended char particulates and volatile tars. A series of sintered metal filters was employed to remove char particles. The filters were 2-3/4 in. (7 cm) in diameter and 24 in. (61 cm) long, with a pore size of 10 μ m. They were suspended inside 5-in. (12.7-cm) Sch 40 black iron tees, as shown in Figure 6. The bottom thimble was removable so that collected char could be sampled and weighed. In some situations, the filter element was replaced by an open downtube. Solids simply settled onto the bottom of the thimble.

FIGURE 5. Char Removal System

Gas Cleanup Filters

Gases leaving the secondary reactor still contained suspended particulates and tar vapors. Separation of chars and tars, which was necessary for efficient gas cleaning, was found to be very difficult. If the temperature of the gas stream dropped below the dew point of the tars, tars and char particles plugged lines very quickly.

For the low product flow rates associated with the bench-scale gasifier, sintered metal filters followed by a condenser/knockout pot were first installed (Figure 7). This was essentially the same system that was very

FIGURE 6. Filter Vessel

successful on the 1-ton/day PRU (Mudge et al. 1983). However, in these bench-scale studies, the filters exhibited plugging problems. Larger filters were procured to reduce the face velocity.

Plugging problems continued in the condenser section, and eventually the condenser-knockout pot system was replaced by a submerged-bed scrubber (Figure 8). Dirty inlet gases were sparged through cooled condensate to precipitate any tars and collect both tars and char. The scrubber was filled with 1/2-in. (1.27-cm) Intalox saddles to break up the gas bubbles and provide

FIGURE 7. Original Gas Cleaning System

maximum gas-liquid contact. A sight glass (not shown in Figure 8) was used to monitor and maintain the liquid level in the scrubber. The scrubber has performed perfectly since installation.

A small glass-fiber coalescing filter removed any small tar, oil, and water droplets which were not removed by the submerged-bed scrubber. The cleaned gases were then metered through an orifice and a dry test meter before being sampled and vented.

Gas Samplers

Product gases from the bench-scale gasifier were sampled at two points. The first point was after the primary gasifier but before the secondary catalytic reactor. The second was downstream of the secondary catalytic reactor. A Carle AGC-S gas chromatograph equipped with a thermal conductivity detector gave on-line gas analyses at approximately 20-minute intervals. Gases were also sampled for tars and oils by extraction into methylene chloride, as shown in Figure 9. The methylene chloride solution was analyzed with a Hewlett-Packard 5992B gas chromatograph to determine the tar content of the solution. The acetone rinse solution was evaporated and analyzed to determine the amount and elemental composition (C, H, and O). The resulting data

FIGURE 8. Submerged-Bed Scrubber

regarding yield of condensible organics are reported in Appendix A. Solids were sampled and analyzed for C, H, O, and ash. Some solid samples were analyzed for inorganic elements by inductively coupled argon plasma atomic emission spectroscopy (ICP).

FIGURE 9. Methods for Tar Sampling and Recovery

MATERIALS

Materials used in the bench-scale studies included wood feedstock, primary catalysts, secondary catalysts, and inert materials. These materials and their sources are described below.

Wood Feedstock

The wood feed used in the bench-scale studies was densified pine flakes obtained from Thomas A. Miles Consulting Engineers, Portland, Oregon. Characteristics of the densified flakes are presented in Table 1. Screen fractions used in the study are given in the tables of test results in Appendix A.

TABLE 1. Characteristics of Densified Flakes

<u>Element</u>	<u>wt%</u>		
C	50.3		
H	6.4		
O	42.7		
Ash	0.6		
		<u>Btu/lb</u>	<u>kJ/kg</u>
Higher heating value		8770	20,400

Primary Catalysts

Sodium carbonate and potassium carbonate were tested for their effectiveness as primary catalysts for wood gasification. Bulk technical-grade chemicals were used for the tests.

Secondary Catalysts

Four secondary (supported metal) catalysts were tested. A catalyst made specially for this project by W. R. Grace and Company, Baltimore, Maryland, NCM, consisted of nickel, copper, and molybdenum salts impregnated on a proprietary, high surface-area support. A commercial steam-reforming catalyst, G90C, was provided by United Catalysts. These were two of the most effective catalysts in laboratory studies. The other two catalysts, RKS-41A and ICI-46-1, are commercially available. Three of the catalysts, G90C, RKS-41A, and ICI-46-1, were in 1/2- to 5/8-in. (1.3- to 1.6-cm) rings when received. These were broken into 1/4- to 1/2-in. (0.6- to 1.3-cm) chunks for the secondary fixed-bed tests and ground to a fine mesh for the fluid-bed tests. In all three configurations, G90C was used; RKS-41A and ICI-46-1 were used only in the secondary fluid bed. Table 2 summarizes the relevant properties of these catalysts.

Inert Materials

Inert materials used to stabilize the fluid bed were sintered bauxite or sand spheres. Bauxite spheres were obtained from the Norton Company Material Division and had a bulk density of 130 lb/ft³ (2 g/cm³). The spheres of

TABLE 2. Properties of Secondary Catalysts

Catalyst	Source	Composition, wt%		BET Surface Area, m ² /g	Metal Surface Area, (a) mg ² /g	Catalyst Sieve (U.S. Sieve)		
		Active Metals	Support			Primary Fluid Bed	Secondary Fluid Bed	Secondary Fixed Bed
NCM	W. R. Grace	9.5% Ni 4.25% CuO 9.25% MoO ₃	SiO ₂ -Al ₂ O ₃	205	5	-40 to +70	-40 to +70	-
G90C	United Catalysts	15% Ni	70% to 76% Al ₂ O ₃ 5% to 8% CaO	3 to 15	-	-40 to +70	-40 to +70	-1/2 to +1/4 in.
RKS-41A	Haldor Topsoe	Ni	MgO Al ₂ O ₃	-	-	-	-20 to +70	-
ICI-46-1	Imperial Chemical Industries	16.5% Ni (21% NiO)	14% SiO ₂ 29% Al ₂ O ₃ 13% MgO 13% CaO 7% K ₂ O 3% Fe ₂ O ₃	11.0	-	-	-20 to +70	-

(a) Determined by hydrogen adsorption.

bauxite were in the size range of -40 to +70 U.S. Sieve No. (0.42 to 0.21 mm). Bauxite can withstand temperatures above 2000°F (1093°C) and is extremely fracture resistant.

Silica sand was obtained from Martin Marietta Industrial Sand Division and was 99.88% silica. The bulk density of the sand was 100 lb/ft³ (1.6 g/cm³), and the size range of the sand particles was -30 to +100 U.S. Sieve No. (0.895 to 0.149 mm).

PROCEDURES

Safe operating procedures were established for operation of the bench-scale gasifier. A general description of these procedures is presented in this section.

For each test, feedstock was prepared for loading into the feed hopper on the day before the test. For tests with a primary catalyst, wood was impregnated with alkali carbonate and dried overnight. An inert material (sand or bauxite) was added to the wood to maintain a constant composition in the fluid bed while keeping the bed depth constant during the test. A weighed quantity of feedstock sufficient for the entire test was added to the feed hopper on the day of the test.

Catalysts were weighed and added to either the gasifier or secondary vessel. For many tests the secondary catalyst was still in the reactor from the previous test, and no preparation was necessary. For single-vessel tests with a secondary catalyst, a weighed quantity of catalyst was added to the gasifier; no attempt was made during the tests to replace catalysts withdrawn with the char overflow.

The gasifier was filled to the desired operating depth with bed material (usually char and inert material or char and secondary catalyst). The furnaces were then heated to the required operating temperatures while the system was purged with nitrogen. Steam flow was started just prior to wood flow, and nitrogen flow was decreased to about a 300-mL/min purge through the hopper to prevent diffusion of steam into the wood feed. Wood flow was initiated by starting the feed auger at the rate required for the test. Steam flow was

controlled by a variable-speed metering pump on the feedwater. Flow conditions used in the tests are included in tables of test results in Appendix A.

Steady-state operation was achieved almost immediately. When catalyst activity was steady, gas flows and compositions remained constant. Bed material was withdrawn each hour to keep the bed level fairly constant. More frequent withdrawals (every 15 min) were tested but found to be unnecessary. Gases were sampled and analyzed every 30 min. Condensibles were collected and analyzed at the end of each test, as were the solid materials from the fluid bed and gas filters. Loss of catalyst activity was evident from several observations: 1) decreased gas flow; 2) increased hydrocarbon content in the gas; and 3) oils in the condensate.

DISCUSSION OF RESULTS

Bench-scale tests were completed with alkali carbonate catalysts (sodium and potassium carbonate) impregnated on wood and with secondary (supported metal) catalysts in different contact configurations. Supported metal catalysts were tested in contact with wood and char in the gasifier and in a secondary catalytic reactor where gases and volatiles from the gasifier contacted the catalyst. Catalysts in the second reactor were tested as a fixed bed and as a fluid bed. Results of tests with these catalysts are presented in the following sections.

SECONDARY CATALYSTS

Tests with supported metal catalysts were conducted in three modes: 1) catalyst in the fluid-bed gasifier, 2) catalyst in a secondary fixed-bed reactor, and 3) catalyst in a secondary fluid-bed reactor. All three modes of operation are described below. The majority of the tests using secondary catalysts were conducted under the conditions shown in Table 3.

In all the tests with the catalysts shown in Table 2, catalyst activity was initially high. The gas consisted primarily of H_2 , CO, CO_2 , and a trace of methane. No tars or oils were initially present. Typical start-of-run data are shown in Table 4. Several uncatalyzed tests were made to provide a

TABLE 3. Typical Conditions for Tests Using Secondary Catalysts

<u>Variable</u>	<u>Range</u>	<u>Variable</u>	<u>Range</u>
Wood Feed Rate		Gasifier Pressure, kPa	101
g/min	12 to 16	Catalyst Loading, g	600 to 700
kg/m^2-h (lb/ft^2-h)	170 (35)	Catalyst Bed Height, cm	23 to 25
kg/m^3-h (lb/ft^3-h)	560 (35)	Char Residence Time, min	30 to 40
Steam Rate, g/min	11 to 13		
Temperature, °C			
Gasifier	750		
Secondary Reactor	750		

TABLE 4. Typical Results with a Fresh Catalyst and with No Catalyst

	<u>Fresh Catalyst</u>	<u>No Catalyst</u>
Gas Composition, vol%		
H ₂	60	41
C ₃ H ₆ , C ₃ H ₈	--	1
CO ₂	16	16
C ₂ H ₄ , C ₂ H ₆	--	4
CH ₄	1	10
CO	23	28
Gas Production, m ³ /kg		
Total	2.6	1.2
Synthesis Gas (H ₂ + CO)	2.1	0.8
Cold Gas Efficiency ^(a)	1.3	0.87
Carbon Conversion, wt%		
Gas	90	80
Solid	10	13
Liquid	--	7

(a) Btu in gas/Btu in wood feed.

comparison. A decreased yield of synthesis gas, an increase of light hydrocarbon gases, and the appearance of tar in the condensate from the gasifier were used as indicators of catalyst deactivation.

Tests with Catalyst in the Gasifier

These tests were conducted to confirm results obtained previously in the 1-ton/day fluid-bed PRU. The catalysts tested in the PRU were a Ni/Al₂O₃ hydrocracking catalyst supplied by W. R. Grace (Mudge et al. 1981) and the NiCuMo catalyst (NCM) tested in the bench-scale tests (Mudge et al. 1983). Both lost activity rapidly, as shown in Figure 10.

This rapid deactivation was originally thought to be due to the instability of short-term tests in the PRU, which involved large temperature variations

FIGURE 10. Catalyst Deactivation in Gasifier

during startup and shutdown (Mudge et al. 1981). However, similar deactivation occurred in the bench-scale tests in longer, more stable tests using both NCM and G90C catalysts (see Figure 10).

Loss of catalyst activity is apparently caused by buildup of carbon that blocks access to the catalyst pores. Figure 11 shows carbon buildup in the bench-scale tests and in PRU tests with bagasse.

Some catalyst was carried out of the gasifier with the product gas, which probably accelerated the apparent loss of catalyst activity. However, the large amount of carbon on the catalyst remaining in the bed indicated that the catalyst had little activity; even if the bed were still full, there would be little overall improvement in catalyst effectiveness.

Tests with Catalyst in a Separate Fixed-Bed Reactor

One extended test was performed with G90C in a secondary fixed-bed reactor to compare to previous results obtained in laboratory gasification tests. The initial loss of activity was similar to that seen in the laboratory (see

FIGURE 11. Carbon Accumulation on Catalyst in Gasifier

Figure 12). In the laboratory tests, catalyst activity stabilized after 15 to 20 hours at a synthesis gas yield of 20 to 21 scf/lb (1.25 to 1.30 nm^3/kg wood), and no further deactivation was noted.

In the bench-scale tests, G90C continued to deactivate down to a synthesis gas yield of about 16 scf/lb (1.0 m^3/kg). After 16 hours of exposure, the catalyst had accumulated 6 wt% of carbon deposits, compared to less than 1 wt% after 40 hours of exposure in the laboratory unit. After about 1200 hours of exposure in the laboratory unit, NCM had accumulated only 4 wt% of carbon deposits.

Tests with Catalyst in a Separate Fluid-Bed Reactor

The NCM catalyst was available only in -40 to +70-mesh (-0.42 to +0.21-mm) spheres; to test it in a separate bed required construction of a fluid-bed reactor. The initial activity of NCM was high in the fluid bed. Some activity was lost in the first 8 to 10 hours, but no further loss of activity was noted during the remaining 34 hours of testing. Synthesis gas yield leveled off at about 24 scf/lb (1.5 nm^3/kg), 20% higher than that achieved in laboratory gasification tests.

FIGURE 12. Catalyst Deactivation in a Secondary Fixed Bed

This test was so encouraging that three other catalysts (G90C, ICI-40-1, and RKS-41A) were also tested in this mode. Only RKS-41A deactivated rapidly. Tests using G90C and ICI-40-1 yielded results similar to those using NCM. Results of these four tests are shown in Figure 13. NCM, G90C, and ICI-40-1 all reached a "steady-state" activity with a synthesis gas yield of about 24 scf/lb (1.5 nm³/kg). Table 5 shows typical results during this steady-state period. These can be compared to the results shown in Table 4 of tests using a fresh catalyst and no catalyst.

Carbon deposition on the catalysts in the separate fluid-bed reactor was dramatically reduced compared to that found on catalysts mixed in the gasifier or in a separate fixed-bed reactor. Carbon deposition leveled off at about 3 wt% for G90C and 1 wt% for NCM, as shown in Figure 14.

Tests with Supported Metal Catalysts

The primary finding of the bench-scale studies using supported metal catalysts was that the placement of the catalyst (gasifier versus separate bed) and the mode of contact (fluid bed versus fixed bed) have a dramatic effect on

FIGURE 13. Catalyst Deactivation in a Secondary Fluid Bed

catalyst deactivation. Figure 15 summarizes the rate of coke formation and catalyst deactivation for all three systems.

We previously theorized that the rapid coke formation on the catalysts in the primary gasifier was due to secondary tar reactions that produce coke and light gases (Baker and Mudge 1984b). Schafizadeh and Fu (1973) and Milne, Evans, and Solty (1983) concluded that tar is the primary product of high-temperature pyrolysis and that the char and gases produced result largely from secondary tar reactions. Placing the catalyst in a separate vessel allows the primary tar to react uncatalyzed in the gasifier, so that the catalyst treats only the resulting secondary tar. The bench-scale tests support this theory, because moving the catalyst to a separate vessel dramatically reduced coke formation and the resultant catalyst deactivation.

Operating the separate catalytic reactor as a fluid bed, as opposed to a fixed bed, further reduced coke formation on the catalyst and catalyst deactivation. Improved heat transfer and improved mass transfer in the fluid bed are the only apparent differences between the two contact modes.

TABLE 5. Typical Results with "Steady-State" Catalyst

Gas Composition, vol%	
H ₂	55
C ₃ H ₆ , C ₃ H ₈	--
CO ₂	14
C ₂ H ₄ , C ₂ H ₆	1
CH ₄	6
CO	24
Gas Production, nm ³ /kg	
Total	1.9
Synthesis Gas (H ₂ + CO)	1.5
Cold Gas Efficiency ^(a)	1.1
Carbon Conversion, wt%	
Gas	88
Solid	10
Liquid	2

(a) Btu in gas/Btu in wood feed.

FIGURE 14. Carbon Accumulation on Catalysts in a Secondary Fluid Bed

FIGURE 15. Comparison of Observed Trends for Catalyst Deactivation Versus Carbon Accumulation in Different Operating Modes (G90C, NCM, and ICI-46-1)

Previous equilibrium studies showed that at a 1:1 steam:wood ratio, the equilibrated product gas shows no affinity for carbon formation at temperatures above 600°C (Mudge et al. 1981). In an open thermodynamic system, carbon may still be stable in a steady state, and accumulation of carbon may result. The question of whether there is a net buildup of carbon and subsequent catalyst deactivation depends on the relative rates of the carbon-forming and carbon-removing reactions. In the closed system employed for the bench-scale tests, the primary carbon-forming reactions are thermal cracking of tars and olefin polymerization (Baker and Mudge 1984a):

tars → coke + light hydrocarbons + gases

$C_nH_{2n} \rightarrow \text{polymers} \rightarrow \text{coke}$

The main carbon-removal reaction is the water-gas reaction:

Carbon can also be gasified by carbon dioxide and hydrogen, but these reactions are slower than the water-gas reaction.

Due to the strongly endothermic nature of the reactions that take place on the catalyst, poor heat transfer in the fixed-bed reactor could result in the catalyst pellets being significantly cooler than the measured bulk gas temperature. Increased carbon deposition could then result from the pellets' dropping below the critical temperature at which carbon is thermodynamically stable (~600°C). It may also be that the lower temperature reduces the rate of carbon gasification on the catalyst pellet below the rate of carbon formation. The effect of heat transfer on catalyst temperature is discussed in the following section.

HEAT AND MASS TRANSPORT CONSIDERATIONS

Catalytic chemical reactions are usually not isothermal. Many require participant reactants to diffuse through a boundary layer to react at or be removed from a catalyst surface. Heat and mass transfer restrictions are of paramount importance in both the experimental and design phases of a project. Adequate heat transfer in this particular situation may mean the difference between an active or an inactive catalyst.

Secondary Reactions

Catalytic steam gasification is a complicated series of simultaneous reactions that are as yet not fully understood. Baker and Mudge (1984b) provide a potential explanation of the interrelated reactions that occur during steam gasification. Figure 16 outlines the overall reaction scheme. The matching reactions are listed in Table 6.

FIGURE 16. Reaction Pathways

For the production of synthesis gas with an active nickel catalyst at 750°C, reactions of importance are conversion of methane, light hydrocarbon gases and tar to gas, and shifting carbon monoxide to hydrogen. With a fresh nickel catalyst, all of the hydrocarbons and tars are converted to gases, and the methane-reforming and shift reactions are driven to equilibrium.

Reaction 9 (see Table 6) represents the ultimate fate of the tar with a fresh catalyst; however, direct reaction of tar with steam is probably small (Wen 1983). Reaction 9 most likely represents the addition of reactions 7, 3, 8, and 10.

The endothermic nature of most cracking and reforming reactions is illustrated in Table 7. This table shows the extremely high heats that are required for the methane-reforming, tar-reforming, and gasification reactions. Reactions such as the Boudouard reaction ($2\text{CO} \rightarrow \text{C} + \text{CO}_2$) and the water-gas shift are exothermic but not favored at the high temperatures found in gasifiers.

TABLE 6. Secondary Reaction Pathways in Steam Gasification of Biomass

Reaction No.	Pathway	Description
1	$\text{CH}_4 + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}$	Steam reforming/methanation
2	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$	Shift reaction
3	$\text{C}_n\text{H}_m + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$	Steam reforming light hydrocarbons
4	$\text{C}_n\text{H}_{2n} + \text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+2}$	Hydrogenation
5	$2\text{CO} \rightarrow \text{CO}_2 + \text{C}$	Boudouard reaction
6	$\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$	Methane decomposition
7	Tar $\rightarrow$ coke + lighter hydrocarbons + gas	Thermal or catalytic cracking
8	Tar + $\text{H}_2 \rightarrow$ lighter hydrocarbons + gas	Hydrogenation/hydrocracking
9	Tar + $\text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$	Tar reforming
10	Coke + $\text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$	Steam gasification
11	$\text{C}_2\text{H}_6 + \text{H}_2 \rightarrow 2\text{CH}_4$	Hydrogenolysis of ethane

TABLE 7. Selected Heats of Reaction^(a)

Reaction No.	Description	ΔH°_{298}
1	Methane reforming	206.2 kJ/mole
2	Water/gas shift	-41.2 kJ/mole
3	Tar reforming	95.5 kJ/mole
5	Boudouard reaction	-172.4 kJ/mole
6	Methane decomposition	+74.9 kJ/mole
10	Carbon/steam gasification	131.5 kJ/mole

(a) Based on $H_f = 36$ kJ/mole for tars (naphthalene).

Thermodynamic Equilibrium and Kinetics

Reaction equilibrium in catalytic gasification can be modeled by solving the nonlinear simultaneous equations representing the pathways given in Figure 16. Newton-Raphson methods (Carnahan, Luther, and Wilkes 1969) are used to predict equilibrium gas compositions of combustion processes. Brown and Mitchell (1983) used similar techniques to predict equilibrium in various

gasifiers and reformers. For the rationale presented here, equilibrium is defined as either "carbon forming" or "noncarbon forming."

Supported metal catalysts employed for catalytic gasification act primarily on the methane, oils, and tars evolved during pyrolysis. These catalysts enable a faster, more complete approach to equilibrium than would otherwise be possible. The "principle of equilibrated gas" (Rostrup-Nielson 1984) states that "carbon formation is to be expected if the gas shows affinity for carbon after the establishment of the methane-reforming and shift equilibrium." At low gasification temperatures (below 600°C) and low steam/carbon ratios, carbon deposition becomes thermodynamically favored. This carbon-forming threshold depends specifically on the gas composition, the reaction temperature, and the total pressure. This is illustrated by Figures 17 and 18 for biomass (Mudge et al. 1981). Carbon deposition is also related to the elemental composition or structure of the feedstock (Figures 19 and 20). Olefins and unsaturates are known precursors to coke formation (Rostrup-Nielson 1984; Baker and Mudge 1984b). Larger molecules may be cracked to olefins during the initial pyrolysis and subsequently polymerize.

By definition, thermodynamic equilibrium is independent of time. That is, the speed of each reaction plays no role in the final equilibrium concentrations. Kinetics, then, is an important factor in determining dynamic concentrations of various species. Rostrup-Nielson compares kinetics in terms of a "turnover frequency," which is a reaction rate corrected for active surface area. Table 8 shows typical turnover frequencies for various reactions on a Ni/ZrO₂ catalyst (Rostrup-Nielson 1984). Each reaction proceeds at its own speed, with the dynamic concentrations of the participating species being functions of both the kinetic expressions and the thermodynamic driving force.

Catalyst deactivation in the bench-scale experiments was found to be due to carbon buildup on the catalyst. Although carbon formation is not favored thermodynamically, actual accumulation depends on the relative kinetics of the carbon-forming reaction 5 and the carbon-removing reaction 8 (Baker and Mudge 1984a,b).

FIGURE 17. Effects of Temperature on the Dry Gas Equilibrium Composition at Atmospheric Pressure for Steam-to-Wood Ratio of 1

FIGURE 18. Effect of Pressure on Methanol Synthesis Gas Production

Heat/Mass Transport

A cross section of a typical spherical catalyst pellet is shown in Figure 21. Reactants diffuse through the gas film boundary layer and react within the porous substrate of the pellet. Products must then diffuse back out through this film to the bulk phase. The heat of reaction must be added or removed through this film as well.

Deactivation of supported metal catalysts by carbon deposition was found to be influenced by kinetics. Heat and mass transfer effects play an important role in determining overall kinetics. For an endothermic reaction such as methane reforming, the heat of reaction required can be appreciable. In commercial steam reformers, a catalyst is employed in large tubes inside a furnace. The furnace burns some of the feed to supply the required heat. Large

FIGURE 19. Carbon Formation from Different Hydrocarbons. Thermogravimetric studies, 0.7 g Ni/MgO/catalyst. $H_2O/C = 2$, 0.1 MPa, 773K (Rostrup-Nielson 1984).

mass velocities in the range of 8200 to 14,300 lb/h-ft² (40,000 to 70,000 kg/m²-h) are employed to minimize heat and mass transfer restrictions. Even so, temperature of the catalyst pellets may drop 10 to 20K more than that of the gas film. Diffusional restrictions usually exist within catalyst particles, causing concentration gradients within the particle.

The role of heat and mass transport in porous catalysts has been well analyzed. One of the first efforts to quantify diffusional effects was that of Theile (1939). Most researchers acknowledge premier works in this area to be those of Carberry (1961) and Weisz and Hicks (1962). They derived relationships explaining heat and mass transfer using nonlinear kinetic expressions for both exothermic and endothermic reactions. Numerous authors have expanded on this subject (Bischoff 1967). Carberry (1975) declared the relative importance of the internal/external temperature and concentration gradients. For most

FIGURE 20. Equilibrium C-H-O Diagram Showing Carbon Isotherms at 450°C and 1.4 atm. Points A and B correspond to compositions of $\text{H}_2\text{O}/\text{CH}_4 = 0.1$ and $\text{H}_2\text{O}/\text{CH}_4 = 2.0$, respectively. Point A is in the region above the isotherms where carbon is predicted to form (Bartholomew 1982).

TABLE 8. Turnover Frequencies for Selected Reactions

Reaction No.	Reaction	Temperature, K	Turnover Frequency, s^{-1}
3	C_2H reforming	773	0.02
1	CH_4 reforming	773	0.01
11	C_2H_6 hydrogenolysis	573	0.08
(-6)	Methane formation	523	0.80
	$2\text{NH}_3 \rightarrow 3\text{H}_2 + \text{N}_2$	773	0.40

FIGURE 21. Catalyst Particle Heat Transfer

gas-solid reactions, the bulk of the concentration gradient occurs on the interior of the pellet, while the temperature differences occur in the gas film.

During catalytic gasification, bulk gas temperatures may range from 650 to 800°C, with 750°C being a norm. Catalyst pellet temperatures, however, may be significantly less due to the endothermic nature of the reactions. Pellet temperatures were predicted by two methods (see Appendix D). Finlayson (1980) presents a complete analysis of heat and mass transfer in catalyst pellets. The highly nonlinear differential equations derived from mass and energy balances are solved on a computer by orthogonal collocation. This model gives concentration and temperature profiles within the pellet and also calculates the differences across the boundary layer.

An iterative isothermal pellet heat transfer analysis was also done. This model assumes that all of the temperature drop is in the film and that the pellet is isothermal. Furthermore, it assumes that there is no resistance to diffusion within the pellet and that the entire active surface of the pellet sees the bulk phase concentrations (very slow reactions).

Calculations show that the temperature of a catalyst pellet may drop as much as 400K from a bulk gas temperature of 1023K with methane reforming

(Figure 22). A temperature drop of this magnitude will definitely affect the equilibrium. Carbon deposition is thermodynamically favored for this gas below 600°C, and the carbon-steam gasification reaction is slow at temperatures below 700°C. The question of carbon deposition then becomes a matter of kinetics.

Temperature and concentration profiles in a single, nonisothermal pellet of catalyst were calculated for reforming of methane, a highly endothermic reaction. Results of these calculations are plotted in Figure 23. The x-axis on the plot is the distance from the pellet center divided by the pellet radius. Dimensionless concentration of methane, c/c_∞ , and temperature are plotted on the vertical axis. Figure 23 shows that the temperature drop and concentration change across the gas film are significant. The catalyst pellet

FIGURE 22. Heat Transfer Coefficient to a Catalyst Particle

FIGURE 23. Pellet Concentration and Temperature Profiles for Reforming of Methane

is at a much lower temperature (900K) than the bulk gas temperature (1023K). Details of these calculations are reported in a thesis by Brown (1986), and results are reported in the literature (Brown et al. 1986).

If deactivation due to carbon deposition is a kinetic problem, then how can we maintain adequate activity on a catalyst? Unfortunately, carbon will be locally deposited by tar cracking and polymerization of larger fragments in a gasification/pyrolysis situation. The rate of carbon formation is kinetically influenced by the temperature and the selectivity of the catalyst. Carbon can also be removed by the carbon-steam reaction if the reaction conditions in the gasifier fall in the carbon-free region thermodynamically. If the temperature is below the carbon threshold, then there is no thermodynamic incentive to remove carbon. Above the carbon-forming region, competing reactions still

occur. Figure 24 illustrates a probable carbon-deposition reaction (tar cracking) versus carbon removal reaction (char gasification). Below about 700°C, the char gasification reaction is slow, and carbon is deposited. Above that, carbon may actually be removed.

The rate of heat transfer to the catalyst is affected primarily by the Reynolds number (Re) of the flowing gas stream. Zenz and Othmer (1960) compiled data of Nusselt number (Nu) versus Reynolds number (Re) for both fixed and fluid beds of particles. These data relate gas-to-particle heat transfer coefficients (h) to Reynolds number. Heat transfer coefficients of 5 to 100 Btu/h-ft²-°F (100 to 2000 kJ/m²-h-K) are reasonable for fixed- and fluid-bed catalytic reactors. Commercial steam reformers typically operate with mass

FIGURE 24. Carbon Deposition on Catalyst

velocities from 8200 to 14,300 lb/ft²-h (40,000 to 70,000 kg/m²-h) (Rostrup-Nielson 1984). This corresponds to Reynolds numbers from 6,000 to 10,000 and heat transfer coefficients around 60 to 100 Btu/h-ft²-°F (1250 to 2000 kJ/m²-h-K).

Berty Reactor Studies

Two wood tar cracking experiments were completed in a "Berty" gradientless recycle reactor to examine further the effects of Reynolds number on pellet temperature and deactivation. Baker and Mudge (1985) performed similar studies using coal tar. G90C commercial steam reforming catalyst (see Table 2) crushed to -6 to +10 mesh was used at 700°C. The Reynolds number was controlled by doubling the gas-recycle-fan rate from 1000 to 2000 rpm. The effect of varying the Reynolds number can be seen in Figure 25. Ethane and ethylene concentrations are an indication of catalyst deactivation.

FIGURE 25. Results of Berty Reactor Studies

The presence of measurable amounts of these components is an indication of impending deactivation. Figure 25 clearly shows that deactivation is postponed by increased Reynolds numbers (and thus higher pellet temperatures). Reynolds numbers attainable in the Berty reactor are not large (100 to 1000) at low pressure because of the low gas density and high temperature. Further testing using small, fixed-bed reactors at high Reynolds numbers is advised.

Design Implications

The previous section indicates that heat transfer to the catalyst pellets is of primary importance in maintaining catalyst activity for the long term. Pore diffusion effects on catalyst deactivation appear minimal. We have also shown that catalytic gasification is not possible in a single bed at 750°C. Therefore, there are two options for further development: a fixed- or fluid-bed gasifier followed by a fixed or fluid bed of catalyst. The primary gasifiers represent well-researched and available technology. The secondary catalytic reactors can be designed and built using good engineering practice coupled with information concerning catalysts and carbon deposition obtained in these studies.

The question of whether to use a fixed- or a fluid-bed catalytic unit is one that depends entirely on the situation. Fluid beds generally have low Reynolds numbers and, consequently, low gas-to-solid heat transfer coefficients; they have large solid-to-solid heat transfer coefficients and are nearly isothermal. In most cases a fluid bed behaves like a stirred tank reactor with solid reactants and a plug flow reactor with respect to the gas. The catalyst is not fixed, however, and is free to move about within the bed. It can exchange heat with the walls and other catalyst pellets. The overall reaction is equally distributed over a much larger mass of catalyst than in a fixed bed.

Most fixed-bed reformers have a layer of catalyst near the entrance that takes the brunt of the reaction, has the highest temperature drop, and consequently deactivates. This inactive layer moves through the reactor until the entire catalyst bed is deactivated. Fixed-bed units may be usable due to the

limited diffusional restrictions for tar cracking. Large mass velocities similar to those used in methane reforming will be needed to supply the needed heat of reaction. Further research is needed in this area.

STUDIES WITH PRIMARY CATALYSTS

Alkali carbonate catalysts using biomass feedstocks are known to have a significant effect on both pyrolysis and char gasification (Baker and Mudge 1984a). They have previously been tested extensively in the laboratory gasifier, and a limited number of tests have been completed in the PRU. Data on the kinetics of the steam-char reaction were obtained on the laboratory scale (Mudge et al. 1981; Baker and Mudge 1984a). The objective of the bench-scale tests was to confirm laboratory-scale results on a larger scale. In particular, there was a need for data on the kinetics of char gasification on a larger scale.

Table 9 shows the test matrix for the primary catalyst tests. Twenty-two tests were completed. Several other tests were terminated prematurely. Two sets of data were obtained for each test. The gasifier was operated at steady state with continuous wood feed for 2 to 4 hours to provide information on the pyrolysis step. At that point wood feed was terminated and the char remaining in the bed was gasified with the feed gas to obtain kinetic data on char gasification.

All tests used 14-mesh pine flakes (see Table 9) as feed, except where noted. The wood feed rate was typically 1.3 to 2 lb/h (10 to 15 g/min). The steam feed rate was the same, giving a steam:wood ratio of about 1 for most of the tests. In tests with CO_2 , the CO_2 molar feed rate was approximately the same as the high molar steam feed rate used in the steam tests, which corresponds to a CO_2 feed rate of 0.6 scfm (18 L/min) or 4.4 lb/h (33 g/min).

Two catalysts, K_2CO_3 and Na_2CO_3 , were impregnated at two concentrations, 0.015 and 0.0075 moles per mole of carbon. These values correspond to 8 wt% and 4 wt% for K_2CO_3 and 6 wt% and 3 wt% for Na_2CO_3 . Results of the kinetic and pyrolysis studies are presented in the following sections.

TABLE 9. Primary Catalyst Test Matrix

Catalyst	Gasification Agent	Temperature, °C	Run No.	Date
None	Steam	750	U-1	2/1/85
None	Steam	750	U-2	2/13/85
None	Steam	750	U-3(a)	3/8/85
None	Steam	750	U-4(b)	3/15/85
None	Steam	750	U-8	8/14/85
None	Steam	650	U-5	6/13/85
None	Steam	650	U-6	6/18/85
None	CO ₂	750	C-1	3/22/85
None	CO ₂	650	U-7	7/10/85
8 wt% K ₂ CO ₃	Steam	750	K-1	1/30/85
8 wt% K ₂ CO ₃	Steam	750	K-3	2/26/85
8 wt% K ₂ CO ₃	CO ₂	750	C-4	4/16/85
4 wt% K ₂ CO ₃	Steam	750	K-2	2/7/85
4 wt% K ₂ CO ₃	CO ₂	750	C-3	3/28/85
4 wt% K ₂ CO ₃	CO ₂	750	C-5	4/21/85
4 wt% K ₂ CO ₃	Steam	650	K-4	6/26/85
6 wt% Na ₂ CO ₃	Steam	750	N-1	5/1/85
3 wt% Na ₂ CO ₃	CO ₂	750	N-3	5/9/85
3 wt% Na ₂ CO ₃	Steam	750	N-2	5/3/85
6 wt% Na ₂ CO ₃	CO ₂	750	N-4	5/16/85
3 wt% Na ₂ CO ₃	Steam	650	N-5	7/3/85
3 wt% Na ₂ CO ₃	CO ₂	650	N-6	7/16/85

(a) -12 to +20-mesh wood feed.

(b) -20-mesh wood feed.

Char Reaction Kinetics

Kinetics of the steam-char and CO₂-char reactions were studied in the following manner. The gasifier was started, feeding wood, inert material, and steam (or CO₂) continuously. Char and inert material were removed from the top of the bed intermittently to maintain a constant bed depth. When steady state was reached, indicated by consistent gas flows and compositions, the wood/inert feed was stopped. Steam (or CO₂) continued to flow to the gasifier. A sample of the bed material was taken at that time to determine the amount of char in the bed. Gasification rates were determined by measuring the gas flow and

analyzing the product gas with the gas chromatographs. At the end of the run, the bed was analyzed to determine the amount of char remaining. The total carbon gasified as measured by the bed samples and by the gas analyses generally agreed within $\pm 10\%$.

The results of four uncatalyzed steam-char tests are shown in Table 10. The gasification rates dropped steadily over the first few minutes of the test

TABLE 10. Gasification Rates for Uncatalyzed Cases
(750°C steam at 13 to 15 g/min)

Run No.	Time, min	Gasification Rate, ^(a) g/g-min $\times 10^2$	Burnoff, ^(b) %
U-1	0	1.6	0
	5	1.3	6
	20	1.0	20
	40	0.9	33
	80	0.9	52
	120	0.9	65
U-2	0	3.6	0
	6	2.9	15
	19	1.6	30
	43	1.0	44
	78	0.9	58
U-3	0	4.4	0
	5	2.3	14
	10	1.7	22
	20	1.6	32
	40	1.7	50
U-4	0	2.5	0
	5	1.8	9
	10	1.3	16
	20	1.0	24
	40	1.0	38
	60	1.0	50

(a) Rates are given as grams of carbon gasified per gram of carbon remaining as char per minute.

(b) % burnoff is the percentage of carbon that has been gasified.

and then leveled off. For runs U-1, U-2, and U-4, the gasification rate leveled off at 0.009 to 0.01 g/g-min. For run U-3, the gasification rate leveled off at about 0.016 to 0.017 g/g-min. For runs U-1 and U-2, -14-mesh wood particles were used; for run U-4, -20 mesh wood particles. There does not appear to be much difference in the results. For run U-3, -12 to +20-mesh particles were used (no fines), and the gasification rate was faster. If gasification reactions were surface area phenomena, the rate would decrease with the use of larger particles because the surface area to mass ratio would be reduced. These results do not agree with the surface area postulate.

The high initial steam-char reaction rates (uncatalyzed) were most likely due to residual pyrolysis of the fresh char in the bed. The rate of actual char reaction with steam at 750°C was about 0.01 g/g char/min. The high initial rate of char gasification and pyrolysis appeared to be a function of the "average char age" or residence time in the continuous-feed portion of the test, as shown in Figure 26. For a long char residence time (see Appendix B) as in run U-1 (about 50 min), there was little residual pyrolysis at the start of the kinetic test portion of the run. At shorter residence times, there was significant residual pyrolysis at the start of the kinetic runs.

The pseudo-first-order rate constants at 750°C for steam-char reaction were 1.5×10^{-4} to $2.7 \times 10^{-4} \text{ s}^{-1}$. This agrees quite well with previous laboratory kinetic tests where rate constants averaged about $2.0 \times 10^{-4} \text{ s}^{-1}$ at 750°C.

Results for the CO₂-char reaction with no catalyst are shown in Table 11. The rates in terms of grams of carbon gasified per grams of carbon remaining as char per minute are fairly constant at 0.009. The pseudo-first-order rate constant for the CO₂-char reaction from these data is about $1.4 \times 10^{-4} \text{ s}^{-1}$.

Potassium carbonate was tested as a gasification catalyst at loadings of 4 wt% and 8 wt%. The results of the kinetic tests of the steam-char reaction are shown in Table 12. Steam-char reaction rates are much higher than the uncatalyzed cases (Table 10): 0.06 to 0.08 g/g-min in the early stage, increasing to 0.08 to 0.1 g/g-min at 60% to 80% burnoff and then falling

FIGURE 26. Effect of Char Age on Initial Gasification Rate

TABLE 11. Uncatalyzed Char Gasification Rates with CO₂ (750°C, 1 atm)

	Time, min	Gasification Rate, g/g-min $\times 10^2$	Burnoff, %
Run C-1	0	0.60	5
	10	0.90	9
	20	0.93	17
	45	0.88	33
	90	0.78	54
	113	0.84	62

TABLE 12. Steam-Char Reaction Rates for Potassium Catalyzed Tests (750°C, 1 atm)

	<u>Time, min</u>	<u>Gasification Rate, g/g min x 10²</u>	<u>Burnoff, %</u>
Run K-1	0	8.0	0
	10	10.0	60
	16	7.8	78
	32	3.0	90
	60	3.0	96
Run K-2	0	6.0	0
	10	6.1	42
	20	7.7	71
	30	9.6	88
	40	3.0	9

TABLE 13. CO₂-Char Reaction Rates With Potassium Carbonate Catalyst (750°C)

	<u>Time, min</u>	<u>Gassification Rate, g/g min x 10²</u>	<u>Burnoff, %</u>
Run C-4 (K ₂ CO ₃ , 8 wt%)	0	3.2	0
	10	4.2	28.5
	18	5.4	53.4
	40	3.5	88.9
	60	1.2	93.5
Run C-5 (K ₂ CO ₃ , 4 wt%)	0	1.6	0
	5	1.8	8
	10	2.2	17
	20	2.6	34
	35	3.8	59
	50	5.6	79
	65	4.6	91
	95	2.3	98

sharply at over 90%. Reaction rates for CO_2 -char catalyzed with potassium carbonate are shown in Table 13 and are about one-third the rates obtained with steam.

In potassium carbonate catalyst tests, the majority of the reaction occurs in the first 20 minutes. Results indicate two kinetic regimes in potassium carbonate catalyzed reactions. In the early period, the gasification rate in grams of carbon gasified per grams of carbon remaining per unit time remains fairly constant, independent of the amount of carbon remaining in the fluid bed. Figure 27 shows the gasification rate expressed as grams of carbon gasified per min per grams of carbon remaining as a function of burnoff (carbon conversion). Expressed in this manner, the rate increases to a maximum of 0.1 g/g-min with steam and 0.05 g/g-min with CO_2 . These maxima occur at about 60% burnoff with 8% K_2CO_3 and at about 80% burnoff with 4% K_2CO_3 .

Our interpretation of these data is that during the initial period of high reaction rate, the rate is dependent not on the amount of carbon remaining but rather on the number of catalytically active gasification sites; that is, the rate depends on concentration of catalyst. During this period the gasification rate with 8% K_2CO_3 is approximately double the rate with 4% K_2CO_3 for both steam and CO_2 .

Eventually the remaining carbon becomes the rate-limiting factor at about 60% burnoff for 8% K_2CO_3 and at about 80% burnoff for 4% K_2CO_3 . In both cases this change occurs at a K:C molar ratio of about 0.2. At this point one would expect the reaction to be first order with respect to the remaining carbon. The rate appears to decrease even faster than first order, possibly due to diffusional resistance from the large amount of K_2CO_3 present.

The results with sodium carbonate catalyst (shown in Table 14) were not as easy to interpret. With steam the gasification rate in grams of carbon gasified per gram of carbon remaining as char per minute was fairly constant as a function of burnoff, indicating first-order kinetics with respect to remaining carbon. Throughout the tests the rate with 6% Na_2CO_3 was about double that with 3% Na_2CO_3 , indicating a first-order dependence on the catalyst. Because the Na:C molar ratio constantly increased through each test, these conditions cannot both be true.

FIGURE 27. Gasification Rates as a Function of Char Burnoff

With carbon dioxide the results with the sodium carbonate catalyst were again difficult to interpret. Rates were quite low in the beginning, about equal to the rate with no catalyst (see Table 11). The rate increased throughout the test and peaked at 80% to 90% burnoff, similar to the results with potassium carbonate.

TABLE 14. Char Gasification Rates with Sodium Carbonate Catalyst (750°C, 1 atm)

<u>Run No.</u>	<u>Time, min</u>	<u>Gasification Rate, g/g-min x 10²</u>	<u>Burnoff, %</u>
N-1 (6% Na ₂ CO ₃ / steam)	0	4.7	0
	5	7.1	25
	10	7.2	48
	15	6.0	63
	20	5.8	72
	25	5.6	79
N-2 (3% Na ₂ CO ₃ / steam)	0	3.2	0
	6	4.2	19
	12	3.4	37
	19	2.6	49
	30	2.1	60
	60	2.3	79
	90	2.6	79
N-3 (3% Na ₂ CO ₃ / CO ₂)	0	1.2	0
	5	1.3	6
	18	1.6	21
	45	1.9	52
	60	2.0	64
	90	4.6	85
	120	2.2	96
N-4 (6% Na ₂ CO ₃ / CO ₂)	0	0.5	0
	10	0.8	6
	40	1.6	34
	60	1.7	56
	80	4.2	77
	100	7.3	92

Effect of Alkali Carbonates on Pyrolysis/Gasification

As described previously, alkali carbonates had a significant effect on steam pyrolysis of biomass (Baker and Mudge 1984a,b). The results obtained in the bench-scale unit were very similar to previous laboratory and PRU tests.

Gas yields were higher for all the catalysts in Table 15, except with 3 wt% Na_2CO_3 . Alkali carbonates increased the yield of hydrogen and carbon dioxide by catalyzing the shift reaction. They decreased the yield of carbon monoxide, methane and other light hydrocarbon gases, and tars.

Char yields with the alkali carbonates were about the same as in the uncatalyzed cases. Char yield was lowest with 6 wt% Na_2CO_3 and highest with 3 wt% Na_2CO_3 .

Tests were also conducted with CO_2 instead of steam (see Table 16). Gas yields with CO_2 were higher than with steam; however, this was due to the unreacted CO_2 in the gas. The H_2/CO ratio was much lower with CO_2 than with steam. The carbon dioxide and the lack of steam forced the water-gas shift reaction toward carbon monoxide (CO).

Gasification with carbon dioxide in the presence of alkali carbonates resulted in a higher yield of char than uncatalyzed gasification with carbon dioxide and more char than all of the tests with steam, both catalyzed and uncatalyzed. All tests with carbon dioxide produced less tar than tests with steam. This is discussed in more detail in the section on tar yield.

Recovery of Alkali Carbonate Catalyst

In previous studies a 99% accountability of potassium carbonate was demonstrated for gasification of bagasse in the PRU (Baker and Brown 1984). Solid residues from gasification of bagasse were washed on a filter with successive flushes of water, using about 50 g of water for each gram of char.

TABLE 15. Effect of Primary Catalysts on Gas Composition and Yields from Steam Pyrolysis

Catalyst	Gas Composition, vol%						Gas Yield, m ³ /kg wood	Tar Yield, g/kg wood	Char Yield, g/kg wood
	C ₃	H ₂	CO ₂	C ₂	CH ₄	CO			
None	0.6	44.5	20.0	3.2	8.9	23.0	1.35	45 to 70	100
K ₂ CO ₃ , 8 wt%	-	59.4	21.0	1.1	3.5	15.0	1.95	20	107
K ₂ CO ₃ , 4 wt%	-	52.4	23.6	1.6	4.8	17.4	1.74	-	94
Na ₂ CO ₃ , 6 wt%	0.2	56.4	23.8	1.1	3.6	14.8	1.72	28	78
Na ₂ CO ₃ , 3 wt%	0.4	53.9	22.7	1.9	5.9	15.5	1.26	29	135

TABLE 16. Effect of Primary Catalysts on Pyrolysis with Carbon Dioxide

Catalyst	Gas Composition, vol%						Gas Yield, m ³ /kg wood	Tar Yield, g/kg wood	Char Yield, g/kg wood
	C ₃	H ₂	CO ₂	C ₂	CH ₄	CO			
None	0.3	7.0	69.3	1.6	4.0	17.1	2.00	28	100
K ₂ CO ₃ , 8 wt%	0.3	16.1	53.9	0.8	2.6	25.9	2.17	20	140
K ₂ CO ₃ , 4 wt%	0.3	12.3	64.4	1.1	3.1	18.7	2.00	14	135
Na ₂ CO ₃ , 6 wt%	0.4	11.6	66.8	1.3	4.0	16.3	2.01	15	168
Na ₂ CO ₃ , 3 wt%	0.3	16.9	58.1	1.3	4.2	19.5	1.56	-	120

Recovery of potassium carbonate was tested for CO₂ gasification of wood using a procedure identical to that used for the bagasse gasification. Recovery was drastically reduced, as shown in Table 17. Concentration of the wash solutions ranged from 1 to 5 g of potassium per liter.

The data indicated that potassium did not readily leach from the wood char residue, as it did from the bagasse char. Different analytical methods were used to determine potassium concentration in the solutions from bagasse char

TABLE 17. Recovery of Potassium Carbonate

<u>Run No.</u>	<u>% K₂O₃ in Feed</u>	<u>% K₂CO₃ in Char Overflow</u>	<u>% K₂CO₂ in Entrained Char</u>	<u>Total % K₂CO₂ Recovered</u>
C-4	8	25	32	57
C-5	4	36	33	69

washing and from wood char washing, but both methods should be accurate within 0.5%. Accountability of materials should be better in the bench-scale equipment than in the PRU. From the data it appeared that the unaccounted potassium was in the char overflow. A representative sample of this stream was difficult to obtain.

TAR YIELD AND COMPOSITION

A major effort was made to determine the amount of tar produced during the gasification tests and to evaluate the effect of catalysts on tar yield. In addition, an attempt was made to identify the major components of the tars.

Analytical Method

Measuring the tar yield from biomass gasification with accuracy was difficult due to the high viscosity of the heavier tar components and the affinity of some of the lighter components for water. The high viscosity caused some of the tar to stick to piping and the condenser walls. Once condensed, the tar was difficult to separate from the aqueous condensate. Several methods for tar recovery and analysis were tested and compared (see Figure 9).

After the gas passed through the secondary catalyst vessel, it was cooled to condense tars as described previously. The condensate was separated from the gas and collected in 1-gal (4-L) plastic bottles. After at least 24 hours, the aqueous phase was decanted off, and the remaining tar was weighed. A sample of the aqueous phase was taken for total organic carbon (TOC) analysis. The aqueous phase still contained small, dispersed droplets of tar, which were extracted with methylene chloride. The sample for TOC analysis was filtered to remove droplets prior to analysis.

This method may result in some "double counting," as the methylene chloride will extract some water soluble compounds, such as phenol and cresol, from the aqueous phase; these compounds will then contribute to the TOC analysis. However, taking the TOC sample prior to extraction gave a better indication of the quality of the condensate than would be obtained in a commercial unit using just gravitational separation.

Following a test the condenser was rinsed with acetone. The rinse solution was evaporated to leave the residual tar. All tar fractions were weighed, and selected samples were analyzed for carbon, hydrogen, oxygen, and nitrogen.

In nickel catalyzed tests, naphthalene crystals were found floating in the condensate, in the condenser, and in piping downstream of the condenser. The method previously described for tar recovery was not effective for recovering naphthalene.

To obtain a quantitative measure of the naphthalene present, a slipstream of the gas (taken both before and after the secondary catalyst) was scrubbed with methylene chloride to remove any condensible organics in the gas. The slipstream gas volume was measured with a wet test meter. The methylene chloride solution was then analyzed by gas chromatography to determine the quantity of organics present.

Nitrobenzaldehyde was used as an internal standard to determine the weight of components in the methylene chloride. This method worked well for the nickel catalyzed runs, where the only major components were benzene, toluene, xylene (BTX), and naphthalene. In the uncatalyzed cases and the alkali carbonate catalyzed tests, where more components were present in the tar, this method was not accurate compared to the previous method.

Tar Yield

Table 18 summarizes the tar yield and the organic carbon soluble in the condensate for the various cases tested in the bench-scale unit. In uncatalyzed tests with steam, tar yield ranged from 2.3 to 7.0 g/100 g of wood. The upper end of the range is probably more accurate. The lower end probably represents less than complete recovery of the tar. Between the tar and the water

TABLE 18. Tar Yields from Wood Gasification^(a)

	Steam Gasification				Carbon Dioxide Gasification		
	Uncatalyzed	Secondary Catalyst ^(b)		Alkali Carbonates	Uncatalyzed	Steady-State Nickel	Alkali Carbonate
		Fresh	Steady-State				
Tar and Oil Yield							
g/100 g wood	2.3 to 7.0	0	1.4 to 1.6	2.0 to 2.9	2.8	--	1.4 to 2.0
% C to tar and oil	3.9 to 11.9	0	2.4 to 2.7	3.4 to 4.9	4.8	--	2.4 to 3.4
Water-Soluble Organic Carbon							
ppm in condensate	7700 to 8700	0	328 to 1600	1660	--	464	--
% C to water soluble carbon	2.3 to 2.6	0	0.05 to 0.2	0.4	--	0.02	--

(a) Typical conditions: 750°C (both primary and secondary vessel); wood feed rate, 10 to 15 g/min; steam/wood, 0.8 to 1.2.

(b) NCM, G-90C, and ICI-46-1 (see Table 2 for catalyst compositions).

soluble organic carbon, liquids in uncatalyzed tests accounted for 7 to 14 wt% of the carbon originally in the wood. Again, the upper end of the scale is probably more accurate.

With fresh nickel catalysts, tars and oils were completely eliminated. As the catalyst aged, some hydrocarbons remained, in the range of 1.4 to 1.6 g/100 g wood when catalyst activity had leveled off at steady state (see Figure 13). Liquids accounted for 2.4 to 2.9% of the carbon originally in the wood. With alkali carbonate catalysts, liquids were reduced to levels somewhat above the level achieved with the steady-state nickel catalysts, about 4.0 to 5.3% of the carbon in the wood. Overall carbon accountability in the tests ranged from 90 to 100+%, as shown by data in Appendix A.

Tar Composition

Using both standards and data from the mass spectrometer, some of the major components in the tars were identified. Table 19 shows the major peaks identified for five different cases. Those in italics were the major components. A complete list of components identified is included in Appendix C.

The tar produced by uncatalyzed steam gasification was the most complex, ranging from benzene to a four-ring aromatic compound, chrysene. With a nickel secondary catalyst, the only components of any significance in the tar were BTX and naphthalene. At condenser conditions the BTX remained primarily in the product gas, and the naphthalene crystals were floating in the condensate. With a primary catalyst, the primary components of the tar were BTX, phenol, cresol, xylene, and naphthalene.

Replacing the steam with CO₂ reduced the uncatalyzed tar yield, as noted previously. The major components were BTX, phenol, and indene; and chromatographic analysis produced a peak tentatively identified as dihydropyranone. The tar produced with CO₂ and primary catalysts was very similar to the tar produced with steam and primary catalysts.

Effect of Temperature

All the previous tests were at 750°C. In uncatalyzed tests at 650°C, the tar yield rose to about 9 g/100 g of wood, and the TOC in the condensate increased to about 11,100 mg/L. Liquids accounted for about 18% to 25% of the

TABLE 19. Major Components of Tars

Steam Gasification			Carbon Dioxide Gasification	
Uncatalyzed	Secondary Catalyst	Primary Catalyst	Uncatalyzed	Primary Catalyst
<i>benzene</i> (a)	<i>benzene</i>	benzene	<i>benzene</i>	<i>benzene</i>
toluene	<i>toluene</i>	toluene	<i>toluene</i>	<i>toluene</i>
xylene + styrene	xylene	xylene	<i>xylene</i>	xylene
<i>phenol</i>	<i>naphthalene</i>	phenol	<i>phenol</i>	phenol
<i>cresol</i>		cresol	cresol	
indene		naphthalene	<i>indene</i>	
methyl indene			naphthalene	
<i>naphthalene</i>			<i>dihdropyranone</i>	
<i>methyl naphthalene</i>				
acenaphthylene				
acenaphthene				
phenanthrene				

(a) Italics indicate major components.

carbon in the wood feed. The major components of the tar were similar, except that the tar produced at 650°C had more of the oxygenated components, such as benzaldehyde, phenol, cresol, xyleneol, and methyl benzaldehyde.

CONCLUSIONS

Three catalysts--NCM, G90C, and ICI-46-1--maintained their activity for generation of synthesis gas from wood at 750°C when the catalysts were contained in a separate fluid-bed reactor. Bench-scale studies succeeded in identifying conditions under which these catalysts maintain their activity. A configuration that separates the catalyst from primary tar reactions and provides rapid heat transfer to the catalyst particle is needed to avoid catalyst deactivation. Based on previous results obtained in the laboratory, where NCM was tested for over 1200 hours and remained active, it is projected that the activity of these three catalysts can be maintained indefinitely when contained in a separate fluid-bed reactor.

Containment of nickel-based catalysts in a separate fluid-bed reactor allows their use with any biomass gasification system. These catalysts are highly effective for destroying condensible organics, which are major waste water and environmental contaminants, while increasing product gas yields.

Bench-scale studies successfully resolved differences in catalyst behavior noted between previous laboratory and PRU results. The long catalyst lifetime achieved in the previous laboratory tests can be attained with proper exposure of the catalyst to gasification conditions.

Secondary (supported metal) catalysts eliminate complex tars formed from wood pyrolysis. Tars that remain are mainly benzene, toluene, xylene, and naphthalene. Fewer and less complex tars are generated by carbon dioxide gasification of wood than by steam gasification at 750°C. These results were obtained with gasification of dry pine flakes.

The major cause of secondary catalyst deactivation was attributed to carbon deposition. Heat and mass transfer to the catalyst are important considerations when designing equipment to avoid conditions that favor carbon deposition.

The rate of the char/steam reaction catalyzed by potassium carbonate at 750°C was found to be dependent on the number of active sites. This was not

the case for sodium carbonate-catalyzed char/steam reaction or char/carbon dioxide reaction. Reaction rates were determined with in situ char produced in the fluid-bed gasifier.

Primary catalysts also are effective for reducing the tar yield from wood pyrolysis and for altering the tar composition. Potassium carbonate is more effective than sodium carbonate as a gasification catalyst.

Despite the large increase in the char/steam reaction rate with potassium carbonate, the overall effect on carbon conversion in steam gasification of wood is negligible. Potassium carbonate also affects wood pyrolysis by increasing the yield of char. Taken with the increased char/steam reaction rate, the net effect of potassium carbonate on carbon conversion in a fluid-bed gasifier is negligible.

Primary catalysts are less effective than nickel-based catalysts for generation of synthesis gas from wood at 750°C. Yields are not improved if both primary and secondary catalysts are used, because the char yield increases when primary catalysts are used.

Recovery of potassium carbonate catalyst by washing the wood char residue ranged from 60 to 70%. This is much less than the 99% recovery by similar washing of bagasse char residue in previous PRU studies.

RECOMMENDATIONS

Bench-scale studies have identified several nickel-based catalysts that show considerable promise for application to biomass gasification. Continued development of these catalysts is recommended. Development studies should include investigations on a large scale with a secondary catalytic reactor in an operating PRU.

The superiority of a fluid bed compared to a fixed bed as the secondary catalytic reactor indicates that inadequate heat transfer to the catalyst surface can lead to excessive carbon deposition, which causes catalyst deactivation. This apparent fouling mechanism should be confirmed. Conditions and designs that provide sufficient heat transfer should be developed. These studies could lead to designs that allow use of a fixed bed of catalyst in the secondary reactor. Special reactor designs in which a separate bed of catalyst is part of the gasifier should be investigated.

Development of catalysts for use with conventional biomass gasifiers (air/steam and oxygen/steam blown) should be studied. Results of these and related studies on destruction of tars in coal-derived gases show that catalysts are effective for converting tars to compounds that enrich the gas stream and do not pollute wastewater. Use of catalysts with commercial gasifiers has the potential to increase gas yields while destroying tars, which are major wastewater contaminants.

Regenerable catalysts that are effective for tar destruction in the 400 to 600°C range should be developed. Inexpensive catalysts, such as zeolites that are regenerable with air, could be applicable to biomass gasification systems.

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APPENDIX A

EXPERIMENTAL DATA

APPENDIX A

EXPERIMENTAL DATA

Tables of experimental data from all bench-scale tests are presented in this appendix. Tar and char compositions listed in the tables are approximate values, which are included for the spreadsheet calculation of material balances. Blank entries indicate that the required data are not available.

Terms used in the table entries are described below. Data are presented for the different process configurations tested in the bench-scale studies.

DEFINITION OF TABLE ENTRIES

A brief description of the table entries is given below to help clarify the data. Some tests include data from the gasifier and from the secondary catalytic reactor. For those tests, a second column with the test number followed by an "a" is used to designate yields from the catalytic reactor. Wood and steam feed rates are repeated for the catalytic reactor, but of course wood is fed to the gasifier only.

Temp, °C - Temperature of the gasifier in °C.

Temp cat, °C - Temperature of the catalytic reactor in °C.

Catalyst - Catalyst designation is as follows (see Table 2): Ni-1 is a nickel on a alumina hydrocracking catalyst used in shakedown tests; NCM is NiCuMo on silica-alumina obtained from W. R. Grace and Company; G90C is Ni on α -alumina from United Catalyst; RKS-41A is the steam-reforming catalyst from Haldor Topsoe; ICI-46-1 is the steam reforming catalyst from Imperial Chemical Industries; 8% K is 8 wt% K as K_2CO_3 on wood; 4% K is 4 wt% K as K_2CO_3 on wood; 6% Na is 6 wt% Na as Na_2CO_3 on wood; and 3% Na is 3 wt% Na as Na_2CO_3 on wood.

Inert Material - Designates the inert material used to stabilize the fluid bed in the gasifier.

Wood Mesh Size - U.S. Sieve number for the wood feedstock used in the test.

Hours - Length of steady-state operation.

Ht, ft - Bed height in the gasifier or secondary catalytic reactor.

Wt cat, g - Weight of the secondary catalyst in grams used for the test.

g/min wood - Wood feed rate in grams per minute of dry (0 moisture) wood.

g/min steam - Steam addition rate in grams per minute.

l/min CO₂ - CO₂ addition rate in liters per minute.

steam/wood - Steam to dry wood weight ratio.

CO₂/wood, g/g = CO₂ to dry wood weight ratio.

slv, ft/sec - Linear velocity of gas (steam or CO₂) in the reactor based on its cross-sectional area and reactor conditions.

lb/h ft₃ - Mass feed rate of wood based on the volume of the fluid bed.

K, 1/sec - Pseudo-first-order reaction rate constant.

Wt wood, g - Total weight of wood (dry, 0 moisture, 8770 Btu/lb) fed to the gasifier during the test.

Wood/catalyst - Weight of dry wood gasified per unit weight of catalyst for that particular test.

Wood comp, wt% - Elemental composition of the feedstock.

Gas comp, vol% - Volumetric composition of the product gas.

H₂/CO - Molar ratio of H₂ to CO in the product gas.

Gas flow, l/g - Volume of product gas generated in liters per gram of feedstock.

Pot MeOH Yield - Potential yield of methanol in kg per kg of wood if all CO plus H₂ in the product gas is converted.

Fr. H in gas - Fraction of hydrogen in the wood that is in the product gas.

Char yield, g - Net weight of char collected during the test.

Char in bed, g - Inventory of char in the fluid bed at end of test.

Char comp, wt% - Elemental composition of char used for material balance calculations.

% C to char - Percent of wood carbon in the char residue.

Min char res t - Residence time in minutes of char in the gasifier as calculated by the method explained in Appendix B.

Wt tar, g - Weight of water insoluble tar obtained during the test.

Tar comp, wt% - Elemental composition of tar used for material balance calculations.

% C to Tar - Percent of wood carbon in the water insoluble tar.

Wt cond, g - Weight of condensate collected during the test.

TOC, mg/L - Total organic content of the condensate.

% C to cond - Percent of wood carbon converted to water-soluble organics and collected in the condensate.

C Balance, % - Percent of wood carbon recovered in the test or percent carbon accountability.

SINGLE-VESSEL TESTS WITH SECONDARY CATALYST

Data from bench-scale tests with the secondary catalyst contained in the fluid-bed basifier are shown in Table A.1. Catalyst was included in the fluid bed at the start of wood feeding, and no makeup catalyst was added during the test. Bed material, which included catalyst, was removed to keep the fluid-bed depth constant. Some depletion of catalyst occurred during each test.

TABLE A.1. Results with Catalyst in a Single Vessel

Test number->	SD-1A	SD-1B	SD-2A	SD-2B	NCM-1	NCM-2	NCM-3	G-1	G-2
Temp, C (a)	750	760	780	750	750	750	750	780	770
Catalyst	Ni-1	Ni-1	Ni-1	Ni-1	NiCuMo	NiCuMo	NiCuMo	G-90C	G-90C
Ht, ft	1	1	1	1	1	1	1	1	1
Wt cat, g	650	650	541	541	488	416	230	630	411
g/min wood	18.3	12.4	19.9	13.3	9.8	8.5	9.7	10.2	11.3
g/min steam	7.6	7.6	17.1	17.1	9.1	12.5	12.3	12.7	12.9
Steam/wood	.42	.61	.86	1.29	.93	1.47	1.27	1.25	1.14
slv, ft/sec	.42	.43	.98	.96	.51	.70	.69	.73	.74
lb/hr-ft ³	49.31	33.41	53.62	35.84	26.41	22.90	26.14	27.49	30.45
Wt wood, g	932	777	695	955	1560	2370	1720	2450	1950
Wood/catalyst	1.43	1.20	1.28	1.77	3.20	5.70	7.48	3.89	4.74
Wood comp, wt%									
C	50.3	50.3	50.3	50.3	50.3	50.3	50.3	50.3	50.3
H	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4
O	42.7	42.7	42.7	42.7	42.7	42.7	42.7	42.7	42.7
Ash	.6	.6	.6	.6	.6	.6	.6	.6	.6
Gas comp, vol%									
H ₂	46.3	54.1	54.4	53.6	53.4	47.6	43	57.1	50.9
CO ₂	9.6	11.4	13.8	20	14.6	20	18.8	17.2	19.1
C ₂	.1	.2	.4	1.2	.2	1.7	2.6	0	1.5
CH ₄	2.3	1	1.4	3.1	2.7	4.9	7.8	.7	4.9
CO	41.8	33.3	30	22.2	29.2	24.9	27.7	25	23.6
H ₂ /CO	1.11	1.62	1.81	2.41	1.83	1.91	1.55	2.28	2.16
Gas flow, l/g	1.68	1.9	1.89	1.87	1.72	1.5	1.39	2.19	1.93
% C to gas	90	87	86	89	80	79	82	93	97
Pot MeOH yield	.66	.74	.71	.63	.63	.48	.44	.80	.64
Char yield, g	50	50	34	33	181	196	101	46	115
Char in bed, g	109	109	118	118	91	105	137	157	162
Char comp, wt%									
C	87	87	87	87	85	85	60	82	82
H	6	6	6	6	2	2	0	1	1
N									
O									
% C to char	9	11	8	6	20	14	7	3	10
Min char res t	20	29	20	30	31	41	47	51	48
Wt tar, g	0	0	0	8.5	1.4	11.4	25.2	.6	14.2
Tar comp, wt%									
C				57	82	85	87	87	87
H				8	6	6	6		
N									
O				35	12	9	7		
% C to tar	0.00	0.00	0.00	1.01	.15	.81	2.53	.04	1.26
Vol cond, cc	150	289	251	928	806	1667	1593	1323	1621
TOC, g/l	.0023	.0023	.0032	.0032	.0015	.0054	.0085	.0014	.0026
% C to cond	.07	.17	.23	.62	.15	.76	1.57	.15	.43
C Balance, %	99	98	95	96	100	95	93	97	108

(a) See Pages A.1 to A.3 for definitions of table entries.

DUAL-VESSEL TESTS WITH SECONDARY CATALYSTS

Tests were conducted with secondary (supported metal) catalysts in a separate vessel. The dual-vessel system was operated with a secondary fixed bed and with a secondary fluid bed of catalyst. Properties of the catalysts were given in Table 2. Only G90C was used as a fixed bed. Data from tests with a secondary fixed bed are given in Table A.2. Data from tests with a secondary fluid bed are shown in Table A.3.

TABLE A.2. Dual Vessel Tests with a Secondary Fixed Bed

Test number-->	2G-1	2G-2	2G-3	2G-4A	2G-4B	2G-5	2G-6	2G-7	2G-8	2G-9	2G-10
Temp, C (a)	760	750	750	750	740	750	750	750	760	750	750
Temp cat, C	740	750	760	760	750	760	760	750	760	800	800
Catalyst	G-90C	G-90C	G-90C	G-90C	G-90C	G-90C	G-90C	G-90C	G-90C	G-90C	G-90C
Wood Mesh Size	-7+20	-20	-20	-20	-20	-20	-20	-20	-20	-20	-14
Ht, ft	1	1	1	1	1	1	1	1	1	1	1
Wt cat, g	711	680	680	680	680	680	680	680	680	680	680
g/min wood	15.1	13.9	12.5	12.4	11.3	10.5	10.9	13.8	14.6	10	10.4
g/min steam	14.6	14.8	13.5	13.1	12.5	14.2	14	13	13.8	14	13.8
Steam/wood	.97	1.06	1.08	1.06	1.11	1.35	1.28	.94	.95	1.40	1.33
slv, ft/sec	.82	.83	.75	.73	.69	.79	.78	.73	.78	.78	.77
lb/hr-ft ³	41	37	34	33	30	28	29	37	39	27	28
Wt wood, g	2051	3850	2330	4460	1630	1680	820	2180	5316	3306	2923
Wood/catalyst	2.88	5.66	3.43	6.56	2.40	2.47	1.21	3.21	7.82	4.86	4.30
Wood comp, wt%											
C	50.3	50.3	50.3	50.3	50.3	50.3	50.3	50.3	50.3	50.3	50.3
H	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4
O	42.7	42.7	42.7	42.7	42.7	42.7	42.7	42.7	42.7	42.7	42.7
Ash	.6	.6	.6	.6	.6	.6	.6	.6	.6	.6	.6
Gas comp, vol%											
H ₂	58.9	53.3	51	58.4	54.5	54.8	50.8	49.6	46.6	59.9	54.7
CO ₂	16.8	16.6	19.2	18.2	19.6	21.2	21	22.6	19	17.9	18.5
C ₂		.8	1.5	.3	.6	.9	1.3	2.4	1.3		.6
CH ₄	.3	3	5	1.8	4.3	4.8	6.2	5.7	6.7	.6	3.4
CO	24.3	26.2	23.2	21.3	20.9	18.5	20.6	19.7	26.3	22	22.8
H ₂ /CO	2.42	2.03	2.20	2.74	2.61	2.96	2.47	2.52	1.77	2.72	2.40
Gas flow, l/g	2.16	1.94	1.77	2.17	2.05	1.79	1.69	1.42	1.62	2.45	2.22
% C to gas	89	91	89	90	94	82	85	75	88	99	102
Pot MeOH yield	.80	.69	.58	.77	.69	.58	.54	.44	.52	.89	.76
Char yield, g	84	60	43	81	33	90	38	61	274	105	94
Char in bed, g	182	157	171	134	163	196	254	156	149	156	206
Char comp, wt%											
C	85	85	85	85	85	85	85	85	85	85	85
H	1	1	1	1	1	1	1	1	1	1	1
N											
O	14	14	14	14	14	14	14	14	14	14	14
% C to char	6.92	2.63	3.12	3.07	3.42	9.05	7.83	4.73	8.71	5.37	5.43
Min char res t	40	38	46	36	48	62	78	38	34	52	66
Wt tar, g	0	17.8	16.1	0	0	3.5	1.6	34.9	50	1.9	4.6
Tar comp, wt%											
C	85	85	85	85	85	85	85	85	85	85	85
H	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2
N											
O	8.8	8.8	8.8	8.8	8.8	8.8	8.8	8.8	8.8	8.8	8.8
% C to tar	0.00	.78	1.17	0.00	0.00	.35	.33	2.71	1.59	.10	.27
Vol cond, cc	1056	2088	1771	2495	998	1482	695	1318	3758	2502	2258
TOC, mg/l	262	1615	2720	468	468	1500	1500	7700	3074	214	723
% C to cond	.03	.17	.41	.05	.06	.26	.25	.93	.43	.03	.11
C Balance, %	96	95	93	94	97	92	93	83	99	104	108

(a) See Pages A.1 to A.3 for definitions of table entries.

TABLE A.3. Dual Vessel Tests with a Secondary Fluid Bed

Test number->	2NCM-2	2NCM-3	2NCM-4	2NCM-5	2NCM-6	2NCM-7
Temp, C (a)	750	750	750	750	750	750
Temp cat, C	750	750	750	750	750	750
Catalyst	NCM	NCM	NCM	NCM	NCM	NCM
Wood Mesh Size	-20	-20	-20	-20	-20	-20
Ht, ft	1	1	1	1	1	1
Wt cat, g	680	680	680	680	680	680
g/min wood	14.6	12.4	12	8.6	12.7	12
g/min steam	13.3	12.6	13	13.3	12.2	13.1
Steam/wood	.91	1.02	1.08	1.55	.96	1.09
slv, ft/sec	.74	.70	.73	.74	.68	.73
lb/hr-ft ³	39	33	32	23	34	32
Wt wood, g	5264	5920	3600	2588	5398	2016
Wood/catalyst	7.74	8.75	5.29	3.81	7.94	2.96
Wood comp, wt%						
C	50.3	50.3	50.3	50.3	50.3	50.3
H	6.4	6.4	6.4	6.4	6.4	6.4
O	42.7	42.7	42.7	42.7	42.7	42.7
Ash	.6	.6	.6	.6	.6	.6
Gas comp, vol%						
H ₂	60.8	55.7	57.6	57.6	56	55.9
CO ₂	13.6	14.8	16.2	17.2	14.6	16.7
C ₂	.1	.8	.7	.6	.8	.9
CH ₄	2.6	5.2	4.6	4.5	5.3	5.6
CO	23.2	23.3	20.9	20.2	23.1	20.9
H ₂ /CO	2.62	2.39	2.76	2.85	2.42	2.67
Gas flow, l/g	2.12	1.9	1.83	2.02	1.94	1.93
% C to gas	83	85	78	87	86	86
Pot MeOH yield	.79	.67	.64	.70	.68	.66
Char yield, g	393	445	269	193	403	151
Char in bed, g	162	167	150	158	176	190
Char comp, wt%						
C	85	85	85	85	85	85
H	1	1	1	1	1	1
N						
O	14	14	14	14	14	14
% C to char	12.62	12.64	12.63	12.60	12.62	12.66
Min char res t	37	45	42	61	46	53
Wt tar, g	.2	1	2.3	1.2	2.5	1.2
Tar comp, wt%						
C	85	85	85	85	85	85
H	6.2	6.2	6.2	6.2	6.2	6.2
N						
O	8.8	8.8	8.8	8.8	8.8	8.8
% C to tar	.01	.03	.11	.08	.08	.10
Vol cond, cc	2333	4287	2533	7588	5398	2016
TOC, mg/l	417	1031	1066			1266
% C to cond	.04	.15	.15	0	0	.25
C Balance, %	96	98	91	99	99	99

(a) See Pages A.1 to A.3 for definitions of table entries.

TABLE A.3. (contd)

Test number->	2NCM-8	2NCM-9	2NCM-10	2NCM-11	2FG-1	2FG-2	2FG-3
Temp, C (G)	750	750	750	750	750	750	750
Temp cat, C	750	750	750	750	750	750	750
Catalyst	NCM	NCM	NCM	NCM	G-90C	G-90C	G-90C
Wood Mesh Size	-20	-20	-20	-20	-20	-20	-20
Ht, ft	1	1	1	1	1	1	1
Wt cat, g	680	550	360	262	680	640	604
g/min wood	16.2	15.4	16.2	16.8	11.7	16.5	16.2
g/min steam	12.9	13.7	13.8	12.8	12.3	12.4	12.9
Steam/wood	.80	.89	.85	.76	1.05	.75	.80
slv, ft/sec	.72	.77	.77	.72	.69	.69	.72
lb/hr-ft ³	44	41	44	45	32	44	44
Wt wood, g	5160	4390	3923	2100	4565	6750	8220
Wood/catalyst	7.59	7.98	10.90	8.02	6.71	10.55	13.61
Wood comp, wt%							
C	50.3	50.3	50.3	50.3	50.3	50.3	50.3
H	6.4	6.4	6.4	6.4	6.4	6.4	6.4
O	42.7	42.7	42.7	42.7	42.7	42.7	42.7
Ash	.6	.6	.6	.6	.6	.6	.6
Gas comp, vol%							
H ₂	60.1	54.8	54.3	51.9	62.7	56.1	51.6
CO ₂	14.2	15.5	15.3	15.1	16.3	13.6	13.4
C ₂	.2	1.1	1.1	1.6	.2	.8	1.3
CH ₄	3.3	6	6.1	7	1.7	5.1	6.8
CO	22.4	22.6	23.2	23.8	19.1	24.4	26.8
H ₂ /CO	2.68	2.42	2.34	2.18	3.28	2.30	1.93
Gas flow, l/g	2.13	1.88	1.86	1.78	2.52	2.03	1.85
% C to gas	85	87	87	87	94	90	91
Pot MeOH yield	.78	.65	.64	.60	.92	.73	.64
Char yield, g	367	313	274	148	164	336	464
Char in bed, g	180	195	178	176	129	137	135
Char comp, wt%							
C	85	85	85	85	85	85	85
H							
N							
O							
% C to char	12.02	12.05	11.80	11.91	6.07	8.41	9.54
Min char res t	37	42	37	35	37	28	28
Wt tar, g	.2	5.8	7.3	.7	3	1.3	1
Tar comp, wt%							
C	85	85	85	85	85	85	85
H	6.2						
N							
O							
% C to tar	.01	.22	.31	.06	.11	.03	.02
Vol cond, cc	1990	2811	2174	1550	2932	3431	3700
TOC, mg/l	550	1800	1768	3358		1331	1880
% C to cond	.04	.23	.19	.49	0	.13	.17
C Balance, %	97	99	99	99	100	99	101

(a) See Pages A.1 to A.3 for definitions of table entries.

TABLE A.3. (contd)

Date	7/19/85	7/19/85	7/25/85	7/26/85	7/29/85
Test number->	RKS-1	RKS-1d	ICI-1	ICI-2	ICI-3
Temp, C (a)	750	750	750	750	750
Temp cat, C	750	750	750	750	750
Catalyst	RKS-4SA	RKS-4SA	ICI-46-1	ICI-46-1	ICI-46-1
Inert Material	Sand	Sand	Sand	Sand	Sand
Wood Mesh Size	-14	-14	-14	-14	-14
Hours	2.8	2.8	4.8	3	6
Ht, ft	1	1	1	1	1
Wt cat, g	700	700	618	618	618
Wt cat at end, g	611	611			502
g/min wood	13.7	13.7	15.7	15.8	12.6
g/min steam	13.5	13.5	13.2	11.9	13.3
Steam/wood	.99	.99	.84	.75	1.06
slv, ft/sec	.75	.75	.74	.67	.74
lb/hr-ft ³	37	37	42	43	34
Wt wood, g	2307	2307	4543	2780	4520
Wood/catalyst	3.30	3.30	7.35	4.50	7.31
Wood comp, wt%					
C	50.3	50.3	50.3	50.3	50.3
H	6.4	6.4	6.4	6.4	6.4
O	42.7	42.7	42.7	42.7	42.7
Ash	.6	.6	.6	.6	.6
Gas comp, vol%					
H ₂	65	46.9	61.7	57.3	56.4
CO ₂	17.9	17.2	14.2	16.6	18.5
C ₂	0	3	.2	.9	1.1
CH ₄	1.2	8.4	1.8	5.1	5.7
CO	16	24.5	22.1	20.2	18.2
C ₃					
H ₂ /CO	4.06	1.91	2.79	2.84	3.10
Gas flow, l/g	2.56	1.74	2.24	1.98	1.98
% C to gas	90	98	86	87	88
Pot MeOH yield	.92	.55	.83	.68	.66
Char yield, g	175	175	252	154	251
Char in bed, g	147	147	110	118	120
Char comp, wt%					
C	85	85	85	85	85
H	1	1	1	1	1
N					
O	14	14	14	14	14
% C to char	13	13	9	9	9
Min char res t	36	36	23	25	32
Wt tar, g					
Tar comp, wt%					
C	85	85	85	85	85
H	6.2	6.2	6.2	6.2	6.2
N					
O	8.8	8.8	8.8	8.8	8.8
% C to tar	0.00	0.00	0.00	0.00	0.00
Wt cond, g	1170	1170	1560	1150	2570
TOC, mg/l				864	876
% C to cond	0.00	0.00	0.00	.07	.10
C Balance, %	103	110	96	96	98

(a) See Pages A.1 to A.3 for definitions of table entries.

UNCATALYZED TESTS

Baseline yields were established in tests without a catalyst. Data from these uncatalyzed tests are presented in Table A.4.

TABLE A.4. Uncatalyzed Tests

Date	JAN/85	FEB/85	MAR/85	MAR/85	6/18/85	8/14/85
Test number->	U-1	U-2	U-3	U-4	U-6	U-8
=====	=====	=====	=====	=====	=====	=====
Temp, C (a)	750	750	750	750	650	750
Catalyst	None	None	None	None	None	None
Inert Material	Bauxite	Sand	Sand	Sand		Sand
Wood Mesh Size	-20	-20	-12+20	-20	-14	-14
Hours	2.33	6.42	1	2.2	1.8	2.5
Ht, ft	1	1	1	1	1	1
Wt cat, g						
g/min wood	16.2	15.4	20.5	19.7	12.2	28.5
g/min steam	16.7	12.5	13.3	15.7	13.3	28
Steam/wood	1.03	.81	.65	.80	1.09	.98
slv, ft/sec	.93	.70	.74	.88	.67	1.57
lb/hr-ft ³	44	41	55	53	33	77
K, 1/sec	.00019					
Wt wood, g	2279	5922	1263	2634	1309	4281
Wood comp, wt%						
C	50.3	50.3	50.3	50.3	50.3	50.3
H	6.4	6.4	6.4	6.4	6.4	6.4
O	42.7	42.7	42.7	42.7	42.7	42.7
Ash	.6	.6	.6	.6	.6	.6
Gas comp, vol%						
H ₂	44.5	41.6	40.7	38.5	34.1	36.5
CO ₂	20	15.7	16.2	15.7	22.4	15.5
C ₂	3.2	4	4	4.3	3.3	4.3
CH ₄	8.9	9.9	10.6	10.6	11.2	10.7
CO	23	28.2	30.1	30.1	28.4	32
C ₃	.6	.6	.8	.9	1.3	1
H ₂ /CO	1.93	1.48	1.35	1.28	1.20	1.14
Gas flow, l/g	1.25	1.31	1.03	.96	.64	1
% C to gas	75	83	69	65	46	70
Char yield, g	300	377	114	159	240	214
Char in bed, g	166	75	64	113	159	92
Char comp, wt%						
C	85	85	85	85	85	85
H	1	1	1	1	1	1
N						
O	14	14	14	14	14	14
% C to char	22	11	15	10	31	8
Min char res t	34	16	10	19	43	11
Wt tar, g	51.3		55	144	150	
Tar comp, wt%						
C	85	85	85	85	85	85
H	6.2	6.2	6.2	6.2	6.2	6.2
N						
O	8.8	8.8	8.8	8.8	8.8	8.8
% C to tar	3.80	0.00	7.36	9.24	19	0.00
Wt cond, g	3666	2650	1874	3841	3810	3730
TOC, mg/l	8000	1503	8713	8711	11100	
% C to cond	2.56	.13	2.57	2.53	6.42	0
C Balance, %	104	94	95	87	103	78

(a) See Pages A.1 to A.3 for definitions of table entries.

STEAM GASIFICATION OF WOOD WITH PRIMARY CATALYSTS

Potassium and sodium carbonates were impregnated on wood and tested as primary catalysts. Data from tests with steam as the gasifying agent are given in Table A.5.

TABLE A.5. Tests with Primary Catalysts

Date	FEB/85	FEB/85	FEB/85	5/1/85	5/3/85	6/26/85	7/3/85
Test number->	K-1	K-2	K-3	N-1	N-2	K-4	N-5
Temp, C (a)	750	750	750	750	750	650	650
Catalyst	8% K	4% K	8% K	6% Na	3% Na	4% K	3% Na
Inert Material	Bauxite	Bauxite	Bauxite	Bauxite	Bauxite	Bauxite	Bauxite
Wood Mesh Size	-20	-20	-20	-14	-14	-14	-14
Hours	2.25	4	2.83	3.4	3.4	1.2	2
Ht, ft	1	1	1	1	1	1	1
Wt cat, g							
g/min wood	13.1	14.4	13.4	11.3	10.1	5.8	7
g/min steam	16.9	15	15.3	16.3	15	11.2	12.6
Steam/wood	1.29	1.04	1.14	1.44	1.49	1.93	1.80
slv, ft/sec	.94	.84	.86	.91	.84	.57	.64
lb/hr-ft ³	35	39	36	30	27	16	19
Wt wood, g	1763	3465	2275	2430	2089	414	835
Wood comp, wt%							
C	50.3	50.3	50.3	50.3	50.3	50.3	50.3
H	6.4	6.4	6.4	6.4	6.4	6.4	6.4
O	42.7	42.7	42.7	42.7	42.7	42.7	42.7
Ash	.6	.6	.6	.6	.6	.6	.6
Gas comp, vol%							
H ₂	59.4	52.4	53.3	56.4	53.9	62.3	47
CO ₂	21	22.6	21.2	23.8	22.7	28.3	30
C ₂	1.1	1.6	2.4	1.1	1.9	.8	1.9
CH ₄	3.5	4.8	6.4	3.6	5.9	3	8.3
CO	15	17.4	16.4	14.8	15.5	5.7	12.5
C ₃	--	--	--	.2	.4	.35	.7
H ₂ /CO	3.96	3.01	3.25	3.81	3.48	10.93	3.76
Gas flow, l/g	1.95	1.74	1.41	1.72	1.26	1.45	.86
% C to gas	81	84	69	76	60	56	47
Pot MeOH yield	.64	.54	.44	.54	.39	.44	.23
Char yield, g	189	324	285	190	281	156	200
Char in bed, g	49	85	15	76	76	150	140
Char comp, wt%							
C	85	85	85	85	85	85	85
H	1	1	1	1	1	1	1
N							
O	14	14	14	14	14	14	14
% C to char	18	16	21	13	23	64	40
Min char res t	12	20	4	22	25	86	67
Wt tar, g	35	2.5	45	59	60		22.3
Tar comp, wt%							
C	85	85	85	85	85	85	85
H	6.2	6.2	6.2	6.2	6.2	6.2	6.2
N							
O	8.8	8.8	8.8	8.8	8.8	8.8	8.8
% C to tar	3.35	.12	3.34	4.10	4.85	0.00	4.51
Wt cond, g	1625	3000	1936	2830	4210	1260	2420
TOC, mg/l	1717	266	719			2940	5056
% C to cond	.31	.05	.12	0	0	1.78	2.91
C Balance, %	103	99	93	93	88	121	95

(a) See Pages A.1 to A.3 for definitions of table entries.

CARBON DIOXIDE GASIFICATION WITH PRIMARY CATALYSTS

Data from tests with carbon dioxide as the gasifying agent are shown in Table A.6. Tests with CO₂ were made with and without catalysts. Both primary and secondary catalysts were tested.

TABLE A.6. CO₂ Gasification Tests

Date	3/21/85	3/21/85	3/28/85	3/28/85	4/16/85	4/16/85	4/25/85	4/25/85
Test number→	C-1	C-1a	C-3	C-3a	C-4	C-4a	C-5	C-5a
Temp, C (°)	750	750	750	750	750	750	750	750
Temp cat, C		750		750		750		750
Catalyst	None	NCM	4%K	NCM	8% K	NCM	4%K	6-90C
Inert Material	Sand		Bauxite		Bauxite		Bauxite	
Wood Mesh Size	-14		-14		-14		-14	-20
Hours	1	1	2.8	2.8	1.8	1.8	1.7	1.7
Ht, ft	1	1	1	1	1	1	1	1
Wt cat, g								680
g/min wood	12.9	12.9	14.5	14.5	15	15	17.5	17.5
l/min CO ₂	18	18	18	18	18	18	18	18
CO ₂ /Wood, g/g	2.56	2.56	2.28	2.28	2.20	2.20	1.89	1.89
slv, ft/sec	.74	.74	.74	.74	.74	.74	.74	.74
lb/hr-ft ³	35	35	39	39	40	40	47	47
Wt wood, g	772	772	2428	2428	1620	1620	1750	1750
Wood/catalyst	--	--	--	--	--	--	--	2.57
Wood comp, wt%								
C	50.3	50.3	50.3	50.3	50.3	50.3	50.3	50.3
H	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4
O	42.7	42.7	42.7	42.7	42.7	42.7	42.7	42.7
Ash	.6	.6	.6	.6	.6	.6	.6	.6
Gas comp, vol%								
H ₂	7	18	12.3	19.7	16.1	22.3	15.9	23.3
CO ₂	69.3	49.2	64.4	49.7	53.9	47	57.1	44.8
C ₂	1.6	.2	1.1	.2	.8	.2	1.3	.4
CH ₄	4	2.6	3.1	1.9	2.6	2.3	3.7	3.1
CO	17.1	29.6	18.7	28	25.9	28.1	22.2	28.7
C ₃	.3	0	.3	0	.3	0	.3	
H ₂ /CO	.41	.61	.66	.70	.62	.79	.72	.81
Gas flow, l/g	2	2.66	2	2.54	2.17	2.47	2.11	2.24
% C to gas	49	78	54	79	64	72	80	71
Fr. H in gas	.52	.82	.58	.79	.69	.88	.76	.89
Char yield, g	77	77	326	326	226	226	202	202
Char in bed, g	101	101	98	98	56	56	0	0
Char comp, wt%								
C	85	85	85	85	85	85	85	85
H	1	1	1	1	1	1	1	1
N								
O	14	14	14	14	14	14	14	14
% C to char	17	17	23	23	24	24	20	20
Min char res t	26	26	23	23	12	12	0	0
Wt tar, g	21.6	0	34	0	32.4	0	30.8	0
Tar comp, wt%								
C	85	85	85	85	85	85	85	85
H	6.2	6.2	6.2	6.2	6.2	6.2	6.2	6.2
N								
O	8.8	8.3	8.8	8.8	8.8	8.8	8.8	8.8
% C to tar	4.73	0.00	2.37	0.00	3.38	0.00	2.97	0.00
Wt cond, g	500	500	660	660	600	600	570	570
TOC, mg/l	464	464	0	0	580	580	962	962
% C to cond	.06	.06	0.00	0.00	.04	.04	.06	.06
C Balance, %	71	95	80	102	91	96	102	90

(a) See Pages A.1 to A.3 for definitions of table entries.

TABLE A.6. (contd)

Date	7/10/85	7/16/85	5/9/85	5/16/85
Test number->	U-7	N-6	N-3	N-4
=====	=====	=====	=====	=====
Temp, C (a)	650	650	750	750
Temp cat, C				
Catalyst	None	3% Na	6% Na	3% Na
Inert Material				
Wood Mesh Size	-14	-14	-14	-14
Hours	2.5	2	2.8	1.9
Ht, ft	1	1	1	1
Wt cat, g				
g/min wood	20.6	10.6	14.1	20.4
l/min CO ₂	18	18	18	18
CO ₂ /Wood, g/g	1.60	3.11	2.34	1.62
slv, ft/sec	.67	.67	.74	.74
lb/hr-ft ³	56	29	38	55
Wt wood, g	3025	1249	2333	2324
Wood/catalyst	--	--	--	--
Wood comp, wt%				
C	50.3	50.3	50.3	50.3
H	6.4	6.4	6.4	6.4
O	42.7	42.7	42.7	42.7
Ash	.6	.6	.6	.6
Gas comp, vol%				
H ₂	4.8	5.3	11.6	16.9
CO ₂	80.4	85.4	66.8	58.1
C ₂	.8	.4	1.3	1.3
CH ₄	3	2	4	4.2
CO	11.1	6.7	16.3	19.5
C ₃	.4	.2	.4	.3
H ₂ /CO	.43	.79	.71	.87
Gas flow, l/g	1.57	2.22	2.01	1.56
% C to gas	65	42	55	45
Fr. H in gas	.29	.32	.63	.60
Char yield, g	282	332	392	279
Char in bed, g	140	156	72	75
Char comp, wt%				
C	85	85	85	85
H	1	1	1	1
N				
O	14	14	14	14
% C to char	16	16	28	20
Min char res t	23	49	17	12
Wt tar, g	263	13	34	
Tar comp, wt%				
C	85	85	85	85
H	6.2	6.2	6.2	6.2
N				
O	8.8	8.8	8.8	8.8
% C to tar	14.69	1.76	2.46	0.00
Wt cond, g	910	925	570	627
TOC, mg/l	54060	12301		
% C to cond	3.23	1.81	0	0
C Balance, %	99	91	86	65

(a) See Pages A.1 to A.3 for definitions of table entries.

APPENDIX B

CHAR RESIDENCE TIME

APPENDIX B

CHAR RESIDENCE TIME

The char residence time shown in the tables in Appendix A was calculated by estimating the char production rate. The usual method for calculation of residence time could not be used without knowing the char inventory in the gasifier and the rate of char input to the gasifier.

The formula used for calculation of char residence time is

$$t = \frac{W}{0.3F}$$

where t is the residence time, W is the weight in grams of char in the gasifier (char in bed) at the end of a test, and F is the wood feed rate in grams per minute. The 0.3 in the formula is the assumed fraction of wood that is instantaneously converted to char upon entering the gasifier.

Calculation of char residence time with this formula assumes that the inventory of char in the gasifier, W , remains constant. The amount of char in the gasifier at the end of a test was usually about the same as the amount of char in the gasifier at the end of a test was usually about the same as the amount of char in the bed at the start of a test.

Attempts to correlate char residence time with char conversion were unsuccessful. Even if the factor used for wood conversion to char (0.3) were wrong, the relative effect on residence time should be the same in different tests. Often, a high char conversion resulted in a low char inventory in the fluid bed, which then gave a relatively short residence time.

APPENDIX C

COMPARATIVE ANALYSIS OF CATALYZED AND UNCATALYZED BIOMASS GASIFICATION TARS

APPENDIX C

COMPARATIVE ANALYSIS OF CATALYZED AND UNCATALYZED BIOMASS GASIFICATION TARS

The following discussion was prepared by D. C. Elliott of the Pacific Northwest Laboratory (PNL). Tars produced in the bench-scale studies were analyzed as described below.

INTRODUCTION

Four biomass gasification tar samples were analyzed by gas chromatography/mass spectrometry (GC/MS) to determine the effect of catalysts on the chemical composition. The mass spectra were used to identify the chemical components, while a similar gas chromatograph produced with a flame ionization detector was used to quantify the components. The four tars were collected in a methylene chloride scrubber in a slip stream from the gas produced in the bench-scale gasifier at PNL. The tars, produced at 750°C, represent the products from uncatalyzed gasification, potassium catalyzed gasification, potassium catalyzed gasification followed by nickel catalyzed reforming, and uncatalyzed gasification in carbon dioxide followed by nickel catalyzed reforming. The sample from the test with carbon dioxide was analyzed for lack of a sample from a nickel catalyzed test performed with steam (steam was used in the other three tests). Significant differences in the amounts of tar produced in the presence and absence of catalyst are well documented; however, the content of the different tar products has never been investigated in detail until recently.

RESULTS AND DISCUSSION

Table C.1 is a list of the major components in the tar fractions. The identities of the components are given with good certainty with the exception of the two complex oxygenated components, dihydropyranone and bicyclocetene-dione, which were very tentatively identified only by evaluation of the mass spectra without standards available for comparison. It is obvious from this

TABLE C.1. Major Condensible Organic Products (mg/100 g wood feed)

Component	Nickel Catalyzed (steam)	Uncatalyzed (steam)	Potassium Catalyzed (steam)	Potassium Plus Nickel Catalyzed (steam)	Uncatalyzed (CO ₂)
Phenol	7	1,183	109	1	52
Cresol	1	1,155	108	<1	39
Naphthalene	164	868	33	40	52
Methylnaphthalenes	29	511	37	10	34
Indene	9	488	1	<1	94
Methylindenes	<1	278	10	1	19
Acenaphthylene	5	301	27	2	23
Acenaphthene	2	170	15	1	15
Benzene	421	1	<1	<1	5
Toluene	198	40	<1	<1	47
Xylene + styrene	53	205	<1	<1	140
Methylstyrene	2	134	1	<1	38
Phenanthrene	2	158	20	31	12
Fluorene	3	93	13	10	16
Dihydrophranone ^(a)	--	68	<1	<1	126
Bicyclooctenedione ^(a)	--	100	5	<1	29
Benzofuran	2	108	1	<1	34
Dibenzofuran	3	14	2	10	1
Biphenyl	7	71	6	6	7
Percent yield of tar	0.9	9.3	0.7	0.2	1.1
Major components as percent of total	98	63	53	66	70

(a) Tentatively identified by evaluation of the mass spectra without standards for comparison.

table that the relative ratios and the actual amounts of the various components can be changed dramatically by the catalysts in the system. Table C.1 must be tempered with the knowledge that the samples analyzed may be somewhat deficient in the most volatile components, since the samples had been in storage for 3 to 4 months before these analyses were made. During storage the dichloromethane solvent had actually evaporated and had to be replenished for these analyses.

Table C.1 shows that the most plentiful tar products from gasification are the phenols and naphthalenes. A large number of other alkylated phenols and naphthalenes were also detected in lesser quantities (see Table C.2). Other aromatic hydrocarbon products, varying from one to three rings, are the other major products. Some oxygenated products, including the benzofurans and cyclic ketones, were also detected in significant quantities. With the addition of potassium the amount of the tar components is generally cut by a factor of about 10. However, the amount of the lighter aromatic hydrocarbons (one and two rings) is reduced by a much greater factor, such that the group of alkylated benzenes (BTX and styrenes) is nearly eliminated. The amounts of furans and ketones are also greatly reduced, with the exception of the dibenzofuran. Dibenzofuran shows the smallest factor of reduction of any of the components, which suggests that it is a later decomposition (condensation) product of other tar components. These changes cause the tar from the potassium catalyzed test to have a higher concentration of phenolics relative to the other compound groups.

The addition of the nickel reforming catalyst also has a dramatic effect on the gas composition. In combination with the potassium catalyst, the nickel catalyst causes nearly complete removal of phenolics and ketones. The dominant constituents are the nonsubstituted polycyclic aromatic hydrocarbons (PAH). In fact, the amount of naphthalene and phenanthrene appears to actually increase with the use of the nickel reformer, apparently due to demethylation of substituted PAH. The less condensed PAH, such as indene, acenaphthylene and acenaphthene, appear to be susceptible also to reaction with the nickel. The large yield of dibenzofuran appears to be the stable end product of reforming other oxygenated components.

TABLE C.2. Detailed Listing of Components in Biomass Gasification Tar

Chemical	U 0308 (uncatalyzed)			N 0226 (potassium only) intermediate gas			N 0226 (potassium & nickel bed) product gas			C 0322 (uncatalyzed CO ₂)		
	FID Time	MS Time	FID Area	FID Time	MS Time	FID Area	FID Time	MS Time	FID Area	FID Time	MS Time	FID Area
1,4-cyclohexadiene	3.30	1.76	44.67							2.13	1.76	287.18
1,3-cyclohexadiene	3.36	1.82	38.42							2.18	1.76	180.48
benzene	3.56		4	2.38		3.86	3.27	1.94	96.35	2.38	1.94	1281.37
cyclohexene	3.76	2.26	2	2.60	2.12	326.99	3.36	2.12	293.71	2.60	2.12	398.47
C ₆ ketone		2.88										
4methyl-2-cyclopentenone										3.40	2.88	187.96
methylfuran?										3.66	3.06	19.27
toluene	3.91	3.32	142.36	3.87	3.34?	6.45	4.39	3.32	39.59	3.88	3.32	71722.38
cyclopentanone	4.63	3.68	13.27							4.23	3.68	82.90
n-butylacetate							5.01	4.00		4.62	4.06	1499.12
HC/ketone?	5.42	4.00	35.77									
2-methylcyclopentanone										4.85	4.32	20.61
furfural	6.19	4.38	87.02							4.97	4.44	333.46
methylfuran?	6.65	4.56	108.99									
xylene	7.25	4.88	38.62							5.52	4.94	2221
xylene	7.39	5.00	98.00	5.00	--	8.94	5.97	5.06	9.82	5.67	5.12	4141
phenylacetylene	7.53	5.12	22.82							5.79	5.18	1199
xylene + styrene	7.82-8	5.38	520.65				6.33	5.50	13.28			
cyclooctatetraene										6.10	5.56	16293.5
dimethylfuran??/methyl												
cyclopentenone	8.10	5.82	25.14									
dihydropyranone?	8.20	6.00	140.5							6.56	6.06	10453
C ₃ = benzene	8.90	6.44	8.28							6.75	6.18-32	4319
3-phenyl-1-propene?										6.90	6.50	477.6
benzaldehyde	9.20	6.68	121.49	7.34	6.82	63.32						
C ₂ benzene										7.36	6.76	1518.6
Cumene		6.82										
trimethylbenzene										7.47	6.94	329.9
phenol	9.36	7.06	2849.1	7.62	7.06	5452.2	7.73	7.00	365.1	7.64-.79	7.18	5359
methylstyrene				7.95	7.38	56.34				7.97	7.44	5006
C ₃ =benzene	9.82	7.32	423.7									
benzofuran	9.93	7.38	298.4	8.02	7.44	68.10	8.19	7.44	10.17	8.04	7.50	3892
HC?	10.22	7.68	132.6									
ethylmethylbenzene/												
mesitylone		7.82								8.33	7.82	4729
C ₃ =benzene		7.88										
methylstyrene										8.48	7.94	1099
C ₄ cyclohexadiene	10.52	8.06	31.10									
C ₃ =benzene	10.50	8.12	31.34									
Nadic maleic anhydride??										8.67	8.06	793.8
indan										8.75	8.18	291.4
o-cresol + indene	10.76 (17% cresol)		834.6	8.90	8.38	1717.66	9.04	8.32	68.45	8.95	8.38	12922
	10.86	8.32	1553.5	9.01 (5% indene)		94.54		(0% cresol)			(<5% cresol)	
	10.98	8.50	60.12									
C ₃ phenol?										9.09	8.56	956.87
phenylacetate										9.29-.38	8.82	3622.3
m-,p-cresol	11.12-.32	8.76	1945.7	9.27	8.76	3680.6	9.38	8.76	86.42			

TABLE C.2. (contd)

C ₄ benzene						9.68	8.94	18.31			
C ₄ =benzene									9.50	8.94	306.1
C ₄ =benzene									9.56	9.00	596.4
ethyl styrene									9.63	9.06	138.7
bicyclo(1,2,3)oct-3-ene-2,5dione	11.68	9.12	245.9	9.71	9.18	269.2			9.72	9.18	2953.3
vinylbenzaldehyde	11.81-3	9.18	99.98								
methylbenzofuran	11.90	9.32	136.8	9.82	9.32	51.26	10.04	9.32	13.77	9.79-.84	9.26 687.2
methylbenzofuran	12.00	9.38	149.9	9.91	9.38	136.9				9.92	9.38 731.6
methylbenzofuran							10.12	9.44	16.75	10.00	9.44 264.4
methylindene										10.05	9.50 439.7
trimethylcyclohexanone	12.24	9.62	140.3	10.20	9.68		10.31	9.62	744.03	10.22	9.68 950.9A
methylanisole or xylene	12.46-.59	9.94	405.49	10.53	10.00	372.7				10.40	9.82 38.67
methylindene	12.74	10.12	642.5	10.71	10.18	260.1	10.83	10.18	12.69	10.72	10.12 1033.4
methylindene+ethylphenol	12.86	10.26	402.9	10.83	10.32	1266.2	10.95	10.26	25.72	10.83	10.32 1680.5
		(48% indene)			(19% indene)			(100% indene)			(29% phenol)
methylindene	12.99	10.38	54.98	11.03	10.44	167.9				11.00	10.44 316.3
methylbenzaldehyde	13.24	10.50	102.1								
xylene	13.06	10.44	90.54		10.56						
naphthalene	13.44	10.82	2714	11.34	10.82	2178.1	11.50	10.88	12311	11.37	10.82 6913.7
vinylphenylether?				11.49	11.00	881.9					
methylbenzaldehyde	13.60	10.94	256.5								
methylbenzaldehyde	13.82	11.06	69.6								
o-tolylaldehyde										11.51	11.00 843.3
dimethylbenzofuran										11.65	11.06 111.5
naphthol	14.11	11.44	52.3	12.03	11.56	108.2				12.04	11.50 157.1
dimethylindene or H ₂ naph	14.32	11.62	49.07	12.26	11.76	24.04					
methylethyl phenol	14.44	11.76	6.44	12.31	11.82	76.52					
dimethylindene?	14.46	11.82	4.15								
dimethylindene?	14.51	11.88	18.07								
methylazulene?	14.87	12.18	112.2	12.76	12.26	158.9				12.77	12.18 213.2
indanone	15.00	12.32	218.7	12.85	12.32	241.6	12.96	12.32	51.78	12.85	12.32 960.9
methylazulene?	15.08	12.38	89.06	12.97	12.44	274.6				12.98	12.44 261.6
methylnaphthalene	15.24	12.50	921.0	13.09	12.56	1271.1	13.20	12.56	1775.5	13.11	12.56 2500.6
methylnaphthalene	15.54	12.82	676.7	13.37	12.82	1105.4	13.48	12.82	1334.4	13.39	12.82 1896.5
vinylbenzaldehyde?	15.70	12.94	42.5								
nitrobenzaldehyde	15.80	13.26	916.4	13.75	13.26	6643.2	13.88-14.05	13.44-.50	29586.	13.82-.99	13.38-.56 40752. **
vinylbenzaldehyde?	15.96	13.32	222.9								
biphenyl	16.49	13.76	270.8	14.33	13.76	461.8	14.46	13.88	2368	14.36	13.82 1251.
ethylnaphthalene	16.76	13.94	173.8								
ethylnaphthalene	16.83	14.00	42.9	14.57	14.00	410.1				14.60	14.06 460.3
dimethylnaphthalene	16.92	14.12	141.3	14.73	14.08	294.5	14.85	14.18	100.0	14.75	14.18 666.7
acenaphthene isomer	17.05	14.26	91.1	14.85	14.32	159.6				14.88	14.32 255.4
dimethylnaphthalene	17.16	14.32	140.6	14.96	14.38	303.5				14.99	14.44 497.3
dimethylnaphthalene	17.22	14.38	114.6	15.01	14.44	229.8	15.07	14.44	144.3	15.04	14.50 379.2
acenaphthene	17.30	14.50	518.4	15.09	14.50	925.8	15.20	14.50	183.8	15.12	14.56 1863
dimethylnaphthalene	17.48	14.62	59.0	15.25	14.68	154.7				15.28	14.68 298.0
dimethylnaphthalene	17.54	14.68	65.2	15.31	14.76	122.4	15.37	14.68	58.0	15.35	14.76 254.3
acenaphthylene	17.72	14.88	917.2	15.45	14.88	1734.2	15.59	14.88	609.1	15.51	14.88-.94 3040.5
diphenylmethane	18.01	15.18	113.6	15.81	15.18	215.2	15.93	15.18	300.5	15.85	15.26 487.0
dimethylazulene?	18.21	15.32	221.4	15.93	15.38	523.6	16.06	15.32	300.9	16.05	15.44 64.2
isopropylnaphthalene	18.34	15.44	28.24	16.10	15.50	70.3				16.15	15.50 104.0

C.5

TABLE C.2. (contd)

C ₃ naphthalene	18.58-.63	15.68	245.5	16.20	15.68	57.5							
methylbiphenyl	18.90	16.00	108.4	16.34	15.76	649.5				16.40	15.76	842.9	
methylbiphenyl	19.06	16.06	8.8	16.63	16.00	331.5				16.69	16.00	486.9	
methylbiphenyl				16.73	16.12	166.5					16.18		
methylbiphenyl	19.15	16.26	73.7	16.87	16.26	328.9	17.0	15.26	19.8	16.92	16.26	440.5	
methylacenaphthylene	19.32	16.32	112.4	17.00	16.38	298.1		15.4	517	17.07	16.44	665.5	
dibenzofuran	19.41	16.44	35.5	17.09	16.50	85.3	16.4-.51	15.76	2688	17.14	16.50	171.4	
methylacenaphthylene	19.52	16.56	78.3	17.19	16.56	256.0							
fluorene	19.58	16.62	270.6	17.25	16.62	796.0	17.40	15.62	3021.2	17.30	16.62	1914.8	
methylfluorene?	19.64-.82	16.76	160.0										
PAH180/dihydrophenanthrene?				17.47	16.82	126.2							
methylacenaphthylene	19.93	16.88	112.9	17.53	16.94	265.8							
methylacenaphthylene?	20.04	17.05	137.7	17.60	17.00	193.6							
hydroxyfluorene?, xanthene?							17.82	17.06	309.8	17.74	17.06	404.8	
methylacenaphthylene?	20.17	17.12	230.1	17.72	17.12	404.4	17.93	17.18	102.2	17.85	17.18	561.5	
PAH182, hydroxyfluorene?, xanthene?		17.18		17.90	17.26	160.0	18.00-.15	17.26-.38	415.6	17.92	--	282.7	
dimethylbiphenyl	20.34	17.32	31.2	18.04	17.38	71.2				18.05	--	101.7	
phenylbenzaldehyde?				18.14	17.50	68.6	18.30	17.50	128.1				
methylfluorene??	20.61	17.56	38.3							18.41		106.2	
C ₄ guaiacol				18.26	17.62	88.6							
methylfluorene??	20.73	17.68	36.9										
dimethylbiphenyl?					17.88								
phenylphenol	20.89	17.88	16.2										
anthracene isomer?	21.07	18.00	218.7				18.80	18.00	314.4				
methylfluorene??	21.18	18.06	118.4				18.90	18.12	147.6	18.81		275.6	
methylfluorene??	21.34	18.26	50.3				19.05	18.26	108.4				
methylfluorene??	21.61	18.50	95.5										
diphenylacetylene?				18.70	18.06	652.3							
C ₄ guaiacol??				18.81	18.12	258.5							
C ₄ guaiacol?? (2)				18.95	18.32-.38	206.1							
C ₄ guaiacol??				19.10	18.50	101.8							
ditolylmethane										19.10		95.3	
fluorenone?, methylfluorene?				19.23	18.56	347.70	19.20	18.38	35.1	19.22		420.7	
ditolylmethane??							19.34	18.56	135.0	19.34		67.5	
phthalate?							19.44	18.68	30.7				***
C ₄ guaiacol??				19.50	18.82	126.4							
phenanthrene	22.22	19.06	448.3	19.78	19.06	1202.3	19.93	19.12	8683.3	19.78	19.1	1413.1	
anthracene	22.35	19.18	106.6	19.90	19.18	313.5	20.02	19.18	475.8	19.89		302.9	
methylphenanthrene	22.51	19.26-.32	1.2							20.01		64.3	
methylphenanthrene	22.53	19.38	11.6							20.07		95.6	
dimethylfluorene(2)	22.70-.89	19.50-.68	26.9							20.17		90.2	
dibenzoheptafulvene/204PAH	23.00	19.82	4.7				20.68	19.82	142.0				
methylphenanthrene	23.08	19.88	11.3				20.76	19.94	94.3	20.65		116.1	
methylphenanthrene	23.55	20.32	37.2	21.08	20.32	133.9	21.17	20.32	136.0	21.07		147.9	
methylphenanthrene	23.62	20.38	67.07	21.16	20.44	302.6	21.24	20.38	227.0	21.15		270.1	
methylphenanthrene	23.74	20.44	78.44	21.26	20.50	227.8	21.36	20.50	65.3	21.25		169.2	

TABLE C.2. (contd)

dibutylphthalate	23.89	20.62	142.1	21.39- .45	20.62	743	21.55	20.62	1524.7	21.38- .45	20.6	848	***
dibenzoheptafulvene/204PAH	24.35	21.06	55.7	21.88	21.12	124.6	21.97	21.06	276.6	21.87		151.4	
phenanthrenequinone?							22.04	21.12	220.8	21.94		68.9	
dimethylphenanthrene	24.79	21.44	12.2	22.29	21.50	144.3	22.38	21.50	33.4	22.28		98.3	
dimethylphenanthrene?				22.39	21.62	47.9				22.38		16.7	
dimethylphenanthrene?				22.57	21.82	118.9				22.58		48.5	
dibenzoheptafulvene/204PAH	25.23	21.88	85.4	22.72	21.88	573.9				22.71		300.1	
204PAH	25.40	22.00	18.7										
dimethylphenanthrene				22.87	22.06	59.8				22.85		43.8	
fluoranthene/pyrene	25.54	22.12	67.5	22.97	22.18	165.5	23.07	22.12	278.4	22.96		132.6	
218 PAH?										23.12		8.8	
202 PAH?				23.23		113.3	23.33	22.38	25.2	23.22		79.1	
diphenylacetylene??	26.18	22.68	163.6							23.55		152.5	
218 MW?							23.83	22.88	118.9				
BHT (C ₉ phenol?)				23.83		138.7				23.81		84.4	
218 MW?							24.00	23.06	43.3				
218 MW?							24.26	23.32	40.8				
218 PAH?										24.21		88.0	
methylpyrene + 16?							24.59	23.62- 68	112.8	24.48		103.7	
methylpyrene + 16?							24.76	23.76	173.1	24.66		66.0	
methylpyrene + 16? (3)										24.76- 25.10		88	
butylbenzylphthalate	27.97	24.5	10.1	25.47	24.6	210.1	25.57	24.50	1318.3	25.44	24.4	175.8	***
HC?							26.57	25.44	105.5	26.46		46.0	
chrysene	29.97- 30.14	26.1	25.9	26.81		75.8	26.91	25.82	74.8	26.89		37.3	
phthalate				26.91		80.3				27.07	26.0	56.4	***
HC>C ₁₈							27.46	26.26	113.0	27.35		4.5	
methylchrysene								26.44					
phthalate							28.09	26.76	25.4	28.0		??	***
methyl chrysene								26.94					
HC C ₂₀							28.43	27.06	119.9	28.86		8.9	
phthalate								27.50					***
HC>C ₂₀							29.56	27.88	101.0				
phthalate							30.40	28.44	64.3				***
HC							30.88	38.88	102.5				
phthalate							31.48	29.50	33.1				***
benzpyrene or perylene								29.68					
benzpyrene or perylene								29.88					
HC C ₂₃							32.48	29.94	88.8				

* cyclohexene is a dichloromethane (solvent) impurity

** nitrobenzaldehyde was added as an internal quantitative standard

*** phthalates are believed to be derived from the sample jar lid liners

A peak was identified as methylphenylacetate

B peak was tentatively identified as a hydrocarbon make up of 13 carbons (C₁₃HC)C peak was very tentatively identified as a guaiacol with a total of four carbons as alkyl substituents (C₄ guaiacol)

The result with uncatalyzed CO_2 gasification tar is a curious mix of components. The BTX and styrenes are the most abundant. The next most abundant component is that tentatively identified as a dihydropyranone. This component appears to be twice as abundant as in the uncatalyzed case with steam. The mechanism of formation of the dihydropyranone is unknown, and speculation would be of doubtful value until the structure is known for certain. The amount of phenols is reduced by a factor of two, a greater reduction than in the potassium-catalyzed-only case. The amounts of PAH appear to be similar to those in the potassium-catalyzed-only case. Based on the more complete data given in Table C.2, it is evident that numerous other alkylated benzenes are present in the CO_2 uncatalyzed tar and not in the steam uncatalyzed.

The nickel-catalyzed only case demonstrates again the strong activity of the nickel to deoxygenate the tar. The tar components are primarily benzenes and naphthalenes. The phenols are reduced by 2 to 3 orders of magnitude. Actual cracking of higher molecular weight hydrocarbons is also shown by the reduced levels of naphthalenes, phenanthrenes, and larger molecules.

CONCLUSIONS

Based on these results, a clearer understanding of the catalytic tar reforming chemistry is possible. As expected from earlier studies of biomass tars, the steam uncatalyzed biomass gasification tar produced at 750°C is a mixture of phenols and PAH with only small amounts of the highly oxygenated components from primary pyrolysis of biomass. The alkali catalyst reduces the tar yield by a factor of 10 for most of the components in the tar, with somewhat stronger activity for one- and two-ring aromatics and the ketone/furan oxygenates. With the addition of the nickel catalyst bed, the phenolic component is further reduced nearly to extinction, and the remaining PAH are demethylated. This results in the high concentration of naphthalene in the product gas stream which has been reported earlier. Based on this analysis, phenanthrene and naphthalene are the primary products of the combined catalyst systems, though they are both present in much lower yields than in the uncatalyzed cases. The BTX and higher alkylated benzenes appear to be maximized in uncatalyzed gasification with CO_2 . Oxygenated components are

reduced, as are the PAH. A major product of the CO₂ uncatalyzed tar has been tentatively identified as a dihydropyranone, but verification is required.

The catalyst systems tested here can significantly reduce tar generation and, presumably, increase gas yield in a biomass gasification system. The alkali catalyst within the gaisifer is generally effective in reducing the production of all components but is particularly effective in reducing production of alkylated benzenes. The mechanism of this reduced production could be either stopping their formation initially or catalyzing their decomposition. Further studies would be necessary to determine the mechanism. The combined catalyst system results in a PAH concentrated tar but at very low yields.

APPENDIX D

HEAT AND MASS TRANSFER CALCULATIONS

APPENDIX D

HEAT AND MASS TRANSFER CALCULATIONS

This appendix includes supporting calculations, computer program documentation, and results of heat and mass transport analyses for the catalytic steam reforming of biomass gases. Process configurations that have been analyzed include both fixed and fluid beds. The effect of particle size and Reynolds number are examined with respect to pellet temperatures and effectiveness factors. This is a preliminary compilation of the analysis of heat and mass transfer. Details are presented in a 1986 thesis by Brown.

For a catalyst sphere with a diameter of 425 μm ,

$$\begin{aligned}\text{surface area} &= 4\pi R^2 \\ &= 5.67 \times 10^{-7} \text{ m}^2 \\ \text{volume} &= 4/3 \pi R^3 \\ &= 4.02 \times 10^{-11} \text{ m}^3\end{aligned}$$

For NiCuMo catalyst,

$$\text{activity surface area} \cong 2 \text{ m}^2/\text{g}$$

For a single pellet,

$$\text{active surface area} = 4.02 \times 10^{-11} \text{ m}^3 \left(\frac{1.24 \text{ g}}{\text{cm}^3} \right) \left(\frac{100^3 \text{ cm}^3}{\text{m}^3} \right) \left(\frac{2 \text{ m}^2}{\text{g}} \right)$$

$$\text{reactive area} = 1 \times 10^{-4} \text{ m}^2$$

Assume that the biomass gas reforming reaction can be adequately described for heat and mass transfer by the following formula:

$$\Delta H_{\text{rxn},1023} = +164 \text{ KJ g-mole}^{-1}$$

$$\Delta E = 130 \text{ KJ g-mole}^{-1}$$

Rostrup-Nielsen (1984) gives the reaction rate of the preceeding reaction as follows:

$$r = 1.1 \times 10^9 \exp [-15.6 \times 10^3 / T] \left\{ \frac{1}{1 + 0.5(P_{\text{H}_2\text{O}}/P_{\text{H}_2}) + 20 P_{\text{CO}}} \right\} P_{\text{CH}_4}$$

where $r = \text{mole m}^{-2} \text{ h}^{-1}$

$T = \text{temperature, K}$

$P = \text{partial pressure, MPa.}$

For a total pressure of 0.101 MPa (1 atm) and an assumed gas composition of:

<u>Component</u>	<u>mole%</u>	<u>Partial Pressure, MPa</u>
CH ₄	10	0.01
H ₂ O	50	0.05
H ₂	20	0.02
CO	10	0.01
CO ₂	10	0.01

At 750°C (1023K)

$$r = 1.1 \times 10^9 \exp [-15.6 \times 10^3 / 1023] \left\{ \frac{1}{1 + 0.5(0.05/0.02) + 20 (0.01)} \right\} 0.01$$

$$= 1.07 \text{ mole m}^{-2} \text{ h}^{-1}.$$

ISOTHERMAL PELLET HEAT TRANSFER

For the calculated reaction rate and an isothermal pellet, the pellet temperature can be calculated by a simple nonlinear energy balance. For this model there is no diffusional resistance to mass transfer.

heat in + heat rxn = heat out + heat accumulated

$$hA (T_{\infty} - T_c) + r(T)SA (-\Delta H_{rxn}) = hA \Delta T + \frac{dH}{dt}$$

where h = heat transfer coefficient, $\text{KJ m}^{-2}\text{h}^{-1}\text{K}^{-1}$

T_{∞} = gas stream bulk temperature, K

T_c = catalyst temperature, K

A = outside surface area of pellet, m^2

$r(T)$ = reaction rate, $\text{mole m}^{-2}\text{h}^{-1}$

SA = active surface area, m^2

ΔH_{rxn} = heat of reaction, KJ gmole^{-1}

dH/dt = change in enthalpy over time, zero for steady state.

If we solve for T_c ,

$$T_c = T_{\infty} - \frac{r(T)SA \Delta H_{rxn}}{hA}$$

where $r(T)$ is nonlinear in temperature.

To solve for T_c an iterative solution is required. The following program was used to predict catalyst temperature as a function of heat transfer coefficient.

```

10 ! THIS PROGRAM PREDICTS ISOTHERMAL CATALYST PELLET TEMPERATURES
20 ! BY A NON-LINEAR REACTION RATE EXPRESSION AND HEAT BALANCE
30 ! OVER A SINGLE CATALYST PELLET
40 !
50 !
60 ! WRITTEN BY M.D.BROWN
70 ! REV 0 9/11/85
80 !
90 !
100 ! VARIABLE DEFINITIONS
110 !
120 ! T0 = INITIAL TEMP (K)
130 ! I = ITERATION NUMBER
140 ! A1 = REACTION SURFACE AREA (M2)
150 ! A2 = OUTSIDE SURFACE AREA (M2)
160 ! H1 = HEAT OF REACTION (KJ/MOL)
170 ! H = HEAT TRANSFER COEFFICIENT (KJ/HR M2 K)
180 ! R = REACTION RATE MOL/M2HR
190 ! T = CATALYST SURFACE TEMPERATURE (K)
200 !
210 ! SET INITIAL VALUES
240 A1=.0001
250 A2=.0000000567
260 H1=164
261 T0=1023 @ I=1
270 ! READ HEAT TRANSFER COEFFICIENT
280 READ H
290 IF H=0 THEN GOTO 1000
300 PRINT "HEAT TRANSFER COEFFICIENT IS ":H
301 PRINT "ITERATION    TEMPERATURE(K)"
310 ! CALCULATE REACTION RATE
320 R=4490000*EXP(-(15600/T0))
330 ! HEAT BALANCE
340 T=T0-R*A1*H1/H/A2
351 I=I+1
360 IF ABS(T-T0)>.1 THEN T0=T @ GOTO 320
369 PRINT USING "3X,DDD.12X,DDDD.D" : I,T
370 PRINT "CONVERGED" @ PRINT @ PRINT
380 GOTO 261
1000 END
2000 ! HEAT TRANSFER COEFFS
2010 ! KJ/M2 HR K
2020 DATA 102.2,204.5,409,1022,2045,0

```

HEAT TRANSFER COEFFICIENT IS 102.2
ITERATION TEMPERATURE(K)
245 670.4
CONVERGED

HEAT TRANSFER COEFFICIENT IS 204.5
ITERATION TEMPERATURE(K)
334 690.9
CONVERGED

HEAT TRANSFER COEFFICIENT IS 409
ITERATION TEMPERATURE(K)
359 712.8
CONVERGED

HEAT TRANSFER COEFFICIENT IS 1022
ITERATION TEMPERATURE(K)
392 744.0
CONVERGED

HEAT TRANSFER COEFFICIENT IS 2045
ITERATION TEMPERATURE(K)
419 769.5
CONVERGED

HEAT AND MASS TRANSFER

For a nonisothermal catalyst pellet, the problem becomes much more complicated. The solutions to the following equations include both nonlinear temperature and concentration profiles. For a single catalyst pellet, the development of simultaneous mass and energy balances is summarized in Weisz and Hicks (1962), Carberry (1961, 1975), and particularly Finlayson (1980). Conservation of mass and energy for spherical system gives

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dC}{dr} \right) = \phi^2 R(C, T) \quad (1)$$

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dT}{dr} \right) = -\beta \phi^2 R(C, T) \quad (2)$$

where r = dimensionless radius, r'/R
 T = dimensionless temperature, T'/T_0
 C = dimensionless concentration, C'/C_0
 ϕ = Thiele modulus, $k_0 R^2 C_0^{n-1} / D_e$
 β = dimensionless heat of reaction, $-H_r C_0 D_e / k_e T_0$
 D_e = effective diffusivity
 k_e = effective thermal conductivity
 $R(C, T)$ = dimensionless reaction rate.

The boundary conditions are

$$\text{at } r = 0 \quad \frac{dC}{dr} = \frac{dT}{dr} = 0$$

$$\text{at } r = 1 \quad \frac{-dC}{dr} = Bi_m (C-1)$$

$$\frac{-dT}{dr} = Bi (T-1)$$

where Bi_m = Biot number for mass transfer, kR/D_e

Bi = Biot number for heat transfer, hR/K_e .

These two equations can be combined to yield

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dC}{dr} \right) = \phi^2 f[C(r), C(1), \beta, \gamma] \quad (3)$$

with the following boundary conditions: $\frac{dC}{dr} = 0$ at $r=0$

$$\frac{-dC}{dr} = B_{im}[C(1)-1] \text{ at } r=1$$

where $f[C(r), C(1), \beta, \gamma] = c^n(r) \exp \left(\gamma - \frac{\gamma}{T(r)} \right)$

$$T(r) = -\beta C(r) + 1 + \beta C(1) + \beta \delta [1 - C(1)]$$

γ = dimensionless activation energy, E/RT

$$\delta = B_{im}/Bi$$

n = reaction order (1 for this case).

Applying the method of orthogonal co-location (Finlayson 1980) to Equation (3) gives

$$\sum_{i=1}^{n+1} B(ji)C_i = \phi^2 f[C_j, C(n+1), \beta, \delta] \quad (4)$$

$$-\sum_{i=1}^{n+1} A(n+1,i)C_i = B_{im} [C(n+1) - 1] \quad (5)$$

The A and B matrices are the first derivative and Laplacian coefficients, respectively, and can be calculated by routines given in Finlayson (1980). This now gives a series of simultaneous nonlinear equations which are soluble by Newton methods.

A computer program to solve these equations was written by Finlayson (1980) and modified here to calculate temperature profiles along with concentration profiles. This program was used to relate catalyst temperatures to reactor types and heat transfer considerations.

COMPUTER PROGRAM - OCRXN

The computer program OCRXN (Finlayson 1980) solves the following equations:

$$\text{Del}^2 \text{Del } C = \text{Phi}^2 R(C)$$

$$-DC/DR = B_{im} [C - 1] \text{ at } R = 1$$

by orthogonal co-location. A complete listing follows. Modifications were made to the original program to calculate temperatures within the catalyst particles. Additional comments were also added to make the program easier to understand.

N = the number of interior co-location points (6 max)

AS = the geometry factor

= 1 for the planar

= 2 for cylindrical

= 3 for spherical

PHI = Thiele Modulus

B_{im} = Biot number for mass transfer

Bi = Biot number for heat transfer

CGUESS = Initial guess for concentrations, a constant

Beta = Dimensionless heat of reaction

Gamma = Dimensionless activation energy.

Input variables for the biomass gas reforming case are calculated and tabulated below. Sample output from the program is also included.

$$\text{For CH}_4 \quad C_0 = 0.10 \left(\frac{\text{mole}}{22.4\text{L}} \right) \left(\frac{\text{L}}{1000 \text{ cm}^3} \right) \left(\frac{100^3 \text{ cm}^3}{\text{m}^3} \right)$$

$$C_0 = 4.47 \text{ g-mole m}^{-3}$$

For fixed bed catalysts $R = 0.5 \text{ cm}$

For fluid bed catalysts $R = 0.0425 \text{ cm}$

$N = 6$ interior co-location points

$AS = 3$, spherical catalyst pellet

$$PHI = \text{Thiele Modulus} \sqrt{k_o R^2 C_o^{n-1} / D_e}$$

$$k_o C_o^{n-1} = 1.1 \times 10^9 (6.82 \times 10^6 \text{ m}^2/\text{m}^3) \exp (-15.6 \times 10^3/T)$$

$$D_e = 0.036 \text{ m}^2\text{-s}^{-1}$$

$$PHI = 94.7 \text{ (fluid bed), } 1100 \text{ (fixed bed)}$$

$$\text{Beta} = \beta = \frac{\Delta H_r C_o D_e}{k_e T_o}$$

$$\beta = \frac{-164 \frac{\text{KJ}}{\text{g-mole}} \frac{\text{cal}}{4.184 \text{ KJ}} 4.5 \frac{\text{gmol}}{\text{m}^3} 0.036 \frac{\text{m}^2}{\text{h}}}{0.21 \frac{\text{kcal}}{\text{m}^2 \cdot \text{h} \cdot \text{K}} 1023 \text{K}}$$

$$\beta = -0.029$$

$$\text{GAMMA} = \gamma = E/RT$$

$$= \frac{130 \frac{\text{KJ}}{\text{gmol}}}{0.08314 \frac{\text{KJ}}{\text{g-mole K}} (1023 \text{K})}$$

$$\gamma = 1.53$$

Bi and Bi_m vary between 0-100 and 0-300, respectively, based on information presented in Finlayson (1980) and Zenz and Othmer (1960).

For a given Reynolds number, both Bi and Bi_m can be calculated from Figure D.1. Table D.1 shows pertinent values used during the calculations with Reynolds numbers between 1 and 10^4 for both fixed- and fluid-bed reactors. The procedure is as follows:

1. Set reynolds number $\frac{DG}{\mu}$.
2. Obtain Nusselt number (hD/K) from Figure D.1.
3. Calculate heat transfer coefficient, h .
4. Calculate heat transfer Biot number.
5. Obtain Colburn j factor for mass transfer, j from Figure D.1.
6. Calculate mass velocity, G based on Reynolds number.
7. Calculate the mass transfer coefficient, k_G from the following equation

$$k_G = \frac{j_d}{MW} \frac{G}{P} \left(\frac{\mu_f}{\rho_f D} \right)^{-2/3}$$

8. Calculate the mass transfer Biot number.

FIGURE D.1. Chu's Generalized Correlation of Mass Transfer
(adapted from Zenz and Othmer 1960, p. 473)

TABLE D.1. Heat and Mass Transfer Biot Numbers

	$\frac{D_p G}{\mu}$	$\frac{h D_p}{k_f}$	$(\text{kcal m}^{-2} \text{h}^{-1} \text{K}^{-1})$	Biot-Heat h/k_e	j_d	$(\text{kgm}^{-2} \text{h}^{-1})$	$\text{kg mol}^{-1} \text{h}^{-1} \text{m}^{-2} \text{atm}$	Biot-Mass $k_G r/D_{epm}$
Fluid Bed $D_p=0.00042 \text{ m}$	1	0.02	0.706	0.001	10	0.049	0.065	0.645
	10	0.3	10.7	0.022	1	0.49	0.065	0.645
	100	5	178.6	0.361	0.2	4.9	0.130	1.29
Fixed Bed $D_p=0.01 \text{ m}$	100	20	60	1.43	0.2	0.49	0.011	1.29
	1000	100	300	7.14	0.08	4.0	0.042	4.9
	10000	300	900	21.4	0.03	40.0	0.159	18.5

```

CCC
CCC PROGRAM OCRXN.F77
CCC
    DIMENSION A(7,7), B(7,7), Q(7,7), XC(7), W(7), AA(49), D(7), TH(7)
    DIMENSION TEMP(7)
    COMMON /REAC/ PAR(8)
    INTEGER DONE

CCC
CCC THIS PROGRAM USES ORTHOGONAL COLLOCATION TO SOLVE
CCC
CCC     DEL**2 C = PHI*PHI*R(C)
CCC
CCC     -DC/DR = BIM*(C - 1 ) AT R = 1
CCC
CCC VARIABLES
CCC
CCC     N = NUMBER OF INTERIOR COLLOCATION POINTS
CCC     AS = GEOMETRY FACTOR
CCC         = 1 PLANAR
CCC         = 2 CYLINDRICAL
CCC         = 3 SPHERICAL
CCC     PHI = THIELE MODULUS
CCC     BIM = BIOT NUMBER FOR MASS TRANSFER
CCC     BI = BIOT NUMBER FOR HEAT TRANSFER
CCC     CGUESS = INITIAL GUESS FOR C(R), A CONSTANT
CCC     PAR(1) = BETA (DIMENSIONLESS HEAT OF REACTION) EQ 4-124
CCC     PAR(2) = GAMMA (DIMENSIONLESS ACTIVATION ENERGY) EQ 4-125
CCC
    5 WRITE (1,10)
    10 FORMAT (' ENTER N, AS, PHI,BIM,BI,CGUESS ')
    READ (1,*) N,AS,PHI,BIM,BI,CGUESS
    WRITE (1,15)
    15 FORMAT (' ENTER FOUR REACTION RATE PARAMETERS ')
    READ (1,*) PAR(1),PAR(2),PAR(3),PAR(4)
    N1 = N+1
    N2 = N*N
    DEL = BIM/BI
    DELTA = PHI*PHI
CCC SET INITIAL CONDITION
    DO 20 I=1,N1
    20 TH(I) = CGUESS
CCC CALCULATE COLLOCATION MATRICES
    CALL COLL (A,B,Q,XC,W,7,N,AS)
CCC BEGIN ITERATION
    DO 50 ITER=1,20
CCC SET THE SYSTEM MATRICES
    DO 25 I=1,N2
    25 AA(I) = 0.
    DO 35 J=1,N
        CALL RXN (TH(J),RATE,DR)
        D(J) = DELTA*(RATE-DR*TH(J))
        D(J) = D(J)-BIM*B(J,N1)/(A(N1,N1)+BIM)
        DO 30 I=1,N
            KN = N*(I-1)+J
            AA(KN) = B(J,I)-B(J,N1)*A(V1,I)/(A(N1,N1)+BIM)
            IF (I.EQ.J) AA(KN) = AA(KN)-DELTA*DR
    30 CONTINUE

```


CCC

```

35  CONTINUE
CCC  DO THE LU DECOMPOSITION ON AA
    CALL INVERT (N,1,AA,D,1)
CCC  SOLVE FOR THE CONCENTRATIONS
    CALL INVSU (N,1,AA,D,1)
CCC  FIND MAXIMUM CHANGE IN SOLUTION
    ER = 0.
    DO 40 I=1,N
        ERR = ABS(TH(I)-D(I))
        TH(I) = D(I)
        IF (ERR.GT.ER) ER = ERR
40  CONTINUE
    WRITE (1,45) ITER,ER
45  FORMAT ('*ITERATION*',I3,'* ERROR IS ',E15.4)
    IF (ER.LT.1.E-6) GO TO 55
50  CONTINUE
    WRITE(1,54)
54  FORMAT('*** 20 ITERATIONS -- DID NOT CONVERGE ***')
CCC  CALCULATE THE EFFECTIVENESS FACTOR
CCC  ETA1 USES EQ. 4-228
55  SUM = 0.
    DO 60 I=1,N
60  SUM = SUM+A(N1,I)*D(I)
    D(N1) = (B1N-SUM)/(A(N1,N1)+B1N)
    SUM = 0.
    SUM1 = 0.
    DO 65 I=1,N1
        CALL RXN (D(I),RATE,DR)
        SUM1 = SUM1+W(I)
65  SUM = SUM+W(I)*RATE
    ETA1 = SUM/SUM1
    WRITE (1,70) ETA1
70  FORMAT ('* EFF. FACTOR ',F20.15)
    WRITE (1,75)
75  FORMAT ('* DO YOU WANT TO SEE THE SOLUTION */* IF SO ENTER 1, OTH
SERVISE 0*)
    READ (1,*) KON
    IF (KON.EQ.0) GO TO 5
    DO 79 I=1,N1
        TEMP(I) = -PAR(1)*D(I)+1+PAR(1)*D(N1)+PAR(1)*DEL*(1-D(N1))
79  CONTINUE
    WRITE (1,80) (D(I),I=1,N1)
80  FORMAT ('*CONCENTRATIONS*/,7F10.6,/)
    WRITE (1,81) (TEMP(I),I=1,N1)
81  FORMAT ('*TEMPERATURES*/,7F10.6,/)
    WRITE (1,85)
85  FORMAT ('*MORE CASES?*/,/* IF YES ENTER 1, OTHERWISE ENTER 2*)
    READ (1,*) DONE
    IF (DONE.EQ.1) GOTO 5
    STOP
    END
    SUBROUTINE RXN(C,R,DR)
CCC
CCC  THIS SUBROUTINE CALCULATES THE REACTION KINETIC EXPRESSIONS R AND
CCC  DR/DC GIVEN THE CONCENTRATIONS. ALL OF THESE ARE DIMENSIONLESS
CCC  PARAMETERS AND RATES.
CCC

```

```

CCC

CCC      INPUTS:
CCC      C = VECTOR OF CONCENTRATIONS
CCC      PAR(1) = BETA (DIMENSIONLESS HEAT OF REACTION--EQ 4-124)
CCC      PAR(1) = GAMMA (DIMENSIONLESS ACTIVATION ENERGY--EQ 4-125)
CCC
CCC      OUTPUT:
CCC      R = DIMENSIONLESS REACTION RATE
CCC      DR/DC = DERIVATIVE OF R
CCC
      COMMON /REAC/ PAR(8)
      T = 1./PAR(1)*(1.-C)
      E = EXP(PAR(2)*(1.-1./T))
      R = C*E
      DR = E*(1.-PAR(1)*C*PAR(2)/T**2)
      RETURN
      END
      SUBROUTINE INVR(A,N,NI)

CCC      THIS SUBROUTINE CALLS DECOMP ONCE AND SOLVE SEVERAL TIMES
CCC      TO CONSTRUCT THE INVERSE. IT SOLVES AX=I WHERE EACH MATRIX
CCC      IS N BY N.
CCC
CCC      INPUT
CCC      A(N,N) - AN N BY N ARRAY, STORED IN MATRIX WITH DIMENSIONS
CCC      NI BY NI
CCC      N - THE SIZE OF THE MATRIX TO BE INVERTED, <=20
CCC      NI - THE SIZE OF THE DIMENSION OF A
CCC      OUTPUT
CCC      A(N,N) - ON OUTPUT THIS IS THE INVERSE OF THE ORIGINAL A
CCC      THE ORIGINAL A IS DESTROYED
CCC
      DIMENSION A(NI,NI), B(20), C(400)
CCC      PACK A DENSELY INTO C
      DO 5 J=1,N
        IND = N*(J-1)
        DO 5 I=1,N
          C(IND+I) = A(I,J)
5      CONTINUE
CCC      PERFORM AN LU DECOMPOSITION ON C
      CALL INVERT (N,1,C,B,1)
CCC      SOLVE AX=I
      DO 20 J=1,N
        DO 10 I=1,N
          B(I) = 0.
          B(J) = 1.
          CALL INVSU (N,1,C,B,1)
CCC      PUT B INTO INVERSE A
          DO 15 I=1,N
            A(I,J) = B(I)
15      CONTINUE
20      CONTINUE
      RETURN
      END
      SUBROUTINE INVERT(N,NL,A,B,ITYPE)
      DIMENSION A(1000,3), B(N), A1(1000), B1(1000), C1(1000)
CCC
CCC      THIS SUBROUTINE CALLS DECOMP, LUDECOM, OR INVTRI TO PERFORM LOWER

```

CCC

```

CCC  UPPER DECOMPOSITION DEPENDING ON WHETHER THE MATRIX A IS
CCC      ITYPE      A
CCC      1          DENSE
CCC      2      BLOCK TRIDIAGONAL
CCC      3          TRIDIAGONAL
CCC  IF A IS DENSE THE MATRIX IS STORED AS A(N,N)
CCC  IF A IS BLOCK DIAGONAL THE MATRIX IS STORED AS A(N,N,NE)
CCC  IF A IS TRIDIAGONAL THE ELEMENTS A,B,C ARE STORED AS A(N,1) = A(N),
CCC      A(N,2) = B(N), A(N,3) = C(N)
CCC  N IS LIMITED TO 201 WITHOUT CHANGING DIMENSION STATEMENT FOR A(N),
CCC      B(N), C(N)
CCC  THE MATRICES ARE DIMENSIONED AS A(N,N), A(N,N,NE) OR A(N,3)
CCC
      GO TO (5,10,15), ITYPE
      5 CALL DECOMP (N,A)
      RETURN
      10 NP = (N-1)/NE+1
      C   CALL LUDECOM (NP,NE,A)
      CALL LUDCOM (NP,NE,A)
      RETURN
      15 DO 20 K=1,N
      A1(K) = A(K,1)
      B1(K) = A(K,2)
      C1(K) = A(K,3)
      20 CONTINUE
      CALL INVTRI (N,A1,B1,C1)
      DO 25 K=1,N
      A(K,1) = A1(K)
      A(K,2) = B1(K)
      A(K,3) = C1(K)
      25 CONTINUE
      RETURN
      END
      SUBROUTINE INVSU(N,NE,A,B,ITYPE)
CCC
CCC  THIS SUBROUTINE DOES THE FORWARD AND BACKWARD SWEEP TO SOLVE AX=B
CCC  WITH THE SOLUTION X STORED IN B ON RETURN. A MUST BE PACKED (WITH
CCC  "INVR" OR EQUIVALENT) AND LU DECOMPOSED (AS IN INVERT) BEFORE THIS
CCC  SUBROUTINE CAN BE CALLED.
CCC
CCC  INPUTS:
CCC      N = ARRAY DIMENSION
CCC      NE = ARRAY DIMENSION IN CALLING PROGRAM
CCC      A = PACKED, LU TRIANGULAR MATRIX OF A IN AX=B
CCC      B = MATRIX OF RHS COEFFICIENTS
CCC
CCC  OUTPUT:
CCC      B = SOLUTION MATRIX X ON RETURN
CCC
      GO TO (30,35,40), ITYPE
      30 CALL SOLVE (N,A,B)
      RETURN
      35 CALL FAS (NP,NE,N,A,B)
      RETURN
      40 CALL SWEEP (N,A1,B1,C1,B)
      RETURN
      END

```

CCC

```

SUBROUTINE SING(I)
CCC
CCC THIS SUBROUTINE IS AN ERROR ROUTINE FOR A SINGULAR MATRIX
CCC
    GO TO (5,15), I
    5 WRITE (1,10)
    10 FORMAT (////, ' MATRIX WITH ZERO ROW IN DECOMPOSE '////)
    RETURN
    15 WRITE (1,20)
    20 FORMAT (////, ' SINGULAR MATRIX IN DECOMPOSE. ZERO DIVIDE IN SOLVE
    S      . '////)
    RETURN
    END
SUBROUTINE DECOMP(N,A)
CCC
CCC THIS SUBROUTINE PERFORMS THE LOWER-UPPER DECOMPOSITION ON A
CCC AND RETURNS THE TRIANGULAR LU VERSION OF A STORED IN "A"
CCC
CCC INPUTS:
CCC     N = ARRAY DIMENSION
CCC     A = MATRIX TO BE DECOMPOSED
CCC
CCC OUTPUT:
CCC     A = TRIANGULAR LU MATRIX OF A
CCC
    DIMENSION A(N,N)
    COMMON /DENSE/ IPS(201),SC(201)
CCC PAGE 68, FORSYTH AND MOLER
CCC INITIALIZE IPS, A AND SCALES
    IF (N.EQ.1) RETURN
    DO 25 I=1,N
        IPS(I) = I
        ROWNRM = 0.0
        DO 10 J=1,N
            IF (ROWNRM-ABS(A(I,J))) 5,10,10
            5 ROWNRM = ABS(A(I,J))
        10 CONTINUE
        IF (ROWNRM) 15,20,15
        15 SC(I) = 1./ROWNRM
        GO TO 25
C
    20 CALL SING (1)
        SC(I) = 0.
    25 CONTINUE
CCC GAUSSIAN ELIMINATION WITH PARTIAL PIVOTING
    NM1 = N-1
    DO 65 K=1,NM1
        BIG = 0.
        DO 35 I=K,N
            IP = IPS(I)
            SIZE = ABS(A(IP,K)*SC(IP))
            IF (SIZE-BIG) 35,35,35
        30 BIG = SIZE
            IDXPIV = I
        35 CONTINUE
        IF (BIG) 45,40,45
        40 CALL SING (2)

```

CCC

```

        GO TO 65
C
45  IF (IDXPIV-K) 50,55,50
50  J = IPS(K)
    IPS(K) = IPS(IDXPIV)
    IPS(IDXPIV) = J
55  KP = IPS(K)
    PIVOT = A(KP,K)
    KP1 = K+1
    DO 60 I=KP1,N
        IP = IPS(I)
        EM = -A(IP,K)/PIVOT
        A(IP,K) = -EM
        DO 60 J=KP1,N
            A(IP,J) = A(IP,J)+EM*A(KP,J)
CCC INNER LOOP
60  CONTINUE
65  CONTINUE
    KP = IPS(N)
    IF (A(KP,N)) 75,70,75
70  CALL SING (2)
75  CONTINUE
    RETURN
    END
    SUBROUTINE SOLVE(N,A,B)
CCC
CCC  THIS SUBROUTINE PERFORMS THE FORWARD SWEEP AND BACK SUBSTITUTION
CCC  TO SOLVE FOR X IN AX=B WHERE A IS THE TRIANGULAR LU DECOMPOSITION
CCC  OF A (DENSE CASE). THE SOLUTION X RETURNS AS B.
CCC
CCC  INPUTS:
CCC      A = TRIANGULAR LU DECOMPOSITION OF A
CCC      B = VECTOR OF RIGHT HAND SIDE COEFFICIENTS
CCC
CCC  OUTPUT:
CCC      B = SOLUTION VECTOR X
CCC
    DIMENSION A(N,N), B(N)
    COMMON /DENSE/ IPS(201),SC(201)
CCC PAGE 69, FORSYTH AND MOLER
CCC FORWARD SWEEP DENSE MATRIX
    IF (N.GT.1) GO TO 5
    B(1) = B(1)/A(1,1)
    RETURN
5  CONTINUE
    NP1 = N+1
    IP = IPS(1)
    SC(1) = B(IP)
    DO 15 I=2,N
        IP = IPS(I)
        IM1 = I-1
        SUM = 0.
        DO 10 J=1,IM1
            SUM = SUM+A(IP,J)*SC(J)
10    CONTINUE
        SC(I) = B(IP)-SUM
15  CONTINUE
```

CCC

```
CCC BACK SUBSTITUTION
    IP = IPS(N)
    SC(N) = SC(N)/A(IP,N)
    DO 25 IBACK=2,N
        I = NP1-IBACK
        IP = IPS(I)
        IP1 = I+1
        SUM = 0.
        DO 20 J=IP1,N
            SUM = SUM+A(IP,J)*SC(J)
20    CONTINUE
        SC(I) = (SC(I)-SUM)/A(IP,I)
25 CONTINUE
    DO 30 I=1,N
30 B(I) = SC(I)
    RETURN
    END
    SUBROUTINE FAS(NP,NE,NT,A,B)
```

```
CCC
CCC THIS SUBROUTINE PERFORMS THE FORWARD SWEEP AND BACK SUBSTITUTION
CCC TO SOLVE AX=B WHERE A IS THE TRIANGULAR LU DECOMPOSITION OF A
CCC (BLOCK DIAGONAL CASE). THE SOLUTION X RETURNS AS B.
CCC THE IMPORTANT INPUT VARIABLES ARE THE SAME AS FOR "SOLVE".
CCC
```

```
    DIMENSION A(NP,NP,NE), B(NT)
CCC FORWARD SWEEP BLOCK DIAGONAL MATRIX
    NP1 = NP
    DO 10 L=1,NE
        DO 10 I=2,NP1
            I2 = (L-1)*(NP-1)+I
            S = 0.
            I1 = I-1
            DO 5 J=1,I1
                J2 = I2-I+J
                S = S+A(I,J,L)*B(J2)
5            CONTINUE
            B(I2) = B(I2)-S
10 CONTINUE
CCC BACK SUBSTITUTION
    DO 25 L1=1,NE
        L = NE-L1+1
        IF (L.NE.NE) GO TO 15
        B(NT) = B(NT)/A(NP,NP,NE)
15    N1 = NP-1
        DO 25 K=1,N1
            I = N1+1-K
            I2 = (L-1)*(NP-1)+I
            M = I+1
            N2 = N1+1
            S = 0.
            DO 20 J=M,N2
                J2 = (L-1)*(NP-1)+J
20            S = S+A(I,J,L)*B(J2)
            B(I2) = (B(I2)-S)/A(I,I,L)
25 CONTINUE
    RETURN
    END
```

CCC

SUBROUTINE LUDCOM(NP,NE,A)

CCC

CCC THIS SUBROUTINE PERFORMS THE LOWER-UPPER DECOMPOSITION OF A

CCC FOR THE BLOCK DIAGONAL MATRIX CASE. A(LU) RETURNS AS A.

CCC THE MAIN VARIABLES ARE THE SAME AS FOR "DECOMP".

CCC

DIMENSION A(NP,NP,NE)

N1 = NP-1

DO 10 L=1,NE

DO 5 K=1,N1

K1 = K+1

DO 5 I=K1,NP

S = A(I,K,L)/A(K,K,L)

A(I,K,L) = S

DO 5 J=K1,NP

A(I,J,L) = A(I,J,L)-S*A(K,J,L)

5 CONTINUE

IF (L.EQ.NE) RETURN

A(1,1,L+1) = A(NP,NP,L)

10 CONTINUE

END

SUBROUTINE INVTRI(N,A,B,C)

CCC

CCC THIS SUBROUTINE PERFORMS THE LU DECOMPOSITION OF A FOR THE TRIDIAGONAL

CCC MATRIX CASE. A(LU) RETURNS AS A. VARIABLES ARE THE SAME AS FOR

CCC THE SUBROUTINE "DECOMP".

CCC

DIMENSION A(N), B(N), C(N)

CCC SOLVES $A(I-1) \cdot T(I-1) + B(I) \cdot T(I) + C(I+1) \cdot T(I+1) = D(I)$

DO 5 L=2,N

S = A(L)/B(L-1)

B(L) = B(L)-S*C(L-1)

5 A(L) = S

RETURN

END

SUBROUTINE SWEEP(N,A,B,C,D)

CCC

CCC THIS SUBROUTINE PERFORMS THE FORWARD SWEEP AND BACK SUBSTITUTION TO

CCC SOLVE FOR X IN $AX=B$ WHERE A IS THE TRIANGULAR LU DECOMPOSITION OF A

CCC FOR THE TRIDIAGONAL CASE. THE SOLUTION X RETURNS AS B. VARIABLES

CCC ARE THE SAME AS FOR "SOLVE"

CCC

DIMENSION A(N), B(N), C(N), D(N)

CCC

FORWARD SWEEP

DO 5 L=2,N

5 D(L) = D(L)-A(L)*D(L-1)

CCC BACK SUBSTITUTION

D(N) = D(N)/B(N)

DO 10 L=2,N

K = N-L+1

10 D(K) = (D(K)-C(K)*D(K+1))/B(K)

RETURN

END

SUBROUTINE COLL(A,B,Q,X,W,N,AA)

DIMENSION A(ND,ND), B(ND,ND), Q(ND,ND), X(ND), W(ND)

DIMENSION QINV(7,7), Z(7), C(7,7), D(7,7)

CCC

CCC

CCC THIS SUBROUTINE COMPUTES THE MATRICES FOR ORTHOGONAL
CCC COLLOCATION USING SYMMETRIC POLYNOMIALS. TABLE 4-5, 4-6

CCC INPUT VARIABLES

CCC N = NUMBER OF INTERIOR COLLOCATION POINTS
CCC ND = ARRAY DIMENSION OF MATRICES IN CALLING PROGRAM
CCC AA = GEOMETRY FACTOR
CCC = 1 PLANAR
CCC = 2 CYLINDRICAL
CCC = 3 SPHERICAL

CCC OUTPUT VARIABLES

CCC A = MATRIX FOR FIRST DERIVATIVE, EQ. 4-205
CCC B = MATRIX FOR LAPLACIAN, EQ. 4-205
CCC Q = MATRIX FOR Q INVERSE, EQ. 4-203
CCC X = VECTOR OF COLLOCATION POINTS, TABLE 4-5
CCC W = VECTOR OF WEIGHTS, EQ. 4-207
CCC

DIMENSION X1(6,6), X2(6,6), X3(6,6)

DATA X1/.4472135955,0.000000000,0.000000000,0.000000000,0.000000000,0.000000000,
\$000000000,0.000000000,0.000000000,0.000000000,0.3399810436,.8611363114,0.
\$000000000,0.000000000,0.000000000,0.000000000,0.000000000,.2386191861,
\$6612093865,.9324695142,0.000000000,0.000000000,0.000000000,0.000000000,
\$1834346425,.5255324099,.7965564774,.9602898565,0.000000000,0.000000000,
\$000000000,.1488743390,.4333953941,.6794095663,.8650633667,
\$9739065285,0.000000000,.1252334085,.3678314990,.5873179543,
\$7699026742,.9041172564,.9815606342/
DATA X2/.5773502692,0.000000000,0.000000000,0.000000000,0.000000000,0.000000000,
\$000000000,0.000000000,0.000000000,0.000000000,.4597008434,.8880738340,0.
\$000000000,0.000000000,0.000000000,0.000000000,0.000000000,.3357106870,
\$7071067812,.9419651451,0.000000000,0.000000000,0.000000000,0.000000000,
\$2634992300,.5744645143,.8185294874,.9646596062,0.000000000,0.000000000,
\$000000000,.2165873427,.4803804169,.7071067812,.8770602346,
\$9762632447,0.000000000,.1837532119,.4115766111,.6170011402,
\$7869622564,.9113751660,.9829724091/
DATA X3/.6546536707,0.000000000,0.000000000,0.000000000,0.000000000,0.000000000,
\$000000000,0.000000000,0.000000000,0.000000000,.5384693101,.9061798454,0.
\$000000000,0.000000000,0.000000000,0.000000000,0.000000000,.4058451514,
\$7415311856,.9491079123,0.000000000,0.000000000,0.000000000,0.000000000,
\$3242534234,.6133714327,.8360311073,.9681602395,0.000000000,0.000000000,
\$000000000,.2695431560,.5190961292,.7301520056,.8870625498,
\$9782286581,0.000000000,.2304583160,.4484927510,.6423493354,
\$8015780907,.9175983992,.9841830547/
WRITE (1,5)

5 FORMAT (' THE COLLOCATION POINTS ARE '/')

N1 = N+1

DO 25 LL=1,N

IA = AA+0.001

GO TO (10,15,20), IA

10 X(LL) = X1(LL,N)

GO TO 25

C

15 X(LL) = X2(LL,N)

GO TO 25

C

20 X(LL) = X3(LL,N)

25 CONTINUE

CCC

```
      X(N1) = 1.0
      DO 30 I=1,N1
        AI = I
        Z(I) = 1./((2.*AI+AA-2.))
30    CONTINUE
      DO 35 I=1,N1
        Q(I,1) = 1.
        QINV(I,1) = 1.
        DO 35 J=2,N1
          Q(I,J) = X(I)**(2+J-2)
35    QINV(I,J) = Q(I,J)
      DO 40 J=1,N1
        CA = 2.*J-2.
        DA = (2.*J-2.)*(2.*J+AA-4.)
        DO 40 I=1,N1
          C(I,J) = CA*X(I)**(2+J-3)
          D(I,J) = DA*X(I)**(2+J-4)
40    CONTINUE
      CALL INVR (QINV,N1,7)
      DO 50 I=1,N1
        W(I) = 0.0
        DO 50 J=1,N1
          A(I,J) = B(I,J) = 0.0
C      A(I,J) = 0.0
      B(I,J) = 0.0
        DO 45 K=1,N1
          A(I,J) = A(I,J)+C(I,K)*QINV(K,J)
          B(I,J) = B(I,J)+D(I,K)*QINV(K,J)
45      CONTINUE
        Q(I,J) = QINV(I,J)
        W(I) = W(I)+Z(J)*QINV(J,I)
50    CONTINUE
      WRITE (1,55) (X(I),I=1,N1)
55    FORMAT (7E15.5//)
      RETURN
      END
```

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