PRODUCTION OF CLEAN MEDIUM Btu GAS FROM GASIFICATION OF SLUDGE WASTES

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Experimental tests were conducted to assess performance of an indirectly-heated, fluidized bed, sludge gasification process employing pulse enhanced heat transfer. Feedstocks included sewage sludge, RDF, lignite, sub-bituminous coal, mild gasification char, SRC residue and black liquor and wastes from pulp mills. Feedstocks were reacted with steam at temperatures of 1150°F - 1500°F to produce a clean medium Btu fuel gas with a higher heating value of approximately 400 Btu/SCF. Heat for the gasification reaction was supplied by means of an integrated pulse combustion system consisting of multiple firetubes immersed within a fluidized bed. This process is being scaled up from laboratory scale (20 lb/hr) to field test demonstration units (2,000 to 6,000 lb/hr). This unique gasification process does not require an oxygen plant to produce medium-Btu gas, thus reducing capital costs significantly. This paper presents the detail of results and progress of scale-up activities.

INTRODUCTION

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

The 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 percent moisture as delivered from a belt press. Many mills are currently installing screw presses to reduce the moisture content to 50 percent. The presence of chlorinated organics (such as dioxins) in the sludges from virgin pulp mills, and plastics in the sludges from recycling mills poses serious problems for the landfilling of these wastes. The Hazardous and Solid Waste Act of 1984 (HSWA) restricts land disposal and requires pretreatment at the source prior to final disposal. Increasing disposal costs, diminishing landfill sites, and social and environmental factors are forcing mills to find unique solutions.

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 replacing natural gas.

BACKGROUND

A pulse-enhanced, indirectly heated fluidized bed gasifier system was constructed and tested by MTCI during 1985-1986 for gasification of waste feedstocks under the Phase II of a 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 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 since the existing technology has significant economic, safety, and environmental shortcomings.

Preliminary feasibility tests were conducted in a 33 lb/hr 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; the Weyerhaeuser Company; and the California Energy Commission's Energy Technologies Advancement Program (ETAP). A scale-up reactor (200 lb/hr) 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. 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 these waste products, the MTCI gasifier operated without problems.

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 3 to 5 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 sometime plague conventional combustion, however, pulsations or combustion-driven oscillations are induces 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 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 Figure 2. In the first step (Figure 2-1), 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 (Figure 2-2), 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 (Figure 2-3), the momentum of the out-rushing 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 (Figure 2-4) 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 are commonly achieved in pulse combustors. These pressure fluctuations are translated into velocity fluctuations of 600 ft/sec 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 Figure 3, the pulse combustors are constructed in modules which can be inserted into the side-wall 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 comprise 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 has tested individual pulse combustors at firing rates of 6 MMBtu/hr 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 to 50 $Btu/hr/ft^2/°F$) which is about five times higher than that for conventional firetubes. Thus, the characteristics for the pulse-enhanced, indirectly-heated gasifier overcomes 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 of a 20 cm fluid bed reactor (35 lb/hr) 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/hr) containing eight pulse combustor resonance tubes. The larger unit was intended to provide scale-up design criteria for integration of large, multi-tube, 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 Figure 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 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.

In a commercial operation, 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 generation of export steam to be used elsewhere in an integrated plant.

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, woodchips, and rice hulls; two different sludge waste products from a recycle paper mill; and a Kraft mill sludge (the two sludge wastes differed primarily in their plastic content). Table 1 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 is composed of short fiber and plastic reject material which is recovered from a clarifier. The dilute waste stream is dewatered in a belt press and delivered to a pile where some additional draining occurs. Currently, the product is hauled by truck to a landfill site for disposal. Disposal costs represent a significant expense for the mill and exceeds $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 2 summarizes the operating conditions for the various test runs. Temperatures were varied over the range of approximately 1215°F to 1450°F. Steam to biomass ratios varied from approximately .75 to 2.6. Test run durations typically ranged from four to ten hours. 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 3. The methane content appears to be relatively constant (8 percent to 12 percent) 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 appear relatively constant. The dry gas heating value typically ranged from 370 to 418 Btu/scf.

As seen in Table 3, carbon conversion to dry gas ranged from 92 percent to 94 percent for pistachio shells and woodchips. Char and tar/oil yields for pistachio shells diminished noticeably with increasing temperature (1.3 percent 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 is 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. 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 Biological Oxygen Demand (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 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 Tables 4 and 5. As seen in Table 4, 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 percent. 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 studies (Ref. Hagenmaier, H., et al) 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 575°F. Above 1100°F 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:

$$\begin{array}{lcl} CaCl_2 + \tfrac{1}{2}O_2 & \rightarrow & CaO + Cl_2 \\ CaO + 2HCl & \rightarrow & CaCl_2 + H_2O \\ \hline 2HCl + \tfrac{1}{2}O_2 & \rightleftharpoons & H_2O + Cl_2 \end{array}$$

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.

ASH TOXICITY

EP toxicity extract tests were performed on a typical feed, bed and cyclone ash materials. The results of tests are summarized in Table 6. 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 data base for preparing designs at the 50 ton/day level. MTCI will field demonstrate the gasifier at a commercial paper mill in the fall of 1991.

SCALE-UP AND COMMERCIALIZATION PLANS

MTCI is currently engaged in the design of scaled up units for 2 ton/hr (TPH) black liquor gasification and 1 TPH mill sludge gasification. The 2 TPH black liquor gasifier will be constructed and field-tested in 1991-1992, and the sludge gasifier will be constructed and operated in 1991-1992. The list of sponsors of these field test plants includes California Energy Commission, Department of Energy, Weyerhaeuser Paper Company, James River Paper Co., and Mead Paper Company. There are other paper companies interested in MTCI technology.

REFERENCES

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TABLE 1
ANALYSIS FOR FEEDSTOCKS TESTED IN PULSE-ENHANCED INDIRECT GASIFIER

ULTIMATE (MAF Basis)	Pistachio Shells	Wood Chips	Rice Hulls	Recycle Mill Fiber Waste	Kraft Mill Sludge	RDF Sand Bed	MSW Sand Bed
Carbon	49.51	49.33	49.09	50.00	59.36	46.96	58.20
Hydrogen	6.18	6.74	6.17	6.55	6.90	7.58	8.42
Oxygen	43.96	43.67	44.19	42.76	28.02	43.84	26.45
Sulfur	0.11	0.16	0.04	0.31	1.04	0.86	1.63
Nitrogen	0.24	0.10	0.51	0.38	4.68	0.77	5.30
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00
PROXIMATE (As rec'd wt %)							
Moisture	8.74	20.46	8.67	49.50	62.40	17.04	5.47
Ash	0.41	0.18	20.48	2.80	7.10	12.66	32.58
Volatile	N/M	N/M	N/M	N/M	N/M	60.23	60.82
Fixed Carbon	N/M	N/M	N/M	N/M	N/M	10.07	1.13
Total	9.15	20.64	29.15	52.30	69.50	100.00	100.00
HHV (Btu/lb), dry	8334	8334	8334	8850	10353	7515	6607

TABLE 2
OPERATING AND PROCESS CONDITIONS FOR BIOMASS TEST RUNS

FEEDSTOCK	TEMP. (F)	AVERAGE FEED RATE (lb/hr)	STEAM RATE (lb/hr)	STEAM TO BIOMASS (lb/lb)	TOTAL FEED (lbs)
Pistachio Shells	1317	35.5	26.0	0.73	337.1
Pistachio Shells	1216	30.6	31.5	1.03	115.3
Wood Chips	1286	22.9	31.4	1.37	205.7
Rice Hulls	1326	30.8	26.0	0.84	185.5
Recycle Paper Mill Sludg	1250	17.6	36.5	2.07	118.8
Kraft Mill Sludge Waste	1250	17.6	36.5	2.07	299.6
RDF (sand bed)	1450	11.0	29.0	2.64	66.0
MSW (sand bed)	1410	12.0	28.0	2.33	62.0
MSW (limestone bed)	1306	15.2	27.0	1.78	84.0

TABLE 4
DIOXIN LEVELS IN PAPER MILL SLUDGE
FEED AND GASIFIER EFFLUENTS
(In parts per trillion, ppt)

	DIOXIN	TCDD	TCDD	PCDD	HXCDD	HPCDD	OCDD
FEED SLUDGE	1543	74	33	69	580	150	670
BED MATERIAL	10.0	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

TABLE 5
DIOXIN AND FURAN ANALYSIS OF RDF FEEDSTOCK AND
CYCLONE CAUGHT ASH IN THE DECEMBER 7, 1990 TEST (ng/g)

	RDF FEEDSTOCK		CYCLONE CAUGHT ASH	
	DETECTION LIMIT	CONCEN-TRATION	DETECTION LIMIT	CONCEN-TRATION
DIOXINS				
TOTAL TCDD	0.56	ND	0.089	ND
TOTAL PeCDD	0.76	ND	0.13	ND
TOTAL HxCDD	0.11	ND	0.091	ND
TOTAL HpCDD	*	0.27	0.23	ND
TOTAL OCDD	*	1.70	0.21	ND
FURANS				
TOTAL TCDF	0.30	ND	0.29	ND
TOTAL PeCDD	0.22	ND	0.13	ND
TOTAL HxCDD	0.30	ND	0.20	ND
TOTAL HpCDD	0.23	ND	0.21	ND
TOTAL OCDD	0.48	ND	0.13	ND

* = Not Supplied

TABLE 6
EP TOXICITY METALS ANALYSIS FOR A TYPICAL GASIFIER FEED AND EFFLUENT

ELEMENT	FEED	BED	ASH
	(mg/L in the EP Tox Extract)		
Ag	<.01	<.01	<.01
As	<.1	<.1	<.1
Ba	<.5	<.5	<.5
Cd	<.01	<.01	<.11
Cr	0.01	<.01	<.01
Hg	<.0005	<.0005	<.0005
Pb	<.05	<.05	<.05
Se	<.1	<.1	<.1

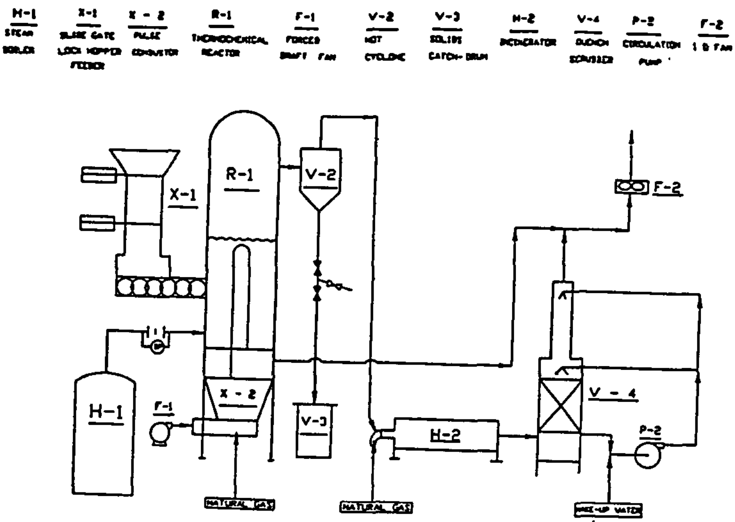

FIGURE 3. PROCESS FOR INDIRECT GASIFICATION PILOT PLANT

TABLE 3
SELECTED GAS COMPOSITIONS AND PRODUCT YIELDS FOR BIOMASS AND MILL SLUDGE TESTS CONDUCTED INPULSE-ENHANCED INDIRECT GASIFIER

COMPOSITION (VOL%)	PISTACHIO SHELLS	PISTACHIO SHELLS	WOOD CHIPS	RICE HULLS	RECYCLE MILL FIBER WASTE	RECYCLED WASTE PAPER W/PLASTIC	KRAFT MILL SLUDGE	RDF SAND BED	MSW SAND BED	MSW LIMESTONE BED
H_2	37.86	35.04	48.11	42.83	38.86	50.50	52.94	45.54	55.21	54.40
CO	18.84	23.43	22.91	19.67	23.34	19.26	11.77	25.26	28.10	25.46
CO_2	28.73	25.20	20.18	24.40	23.27	20.10	21.94	14.51	5.95	5.66
CH_4	10.65	11.31	8.32	11.56	8.31	8.42	8.95	8.30	5.00	5.86
C_2+	3.92	5.02	0.48	1.54	6.40	1.72	3.00	6.38	5.74	8.62
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	98.60	100.00	100.00	100.00
HHV (Btu/scf)	370	406	329	367	412	364	372	418	374	448
TEMP (°F)	1317	1216	1286	1326	1250	1326	1250	1450	1410	1306
YIELD (% CARBON)	94.1	92.1	93.0	N/A	86.8	N/A	56.0	83.6	93.7	83.8

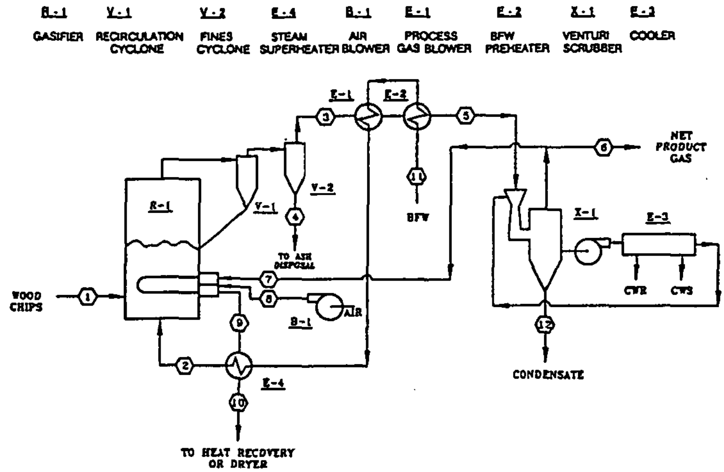

FIGURE 1. PROCESS FLOW DIAGRAM FOR INDIRECT GASIFIER

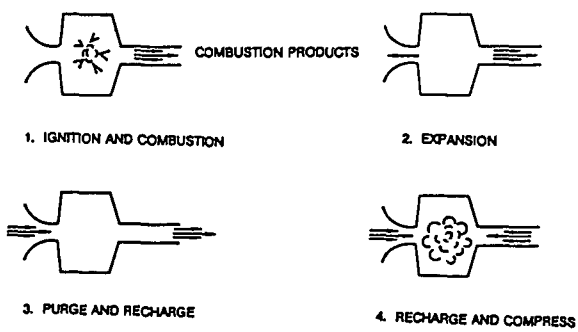

FIGURE 2. OPERATING PHASES OF PULSE COMBUSTOR