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CATALYZED STEAM GASIFICATION OF BIOMASS. PHASE II

Final Research Report

MASTER

By
Roger H. Hooverman

May 24, 1979
Date Submitted

Work Performed Under Contract No. ET-78-C-02-4736

Wright-Malta Corporation
Ballston Spa, New York

U.S. Department of Energy

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Catalyzed Steam Gasification of Biomass
Phase II

Work performed for
Biomass Energy Systems Branch
Division of Solar Technology
U.S. Department of Energy

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FINAL RESEARCH REPORT
REPORT NO. COO/4736-12

by Roger H. Hooverman

Submitted May 24, 1979

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SUMMARY

The Wright-Malta gasification process is characterized by low-temperature, catalyzed steam gasification in a pressurized rotary kiln.

Fresh biomass moves slowly and continuously through the kiln, where it is gradually heated to around 1200°F in an atmosphere of 300 psi steam. During its traverse, pyrolysis and reaction of steam with the nascent char convert nearly all of the organic solids to the gaseous phase. The volatile pyrolysis products pass through the kiln co-currently with the solids and are similarly cracked and steam-reformed within the kiln to fixed gases. Heat for the gasification process is provided by sensible heat recovered from the product gas and the wood decomposition exotherm, making the process inherently very energy-efficient.

This report summarizes the work done during the experimental, laboratory-scale phase of development of the W-M biomass gasification process. Two bench-scale experimental gasifiers were constructed and tested: the "minikiln", a batch-feed, rotating autoclave; and the "biogasser", a stationary, continuous-feed, tubular reactor with zone heating and auger transport.

Studies were carried out in these reactors to determine the extent of conversion of biomass solids to gas, and the makeup of the product gas, over a wide range of process conditions. The process variables that were investigated included reactor pressure and temperature, catalyst type and concentration, moisture content and type of biomass feed.

Further studies, both experimental and theoretical, established the heat requirements for the process and the heat transfer properties of the biomass materials within the kiln.

This phase of the work has proven the process and has indicated the preferred conditions for reactor operation as follows:

The best feed for the biomass gasifier is a fast-growing open wood like poplar or a non-woody biomass, with a moisture content about 50% by weight. The best catalysts are the soluble alkaline carbonates, their effectiveness increasing linearly with concentration up to and beyond 10% by weight. Reactor pressure exhibits a broad optimum around 300 psi, which is about the maximum pressure desired for practical reactor design. A maximum temperature in the neighborhood of 1200°F is found to be adequate for nearly complete gasification of biomass, and it appears that the heat derivable from product gas and exotherm will be sufficient to attain this in a commercial reactor.

Under optimum conditions, about 95% of the mass, or 90% of the fuel value, of the organic feed can be converted into gas. The product gas is a clean mixture of fixed gases, principally CH₄, CO₂, H₂, and water vapor, with a composition close to that of an equilibrium mixture at the given pressure and temperature. Its heating value is typically around 300 Btu/scf, and it is suitable for use either as a fuel or as a chemical feedstock.

The next phase of the work will be a scaling up of the process, with the construction and testing of a 6 ton/day process development unit.

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SECTION I

INTRODUCTION TO THE W-M GASIFICATION PROCESS

A. Highlights of the W-M Process

There is no need in this report to reiterate our nation's need to develop alternate sources of energy and chemical feedstocks. Nor is there need to point out the potential inherent in our largely untapped resources of biomass and organic wastes. The question before us is only how to best utilize these resources--to develop practical and commercially viable processes to recover energy and chemicals from our forestry and farm residues, our municipal and industrial wastes, and the future harvests from dedicated biomass plantations.

Since 1973, Wright-Malta Corporation has been developing such a process.

The W-M process can be characterized as low-temperature catalyzed steam gasification. Fresh biomass, or other organic material, is heated slowly in the presence of adequate moisture and alkaline catalyst, at a pressure of several hundred psi. By a combination of pyrolysis and steam-gasification, nearly complete conversion of organic solids to low-Btu gas is achieved, at temperatures no higher than about 1200°F. Under typical conditions as much as 95% of the mass of the organic solids, or 90% of its fuel value, can be recovered in the gas.

The pyrolysis gases flow through the kiln co-currently with the solids, and are themselves fully cracked and steam-reformed within the reactor. The product gas thus consists entirely of low-molecular-weight fixed gases; principally methane, ethane, hydrogen, carbon monoxide and dioxide, and water vapor.

Because the W-M process involves steam-gasification, rather than combustion, it can accept feeds with a high moisture content--up to 50% or more by weight. And there is no need for fine shredding, pelletizing, or (in the case of municipal wastes) classification and removal of the inorganic fraction. Fresh wood chips make an ideal feed, as does a mixture of equal parts coarsely shredded municipal solid waste and sewage sludge.

The W-M system is thermally very closely coupled. For a gas plant, the process heat is provided by the sensible heat of the product gas, plus the heat generated by the cellulose decomposition exotherm. When the gasifier is coupled to a gas turbine generator for power production, the "waste" heat from the turbine exhaust provides the process heat. In either case, the W-M system achieves a very high thermal efficiency--up to 83% for the gasifier alone, around 38% for the complete power system.

A W-M plant is also environmentally attractive: It is non-polluting, and the economics of scale are such to encourage small, scattered plants, close to the sources of waste or biomass.

Lastly, preliminary economic analyses have concluded that a W-M plant will be economically profitable. An updated, independent analysis by Bechtel, Inc. will be presented in a separate report as part of the current contract.

This report concentrates on the application of the W-M process to biomass gasification, with fuel gas or chemical feedstock as the product. For a discussion of the W-M power system, fueled by municipal solid and liquid wastes, see: "Power from Wastes by Steam Gasification", JA Coffman and RH Hooverman, ACS Symposium Series No. 76, Jerry L. Jones & Shirley Radding, eds., 1978.

B. A W-M Gasification Plant

Figure 1 is a schematic drawing of a W-M biomass gasification plant. This particular drawing shows the proposed PDU, which will be described in greater detail in an accompanying report. But the same principles will apply to a commercial plant.

To describe how it operates, let us follow a sample of biomass as it moves through the system and is converted into char/ash and gas.

The biomass, normally fresh wood chips, is delivered to the plant on a regular schedule. It may be stored, blended for greater uniformity, or loaded directly into the feed hopper.

W-M BIOMASS GASIFIER SCHEMATIC

Figure 1

A conveyor system carries the biomass from the hopper to the kiln feed system at a controlled rate. Sensors along the conveyor measure both the weight and the moisture content of the feed, both quantities which must be monitored and controlled to assure uniform quantity and quality of product gas. The appropriate proportion of catalyst is sprinkled over the biomass as it passes along the conveyor (not shown).

The feed system is a double-seal system devised by W-M to solve the problem of feeding wood chips into a pressurized system without loss of gas or unacceptable expenditure of energy.

The upper part of the kiln feed system consists of a vertical standpipe, closed by a sealing piston at the top and a ball valve at the bottom. At the beginning of the feed cycle, the conveyor moves a measured amount of biomass and catalyst into this standpipe through a side opening; and then the piston moves down past the opening, closing it off, but not moving so far as to compress the biomass.

The ball valve then opens, presenting a diameter larger than the standpipe, and the biomass falls through the expanding conic section below. The low length/diameter ratio of the standpipe, the increasing diameter of the ball valve, and the conical shape of the lower chamber are all designed to prevent bridging of the charge.

A continuously running auger then feeds the charge into the rotary kiln.

The piston then extends to its full stroke position, flush with the surface of the ball valve, forcing the high-pressure kiln gas from the upper standpipe with much less energy consumption than a conventional pump.

The ball valve is closed and the piston retracted to its full height, completing the feed cycle.

A predictive controller (not shown) controls the frequency of the feed cycle, the speed of the conveyor screw, and the speed of rotation of the kiln.

Within the kiln, lifting and tumbling, the biomass moves forward by gravity and is slowly exposed to higher and higher temperatures.

Around 350°F it begins to thermally decompose, releasing a complex mixture of volatile tars and organic liquids, as well as oxides of carbon and water vapor. Methane starts evolving about 500°F, hydrogen shortly thereafter. Above 900°F, the reactive, nascent char begins reacting with the abundant steam, yielding more H₂ and CO₂. The presence of high pressure steam and alkaline catalyst greatly enhances the conversion of solids to gas. By the time the charge has reached the far end of the kiln, and temperature around 1200°F, nearly all of the initial mass of biomass has been converted to gas.

Meanwhile, the gaseous pyrolysis products are also passing through the kiln, being exposed to higher and higher temperatures and being further cracked and steam-reformed. By the time they have reached the 1200°F end of the kiln, they are completely converted to simple molecules of fixed gases: carbon dioxide and monoxide, hydrogen and methane, with traces of lighter hydrocarbons.

The dwell time in the reactor is about one hour for the solids, a few minutes for the gases.

Ash and residual char are removed from the hot end of the kiln through the ash dump system shown in the diagram. It consists of a pair of ball valves, connected by a short chamber, all rotating with the kiln. The dump cycle takes two revolutions of the kiln. On the first revolution, solid residue falls through the first ball valve into the intermediate chamber. Then the first valve is closed and the pressurized product gas trapped in the chamber is drawn off and utilized to help fuel the boiler/superheater. On the second revolution, the second ball valve is opened, dropping the hot residue onto the ash conveyor.

Upon exposure to air, the small amount of remaining char is quickly consumed, freeing the original catalyst and the wood ash.(itself a catalyst) to be recycled.

The steam boiler/superheater serves primarily to heat the kiln during startup and checkout. In addition, during normal operation, it provides an intermittent backflow of steam to clean the gas filter.

The hot product gas exits through this gas filter, into a plenum at the end of the kiln, and then back into a jacket of coils (or, alternatively, a vaned annular space) surrounding the kiln. The product gas flows through these coils, countercurrently to the charge, from the hotter end of the kiln to the cooler giving up most of its sensible (and latent) heat to the charge within.

The cross-section inset shows the kiln structure: an inner pressure vessel in which the gasification of the biomass occurs, the outer jacket carrying the returning product gas, and outside this a thick layer of insulation.

It is the sensible heat of the product gas, plus the heat liberated in the wood decomposition exotherm, which provides the process heat for the gasification reactions. No additional fuel is consumed. It is this tight thermal coupling and the relatively low reactor temperatures (made possible by the relatively long dwell time) that provides the very favorable overall thermal efficiency of the gasifier.

The cooled product gas leaves the kiln through a sliding seal, and is passed through a condenser to remove the water vapor. The product gas now has a variety of potential applications: as a medium-Btu fuel gas for industrial processes or power generation, or as a feedstock for a number of chemical processes that at present utilize natural gas.

C. Overall Status of W-M Gasifier Project

With the publication of this report, W-M completes the bench-scale experimentation phase of the development of the W-M gasification system.

This work has proven the process, in both batch- and continuous-feed reactors. It has established the minimum conditions for satisfactory gasifier operation, and the quantitative effects of varying process parameters. It has laid the experimental foundation for modeling a commercial plant, including projection of optimum process conditions, establishment of heat cycles and flow charts, and estimation of process efficiency and economic return. In addition, the bench-scale work has provided invaluable technical experience in the mechanical aspects of constructing and operating a pressurized gasifier.

The major contracts completed to date are as follows:

<u>Contract Title</u>	<u>Contract Date</u>	<u>Contractor</u>
■ Construction and Testing of Minikiln Gasifier	7/23/75	Empire State Electric Energy Research Corp. (NY State Utilities)
■ Gasification of Municipal Waste and Sewage Sludge in Minikiln	10/24/75	US EPA
■ Gasification of Coals in Minikiln	3/12/76	NYS Energy Research & Development Authority
■ Engineering Analysis of Power System	4/1/76	US ERDA-Conservation Research & Technology
■ Construction and Testing of Biogasser	9/22/76	US ERDA-Fuels from Biomass Branch, Div. of Solar Energy
■ Continuation Contract- Construction & Testing of Biogasser	1/1/78	US Department of Energy, Biomass Energy Systems, Div. of Solar Technology
I: Biogasser Experimentation		
II: PDU Design		
III: Techno-economic analysis		

This report describes the experimental work and the related analyses carried out under Task I of the final contract. For completeness, it also reviews the major experimental findings from the earlier work so as to provide a definitive summary of the results of the first, laboratory-scale phase of the biomass gasification project.

Separate reports are forthcoming on Task II of the contract, PDU Design, and on Task III, the Techno-economic Analysis.

The next phase of development of the Wright-Malta gasification system will be the construction and operation of a Process Development Unit, which will gasify nominally 6 ton/day of fresh biomass (wood chips). This plant will be built at the Malta Test Station, beginning this summer, with funding from the US Department of Energy, Division of Solar Technology, Biomass Energy Systems.

This gasifier will permit testing of the gasification process--specifically the process chemistry, materials flow, and heat transfer--at the pilot plant scale. It will also provide experience with the technical and mechanical aspects of a larger scale continuous-feed, pressurized gasifier. The experience from this biomass PDU will be applicable to the solid waste program, as well as to the biomass program; and from the PDU it should be possible to proceed directly to commercial-scale plants of both kinds within a few years.

SECTION II

THE EXPERIMENTAL GASIFIERS

Two separate bench-scale gasifiers were used in the experimental work described here. The first was a batch-feed, rotating autoclave, the "minikiln". The second was a continuous-feed reactor, with auger transport, the "biogasser".

These two experimental gasifiers complement one another. The minikiln provides a differential view of the process, step by step, as the solid charge is dried, pyrolyzed, and steam-gasified. The biogasser provides an integrated view of the process and, unlike the minikiln, permits study of the cracking and steam-reforming of the volatile pyrolysis products, as they move on through the hotter parts of the reactor. The availability of both gasifiers has lent versatility to our test facilities, and both have been used in the present project.

This section describes the two experimental gasifiers and their operation.

A. The Minikiln

The minikiln gasifier was designed, built, and tested in 1975-76, with funds from the New York State utilities (ESEERCO) and the US EPA. Its original purpose was to study gasification of solid wastes and sludges; though it is a versatile reactor that can equally well be used to study biomass and other organic materials.

The minikiln is a bench-scale, batch-feed, rotating autoclave. One can think of this device as a segment of a long continuous-feed kiln. By appropriate programming of reactor temperature and atmosphere, one can simulate the passage of a portion of solid material through the longer kiln.

Figure 2 is a scale drawing of the minikiln, showing its major components. Figure 3 is a photograph of the minikiln in its test bay.

The gasification chamber itself is a cylindrical pressure vessel, about 3 feet long and 11 inches in inner diameter. It is constructed of 3/4 inch thick stainless steel, designed to sustain temperatures up to nominally 600°C (1100°F) and pressures up to nominally 3500 kPa (500 psi).

Figure 2
MINIKILN SCALE DRAWING

Figure 3

In an experimental run, the minikiln is loaded with a measured charge through the front port and the cover bolted in place. The drive motor turns the kiln at from one to ten rpm.

Heat is provided to the minikiln by an array of electric resistance heating rods, strapped about the outside of the gasification chamber. The heating rate is determined by the power applied: at maximum power, 24 kW, kiln and contents are raised to peak temperature in about one hour.

As the charge increases in temperature, the moisture evaporates, providing a high-pressure steam atmosphere: pyrolysis and emission of volatiles begin at about 150°C (300°F).

When the kiln pressure reaches a predetermined level, a pneumatic control valve can be opened, permitting excess steam and gases to escape through the hollow axial shaft projecting from the rear of the kiln. The gas flow is regulated throughout the rest of the run to maintain a constant pressure within the kiln. The gas emerges through a rotating valve, passes through a condenser, where it is cooled and the moisture and heavy organics are removed, and is then sampled by a gas chromatograph or flared.

The steam atmosphere within the minikiln is maintained by fresh steam provided by an auxiliary boiler and superheater. Superheated steam passes into the minikiln through a rotating seal, through an annular passage surrounding the axial exit shaft, into a plenum at the rear of the kiln, and thence through an array of perforated tubes lying along the inner wall of the kiln. A cam-operated array of poppet valves permits steam to enter only those tubes lying beneath the bed of solids at a given time, thus maximizing exposure of the solids to the hot steam.

High-pressure air can be injected through the same system, in order to investigate the effects of partial oxidation of the char.

Instrumentation throughout the system provides continuous reporting of the process conditions. A thermocouple projecting through the front plate measures the temperature of the gas within the kiln: this and the kiln pressure are recorded continuously throughout each run. Orifice flowmeters in the air and steam lines permit continuous monitoring of the flow of reactant gases into the kiln. A similar flowmeter in the exit gas line, beyond the condenser, gives a continuous measure of the non-condensable product gases issuing from the kiln. The fixed gases are periodically sampled and analyzed by a gas chromatograph. The condenser can be tapped at any time during a run for collection of the accumulated condensate.

The run continues until peak temperature, normally 600°C (1100°F) is reached. The system is then depressurized and allowed to cool overnight, after which the solid residue remaining in the kiln is removed, weighed and analyzed.

B. The Biogasser

The biogasser was constructed in 1977 with funding from US ERDA, later DOE, specifically for the biomass gasification studies reported herein. Unlike the minikiln, it is a continuous-feed gasifier: fresh biomass moves continually into the cooler end, gasifies as it moves through the reactor, and emerges from the hotter end as gas, ash and char. The biogasser was designed to test reactor pressures as high as 3200 psi (22000 kPa), and for this reason was constructed not as a rotating kiln but as a stationary tubular reactor with auger transport.

Figure 4 is a schematic of the biogasser, as it was originally designed and built, for the gasification of a wood-water slurry. The biomass slurry reservoir, at the left, is about 6 in. i.d. by 6 ft. high; the slanted tubular reactor is 1.77 in. i.d. by 10 ft. long; and the residue collector at the right is about 3 in. i.d. by 3 ft. high. The reactor is built of stainless steel, to minimize corrosion and provide strength at operating temperatures.

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Figure 4

At the beginning of a biogasser run, the fuel reservoir is filled from the top with sawdust or wood chips, water, and catalyst; and the piston and cap are put in place. Electric resistance heaters surrounding the reactor are turned on, and the power adjusted to bring the reactor up to the desired temperature profile, typically ranging from about 100°F at the feed end to about 1100°F at the collector end. The residue collector is also heated to prevent condensation.

Then the auger drive and the hydraulic pump driving the piston are started, and the mixture of wood and water moves from the reservoir into and slowly up the reactor. As the water evaporates, the pressure builds in the reactor, and when it reaches the desired level it is automatically held there by controlled release of gas from the reactor. As the biomass passes through the reactor barrel it dries and then pyrolyzes; the char reacts with the abundant steam, and the pyrolyses gases too pass on through the hotter part of the reactor, where they continue to crack and steam-reform. The final product gases are removed from the top of the residue collector, passed through a water-cooled condenser to remove the water vapor, and analysed with the gas chromatograph and/or flared. The condensate may be sampled at any time for presence of organic liquids or tars. The solid residue falls into the residue collector, from which it can be collected at the end of the run.

After a number of checkout and preliminary runs, it was decided that this initial version of the biogasser needed substantial modification. The most serious problem was with the slurry feed system: sawdust tended to bridge in the feed reservoir, whereupon the piston merely squeezed the water out of it. The only way to assure a constant flow of biomass into the reactor with this system was to wash it in by pumping water into the top of the reservoir, producing a large and uncontrollable water/biomass ratio.

Therefore, the biogasser was re-designed and largely rebuilt to make it a more useful experimental tool.

Figure 5 is a photograph of the modified biogasser, nearly completed in the W-M development shop. The fuel reservoir has been replaced with an external hopper and a double-lock system, which permits continuous feeding of dry or moist sawdust into the pressurized reactor. A similar feed mechanism is incorporated in the design for the process development unit, and is described in detail in that report.

Extending to the left, under its blanket of insulation, is the biogasser barrel, now horizontal. The electric heating units have been re-arranged to increase the original three independent heating zones to five, each covering two feet of the reactor's length. Additional thermocouples have been installed along the reactor wall. A new feed screw now extends the entire length of the barrel (the original screw extended only six feet, to minimize friction). At the far end, one can see the residue collector, now jutting forward for easier cleaning.

Most of the experimental biogasser work described in this report was performed with this second version of the equipment.

Figure 5

SECTION III

PROCESS STUDIES II

EFFECT OF PROCESS CONDITIONS ON SOLIDS CONVERSION

AA. Introduction

A principal goal of the present experimental study is to learn how the completeness of gasification of biomass depends on various process parameters. This information will then help establish the least extreme process conditions that still yield satisfactory levels of conversion of biomass to gas.

In determining "completeness" of gasification, there are two independent quantities that must be measured:

- The amount of char solids remaining after gasification. The char residue gives a direct measure of the weight of biomass solids converted into gas, or, equivalently, the fraction of the fuel value recovered.
- The amount of condensable organic liquids and tars remaining in the product gas. The pyrolysis products ought to be completely cracked and steam reformed to fixed gases (and water) so as to prevent condensation in the gas lines and provide a uniform product.

As it happens, these two determinations cannot easily be made in the same experiment. Best results are obtained using a different experimental gasifier for each.

Char residue is measured most precisely when the test is performed in the mini kiln, as this reactor can be brushed clean of all char residue after each run. In the big gasifier, char tends to build up on the screw, where it can be neither seen nor removed, and then to come free in later runs, making big gasifier residue collections often erratic and unreliable.

On the other hand, cracking of volatile pyrolysis products can be studied only in the big gasifier, where, as in the commercial process, all product gases pass through the hottest part of the reactor before exiting. In the mini kiln, product gases are removed from the reactor as soon as they are evolved, never see a higher temperature, and are given no opportunity for further reaction.

Thus, we have performed two quite distinct categories of gasification tests:

- Those tests designed to study the dependence of char residue on process conditions. Most of those tests were performed with the minikiln, and include studies of the effects of six different process parameters: maximum reactor temperature, reactor pressure, catalyst, type, catalyst concentration, and type of biomass. These are reported in this section.
- Those tests designed to study the cracking of volatiles and the final product gas composition, and their dependence on process conditions. These tests were of necessity all performed in the biogasser, and are described in the following section.

B. Dependence of Solids Conversion on Peak Reactor Temperature

1. Introduction

As the biomass charge moves through a commercial rotary kiln gasifier, to higher and higher temperatures, more and more of the solid charge is thermally decomposed and/or steam-gasified. Since it is highly desirable, from both economic and engineering standpoints, to operate a commercial gasifier at the lowest practical temperature, it is important to know how the completeness of gasification depends on increasing temperature.

The most thorough minikiln study of the temperature-dependence of gasification was performed in 1977 for the EPA, using shredded newspaper as the experimental charge. Newspaper and wood are chemically similar ligno-cellulosic materials, and behave very similarly in the gasifier; so the results of this study are applicable to biomass gasification.

2. Procedure

In these runs, the minikiln was loaded with 1 kg (2.2 lb) torn-up newspaper, about $\frac{1}{2}$ kg crushed limestone for breakers, and about 2 liters (4.4 lb) of water. In some of the runs, 100 g (10% by weight) Na_2CO_3 catalyst was added to the charge.

The kiln was then sealed and set rotating at 1.7 rpm. The minikiln was heated through the run with a uniform power input of 10 kW, giving an average heating rate of about $5^\circ\text{C}/\text{min}$. Kiln pressure was held at 1500 kPa (203 psig) by release of product gas and steam, and fresh steam was injected beneath the charge at a rate between 50 and 100 g/min.

Runs were terminated at various temperatures between 300°C ($\sim 600^\circ\text{F}$) and 600°C ($\sim 1100^\circ\text{F}$). The heating elements were turned off, the steam flow and rotation continued for several minutes to quench the reaction (the steam is cooler than the reactor or the charge); then rotation was stopped and the kiln vented to atmospheric pressure and left to cool overnight.

In the morning, the kiln was opened, the solid residue removed and weighed. The initial weight of the breakers and the known weight of paper ash (4%) was subtracted. Residue weights from catalyzed runs were also corrected for the amount of catalyst remaining in the char residue.

3. Results and Discussion

The results are shown in Figure 6, which shows char residue plotted against the maximum reactor temperature reached. Residue weights are shown as a percentage of the initial organic charge, on a moisture-, ash-free basis.

Two-thirds of the mass of the organic charge (not counting its moisture content) is already volatilized by around 350°C ($\sim 650^\circ\text{F}$). The residue weight begins to plateau at temperatures around 500°C ($\sim 900^\circ\text{F}$), but then begins to drop again around 600°C ($\sim 1100^\circ\text{F}$) due to reaction of steam with the char. At 600°C the (paper) residue in the catalyzed run has been reduced to around 5% of the initial organic charge.

Figure 66

RESIDUAL CHARGE AS FUNCTION OF PEAK
TEMPERATURE, PAPER AT 15000 kPa

The catalyst shows its effect even at the lower temperatures, and continues to exert its influence throughout the range of temperatures tested. This indicates that the catalyst affects several of the reactions comprising the overall gasification process.

44. The Steam-Charr Reaction

At around $500^{\circ}\text{C}/900^{\circ}\text{F}$, steam begins to react with the fresh charr, at an appreciable rate. That this reaction is occurring (and in fact predominating) is evidenced by analysis of the fixed gases being evolved, which show a composition 17.33CO_2 , 27.33H_2 . That the reaction is occurring at such low temperatures indicates that it is being initiated by continued scission of organic bonds, rather than by thermolysis of the water molecules. The onset of this reaction explains why the charr residue begins to decrease more rapidly with temperature in this region. Also, once this reaction has begun, gas continues to be evolved and charr continues to be consumed, even if the temperature ceases to rise.

From flowmeter observations, one can measure the rate at which evolution of H_2 and CO_2 increases with temperature, and thereby calculate an effective activation energy for the steam-charr reaction. One finds approximately:

for paper charr:	800 kcal/mole for	11 atm steam
400	155	300
for wood charr:	500	11
255	155	300

The dependence on pressure suggests that the charr formed at lower pressure is more reactive, possibly because it has been less completely gasified (see the next section).

Because of equipment limitations, tests were not run at peak temperatures above $600^{\circ}\text{C}/1100^{\circ}\text{F}$. But, if the observed behavior can be extrapolated, it appears that at only slightly higher temperatures, say 1200°F , the steam-charr reaction will almost completely consume the charr in a matter of minutes.

C. Effect of Reactor Pressure-Minikiln Study

1. Introduction

The pressure of steam in the reactor is also an important process parameter. Early exploratory experiments in the minikiln revealed that the pressure dependence of the process is strongly non-linear and that steam pressure and catalyst concentration are interrelated, in that the effect of pressure is greater at higher catalyst concentrations. Therefore, any experiment to test the effects of reactor pressure needed to examine at least three levels of pressure, and furthermore had to be planned in a block design, testing at least two concentrations of catalyst at every level of pressure.

The first such systematic study was done with the minikiln as part of the solid waste study for US EPA. That work was then supplemented with a biogasser study, exploring a wider range of pressures, within the present project for US DOE. These two studies are described in this and the following subsection, D.

2. Procedure

In this first, minikiln study, it was decided to test three levels of pressure:

100 kPa (approx 1 atm, or 0 psig)
1500 kPa (approx 15 atm, or 200 psig)
3000 kPa (approx 30 atm, or 420 psig)

and two levels of catalyst: 0 and 10% Na_2CO_3 by weight. All six combinations of these levels were tested, plus a pyrolysis run (no added steam or catalyst) at one atmosphere to provide a baseline.

The biomass charge was poplar chips, obtained by chain-sawing a freshly-cut young tree. A normal minikiln charge consisted of 1 kg (2.2 lb) wood chips, either 0 or 100 g Na_2CO_3 , about $\frac{1}{2}$ kg limestone breakers, and about 2 liters (4.4 lb) water.

The same run procedure was followed as in the previously described experiments with paper. The minikiln was heated at a constant rate of 10 kW for the duration of the run, while steam was injected beneath the charge at a rate between 50 and 100 g/min. When the minikiln reached a temperature of 600°C (1110°F), about three hours after the beginning of run, the heating elements were turned off. Steam was passed through the charge for perhaps another 20 minutes, and then the kiln was depressurized and left to cool overnight.

In the morning, the breakers were picked out and the char residue brushed loose and swept up with a vacuum cleaner. The total material removed from the kiln was weighed and the initial weight of the breakers subtracted. Residues from the catalyzed runs were leached in boiling water to remove residual catalyst, filtered, rinsed, dried and weighed again.

3. Results and Discussion

Figure 7 shows the residues from these seven runs, plotted against reactor pressure. As before, residue is expressed as a percentage of the organic (moisture-free) portion of the charge.

It is seen that increasing pressure reduces the biomass char residue significantly, and that the effect is much more pronounced when alkaline catalyst is added to the charge. At the most favorable conditions tested--10% catalyst, 420 psig pressure, and 1100°F peak temperature, the char residue is only 5% that of the (dry) charge. That is, 95% of the organic material has been converted to gas.

Even without added catalyst, increasing pressure still enhances the gasification of wood chips. However, in similar tests (not reported here) with uncatalyzed newsprint, pressure had no beneficial effect on residue reduction. These observations suggest a natural catalytic effect in the wood, due probably to potassium compounds naturally present in the bark and cambium layers.

Figure 77

RESIDUAL CHAR IN MINIKILN PRUNES,
as percentage of inorganic content of wood chips

D. Effect of Reactor Pressure on Biogas Study

1. Procedure

A series of runs was performed with the continuous feed biogas reactor to test the effect on biomass gasification of pressures higher than those attainable in the minikiln. The pressures tested were: 1 atmosphere, 3000, 6000, 10000, and 30000 psig. (However, no residue data was obtained at 30000 psig because of reactor plugging.)

The reactor wall temperature was held (nearly) fixed, with the hotter end at about 1300°F . (It was difficult to determine the maximum temperature attained by the char and gas, but this was thought to be about 1100°F .) In these runs, a measured amount (0.800 kg/1.766 lb) of wood sawdust was loaded into the feed reservoir, along with a large excess of water and, in some runs Na_2CO_3 catalyst at a level of 5% by weight. The charge was moved totally through the reactor and gasified, and after the run the char residue was removed from the end of the reactor and weighed. For the catalyzed runs, the residues were leached with boiling water, filtered, rinsed, dried, and reweighed.

2. Results and Discussion

The residues from these runs are plotted in Figure 88, as a percentage of the initial fresh weight of the charge. The data from the present biogas experiment are represented by the triangles; for comparison, those from the previous minikiln experiment are also shown, as the circles.

The residues from the biogas runs at one atmosphere and 3000 psig lie slightly below the corresponding minikiln curves, but otherwise the biogas data at low pressures seem consistent with the minikiln data and show a catalyst effect of the same magnitude.

By 6000 psig, however, the effect of the catalyst seems to have disappeared: the residue from the catalyzed biogas run is as large as that from the uncatalyzed run. And at 10000 psig,

Figure 8

RESIDUAL WOOD CHAR vs PRESSURE,
MINIKILN AND BIOGASSER

the single sample of char residue is clearly heavier than those at lower pressures. The exact shape of the curve is not well-defined by these experiments, because of difficulties in maintaining the same peak temperatures in runs at different pressures and because of the difficulty of recovering all the residue from the biogasser. Nonetheless, it is clear that the trends in the lower-pressure minikiln data may not be extrapolated to higher pressures.

Qualitatively, there is also a change in the nature of the residue at higher pressures. In both the minikiln runs and biogasser runs at pressures up to 300 or 400 psig, the char residue is loose, flaky, and granular. In the biogasser runs at 600 and 1000 psig, much of the residue is stuck together in hard lumps, up to 1-2 cm ($\frac{1}{2}$ -1 inch) across. Furthermore, plugging of the reactor screw is a frequent problem at these and higher pressures. (This is the reason for the paucity of residue data at 1000 psig and the absence of data at 3000 psig.)

These observations suggest a new reaction mechanism becoming important at the higher pressures, reversing the trend toward smaller, fluffy residues in the lower pressure range. A prime candidate is disproportionation and recombination of the volatilized organic compounds in the gas phase. Such condensation and polymerization of lighter compounds to heavier at higher pressure is in fact consistent with Le Chatelier's principle.

It is concluded that for maximum conversion of solids to fuel gas, there appears to be a broad optimum in reactor pressure in the neighborhood of 300 psig (2000 kPa). This discovery establishes that there is no advantage to the process in going to extremely high reactor pressures.

E. Effect of Catalyst Type and Concentration

1. Introduction

The minikiln and biogasser studies reported above all examined only one catalyst-- Na_2CO_3 and only two levels of

concentration--0 and 10% (or 5%) by (fresh) weight. And, in all cases, the catalyst was mixed with the biomass and a great excess of water in the reactor at the beginning of the run; the consequences of a dryer mixture or a longer soaking were not investigated.

The minikiln experiments reported in this section examine the relative effectiveness of several potential catalytic compounds, and the effect of catalyst concentration, on the extent of gasification of wood sawdust. They also test the effects of the amount of moisture present and the method of mixing the catalyst with the wood.

2. Procedure

Fresh sawdust--principally white pine--was obtained from a lumber yard, thoroughly mixed, and bagged in individual 4 kg (8.8 lb) charges, to prevent its drying out. Oven-drying of a few samples established the moisture content of this sawdust at 39%, so each bag contained the equivalent of 2.45 kg dry wood.

Four compounds were tested for their catalytic activity: Na_2CO_3 , K_2CO_3 , NaOH and $\text{Ca}(\text{OH})_2$. Three levels of catalyst concentration were tested: 0, 1×10^{-3} , and 3×10^{-3} gram equivalent weights per gram of dry wood. The actual weight of catalyst differed from one compound to another: for Na_2CO_3 , these levels correspond to 0%, 5.3%, and 15.9% by weight of dry wood, respectively.

Two levels of moisture content were tested. In "dry" runs, the catalyst and sawdust were loaded into the minikiln with no added water, and the steam flow into the minikiln was controlled so that little or no liquid water condensed during the run. In the "wet" runs, the catalyst and sawdust were mixed with approximately 4 kg liquid water (equal parts water and fresh wood). Normally, the catalyst was dissolved in the water, the solution thoroughly mixed into the sawdust, and the damp charge allowed to equilibrate overnight before being put into the gasifier.

((The insoluble $\text{Ca}(\text{OH})_2$ was mixed uniformly with the sawdust dry, and then the water added)) In two cases, the water was added in the kiln at the beginning of the run; however, varying the procedure in this way showed no consistent effect on residue weight, so all "wet" runs are here reported together, with no distinction.

Not every possible combination of levels of these three variables was tested, but only a selected subset, chosen to yield the most information in the fewest number of runs.

In a typical run, the mini kiln was loaded with the sawdust charge, and with $\frac{1}{2}$ to 1 kg limestone rocks as breakers. It was then heated at a constant rate to a peak temperature of around 1100°F / 600°C over $22\frac{1}{2}$ hours. Kiln pressure built up and was held at 3300 psig (about 22000 kPa) by the controlled release of product gas and steam. Fresh steam was supplied at pressure at a rate of about 66 kg/hr. For two runs, the mini kiln was operated at atmospheric pressure.

Gas chromatograph samples of the fixed gases evolved were normally taken every ten minutes during the run. No analysis of condenser liquids or char residue was attempted.

After the run, the kiln was allowed to cool overnight, and then the char residue collected and weighed. The breakers were weighed before and after each run, and the weight of any lost rock chips subtracted from the residue weight.

33. Results and Discussion

The residues from these runs are plotted on Figure 99. The different symbols denote different catalysts, as shown in the legend; open and filled symbols signify "dry" and "wet" runs, respectively. The horizontal axis is the catalyst concentration, in units of g name equivalent weight per g dry wood. The vertical axis is the char residue, expressed as a percentage of the initial moisture free weight of wood. For consistency, the char residue is here defined in every case as the total residue weight, less the weight of added catalyst, as carbonate.

Figure 9

Char residues for varying
catalyst type and concentration

First note the three runs with no added catalyst. All yielded essentially the same weight of char residue. Thus, neither the moisture content of the wood, nor the reactor pressure, had in themselves any significant effect on the extent of gasification. This finding is in contrast with the earlier work on poplar chips. The most likely explanation is that the pine sawdust used here, which (unlike poplar chips) is derived principally from heartwood, contains negligible amounts of naturally occurring catalytic compounds.

In general, the "wet" runs yielded lower residues than the "dry" runs. The two exceptions are the one run with Ca(OH)_2 , which is insoluble in water, and the one run at atmospheric pressure, in which all the liquid water would have evaporated before the gasification reactions began. Thus, the residues fall into two quite well defined groups, distinguished by whether or not the alkaline catalyst was dissolved in water at the time the wood was pyrolyzing. Note, however, that even in the drier cases, the catalysts still caused some reductions in char residue.

Among the three soluble compounds tested, sodium carbonate and sodium hydroxide appear equivalent. Potassium carbonate seems slightly more effective than either sodium compound. This is qualitatively consistent with the findings of the Battelle group, who have compared the properties of various catalysts in a somewhat different gasification process.⁽¹⁾

Lastly, we note that, whether "dry" or "wet", the effectiveness of the catalyst increases almost linearly with increasing catalyst concentration, up to quite high levels. This suggests that the intermediate alkali-organic compounds are quite long-lived, binding the catalyst through a good portion of the gasification process.

(1) P.C. Walkup, et.al., "Investigation of Gasification of Biomass in the Presence of Multiple Catalysts", Proceedings of Second Annual Fuels from Biomass Symposium, Troy, NY, June 20-22, 1978.

Two questions are raised by these results, and will be answered in the following two subsections ("FF" and "GU"). First, what is the mechanism behind the difference between the "wet" and "dry" runs?? Does the larger amount of water actually take part in the chemical reactions, or does it merely help incorporate the soluble catalyst into the wood particles. Second, under the optimum conditions tested here, the residues from the pine sawdust were about twice as large as those from the poplar chips in the previous work; can this be attributed simply to differences in biomass materials??

FF. Effect of Moisture Content

11. Introduction

In the study of catalyzed steam gasification of (pine) sawdust reported above, it was noted that the extent of gasification increases with the moisture content of the charge. While higher levels of moisture may aid gasification, lower moisture levels are desired from the standpoint of the heat requirements of a commercial gasifier. It is therefore important to learn more about the extent to which moisture benefits catalyzed wood gasification, and, if possible, why.

22. Test of Varying Moisture Level

The "dry" and "wet" runs reported above were supplemented with further minikiln runs at intermediate and higher moisture levels. Altogether, four levels of moisture were tested: ratios of 0/11, 0.5/11, 1/11, and 3/11 water/fresh wood.

Thus, a typical charge consisted of 44 kg pine sawdust (38% moisture), alkaline catalyst at a level of 3×10^{-3} gm eq wt/gm dry wood ($3900 \text{ kg Na}_2\text{CO}_3$ or $5077 \text{ kg K}_2\text{CO}_3$), and either 0, 22, 44, or 122 kg water. Reactor pressure was held at 3000 psig, unless otherwise noted. Runs were performed and analyzed in the same manner as described previously.

The resultant char residues are plotted as the open symbols on Figure 10. The abscissa is the ratio of total water to dry wood in each case. (The volume of the mini-kiln is such that at 20 atm and saturation temperature, about 0.5 kg water is in the vapor phase; this is in all cases a small fraction of the total water present.)

It is seen that the extent of gasification improves slightly with increasing moisture content, leveling off just above the level of 1/1 water/fresh wood.

3. Test of Mechanism

There appear two explanations for the effect of water in aiding the catalyzed gasification of wood. One is that the liquid water is important in itself, swelling the wood and/or providing a medium wherein the soluble catalyst can react with intermediate products of pyrolysis. The other is that the water merely helps the soluble catalyst to penetrate more deeply into the wood particles. The latter hypothesis can be tested by soaking the sawdust in a catalyst solution, then drying out the added water before commencing gasification.

Four runs were performed with slightly differing procedures. In Run #1, 4 kg sawdust was mixed with 2 kg water, in which 0.370 kg Na_2CO_3 was dissolved; and the moist sawdust was then air-dried back to about 50% moisture. In Run #2, the sawdust was first air-dried, and then catalyst solution added to bring the moisture level up to about 50%. In Runs #3 and #4, the sawdust was mixed with 4 kg water and catalyst--the optimum level from previous tests--and then air-dried back to below its original moisture content. All the runs used the same amount of catalyst and the same run procedure as before.

The residues from these runs are plotted in Figure 10 as the filled symbols, and identified as Runs #1 through #4. They are plotted along the abscissa at the moisture level the charge possessed when it was put into the gasifier.

Figure 10

EFFECT OF MOISTURE CONTENT OF CHARGE ON CHAR RESIDUE

It is apparent that the amount of char residue is determined by the amount of moisture in the wood when it is gasified, and not by the amount present when the catalyst is added. In other words, the value of water in incorporating catalyst into the wood is small, compared to its value as a liquid medium during the gasification reactions in which the catalyst takes part.

4. Conclusions

It appears that a certain amount of liquid water--beyond that normally present in fresh wood--increases the effectiveness of the catalyst.

This finding, however, is probably of little practical value to the W-M biomass gasification process. Thermal considerations limit the moisture content of the feed to around 45-50%, about that of fresh wood. (Cf the projected gasifier heat cycle, discussed in Section VI of this report.) If more water were to be added, more heat transfer surface would have to be incorporated into the gasifier to evaporate the added load. More important, the heat capacity of the additional steam would be so great that the heat liberated in the wood decomposition exotherm would no longer be sufficient to raise the charge to the 1100-1200°F needed to finish off the gasification.

A more practical finding from this study is that there seems to be no practical advantage in soaking the biomass in a catalyst solution to incorporate it into the wood, as long as the biomass must be dried back to its initial moisture content. The effect of the catalyst seems to be no less if it is simply mixed dry with the fresh wood.

G. Comparative Study of Different Biomass Materials

1. Introduction

Most of the experimental work described above by W-M with both biogasser and minikiln used pine sawdust as the biomass

feed. This material was chosen primarily because it is available in large quantities from a local lumber mill, and hence many tests may be run using a uniform charge.

A commercial plant may also use other, perhaps several, biomass types, e.g., poplar from an energy farm, hardwood waste from a wood products industry, forestry or crop residues. It is thus important to learn how a variety of biomass types behave in the W-M gasification process.

It would be impractical at this time to perform an extensive study of the effects of reactor conditions for every biomass type of interest. But it is feasible to compare a limited number of diverse biomass materials under a few selected experimental conditions. In this way one can learn how different biomass types vary in their ease of gasification and product gas composition. And one can learn whether or not the effects of pressure, moisture, and catalyst concentration are similar for different biomass materials. If they are similar, or follow a consistent pattern, then what has been learned in the study of one material can be extended to others.

2. Procedures

Five biomass materials, of varying lignin/cellulose ratios and densities, were tested and compared: three types of wood common to the Northeast--pine, maple, and poplar; cornstalks; and peat.

The pine included in this comparison was the lumberyard sawdust tested previously. The maple and poplar samples were obtained by felling small trees and chain-sawing their trunks into small chips. Cornstalks were of the home garden variety, collected at the end of the season and cut to six-inch lengths. Peat was represented by commercial garden-center peat moss.

Weighed samples of each material were dried in a 350°F oven for 4 to 6 hours, to determine the weight percent of moisture present. A peat sample was also ashed; but the ash content of the others was assumed negligible and not measured.

Table 1 summarizes the properties of the five materials:

Table 1

<u>Material</u>	<u>Typical Particle Size</u>	<u>Moisture Content</u>	<u>Ash Content</u>
maple	1x5x10 mm	33%	-
pine	0.5x1x2 mm	39%	-
poplar	1x5x10 mm	43%	-
cornstalks	½ x 6 in.	63%	-
peat moss	< 1 mm	44%	1.5%

The tests were performed in the batch-feed minikiln, using the same procedures described above. The biomass charge used varied from 2 to 4 kg. About 1 kg limestone rocks were used as breakers.

Runs were made under several process conditions. Three parameters were investigated, each at one of two levels:

reactor pressure: 1 atm or 300 psig
 moisture content: fresh biomass, or equal parts fresh biomass and water
 catalyst concentration: none or 3×10^{-3} gm eq.wt. Na_2CO_3 /gm oven-dried biomass

Not all eight combinations were tested for each biomass type, but selected combinations to gain the most information in a limited number of runs.

All runs were performed with an abundance of steam and with the same heating rate, the reactor reaching a peak temperature of 1100°F after about 3 hours.

During each run, the fixed product gases were analyzed every 10 minutes by gas chromatograph. The charry residue after each run was collected from the minikiln and weighed; the amount of residue was used as a measure of the degree of gasification.

3. Results-Presentation of Data

The residue data are shown in Table 2. Char residue is expressed as a percentage of the weight of initial biomass, on a moisture-free, ash-free basis. Where more than one run was made at a given set of conditions, the mean $\pm$ standard deviation is reported.

Included for comparison are data from the earlier minikiln study reported above in Subsection B. The figures are interpolated from the 1977 data to correspond to the levels of the pressure and catalyst in the present study.

In the runs with catalyst there is some ambiguity in determining how much of the residue is char. Leaching some of these residues with boiling water normally removed between 60 and 80% of the weight of Na_2CO_3 initially added. The exact percentage varies from trial to trial with no apparent pattern. It is not clear how to account for the small apparent loss of catalyst; whether some of the catalyst was converted to a lower weight compound (e.g., NaOH), became bound physically or chemically with the char, blew out as a fine dust with the product gas, or remained caked on the kiln walls.

Thus, for simplicity and consistency, we defined the char residue in every case as the total residue weight (less ash), less the weight of Na_2CO_3 initially added. (This procedure may introduce a small systematic error into the results; but so would any other.)

Table 2
Char Residues Under Various Conditions
(dry basis)
All at 1100°F Peak Temperatures

pine sawdust			
		0 pres	300 psi
0 cat	dry	25.7%	26.1%
	wet	-	25.7 $\pm$.7%
3x10 ⁻³	dry	19.4%	17.7 $\pm$.6%
	wet	14.0 $\pm$ 1.5%	11.6 $\pm$.5%

poplar chips (1977)*			
		0 pres	300 psi
0 cat	dry	25.4%	-
	wet	23.8%	19.3%
3x10 ⁻³	dry	-	-
	wet	18.6%	7.6%

maple chips			
		0 pres	300 psi
0 cat	dry	28.4%	-
	wet	-	24.1%
3x10 ⁻³	dry	20.7%	21.9%
	wet	20.8%	16.0%

poplar chips (1978)			
		0 pres	300 psi
0 cat	dry	24.9%	-
	wet	-	-
3x10 ⁻³	dry	17.8%	-
	wet	-	5.7%

peat moss			
		0 pres	300 psi
0 cat	dry	31.2%	-
	wet	-	26.0%
3x10 ⁻³	dry	26.2%	-
	wet	-	23.0

cornstalks			
		0 pres	300 psi
0 cat	dry	22.1%	-
	wet	-	-
3x10 ⁻³	dry	-	-
	wet	-	-1.2% (see text)

*Interpolated from actual data to correspond to present levels of pressure and catalyst.

(In the one cornstalk run, this formal procedure leads to a "char" residue less than zero. Leaching this residue with boiling water left insoluble charry solids amounting to 4.7% the initial dry weight of the charge.)

4. Results-General Trends

Let us first compare the difference in biomass types at the weakest gasification conditions tested (dry, atmospheric pressure, no catalyst) and the strongest (moist, 300 psig, with catalyst). The residue weights for these two conditions are plotted in Figure 11.

We see a regular progression from peat, the most intractable to gasification--down through maple, pine, and poplar--to cornstalks, the easiest to gasify. Moreover, the easier a substance is to gasify, the more does it respond as the gasification conditions are strengthened. Increasing moisture, pressure, and catalyst from lower to higher levels decreases the peat residue from 31% to 23%; but it decreases the cornstalk residue from 22% to almost nothing.

The ranking of the three wood types is also of interest. They do not follow in order of decreasing lignin/cellulose ratio, as might have been expected, as pine has higher lignin content than either hardwood. Rather the ranking is in order of density--the poplar being the lightest, most "open" wood structure of the three; the maple the densest. We hypothesize that the more open structure permits easier entry of water/steam into the wood, permits more rapid egress of pyrolysis products so they are less likely to recombine, and/or reduces the opportunity for free radical sites on the nascent char to cross-link.

Gas chromatographic analysis of the (fixed) product gases evolved during the runs showed less extreme differences between biomass types. Figure 12 shows some typical graphs of gas composition vs kiln temperature for three runs at the stronger conditions. The major feature of these and other GC traces is

Figure 11

Figure 12
Composition of fixed product gases,
Three typical runs

perhaps their similarity: pyrolysis begins with the evolution of CO_2 and CO , these gases give way to methane, and by the end of the run the steam-char reaction predominates with the production of H_2 and CO_2 . Any changes in this pattern due to difference in process conditions are small compared to random variations from one run to the next.

One does perceive in these and other traces a small but consistent trend toward more methane, less hydrogen, in the series from cornstalks to peat. This may reflect the higher lignin content. (The apparently lower CO_2 , higher CO concentration seen in the early part of the pine run here is not necessarily seen in other pine runs; it seems related to variations in steam flow than in composition of the material.)

There may of course be more marked differences between biomass types in their heavy pyrolysis products. These are not cracked in the minikiln (as they are in a continuous-feed gasifier), but are removed from the gas stream in the condenser, and are not analyzed. But, on the basis of the present information, it is expected that for the variations in feed likely in a commercial gasifier the difference in gas composition will be insignificant.

5. Results-Effect of Process Parameters on Different Materials

Returning to the data of Table 1, we see that, for the different woods, the effects of varying the three parameters are also different.

For pine, in the absence of catalyst, neither increasing water or increasing pressure improves the extent of gasification. Yet for both maple and poplar (as well as peat), increasing moisture and pressure in the absence of catalyst does reduce the char residue.

In the runs with added catalyst, too, pine behaves differently from the hardwoods. For pine, either increasing the water content or increasing pressure reduces the char residue;

and at the higher level of both variables, the char reduction is just the sum of that due to each effect alone. In statistical language, there is no significant interaction between the two variables. Yet, for maple (and apparently for poplar), neither moisture nor pressure alone affect the residue weight, while the two together do. Here there is a statistically significant interaction between the two variables.

If the reasons for these observed differences in behavior could be identified, it might lead to a better understanding of the mechanisms of the gasification process. There are several differences between the pine and hardwood samples:

- The pine, because of its lumberyard origin, is principally heartwood, while the maple and poplar are whole-trunk samples, including bark and cambium layers. These outer layers are not only more open in structure, but are rich in naturally occurring potassium salts, which may have an intrinsic catalytic effect.
- The pine sawdust is of smaller particle size than the hardwood chips. Also, it was collected from a pile that had lain outdoors several days, while the other woods were chipped and bagged while fresh. Thus there was more opportunity for surface drying and oxidation of the pine particles.
- Conifers in general have a somewhat different chemical makeup than hardwoods, containing more resins and a slightly higher ratio of lignin to cellulose. The resins may act to impede the transport of moisture into the wood, and the lignin may be expected to gasify differently than cellulose.

The connection between these factors and the observed gasification behavior is not transparent. At this time, we are not prepared to offer a hypothesis that would adequately explain all the observed differences between the biomass types tested.

6. Conclusions

Different biomass materials can vary widely in their responsiveness to gasification. In general, the denser, more slowly growing woods like maple leave the larger char residues, while the less dense, rapidly growing plants like poplar and corn leave much smaller residues. (It may be speculated that the very rapidly-growing strains of poplar being developed for energy farms would gasify more easily than the natural strain tested here.)

Different materials also respond in different degree to changes in process conditions. This suggests that the optimum conditions for a commercial process may differ according to the feed. For example, for maple and pine, the benefit of increasing reactor pressure is quite small, compared with the effect for poplar and cornstalks. Thus, for a gasifier dedicated to lumbering wastes, composed mainly of the heavier woods, a low pressure reactor with lower capital investment may be more cost-effective. For a gasifier dedicated to an energy farm, where the feed is a fast-growing poplar (or algae, water hyacinths, etc.), a higher-pressure reactor may be the choice because it is capable of a much higher gasification efficiency. These examples are only for purposes of illustration, and do not reflect a calculated projection.

Lastly, because the various biomass types appear to behave quite differently under catalyzed steam gasification, it will probably be necessary to make a separate series of tests on each biomass type, before designing a gasifier dedicated to that material. Such a study is beyond the scope of the present work.

H. Summary

The experiments described in this section have established the effects of various process parameters on the extent of gasification of biomass.

Peak reactor temperature is one of the most significant parameters. The amount of solid residue drops rapidly with increasing temperature, reaching about 5% at 1100°F, for poplar chips under favorable conditions. Above this temperature the steam-char reaction progresses rapidly, accelerating the disappearance of the char.

Reactor pressure, moisture, and soluble alkaline catalyst all show a beneficial effect on biomass gasification. The effect of pressure levels off at about 300 psi, that of moisture at a level of approximately equal parts water and fresh wood. The effect of the catalyst seems linear up to the highest level tested, 3×10^{-3} gm eq.wt./gm dry biomass. These three variables interact, in that the effect of all three together is much greater than the sum of each separately.

These observations suggest the following reaction mechanism: it is postulated that the primary effect of pressure on the process is to maintain water in the liquid phase to higher temperatures. The catalyst then exerts its effect when the organic material pyrolyzes in the presence of an aqueous solution of the alkali. The detailed mechanisms of the catalytic action have not been determined. Ion-catalyzed hydrolysis may play a significant role. It is also likely that the alkali reacts with acidic substrates in the organic material, thereby promoting its disintegration and reaction with water. This would be consistent with the visual observation that the condensate from catalyzed runs tends to contain more oils, as opposed to water-soluble organics, than that from runs without catalyst. The apparent linearity of the response to catalyst concentration, up to quite high levels, suggests that the intermediate alkali-organic compounds are quite long-lived, binding the catalyst through a good portion of the gasification procedure.

Lastly, the experiments show a wide variation in the extent to which different biomass materials can be gasified. In general, the less dense the structure, the more completely can a given (dry)

mass of material be converted to gas, and the greater is its response to increasing pressure, moisture, and catalyst levels. It may be hypothesized that the more open structure permits easier entry of water/steam into the biomass and permits more rapid egress of pyrolysis products, so they are less likely to recombine.

The above discussion is concerned only with maximizing the conversion of biomass to gas. In a commercial gasifier, practical considerations, such as equipment costs and technical feasibility, may well require operation at other, less favorable conditions. It must therefore be recognized that this experimental work, alone, does not necessarily establish the preferred conditions for gasifier operation. The task of evaluating tradeoffs between gasification efficiency and reactor costs lies beyond this experimental phase.

SECTION IV
PROCESS STUDIES II
EFFECT OF PROCESS CONDITIONS ON PRODUCT GAS COMPOSITION

A. Introduction

Section III examined the effects of process conditions on the volatilization and gasification of biomass solids. Section IV considers the remainder of the process: the cracking and steam-reforming of the volatile pyrolysis products--oils, tars, and other organic liquids--to non-condensable fixed gases.

In the W-M process, steam-cracking of the volatile pyrolysis products occurs in the rotary kiln reactor along with the gasification of the solids. The pyrolysis gases, emitted in the 300-500°F region of the kiln, pass on, co-currently with the solids, through the hotter region of the kiln, where the thermal cracking and steam-reforming proceeds.

In the commercial process, it is desirable that the volatiles be completely steam-cracked to simple, fixed gases. Then there is no difficulty with organic liquids condensing in, and perhaps plugging, the lines as the gas cools. Furthermore, complete cracking provides a simpler and more uniform gaseous product.

It is also desirable, given the process conditions, to be able to predict the composition of the product gas. This would permit one to determine its heating value (if it is to be used for fuel), or its appropriateness as a chemical feedstock. Or, within limits, one could specify the reactor conditions to produce a gas of the desired quality.

Therefore, the questions to be answered by the experiments described in this section are: How completely are the heavy organics steam-cracked to fixed gases? What is the composition of the resulting product gas? And, how do these properties of the gas depend on the process conditions?

B. Experimental Procedure

Two separate sets of tests were performed to investigate the composition of product gas from the continuous-feed biogasser. An early test was performed with the original version of the biogasser, using a great excess of water with the wood feed. A later test was performed with the later version of this reactor, using a lower level of moisture. The results of both sets were consistent in all important aspects, so both are described together here.

The biomass charge used in all cases was lumberyard sawdust (white pine). Experience with gasification of different types of biomass, reported in the previous section, would suggest that, had a different biomass material been used, the product gas would not have been significantly different.

For these tests, the biogasser was brought up to temperature, and about one to three kg of sawdust passed through and gasified, at a steady rate. Runs were done both with and without catalyst, and moisture levels ranged from fresh wood with no added water to ratios as high as 10/1 water/wood. During each run, pressure was held fixed at either one atmosphere, 100, 300, 600, 1000, or 3000 psig.

During the runs, which typically lasted several hours, the peak temperature of the reactor was slowly varied, over a range of perhaps a few hundred Fahrenheit degrees. Thus, in a short time, gas samples could be obtained under a range of maximum reactor temperatures, yet otherwise similar reactor conditions.

The product gas was passed through a condenser, where it was cooled and dried, and then sampled by the gas chromatograph. Samples were taken every 10 or 15 minutes, and immediately analyzed for CO, CO₂, CH₄, C₂H₆, and H₂. The instrument used was a Fisher Model 1400 dual-column gas partitioner. The gas analysis not only yielded the gas composition under various process conditions, but also, as will be described, permitted a determination of the extent of cracking.

C. Analysis-Extent of Steam Cracking

There are basically two ways of determining the extent to which pyrolytic liquids and tars are converted to fixed gases: One may examine the condensate formed when the product gas is cooled, or one may analyze the fixed gases passing out of the condenser.

With the present experimental equipment it was not practical to examine the condensate (principally water) for small amounts of organic compounds, because it was so easily contaminated by earlier deposits in the condenser and gas lines. Instead, the degree of steam-cracking was determined quantitatively from the analysis of the fixed product gases as follows:

We introduce the dimensionless parameter ζ (zeta), defined as

$$\zeta = \frac{\frac{1}{2} \times \text{moles H}}{\text{moles O}} = \frac{\% \text{ H}_2 + 2 \times \% \text{ CH}_4 + 3 \times \% \text{ C}_2\text{H}_6}{\% \text{ CO} + 2 \times \% \text{ CO}_2}$$

The second expression shows how zeta is calculated from the gas chromatographic analysis. If the biomass (sawdust) is completely converted to these five fixed gases and water, then zeta will be equal to or slightly greater than 1.0, one-half the ratio of H to O in the fresh wood. If, on the other hand, the product gas contains H-rich oils and tars (which are removed in the condenser), then zeta will be less than unity.

For every run performed, zeta was calculated for each gas sample taken and the results correlated with temperature, pressure, catalyst, and moisture level. It was found that the degree of cracking--as measured by ζ --depends entirely on the reactor temperature. Neither reactor pressure, level of moisture, nor the presence of catalyst seem to have a large enough effect to be of any significance.

Figure 13 shows a plot of ζ against peak wall temperature for a large number of gas samples taken at the same pressures but differing temperatures. Each point represents one gas sample; the solid line is an empirical fit to the data.

The data shown are compiled from six different runs, all at 300 psig. All are from the earlier biogasser series, with a water/wood ratio somewhere between 5/1 and 10/1. These six runs were performed under different conditions of catalyst concentration and feed rate; but since no significant effects of these variables on gas composition were found, all are combined here.

Figure 13

$$\xi \equiv \frac{\text{total H}}{2 \times \text{total O}} \text{ vs } T_{\text{max}}, 6 \text{ runs @ } 300 \text{ psig}$$

Though the individual data points show some scatter, the overall trend is well defined: the extent of cracking, as measured by ζ , increases steadily (in fact linearly) with temperature; and reaches completeness ($\zeta = 1$) at a wall temperature about 1300°F ($\sim 700^{\circ}\text{C}$). Reliable measurements of the actual gas temperature were not obtained; but for reasons that will be discussed later, it is likely the peak gas temperature at completeness is about 200°F lower than this, or about 1100°F (600°C).

Other runs at different pressures show the same pattern and very nearly coincide with the data shown here. There are some indications that, at highest pressures, cracking is accomplished at slightly lower temperatures; but the effect is too small to be of practical importance.

It is significant that zeta reaches unity linearly, rather than asymptotically. From this, it can be inferred that, at temperatures above this point, the gas is essentially free from all heavy organic compounds. If, on the other hand, the curve had approached unity smoothly, one might expect condensibles to be present in the gas to much higher temperatures, at levels too small for the zeta test to detect.

Figure 14 shows a similar plot of ζ vs gas temperature. The data shown are all from a single run, in the later biogasser series, performed at atmospheric pressure, with fresh sawdust (no added water) as charge. In this run, reactor temperature was increased slowly over a period of two hours, with gas samples taken every 10 minutes. The temperature shown on the abscissa is measured by a thermocouple suspended in the residue collector, at the mouth of the biogasser barrel.

The value of ζ again increases steadily with temperature, from 0.5 to 1.0 over about 200°F ; reaching unity at an exit gas temperature of 1000°F ($\sim 550^{\circ}\text{C}$). It must be recognized that the maximum temperature reached by the gas within the biogasser barrel was probably somewhat higher than this, since at the thermocouple location the fresh product gas has had opportunity to mix with the cooler gas in the residue collector.

Figure 14

EXTENT OF CRACKING
vs GAS TEMPERATURE

0 psig

It is unfortunate that, because of the biogasser screw, there is no way to place a thermocouple directly in the hottest part of the gas stream. It would appear that one can only bracket the maximum gas temperature--by the wall temperature above and the exit gas temperature below. In Subsection D, it will be seen how considerations of the gas composition help narrow this uncertainty.

The conclusions from these biogasser runs are very similar to, and consistent with, those from an earlier study by W-M on the steam-cracking of polychlorinated biphenyls (PCB's)⁽²⁾. In that study, a closed container of PCB oil, catalyst, and water, was slowly heated to various final temperatures, and the residue afterward analyzed. It was found that, here, too, the fraction of volatile PCB's remaining uncracked decreased steadily with increasing temperature, reaching zero about 1100°F.

D. Analysis-Composition of Product Gas

The biogasser runs described above have yielded a great deal of information about product gas composition, over a wide range of pressure, temperature, and moisture level. Out of this bulk of data, certain trends become apparent:

In general, one finds the gas composition obeying LeChatelier's principle: Increasing pressure favors production of methane, ethane, and CO₂, at the expense of H₂ and CO; while increasing temperature converts CH₄ and CO₂ back to H₂ and CO. Increasing the moisture level yields more H₂ and CO₂ in the product gas, at the expense of CO and the hydrocarbons. The presence or absence of alkaline catalyst has no perceptible effect on gas composition.

These trends suggest it would be instructive to compare the measured gas composition with that at chemical equilibrium, for the same temperature, pressure and C/H/O ratio.

(2) JA Coffman & RH Hooverman, "Power from Wastes via Steam Gasification", ACS Symposium Series No. 76, Solid Wastes and Residues, Jerry Jones & Shirley Radding, eds.

To calculate the equilibrium composition, a simple Fortran IV program was devised specifically for this project. The calculational procedure amounts to minimizing the total Gibbs free energy for a system comprised of the five molecular species CH_4 , CO , CO_2 , H_2 , and H_2O , with the constraint that the given number of C, H, and O atoms remains fixed.

In making the calculations of gas composition, two assumptions were made: First, that the wood could be represented by the empirical formula $\text{C}_6\text{H}_9\text{O}_4 + \text{X} \cdot \text{H}_2\text{O}$, where the value of X depends on the moisture content of the feed. This corresponds to an elemental analysis which is very close to that for most woods. Second, that all the wood is converted to gas (no char), and that only the five species CH_4 , CO , CO_2 , H_2 , H_2O are present in the final equilibrium mixture. This means that the calculation is applicable only at temperatures high enough that the amount of residual char is negligible and the heavy organic compounds are all steam-cracked.

When the calculated gas compositions are compared with those measured in actual runs, it is found that, at temperatures high enough to steam-crack the heavy volatiles, the remaining fixed gases are indeed very nearly in chemical equilibrium.

Table 2 shows the measured composition of fixed product gases from four biogasser runs with essentially complete cracking (calculated value of zeta near 1.0). T_{max} is the hottest reactor wall temperature reached; T_{gas} is the temperature of the gas as it exits the biogasser barrel. Compositions and temperatures reported are averages over a half-hour or more of approximately steady-state operation.

For comparison, we also show the calculated equilibrium composition for a mixture of CH_4 , CO , CO_2 , H_2 , and H_2O , under three conditions matching those in these experimental runs. The calculation assumes the input to be "dry wood", $\text{C}_6\text{H}_9\text{O}_4$, plus a

TABLE 1
COMPOSITION OF PRODUCT GAS FROM BIOGASSER

		<u>Experimental</u>				<u>Calculated (equilibrium)</u>		
Charge		dry wood		fresh wood		$C_6H_9O_4+3H_2O$	"5H ₂ O	"5H ₂ O
Pressure		0 psig (11/27)	0 psig (12/15)	0 psig (1/24)	300 psig (1/11)	0 psig	0 psig	300 psig
T _{max}		1120°F	1300°F	1330°F	1110°F	1025°F	1050°F	1100°F
T _{gas}		905°F	965°F	975°F	805°F			
vol. comp. dry gas %	CH ₄	23.8	23.0	14.0	29.5	27.1	18.5	37.8
	C ₂ H ₆	2.2	1.6	1.5	5.8	-	-	-
	CO	19.8	21.1	15.1	8.5	18.6	15.6	6.1
	CO ₂	29.7	29.7	28.5	39.8	27.9	27.4	39.6
	H ₂	24.5	24.6	40.9	16.4	26.4	38.5	16.5
	Σ	.99	.94	1.02	1.05	1.08	1.07	1.08
% water in whole gas		?	?	?	?	10.3	17.9	28.6

certain amount of moisture. (Note that the table shows first the relative abundance of only the four fixed gases; the final row shows the amount of water vapor in the whole equilibrium mixture.) The match is quite good, especially considering that the simple computer program used does not consider ethane, and thus overestimates the methane content of the gas.

First, consider what this data and the theoretical fit may tell about the gas temperature necessary for complete cracking. It is clear that the measured values of wall and gas temperature are of limited value. For example, it might appear from the data that, at the higher pressure, cracking is accomplished at a lower temperature. This may or may not be the case. Since the wall-to-gas heat transfer coefficient is much better at higher pressures, the same peak gas temperature might have been reached with a lower wall temperature. It also appears that in November the cracking was accomplished at a lower wall temperature than in December; this is surely due to the fact that an insulating layer of char was slowly building up on that part of the biogasser wall not scraped by the screw. As for the measured "gas" temperature, it must be remembered that this quantity is not measured until after the gas has emerged from the biogasser barrel and may have mixed with the somewhat cooler gas in the residue collector. All that can be said with assurance is that the maximum temperature reached by the gas was at least as high as that measured in the exit chamber, and no higher than the hottest part of the reactor wall.

Now consider the temperatures associated with the theoretical fits to these data. It is important to note that these temperatures were not taken from experimental measurements, but are chosen as those which yield the best fit to the measured compositions. This procedure provides an independent estimate of the temperatures actually reached (or exceeded) by the gases in the biogasser barrel.

The temperatures so derived are much more uniform than those measured in the experiments. They indicate a common temperature for cracking in the neighborhood of 1050°F - 1100°F .

These observations taken together support the previous assertion that the gas is completely steam-cracked by the time it reaches a temperature of 1100°F ($\sim 600^{\circ}\text{C}$).

Now let us return to the observation that, when it is fully cracked, the product gas is very nearly an equilibrium mixture of the fixed gases and water vapor. This fact makes it possible to estimate the composition of the product gas under conditions that have not been tested experimentally. It also provides a guide for choosing reactor conditions that would adjust the gas composition for a specific application.

As an illustration, consider Table 3. This shows the predicted composition of dried product gas from fresh wood at 50% moisture, over a range of temperatures and pressures. This table was generated to investigate the potential of gas from the W-M process as a feedstock for methanol synthesis. For that application, a gas is desired which is high in CO and H_2 , in a 2/1 ratio. Balancing gas quality against practical engineering constraints on the gasifier, it appears that operation at $\sim 1500^{\circ}\text{F}$ peak and 200 psig would provide a good feedstock for a methanol producer.

E. Summary

It has been found that in the continuous-feed biogasser, the product gas is cracked and steam-reformed to simple fixed gases when it reaches a temperature in the neighborhood of 1100°F (600°C).

The temperature at which cracking is complete--or to the extent of cracking at lower temperatures--does not seem to depend strongly on the presence of alkaline catalyst, the moisture level of the feed, or the reactor pressure. Neither does the catalyst appear to affect the fixed gas composition, although the other two

Table 3

Theoretical Predicted Gas Composition From
Gasification of Fresh Wood (50% Moisture)

Temperature OF	Pressure psig	Volume Composition			
		CH ₄	CO	CO ₂	H ₂
1300	100	10.8	18.3	23.3	47.6
	200	16.1	15.5	26.8	41.6
	300	19.5	13.7	28.9	37.9
1400	100	5.4	23.5	18.2	52.9
	200	9.8	21.0	21.2	48.0
	300	12.0	19.2	23.3	44.5
1500	100	2.2	27.1	14.8	55.9
	200	5.1	25.6	16.7	52.6
	300	7.6	24.2	18.4	49.8
1600	100	0.8	29.5	12.7	57.0
	200	2.2	28.8	13.7	55.3
	300	2.9	27.9	14.7	53.5
1700	100	0.3	31.1	11.5	57.1
	200	0.9	30.9	11.8	56.4
	300	1.7	30.5	12.3	55.5
1800	100	0.1	32.5	10.5	56.9
	200	0.3	32.4	10.7	56.6
	300	0.7	32.2	10.9	56.2

variables do markedly affect the gas composition, in accord with LeChatelier's principle.

When cracking is essentially complete, the composition of the fixed gas observed is very nearly that of an equilibrium mixture at the appropriate temperature, pressure, and steam concentration. This observation is of value in predicting gas composition, or in choosing reactor conditions to produce a desired gas.

Lastly, the cracking of the gas seems to be accomplished within a reasonably brief dwell time. At the feed rate used in these experiments, it is estimated that the total residence time of the gas in the reactor at 1 atmosphere is about 3 seconds; at 300 psig, about one minute. The gas is exposed to the hottest temperature region for about one-tenth of this time.

SECTION V

THERMAL STUDIES

A. Introduction

The previous sections have dealt with tests of the W-M process chemistry. These studies have shown how changing the process conditions affects the extent of biomass gasification and the makeup of the product gas.

This section deals with studies of the thermal behavior of the system. There are basically three questions which must be resolved--both experimentally and theoretically--in order to design the PDU and larger systems.

1. The Exotherm. When wood/cellulose decomposes, heat is liberated; and this exotherm is expected to provide a significant portion of the process heat to the reactor. It is necessary to establish how much heat is given off in this exotherm, over what temperature range it occurs, and whether it is affected by changes in the process conditions.
2. Thermal Cycle. The W-M biomass gasifier is thermally very tightly-integrated, with process heat derived entirely from the wood decomposition exotherm and the sensible heat of the returning product gases. It is necessary to establish that this expectation is consistent with both the first and second laws of thermodynamics--that is, that the sensible heat available is adequate, and in the right place, to do the job.
3. Heat Transfer. The greater part of the process heat must enter the reactor by conduction through the reactor walls. It is thus necessary to determine the overall coefficient of heat transfer--from the gas jacket, through the walls, into the gas and solids bed within the reactor. To do so involves experimental measurement of the heat transfer properties of the biomass solids, in various stages of gasification, as well as the calculation of heat transfer between wall and gases.

Once the thermal requirements of the process and the overall heat transfer coefficient have been calculated, one can project the heat transfer surface needed in the rotary kiln, and thus determine adequate heat transfer in a reactor of practical dimensions.

B. Minikiln Calorimeter Experiment

1. Experimental Plan

The purpose of this work was to obtain information about the exotherm associated with the decomposition of wood under conditions of the W-M process. Specifically, it was to determine how much heat is released over what range of temperatures, and whether the nature or magnitude of the exotherm is affected by changes in the process conditions.

Information about the exotherm was obtained by slowly heating the minikiln at a uniform rate of power input and recording the rise in temperature with time. Comparing the rates of rise for full and empty kiln under otherwise identical conditions tells how much heat is being emitted (or absorbed) by the charge.

To express this mathematically we make the simplifying assumption that both the kiln wall and the charge inside are each at a uniform temperature. To help justify this assumption, the kiln is heated at the slowest practical rate (5.0 kW - 285 Btu/min) to allow time for both kiln and charge to approach thermal equilibrium.

Then let:

P = the power input to the reactor (Btu/min)

C_k = the heat capacity of the kiln (Btu/F⁰)

$T_k^0(t)$ = temperature of kiln in Run #0 (empty)

$T_k^1(t)$ = temperature of kiln in Run #1 (with sawdust)

This in Run #00, the rate of uptake of heat by the empty kiln is

$$C_{kk} \frac{dT_{kk}^{00}}{dt} = PP - L(T_{kk}) \quad (1)$$

where $L(T_{kk})$ is the rate of loss from kiln to environment. At $t=0$, kiln and environment are the same temperature and the loss term = 0. Therefore C_{kk} is given by

$$C_{kk} = \left. \frac{PP}{\frac{dT_{kk}^{00}}{dt}} \right|_{t=0} \quad (2)$$

In Run #11, the rate of heat uptake is given by

$$C_{kk} \frac{dT_{kk}^{11}}{dt} = PP + X(T_{kk}) - L(T_{kk}) \quad (3)$$

where $X(T_{kk})$ is the rate of exotherm (Btu/min) at the given temperature. (X less than 0 corresponds to an endotherm) This expression assumes that the heat capacity of the charge and gas is negligibly small, compared to that of the massive kiln, so that essentially all the heat generated (absorbed) by the charge goes into (comes out of) the kiln wall.

The (unknown) loss term is assumed the same for both runs, at the same T_{kk} . Therefore, comparing the rates of temperature rise for the two runs at the same temperatures (not the same times), yields the rate of exotherm (endotherm):

$$X(T_{kk}) = C_{kk} \left[\frac{dT_{kk}^{11}}{dt} - \frac{dT_{kk}^{00}}{dt} \right] \text{ same } T_{kk} \quad (4)$$

2. Experimental Procedure

For these tests, the minikiln gasifier was fitted with two thermocouples, both attached to the removable cover plate and projecting about 12 inches into the kiln. One was a shielded thermocouple that measured gas temperature, the other was spring mounted against the inner kiln wall and measured the wall temperature.

Signals from the thermocouples were taken through a set of slip rings and to a data logger, where they were recorded on punched paper tape for computer interpretation.

The biomass used in these experiments was fresh soft-wood sawdust from a lumberyard. It was mixed thoroughly and then bagged in plastic bags in individual 15-lb. charges. (This amount fills the minikiln just under half-full.)

A measured amount of the sawdust was dried in a microwave oven and re-weighed, establishing the moisture content at 60%. Thus, each 15-lb. bag of sawdust contained 6 lb of "dry wood" and 9 lb. water.

Five runs were made in this series as follows:

- Run 0: empty kiln, to establish baseline heating rate
- Run 1: 15 lb. sawdust, at 1 atm.
- Run 2: 15 lb. sawdust, at 300 psig
- Run 3: 15 lb. sawdust with 10% Na_2CO_3 catalyst, at 300 psig
- Run 1': repeat of Run 1.

In each run, the system was begun at $56 \pm 2^\circ\text{F}$ and heated at a constant rate of $5.00 \text{ kW} \pm 1\%$ until the kiln interior passed 1100°F . The kiln was turned at a steady rate of 2 rpm. Five readings each of wall and gas temperature were taken during every other revolution (once each minute) and averaged.

3. Results-Heating Rates and Exotherm

Figure 15 shows a plot of the wall temperature vs time for three typical runs (Runs #0, #1', and #3).

Run #0 shows the heating rate for the empty kiln with which all other runs are to be compared. In contrast, Run #1' shows a slower rate of temperature rise up to around 400°F, due to the drying of the sawdust, then a faster rate as the wood decomposition exotherm commences. In Run #3, the rate of evaporation of water is initially slower because the kiln pressure is building up. The pressure reaches 300 psig at around 450°F, whereupon the excess steam is released, producing a brief plateau in the temperature profile.

The differences in the heating rates for various runs are more evident in Figures 16 and 17. Here the slopes of the temperature curves, dT/dt , are plotted. Figure 16 compares each of the two atmospheric pressure runs with the empty kiln; Figure 17 compares each of the two runs at 300 psig. Note that for these graphs wall temperature rather than time is the abscissa.

Let us look first at the curve for the empty kiln, Run #0, in the upper part of Figure 16. The rate of temperature rise increases to about 5.5°F/min., then gradually declines with increasing temperature. (The rise is not instantaneous due to the fact that the calrod heaters must first heat up, then warm the kiln by conduction.) The gradual, nearly linear, decrease in dT/dt with increasing temperature is due to the energy loss, $L(T_k)$, which increases roughly as $T_k - T_{\text{environment}}$. If this curve is extrapolated back to the beginning ($T_k = 56^\circ\text{F}$), it identifies an ideal temperature rise in the absence of losses, also 5.5°F/min. Using Equation (3), this data fixes the effective heat capacity of the kiln to be

Figure 15

KILN TEMPERATURE vs TIME

for 33 representative runs

$$C_k = \frac{285 \text{ Btu/min}}{5.5 \text{ }^{\circ}\text{F/min}} = 52 \text{ Btu/}^{\circ}\text{F} \quad (5)$$

(This value is consistent with the estimated mass of the minikiln and the known specific heat of stainless steel.)

Now compare the curves for the four sawdust runs with this baseline curve. By Equation (4), the difference between each pair of curves, times C_k , gives the rate of exotherm (or endotherm) at that temperature. In the two runs at atmospheric pressure, there is an endotherm (drying of the sawdust) up to about 400°F, followed by an exotherm (decomposition of the wood) between about 400 and 800°F. In the two runs at 300 psig the endotherm region persists to higher temperatures, at least partly due to the fact that water is remaining longer in the condensed phase.

Quantitative interpretation of these curves is made difficult by their irregularity, which introduces uncertainty in the values of dT/dt for the runs with charge. It is possible to reduce this uncertainty by making some reasonable assumptions about the sources of the irregularities, and hence obtain the most appropriate value for the rate of change of temperature. The assumptions used are as follows:

- The irregular heating rate observed during the drying phase is due to steam condensing on the cooler portion of the reactor and running back down, to be re-evaporated. Therefore, the minima in the jagged heating rate curve are meaningless; a smooth curve drawn through the peaks of the jagged curve represent the actual rate of heat uptake by the charge.
- This hypothesis can be checked by the expectation that the total heat uptake by the charge drying should sum to about 1200 Btu per lb. of water present.

- The irregular heating rate during the exotherm phase is due to local inhomogeneities in the progress of the exotherm, because of incomplete mixing of the charge. Therefore, a smooth curve averaging the irregular heating rate observed gives the best depiction of the rate of evolution of heat vs temperature.
- The behavior of the exotherm for the pressurized run without catalyst is not different from that for the unpressurized runs (because both cases give the same residues)--the lower net heating rate observed in the pressurized case being due only to the persistence of the drying phase into the exotherm region. However, the exotherm for the pressurized run with catalyst may be different from the others.

This approach, applied to the aforementioned data, does in fact yield a consistent and plausible analysis which is shown graphically in Figure 18. In these curves, the rate of heat transfer in Btu/F⁰, is plotted vs charge temperature. This figure shows separately the rate of heat uptake by 1 lb. of water, and the rate of heat evolution by 1 lb. of dry wood, under various process conditions. For any given run, the observed rate of heat transfer would be given by the algebraic sum of the appropriate water and wood curves, weighted according to the moisture content of the given charge.

The two lower curves show the heat absorbed by 1 lb. of water, when it is soaked into a comparable mass of dry wood, at both 1 atmosphere and 300 psig. In the atmospheric pressure case, drying of the charge is seen to extend up to 400°F, with the most rapid rate of evaporation occurring around 300-325°F (not, as might have been expected, 212°F). At 300 psig, the data are consistent with the water remaining in the condensed phase up to around 600°F. In both cases, as required, the area within the curves is about 1200 Btu/lb. water.

Figure 18

HEAT FLOWS DERIVED FROM CALORIMETRY EXPERIMENT

The two upper curves show the heat generated by 1 lb. dry wood (in the presence of a comparable amount of water). The first curve is consistent with the data for wood at both 1 atm. and 300 psig in the absence of catalyst. The second curve describes the wood exotherm at 300 psig steam pressure with alkaline catalyst. The total heat released in the first case is about 900 Btu/lb. dry wood--or 10% of the heating value of the charge. The second curve is depressed during the earlier part of the exotherm, when water is still present in the condensed phase. As a result, the total heat emitted is only about 600 Btu/lb. dry wood.

This observation, which arose independently out of this analysis of the data, is wholly consistent with--and lends support to--a reaction mechanism postulated earlier in this report. As discussed in Section III-H it is known that the char residue is markedly reduced under the combined conditions of both high pressure and presence of alkaline catalyst. It was postulated that the effect of pressure was to maintain moisture in the condensed phase to higher temperatures, and that the (endothermic) reaction of water with organic radicals occurred only in the combined presence of condensed-phase water, alkaline catalyst, and decomposing organic material. In this case, one would expect the normal wood-decomposition exotherm to be partially suppressed by the endothermic water reactions, exactly as observed here.

Figure 19 shows the estimated heat flow for the specific case of 1 lb. fresh wood (50-50 water-dry wood) at 300 psig with catalyst. The curve is the algebraic sum of two appropriate curves from Figure 18. A dip has been added around 1000-1100°F to represent the endothermic steam-char reaction known to occur there.

Figure 19

ESTIMATED HEAT FLOW - 1 lb "fresh wood" (50-50)

300 psig with catalyst

C. Projected Biomass Gasifier Thermal Cycle

The above information about endotherms and exotherms now permits the projection of the complete thermal cycle of a continuous-feed biomass gasifier. If the curve of Figure 19 is integrated up to a given temperature, the result is the net heat input to 1 lb. of charge as a function of temperature. This relationship provides the first part of the ascending curve of Figure 20.

Figure 20 shows the thermal cycle for 1 lb. fresh wood; first, it is heated, dried, pyrolyzed, and converted to fuel gas; and then as that product gas is cooled, condensed, and returned to ambient temperature. The horizontal scale represents the heat added to 1 lb. of wood from the beginning of the cycle; at the baseline "zero" point, of course, the wood already contains energy equal to its high heating value, here assumed to be 4500 Btu/lb.

The ascending curve, from its beginning to 500°F, is obtained by integrating the empirically-based curve of Figure 19. Above 500°F, the dashed line shows the result of continuing to integrate Figure 19 through the exotherm region. This is the path the system would take if the sensible heat liberated in the exotherm were continually removed. In fact this sensible heat remains in the charge, causing its temperature to ascend rapidly, as estimated by the solid line labeled "exotherm".

At 1200°F, the solids should all be gasified. At this temperature, the curve we have been following intersects with the upper curve in the figure, which describes the corresponding heat-temperature relationship for the product gas. This second curve is calculated from the heating values and enthalpies of the fixed gases and steam using the gas composition observed in previous biogas experiments.

If this gas/steam mixture is then cooled, it follows the second, descending curve. Condensation of steam begins at 360°F.

Figure 200

On further cooling to ambient temperature, the final heat content of the gas ends up some 300 Btu below that of the initial wood charge. That is, the high heating value of the gas produced from 1 lb. fresh wood is 4200 Btu, or 300 Btu less than the initial heating value of the wood. The difference is the net exothermicity of the overall set of gasification reactions.

In the PDU (and subsequent commercial gasifiers), the product gas will pass through a heat exchanger coil surrounding the reactor, so that the heat it gives up as it cools and condenses provides the process heat for the countercurrently moving charge. The vertical separation between the two curves of Figure 20 then has an important physical significance: it is the temperature difference driving the heat transfer.

From this figure, one can make two projections concerning the operation of the gasifier:

- As the figure is drawn, the wood decomposition exotherm provides enough heat to raise the charge to around 1200°F and complete the solids gasification and steam-cracking. In principle, there is enough energy in the exotherm to do this. Whether it will occur in practice will not be verified until the PDU is put into operation. It could not be demonstrated in the laboratory-scale gasifiers, because at this small scale the heat capacity of the metal reactors rapidly absorbs the heat generated by the charge.
- The temperature difference between the hot gas and the charge is always positive and typically several hundred degrees Fahrenheit. At its smallest, this temperature difference is about 100°F, and this occurs when heat transfer is particularly good (condensing steam to damp wood). Thus, there are favorable conditions for heat transfer along the entire length of the reactor.

D. Heat Transfer Properties of Biomass Solids

In order to design a process development unit, or to evaluate the feasibility of a commercial plant, one must be able to estimate the heat transfer surface required to provide process heat to the reactor.

The first step in this projection is to determine the coefficient of heat transfer between the kiln wall and the tumbling solids bed. This is both a theoretical and an experimental problem, and is dealt with below. In the following Subsection E, these results are combined with the theoretically calculable wall-to-gas coefficient to determine the overall heat transfer properties of the system.

1. Derivation of Wall-to-Solids Coefficient

The rate of transfer of heat from kiln wall to the tumbling solids bed depends on properties of the kiln such as its fullness and rotation rate, as well as on the materials making up the bed. Fortunately, it is not necessary to measure this complicated dependence experimentally. One can develop a simplified conceptual model of the tumbling bed, and derive the relationship mathematically, as follows:

The diagram below shows a cross-section of a rotating kiln, of radius R , and bed depth d , turning at N revolutions per hour.

The net flow of heat from wall to bed is described by

$$\frac{dQ}{dt} = AA \cdot (T_w - T_b) \cdot hh \quad (66)$$

where:

AA == area of wall in contact with the bed, ft^2
 T_w, T_b == average temperatures of wall and bed, $^{\circ}\text{F}$
 hh == coefficient of heat transfer, $\text{Btu/hr-ft}^2-^{\circ}\text{F}$

We assume the heat transfer occurs as a two-step process: first, heat flows from the wall into the bed by conduction, heating a shallow layer of the charge; then when this material, turning, reaches the surface of the bed, it tumbles down the slope and mixes with the rest of the bed.

We assume negligible film resistance between wall and bed to-mass particles. We further assume that the layer of charge that is heated is thin compared to the bed depth, and that when the heated material tumbles down the face of the bed, it mixes uniformly and instantaneously with the rest of the charge.

Then, from the equations for transient conduction into a thick slab, one can derive the following expression for the heat transfer coefficient.

$$hh = 22 \sqrt{\frac{cc \rho \phi k N}{\phi \phi}} \quad (67)$$

where:

cc == specific heat capacity of the material, $\text{Btu/lb-}^{\circ}\text{F}$
 ρ == bulk density, lb/ft^3
 k == thermal conductivity, $\text{Btu/hr-ft-}^{\circ}\text{F}$
 N == rotation rate, turns/hr
 ϕ == geometrical factor describing fullness of kiln

$$= \sin^{-1} \sqrt{22 \left(\frac{d}{R} \right) - \left(\frac{d}{R} \right)^2} \quad (\text{see diagram}) \quad (68)$$

This equation was derived independently, and later discovered in the literature.⁽³⁾

The value of this equation is that it predicts the heat transfer coefficient for material tumbling in a rotating kiln, in terms of bed geometry, rotation rate, and the thermal properties of the quiescent material: its specific heat, bulk density, and thermal conductivity. These can easily be determined independently of any particular reactor, and the results applied to a rotary kiln of any reasonable size, bed depth, and tumbling frequency.

It should be pointed out that as the tumbling frequency is increased, the heat transfer coefficient cannot, of course, increase without bound as the equation would suggest. It is limited by the wall-to-particle surface coefficient. Information from the literature indicates that this limit is reached at a tumbling frequency of about $N = 20$ revolutions per minute.

Otherwise, the model is conservative. It neglects other mechanisms which will transfer additional heat to the charge: evaporation of moisture at the kiln wall followed by condensation on cooler parts of the bed; radiation from the wall to the charge; and contact of the upper surface of the bed with hot, turbulent gas.

2. Measurement of Thermal Properties of Wood Particles

From the relationship above, the heat transfer coefficient for materials tumbling in a rotating kiln can be predicted, if the thermal conductivity, specific heat capacity, and bulk

(3) V.W. Uhl and W.L. Root, Chem. Eng. Prog., July 1967.

density of the charge are known. These properties for wood can usually be found in handbook tabulations, but such listings often disagree with one another and do not normally specify the type of wood, the moisture content, or the particle size.

Therefore a series of tests were performed specifically to measure the thermal properties of the materials of interest in this project: fresh sawdust, of varying degrees of wetness and compression, wood chips, and char.

The experimental equipment consisted of a cylindrical container, insulated at either end, with an electric heating coil along its axis and a cooling coil carrying tap water around the outside. The magnitude of the temperature difference set up between the inner and outer coils gives a direct measure of the conductivity of the material in the container. The rate at which this temperature difference is established is determined by both the conductivity and the specific heat capacity, and thus yields c for the material.

The equipment was constructed as follows: A piece of cylindrical stovepipe, 8" in diameter and 24" long, provides the outer wall of the container. The inner cylinder is a 24" long, 1" diameter plastic pipe, whose central 16" is wrapped tightly with resistance wire and covered with protective foil. Three thermocouples are fixed at 4, 8, and 12" along this coil. Two 4"-thick pieces of polyurethane insulation, round with 8" diameter and 1" central hole, fit into the ends of the cylinder, insulating the ends of the experimental chamber and supporting the heating coil along the axis. The cavity for the charge is thus 16" long, by 8" in diameter.

The cooling coil is constructed of $\frac{1}{2}$ " copper tubing, wrapped tightly around the central 16" of the outer wall of the container. Two thermocouples measure the temperature of the cooling water as it enters and leaves the coil.

The experimental procedure was as follows: The cylindrical container was filled with the material to be investigated and topped with the polyurethane insulator. Tap water at 50°F was circulated through the cooling coil, and the entire apparatus was allowed to sit overnight to come to constant temperature. In the morning, the heating coil was energized at 8 to 10 watts, and its temperature recorded every 10 minutes for several hours. The water temperature and coil power were also recorded, so any variations could be noted.

Heat flows from the resistance coil, into and through the experimental material, and into the cooling water. At steady state, the temperature difference between the inner and outer cylinders is inversely proportional to the thermal conductivity of the material within. For cylindrical symmetry, the relationship is⁽⁴⁾

$$k = \frac{\ln (r_{\text{out}}/r_{\text{in}})}{2\pi L \Delta T} q \quad (9)$$

where L is the length of the cylinder, and q is the heat input in Btu/hr. For the given equipment, this becomes

$$k = \frac{0.488 P}{\Delta T_f} \quad (10)$$

where P is the power input in watts, and ΔT_f the (final) temperature difference in F°.

In practice, the given system takes many hours to approach steady state; and therefore the "final" temperature difference was not measured directly but was determined mathematically from the rate of temperature change at earlier times. After some initial transients, the temperature T at any point within the charge proceeds toward its final value T_f exponentially with time:

(4) McAdams, Heat Transmission, p.13

$$(T-T_o) = (T_f-T_o) \left[1 - e^{-\beta(t-t_o)} \right] \quad (11)$$

For a long cylinder of radius r , the time constant β is related to the thermal diffusivity of the material, α , by

$$\beta = \frac{5.76}{r^2} \alpha \quad (12)$$

where $\alpha = k/\rho c$, in units ft^2/hr ⁽⁵⁾.

Thus the data from these runs were analyzed in the following way: For each run, the first hour's data were discarded, as were any portions of the data which were unaccountably irregular or which were taken while input power or water temperature were not constant. The remainder of the data from each run were fitted to the above exponential curve, values of T_f and β being chosen to optimize the fit. In almost every case, a coefficient of determination of at least $r^2 = 0.999$ could be achieved.

These two parameters then uniquely determine the conductivity k and the volumetric heat capacity ρc for the given charge. The specific heat capacity c , if desired, be determined by independent measurement of the material's bulk density. (For calculating the heat transfer coefficient h , only the product ρc is needed; but in this work we determined p and c independently, to check the reasonableness of the results.)

The question was raised whether the heat capacity of the core containing the heating coil would bias the measurement of thermal diffusivity. As a check, two runs were performed with the core removed and the three thermocouples

(5) McAdams, p. 41

positioned along the center line of the container on a thin dowel. In these runs, the system was allowed to equilibrate at ambient temperature (70-80°F) overnight; and then in the morning the flow of cooling water at 50°F was started. The temperature at the center of the charge was recorded as it cooled, and the data was fit to the exponential curve as before. For both fresh and dried sawdust, values determined for β were consistent with those from the other configuration, within an experimental error of 5%.

Several experimental materials were tested. Fresh softwood sawdust and wood chips were obtained from a local lumber yard. Some of the sawdust was air dried for several days to obtain material of varying moisture content. The moisture content was determined by heating samples in a 250°F oven for 8 to 24 hours and measuring the weight loss. Char residue from gasification of softwood sawdust in the minikiln was also studied.

The results are shown in Figure 21. Here the values obtained for bulk density ρ , specific heat capacity c and conductivity k , are shown graphically for both sawdust and wood chips, as a function of moisture, and also for the char.

For all three properties, the difference between sawdust (•) and wood chips (□) is negligible. Thus, it seems that particle size is not an important variable in predicting heat transfer properties (at least as long as the particle shapes are similar, as is the case here).

One run (+) was performed with sawdust compressed to about 1/3 again its normal (loosely packed) density. In this case the thermal conductivity k was increased by only 10%. We conclude that any effect of greater bed depth in improving thermal contact by lightly compressing the charge bed is not significant.

THERMAL PROPERTIES OF MATERIALS

Figure 21

- sawdust (loose)
- + compressed sd.
- wood chips
- * char

As expected, all three properties depend strongly on the moisture content of the material. On the graph of density vs moisture content, the solid line is a theoretical curve. It is obtained by assuming the given mass of dry wood takes up space at 8 lb/ft^3 , the given mass of water takes up space at 62.4 lb/ft^3 , and the combined density is given by the total mass divided by the total volume. Although this model does not allow for water filling air spaces in the wood, it provides a neat summary of the empirical results.

On the graph of heat capacity vs moisture, the solid line is also a theoretical curve, based on the assumption that the heat capacity is simply the weighed average of that for dry wood (assumed $0.45 \text{ Btu/lb-F}^\circ$) and that for water (1.0).

On the graph of thermal conductivity, the curve is drawn through the data points. It curves down to $0.03 \text{ Btu/ft-hr-F}^\circ$ at the low end, a handbook value for dry wood. At the upper end, it curves sharply upward, toward a value of about 0.35 for water.

From these results one can now calculate the coefficient of heat transfer from the kiln wall into a tumbling bed of wood chips or char.

E. Heat Transfer Requiements for the Rotary Kiln Gasifier

1. Introduction

In this section are calculated the projected heat transfer coefficients relevant to the rotary kiln gasifier. These include the wall-to-bed and wall-to-gas coefficients, as well as the overall coefficients of heat transfer from the returning gas in the exterior coil to the interior charge and gas. The calculations are based partly on established engineering formulae and partly on our own measurements on thermal properties of sawdust at various stages of gasification.

Because the process is still under development, these calculations have had to involve approximations in a number of crucial points. It is believed that the values presented here have an uncertainty of perhaps 20%. For this reason, only the major factors determining the heat transfer coefficients were taken into account.

2. Wall-to-Bed Heat Transfer Coefficient

The wall-to-bed heat transfer coefficient was calculated using the derived equation,

$$h_{wb} = 2 \sqrt{\frac{c \rho k N}{\phi}} \quad (13)$$

where

c = specific heat capacity of the bed material

ρ = bulk density of the bed

k = thermal conductivity of the bed

N = turns/hr of the kiln

ϕ = half the angle subtended by the bed at the axis

The previous subsection reported measured values of c , ρ , and k for a typical wood sawdust at various stages of drying, and as char. Using these data, the value of h_{wb} was calculated as a function of kiln temperature, for values of N between 1 and 10 rpm. The results are displayed in Figure 22(a).

The behavior of h_{wb} with temperature can be understood as follows: At first, as the biomass dries and chars, the heat transfer decreases. Then, as the char gasifies and the bed depth decreases, the bed tumbles more frequently with each turn of the kiln and the rate of heat transfer increases again.

3. Wall-to-Gas Heat Transfer Coefficient

The flow velocity of the gas through the kiln is far from turbulent (the Reynolds number varies from 300 at the cooler end to around 1000 at the hotter). Transfer by natural convection is however not insignificant, because of the relatively higher density of the gas at 20 atmospheres. Standard equations for convective heat transfer in enclosed spaces yield h_{wg} about $10 \text{ Btu/ft}^2\text{-hr-F}^\circ$, nearly independently of the temperature of location along the kiln. (This may be an underestimate, as there is some forced mixing due to the tumbling of the bed.)

At the hotter end of the kiln, heat transfer to the gas is augmented by radiation (the dense, H_2O -and CO_2 -rich gas is an IR absorber) to the extent of approximately $2 \text{ Btu/ft}^2\text{-hr-F}^\circ$ additional.

We therefore estimate h_{wg} as shown in Figure 22(b).

4. Bed-to-Gas Heat Transfer

The rate of heat transfer between bed and gas depends strongly on what is happening physically at the interface. As the bed turns and tumbles, the particles will, to some extent, fall through the gas, and entrap gas within the bed. This gas-solids mixing could be more pronounced if the kiln were equipped with internal fins wherein the effective area of contact between solids and gases will be several times that between wall and gas, or wall and bed.

Thus, we may expect the average temperature difference between bed and gas to be much smaller than that between the wall and either bed or gas. This provides the justification for an assumption which simplifies the calculation: we assume that both bed and gases, at a given station along the kiln, have the same, uniform temperature, T_i .

Figure 22

5. Total Wall-to-Interior Heat Transfer

It follows that the transfer of heat from kiln wall to interior can be described by a single heat transfer coefficient, h_{wi} , which is the average of h_{wb} and h_{wg} , weighted according to the area of wall in contact with bed and gas:

$$h_{wi} = \frac{\phi}{\pi} h_{wb} + \left(\frac{\pi-\phi}{\pi}\right) h_{wg} \quad (14)$$

The fullness parameter ϕ decreases from nearly $\pi/2$ at the beginning to essentially zero at the end of the kiln, as seen in Figure 22(c). This curve is based on data from minikiln runs that were terminated at intermediate temperatures.

The calculated values of the two terms making up h_{wi} and h_{wi} itself, as functions of temperature, are shown in Figure 23.

6. Overall Heat Transfer Coefficient

The process heat is supplied by sensible and latent heat of the product gas, in counterflow through a heat transfer coil surrounding the kiln. The total path for heat transfer is therefore from this gas, through the walls of coil and kiln, and only then into the kiln interior. The overall heat transfer coefficient U is given by an expression of the form

$$\frac{1}{U} = \frac{1}{h_{wi}} + \frac{1}{k_x} + \frac{1}{h_f} + \frac{1}{h_{ow}} \quad (15)$$

Clearly, the h_{wi} term will be controlling.

We assume that the coil is good thermal contact with the kiln, and that breakers are used to scour the kiln interior wall. Then the terms describing the thermal resistances of walls and films become negligibly small. Furthermore, below 350°F coil temperature (250°F kiln temperature), condensation of steam in the return coil makes h_{ow} large enough that it does not contribute measurably to U .

Figure 23

Above this temperature, the coefficient for heat transfer from returning gas to wall, h_{ow} , is large but not ignorable. Its precise value depends strongly on the diameter and number of parallel channels making up the return coil. A typical value would be in the range of 50 to 100 Btu/ft²-hr-F⁰, larger toward the hotter end because of the higher gas velocity there.

Our estimate for the overall U is therefore just slightly less than that for h_{wi} , as shown in Figure 24(a).

7. Heat Flux

The rate of flow of heat from this returning gas to the kiln interior, per unit kiln area, is thus

$$\frac{\Delta \dot{q}}{\Delta s} = U (T_o - T_i)$$

The temperature difference $T_o - T_i$ is obtained from the graph of the projected gasifier heat cycle (Figure 20, page V-15). This temperature difference is plotted against T_i as Figure 24(b).

The resulting heat flux, as a function of T_i , is then as shown in Figure 24(c).

8. Heat Required for the Process

The question remaining is: how much heat transfer area is required for the above flux to supply the required heat for the gasification process?

The heat cycle diagram, Figure 20, shows the cumulative heat input to one pound of biomass, as a function of the temperature. The derivative of this curve, $\Delta q / \Delta T$, gives the incremental heat required to raise 1 lb. of charge 1 F⁰. Multiplying this function by the projected PDU feed rate of 500 lb/hr. yields the required flow rate of heat, for each 1 F⁰ increment along the kiln. This quantity, $\Delta \dot{Q} / \Delta T$ is plotted, as a function of T_i , in Figure 25(a).

Figure 24

Figure 25

The curve drops to zero at 600°F, as at this temperature the exotherm takes over, providing the thermal energy to carry the process to completion.

9. Heat Transfer Area Required for the PDU

Lastly, taking the ratio of the two preceding functions yields $\Delta s/\Delta T$, the incremental surface needed to supply heat to raise 500 lb/hr. of the charge by 1 F°. This function is plotted as Figure 25(b). The area under the curves gives the total heat transfer surface needed to raise the charge to 600°F. This surface area, as here computed, ranges from 140 ft² for N=1 rpm down to about 70 ft² for N=10 rpm.

The W-M designed PDU kiln measures 2 by 30 feet, providing 160 ft² of surface area for heat transfer. A rotary kiln gasifier of these dimensions is thus in no way heat transfer limited for a rating of 500 lbs/hr.

SECTION VI

QUALITATIVE OBSERVATIONS AND CONCLUSIONS

A. Introduction

The preceding sections of this report have dealt primarily with the quantitative results of a number of tests, experiments, and calculations, most of them planned to answer specific questions.

In addition, during the course of these studies, a number of qualitative observations have also been made, often as a byproduct of the particular investigation. These observations have been important in proving the process and determining the design and operation of the PDU and subsequent commercial gasifiers. Some of them merely confirmed expected behavior, but others significantly altered initial gasifier concepts.

The more important of these observations, and the conclusions drawn from them, are compiled in this section.

B. Caking in the Reactor

All the experience with minikiln and biogasser indicates that, although caking of biomass in the reactor can occur, it need not be a problem.

In most runs in the minikiln, limestone breakers ($\frac{1}{2}$ to 1 kg coarse gravel) were added with the biomass charge. This was more than sufficient to prevent agglomeration of the charge and to break down the charring wood particles to fine granules and powder. There was some buildup of char on the end walls of the minikiln, and along the lateral walls behind the steam injection pipes, where the breakers could not reach. But for the most part, the side walls remained free of significant char accumulation.

It may be noted, in passing, that the breakers used in the minikiln were sufficient to break down quite large pieces of wood. Even slabs of poplar trunk up to several inches across were found to become so brittle when charred that they were quickly broken down to fine particles, and the overall extent of conversion to gas was not noticeably less than when wood chips or sawdust were the starting material. It is concluded that there is no need to reduce the biomass to small particles for the sake of the gasification process; the only restraint on particle size is ease of materials handling and passage through the reactor feed system.

In the biogasser, inorganic breakers were not used, as they would damage sealing surfaces in the feed system and perhaps jam in the screw. There was thus some concern that the pyrolyzing biomass might become tacky, causing the wood particles to stick together, adhere to the screw surface, and perhaps plug the reactor. However, in all the situations tested, there was never any indication of such stickiness occurring, with either wet or dry wood.

There was a tendency for a char cake to build up gradually on the upper portion of the biomass wall not reached by the screw, and also on the trailing surface of the screw flights. The leading edges of the flights, which were constantly being scrubbed by the biomass or char, stayed free of any buildup. Changes in reactor response during the series of tests indicated that the buildup on the upper wall was seriously reducing the heat transfer from wall to gas.

It is concluded that char buildup in the gasifier can occur, with detrimental effects on heat transfer, and so it must be avoided. In a rotary kiln, it is easy to prevent char buildup by the inclusion of breakers.

C. Behavior of Steam in Reactor

As the sawdust in the reactor is heated and dried, the first gas to be emitted is water vapor. In the conceptual stage of gasifier design, there was some question about where this steam would go: Would it flow backward and condense upon the cooler parts of the reactor, or would it all move forward with the product gases, while the air admitted with the sawdust formed a pocket in the cooler end of the reactor?

Biogasser studies have now verified that at least some of the steam flows backward and condenses. This was revealed in the biogasser tests by the gradual rise in temperature of the cool end of the reactor, until it reached the condensation temperature of steam at reactor pressure.

The consequences of this fact are of considerable significance to design and operation of future gasifiers. Previous concepts of the W-M system have shown the process heat for drying and gasification to be supplied by the product gas as it cools--and some of its steam condenses--in a jacket surrounding the reactor. The heat cycle described in the previous section is based on this presumption (though these later findings do not invalidate those conclusions). It is now seen that it will be impossible to cool the product gas in the jacket below the temperature at which steam condenses in the reactor; and at this temperature, no steam will condense from the product gas. It is not, therefore, possible to draw enough heat from the product gas to carry out this drying and gasification.

A solution is to modify the reactor design, so that the heat transfer from product gas to biomass is carried out in two separate stages: a preheater, in which the biomass is heated to the "boiling point", and then the rotary kiln gasifier for the rest of the process. The product gas can be cooled as far as possible in the gasifier jacket, then can be further cooled, and some of its steam condensed, in a preheater. The situation is analogous to making superheated steam: It can't be done in a single device; one needs a separate boiler and superheater.

(One option that seems very attractive is to make the preheater the standpipe in which the biomass is held before dropping through the ball valve into the reactor. It seems feasible that, during this part of the feed cycle, the warm product gas from the kiln jacket could be passed into and through the standpipe, in direct contact with the biomass. By direct transfer of sensible heat, and condensation of some of the steam onto the biomass, the charge would be brought up to temperature very quickly. As a bonus, the biomass would act as a scrubber, filtering particulates and absorbing organic vapors that may remain in the gas. The acceptance of this option will depend upon the effectiveness of the biomass as a gas filter, the ability of the moistened biomass to feed freely, and the detailed thermodynamic calculation of the modified heat cycle.)

D. Choice of Rotary Kiln Over Auger Reactor

At the time this contract was awarded, W-M was developing, in parallel, two distinct reactor configurations: a rotary kiln, suitable for gasifying coarsely-shredded municipal wastes; and a stationary, tubular reactor with auger transport, designed for shredded biomass. During the course of the present work, it became apparent that the rotary kiln was preferable over the auger reactor for either application.

We were led to this conclusion as a result of trying to design adequate heat transfer into an auger-fed biomass PDU. However, there are mechanical as well as thermal considerations that support the choice of kiln over auger reactor. The major points are summarized below.

Originally, there were two reasons for preferring the auger reactor for biomass gasification. 1) It was thought that the biomass gasifier would be operated at very high (e.g. critical) pressure; this would require a reactor of small diameter, and would preclude a rotating vessel with sliding seals. 2) It was expected that, at high pressure, the fresh green biomass would cook down into a thick soup, for which positive transport could best be accomplished by an Archimedes screw. The experimental biogasser was designed to provide these conditions.

The exploratory tests with the biogasser, completed in the fall of 1977, showed these presumptions incorrect. The optimum reactor pressure was found to be around 300 psig (approximately the pressure already planned for the rotary kiln solid waste gasifier). And, at this pressure, the sawdust maintains its particulate nature as it dries, pyrolyzes and gasifies.

On the other hand, there are numerous arguments in favor of utilizing a rotary kiln for gasifying biomass as well as solid wastes. Heat transfer from reactor wall to charge is better in a rotating kiln than in an auger reactor. Because of the low thermal conductivity of materials like wood chips and char,

heating of the bulk of the charge occurs through a two-stage process: first a shallow layer along the reactor wall is heated by conduction; secondly this heated portion is mechanically mixed and distributed through the rest of the bed. In the rotating kiln, this mixing occurs freely and frequently, every time the kiln turns. In the auger reactor, the charge does not mix as thoroughly, but tends to be pushed along as a plug or "rope".

Further, because of the simpler pattern of particle motion, the heat transfer properties of the rotating kiln can be modeled more easily than can those of the auger, as discussed earlier in this report. Having such a model permits design of the PDU and of the projected commercial plants of Task III, with reasonable confidence in the validity of scaling up.

Another consideration relating to heat transfer is that in a rotating kiln the whole lateral surface of the reactor is heat transfer area. Even that part of the wall that is above the solids bed at a given time is continuously heated by the returning gas in the surrounding coil, and transfers this stored heat to the bed as it turns under the charge. In an auger reactor only the lower surface of the reactor comes in contact with the solids bed.

There are also economic considerations tending to support the choice of a kiln as a gasifier, such as lower power consumption, greater feedstock versatility, and lower projected cost.

For these reasons, the process development unit has been designed with a rotary kiln on the biomass gasification vessel.

E. General Conclusions

This report concludes the experimental phase of development of the W-M gasification system. The work reported here has proven the process in both batch- and continuous-feed bench-scale reactors. It has determined the effects of various process parameters and the magnitude of those effects, on both gasification of solids

and steam-cracking of volatiles, thus permitting a projection of optimum operating conditions for a full-scale reactor. And it has provided a quantitative basis for modeling such a plant: determining material flows and thermal cycles, estimating overall plant efficiency, and projecting its economics.

These results, conclusions, and projections are supportive of further development of the W-M gasification system.

The principal questions remaining at this time have to do with scaling up the process to commercial sizes: What will the flow path of gases in a large rotary kiln be? How well will the solids and gases intermix in the kiln, and what effect will this have on interaction of steam with the char? How good is the transfer of heat from kiln wall to solids and gases, and--more important because it cannot be calculated even approximately--the transfer of heat between the tumbling solids and the gases? And what effect will this heat transfer have on the progress of the wood decomposition exotherm? These questions about materials flow and heat transfer involve phenomena that in general do not scale easily, and must be determined empirically in an intermediate-scale system before the process can be said to be fully defined.

Other questions remaining are technical and mechanical in nature, relating to construction and control of a large-scale, continuous-feed pressurized rotary kiln. Chief among the engineering challenges are the lock valve feed system, rotating seals for the pressurized kiln, techniques for handling the hot residue, the heat transfer systems in the kiln and pre-heater, and start-up/shutdown procedures. Engineering designs of these systems have been prepared and will be tested in the PDU before they are applied to commercial plants.