

Indirect steam gasification of paper mill sludge waste

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The clean gas generated by an indirect gasifier can replace premium fuels used elsewhere in the mill.

The potential for recovering energy from renewable sources and organic waste products has been recognized for many years. In recent years, we have been confronted with the realization that fossil fuels—oil and gas in particular—are unrenowable and being depleted at an accelerated rate. Thus the need for an effective technology for utilizing renewable organic sources of energy is a prime consideration for U.S. energy policy.

Paper mill biomass waste is representative of materials discharged from virgin pulp mills and recycle mills located throughout the United States. These sludges typically contain 70% moisture as delivered from a belt press. Many mills are currently installing screw presses to reduce the moisture content to 50%. Increasing disposal costs, diminishing landfill sites, and social and environmental factors are forcing mills to find unique solutions.

Manufacturing and Technology Conversion International (MTCI) has developed a unique process that reduces the volume of the solid wastes, destroys the chlorinated organics such as dioxins, and produces clean fuel gas for use in the mill as a replacement for natural gas.

Background

A pulse-enhanced, indirectly heated fluidized bed gasifier system was constructed and tested by MTCI during 1985–86 for gasification of waste feedstocks under Phase II of a Department of Energy/Small Business Innovative Research (DOE/SBIR) program. The results of these tests confirmed the technical feasibility of the steam gasification of various feedstocks using the resonance tubes of the MTCI pulse combustor technology as an in-bed heat exchanger. In fact, the system demonstrated a capability

for generating a medium-Btu product gas of a quality superior to that attainable in an air-blown, direct gasification system. The system's overall simplicity, due to the compact nature of the pulse combustor and the high heat transfer rates attainable within the pulsating flow resonance tubes, provided a decided and near-term potential economic advantage for the MTCI system when compared to alternative direct or indirect gasification systems.

Under Phase II of this DOE/SBIR grant, testing of the gasifier was limited to biomass feedstocks only. In early 1987, Weyerhaeuser Paper Company expressed an interest in testing the MTCI gasifier using black liquor feedstocks. The pulp and paper industry has an ongoing and substantial interest in developing new black liquor recovery methods because the existing technology has significant economic, safety, and environmental shortcomings.

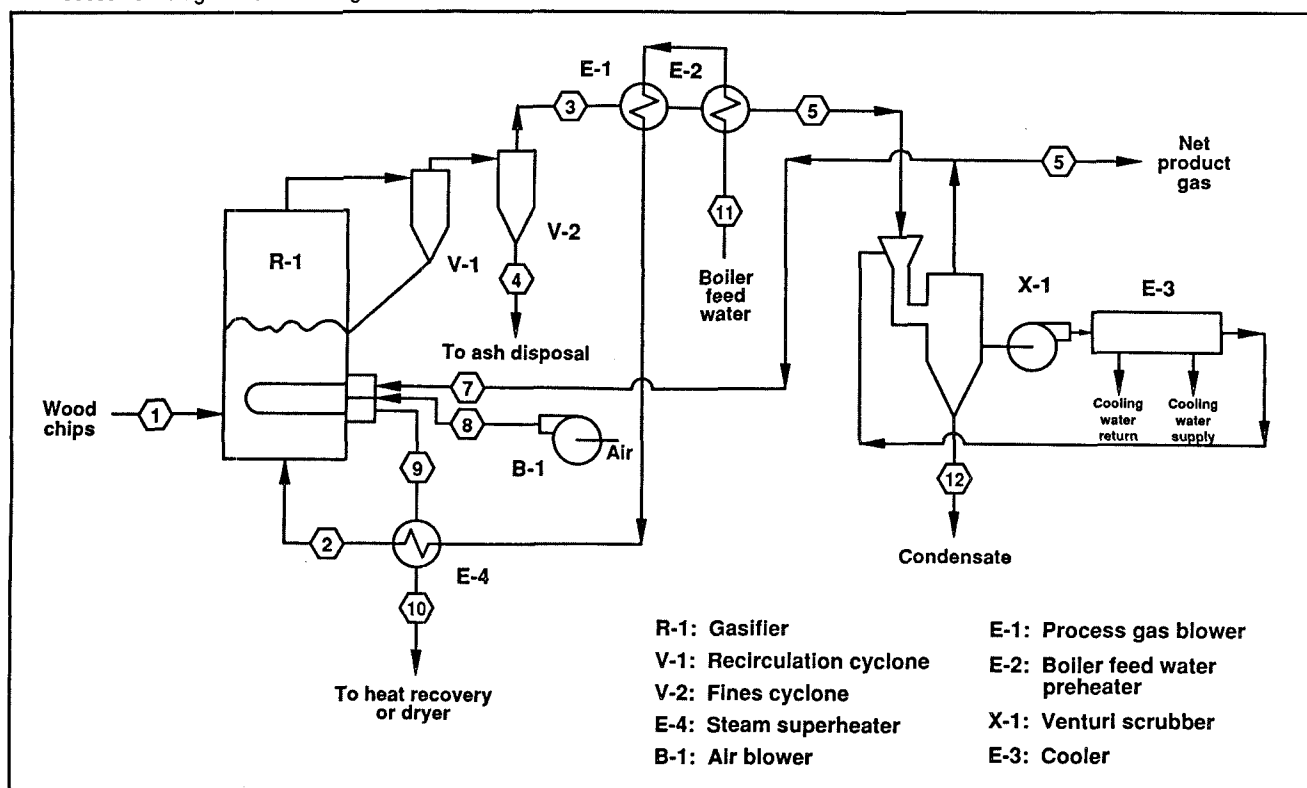
Preliminary feasibility tests were conducted in a 15 kg/h reactor, which verified the feasibility of the MTCI gasifier with black liquor feedstocks. In order to further develop this technology for mill sludge waste gasification and black liquor recovery, MTCI received funding from the Department of Energy (DOE), Weyerhaeuser Paper Company, and the California Energy Commission's Energy Technologies Advancement Program (ETAP). A scale-up reactor (90 kg/h) was constructed and tested for verification of the technology. The tests emphasized the collection of definitive process data on conditions and with a broad range of feedstocks.

These projects were completed in 1989 and have yielded extremely successful results confirming the commercialization potential of the MTCI technology to process a wide spectrum of biomass feedstocks as well as the ability to process mill biomass waste from recycling operations.¹ In these tests, the MTCI gasifier was operated using samples of paper mill biomass waste provided by the Gaylord Container Corporation. This waste is currently being landfilled at a significant expense to Gaylord. Despite the high moisture content and presence of plastic material in

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¹"Testing of an advanced thermochemical conversion system," MTCI, DOE Contract No. DE-AC06-76RL01830, January 1990.

1. Process flow diagram for indirect gasifier



these waste products, the MTCI gasifier operated without problems.

Process description

A schematic of the MTCI indirect steam gasifier is given in Fig. 1. It consists of a fluidized bed reactor with in-bed heater tubes, which are part of a pulse combustor. The pulse combustor, which will be described later, allows for very high heat transfer rates. Thus fewer heat exchanger tubes are necessary to supply the endothermic heat required for the gasification reaction.

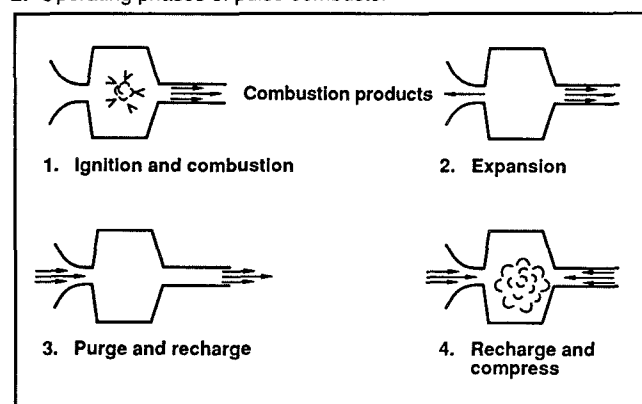
As indicated in Fig. 1, biomass is fed to gasifier R-1 using an injection screw. The gasifier is fluidized with superheated steam from E-4. Product gases are routed to cyclones V-1 and V-2 to remove the bulk of entrained particulate matter. Char and ash collected from V-2 are discharged for disposal.

The hot process gases are cooled in process gas boiler E-1 and boiler feed water preheater E-2. The quantity of steam generated in E-1 is sufficient to meet the process needs of the plant. The cooled gases are then quenched and scrubbed in venturi scrubber X-1. Heat is removed from the circulating quench water using cooler E-3. The product gases, having been cooled to 120°F or less, are substantially free of particulate and water vapor.

A portion of these medium-Btu product gases would be delivered to the pulsating heat exchanger as a fuel source. Combustion of these gases provides the heat necessary for the indirect gasification process.

Waste heat at the exit of the pulsating heat exchanger is utilized to superheat the process heat. Additional waste heat is available for feedstock drying, if necessary, or for

2. Operating phases of pulse combustor



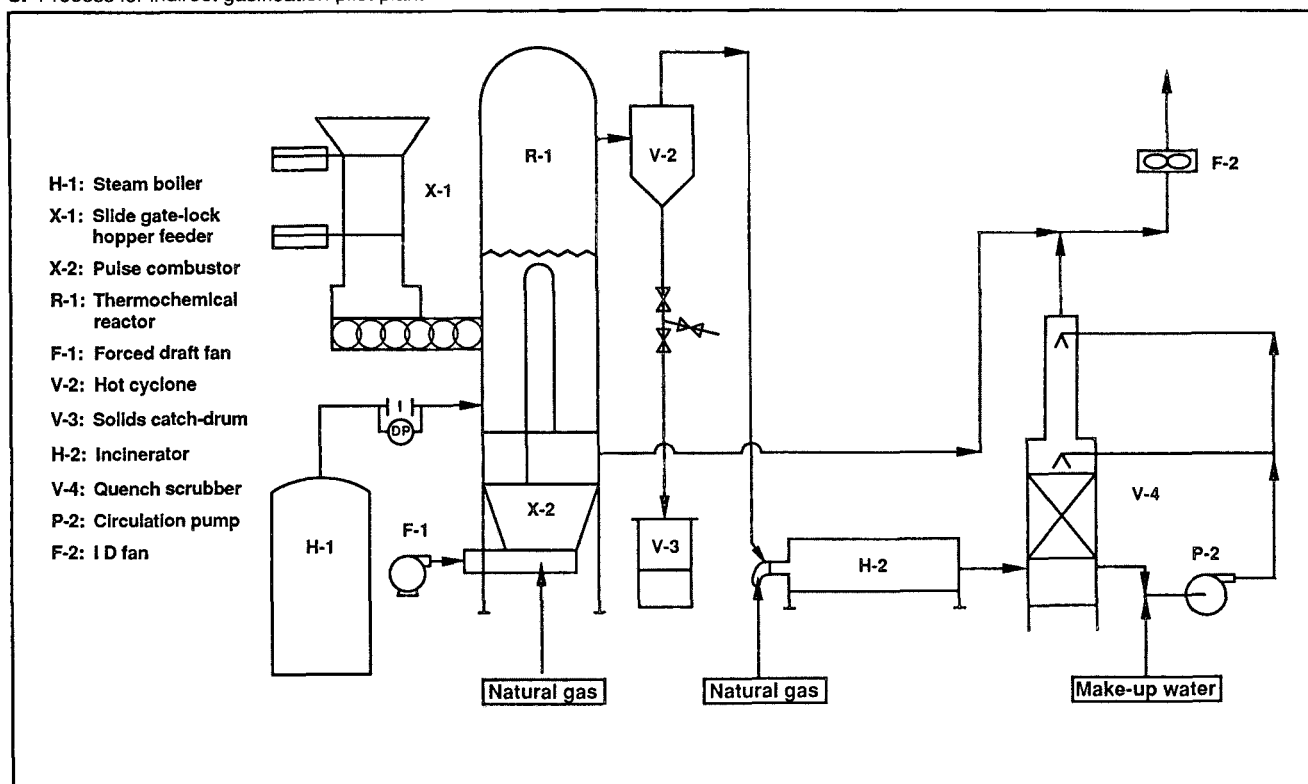
generation of export steam to be used elsewhere in an integrated plant.

Description of the pulse combustor

The indirect gasifier tested under this program is supplied heat through the resonance tubes of a pulse combustor. The use of pulse combustion significantly enhances the performance and economics of the indirectly heated gasifier since heat transfer coefficients can be obtained which are three to five times that achievable in steady-flow systems.

The physical principles involved in the operation of a pulse combustor are essentially the same as those which govern the undesirable pulsations that sometimes plague conventional combustion. However, pulsations or

3. Process for indirect gasification pilot plant



combustion-driven oscillations are induced by design and are intended to improve combustion rates, heat transfer, and system performance. The frequency, intensity, and nature of these self-induced combustion oscillations depend upon the precise geometry of the pulse combustion apparatus.

The pulse combustor consists of three main components: an air inlet valve, a combustion chamber, and a tailpipe or resonance tube. The pulse combustor operates over a natural oscillation cycle, as shown in Fig. 2. In the first step, fuel and air ignite within the combustion chamber. Ignition is spontaneously triggered from hot gases of the previous cycle and is not controlled by a spark plug or other external means. In the second step, the combustion-induced pressure rise forces the burning mixture to expand outward toward the tailpipe exit. Although some gases escape through the air inlet, the fluidic design of the air valve significantly impedes flow in this direction. In the third step, the momentum of the outrushing combustion gases creates a suction within the combustion chamber. This results in the purging and recharging of the chamber with fresh air and fuel. The fourth and final step involves recompression of the fuel/air mixture within the chamber. This is followed by spontaneous ignition to repeat the natural pulsation cycle.

Chamber pressure fluctuations of 34.5 kPa (± 5 psi) are commonly achieved in pulse combustors. These pressure fluctuations are translated into velocity fluctuations of 180 m/s (600 ft/s) within the resonant tailpipe. The velocity fluctuations, which occur at a frequency characteristic of the combustor (30–300 Hz), intensely scrub the convective boundary layer inside the tube surface, thereby enhancing heat transfer rates.

In the conceptual commercial gasifier designed for atmospheric operation, as shown in Fig. 3, the pulse combustors will be constructed in modules which can be inserted into the sidewall of a refractory-lined containment vessel. The pulse combustor modules can be installed using techniques employed for conventional heat exchange tube bundles. Each pulse combustor will include an individual combustion chamber connected to a multitude of resonant heat exchange tailpipes. Since the pulse combustor is of a modular construction, scale-up of the gasifier is anticipated to be straightforward. In fact, MTCI had tested individual pulse combustors at firing rates of 1.5×10^6 kcal/h (6 MMBtu/h), which are comparable to the size expected for use in commercial systems.

Using the resonance tubes as a firetube bundle substantially alleviates heat transfer limitations on the flue gas side. This is due to the presence of a vigorous oscillating flow field contained within the resonance tubes. The oscillatory flow field, which causes periodic flow reversal, induces a significant level of turbulence in the boundary layer on the inner walls of the firetubes. This, in turn, gives rise to effective heat transfer coefficients (40–50 Btu/h/ft²/°F) about five times higher than that for conventional firetubes. Thus, the characteristics for the pulse-enhanced, indirectly heated gasifier overcome many of the limitations of the state-of-the-art gasifier systems.

Gasification tests

Test systems

Two separate pulse-enhanced gasifier systems were constructed under this program. The first unit consisted

I. Analysis for feedstocks tested in pulse-enhanced indirect gasifier

	Ultimate analysis, MAF wt%				
	<i>Pistachio shells</i>	<i>Wood chips</i>	<i>Rice hulls</i>	<i>Recycle paper mill sludge</i>	<i>Kraft mill sludge</i>
Carbon	49.51	49.33	49.09	50.00	59.36
Hydrogen	6.18	6.74	6.17	6.55	6.90
Oxygen (by diff.)	43.96	43.67	44.19	42.76	28.02
Sulfur	0.11	0.16	0.04	0.31	1.04
Nitrogen	0.24	0.10	0.51	0.38	4.68
Total	100.00	100.00	100.00	100.00	100.00
Heating value (MJ/kg)	19.4	19.4	19.4	20.6	24.1
Ash (as rec'd. wt%)	0.41	0.18	20.48	2.8	7.10
Moisture (as rec'd. wt%)	8.74	20.46	8.67	49.5	62.4

II. Operating summary and process conditions for biomass test runs

<i>Feedstock</i>	<i>Temperature, °K</i>	<i>Average feed rate, kg/h</i>	<i>Steam rate, kg/h</i>	<i>Steam to biomass, kg/kg</i>	<i>Total feed, kg/h</i>
Pistachio shells	987	16	12	0.73	152.9
Pistachio shells	931	14	14	1.02	52.3
Wood chips	970	10	14	1.37	93.3
Rice hulls	992	14	12	0.84	N/M
Recycle mill sludge waste	950	8	17	2.07	53.9
Kraft mill sludge waste	950	14	16	1.2	135.9

III. Selected gas compositions and product yields for biomass and mill sludge tests conducted in pulse-enhanced indirect gasifier

<i>Composition, vol %</i>	<i>Pistachio shells</i>	<i>Pistachio shells</i>	<i>Wood chips</i>	<i>Rice hulls</i>	<i>Recycle mill fiber waste</i>	<i>Recycled waste paper w/plastic</i>	<i>Kraft mill sludge</i>
H ₂	37.86	35.04	48.11	42.83	38.86	50.50	52.94
CO	18.84	23.43	22.91	19.67	23.34	19.26	11.77
CO ₂	28.73	25.20	20.18	24.40	23.27	20.10	21.94
CH ₄	10.65	11.31	8.32	11.56	8.31	8.42	8.95
Ethylene	2.12	2.86	0.05	N/D	3.44	N/D	0.96
Ethane	0.28	N/D	N/D	N/D	N/D	N/D	0.43
Propylene	0.95	1.31	0.04	N/D	2.19	N/D	0.85
Propane	0.18	0.12	0.03	0.48	0.42	0.57	0.26
I-Butane	N/D	N/D	N/D	0.29	0.27	0.32	0.24
N-Butane	0.36	0.72	0.06	0.40	0.07	0.46	0.26
I-Pentane	0.03	0.01	0.30	0.37	0.01	0.37	N/D
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00
HHV, MJ/m ³	13.7	15.0	12.2	13.6	15.2	13.5	13.7
HHV, Btu/scf	370	406	329	367	412	364	372
Temperature, °K	987	931	970	992	950	992	950
Yield, % carbon							
Dry gas	94.1	92.1	93.0	N/A	86.8	N/A	56.0
Char	4.6	5.8	4.0	18.1	8.5	N/A	37.0
Tar/oil	1.3	2.1	3.0	N/A	4.7	N/A	7.0

of a 20 cm fluid bed reactor (16 kg/h) enclosing two pulse combustor resonance tubes. This unit was employed to define essential gasification process data. The second gasifier consisted of a 48 cm reactor (90 kg/h) containing eight pulse combustor resonance tubes. The larger unit was intended to provide scale-up design criteria for integration of large, multitube heat exchange bundles. Both of these reactors shared essentially similar basic designs.

The main components of the gasifier test rigs used until 1989 are shown in Fig. 3. Steam was supplied to the fluidized bed reactor (R-1) from a boiler (H-1) where it was injected at the base of the bed through a series of sparge tubes. The fluidized bed consisted of sized calcium carbonate (limestone) particles. The pulse combustor (X-2) was fixed to the base of the reactor with its resonance tubes positioned to penetrate the bed in a U-tube arrangement. Combustion gases were then vented through an induced draft fan (F-2). The feed was injected into the fluid bed using a screw feeder. The feeder was charged periodically with a lock hopper.

Product gas from the reactor entered a hot cyclone (V-2) and disengaged particulate matter, which was collected in a drum (V-3). The product gas was then incinerated (H-2) and scrubbed (V-4) prior to being vented to the atmosphere. In 1990, a quench scrubber and a condensate heat exchanger were added to remove the water from product gas.

Gas samples were extracted downstream of the hot cyclone. The sample gas was cooled in a condenser and knock-out pot prior to being analyzed by gas chromatography. The condensate was collected and sent to an independent laboratory for analysis of tars and oils. In addition, a screw sample valve, located on the reactor shell, allowed continuous monitoring of the bed carbon content.

Test results

System testing of the indirect gasifier on biomass/waste feedstocks was conducted. The test results provided detailed information on gas compositions, char and tar/oil yields, and bed carbon inventory levels.

Tests were performed using three different biomass feeds (pistachio shells at two different temperatures, wood chips, and rice hulls); two different sludge waste products from a recycle paper mill; and kraft mill sludge (the two sludge wastes differed primarily in their plastic content). **Table I** summarizes the ultimate analysis for mill waste and other biomass feedstocks employed in the test program. The ash content of the sludge waste exhibited a high degree of statistical variation.

The waste paper sludge was obtained from a mill located in northern California. The sludge fraction was composed of short fiber and plastic reject material which was recovered from a clarifier. The dilute waste stream was dewatered in a belt press and delivered to a pile where some additional draining occurred.

Currently, the product is hauled by truck to a landfill site for disposal. Disposal costs represent a significant expense for the mill, exceeding US\$ 600,000 annually. These sludge wastes are representative of high moisture waste materials which are generated in similar mills located throughout the United States.

Table II summarizes the operating conditions for the

various test runs. Temperatures were varied over the range of approximately 930°K to 992°K. Steam-to-biomass ratios varied from approximately 0.75 to 2.0. Test run durations typically ranged from 4 h to 10 h. No process operating problems were encountered for any of the runs, including those with rice hulls, which have a high ash content and low ash fusion point.

Selected gas compositions for the various feedstocks are summarized in **Table III**. The methane content appears to be relatively constant (8-12%) over the range of feeds and processing conditions tested. Higher hydrocarbons show a decreasing trend, with increasing temperature and a concomitant increase in hydrogen yields. The ratio between carbon monoxide and carbon dioxide appears relatively constant. The dry gas heating value typically ranged from 13.7-15.2 MJ/m³.

For each test run, cyclone product samples were measured and analyzed for organic content to calculate char yields. Condensate samples were also collected and measured for organic carbon to calculate tar/oil yields. The product yields for each of the test runs are also listed in **Table III**.

Carbon conversion to dry gas ranged from 92% to 94% for pistachio shells and wood chips. Char and tar/oil yields for pistachio shells diminished noticeably with increasing temperature (1.3% at 987°K). Significantly higher char yields were obtained for both rice hulls and paper mill sludge wastes. The increase in char yields for rice hulls is probably due to the associated high ash content of this feed, which tends to inhibit the gasification reaction. The higher char yields for the sludge waste are believed to be due to high rates of entrainment exhibited by this fine, fibrous material. Also, since the sludge waste contained high moisture levels, vaporization of the feed moisture resulted in gas superficial velocities within the fluid bed which were generally higher than for the other feeds tested, thus further exacerbating the entrainment problem. Entrainment of the feedstock into the gasifier freeboard region also increased tar/oil yields for these materials. It is anticipated that closer control of gasifier superficial velocities and modest recycle of fly ash can significantly enhance carbon utilization rates. It should be noted that the char and tar/oil levels obtained in these tests are comparable to those achieved for similar feeds in other gasifiers which operate at significantly higher temperatures.

Condensate

Effluent from the gasifier includes condensed steam which contains tar/oil and particulate products. The BOD level for the condensate was measured at 3920 mg/L. However, a significant portion of the BOD is in the form of carbon particulate which can be clarified or filtered. Further investigation will be needed to determine the achievable quality of wastewater discharge from the gasification plant.

Dioxin reduction

A key objective of the sludge gasification trial was to determine the dioxin destruction efficiency of the indirect gasifier. Dioxin, which is present in the feed sludge, has

IV. Dioxin levels in sludge feed and gasifier effluents, ppt

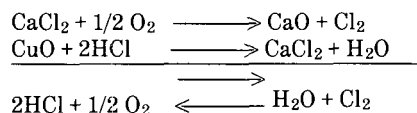
	Total dioxin	TCDD	2, 3, 7, 8 TCDD	PCDD	HXCDD	HPCDD	OCDD
Feed sludge	1543	74	33	69	580	150	670
Bed material	10.1	N/D	N/D	N/D	N/D	2.9	7.2
Cyclone ash	100.2	53	27	14	14	9.5	9.7
Condensate	0.33	0.23	0.07	N/D	N/D	N/D	0.33

N/D: Not detectable

been attributed to the pulp bleaching operation, which includes a chlorination step. Dioxin levels were measured for the feed sludge, cyclone ash, condensate, and gasifier bed material. The dioxin feed and effluent results are summarized in Table IV. The feed sludge contains a total dioxin concentration of 1543 ppt. By comparison, the gasifier ash effluent contains only 100.2 ppt of dioxin. Including the effect of mass reduction, the net dioxin destruction efficiency is approximately 97.5%. It should be noted that dioxin concentrations in the gas product were not measured. However, the gas condensate showed very low dioxin levels, and any dioxin that might be present in the gas phase is likely to be destroyed with high efficiency upon subsequent combustion.

The high destruction efficiency for the indirect gasifier is thought to be attributed to the use of calcium material within the fluid bed, which serves to absorb HCl released during gasification, and the absence of oxygen in the reducing environment of the reactor.

Recent studies² on the occurrence of dioxin in fly ash from waste incinerators have implicated a metal-catalyzed dioxin formation reaction which is facilitated by the presence of surplus oxygen at a temperature regime of approximately 300°C. Above 600°C, dioxin destruction rates exceeded dioxin formation rates. However, at somewhat lower temperatures, it was postulated that a Deacon-type mechanism was responsible for the release of molecular chlorine as shown below:



Under this assumption, oxygen in the incinerator flue gas reacts with CaCl_2 or other metal chlorides contained in the fly ash to form chlorine, which subsequently gives rise to the formation of organochlorine compounds and finally dioxins.

These studies further showed that no such dioxin formation occurred in an oxygen-deficient (nitrogen) environment. On the other hand, dioxin formation increased in an air stream spiked with HCl.

Based on this evidence, there is reason to conclude that gasification of chlorinated waste material may avoid the dioxin-forming reactions that contribute to dioxin emissions from incineration processes.

V. EP toxicity metals analysis for a typical gasifier feed and effluent

Element	mg/L in the EP Tox extract		
	Feed	Bed	Ash
Ag	<0.01	<0.01	<0.01
As	<.1	<.1	<.1
Ba	<.5	<.5	0.7
Cd	<0.01	<.01	0.11
Cr	0.01	<0.01	<0.01
Hg	<.0005	<.0005	<.0005
Pb	<.05	<.05	<.05
Se	<.1	<.1	<.1

Ash toxicity

EP toxicity extract tests were performed on typical feed, bed, and cyclone ash materials. The results of these tests are summarized in Table V. The results indicate that cyclone char/ash disposal should not present a problem.

Conclusions

The test results confirmed the ability of the MTCI indirect gasifier to handle a wide range of biomass feedstocks, including those with high moisture content, low ash fusion temperature, and high plastic materials content. Also, product gas quality was shown to be quite insensitive to feedstock moisture level.

The gasifier does not require any special feedstock preparation such as pelletization. The gasifier produces a medium-Btu gas without the consumption of oxygen. The reactor is easily scaled, since the pulse combustor tube bundles are constructed in modules. The gasifier produces a gas with a hydrogen-to-carbon-oxide ratio considerably higher than oxygen-blown systems, thus making it particularly attractive for methanol production. The gasifier integrates well with both methanol and high purity hydrogen plants.

The results of these tests have provided a significant database for preparing designs at the 50 tons/day level. MTCI plans to field demonstrate the gasifier at a commercial paper mill in the near future.

Scale-up and commercialization plans

MTCI is currently engaged in the design of scaled-up units for 1 ton/h black liquor gasification and 2 ton/h mill sludge

²Hagenmaler, H., Kraft, M. Brunner, H. and Haag, R., Environ. Sci. Technol. 21:1090-1084(1987).

gasification. The 1 ton/h black liquor gasifier is being constructed and field-tested, and the sludge gasifier will be constructed and operated in 1991-92. The list of sponsors of these field test plants includes California Energy Commission, the DOE, Weyerhaeuser Paper Company, James River Paper Company, and Mead Paper Company. Other paper companies are also interested in MTCI technology.□

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