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Catalysis in Biomass Gasification

E. G. Baker
L. K. Mudge

June 1984

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

Pacific Northwest Laboratory
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by Battelle Memorial Institute

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Pacific Northwest Laboratory
Richland, Washington 99352

SUMMARY

The Pacific Northwest Laboratory is conducting studies, sponsored by the Biomass Energy Technology Division of the U.S. Department of Energy, on the use of catalysts in biomass gasification. The overall objective of these studies is to evaluate the technical and economic feasibility of producing specific gas products by catalytic gasification of biomass. Catalyst performance is a key factor in the feasibility of catalytic wood gasification processes. This report presents the results of studies designed to gain a fundamental understanding of catalytic mechanisms and of the causes of deactivation, and discusses the state-of-the-art of related catalytic processes.

Experiments with primary and secondary catalysts were conducted in a 5-cm-diameter, continuous-wood-feed, fixed-catalyst-bed reactor. The primary catalysts used in the experiments were alkali carbonates mixed with the biomass feed; the secondary catalysts included nickel or other transition metals on supports such as alumina, silica, or silica-alumina. The primary catalysts were found to influence wood pyrolysis as well as the char/steam reaction. Secondary catalysts were used in a fixed-bed configuration to direct gas phase reactions. Results of the performance of these catalysts for wood gasification in the laboratory system are presented. Secondary catalysts were found to be highly effective for conversion of biomass to specific gas products: synthesis gases and methane-rich gas. With an active catalyst, equilibrium gas compositions are obtained, and all liquid pyrolysis products are converted to gases.

The major cause of catalyst deactivation was carbon deposition, or coking. Loss of surface area by sintering was also an important factor. Catalyst deactivation by sulfur poisoning was observed when bagasse was used as the feedstock for catalytic gasification. Mechanisms of catalyst activity and deactivation are therefore discussed. Model compounds (methane, ethylene, and phenol) were used to determine coking behavior of catalysts. Carbon deposition is more prevalent with ethylene and phenol than with methane. Catalyst formulations that are resistant to carbon deposition are presented.

Several types of carbon deposition on nickel catalysts are known to occur in steam-reforming of hydrocarbons. The mechanisms for formation of polymer, whisker, and pyrolytic carbons are discussed.

These studies have revealed promising approaches to the development of effective catalyst systems for gasification of biomass. The influence of process variables, such as char residence time, gas velocity, and biomass particle size, has been shown to be important to the catalytic process design.

CONTENTS

SUMMARY.....	iii
INTRODUCTION.....	1
BACKGROUND.....	1
EXPERIMENTAL FACILITIES.....	3
CONCLUSIONS AND RECOMMENDATIONS.....	9
PRIMARY CATALYSTS.....	11
CARBON/STEAM REACTION.....	12
Effect of Catalyst Type.....	14
Effect of Catalyst Loading.....	14
Effect of Catalyst Contacting Method.....	16
EFFECT ON PYROLYSIS AND OTHER REACTIONS.....	16
Tar and Light Hydrocarbon Yield.....	16
Water-Gas Shift Reaction.....	18
CATALYST RECOVERY.....	20
SECONDARY CATALYSTS.....	23
PRODUCTION OF SPECIFIC GASES.....	23
CATALYST LIFETIME AND DEACTIVATION.....	30
Catalyst Deactivation Studies.....	31
Attrition.....	39
MECHANISMS OF CATALYTIC GASIFICATION.....	41
PRIMARY CATALYSTS.....	42
Pyrolysis.....	43
Gasification.....	44
Secondary Reactions.....	44

SECONDARY CATALYSTS.....	46
Catalytic Effects.....	46
Mechanisms of Carbon Deposition.....	47
REFERENCES.....	55
APPENDIX A - GAS-PHASE REACTOR STUDIES WITH SECONDARY CATALYSTS.....	A.1
APPENDIX B - DATA FROM FIXED-BED LABORATORY TESTS.....	B.1

FIGURES

1	Continuous-Feed Laboratory Reactor.....	5
2	Gas-Phase Reactor.....	6
3	Catalytic Effect of K_2CO_3 -Impregnated Wood as a Function of Catalyst Loading and Temperature.....	15
4	Effect of Water/Residue Ratio on Potassium Recovery.....	20
5	Steam-Reforming of Phenol and Methane.....	27
6	Effect of Metal Surface Area on Catalyst Lifetime at 550°C.....	31
7	Effect of Catalyst Age on Yield at 750°C.....	32
8	Catalyst Deactivation in PDU with Ni/Al_2O_3	35
9	Catalyst Deactivation in PDU with $NiCuMo/SiO_2-Al_2O_3$	36
10	Reaction Pathways for High-Temperature Steam Gasification of Biomass.....	42
11	SEM Micrograph of Catalyst Coked at 750°C.....	51

TABLES

1	Maximum Stoichiometric Yield of Specific Gas Products from the Reaction of Biomass with Steam.....	2
2	Rate Constants for Catalyzed and Uncatalyzed Carbon/Steam Reaction.....	12
3	Effect of K_2CO_3 at Various Temperatures.....	13
4	Effect of K_2CO_3 on Various Feed Materials.....	14
5	Comparison of K_2CO_3 and Na_2CO_3 at 3.0×10^{-3} mole alkali/g wood.....	15
6	Effect of Alkali Carbonate Catalysts on Yields.....	17
7	Effect of Potassium Carbonate on the Methane Yield in PDU Tests at $750^\circ C$	17
8	Effect of Alkali Carbonates on Methane Yield.....	18
9	Comparison of Alkali and Nickel Catalysts for the Water-Gas Shift Reaction in PDU Tests.....	18
10	Effect of Alkali on H_2/CO Ratio in Laboratory Gasification Tests in a Continuous Reactor.....	19
11	Secondary Reactions in Steam Gasification.....	24
12	Gas Compositions for Various Catalysts Tested for Synthesis Gas Production.....	25
13	Production of Specific Gases from Biomass by Steam Gasification.....	28
14	Typical Results of Various Catalytic Biomass Conversion Studies with Nickel Catalysts.....	29
15	Catalytic Gasification with Various Metal Oxide Catalysts at $700^\circ C$	30
16	Carbon Deposition on Catalysts Used for Methanol Synthesis Gas at $750^\circ C$, 1 atm.....	33
17	Effect of Steam Rate on Carbon Deposition with Phenol.....	34
18	Sulfur Analyses for Biomass Gasification.....	36
19	Effect of Sodium Carbonate on Carbon Conversion to Gas for Model Compounds Reacted with Steam at $600^\circ C$	45

20	Different Types of Carbon Formation in Steam-Reforming of Hydrocarbons.....	48
21	Effect of Feed on Carbon Deposition.....	50
22	Effect of Catalyst Support on Carbon Deposition at 750°C.....	51
A.1	Results of Fixed-Bed Gas-Phase Reactor Studies.....	A.1
B.1	Results of Primary Catalyst Tests in Continuous Laboratory Reactor.....	B.1

INTRODUCTION

In studies sponsored by the Biomass Energy Technology Division of the U.S. Department of Energy (DOE), the Pacific Northwest Laboratory (PNL)^(a) has developed a catalytic steam gasification process that converts wood to specific product gases in one step using catalysts in the gasifier. This report summarizes the catalyst development studies performed in support of the PNL catalytic steam gasification process.^(b) It also reviews state-of-the-art catalysis as it applies to gasification of biomass.

BACKGROUND

A variety of specific gas products can be produced by the reaction of biomass and steam, as shown in Table 1. Without catalysts, however, gasification of biomass produces a wide variety of gases as well as char and tar by-products. The objective of PNL's catalytic biomass gasification program is to maximize production of specific gas products through the use of catalysts.

The yield of a specific gas from biomass may be limited by kinetics, thermodynamics, or both. High temperature alone will increase the yield of gases at the expense of by-product char and tar. However, this may be expensive and often has an adverse effect on the equilibrium concentration of the desired gas, thus reducing its yield.

The catalysts used in biomass gasification serve two primary functions: 1) to increase the yield of gases at the expense of tar and char at lower temperatures than are possible without catalysts, and 2) to catalyze secondary reactions to produce the specific product desired.

(a) Operated for the DOE by Battelle Memorial Institute.

(b) The PNL catalytic gasification studies were initiated late in 1977. Mudge et al. (1981) described the laboratory studies performed in 1978, 1979, and 1980 and the atmospheric-pressure process development unit (PDU) tests of 1979 and 1980. Laboratory studies in 1981 and 1982 and the 1982 pressurized (10 atm) PDU tests are summarized by Mudge et al. (1983). Additional laboratory and PDU tests conducted in 1983 with bagasse are described by Baker and Brown (1984). The results of laboratory studies in 1983 are also included in Appendices A and B of this report.

TABLE 1. Maximum Stoichiometric Yield of Specific Gas Products from the Reaction of Biomass with Steam

	<u>Gas Composition</u>	<u>Yield, nm³/kg wood</u>	<u>Standard Heat of Reaction, kJ/kg wood</u>
Methane			
$C_4H_6O_{2.9} + 1.1 H_2O \longrightarrow 2.0 CH_4 + 2.0 CO_2$	50% CH ₄ , 50% CO ₂	0.45	-2010
Methanol or hydrocarbon synthesis gas			
$C_4H_6O_{2.9} + 2.4 H_2O \longrightarrow 5.4 H_2 + 2.7 CO + 1.3 CO_2$	57% H ₂ , 29% CO, 14% CO ₂	1.8	+3250
Hydrogen			
$C_4H_6O_{2.9} + 5.1 H_2O \longrightarrow 8.1 H_2 + 4 CO_2$	67% H ₂ , 33% CO ₂	1.8	+3280
Ammonia synthesis gas			
$C_4H_6O_{2.9} + 4.0 H_2O \longrightarrow 2.3 N_2 + 4 CO_2$	53% H ₂ , 17% N ₂ , 30% CO ₂	2.1	-120

Two types of catalysts have been studied. Primary catalysts, usually alkali carbonates, are doped on or mixed with the biomass. They are well-known catalysts for the carbon/steam reaction, and have also been found to have a significant effect on biomass pyrolysis. Secondary catalysts--nickel or other transition metals on supports such as alumina or silica-alumina--are used to catalyze secondary gas phase reactions such as steam-reforming, methanation, and the water-gas shift reaction.

Two terms that will be used throughout this report are catalyst loading and catalyst lifetime. Catalyst loading refers to the mass of primary catalyst doped on the biomass feedstock per unit mass of biomass and is given in wt% or in moles of metal ion per unit mass of biomass. Catalyst lifetime is associated with secondary catalysts, and is the mass of biomass fed to the gasifier per unit mass of catalyst in the gasifier before the catalyst shows a serious loss of activity. In all of the gasifier systems, biomass is fed to the reactor at approximately one mass unit of biomass per mass unit of catalyst per hour. Catalyst lifetime is therefore also approximately equal to the number of hours onstream before deactivation, as shown below:

$$\frac{\text{wt biomass gasified}}{\text{wt catalyst in gasifier}} \times \frac{\text{wt catalyst in gasifier} \cdot \text{hour}}{\text{wt biomass}} = \text{hours}$$

(lifetime) (feed ratio)

Laboratory tests have shown that a feed ratio of one provides sufficient residence for secondary reactions to reach equilibrium.

EXPERIMENTAL FACILITIES

The catalytic gasification studies at PNL were conducted primarily in laboratory-scale reactors operated at atmospheric pressure and at temperatures ranging from 550 to 850°C. A batch feed reactor was used in the primary catalyst studies to obtain kinetic data (Mudge, Sealock, and Weber 1979; Mudge et al. 1981). Wood samples 5 to 15 g in size were charged to the preheated reactor. The evolution of gases was measured over time to determine the rate of gasification. Two continuous-wood-feed reactors were designed to screen secondary catalysts (Mudge et al. 1981, 1983). Wood was fed at a rate of 8 to 12 g/h into the top of reactor, where it pyrolyzed. The pyrolysis products

passed over a fixed bed of catalyst (10 to 20 g). Char that accumulated on top of the catalyst bed was vacuumed out periodically.

To study primary catalysts in a continuous reactor, one of the reactors used for secondary catalyst studies was modified to provide continuous char removal, as shown in Figure 1. By adjusting the speed of the rotating grate, the rate of char removal could be controlled, allowing operation at varying residence times.

A fixed-bed gas-phase reactor (shown in Figure 2) was built to study carbon deposition on secondary catalysts using model compounds. Feed materials passed through a preheating zone and then over a bed of catalyst (5 to 10 g).

Many of the results obtained in the laboratory gasifiers have been verified in a 1-ton/day PDU. The PDU is a fluidized-bed gasifier that has been operated at 100 to 1000 kPa and 500 to 750°C. A description of the facility and operations at atmospheric pressure (Mudge et al. 1981; Mitchell et al. 1980) and at 10 atmospheres (Mudge et al. 1983; Baker et al. 1983) have been given previously.

Wood has been the primary feedstock for both laboratory and PDU tests. Other materials used in laboratory tests have included bagasse, rice straw, alfalfa, and almond hulls. Bagasse has also been tested in the PDU. Proximate and ultimate analyses, and the heating value of these materials, are given by Mudge et al. (1983) and Baker and Brown (1984).

Catalysts used in the PNL studies were of the following origins:

- commercially available (primarily Harshaw and United Catalysts)
- prepared for PNL by W. R. Grace, Inc.
- prepared at PNL, either by metal impregnation on commercial supports or by coprecipitation.

The analytical methods were basically the same for all of the gasifier systems. The product stream from the gasifier was cooled and the liquids condensed and separated. Gas flow was measured and the gas was analyzed with a Carle AGC-S gas chromatograph. Gas analysis included H₂, CO, CO₂, and hydrocarbon gases C₁ through C₄. Tars were collected and weighed and then analyzed with a Perkin-Elmer 240 elemental analyzer. A Dohrmann DC-80 carbon analyzer

FIGURE 1. Continuous-Feed Laboratory Reactor

FIGURE 2. Gas-Phase Reactor

was used to determine the water-soluble organics content of the condensate. Char was collected and weighed, and its elemental content was determined. Sulfur analyses were performed on a limited number of feedstocks and product gases.

CONCLUSIONS AND RECOMMENDATIONS

This study has examined the effects of two types of catalysts on high-temperature steam gasification of biomass. Primary catalysts (alkali carbonates) alter pyrolysis reaction pathways and catalyze various secondary reactions, significantly altering the final product distribution. Some insights have been gained on the effect of alkali carbonates on pyrolysis and secondary reactions, but a better understanding of the mechanisms involved would lead to more efficient use of these catalysts. Alkali carbonates do catalyze the reaction of biomass char with steam, but they have little net effect on char yield in the fluidized-bed PDU. The physical characteristics of the gasifier, residence time, superficial gas velocity, and the particle size of the biomass appear to have a much larger effect on overall conversion than do primary catalysts. This will be studied in more detail in the bench-scale fluidized bed.

Supported-nickel catalysts are the most effective catalysts for maximizing production of specific gases. With an active catalyst, equilibrium gas-phase compositions are achieved and all liquid products are converted to gases. At 550°C and low steam rates a methane-rich gas is produced; at 750°C and somewhat higher steam rates a high-quality synthesis gas or hydrogen-rich gas is produced.

Unfortunately, nickel catalysts are subject to deactivation. Deactivation can be caused by coking (carbon deposition), sintering, or sulfur poisoning. With wood, coking was found to be the major cause of deactivation. At 550°C carbon deposition was quite severe and all catalysts tested rapidly lost their activity. At 750°C in the laboratory gasifiers (where the catalyst is physically separated from biomass during pyrolysis) carbon deposition was less severe and several catalysts were found to maintain much of their original activity for an extended period of time. Coking in the laboratory gasifier at 750°C was the result of pyrolysis and cracking of tars and light hydrocarbons on the catalyst support. At 550°C other types of carbon deposition such as whisker formation may occur. This type of coking is more rapid and results in larger carbon accumulations. It is also possible that a different mechanism

for coking is involved in the PDU, where the catalyst is intimately mixed with biomass during pyrolysis.

As part of the bench-scale fluidized-bed testing now in progress, the mechanism by which carbon deposition occurs when the catalyst is intimately mixed with biomass during pyrolysis will be investigated at both 750°C and 550°C. An understanding of the coking mechanism will facilitate the choice of catalyst and operating conditions to reduce coking.

PRIMARY CATALYSTS

The application of alkali catalysts to coal gasification has long been known (Taylor 1921) and has been studied extensively in recent years.^(a) The primary effect of these catalysts in coal gasification is to increase the rate of the reaction of char with steam and carbon dioxide:

Alkali catalysts have also been studied in relation to biomass.^(b) However, because of the high reactivity of biomass (a large portion of the carbon can be volatilized at relatively low temperatures), the overall effect of alkali catalysts is more difficult to evaluate.

When biomass is contacted with steam at elevated temperatures, a series of complex physical changes and chemical reactions are initiated. A simplified model describes the gasification process in two stages: 1) rapid volatilization to yield gases, condensable liquids, and char; followed by 2) secondary reactions of steam with the char and pyrolysis products. Studies at PNL have shown that alkali catalysts have a significant effect on both stages of gasification. The overall effect is a combination of the two and must be evaluated as such. For example, the Exxon catalytic coal gasification (CCG) process uses K_2CO_3 to catalyze the steam/char reaction. To reach 90% carbon conversion to gas, the residence time in the CCG gasifier with the catalyst is 6 to 10 h at 700°C (Nahas 1983). In contrast, with biomass, high carbon conversion to volatiles can be achieved at 550 to 750°C without catalysts and with residence times of less than one hour. The effect of alkali catalysts on the yields of specific products from pyrolysis becomes much more important for biomass than for coal.

(a) Haynes, Gasior, and Forney 1974; Willson et al. 1974; Veraa and Bell 1978; McKee et al. 1983; Walker et al. 1983; McCoy 1983; Nahas 1983.

(b) Mudge, Sealock, and Weber 1979; Mudge et al. 1981; Sealock, Elliott, and Hallen 1982; Hawley et al. 1983; Ross and Fong 1981; Tran and Rai 1978.

CARBON/STEAM REACTION

To evaluate the effect of alkali on the carbon/steam reaction, samples of wood were gasified in a batch reactor with flowing steam. Temperatures from 550 to 850°C were studied with different catalyst systems. Carbon conversion to gas was measured as a function of time. The percentage of carbon remaining was defined as the difference between the carbon charged to the reactor and the carbon in the gas. Assuming pseudo-first-order-reaction kinetics, the carbon/steam reaction rate constant can be expressed as:

$$K = \frac{1}{t_2 - t_1} \ln \left(\frac{C_1}{C_2} \right)$$

where C_1 is the carbon remaining at time t_1 , and C_2 is the carbon remaining at time t_2 .

Following the rapid-rate pyrolysis period, a plot of the log of the remaining carbon versus time is generally linear, confirming first-order kinetics (Mudge, Sealock, and Weber 1979; Mudge et al. 1981). The slope of the line is the rate constant for the carbon/steam reaction. Table 2 shows rate constants for Douglas fir at 550°C, 650°C, and 750°C with 17 wt% K_2CO_3 . Similar results have been obtained by Sealock et al. (1981) and Sealock, Elliott, and Hallen (1982).

Table 3 presents the ratio of catalyzed to uncatalyzed rates for several different investigations. The effect is small at 550°C but increases at 650°C

TABLE 2. Rate Constants for Catalyzed and Uncatalyzed Carbon/Steam Reaction

Temperature, °C	wt% Catalyst	Rate Constant, s ⁻¹	Ratio of Catalyzed to Uncatalyzed Rate
550	17	1.4×10^{-4}	1.27
550	-	1.1×10^{-4}	
650	17	3.4×10^{-4}	3.5
650	0	9.6×10^{-5}	
750	17	9.9×10^{-4}	4.9
750	0	2.0×10^{-4}	

TABLE 3. Effect of K_2CO_3 at Various Temperatures

Temperature, °C	Ratio of Catalyzed Rate to Uncatalyzed Rate		
	Douglas Fir ^(a) and 17 wt% K_2CO_3	Douglas Fir ^(b) and 8 wt% K_2CO_3	Jack Pine Bark Char ^(c) and 5 wt% K_2CO_3
550	1.3	2.6	1.0
650	3.5	5.4	2.3
750	4.9	4.7	-
850	3.5	-	-

(a) Data from Mudge et al. (1981).

(b) Data from Sealock, Elliott, and Hallen (1982).

(c) Data from Ross and Fong (1981).

and 750°C, and may fall off at higher temperatures. Ross and Fong (1981) found that 5 wt% K_2CO_3 reduced the gasification rate of jack pine bark char at temperatures below 550°C.

McKee et al. (1983) have studied the relationship between the magnitude of the catalytic effect produced by alkali metal salts and coal rank. These results are compared in Table 4 to those obtained at PNL with biomass. Char from lignite was the most reactive char tested, and the addition of 10 wt% K_2CO_3 increased the reactivity about fourfold. Graphite char was the least reactive, but the effect of adding alkali was quite large. Winter, Malcosky, and Hong (1982) observed a similar effect with Na_2CO_3 and a bituminous coal, a subbituminous coal, and a lignite. Biomass falls near the lignite end of the scale, as might be expected due to its high reactivity.

Rate constants obtained at various temperatures were used to calculate the activation energies of the carbon/steam reaction for wood. The activation energy, E_a , is obtained from a plot of $\ln k$ versus $1/T$. The activation energy is proportional to the slope as dictated by the Arrhenius equation:

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

TABLE 4. Effect of K_2CO_3 on Various Feed Materials

	Temperature, °C	wt% K_2CO_3	$\frac{\text{Catalyzed Rate}}{\text{Uncatalyzed Rate}}$
Biomass ^(a)	750	17	4.9
Lignite	700	10	3.8
Subbituminous coal	700	10	7.5
Bituminous coal, hvA	800	10	11
Bituminous coal, hvB	700	10	16
Anthracite	800	10	25
Graphite	900	10	470

(a) Data from Mudge et al. (1981).

where k_1 is the rate constant at T_1 , k_2 is the rate constant at T_2 , and R is the gas constant. The sensitivity of the carbon/steam reaction to changes in temperature is reflected by the activation energies.

Activation energies determined at PNL for the carbon/steam reaction with wood ranged from 92 to 125 kJ/mole for uncatalyzed wood and from 71 to 125 kJ/mole when alkali catalysts were used (Mudge et al. 1981; Sealock et al. 1981). In general, the activation energies were somewhat lower in the presence of catalysts, but the difference was not large.

Effect of Catalyst Type

Three catalysts have been studied extensively at PNL: K_2CO_3 , Na_2CO_3 , and Cs_2CO_3 . Table 5 shows that K_2CO_3 and Na_2CO_3 have nearly the same catalytic effect on the carbon/steam reaction. Sealock, Elliott, and Hallen (1982) also found K_2CO_3 and Na_2CO_3 to be similar in their catalytic effect on Douglas fir gasification. They found Cs_2CO_3 to be slightly more effective.

Effect of Catalyst Loading

Figure 3 shows the relationship between catalyst loading and catalytic effect for K_2CO_3 -impregnated wood. At 650°C and 750°C catalyst effectiveness increased with increased loading up to 12 wt% (2.25×10^{-3} mole alkali/g wood). At 17 wt% the effectiveness was about equal to that at 12 wt% (750°C) or somewhat reduced (650°C). At 550°C the char/steam reaction is quite slow and the effect of the catalyst is quite small.

TABLE 5. Comparison of K_2CO_3 and Na_2CO_3 at 3.0×10^{-3} mole alkali/g wood

Temperature, °C	Catalyzed Rate/Uncatalyzed Rate	
	K_2CO_3	Na_2CO_3
550	1.3	1.2
650	3.5	3.5
750	4.8	4.3

FIGURE 3. Catalytic Effect of K_2CO_3 -Impregnated Wood as a Function of Catalyst Loading and Temperature

In the continuous reactor, increased loadings (up to 3×10^{-3} mole alkali/g wood) increased effectiveness at short residence times. However, at longer residence times and high conversions, high loadings reduced the rate of char gasification. Diffusion through the ash layer may limit the gasification rate under these conditions.

Effect of Catalyst Contacting Method

Previous PNL laboratory studies concluded that impregnation was a more effective means of adding catalyst than dry-mixing, although a significant catalytic effect was still achieved by dry-mixing the catalyst (Mudge et al. 1981). Sealock, Elliott, and Hallen (1982) concluded that there was little difference between impregnation and dry-mixing. Tests in the fluidized-bed PDU showed Na_2CO_3 to be almost totally ineffective when physically mixed with wet wood chips. Tests with K_2CO_3 mixed with wet wood chips were much more successful. The higher solubility of K_2CO_3 enabled it to absorb into the wet wood chips almost entirely, while the Na_2CO_3 remained primarily a solid when mixed with the wood chips. The lack of effectiveness of Na_2CO_3 dry-mixed at the PDU is not understood at this time.

EFFECT ON PYROLYSIS AND OTHER REACTIONS

The effect of alkali catalysts on the pyrolysis of biomass is not as well known as their effect on the gasification of the char residue. However, because biomass has much more volatile carbon than fixed carbon, the effect of alkali on the pyrolysis reactions of biomass becomes more important than on those of coal. PNL studies have shown that at 550 to 750°C and atmospheric pressure, alkali catalysts reduce or eliminate tars, oils, and soluble organics, reduce the yield of methane and other light hydrocarbons, and catalyze the water-gas shift reaction.

Tar and Light Hydrocarbon Yield

The effect of alkali on the yield of tars and light hydrocarbon gases at 750°C is shown in Table 6. These data are from the continuous-feed reactor system. With no catalyst the yield of tar and condensible organics was 11% (weight of original carbon present as condensible organics). With various alkali metal salt catalysts almost no tar was detected. Analysis of the condensate showed that almost no soluble organic material was present.

There was some reduction in the amount of methane and other light hydrocarbon gases in the continuous laboratory gasifier (Table 6). The effect of alkali on methane yield is more dramatic in PDU tests (Table 7). Veraa and

TABLE 6. Effect of Alkali Carbonate Catalysts on Yields
(750°C, residence time ~20 min)

Product Yield from Carbon Conversion	Percent of Total Carbon in Wood Converted				Uncatalyzed
	13 wt% Na ₂ CO ₃	8.5 wt% K ₂ CO ₃	6.5 wt% Na ₂ CO ₃	17 wt% K ₂ CO ₃	
Synthesis gas (CO, CO ₂ , H ₂)	53	57	58	60	42
CH ₄	8	7	9	8	10
C ₂ H ₆ , C ₂ H ₄	5	4	4	5	5
Total gas	66	68	71	73	57
Tar	tr(a)	tr	tr	tr	8
Water-soluble organics	tr	tr	tr	tr	3
Char	34	31	28	27	32

(a) tr = trace quantity, probably less than 0.1%.

TABLE 7. Effect of Potassium Carbonate on the Methane
Yield in PDU Tests at 750°C

	CH ₄ Yield, nm ³ /kg dry wood	
	1 atm	10 atm
Uncatalyzed	0.133	0.182
Catalyzed (K ₂ CO ₃)	0.045	0.108
Equilibrium ^(a)	0.004	0.098

(a) Gas phase equilibrium assuming 80% carbon conversion to gas.

Bell (1978) also noted that high loadings of K₂CO₃ suppressed formation of methane during gasification of coal at atmospheric pressure and at temperatures ranging from 700 to 900°C.

The overall effect of the decreased yield of tar and methane is a significant increase in yield of hydrogen and carbon monoxide (synthesis gas).

Exxon found that K₂CO₃ mixed with coal char increased methane yield at temperatures of 700°C or more and elevated pressure. The methanation reaction was essentially brought to equilibrium (Nahas 1983). In other PNL studies, Sealock, Elliott, and Hallen (1982) found that at atmospheric pressure 17 wt% K₂CO₃ had little effect on methane yield at 550°C and 650°C but decreased the

yield by almost 50% at 750°C (Table 8). At 1000 kPa the effect of K_2CO_3 on CH_4 yield was smaller. With 13 wt% Na_2CO_3 the yield of methane was significantly increased at all three temperatures and atmospheric pressure. At pressure Na_2CO_3 had little effect on the methane yield.

The effect of alkali carbonates on methane yield appears to vary significantly depending on the conditions (Table 8). Residence time may play an important part and should be investigated further.

Water-Gas Shift Reaction

Alkali carbonates impregnated on wood significantly affect the H_2/CO ratio of the gas produced by gasification. This can be seen in the PDU (Table 9)

TABLE 8. Effect of Alkali Carbonates on Methane Yield (nm^3/kg dry wood)^(a)

	550°C		750°C	
	1 atm	10 atm	1 atm	10 atm
Uncatalyzed	0.015	0.071	0.058	0.122
17 wt% K_2CO_3	0.021	0.053	0.032	0.106
13 wt% Na_2CO_3	0.027	0.046	0.070	0.103

(a) Data from Sealock, Elliott, and Hallen (1982).

TABLE 9. Comparison of Alkali and Nickel Catalysts for the Water-Gas Shift Reaction in PDU Tests

	Catalyst		
	10 wt% K_2CO_3	Ni/Alumina	None
Steam rate, kg/kg dry bagasse	0.95	1.0	1.1
Gas composition			
H_2	55	57	36
CO_2	24	20	23
CH_4	4	2	13
CO	11	21	26
C_2 and C_3	1	tr	2
H_2/CO ratio	5.0	2.8	1.4

where the H_2/CO ratio was 5.0 for the catalyzed case compared to 1.4 with no catalyst, and in laboratory tests (Table 10) where it increased from 2.1 to 3.4 when K_2CO_3 was used. In both cases all other conditions were nearly the same. Sealock, Elliott, and Hallen (1982) also found that alkali affected the H_2/CO ratio in biomass gasification tests. To check the catalytic effect, CO and H_2O were passed over Na_2CO_3 at $600^\circ C$ and H_2 and CO_2 were produced. Without a catalyst, little or no shift was detected.

In PDU tests with bagasse K_2CO_3 was apparently a more effective shift catalyst than were nickel catalysts, as shown in Table 9. In fact the H_2/CO ratio is higher than the calculated equilibrium ratio at $750^\circ C$ and 1 atmosphere. One possible explanation for the high H_2/CO rate with alkali in the PDU is that the gas continues to react with the alkali-impregnated char that is carried out of the gasifier. At the lower temperatures in the off-gas system a H_2/CO ratio higher than the equilibrium value at $750^\circ C$ could be attained. Gas samples are taken after the char has been removed in a filter vessel (which operates at about $300^\circ C$) and may show a higher H_2/CO ratio than is actually produced in the gasifier.

TABLE 10. Effect of Alkali on H_2/CO Ratio in Laboratory Gasification Tests in a Continuous Reactor^(a)

Gas composition, vol%	Catalyst	
	17 wt% K_2CO_3	None
H_2	52.4	39.0
CO_2	25.3	28.8
CH_4	5.4	10.9
CO	15.2	18.1
C_2	1.6	3.3
H_2/CO ratio	3.4	2.1

(a) $750^\circ C$, 1 atm, $H_2O/wood = 1$, residence time ~15 min.

CATALYST RECOVERY

The cost of alkali metal catalysts and the loadings required necessitates the recovery of the catalyst from the gasification residue (char, ash, catalyst). Catalyst recovery tests were performed on residue from laboratory gasification tests with both wood and bagasse (Mudge et al. 1981; Baker and Brown 1984). The wood residue contained about 50% char and 50% ash which was almost entirely from the K_2CO_3 doped on the wood. With a water wash of 10 mL/g residue, about 95% of the potassium was recovered; with 100 mL/g of residue, about 98% was recovered.

The bagasse residue generally contained about 40% char and 60% ash. About 30% of the ash was from the bagasse, the remainder from the K_2CO_3 doped on the bagasse. Figure 4 shows the effect of water/residue ratio on potassium recovery. About 80% recovery was obtained with as little as 2 mL of water per gram of residue. Additional water did not significantly improve recovery.

The remainder of the potassium probably reacts with mineral matter in the bagasse to form water-insoluble compounds. Wood produces very little ash of its own, so higher recoveries are possible. Exxon digests the char from their

FIGURE 4. Effect of Water/Residue Ratio on Potassium Recovery

CCG process with $\text{Ca}(\text{OH})_2$ to free additional water-soluble catalyst and increase recovery to 90% (Furlong and Nahas 1978; Fant and Euker 1980). This method could probably be used with bagasse char to increase the recovery of potassium. Lower wash water/residue ratios should also be investigated.

The filtrate from the potassium recovery tests with wood was recycled and used in subsequent gasification tests, with no noticeable loss of catalyst effectiveness.

SECONDARY CATALYSTS

Pyrolysis of biomass yields a variety of volatile products (CO , CO_2 , H_2 , CH_4 , light hydrocarbon gases, tars, oils, soluble organics, etc). For many uses, however, a specific product is required (such as CH_4 for high-Btu gas, or H_2 and CO for methanol or hydrocarbon synthesis). By catalyzing the secondary reactions of pyrolysis products it is possible to tailor the product gas to specific applications. Biomass has several advantages over coal. Because of the high reactivity of biomass (only about 20 wt% fixed carbon), high carbon conversion can be obtained at relatively low temperatures without the use of oxygen. The sulfur and ash contents of biomass are also quite low. These factors make it possible to use supported-metal catalysts in or directly following the gasifier.

PRODUCTION OF SPECIFIC GASES

Studies at the University of Wyoming were among the first to use supported-metal catalysts in gasification. At 650°C and 2 to 3 atm, a gas containing primarily methane and carbon dioxide (31.7 MJ/m^3 on a CO_2 -free basis) was successfully produced in one step with a combination of potassium carbonate and commercial nickel methanation catalysts (Hoffman et al. 1972; Willson 1974). The nickel catalysts were eventually deactivated by the sulfur in the coal. Several approaches for alleviating the problem were studied but none was completely successful (Cox and Sealock 1974).

Catalytic biomass gasification studies were initiated at PNL in 1977. Catalysts and operating conditions were screened in a laboratory gasifier to optimize production of methane-rich gas, methanol or hydrocarbon synthesis gas ($2\text{H}_2/\text{CO}$), hydrogen-rich gas, and ammonia synthesis gas. Efforts to produce a CO -rich gas were unsuccessful.

The reactions affected by the secondary catalysts are shown in Table 11. The conditions and catalysts used for similar commercial applications in the hydrocarbon processing industry are also shown. For all the cases studied, elimination of tars, soluble organics, and light hydrocarbon gases was desirable. Catalysis of the shift reaction was usually necessary also. The primary

TABLE 11. Secondary Reactions in Steam Gasification^(a)

Reaction	Temperature, °C	Pressure, kPa	Catalyst
1. <u>Methanation/steam-reforming</u> (methanation)	230 to 450	100 to 3000	Ni on silica, alumina, refrac- tory supports
$\text{CO} + 3 \text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$ (steam-reforming)	550 to 1000	100 to 4000	Ni on refractory supports
2. <u>Shift reaction</u>			
$\text{CO} + \text{H}_2\text{O} \longrightarrow \text{H}_2 + \text{CO}_2$	315 to 485	100 to 2000	Metal oxides Fe, Cr, Cu, Zn
3. <u>Steam-reforming</u> <u>Tars and other oxygenated hydrocarbons</u>			
$\text{Tar} + \text{H}_2\text{O} \longrightarrow \text{CO} + \text{H}_2$	550 to 1000	100 to 4000	Ni on refractory supports
<u>Light hydrocarbon gases</u>			
$\text{C}_n\text{H}_m + \text{H}_2\text{O} \longrightarrow \text{CO} + \text{H}_2$	550 to 1000	100 to 4000	Ni on refractory supports
4. <u>Hydrocracking</u>			
$\text{Tar} + \text{H}_2 \longrightarrow \text{lighter hydrocarbons} + \text{gases}$	250 to 500	200 to 2000	Ni-W on silica- alumina, Pd on zeolite
5. <u>Catalytic cracking</u>			
$\text{Tar} \longrightarrow \text{coke} + \text{lighter hydrocarbons} + \text{gases}$	450 to 600	100 to 300	Acidic

(a) Thomas 1979; Venuto and Habib 1979; Rostrup-Nielsen 1975; Gates, Katzer, and Schuit 1979; Satterfield 1980.

difference among the cases was the fate of methane. For production of a methane-rich gas, catalysis of the methanation reaction was required; for the other cases, steam-reforming of methane to produce synthesis gas was necessary.

Silica-alumina cracking catalysts eliminated tars at 750°C and above, but had little effect on other gas-phase reactions (shift, reforming, or methanation). For production of synthesis gas, nickel-based catalysts were the most effective supported-metal catalysts tested. Others that were less effective included a CoMo/Al₂O₃ hydrotreating catalyst, a NiMo/Al₂O₃ hydrodesulfurization/hydrocracking catalyst, a Pd hydrocracking catalyst, a CuZn shift catalyst, and a triple-promoted Fe₂O₃ ammonia synthesis gas catalyst. In general, these catalysts reduced or eliminated tars but had little effect on the other gas phase reactions, except that the CuZn catalyst was an effective shift catalyst. Typical gas compositions achieved with some of these catalysts are shown in Table 12. A complete list of catalysts tested is given by Mudge et al. (1983).

Nickel catalysts were also found to be the most effective for the methanation reaction. Other types of catalysts tested included SiO₂-Al₂O₃ cracking catalysts, Ru/Al₂O₃, Rh/Al₂O₃, Pd/Al₂O₃, and CoMo/Al₂O₃.

TABLE 12. Gas Compositions for Various Catalysts Tested for Synthesis Gas Production^(a)

Gas Composition	Catalyst				
	SiO ₂ -Al ₂ O ₃	CoMo/Al ₂ O ₃	NiMo/Al ₂ O ₃	SiO ₂ -Al ₂ O ₃ Ni/Support	Ni/Support
H ₂	36	44	31	58	56
CO	26	16	28	27	29
CO ₂	21	28	22	14	14
CH ₄	14	11	14	1	1
C ₂ and C ₃	3	2	5	-	-

(a) 750°C, 1 atm, H₂O/wood ~0.7.

With fresh nickel catalysts the methanation/reforming reaction

is brought to equilibrium. Methane was almost completely converted to H_2 and CO at 850°C and increased to about 25 mol% at 550°C . The minimum temperature for a single-bed process was set at 550°C ; below this temperature the rate of gas production was too low to be practical. Higher methane concentrations were achieved at lower temperatures using a dual-bed scheme in which the catalyst temperature was kept lower than the gasification temperature.

For the production of hydrocarbon synthesis gas, hydrogen, and ammonia synthesis gas, the secondary reactions are quite endothermic. Later PDU studies and a feasibility study of full-scale plants indicated that the maximum practical operating temperature would be limited to about 750°C by heat input requirements and materials considerations.

These secondary reactions are quite fast in the presence of a catalyst. As Figure 5 shows, methane and phenol are almost completely converted to hydrogen and CO at residence times longer than 0.2 s at 750°C .

Steam rates were varied from 0.1 g/g wood up to 6 g/g wood. Methane production is thermodynamically favored at low steam rates while production of hydrogen is favored at high steam rates. At low steam rates (<0.3 g/g wood) carbon conversion begins to decrease, otherwise steam rate had little effect on conversion.

Table 13 shows the optimal operating conditions and catalyst type for the various product gases along with typical results for each case. Comparison of the obtained yields to the maximum theoretical yields (see Table 1) is enlightening. The best methane yield achieved was a little over 50% of the maximum theoretical. At high temperatures the yield is limited primarily by thermodynamic equilibrium; at lower temperatures, by the kinetics of gasification. A dual-bed system operating at different temperatures is necessary to increase the yield.

FIGURE 5. Steam-Reforming of Phenol and Methane

The yield of methanol synthesis gas is nearly 80% of theoretical and is limited by the kinetics of gasification and the ability of the catalyst to reform methane to synthesis gas. Hydrogen production, shown in Table 13, is about 70% of maximum theoretical and is limited by gasification kinetics and, at high temperatures, by the water-gas shift equilibrium. Ammonia synthesis gas yield in Table 13 is about 60% of theoretical and is limited by the same factors as hydrogen production.

The type of nickel catalyst that was most effective varied from case to case. For methanation, catalysts with high nickel loadings (>30 wt% Ni) and high surface areas were most effective. They produced a gas containing essentially the equilibrium methane concentration. With lower-surface-area catalysts containing less nickel the methane concentration was somewhat lower. For synthesis gas production the difference in activity between various nickel catalysts was small.

TABLE 13. Production of Specific Gases from Biomass by Steam Gasification

	Product Gas/Catalyst				
	Methane-Rich Gas		Methanol Synthesis Gas	Ammonia Synthesis Gas	Hydrogen
	Nickel	Nickel	Nickel	Nickel + Shift	Nickel + Shift
Gasification temperature, °C	650	550	750	650	750
Catalyst temperature, °C	350	550	750	650	750
Steam/wood, g/g	0.16	0.33	0.70	1.60	5.7
Air/wood, g/g	--	--	--	0.65	--
Carbon conversion to gas, % ^(a)	50	68	90	65	78
Gas composition, vol%					
H ₂	5	30	53	51	64
CO ₂	42	34	16	21	30
CO	tr ^(b)	11	28	7	6
CH ₄	53	25	3	3	tr
C ₂ and C ₃	tr	tr	tr	tr	tr
N ₂	--	--	--	18	--
Yield/kg, nm ³	0.25	0.22	1.4	1.3	1.25

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

(b) tr = trace quantity, probably less than 0.1%.

Research on catalytic gasification of biomass with supported-metal catalysts is also under way in France (Anonymous 1983), Japan (Yamazaki et al. 1983; Yokayama et al. 1983), and Sweden (Lindman et al. 1981; Ekstrom, Lindman, and Pettersson 1982). Typical results from these studies are shown in Table 14. All three use some form of nickel catalyst. The Japanese and Swedish studies are directed toward production of methanol or hydrocarbon synthesis gas and the gasification temperature, 700 to 750°C, is the same as that used at PNL.

TABLE 14. Typical Results of Various Catalytic Biomass Conversion Studies with Nickel Catalysts

	France	Japan	Sweden	U.S.
Organization	Azote et Produits	Toyohashi University	Royal Institute of Technology	PNL
Reactor size and type	Pilot-scale, dual vessel	Laboratory, batch, single vessel	Bench-scale and pilot-scale, dual vessel	Laboratory and fluidized bed PDU
Operating conditions				
Catalyst	Ni, proprietary	Ni/Al ₂ O ₃	Ni-reforming	Ni/Al ₂ O ₃
Reactant	Steam	Steam	Steam, oxygen	Steam
Temperature, °C	NA	700	750, 950	700
Pressure, MPa	NA	0.1	3	0.1
Carbon conversion to gas	NA	87	98	80
Dry gas composition, mol%				
H ₂	50	56	43	55
CO	28	31	35	21
CO ₂	16	11	22	21
CH ₄	6	3	tr ^(a)	2
C ₂ and C ₃	--	--	--	--
Tar	NA	NA	None	tr

(a) tr = trace quantity, probably less than 0.1%.

In Sweden, Lindman et al. use oxygen as well as steam and a separate secondary catalyst bed operating at 950°C. This setup results in very high carbon conversion to gas and almost complete elimination of hydrocarbon products.

Yamazaki et al. tested eight different metal oxide catalysts at 700°C in the presence of steam. The results are shown in Table 15. They concluded that NiO/Al₂O₃ was the most effective catalyst for production of methanol synthesis gas, followed by CuO and Fe₂O₃. Several of the catalysts normally used for

TABLE 15. Catalytic Gasification with Various Metal Oxide Catalysts at 700°C^(a)

	Catalyst							
	<u>V₂O₅</u>	<u>CoO</u>	<u>MoO₃</u>	<u>Mn₂O₃</u>	<u>Cr₂O₃</u>	<u>CuO</u>	<u>Fe₂O₃</u>	<u>NiO</u>
Carbon conversion to gas, wt%	81	83	81	77	77	89	79	87
Gas composition, % of total gas produced								
H ₂	46	44	40	58	44	59	55	56
CO	6	13	7	18	30	19	32	31
CH ₄	2	1	1	11	12	7	7	3
CO ₂	46	42	52	13	15	15	5	11
Synthesis gas yield, nm ³ /kg dry wood	0.71	0.77	0.58	1.27	0.93	1.53	1.40	1.55
Total gas yield, nm ³ /kg dry wood	1.36	1.35	1.22	1.66	1.25	1.96	1.60	1.78

(a) Data from Yamazaki et al. (1983).

oxidation reactions produced large quantities of CO₂. Material balances indicate that much of the oxygen must come from the catalyst and not from the wood or steam.

CATALYST LIFETIME AND DEACTIVATION

An effective catalyst for catalytic steam gasification of biomass will:

- have the chemical and physical properties needed to promote the desired reactions
- be resistant to deactivation or be easily regenerated
- be physically durable in fluidized-bed operations.

Preliminary catalyst screening studies at PNL identified numerous active nickel-based catalysts and the optimal operating conditions for producing a variety of gases. Studies were then initiated to determine the active lifetime of nickel catalysts used for synthesis gas and methane-rich gas production in

laboratory gasifiers. In addition, the attrition rate of various catalysts was measured in a laboratory fluidized bed.

Catalyst Deactivation Studies

Three possible causes of loss of catalyst activity were identified in laboratory tests: 1) catalyst fouling by carbon deposition, 2) loss of nickel surface area due to sintering, and 3) sulfur poisoning. The rate of catalyst deactivation was measured in terms of the weight of wood processed per unit weight of catalyst before deactivation. Some loss of activity is noted for all catalysts, so the presence of tars in the product gas was used to define the point at which a catalyst was deactivated.

In tests at 550°C all catalysts tested were deactivated quite rapidly. The active lifetime of the catalyst seems to be primarily related to the amount of metal surface area on the catalyst, as shown in Figure 6. The longest active lifetime achieved was 73 g wood/g catalyst.

FIGURE 6. Effect of Metal Surface Area on Catalyst Lifetime at 550°C

At 750°C some catalysts were completely deactivated rapidly, but several were found that retained much of their activity, as shown in Figure 7. All of the catalysts lost some of their initial activity for reforming methane, which accounts for the small drop in activity for the NiCuMo/SiO₂-Al₂O₃ and Ni/α-Al₂O₃ (G-90C). Catalyst lifetimes ranged from 16 to 1470 g wood/g catalyst. Several of the tests, including the two shown in Figure 7, were terminated while the catalyst was still active.

Carbon Deposition. Almost all catalysts tested at PNL had some carbon on them at the end of a run. Carbon deposition in the laboratory tests is primarily a function of temperature and catalyst type.

At 550°C carbon deposition was quite severe on all catalysts tested. Generally the catalysts contained 15 to 30 wt% carbon. At 750°C, carbon deposition was significantly reduced, but was still a serious problem. The amount of carbon on the used catalysts at 750°C was generally less than 10 wt%.

FIGURE 7. Effect of Catalyst Age on Yield at 750°C

Studies in Sweden found that between 700°C and 850°C the nickel-based catalysts used in the MINO process were deactivated for methane-reforming, but not for tar-reforming or the water-gas shift reaction. Carbon deposition was shown to be the cause of deactivation. Above 900°C, catalysts used for the MINO process were not deactivated, but at low steam rates carbon formation in the catalyst bed resulted in increased pressure drop (Ekstrom, Lindman, and Pettersson 1982). In limited PNL tests at 850°C it appeared that carbon deposition was less than at 750°C.

The effect of catalyst type on carbon deposition was most apparent at 750°C, as shown in Table 16. Many commercial nickel catalysts such as Ni-3266 and C-13-3 were deactivated for tar-reforming at lifetimes of less than 100 g wood/g catalyst. However, three types of catalysts show promise for achieving economic lifetimes:

- trimetallic catalysts containing NiCuMo or NiCoMo
- steam-reforming catalysts supported on low-surface-area ceramic materials such as α -alumina, magnesia, and magnesium aluminum spinel
- catalysts doped with alkali.

TABLE 16. Carbon Deposition on Catalysts Used for Methanol Synthesis Gas at 750°C, 1 atm

Catalyst	Carbon on Used Catalyst, wt%
Harshaw Ni-3266	20
United C-13-3	21
Grace NiCoMo/SiO ₂ -Al ₃ , 2% Na	7,5,4
NiCuMo/Al ₂ O ₃ , 2% Na	7
NiCoMo/Al ₂ O ₃	3
NiCoMo/Al ₂ O ₃ , 2% Na	4
NiCuMo/SiO ₂ -Al ₂ O ₃	2
NiCuMo/SiO ₂ -Al ₂ O ₃ (a)	13
United G-90C	0.1
PNL K ₂ CO ₃ /SiO ₂ -Al ₂ O ₃	0.4
PNL Ni/Na ₂ CO ₃ /Al ₂ O ₃	0.4

(a) Tested at 650°C.

A NiCoMo/SiO₂-Al₂O₃ catalyst doped with 2 wt% Na reached a lifetime of 1470 g wood/g catalyst. At the end of the run 6 wt% carbon had accumulated on the catalyst, which had lost some of its activity for methane-reforming but was still active for tar-reforming and the shift reaction.

A steam-reforming catalyst, nickel on α -alumina (G-90C), reached a lifetime of 60, maintained much of its initial activity, and had essentially no carbon on it at the end of the run. This was the only tested nickel-based catalyst on which carbon did not accumulate. A catalyst made at PNL containing 25 wt% Na₂CO₃ and 10 wt% Ni had very little carbon on it after a lifetime of 90 but its initial activity was significantly less than that of other nickel catalysts.

In the laboratory gasifier tests with NiCuMo/SiO₂-Al₂O₃ and NiCoMo/SiO₂-Al₂O₃, steam rates between 0.5 g and 6 g/g wood had little effect on carbon deposition at 750°C. In model compound studies, carbon deposition with phenol was low (0.5 to 3.4 wt% on the catalyst) at steam rates above 3 moles steam/mole of carbon (Table 17). At lower steam rates carbon deposition increased dramatically. This represents a much lower steam/tar (phenol) ratio than that to which the catalyst is exposed in the laboratory gasifier.

Only limited information has been obtained from the POU with respect to carbon deposition and catalyst lifetime but it appears that coking may be more

TABLE 17. Effect of Steam Rate on Carbon Deposition with Phenol

Moles Steam/Mole Carbon	Space Velocity (GHSV)	wt% Carbon on Catalyst
5.8	2000	3.4
4.7	1900	(a)
4.4	3500	(a)
3.7	2400	0.4
3.6	2400	1.6
1.2	4300	22.4
1.2	1100	18.9

(a) Part of a series of runs. Wt% carbon at the end of the series was 6.3.

severe in the PDU. Catalysts usually pick up 10 to 20 wt% carbon by the end of a one-day PDU run. It is not clear whether this increase in carbon deposition is due to 1) intrinsic differences between the fluidized-bed PDU and the fixed-bed laboratory gasifiers or 2) the unsteady-state operations of the PDU. Figure 8 shows the loss of activity for a series of runs with $\text{Ni}/\text{Al}_2\text{O}_3$ in 1980. The loss of activity seems to correspond to the shutdowns between runs. When the system operated smoothly, as in runs 3 and 5, the catalyst appeared to maintain its activity. After run 4 the catalyst was regenerated with steam at 750°C . Figure 9 shows the activity of $\text{NiCuMo}/\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst with bagasse and wood. With wood there was some noticeable loss of activity near the end of the run but it occurred immediately following a plant upset. With bagasse there was a gradual loss of activity that apparently was a function of the sulfur content of the bagasse (see section on sulfur poisoning).

Although loss of activity seems to correspond to unsteady-state operations, similar conditions were encountered many times in the laboratory life-time runs without loss of activity.

Sulfur Poisoning. Hydrogen sulfide is a known poison for nickel catalysts (Rostrup-Nielsen 1975; Satterfield 1981). Biomass contains relatively small

FIGURE 8. Catalyst Deactivation in PDU with $\text{Ni}/\text{Al}_2\text{O}_3$ (synthesis gas production at 750°C , 1 atm)

FIGURE 9. Catalyst Deactivation in PDU with NiCuMo/SiO₂-Al₂O₃ (synthesis gas production at 750°C)

quantities of sulfur compared to other solid fuels; however, sulfur poisoning still must be considered as a possible cause of catalyst deactivation. Table 18 lists the sulfur contents of various biomass materials and the H₂S contents of the raw gas produced by uncatalyzed steam gasification at 750°C.

With wood as a feedstock, there were no indications that sulfur contributed to catalyst deactivation at any of the conditions tested. In recent tests with bagasse, however, sulfur poisoning appeared to be one of the major causes of catalyst deactivation. Two factors indicate that the deactivation mechanism with bagasse is different from that observed with wood:

- Catalyst lifetimes were much shorter (<100 g wood/g catalyst).
- A catalyst with greater active-metal surface area (Ni/Al₂O₃) takes longer to deactivate than does NiCuMo/SiO₂-Al₂O₃.

That H₂S is involved in the deactivation mechanism with bagasse is suggested by the following:

- There is a close correlation between the amount of sulfur on the catalysts when they lose activity and the amount of sulfur required to sulfide the active-metal surface area of the catalyst.
- There is good correlation between the time that should be required to sulfide the catalyst and the time at which deactivation occurs.

TABLE 18. Sulfur Analyses for Biomass Gasification

	ppm S by weight in feed	ppm H ₂ S in raw gas
Wood	47 to 145	20 to 30
Bark	204 to 330	--
Bagasse	230 to 375	80 to 240

- Mixing a ZnO sulfur guard catalyst with a nickel catalyst extends the life of the nickel catalyst.

Wood does contain some sulfur, although less than bagasse, and NiCoMo/SiO₂-Al₂O₃ ran for over 1000 hours in a laboratory test with wood without deactivating. Rostrup-Nielsen (1975), in studies of chemisorption of hydrogen sulfide on steam-reforming catalysts, found the chemisorption of hydrogen sulfide on nickel to be reversible, the coverage on the catalyst being a function of the ratio p_{H₂S}/p_{H₂}. The amount of absorbed sulfur in equilibrium with the H₂S in the gas increases with increasing H₂S concentration until constant fractional coverage of the surface is reached. It appears that the sulfur level in wood allows enough of the nickel on the catalyst to remain exposed and active.

Heavy carbon deposition was also found on catalysts used with bagasse, particularly those from the PDU, and one could conclude that the sulfided catalysts are more susceptible to the carbon deposition that actually causes loss of activity. However, it is generally agreed that sulfiding nickel-reforming catalysts decreases carbon formation on the catalyst (Rostrup-Nielsen 1975; McCarty et al. 1981).

From these studies it is not possible to positively identify the exact mechanism for deactivation with bagasse, but it definitely appears to be a function of the sulfur content. Coking may also play a part but the exact relationship between the sulfur adsorption and carbon deposition is not known.

Sintering. Thermal sintering, or agglomeration, can also cause loss of catalyst activity. Sintering is the loss of metal surface area due to growth in nickel particle size on the catalyst support. Nickel is mobile at high temperatures and the small crystals agglomerate to form larger particles, reducing the nickel surface area.

Sintering is particularly troublesome with high-surface-area dispersed metal catalysts such as Harshaw Ni-3266. A sample of Ni-3266, which had 20 wt% carbon on it after a lifetime test, was regenerated with steam at 750°C for 64 hours. Despite removal of all the carbon the catalyst was not active and the surface area as measured by hydrogen chemisorption was the same as that of the coked catalyst, and much less than that of the fresh catalyst. On the other hand, a sample of NiCoMo/SiO₂-Al₂O₃ catalyst, with a much lower surface area than a fresh catalyst, showed a significant increase in activity and surface area after steaming at 750°C to remove carbon.

The fact that regeneration of Ni-3266 did not increase its metal surface area indicates that sintering was responsible for much of the surface area loss. With NiCoMo/SiO₂-Al₃O₃, the metal surface area increased after regeneration although it did not return to its original value. Some of the surface area was permanently lost, due probably to sintering. Pederson, Skov, and Rostrup-Nielson (1980) studied sintering of a high-surface-area methanation catalyst (Ni/γAl₂O₃) and a low-surface-area steam-reforming catalyst (Ni/ceramic). The Ni/γAl₂O₃ lost over 70% of its surface area at 750°C while the Ni/ceramic lost less than 10% of its surface area.

Tammann's rule says that sintering can be expected at temperatures 0.5 times the melting point in degrees K (Gregg 1965). The melting point of nickel is 1726K, so sintering can be expected at temperatures above 590°C (863K). However, for supported catalysts the metal particles are restricted to a size less than the pore diameter of the support. This means that a stabilized micro-pore system in the support can help prevent sintering of the nickel crystals.

At the temperatures encountered in the gasifier, even some support materials lose their porosity and are not suitable supports. Most industrial catalysts for steam-reforming, which operates at temperatures similar to those in gasification, use catalyst carrier materials of α-alumina, MgO, and magnesium aluminum spinel. High-surface-area supports such as γ- or η-Al₂O₃ are susceptible to sintering at high temperatures and can not be used without stabilizing additives. Silica, being volatile at high temperatures in steam, is now normally excluded from catalysts for steam-reforming (Marschner and Renner 1982; Rostrup-Nielson 1975).

In summary, sintering of nickel can be expected at gasification temperatures. Sintering can be controlled by choosing a support with sufficient surface area ($>5 \text{ m}^2/\text{g}$) that retains its micropore structure at gasification temperatures.

Attrition

Another factor which must be considered when evaluating catalyst lifetime is physical breakdown, or attrition, of the catalyst. If the catalyst is located outside of the gasifier in a fixed bed, attrition will not be a serious problem. However, if the catalyst is the fluidizable material in the gasifier bed, attrition may be significant.

Because the wood must also be fluidized the catalyst particles used in PNL's PDU gasifier are quite large (30 to 80 mesh) for fluidized-bed catalysts. Data for this catalyst size are limited but it appears that fluidization is not as good and attrition is higher than with smaller particles (Kono 1980; Wen and Dutta 1978).

The attrition rate of three different catalysts (Al_2O_3 , $\text{Ni}/\text{Al}_2\text{O}_3$, and $\text{NiCuMo}/\text{SiO}_2\text{-Al}_2\text{O}_3$) in the 30-to-80 mesh size range was measured in laboratory-scale fluidized beds. At flow rates just above the minimum fluidization velocity the steady-state rate of attrition ranged from 0.004 to 0.007 wt% per hour using air at ambient temperature as the fluidizing gas. At 750°C with steam the rate of attrition was 0.007 to 0.008 wt% per hour. This rate is quite low; however, as the superficial linear velocity (V_0) increases, the rate of attrition increases dramatically. For the $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst it was a function of $V_0^{2.1}$; for the $\text{NiCuMo}/\text{SiO}_2\text{-Al}_2\text{O}_3$ it varied as V_0^3 .

The attrition rate in the fluidized-bed PDU has not been measured but appears to be higher than observed in the laboratory tests. The high superficial velocities used in the PDU, up to five times the minimum, are partially responsible for this. Another possibility is that carbon on the catalyst may weaken the particle and increase attrition. In the laboratory fluidized bed the attrition rate with a coked catalyst was about double that of a fresh catalyst. The design of the PDU gasifier also allows catalysts to fall back into the feed screw where some of the catalysts may be crushed.

MECHANISMS OF CATALYTIC GASIFICATION

The focus of the PNL catalytic gasification studies has been to develop a process for producing specific gases in one step. In the course of these efforts it became apparent that a better understanding of the mechanisms involved could lead to significant process improvements in several areas. Mechanistic studies were therefore initiated to develop a fundamental understanding of 1) the overall effect of alkali carbonates on pyrolysis/gasification, and 2) the causes of coking on secondary catalysts.

High-temperature steam gasification of biomass is often considered to be a two-step process: rapid pyrolysis followed by steam gasification of the remaining residue. However, Shafizadeh and Fu (1973) have shown that tar-forming reactions predominate during high-temperature pyrolysis and that levoglucosan is the primary component of the tar. At the Solar Energy Research Institute (SERI), Milne, Evans and Solty (1983) have shown that the decomposition pathways are basically unaffected by temperature in the range from 500 to 900°C, with levoglucosan being the primary product.

These primary tars undergo secondary thermal reactions such as dehydration, disproportionation, decarboxylation, and decarbonylation to produce gases (CO, CO₂, CH₄), water-soluble organics (acids, ketones, alcohols, etc.), char, and water (Shafizadeh 1982).

Char from rapid pyrolysis and secondary tar reactions continues to pyrolyze and reacts with steam (carbon/steam reaction) to produce additional gases. Gases from pyrolysis, secondary tar reactions, and gasification of char can undergo various secondary reactions such as water-gas shift, methanation, and reforming. Only the shift reaction is rapid enough to be significant in the absence of catalysts.

The mechanistic studies showed that catalysts affect the entire process, as shown in Figure 10. The effect of catalysts and primary tars on one another appears to be especially important.

FIGURE 10. Reaction Pathways for High-Temperature Steam Gasification of Biomass

PRIMARY CATALYSTS

Laboratory gasification tests showed that alkali carbonates doped on biomass increase the yield of char from pyrolysis. The char was more reactive than uncatalyzed char and the rate of gasification was increased two- to nine-fold. In the fluidized-bed PDU, however, the net effect of adding K_2CO_3 was to increase the yield of char. Laboratory and PDU tests at $750^\circ C$ both showed that alkali carbonates significantly reduced the tars and decreased the yield of methane.

Pyrolysis

Analysis of high-temperature (300 to 500°C) pyrolysis tar from cellulose shows levoglucosan as a primary component along with other sugar units (Shafizadeh and Fu 1973; Milne, Evans, and Solty 1983). Fundamental pyrolysis studies at SERI have shown that addition of alkali catalysts such as K_2CO_3 , Na_2CO_3 , and KOH eliminates formation of levoglucosan during pyrolysis. These catalysts apparently inhibit transglycosylation, which has been shown to be the primary pathway for decomposition of cellulose to tar (Milne, Evans, and Solty 1983). This appears to be one mechanism by which alkali carbonates reduce the yield of tars.

Shafizadeh (1982) has also shown that alkali increases conversion of levoglucosan to char and gases. This could also partially account for the effect of alkali on gasification. Most of the preceding discussion is based on cellulose but the mechanisms fit very well with the overall results obtained with wood in both laboratory and PDU studies at PNL.

In high-temperature gasification of biomass the amount of methane produced during pyrolysis generally exceeds the equilibrium methane concentration. The effect of alkali is to reduce this concentration toward the equilibrium concentration, although equilibrium is not achieved. Laboratory studies in a gas phase reactor have shown that neither K_2CO_3 nor biomass char, nor a combination of the two, catalyzes the decomposition of methane at temperatures below 800°C. Furthermore, analysis of gases from the top of the continuous reactor during a run with K_2CO_3 -impregnated wood showed a reduction in the methane produced (compared to uncatalyzed runs), and no further reduction was noted after the gas had passed through the char bed and out of the reactor. This suggests that alkali carbonates alter the pyrolysis reaction pathways so as to reduce the formation of methane, rather than acting as a heterogeneous catalyst for reforming methane to H_2 and CO. Veraa and Bell (1978) also found that high concentrations of K_2CO_3 suppressed formation of methane during coal gasification.

Gasification

Alkali carbonates increase the rate of biomass char gasification, although the effect is not as dramatic as has been reported for some coals (see Table 4). The mechanism of alkali-catalyzed gasification of char has been the subject of much research.^(a) McKee (1983) has proposed a mechanism involving the carbo-thermic reduction of alkali carbonates to alkali metal vapor, as shown below:

McKee indicated that alkali intermediates may also interact with the substrate to form free radicals or intercalation compounds, but that insufficient data were available to assess the role of these species in the gasification process. The actual mechanism controlling alkali-catalyzed gasification is still the subject of much debate.

Secondary Reactions

As previously indicated, alkali catalysts reduce the yield of tars, oils, soluble organics, and light hydrocarbon gases from high-temperature gasification of biomass. This is somewhat surprising, as catalysis of decomposition reactions such as dehydrogenation, dehydration, and steam-reforming normally occurs with Group VIII metals, not with alkalis. That alkali carbonates apparently alter the pyrolysis reaction pathways accounts for much of this effect. However, in the course of recent PNL studies it was discovered that alkali carbonates do act as heterogeneous catalysts for some secondary reactions during biomass gasification.

The PNL study used supported- Na_2CO_3 as a secondary catalyst in the fixed-bed continuous-feed laboratory reactor, and found that this catalyst reduced tars and soluble organics but had little effect on gas composition. Hallen,

(a) McKee et al. 1983; McCoy 1983; Veraa and Bell 1978; Wood et al. 1983; Wen 1980.

Sealock, and Cuello (1982) found much the same result in dual-vessel batch gasification tests where Na_2CO_3 was kept in a basket physically separated from the wood.

Hallen, Sealock, and Cuello also investigated the effect of alkali carbonates on the decomposition of model compounds that have been reported as pyrolysis products from cellulose. Alkali carbonates catalyzed the decomposition of alcohols, organic acids, and aldehydes, but had little effect on ketones (Table 19). Especially surprising is the catalytic effect of alkali carbonates on alcohol dehydrogenation, as there is no reference to the use of alkali carbonates as alcohol dehydrogenation catalysts in the literature (Hallen, Sealock and Cuello 1982). PNL also studied the catalytic effect of K_2CO_3 on decomposition of methane and phenol in the gas phase reactor at 750°C . Potassium carbonate catalyzed the decomposition of phenol but was not active for converting methane.

As discussed earlier, studies at PNL indicate that the alkali carbonates suppress formation of methane during pyrolysis and do not act as heterogeneous catalysts to reform methane to H_2 and CO after it is formed. It is interesting to compare these results to those obtained by Exxon in their CCG process.

TABLE 19. Effect of Sodium Carbonate on Carbon Conversion to Gas for Model Compounds Reacted with Steam at 600°C ^(a)

	Catalyst	Feed Rate, g/min	Carbon Converted to Gas, %
Methanol	None	0.46	0.8
	Na_2CO_3	0.46	19.2
Acetic acid	None	0.53	7.2
	Na_2CO_3	0.53	53.9
Acetaldehyde	None	(b)	9.4
	Na_2CO_3	(b)	38.3
Acetone	None	0.46	0.4
	Na_2CO_3	0.46	0.1

(a) Data from Hallen, Sealock, and Cuello (1982).

(b) Preliminary experiments at varied feed rates.

Exxon found that K_2CO_3 impregnated on the coal increased the methane concentration up to the equilibrium concentration at 700°C and 3.6 MPa. Neither K_2CO_3 nor char alone was able to catalyze the methanation reaction, but the two in combination were catalytic (Nahas and Gallagher 1978). This is unusual, because hydrogenation catalysis does not usually involve alkalis. Cabrera, Heinemann, and Somorjai (1982) found that methane could be formed by direct hydrogenation of graphite catalyzed with K_2CO_3 but the concentrations were low.

If alkali carbonates do in fact catalyze formation of methane, they could also be expected to catalyze the reverse reaction, steam-reforming; however, this has not been observed in the PNL studies.

SECONDARY CATALYSTS

The secondary reactions that can be catalyzed during biomass gasification are shown in Table 11. Nickel-based catalysts are the most effective for this combination of reactions.

Catalytic Effects

With an active nickel catalyst the methanation/steam-reforming reaction and the shift reaction are catalyzed to equilibrium concentrations in both the laboratory and PDU gasifiers. At lower temperatures (such as 550°C), nickel catalyzes the methanation reaction. At higher temperatures (such as 750°C), nickel catalyzes steam-reforming of methane (pyrolysis) to hydrogen and carbon monoxide. Over the temperature range studied (550 to 850°C) all tar is converted to gas and/or char when active nickel catalysts are present. This may involve steam-reforming, thermal cracking, catalytic cracking, or a combination.

Rostrup-Nielsen (1977) has presented the following sequence for steam-reforming of naptha:

where S is an active site on the catalyst. The first step is chemisorption of the hydrocarbon on a dual nickel site involving dehydrogenation. This is followed by rupture of the carbon-carbon bond and formation of surface radical CH_x . Adsorption of steam is thought to occur on the support on the basis of the observed influence of support type on the kinetics of the reaction (Bhatta and Dixon 1969). The adsorbed steam (or oxygen) reacts with the surface radical CH_x to produce carbon monoxide and hydrogen.

At higher temperatures ($>700^\circ\text{C}$) cracking reactions may become significant, particularly in the presence of acidic catalysts such as zeolites, silica-alumina, and alumina. Thermal cracking proceeds via free-radical mechanisms. The initial step is the homolysis of a carbon-carbon bond to form free radicals that can continue to undergo scission to form smaller and smaller radicals (Gates, Katzer, and Schuit 1979). Catalytic cracking reactions are highly complex but can be interpreted in terms of carbonium-ion theory (Gates, Katzer, and Schuit 1979; Satterfield 1980). A carbonium ion is formed by abstraction of a proton from a Bronstad acid. The resulting carbonium ion undergoes fission and the process is repeated. Commercial catalytic cracking results in a large buildup of carbon on the catalyst that must be removed by regeneration.

Mechanisms of Carbon Deposition

Reactions that can cause carbon deposition, or coking, of secondary catalysts include:

Carbon can also be removed from catalysts by gasification reactions which include the reverse of reactions 1 and 2 and the carbon/steam reaction

Even though the equilibrated gas may show no affinity for carbon formation, in an open thermodynamic system carbon may be stable in a steady-state, and the accumulation of carbon may continue. The question of whether there is a net buildup of carbon, and subsequent deactivation, is thus a kinetic one and is influenced by the choice of catalysts (Rostrup-Nielsen 1975).

Several types of carbon have been found on nickel catalysts used for steam-reforming and methanation, depending on the test conditions.^(a) These are summarized in Table 20. Whisker carbon results from decomposition of CO,

TABLE 20. Different Types of Carbon Formation in Steam-Reforming of Hydrocarbons^(a)

	Polymer	Whisker	Pyrolytic
Formation	Slow polymerization of hydrocarbon radicals on nickel surface into encapsulating film	Diffusion of carbon through nickel crystal, whisker growth with Ni-crystal at top	Thermal cracking of hydrocarbons. Deposition of C precursors on catalyst
Effects	Progressive deactivation	No deactivation. Breakdown of catalyst, plugging	Encapsulation of catalyst particle and deactivation
Temperature range, °C	<500	>450	>600
Critical parameters	Low temperature Low H ₂ O/C Low H ₂ /C Aromatics	High temperature Low H ₂ O/C	High temperature Low H ₂ O/C High pressure Acidity of catalyst

(a) Data from Rostrup-Nielsen (1982).

(a) Rostrup-Nielsen 1982; Rostrup-Nielsen and Trimm 1977; Trimm 1977; McCarty et al. 1981.

CH₄, and heavier hydrocarbons. Polymer and pyrolytic carbon generally occur only with heavier hydrocarbon feeds.

In steam-reforming of hydrocarbons at low temperatures, coking usually takes the form of progressive deactivation by polymer formation on the nickel surfaces. For a given set of conditions, feedstocks, and catalyst there is a temperature above which this type of coking will not occur.

At higher temperatures (above 450°C) whisker carbon formation predominates. Above 530°C the whiskers become more like layers. These types of carbon can accumulate quite rapidly and in large amounts. At a given set of conditions (temperature, feedstock, catalyst) there is a critical steam/carbon ratio below which whisker carbon will occur. At temperatures above 600°C, thermal cracking and coke formation on the catalyst may occur. Acidic catalyst surfaces are more susceptible to this type of coking.

Polymer carbon deposition results in progressive deactivation. Whisker carbon growth does not cause the loss of intrinsic catalyst activity, but can cause deactivation when the whiskers block the pores. Pyrolytic carbon deposition occurs on the catalyst surface and also causes deactivation by pore blockage.

High-Temperature Coking. Laboratory studies were initiated with various model compounds to determine the cause of carbon deposition. The four feeds tested were a 50/50 H₂/CO mixture, methane, ethylene, and phenol to represent reactions 1 through 4. The results at 750°C with a NiCuMo/SiO₂-Al₂O₃ catalyst are shown in Table 21. Very little carbon was formed with the H₂/CO mixture or with methane. Coking was more severe with ethylene and phenol, indicating that reactions 3 and 4 are primarily responsible for the carbon deposition. These results are similar to those obtained for steam-reforming various hydrocarbons where the relative rate of carbon formation was as follows (Satterfield 1980):

Ethylene > benzene, toluene > heptane > hexane > cyclohexane
> butane ≈ carbon monoxide > methane

TABLE 21. Effect of Feed on Carbon Deposition^(a)

Feed	wt% Carbon on Catalyst After 4 hours
CO/H ₂ (50/50)	0.1
Methane	1.3
Ethylene	6.4
Phenol	6.3

(a) NiCuMo/SiO₂-Al₂O₃ catalyst, 750°C,
~3 moles H₂O/mole C.

A scanning electron microscopy (SEM) micrograph of a catalyst coked at 750°C in a laboratory gasification test (Figure 11) shows a film of amorphous carbon on the catalyst, but whisker growths like those shown by McCarty et al. (1981) and Albright, McConnell and Welther (1979) are not apparent. The conclusion from the gas phase reactor studies and the SEM studies is that cracking of hydrocarbons is the primary cause of carbon deposition.

Several other variables were tested to determine their effect on carbon deposition: steam rate, temperature, catalyst support, bimetallic combinations with nickel, and addition of alkali to the catalyst. Of these variables, the type of catalyst support had the most significant effect on coking, as shown in Table 22. A commercial steam-reforming catalyst, G-90C, nickel-supported on α -alumina, had the lowest amount of carbon deposition both with wood in laboratory gasification tests and with phenol in model compound studies. The other, more acidic supports had more carbon deposition. These results reinforce the conclusion that cracking of tars on the support is the predominant cause of carbon deposition.

Wen (1983) found that petroleum catalytic cracking catalysts were effective in converting coal tar to chars and gases in the temperature range of 350 to 500°C. Carbon buildup on the catalysts was quite rapid and the catalyst effectiveness decreased very rapidly if the coke was not removed.

FIGURE 11. SEM Micrograph of Catalyst Coked at 750°C

TABLE 22. Effect of Catalyst Support on Carbon Deposition at 750°C

Catalyst Support	wt% C on the Catalyst	
	Wood ^(a)	Phenol ^(b)
α -Al ₂ O ₃	0.1	0.4
SiO ₂ -Al ₂ O ₃	2 to 7	6.3
SiO ₂ -Al ₂ O ₃ (γ-zeolite)	-	15
γ-Al ₂ O ₃	21, 20	20

(a) Gasification tests in a laboratory gasifier, various exposure times.

(b) After 4 to 5 hours exposure.

In the Syntar process being developed by the Ralph M. Parsons Company, coal tar is reacted with steam in the presence of catalysts at about 600°C to produce fuel gases. Catalysts with acidic supports were found to be susceptible to coking (Stern 1982).

Increasing the temperature from 750 to 850°C reduced carbon deposition. This effect is similar to the results of Ekstrom, Lindman, and Petterson (1982) with secondary catalysts in the MINO process. Carbon deposition increased at 650°C but not dramatically.

Use of trimetallic or alloy catalysts (NiCuMo or NiCoMo) also appears to reduce carbon deposition in gasification tests. A similar effect has been observed in steam-reforming tests, but it was attributed to the lower adsorption rate and lower activity of the catalyst. The trimetallic catalysts used for gasification were quite active. A NiCoMo/SiO₂-Al₂O₃ catalyst ran for over 1000 hours in the laboratory gasifier at 750°C and retained its activity for converting tars and for the water-gas shift reaction. Its activity for methane-reforming was reduced significantly in the first 100 hours, but no additional loss of activity was noted thereafter. After 100 hours the catalyst had accumulated 7 wt% carbon; however, by the end of the run only 4 wt% remained.

Work on methanation reactions with a NiCu bimetallic catalyst demonstrated that copper dilutes the nickel sites, thus inhibiting carbon formation (Araki and Poniec 1976). A bimetallic NiCu catalyst shows higher rates for cyclohexane dehydrogenation than does pure nickel. Some investigators have attributed this effect to less carbon fouling of the bimetallic surface compared to the pure metal (Cusumano, Dalla Betta, and Levy 1978).

Limited PDU data indicate that coking on the NiCuMo/SiO₂-Al₂O₃ catalyst may be much more severe than was experienced in the laboratory gasifier. In the gas-phase reactor studies, carbon deposition was similar to that experienced in the laboratory gasifier (as shown in Table 22) except at low steam rates with phenol, where coking was quite substantial. Schafizadeh and Fu (1973) and Milne, Evans, and Solty (1983) have concluded that tar is the primary product of pyrolysis at high temperatures and that a large percentage of the gases and char produced at high temperatures is formed from secondary reactions of tar. This tar is very reactive and likely to form carbon (much of the tar is converted to gases and char even without a catalyst present). At 750°C in the laboratory the secondary reactions of tar take place before the product gas contacts the catalyst and coking on the catalyst is limited. In the PDU

the primary tar contacts the catalyst immediately and the large quantity of tar produced results in a low steam/tar ratio. This may produce the same effect as did the reduction of the steam/phenol ratio in the model compound studies discussed earlier.

The increased coking at low steam rates may be the result of increased coking from thermal cracking or it may be that the steam/tar (phenol) ratio has dropped below the critical ratio for whisker carbon formation. Rapid whisker carbon formation can physically break down the catalyst (Rostrup-Nielsen 1982). If this type of carbon is formed in PDU operations it may explain the high attrition rate noted in the PDU.

If the increased coking is due to thermal cracking on the support, catalysts with non-acidic supports, such as G-90C, should be effective. Doping with alkali or using magnesia-supported catalysts should also reduce coking. Alkali reduces the acidity of supports and increases steam adsorption on the support, thereby increasing the rate of carbon gasification. Tests on the effect of doping nickel catalysts with alkali in laboratory gasification studies have produced inconclusive results. In addition, alkalis will be fairly mobile at 750°C and will eventually be lost. Magnesia supports have also enhanced adsorption and have been used successfully for naptha steam-reforming.

If the increased coking is due to whisker carbon growth the solution may be more difficult. Raising the steam rate affects the product gas composition so there is little flexibility in adjusting the steam/tar ratio. Doping with alkali or using magnesia-supported catalysts should help; however, their effects are limited. Placing the catalyst in a secondary reactor and allowing the secondary tar reactions to take place in the gasifier should solve the problem. This is essentially what happens in the laboratory gasification system, where long catalyst lifetimes have been demonstrated.

Low-Temperature Coking (550°C). At lower temperatures more favorable to the production of methane-rich gas, pyrolysis or cracking on the support is probably not significant (Rostrup-Nielsen 1975, 1982; Trimm 1977). However, carbon deposition is considerably more severe than at 750°C, suggesting that a different mechanism for carbon deposition may be involved. In this lower temperature range whisker carbon formation is suspected to be the major type of

carbon deposition. SEM studies of catalysts used at 550°C are planned to verify this conclusion. If whisker carbon growth is the cause the only solution would appear to be to significantly increase the steam rate. This may not be economic in terms of the process, however, because additional steam will cost more and will reduce the equilibrium yield of methane.

REFERENCES

- Albright, L. F., C. F. McConnell, and K. Welther. 1979. "Types of Coke Formed During Pyrolysis of Light Hydrocarbons." Am. Chem. Soc. Adv. Chem. Ser. 183:175-191.
- Anonymous. 1983. "French Fertilizer Manufacturer Testing New Biomass-Gasification Process." Chem. Eng., May 16, p. 17.
- Araki, M., and V. Ponec. 1976. "Methanation of Carbon Monoxide on Nickel and Nickel Copper Alloys." J. Catalysis 44:439-448.
- Baker, E. G., and M. D. Brown. 1984. Catalytic Gasification of Bagasse for the Production of Methanol. PNL-5100, Pacific Northwest Laboratory, Richland, Washington.
- Baker, E. G., et al. 1983. "Methanol Synthesis Gas from Wood Gasification." Energy Progress 3(4):226-229.
- Bhatta, K. S. M., and G. M. Dixon. 1969. Ind. Eng. Chem. Prod. Res. Dev. 8:324.
- Cabrera, A. L., H. Heinemann, and G. A. Somorjai. 1982. J. Catalysis 75:7.
- Cox, J. L., and L. J. Sealock, Jr. 1974. "Sulfur Problems in the Direct Catalytic Production of Methane from Coal-Steam Reactions." Prepr. Am. Chem. Soc. Div. Fuel Chem. 19(1):64-78.
- Cusumano, J. A., R. A. Dalla Betta, and R. B. Levy. 1978. Catalysis in Coal Conversion. Academic Press, New York.
- Ekstrom, C., N. Lindman, and R. Pettersson. 1982. "Catalytic Conversion of Tars, Carbon Black, and Methane from Pyrolysis/Gasification of Biomass." Presented at The Fundamentals of Thermochemical Biomass Conversion Conference, October 19-22, Estes Park, Colorado.
- Fant, B. T., and C. A. Euker, Jr. 1980. "Exxon's Catalytic Coal Gasification Process." Proceedings of the First International Research Conference. Gas Research Institute, Chicago, Illinois.
- Furlong, L. E., and N. C. Nahas. 1978. "Catalytic Coal Gasification - Process Research and Development." Proceedings of the Tenth Synthetic Pipeline Symposium. Gas Research Institute, Chicago, Illinois.
- Gates, B. C., J. R. Katzer, and G. C. A. Schuit. 1979. Chemistry of Catalytic Processes. McGraw-Hill, New York.
- Gregg, S. J. 1965. The Surface Chemistry of Solids. Chapman and Hall, London.

- Hallen, R. T., L. J. Sealock, and R. Cuello. 1982. "Influence of Alkali Carbonates on Biomass Volatilization." Presented at The Fundamentals of Thermochemical Biomass Conversion Conference, October 18-22, Estes Park, Colorado.
- Hawley, M. C., et al. 1983. "Gasification of Wood Char and Effects of Intraparticle Transport." Fuel 62:213-216.
- Haynes, W. P., S. J. Gasior, and A. J. Forney. 1974. "Catalysis of Coal Gasification at Elevated Pressure." Am. Chem. Soc. Adv. Chem. Ser. 131:179.
- Hoffman, E. J., et al. 1972. "Behavior of Nickel Methanation Catalysts in Coal-Steam Reactions." Am. Chem. Soc. Div. Fuel Chem. Prepr. 16(2):64-67.
- Kono, H. 1980. "A New Concept for Three-Phase Fluidized Beds." Hydrocarbon Processing, January, pp. 123-129.
- Kosky, P. G., et al. 1982. Coal Gasification Catalysis Mechanisms. DOE/MC/14591-1397, General Electric Company, Schenectady, New York.
- Lindman, N., et al. 1981. "A New Synthesis Gas Process for Biomass and Peat." Proceedings of the Fifth Energy from Biomass and Wastes Symposium, Institute of Gas Technology, Chicago, Illinois.
- Marschner, F., and H. J. Renner. 1982. "Naphtha Reforming." Hydrocarbon Processing, April, pp. 176-180.
- McCarty, J. G., et al. 1981. Hydrocarbon Reforming for Hydrogen Fuel Cells. DOE/MC/11323-T2. SRI International, Menlo Park, California.
- McCoy, L. R. 1983. Investigations of Coal Gasification Catalysis Reaction Mechanisms. DOE/MC/14592-1419. Energy Systems Research Group, Albany, New York, and Rockwell International Corporation, Thousand Oaks, California.
- McKee, D. W. 1983. "Mechanisms of Alkali Metal Catalyzed Gasification of Carbon." Fuel 62(2):170-175.
- McKee, D. W., et al. 1983. "Catalysis of Coal Char Gasification by Alkali Metal Salts." Fuel 62(2):217-220.
- Milne, T. A., R. J. Evans, and S. Solty. 1983. Fundamental Pyrolysis Studies, Quarterly Report March - May. Solar Energy Research Institute, Golden, Colorado.
- Mitchell, D. H., et al. 1980. "Methane/Methanol by Catalytic Gasification of Biomass." Chem. Eng. Prog. 76(9):53-57.
- Mudge, L. K., L. J. Sealock, Jr., and S. L. Weber. 1979. "Catalyzed Steam Gasification of Biomass." J. Anal. Appl. Pyrolysis 1:165-175.

- Mudge, L. K., et al. 1981. Investigations on Catalyzed Steam Gasification of Biomass (Including Appendices A, B, C, and D), PNL-3695, Pacific Northwest Laboratory, Richland, Washington.
- Mudge, L. K., et al. 1983. Catalytic Gasification Studies in a Pressurized Fluid Bed Unit. PNL-4594, Pacific Northwest Laboratory, Richland, Washington.
- Nahas, N. C., and J. E. Gallagher. 1978. Proc. 13th Energy Conv. Eng. Conf. 3:2143.
- Nahas, N. C. 1983. "Exxon Catalytic Coal Gasification Process." Fuel 62(2):239-241.
- Pederson, K., A. Skov, and J. R. Rostrup-Nielson. 1980. "Catalytic Aspects of High Temperature Methanation." Prepr. Am. Chem. Soc. Div. Fuel Chem. 25(2):89-99.
- Ross, R. A., and P. Fong. 1981. "Catalytic Conversion of Wood Barks to Fuel Gas." Ind. Eng. Chem. Prod. Res. Dev. 20:197-203.
- Rostrup-Nielson, J. R. 1975. Steam Reforming Catalysts. Danish Technical Press, Copenhagen.
- Rostrup-Nielson, J. R. 1977. "Hydrogen via Steam Reforming of Naptha." Chem. Eng. Prog. 73:87-92.
- Rostrup-Nielson, J. R. 1982. "Criteria for Carbon Formation." NATO Adv. Study Inst. Ser., Series E, 54:127-149.
- Rostrup-Nielson, J. R., and D. L. Trimm. 1977. "Mechanisms of Carbon Formation on Nickel-Containing Catalysts." J. Catalysis, 48:155-165.
- Satterfield, C. N. 1980. Heterogeneous Catalysis in Practice. McGraw-Hill, New York.
- Sealock, L. J., et al. 1981. Kinetics and Catalysis of Producing Synthetic Gases from Biomass. Annual Report. GRI-80/0116, Battelle, Pacific Northwest Laboratories, Richland, Washington.
- Sealock, L. J., D. C. Elliott, and R. T. Hallen. 1982. Kinetics and Catalysis of Producing Synthetic Gases from Biomass. Final Report. GRI-82/0038, Battelle, Pacific Northwest Laboratories, Richland, Washington.
- Schafizadeh, F., and Y. L. Fu. 1973. "Pyrolysis of Cellulose." Carbohydr. Res. 29:113.
- Schafizadeh, F. 1982. "Introduction to Pyrolysis of Biomass." J. Anal. Appl. Pyrolysis 3:283.

- Stern, E. W. 1982. Bench-Scale Development of Catalysts for Reforming Aromatic and Heterocyclic Hydrocarbons. DOE/ET/11029-1191, Englehard Corporation, Edison, New Jersey.
- Taylor, H. S., and H. A. Neville. 1921. J. Am. Chem. Soc. 43:2065.
- Thomas, C. L. 1979. Catalytic Processes and Proven Catalysts. Academic Press, New York.
- Tran, D. Q., and C. Rai. 1978. "A Kinetic Model for Pyrolysis of Douglas Fir Bark." Fuel 57:293-298.
- Trimm, D. L. 1977. "Formation and Removal of Coke from Nickel Catalysts." Catal. Rev.-Sci. Eng. 16:155-189.
- Venuto, P. B., and E. T. Habib, Jr. 1979. Fluid Catalytic Cracking with Zeolite Catalysts. Marcel Dekker, New York.
- Veraa, M. J., and A. T. Bell. 1978. "Effect of Alkali Metal Catalysts on Gasification of Coal Char." Fuel 57:194-200.
- Walker, P. L., et al. 1983. "Catalysis of Coal-Derived Cokes and Chars." Fuel 62(2):140-149.
- Wen, W. Y. 1980. "Mechanisms of Alkali Metal Catalysis in the Gasification of Coal, Char, or Graphite." Catal. Rev.-Sci. Eng. 22(1):1-28.
- Wen, W. Y. 1983. Thermal and Catalytic Cracking of Tars and Tar Constituents from Coal Gasification Processes. DOE/MC/14385-1484, Clark University, Worcester, Massachusetts.
- Wen, C. Y., and S. Dutta. 1978. "Research Needs for the Analysis, Design, and Scale-up of Fluidized Beds." AIChE Symposium Series 161(73):1-8.
- Willson, W. G., et al. 1974. "Alkali Carbonate and Nickel Catalysis of Coal-Steam Gasification." Am. Chem. Soc. Adv. Chem. Ser. 131:203.
- Winter, E. M., N. D. Malcosky, and C. C. Hong. 1982. Catalytic Enhancement of Coal Gasification. DOE/ET/11027-1303, Columbia Gas Systems, Columbus, Ohio.
- Wood, B. J., et al. 1983. The Mechanisms of Catalytic Gasification of Coal Char. DOE/MC/14593-1416, SRI International, Menlo Park, California.
- Yamazaki, K., et al. 1983. "Catalytic Gasification of Wood for Methanol Synthesis Gas." Chemistry Letters 1029-1032.
- Yokayama, S., et al. 1983. "Efficient Gasification of Cellulose for the Production of Hydrogen and Carbon Monoxide." Chemistry Letters 151-154.

APPENDIX A

GAS-PHASE REACTOR STUDIES WITH SECONDARY CATALYSTS

TABLE A.1. Results of Fixed-Bed Gas-Phase Reactor Studies

Run	Date	Catalyst	Feed	Temperature, °C	Space Velocity, vol. [feed + H ₂ O] [h] (vol. cat.)	g Steam g Feed	Moles Steam Moles Carbon	wt% Carbon on Catalyst	% Converted	% Unconverted	% Char
1	1-5	NiCuMo/SiO ₂ -Al ₂ O ₃	CH ₄	750	2540	2.9	2.6	1.3	89	10	1
2	7-6	(SMR-2)	CH ₄	750	2160/4130	5.6/5.8	5.0/5.1	1.1	97	1	2
3	1-6		C ₂ H ₄	750	2170	3.6	2.8	6.4	91	0	9
4	1-18		phenol	750	1980	6.7	5.8	3.4	96	0	4
5	1-7		CO/H ₂	750	3120	1.8	2.8	0.1	--	--	--
6	4-27		CH ₄	650	1710/2410	4.3/3.9	3.8/3.4	0.06	98	2	0
7	5-3		CH ₄	550	2200/2410	5.9/3.9	4.8/3.4	0.16	34	66	0
8	5-18	{previously used for C ₂ H ₄ run 3}	CH ₄	750	2520/2680	6.0/4.0	5.3/3.6	3.9	100	0	0
9	7-8		phenol	750	1900/3520/5560	5.3/5.0/5.1	4.7/4.4/4.5	6.3-	94/94/89	<1/trace/5	6/6/6
10	7-13		phenol	650/550	1900	5.1	4.4	5.5	92/84	0.5/trace	7/16
11	7-29	{previously used for phenol run 9}	CH ₄	750	2210	5.2	4.6	4.3-	88	2	10
12	8-5		CH ₄ /phenol	750	1940	2.8	2.5	--	94	0	6
13	8-8		CH ₄ /phenol	750	1960	2.8	2.4	00	95	0.4	4
14	8-9		CH ₄ /phenol	750	2070	2.4	2.1	17.2	90	3	7
15	9-2		CH ₄ /phenol	750	10,680	3.0	2.6	12.6	26	65	9
16	9-8		phenol	750	4320	1.3	1.2	22.4	17	77	6
17	9-13		phenol	750	1130	1.4	1.2	18.9	28	53	19
18	9-21	{doped with 2 wt% Na ₂ CO ₃ }	phenol	750	2110	6.5	5.7	1.2	97	2	1
19	9-23		phenol	750	2350	4.2	3.7	0.4	98	0.4	1.5
20	9-27	{crushed}	phenol	750	2430	4.2	3.6	1.6	98	0.5	1.2

TABLE A.1. (contd)

Run	Date	Catalyst	Feed	Temperature, °C	Space Velocity, vol. (feed + H ₂ O) {h}{vol. cat.}	g Steam g Feed	Moles Steam Moles Carbon	wt% Carbon on Catalyst	% Converted	% Unconverted	% Char
21	2-17	<u>K₂CO₃/Al₂O₃</u>	CH ₄	750	1970	6.1	5.4	0	0.2	99.8	0
22	3-22		C ₂ H ₄	750	1940	3.1	2.4	--	9	91	0
23	2-2		phenol	750	1700	6.2	5.4	21.0	72	12	16
24	2-25	Ni/Ceramic (G-90C <u>broken up</u>)	CH ₄	750	2910/3500	5.8/2.5	5.1/2.2	0.05	99	1	0
25	3-4		phenol	750	2410	5.9	5.2	0.4	99	0	1
26	4-19		C ₂ H ₄	750	2850/3140	3.2/2.1	2.5/1.7	0.1	99	1	0
27	6-22	<u>Ni-1404 1/8"</u>	CH ₄	750	3690	6.7	5.9	0.09	98	1.3	0.5
28	6-24		C ₂ H ₄	750	3650	3.7	2.9	.88	94	~0.2	6
29	6-29		phenol	750	3380	3.8	3.3	.52	94	~0.4	6
30	7-18	<u>Zeolite (LZ-Y-82 1/16")</u>	phenol	750	1330	4.0	3.5	15.4	45	43	12
31	7-22		CH ₄	750	1530	5.0	4.5	0.2	1	99	0
32	7-26	<u>Ni/Mo (HT-100E 1/16")</u>	phenol	750	1910	4.0	3.5	20.2	65	13	21

APPENDIX B

DATA FROM FIXED-BED LABORATORY TESTS

TABLE B.1. Results of Primary Catalyst Tests in Continuous Laboratory Reactor

Run	Temperature, °C	wt Steam/ wt Wood	Catalyst and Loading, wt%	Residence Time, min	Gas Composition						Carbon Conversion		
					H ₂	CO ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	CO	Gas	Char	Tar ^(a)
1A	750	1.0	--	55	46	26	7.1	1.6	0.5	19	80	16	4
3	750	0.9	17 K ₂ CO ₃	18	52	25	5.4	1.0	0.6	15	73	27	0.1
4	750	1.0	17 K ₂ CO ₃	11	52	25	5.2	1.0	0.6	15	70	30	tr
4A	750	0.9	17 K ₂ CO ₃	34	53	24	5.1	1.0	0.5	17	77	23	tr
5	750	1.1	13 Na ₂ CO ₃	50	51	26	5.9	1.0	0.6	16	73	27	tr
6	750	1.0	13 Na ₂ CO ₃	17	50	25	6.3	1.1	0.7	16	66	34	tr
9	750	1.1	8.5 K ₃ CO ₃	21	53	27	5.3	1.0	0.5	14	69	31	tr
11	750	1.2	8.5 K ₃ CO ₃	24	54	24	4.3	0.8	0.4	17	85	15	tr
12	750	1.1	8.5 K ₂ CO ₃	7	51	27	6.6	1.2	0.6	14	65	35	tr
13	750	1.1	8.5 K ₂ CO ₃	50	53	25	4.4	0.9	0.5	17	83	17	tr
16	750	1.1	6.5 Na ₂ CO ₃	49	55	24	5.3	0.8	0.3	14	84	16	tr
17	750	1.2	6.5 Na ₂ CO ₃	49	54	26	6.1	1.0	0.5	13	71	29	tr
18	750	1.2	6.5 Na ₂ CO ₃	10	52	27	6.6	1.1	0.5	12	66	34	tr
19	750	1.1	6.5 Na ₂ CO ₃	21	53	26	5.8	1.0	0.5	14	72	28	tr
20	750	1.3	--	15	39	29	10.9	2.4	0.9	18	57	32	11
21	750	1.2	--	4	37	28	11.9	2.5	0.6	20	47	42	11
22	750	1.7	--	29	45	26	9.3	2.0	0.5	17	68	27	5 ^(b)
23	750	4.0	17 K ₂ CO ₃	10	56	31	5.3	1.2	0.3	7	71	29	tr
24	750	4.3	17 K ₂ CO ₃	24	58	29	4.6	1.0	0.3	7	84	16	tr
25	750	3.7	17 K ₂ CO ₃	18	59	29	4.3	1.0	0.3	7	80	20	tr
26	750	1.1	17 K ₂ CO ₃	82	54	24	4.9	1.0	0.4	15	81	19	tr
27	750	0.6	17 K ₂ CO ₃	26	51	17	4.3	0.7	0.5	26	83	17	tr
28	750	0.6	17 K ₂ CO ₃	34	52	20	5.5	1.0	0.4	21	72	28	tr
29	650	1.1	17 K ₂ CO ₃	213	57	26	4.3	0.4	0.5	11	61	37	2
30	650	1.0	17 K ₂ CO ₃	108	55	27	5.0	0.6	0.6	11	52	48	1
31	650	1.2	17 K ₂ CO ₃	82	31	40	8.6	1.5	1.0	18	28	63	9
32 ^(c)	750	1.5	17 K ₂ CO ₃	16	52	30	7.2	1.7	0.6	9	52	48	tr
33	750	1.0	17 K ₂ CO ₃	12	48	28	7.6	1.7	0.5	13	50	50	tr

B.1

TABLE B.1. (contd)

Run	Temperature, °C	wt Steam/ wt Wood	Catalyst and Loading, wt%	Residence Time, min	Gas Composition						Carbon Conversion		
					H ₂	CO ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	CO	Gas	Char	Tar ^(a)
34	750	1.3	17 K ₂ CO ₃	13	57	22	2.9	0.7	0.4	17	79	21	tr
35 ^(c)	750	1.0	17 K ₂ CO ₃	65	56	23	3.2	0.7	0.4	17	86	14	tr
36 ^(c)	750	0.7	17 K ₂ CO ₃	167	56	17	1.7	0.6	0.3	24	81	19	tr
38	750	0.8	17 K ₂ CO ₃	44	55	18	2.4	0.9	0.5	23	80	20	tr
39 ^(c)	750	1.1	8.5 K ₂ CO ₃	24	47	28	4.1	1.6	0.8	18	60	40	tr
40 ^(c)	650	0.9	8.5 K ₂ CO ₃	288	54	28	5.1	0.7	0.6	13	63	35	2
41 ^(c)	650	1.0	8.5 K ₂ CO ₃	19	50	29	7.1	1.1	1.1	12	50	50	tr
42	750	--	8.5 K ₂ CO ₃	103	38	15	10.0	1.8	1.3	34	54	45	1
43	750	--	--	167	19	14	17.4	3.8	1.4	45	39	52	11

(a) Includes tar and water-soluble organics. "tr" indicates that the quantity was less than 1 wt% of original carbon, and probably less than 0.1 wt%.

(b) Soluble organics not included.

(c) Feed material was densified pine flakes. All other runs with maple/alder headrig sawdust.

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