

Biomass gasification project gets funding to solve black liquor safety and landfill problems

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System forms no smelt and makes clean fuel gas that can be burned in inexpensive, gas-fired power boilers, calciners, or gas turbines

Manufacturing and Technology Conversion International (MTCI), Columbia, Md., U.S.A., has been awarded \$1.2 million of an expected \$4.9 million program to develop an advanced gasification system that will be fueled by low-quality residues from the manufacture of pulp and paper and reduce dependence on explosion-prone boilers.

The main by-product in pulp making is black liquor from virgin fiber; the main by-product in paper recycling is fiber residue. Although the black liquor is recycled for chemical and energy recovery, safety problems plague the boilers currently used to do this. The fiber residue is usually transported to a landfill. The system being developed by MTCI will convert black liquor and fiber residue into a combustible gas, which can then be used for a wide variety of thermal or power generation applications.

The project began in November 1989 and is scheduled for completion in February 1993. It was funded by the United States Department of Energy, the California Energy Commission (CEC), Weyerhaeuser, and other sources.

The MTCI process will reduce the pulp industry's reliance on boilers that are subject to violent explosions, according to information released by the CEC.

20% chance

"Historical trends show that over a 20-year lifetime, a boiler in this operation has a one in five chance of exploding," noted David Warren, MTCI's managing engineer for the project. "Safety modifications have reduced the rate of explosion only modestly in the past 30 years. By gasifying the black liquor rather than combusting it, loss of life and property from explosions are prevented," he said.

The indirect gasifier has significant advantages over conventional recovery technology. The unit operates without smelt formation and thus presents no smelt-water

explosion risk. The unit produces a clean fuel gas, which can be combusted in an inexpensive gas-fired power boiler without fouling problems or the need for soot blowing.

Alternatively, the gas can be used to replace premium fuels in calciners or gas turbines. In the latter case, the heating value of black liquor can be converted to electrical energy at an efficiency 50% greater than for a conventional recovery system.

According to Warren, approximately 50-55% of the heating value in the black liquor solids (BLS) is converted to net fuel gas energy, with an additional 10-15% of the heating value converted to steam.

"Thus, for a 10 tons/h BLS unit, enough fuel gas can be generated to displace up to 70×10^6 Btu/h of premium fuel being consumed elsewhere in the mill. Furthermore, we think these modular units can be constructed at the 5-10 tons/h BLS scale at a specific cost competitive with large recovery boilers, thus allowing incremental capacity expansion," Warren said.

Research

To research its theory, MTCI built a bench-scale integrated gasification train (Fig. 1) and used it to gather data about the process chemistry and performance of the indirect gasifier. Tests have been conducted, mainly at the 30 lb/h level. Also, several hundred hours of operation with spent liquors including kraft black liquor, sulfite liquor, and soda liquor, have been done.

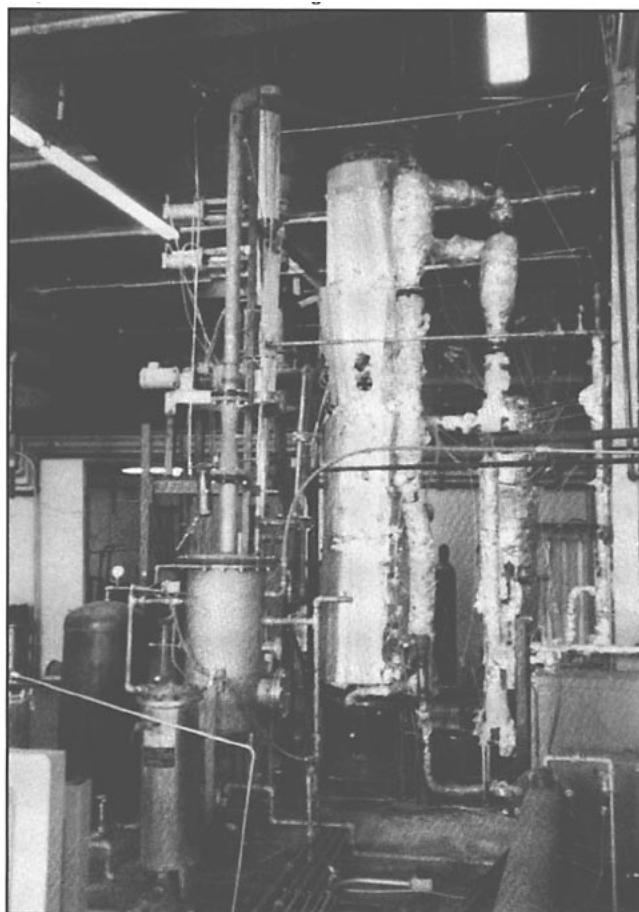
The system also includes a prototype of a full-scale, pulse heater module, which has been tested in a 3 ft $\times$ 10 ft fluid bed. Figure 2 illustrates this pulse heater module, which contains 61 immersed firetubes with a nominal firing rate of 5×10^6 Btu/h and is rated for 0.5 ton/h of BLS.

Prototype development tests are being conducted to ensure the reliable performance of the pulse modules when they are placed in field service. The construction of a nominal 1 ton/h BLS field test gasifier is slated for 1991, and the negotiations for a host site have begun.

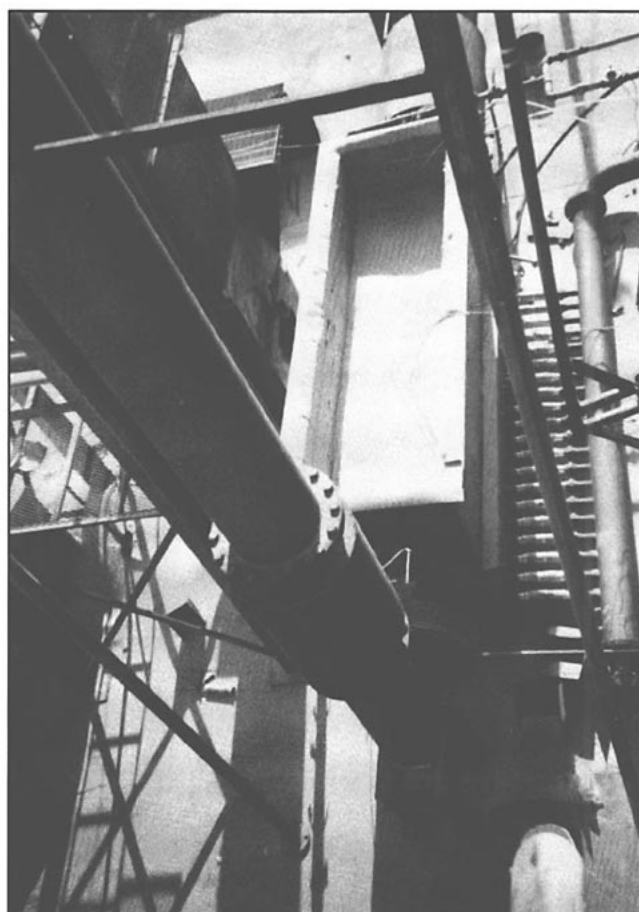
The gasification system also resolves a disposal problem faced by the paper recycling business. Fibers used by the

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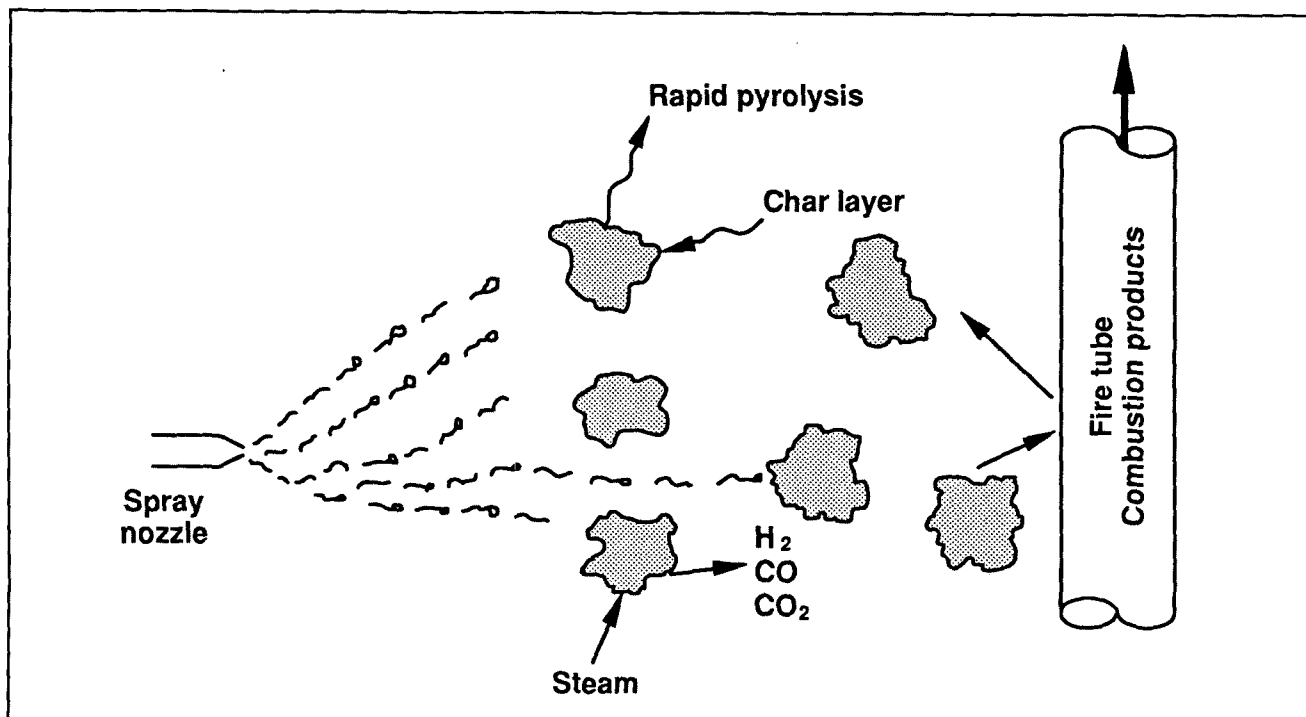
1. Bench-scale integrated gasification train built by MTCI and used to gather data about the indirect gasifier



2. Prototype of a full-scale, pulse heater module being tested in a 3 ft x 10 ft fluid bed



3. Principles of operation. Black liquor is sprayed directly onto a bed of sodium carbonate solids fluidized by steam or recycled process gas or both. This direct contact with the hot bed solids promotes high rates of heating and pyrolysis. A porous char layer forms as a residue on the particle surface and is then gasified in a reaction with the steam. Pulse combustor resonance tubes immersed within the fluid bed supply heat for the process.



wastepaper recycler must be of a minimum length in order to be used as furnish in papermaking. Fibers that are too short have been disposed of in landfills in California. By converting these fibers to fuel, users of the system realize savings in fiber disposal and fuel costs.

A typical sludge output from a recycled old corrugated container mill is about 2 tons/h. At a disposal cost of \$40/ton, this would translate to a monthly expense of \$50,000. The MTCI system would use the underlength fibers as a fuel for gasification, thereby reducing transportation costs and saving landfills for other uses.

Operational principles

In the MTCI process, black liquor is sprayed directly onto a bed of sodium carbonate solids (600 μm), and is transformed into fluid by steam and/or recycled process gas. The droplets uniformly coat the bed solids' surface.

The black liquor's direct contact with the hot bed solids promotes high rates of heating and pyrolysis. The porous char layer, which is formed as a residue on the particle surface, is then gasified in a reaction with the steam. This process is illustrated in **Fig. 3**. Heat for the endothermic steam gasification process is supplied from pulse combustor resonance tubes, which are immersed within the fluid bed.

Smelt formation in the system is avoided at all times by careful control of the conditions within the gasifier.

The sodium carbonate provides an active catalyst with a large surface area on which the rapid steam-char and water-gas shift reactions are promoted. Because gas-char reactions happen without the interphase mass transfer limitations imposed by a molten char bed, efficient gasification of black liquor is done at relatively low temperatures of 600–650°C (1112–1202°F). The operation's thermal efficiency is enhanced by the lower temperature.

The fact that there is no smelt in the system means the potential for a smelt-water explosion is avoided and the use of corrosion-resistant refractory materials is unnecessary.

Sulfur chemistry

In a conventional recovery boiler, Na_2SO_4 is reduced to Na_2S in a smelt bed operating under partially reducing conditions. The smelt is then dissolved to form green liquor. In the MTCI reactor, sodium sulfide is unstable at the low-temperature steam gasification conditions in the MTCI reactor. As Na_2SO_4 is reduced to Na_2S by reaction with carbon monoxide or hydrogen, the Na_2S is rapidly decomposed to form H_2S and Na_2CO_3 .

Table I summarizes the major sulfur reactions that happen in MTCI's gasification process. Each reaction shown exhibits a strong equilibrium driving force from left to right. The reaction's extent is, therefore, dictated only by kinetic rate limitations.

Figure 4 shows a conceptual configuration for an integrated recovery process based upon the indirect steam-gasifier. Black liquor enters the gasifier and reacts with steam to generate a producer gas. The producer gas is then cooled in a heat recovery steam generator (HRSG) before it enters a scrubber. Dry sodium carbonate solids are discharged from the gasifier and dissolved to form an

alkaline solution, which is used to scrub the producer gas of hydrogen sulfide and regenerate the green liquor. Caustic soda may also be used to polish.

Part of the fuel gas is burned to supply indirect heat to the gasifier. The balance of the fuel gas is burned in a gas-fired boiler to generate steam for process use and power generation. Warren said that preliminary heat and material balances indicate that the integrated plant can achieve a greater than 67% net thermal efficiency.

Pulse combustion

The resonance tubes of a pulse combustor supply the heat to MTCI's indirect gasifier. The pulse combustor significantly enhances the performance and economics of the indirectly heated gasifier because heat transfer coefficients can be gotten that are 3–5 times greater than those in steady-flow systems.

The physical principles in pulse combustor operation are essentially the same as those that govern the undesirable pulsations that sometimes plague conventional combustion. The pulsations, or combustion-driven oscillations, are, however, 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 depends upon the precise geometry of the pulse combustion apparatus. The pulse combustor's three main parts are 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. 5**. In step 1, fuel and air ignite within the combustion chamber.

Ignition is spontaneously triggered by hot gases from the previous cycle and is not controlled by a spark plug or other external means.

In step 2, the combustion induced pressure rise forces the burning mixture to expand outward toward the tailpipe exit. Some gases escape through the air inlet, but the fluidics design of the air valve significantly reduces flow in this direction.

Enhanced heat transfer

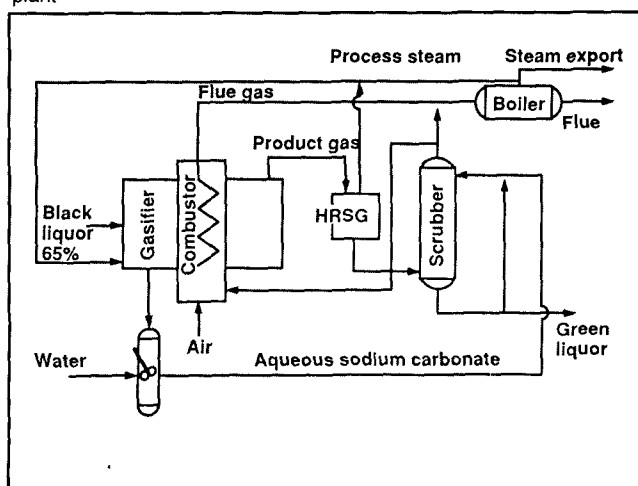
In step 3, the momentum of the out-rushing combustion gases creates a suction within the combustion chamber similar to the tension formed by a mass-on-a-spring. This causes the chamber to be purged and recharged with fresh air and fuel.

In step 4, the fuel and air mixture in the chamber is recompressed. This is then spontaneously ignited to repeat the natural pulsation cycle.

Fluctuations of 34.5 kPa (5 psi) in the chamber pressure are common in pulse combustors. These fluctuations translate into velocity fluctuations of 180 m/s (600 ft/s) in the resonant tailpipe. The velocity fluctuations occur at a frequency characteristic of the combustor (30–300 Hz) and intensely scrub the convective boundary layer inside the tube's surface, which enhances heat transfer rates.

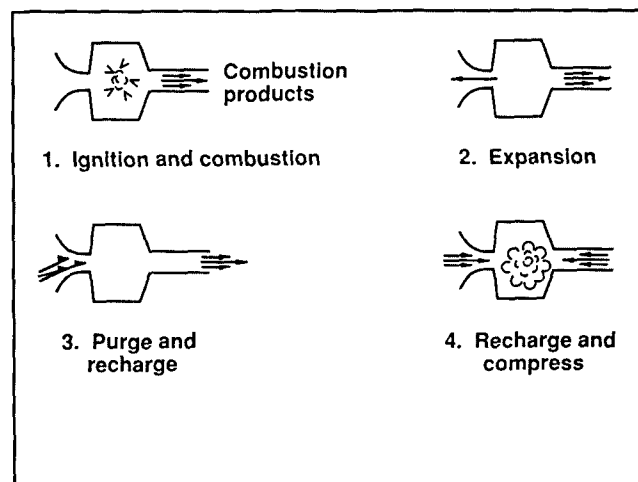
In a commercial gasifier designed for atmospheric operation, the pulse combustors are built in modules that can be put into the side wall of a refractory-lined containment vessel. These modules can be installed with techniques used for conventional heat exchange tube bundles.

4. Conceptual configuration for an integrated black liquor recovery plant



Each pulse combustor consists of an individual combustion chamber connected to many resonant heat exchange tailpipes. The pulse combustor has a modular construction, so scale-up of the gasifier is expected to be straightforward. MTCI has successfully tested full-scale pulse combustor modules (5×10^6 Btu/h). □

5. Operating phases of a pulse combustor



1. Primary sulfur reactions in black liquor gasifier

1. Lignin $\rightarrow$ Organic sulfides + H_2S
2. Organic sulfides + $H_2O \rightarrow CO, CO_2, H_2 + H_2S$
3. $Na_2S + H_2O + CO_2 \rightarrow Na_2CO_3$
4. $Na_2SO_4 + 4CO \rightarrow Na_2S + 4CO_2$