P5 Hot Coal Gas Desulfurization with Manganese-Based Sorbents

ABSTRACT

In this paper, the physical and chemical behavior of several sorbent formulations fabricated from a manganese-containing compound, alundum (Al_2O_3), and a binder are addressed. The thermodynamic feasibility of hydrogen sulfide (H_2S)-removal from hot-simulated coal-gases using these sorbents and their subsequent regeneration with air are established. A formulation, FORM4-A, which consists of $MnCO_3$, alundum, and bentonite exhibits the best combination of capacity and reactivity; whereas, FORM1-A, which consists of Mn-ore, alundum, and dextrin exhibits the best combination of strength and reactivity. One important finding is that the capacity of the pellets for sulfur pickup from a H_2/H_2S mixture (at 950°C) and the kinetics of reduction, sulfidation and regeneration (at 1000°C) improve with recycling without compromising the strength.

The leading formulation, FORM4-A, was subjected to 20 consecutive cycles of sulfidation and regeneration at 900°C in a 2-inch fixed bed reactor. The sulfidation gas was a simulated Tampella U-gas with an increased hydrogen sulfide content of 3% by volume to accelerate the rate of breakthrough, arbitrarily taken as 500 ppmv. Consistent with thermo-gravimetric analysis (TGA) on individual pellets, the fixed bed tests show small improvement in capacity and kinetics with the sulfur-loading capacity being about 22% by weight of the original pellet, which corresponds to approximately 90% bed utilization!

OBJECTIVES

The objective of this study is to develop manganese-based sorbent pellets for the effective desulfurization of coal-derived fuel gases at high temperature (700-1200 °C). A number of formulations are prepared and screened first by testing in a thermogravimetric apparatus (TGA) in which individual pellets are weighed in mixtures of simulated coal-derived fuel gases at atmospheric pressure and high temperatures, and then in a bench-scale fixed bed-reactor. Sorbent screening criteria include measurement of sorbent (fresh, used, and regenerated) crush strength, chemical reactivity by thermogravimetric analysis, surface area, porosity, etc... The superior formulation is tested for long-term durability and chemical reactivity in the TGA apparatus and the bench-scale unit.

BACKGROUND INFORMATION

The Integrated Gasification Combined Cycle (IGCC) is one of the most promising proposed processes for advanced electric power generation that is likely to replace conventional coal combustion. This emerging technology not only will improve considerably the thermal efficiency but will also reduce or eliminate the environmentally adverse effects normally associated with coal combustion. The IGCC process gasifies coal under reducing conditions with essentially all the sulfur existing in the form of hydrogen sulfide (H_2S) in the product fuel gas. The need to remove H_2S from coal-derived fuel gases is a significant concern which stems from stringent government regulations and also, from a technical point of view, a need to protect turbines from corrosion. Westmoreland et al.[1] and Hepworth et al.[2] carried out comparative studies on several proposed sorbent systems which consisted almost entirely of metal oxides. Metal oxides have been proposed because they tend to be more reactive at high temperature where desulfurization is desirable to conserve the sensible heat in gasifier fuel gas. A sulfur concentration limitation of approximately 150 ppmv for IGCC systems has been established; therefore, a sorbent system capable of reducing H_2S concentration from about 5000 to 150 ppmv is sought.[3]

Zinc ferrite and zinc titanate have received much attention over the past twelve years because, from a theoretical point of view, they have desirable properties: high sulfur capacity, ability to remove H_2S from coal-derived fuel gas to levels of a few ppmv, and the feasibility of regeneration with air. Because it is economically necessary to recycle sulfur sorbents for at least 100 cycles, research has focused almost entirely on making the zinc-based sorbents durable. Unfortunately, extensive research carried out by the Morgantown Energy Technology Center (METC) of the Department of Energy (DOE) casts doubt that zinc ferrite or zinc titanate can be utilized even for fixed-bed operation. The desirable properties of Zn-based sorbents as well as their practical limitations will be discussed in detail in a later section of this paper.

Given the limited success of the zinc-based sorbents, METC has shown interest in formulating and testing manganese-based sorbent pellets.[4] There are a number of studies that led to the consideration of Mn-based sorbents.[1,2,5,6,7] This paper addresses the physical and chemical behavior of several sorbent formulations fabricated from manganese-containing compounds, alundum, and a binder and establishes the practical feasibility of H_2S removal from hot simulated coal gases using these sorbents and their subsequent regeneration with air. Experimental tests, utilizing the best formulation were carried out to study the kinetics of regeneration as a function of

temperature. Five repeated sulfidation and regeneration tests were then carried out to investigate the effect of pellet recycling on its chemical reactivity, physical durability, and capacity for sulfur pickup from fuel gases. Finally, the leading Mn-based formulation was subjected to 20 consecutive cycles of sulfidation, using a Tampella U-gas, and regeneration, with air, at 900°C in a 2-inch fixed-bed reactor.

PROJECT DESCRIPTION AND RESULTS

Sorbent Pellet Preparation For reasons which were previously explained,[4] the present investigation employed the following materials: Moanda manganese ore, regular manganese carbonate, alundum, bentonite, and dextrin. Four pellet formulations were prepared using combinations of a manganese-containing compound, an alumina-based matrix, and a binder, based on desired compositions determined on a dry weight-percent basis. After each blend is mixed, an appropriate amount of water is added prior to pelletizing. The composition of the initial make up of the formulations prepared using this procedure is reported in Table I.

Table I. Initial Make up of Formulations

Formulation No.	Raw Material Content in initial make-up, wt.%				
	Moanda Ore	Alundum	MnCO₃	Bentonite	Dextrin
1	68.18	22.73	-	-	9.09
2	73.53	24.51	-	1.96	-
3	-	15.51	75.4	-	9.09
4	-	16.73	81.31	1.96	-

Twenty-four induration campaigns were conducted. Preliminary tests indicated that Moanda ore-based pellets required a temperature of 1200 °C and manganese carbonate-based pellets required an induration temperature of 1250 °C, to produce a required strength of greater than 22 N per mm of pellet diameter (5 lbs/mm). In

addition, two time periods for induration were explored, namely, 1 hour and 2 hours. The strongest formulations are bentonite-bonded as expected. At the conclusion of these tests, four formulations were selected for thermogravimetric analysis (TGA). They were given the following designations: FORM1-A, FORM2-A, FORM2-B, and FORM4-A. Letter "A" corresponds to induration for 2 hours at 1200 °C for the ore-based pellets, and 1250 °C for carbonate-based pellets; whereas, letter "B" corresponds to an induration time of 1 hour.

Table II summarizes the manganese assays and strengths of the formulations which were subjected to TGA analysis.

Table II. Manganese Assays and Strengths of Formulations Studied

Sample Designation	Weight % Mn	Strength, N/mm
FORM1-A	41.14	25.5
FORM2-A	37.48	64.7
FORM2-B	39.83	52.4
FORM4-A	44.22	23.8

Pellet Reactivity via Thermogravimetric Analysis (TGA) The TGA testing is divided into two campaigns; the first being only comparative loading for one cycle, and the second for regeneration studies and repeated cyclic loading and regeneration.

During the first campaign, emphasis was placed upon studying the kinetics of sulfidation using the above four sorbents. The reaction variables included temperature (700 to 1000 °C), fuel gas H_2S content (1%, 2%, and 3% in H_2/H_2S gas mixtures), and pellet diameter in the range 5-10 mm.

Figure 1 is a schematic diagram of the experimental equipment employed for TGA testing. The upper right-hand portion of the diagram shows the Cahn 1000-Series automatic recording balance assembly which holds up to twelve pellets in a nichrome wire-

mesh basket suspended with a nichrome chain from the left pan of the balance. The reactor consists of an alumina tube positioned in a high-temperature molybdenum-wound furnace. The reaction temperature was monitored by using a Pt/Rd thermocouple positioned directly below the sorbent pellets. The weighing unit was constantly blanketed with nitrogen during each test. The gas delivery and data acquisition systems are as depicted. Vent gases are scrubbed in a sodium hypochlorite solution prior to flaring and venting.

For each test, pellets were selected at random from a large batch of indurated pellets. The furnace pressure was 1 atm and the total flowrate was 500 cc/min. Before the heat was turned on, the reactor chamber was evacuated to 0.03 atm and then backfilled with nitrogen. The reactor was heated in a nitrogen atmosphere flowing at 1 l/min to the desired operating temperature before the balance platform was lowered to position the pellets in the center of the 10-cm-long hot zone. Five minutes after the sample was lowered into the hot zone, the nitrogen flow was shut off and the reactive gas mixture was started. Chemically pure (>99.9 %) hydrogen and hydrogen sulfide were metered into the TGA apparatus; flows were regulated by needle valves using calibrated rotameters. Finally, the nitrogen flow was turned on and the pellets were raised into the cold zone.

Figure 2 shows the results of TGA analysis at 1000 °C on the four selected sorbents which were described above. In all subsequent figures, W_0 refers to the mass of the indurated pellet and W to the mass of the reacting pellet as a function of time. Initially, the ratio W/W_0 for all pellets is unity; however, there is a decline in this value (reduction of Mn_3O_4 to MnO) when the pellets are exposed to hydrogen during the initial reduction period. Each reduction phase lasted 45 minutes although all pellets

remained constant in weight for at least 20 minutes. Each of the sorbents appears to have lost the expected percentage of its original weight; FORM4-A pellets, which contain high manganese concentrations lost appreciably more weight than did the pellets containing lower proportions of manganese. Total percent loss at the conclusion of the reduction period ranged from 2% to 5% for FORM2-B and FORM4-A, repectively.

As indicated on the figures, hydrogen sulfide is added at 3% by volume to the gas which is flowing at a rate of 500 cc per minute. In the lower right-hand corner of the diagram are the theoretical maximum weight ratios which the pellets could exhibit based upon total conversion of the manganese in the pellet, as determined by chemical analysis, to the stoichiometry: MnS. Upon examining these calculated values, one should note that the formulation which resulted from manganese originating from purified carbonate (i. e., FORM4-A) has a greater capacity for sulfur than the formulations which originate from the ore because of the higher manganese content of the calcined carbonate. (see Tables I and II). Furthermore, dextrin-based formulations also yield higher sulfur capacities based upon the fact that dextrin volatilizes upon induration of the pellet; whereas, bentonite is a non-volatile impurity which effectively lowers the manganese content of the pellet.

The asymptote for time periods exceeding 90 minutes for formulation 4-A at 1000 °C actually exceeds the calculated value for sulfur capacity, which may indicate that the original sulfur assay is slightly on the low-side. The asymptotic value for formulation 1-A is very close to the calculated value; whereas, the asymptote for 2-A (Moanda ore plus bentonite) falls below the calculated value indicating that some of the manganese may be chemically combined with silicate compounds in the ore and therefore not
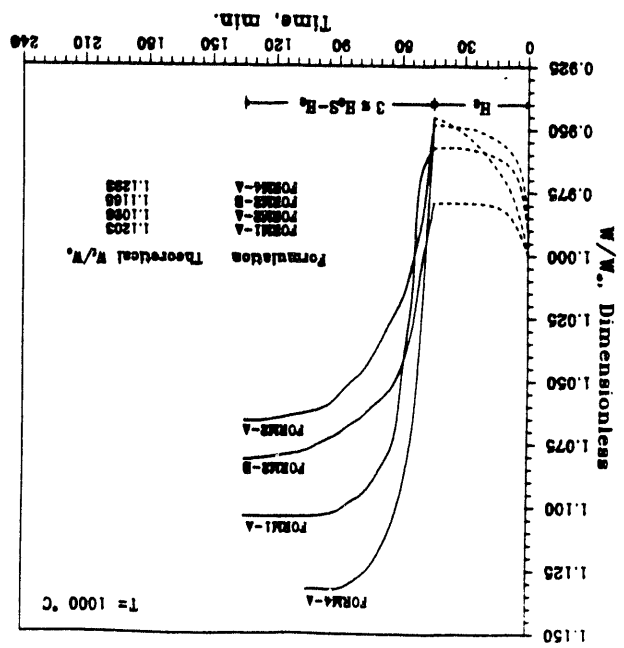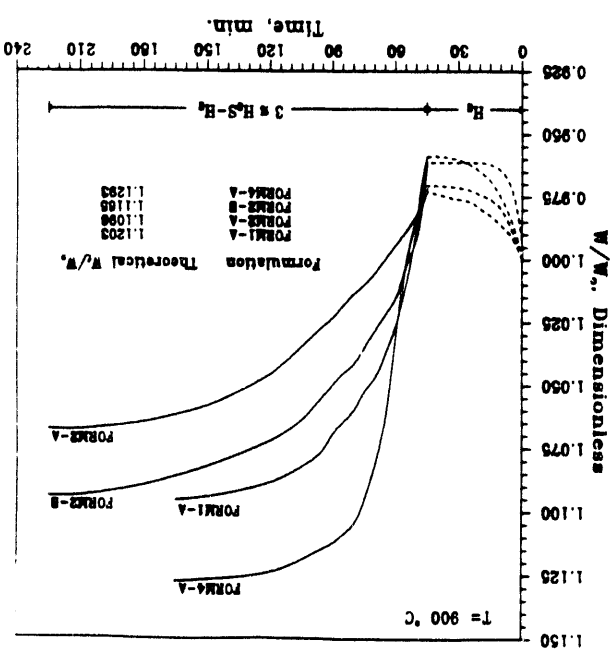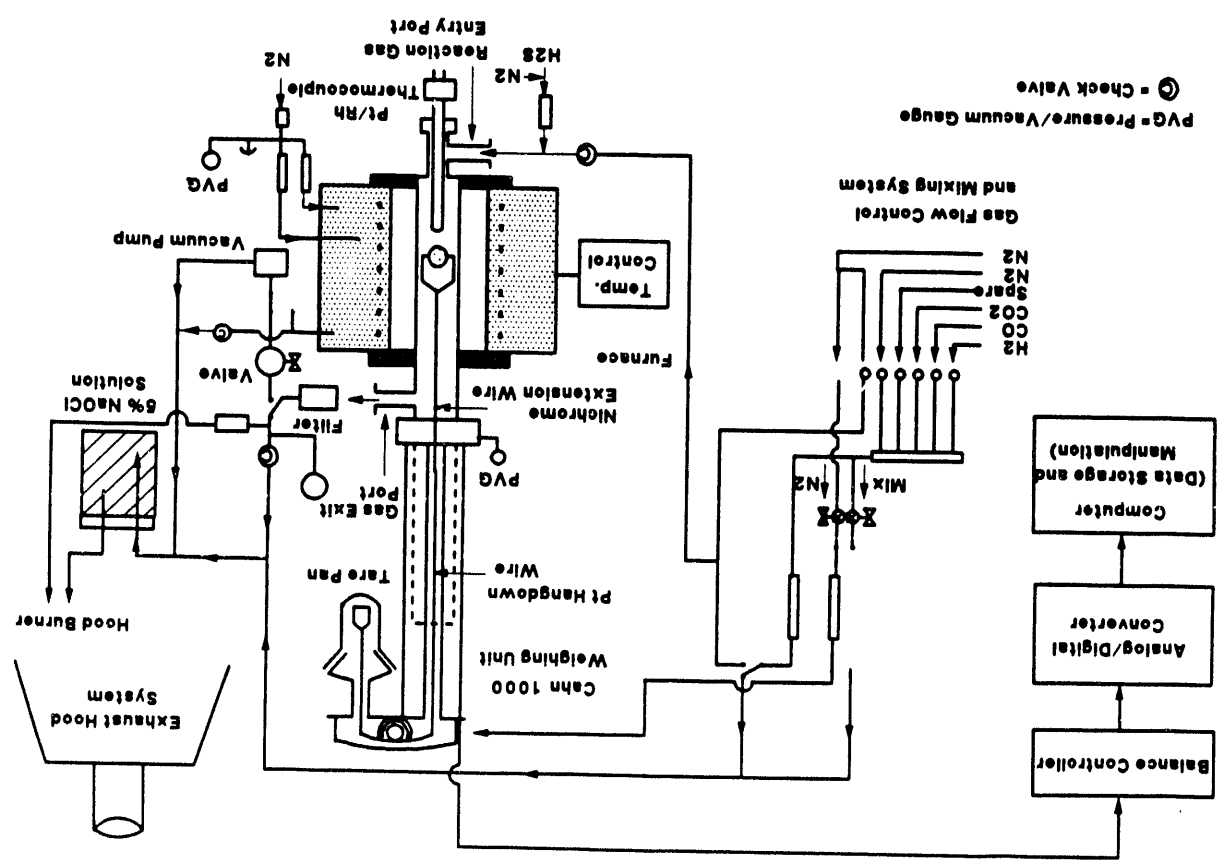
available to react with hydrogen sulfide. In general, however, and at longer reaction times, each curve would approach its final weight corresponding to complete sulfidation.

In continuing the examination of Figure 2, one should note the rapid kinetics upon switching to the loading gas, which is most pronounced in formulation 4-A, i. e. manganese carbonate plus bentonite. Formulation 1-A (ore plus dextrin) has somewhat slower kinetics followed by formulation 2-A (ore plus bentonite). Figure 3 shows similar results for tests conducted at 900 °C. Again formulation 4-A shows the highest sulfur capacity and the most rapid kinetics of the four pellet groups. Tests conducted at 800 °C show somewhat slower kinetics again with the pellet groups showing similar trends in kinetics. Results from similar loading tests at 700 °C indicated that the kinetics are significantly slower so that only a fraction of the pellet capacity is utilized for all four formulations within the time-frame of the three-hour test regime.

Figure 4 is a composite of the data for formulation 4-A, the best of all the formulations studied, for the temperatures 760, 800, 900, and 1000 °C. The theoretical capacity for this formulation is shown as a dashed line on the plot with reactivity rates for all temperatures being rapid.

Regeneration Tests. The TGA tests focused on studying the effects of regeneration parameters (temperature and O_2 content) and on repeated loading and regeneration of the selected FORM4-A pellets. Since up to fifteen pellets may be used in each reduction/sulfidation test, various tests were needed to provide enough fully-loaded pellets for the various regeneration tests planned. This provided an opportunity to determine the reproducibility of the sulfidation tests. The reduction and sulfidation were carried out under standard conditions of 950 °C and 3%
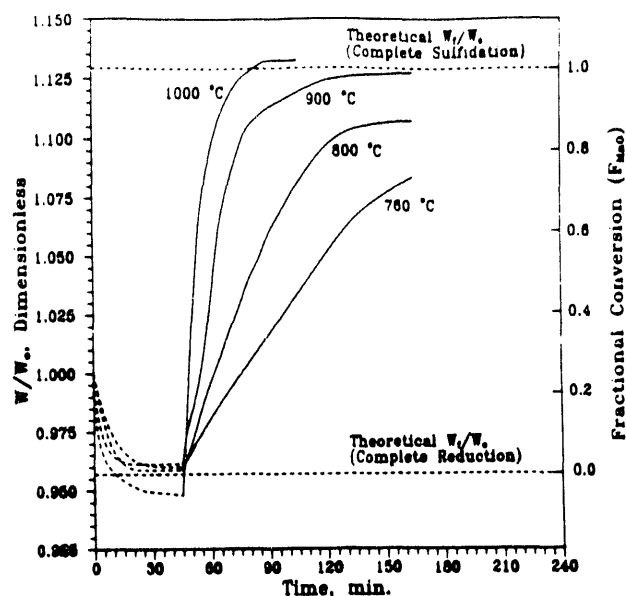

Figure 4. Effect of Temperature on Sulfidation Kinetics of FORM4-A Pellets

H_2S-H_2 gas mixtures at 500 cc/min delivery for a total of approximately 2 grams of pellets. Reduction was carried out with pure hydrogen for the first 45 minutes and then the hydrogen sulfide was added.

Figure 5 shows the reproducibility of loading tests resulting from five separate tests on fresh pellets (i.e., first loading cycle) at 950 °C with 3% by volume hydrogen sulfide in hydrogen. This figure gives the error bars on the data to indicate the range of the results. Although not shown for the reduction portion of the curve the reproducibility is particularly good, with reduction essentially completed in fifteen minutes. Figure 5 shows that deviations in extent of loading occur even though during each test the macroscopic properties (mass and size) of the pellets were kept as constant as possible. These deviations may be due to the difficulty associated with controlling temperature, flow rates, etc. However, the reproducibility of sulfidation is excellent beyond the first 30 minutes after the initial reduction period (total lapse time of 75
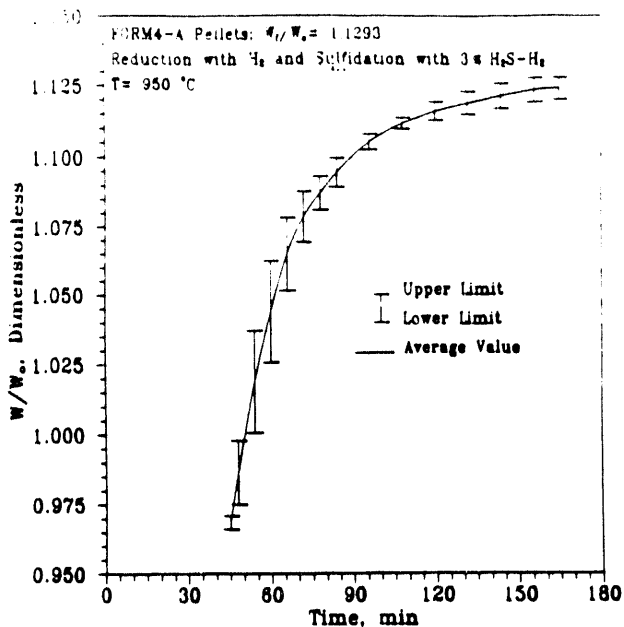
Figure 5. Reproducibility of Loading Tests at 950°C with 3% H_2S-H_2 Gas Mixtures Showing Average Value and Error Bars

Figure 6. Effect of Temperature on Regeneration Kinetics of FORM4-A Mn-Based Pellets.

minutes). The solid line represents the average values and therefore serves as an indication for future test results.

A total of five regeneration tests were then carried out using five pellets during each test. The regeneration gas was air flowing at 500 cc per minute and regeneration temperature varied between 800 and 1000 °C in increments of 50 °C. The purpose was to determine the temperature at which loaded pellets could be fully regenerated in reasonable time. The results from these tests are reported in Figure 6. The loading curve corresponds to the solid line shown in Figure 5; however, the right-hand portion of this figure shows the regeneration portion after a total time lapse of 165 minutes. These results appear to be in strict accordance with thermodynamic predictions, viz.: at 800 °C the loaded pellets first oxidize (and hence lose weight) for about 3 minutes at which time sulfation with an concurrent weight gain becomes predominant. When approximately
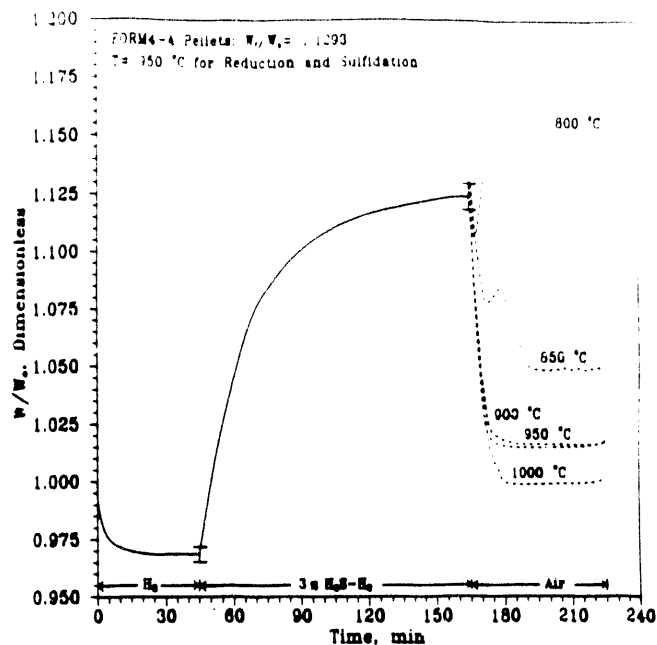
60% of the MnS is converted to $MnSO_4$, sulfate decomposition starts and the pellets begin to show a weight loss. Continuing at higher temperatures, at 850 °C, the same trend is observed; however, the oxidation of the pellets appears to be faster than sulfation; this is reasonable since the driving force for the decomposition of sulfate is greater. Regeneration kinetics appear to be a weak function of temperature over the range 900 to 1000 °C. In this range regeneration is essentially complete in 10 to 15 minutes and sulfation does not occur, as concluded from the prior thermodynamic analysis of the Mn-S-O system. It must be noted, however, that full regeneration (i.e., $W/W_0 = 1$) apparently requires a temperature of 1000 °C or higher.

Multicycle Tests Over a five-day period, one loading and regeneration cycle was completed each day at 950 °C for reduction and sulfidation and 1000 °C for regeneration. The TGA data for these five tests are shown in

Figure 7. The arrows show the direction of increasing cycle sequence numbers, i. e. for loading, the capacity and reaction kinetics improve for each of the five cycles with the change between the first and second cycles being the most pronounced. For the tail of the curve terminating the regeneration step, the weight loss drop is steepest for the fifth
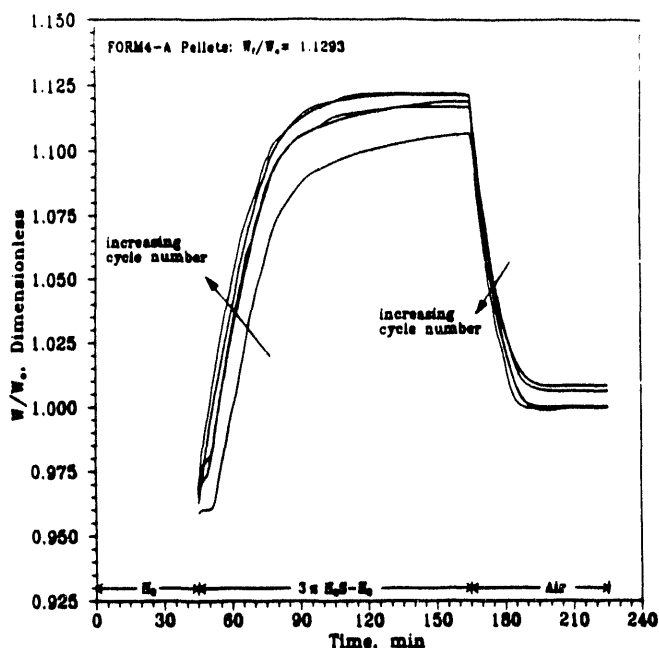

Figure 7. Effect of Repeated Cyclical Loading and Regeneration on the Reaction Kinetics and Capacity of FORM4-A Pellets.

cycle: again showing that the rate of regeneration increases with pellet re-use. An optical examination at 30 magnifications with a binocular microscope as well as petrographic thin sections examined at 100x showed the presence of radial cracks. The penetration distance of the sulfur as exhibited by the higher reflectivity of the manganese sulfide phase was densest adjacent to these cracks, indicating that the diffusion distance for permeation of sulfur (and counter-transport of oxygen) was decreased by the change in diffusion geometry occasioned by the cracking. Whereas the original pellet

experiences diffusion for a gross pellet size of ≈ 2.5 mm in radius; upon cracking of the pellet, the solid-state diffusion distance is somewhat reduced. This permits gaesous species to be transported by the relatively faster mechanism of gaseous diffusion into the cracks compared with the slower process of solid state counter diffusion of oxygen out of the pellet to exchange for sulfur into the pellet.

This is a unique feature of manganese-based pellets, i. e. their retained strength upon micro-cracking and improved kinetics compared with competing sorbents, e. g., zinc titanate, in which the reaction kinetics and sorbent loading capacity and pellet strength decrease upon cyclic loading.

Bench-scale testing The overall schematic diagram of the experimental arrangement for fixed-bed tests is shown in Figure 8. The split or two-zone furnace is positioned with respect to the bed to accomplish gas preheating and careful control of the bed temperature. Gas combinations for flows can be produced via control of bottled gases through the valves and flowmeters shown in the diagram. The water content of the system is controlled by a metering pump acting on liquid water which is discharged into a heated stainless tube to vaporize the water and provide the gas composition required by the Tampella-U Gas composition, as reported earlier.[4]

The details of the reactor system are depicted in Figure 9. This figure shows the two-inch (I.D.) closed-end alumina reactor tube equipped with an alumina perforated-disc plate suspended over alumina chips. The coal-derived fuel gas simulating the Tampella-U Gas is passed through a small central tube (without contacting the reaction zone of manganese pellets) through the perforated disc and into a preheat zone of alumina chips which supports the disc. The gas is then discharged from the small central tube into
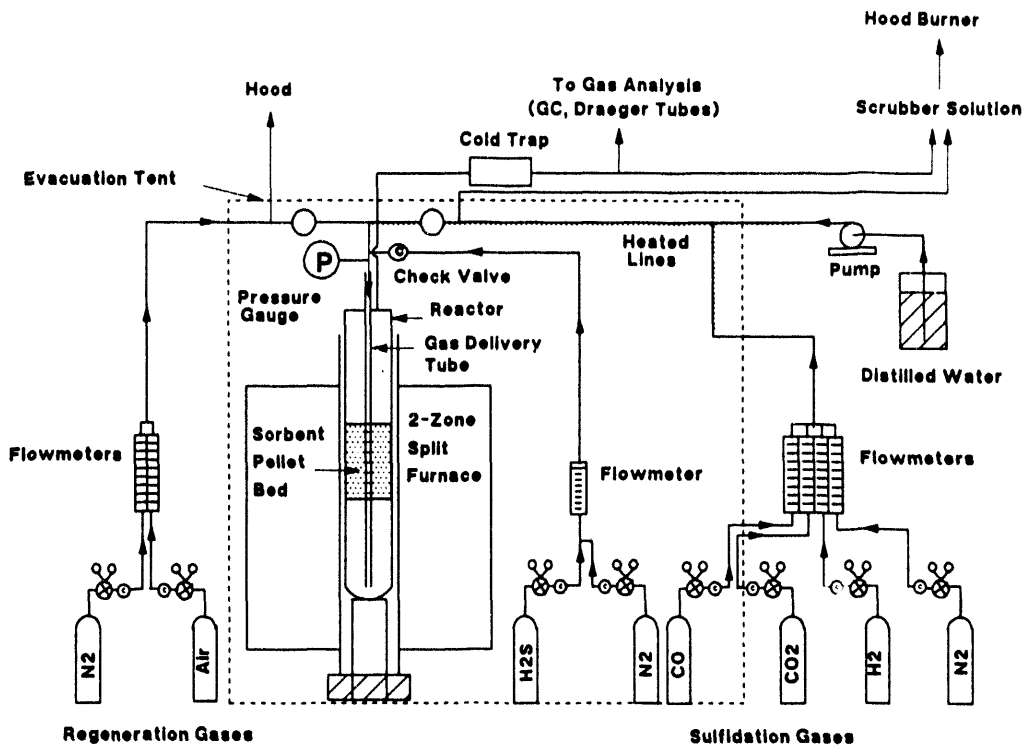
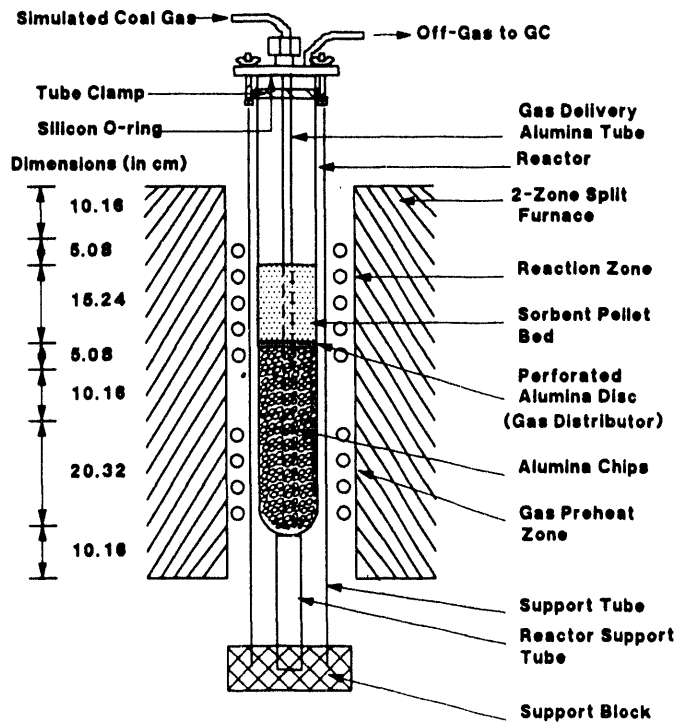**Figure 8.** Schematic of Overall Experimental Arrangement for Fixed-Bed Tests.

Figure 9. Schematic Diagram of Reactor Details.

the larger tube and moves upward, after reaching temperature, into gas preheat zone of a two-zone furnace. The gas, now at temperature, contacts the sorbent bed consisting of pellets ranging in size from 4 to 5 mm in diameter. The off-gas then is flared and discharged to a hood. A sample is taken via gas chromatograph (labelled in Figure 9 as GC).

A minor problem has arisen during the regeneration step in that sulfur tends to form and plug the exit tube during the early stages of regeneration (examination of the plug showed it to be elemental sulfur). This problem was overcome by reducing the air flow rate to limit the rate of heat release by the highly exothermic regeneration reaction and prevent the pellets from sintering. The addition of an after-burner on top of the pellet bed resulted in more oxidizing conditions and hence less tendency for sulfide sulfur (S^-) to oxidize to the intermediate elemental form (S^0) rather than to 4-valent (S^{+4}).

Loading proceeded at a rate of 3.5 liters per minute until breakthrough is observed. Breakthrough is defined as a sudden rise in the sulfur content of the gas as determined by gas chromatography. The bed is then flushed with nitrogen in order to expel remaining hydrogen and a regeneration gas consisting of air is initiated with the sulfur content of the gas being continuously analyzed for sulfur dioxide. The regeneration step is discontinued when the concentration of sulfur dioxide in the exit gas is measured below 500 ppmv. The loading and regeneration cycles are then repeated until twenty (20) cycles are completed.

Figure 10 shows the effect of cycling on the sulfur capacity of FORM4-A pellets at 900°C upon repeated loading and regeneration. The sulfur loading capacity (defined as grams sulfur per 100 grams of original pellet mass) shows a slight improvement with each cycle. The effect diminishes with each cycle since loadings

approaching 23% S, (i. e., is ~90% of the maximum theoretical value) at 12 cycles. This sulfur capacity is calculated using mass balances, based upon gas analyses for H_2S entering and leaving the reactor. Before break-through the H_2S concentration in the cleaned gas approach more closely the equilibrium value, which is an indication of an improvement in pellet reaction kinetics with increasing cyclic loading. These results are consistent with the previous results from TGA tests on individual pellets.

Mn-Based Sorbents vs Zn-Based Sorbents

The theoretical capacity of manganese-based pellets for sulfur compares favorably with zinc ferrite and zinc titanate as shown in Table III. In generating this table, it is assumed that Fe_3O_4 is the stable form of Fe after reduction of $ZnFe_2O_4$, and that the optimized zinc titanate formulation is composed of 1.5 ZnO:1.0 TiO_2. Furthermore, the manganese ore-based formulation is based upon Moanda ore containing 51.2% Mn by weight.

Clearly, even the manganese ore-based sorbent pellet, which has a lower capacity than the Mn carbonate-based formulation, compares favorably with the optimized formulation of zinc titanate which was used extensively in pilot-scale and process development work.

Table III. Theoretical Sorbent Capacities

Sorbent	Theoretical Capacity, g S/100 g of sorbent
Zinc ferrite	39.8
Zinc titanate	23.8
Mn Ore-based	24.0
Mn carbonate-based	34.4

The ultimate degree of desulfurization of manganese-based pellets is less favorable than would be achieved with Zn-based
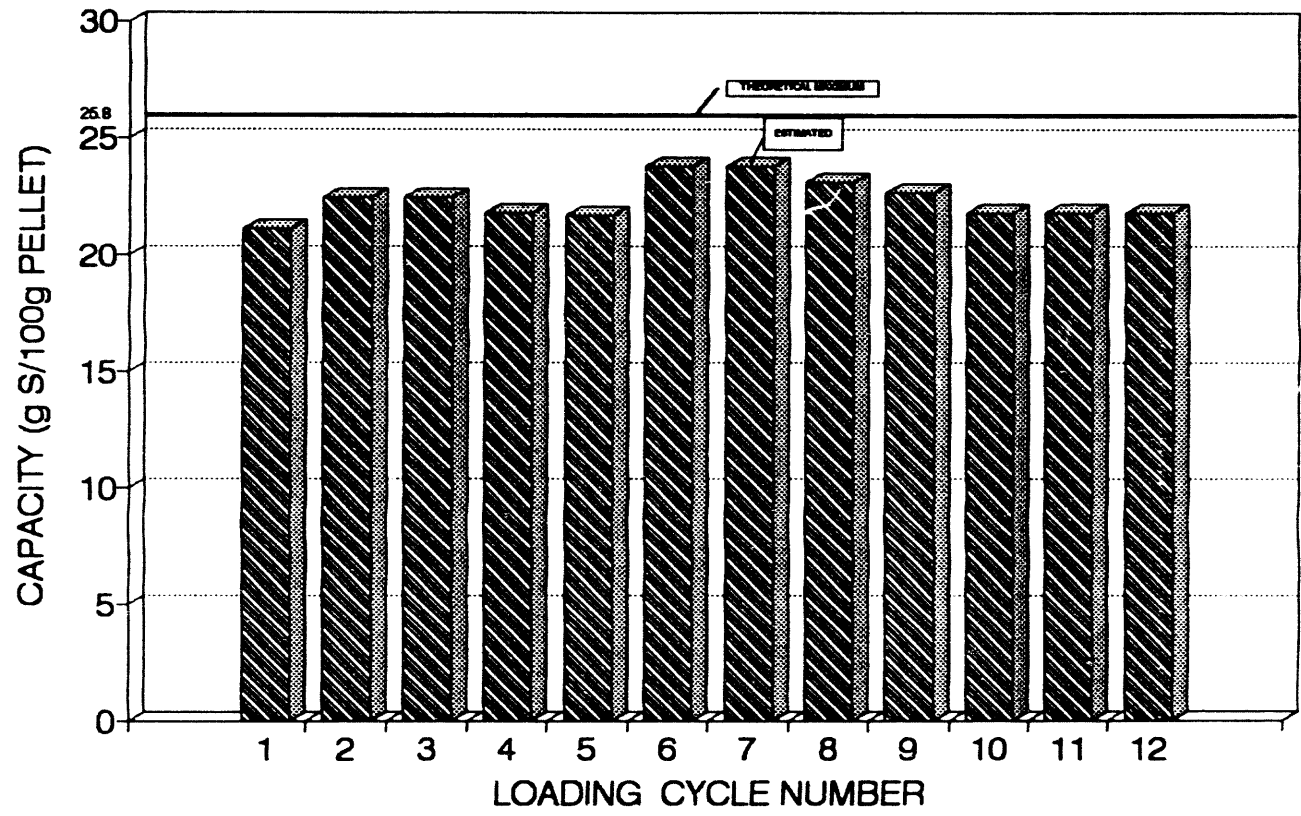
Figure 10. Effect of Cyclic Loading and Regeneration on Sulfur Capacity of FORM4-A Pellets at 900 °C.

sorbents. For example, for a fuel gas containing 5% H_2O and 1% H_2S, desulfurization at 1000 °K (727 °C) achieves 57 ppmv H_2S with MnO and 6 ppmv H_2S with ZnO, based on data compiled by Turkdogan.[8]

To compare the rate of sulfidation of Mn-based pellets with that of Zn-based sorbents, the results from sulfidation tests on L-3140 sorbent[3] at 760 and 870 °C are superimposed on the results reported above in Figure 4, as shown in Figure 11. The goal of exposing the Zn-based sorbent to the H_2S-free reducing gas is to quantify the weight loss which is solely due to ZnO depletion. At 760 °C this physical loss of reactive component is negligible; however, at 870 °C this phenomenon becomes noticibly more severe leading to lower sorbent capacity for sulfur. More importantly, the rate of sulfur pick-up from hot coal-derived fuel gases using Mn-based pellets compares favorably with that which is obtained using Zn-based sorbents.

zinc-based sorbents is sulfate formation which is found to occur whenever SO_2 is present in the regeneration gas. Sulfation leads to volume expansion and swelling of sorbent pellets eventually causing them to spall and crack. For example: a 5 to 6-mm diameter loaded pellet expands to 9 mm after regeneration when sulfate was formed.[9] Certainly, in a fixed-bed operation some of the pellets will be saturated with sulfur and the regeneration gas will contain some SO_2. Therefore, sulfate formation is unavoidable along with accompanying spalling and cracking.

The role of chlorides in the gas system should be considered in any study because of the potential volatility of metal chlorides. The presence of HCl in the coal gas causes extensive volatilization of zinc in the form of $ZnCl_2$. All fuel gases contain some hydrochloric acid, under reducing conditions. Zinc chloride ($ZnCl_2$) has a boiling point of 1005 °K (732 °C); whereas, manganese chloride ($MnCl_2$) has a boiling point of 1504 °K[10] (1231 °C). The higher boiling point of manganese makes it much less susceptible to volatilization and losses from the sorbent than zinc. Losses of zinc as high as 5-10% by weight from the exit of a fixed-bed reactor have been reported,[9] even after one cycle of loading and regeneration. It follows that any gas system which is used as an environment for comparing the cyclic loading and regeneration behavior between manganese oxide and zinc-based sorbents should take into account the presence of chlorides in the fuel gases.

A fortuitous feature of the manganese-oxygen-sulfur system is its resistance to reduction to elemental manganese under the range of most of the fuel gas compositions for which it would be utilized as a sorbent. Furthermore the sulfidation and regeneration can be carried out at the same temperature, for example (800 °C) without the formation of sulfates. Another favorable feature of the
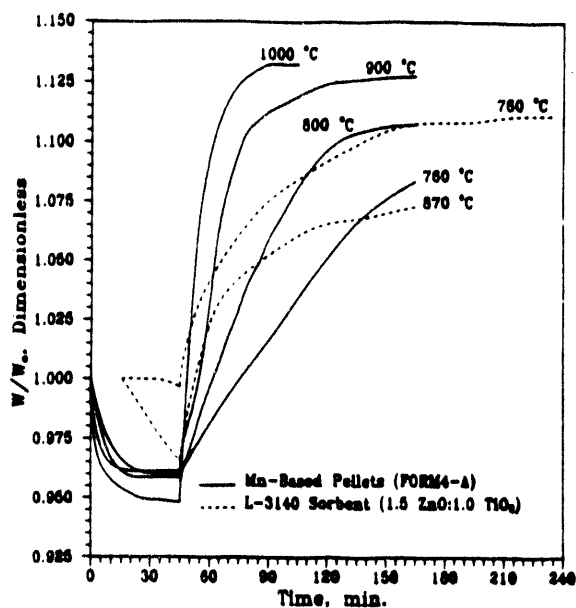
Figure 11. Comparison of Sulfidation Kinetics via Thermogravimetric Analysis of FORM4-A Mn-Based Pellets and L-3140 Zn-Based Sorbents.

One major problem associated with

manganese-oxygen-sulfur system is its resistance to fusion as a result of temperature rises which may occur in the exothermic step of regeneration since the system is relatively refractory and non-volatile (i.e., lacks low melting-point phases) even in the presence of trace chloride impurities. For the case of zinc ferrite, it was found that temperature excursions as small as 50 °C could destroy the sorbent reactivity.[11] Exit gas temperatures from commercial gasifiers are likely to be in excess of 650 °C; in addition, operation of the desulfurization process at higher temperatures increases the overall IGCC plant efficiency. Manganese-based pellets appear to be capable of much higher temperatures of loading and regeneration than zinc without degradation; however, this question remains to be fully explored.

FUTURE WORK

Under the present contract a program was undertaken to optimize pellet formulations and evaluate them by multiple cyclic tests in a fixed-bed reactor; however, now that the FORM4-A pellets have been shown to be highly effective through repeated cycling, effort should be redirected toward exploring several parameters of fixed bed operation which may be more consonant with actual test conditions. For example after ten cyclic loadings of the pellets, a long cycle of loading at a lower H_2S content, more nearly representing the actual fuel gas compositions, should be undertaken. Upon completing this long cycle to break-through, the bed should be examined in vertical layers to explore the degree of sulfidation which has occurred on single pellets.

Also single-particle regenerations on selected pellets from the above long test should be explored by DTA as well as TGA analysis to determine the thermal effects which occur upon oxidation of the sulfides. The results on single pellet tests could then be compared with the thermal effects (e. g., local temperature rises) which would occur in fixed bed environments. The effect of space velocity, i. e. gas flow rates in fixed bed tests could also be explored.

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P6   A Calcium Oxide Sorbent Process for
Bulk Separation of Carbon Dioxide

CONTRACT INFORMATION

Contract Number	DE-AC21-89MC26366
Contractor	Louisiana State University Department of Chemical Engineering Baton Rouge, Louisiana 70803
Contract Project Manager	Douglas P. Harrison
Principal Investigators	D.P. Harrison C. Han
METC Project Manager	Venkat A. Venkataraman
Period of Performance	September 1989 to October 1994

OBJECTIVES

Initial phases of this project investigated the bulk separation of CO_2 from coal-derived gas at moderate to high temperature. The separation process was based upon the reversible noncatalytic reaction

$$CO_2(g) + CaO(s) \leftrightarrow CaCO_3(s). \qquad (1)$$
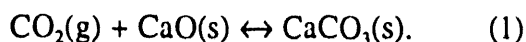
We are presently studying the feasibility of combining CO_2 removal with the water gas shift reaction

$$CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g). \qquad (2)$$
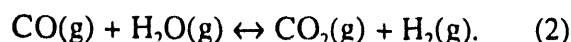
The combined reactions, which are carried out in a single reaction vessel, provide an alternate and potentially simpler process for the production of H_2 from synthesis gas.

In this experimental investigation, a laboratory-scale fixed-bed reactor containing a calcium-based sorbent is being used to study the combined reactions as a function of calcination and carbonation temperature and pressure, synthesis gas composition, reactor space velocity, and sorbent composition and properties.

BACKGROUND INFORMATION

Hydrogen, one of the most important raw materials in both the chemical and petroleum industries, is produced primarily by the steam reforming or partial oxidation of gaseous or liquid hydrocarbons. In the future, coal gasification may become important as the supply of light hydrocarbons decreases. The initial product from all of these processes is a synthesis gas composed primarily of CO, CO_2, H_2, H_2O, and, in some cases, N_2. The water gas shift reaction is then used to produce additional H_2 by reacting the remaining CO.

Because the shift reaction is exothermic and reversible, multiple catalytic reaction steps are necessary to achieve complete CO conversion. Extensive gas-to-gas heat exchange

networks are required to adjust the temperatures at various stages in the process. The CO_2 product is normally removed using wet scrubbing or pressure swing adsorption. The alternate single-step process accomplishes the shift reaction and CO_2 removal in a single reaction vessel, and eliminates the need for expensive catalysts as well as the CO_2 absorber and stripper (or the PSA unit). Heat exchange requirements are minimized since the alternate process occurs at high temperature.

The potential advantages of the single-step process are illustrated by the following thermodynamic comparison. Consider a typical coal-derived synthesis gas containing 22% H_2, 30% CO, 8% CO_2, and 40% H_2O at a reaction temperature of 900K. Equilibrium calculations, using thermodynamic data of Barin et al. (1977), show that the shift reaction alone would result in only 56% conversion of CO. If the shift reaction is carried out in the presence of calcium-based sorbent, equilibrium at 1 atm corresponds to 99% conversion of CO, while effectively 100% conversion of CO will occur at 25 atm. In the later case, total carbon oxide concentration in the equilibrium product gas will be in the ppm level.

PROJECT DESCRIPTION

The laboratory-scale fixed-bed reactor has a capacity of 10 to 15 grams of sorbent. Gaseous feed components are obtained from high pressure cylinders with flow rate controlled by high pressure mass flow controllers. Liquid water is added using a high pressure syringe pump and is vaporized as it mixes with the permanent gases. The combined gas feed is preheated prior to contacting the sorbent.

Reactor product is sampled periodically and analyzed by gas chromatography. Argon is used as the carrier gas and the chromatograph system is equipped with multiple columns, automatic sampling and switching valves, and both thermal conductivity (TCD) and flame ionization (FID) detectors. The TCD is used for analysis of N_2, H_2, and high concentrations of CO and CO_2 ($\geq$ 0.5%). When CO and CO_2 concentrations are below the TCD detection limit, the reactor products pass through a ruthenium-catalyzed methanator which converts CO and CO_2 to CH_4, and analysis is completed using the more sensitive FID. More complete descriptions of the reactor and analytical system, including drawings have been published (Harrison et al., 1993).

A typical reactor response curve showing component concentrations as a function of time is presented in Figure 1. Results from both the TCD and FID are included as indicated. Early in the reaction CO and CO_2 concentrations were effectively constant at about 80 and 300 ppm, respectively, while H_2 concentration was constant at 1.5×10^5 ppm (15%). We refer to this stage as the prebreakthrough period, during which the total fractional removal of carbon oxides was 0.998. After much of the CaO was converted to $CaCO_3$, CO and CO_2 concentrations increased rapidly while H_2 concentration decreased. The slope of the concentration-time curves during this breakthrough period provides a measure of the global rate of the combined reactions. After essentially all of the CaO was converted to $CaCO_3$, a second steady-state, postbreakthrough period, was reached. Only the shift reaction occurred during this stage.

The prebreakthrough period is of primary interest since it is during this period that the true capability of the single-step process for carbon oxide removal and hydrogen production can be evaluated.

RESULTS

The parameters which have been (and are being) investigated include calcination and carbonation temperature and pressure, feed gas composition, reactor space velocity, and the composition and structural properties of the sorbent. Multicycle runs are being carried out because, for the process to be economically attractive, the sorbent must maintain its activity
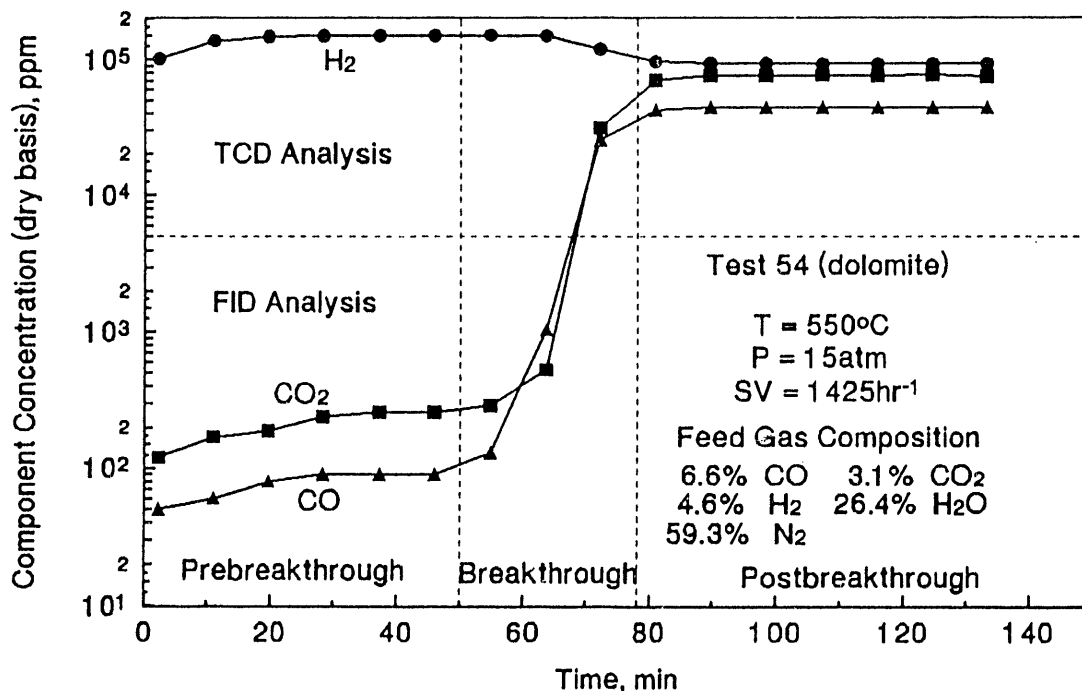
Figure 1. Typical Fixed-Bed Reactor Response Curve

through numerous calcination-carbonation cycles.

Comparison of Sorbents

Dolomite was found to be superior to limestone during the initial phase of this project, and the superiority has subsequently been confirmed in the fixed-bed studies. Figure 2 compares the performance of dolomite and limestone sorbents in a plot of fractional removal of total carbon oxides as a function of time. The product gas analysis in this example is based on the TCD only, so that, early in the reaction, the fractional carbon oxide removal approaches 1.0 with both sorbents. The actual CO and CO_2 concentrations during this period were approximately 80 and 215 ppm, respectively, during the test with limestone, and 22 and 250 ppm for the test with dolomite. These concentrations correspond to fractional removal of total carbon oxides during the prebreakthrough period of 0.996 in both tests.

In addition to the delayed initial breakthrough, the larger slope of the breakthrough curve for dolomite is indicative of larger global reaction rates. Finally, additional data (not shown) indicates that the multicycle durability of dolomite is significantly better.

The favorable properties of dolomite are attributed, to a large degree, on differences between the structural properties of calcined dolomite and calcined limestone. Complete decomposition occurs during the initial calcination phase so that dolomite is converted to (CaO + MgO) while limestone is converted to CaO. Carbonation conditions are such that CaO, but not MgO, reacts with CO_2. Therefore, after initial decomposition, dolomite cycles between fully calcined (CaO + MgO) and half-calcined ($CaCO_3$ + MgO) forms while limestone cycles between CaO and $CaCO_3$. The "excess" pore volume created by $MgCO_3$ decomposition during initial calcination is believed to be responsible for the favorable reaction properties.
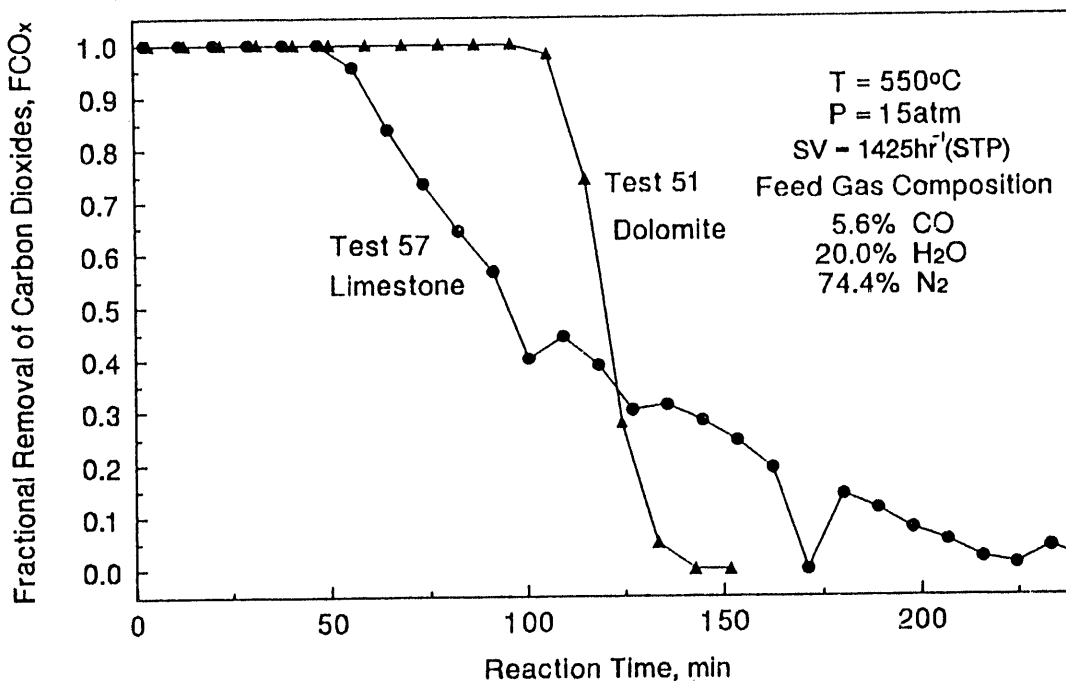
Figure 2. Comparison of the Performance of Dolomite
and Limestone Sorbent Precursors

In a similar manner, a gradual change in structural properties caused by sintering is the suspected cause of the gradual deterioration in sorbent performance observed in multicycle tests (see subsequent discussion).

Calcination

Calcination at the mildest possible conditions is important if sintering is to be minimized and sorbent durability increased. All of the calcination experiments discussed in this paper were carried out at 750°C and 3.3 atm of N_2. At lower temperatures, the calcination rate is too small to be of interest while presently available data indicates more rapid sorbent deterioration at higher calcination temperature. Process analysis, however, suggests that, in order to reduce the required flow rate of calcination sweep gas, it is desirable to operate at more severe calcination conditions. Therefore, the final choice of calcination conditions must balance the conflicting considerations of sorbent durability and sweep gas flow rate.

Shift/Carbonation Temperature and Pressure

Choice of the optimum temperature for the shift and carbonation reactions also represents a balance between equilibrium and kinetic factors, and the desired extent of carbon oxide removal. Since both the shift and carbonation reactions are exothermic, higher temperature has an adverse effect on both equilibrium CO conversion and CO_2 removal. Experimental results shown in Figure 3 indicate that the kinetics during the prebreakthrough period are sufficiently rapid that equilibrium is closely approached at temperatures equal to or greater than 500°C. Minimum prebreakthrough CO and CO_2 concentrations of 3 and 35 ppm, respectively, at 500°C correspond, as shown in the upper portion of Figure 3, to 0.999 fractional carbon oxide removal. This figure also shows that greater
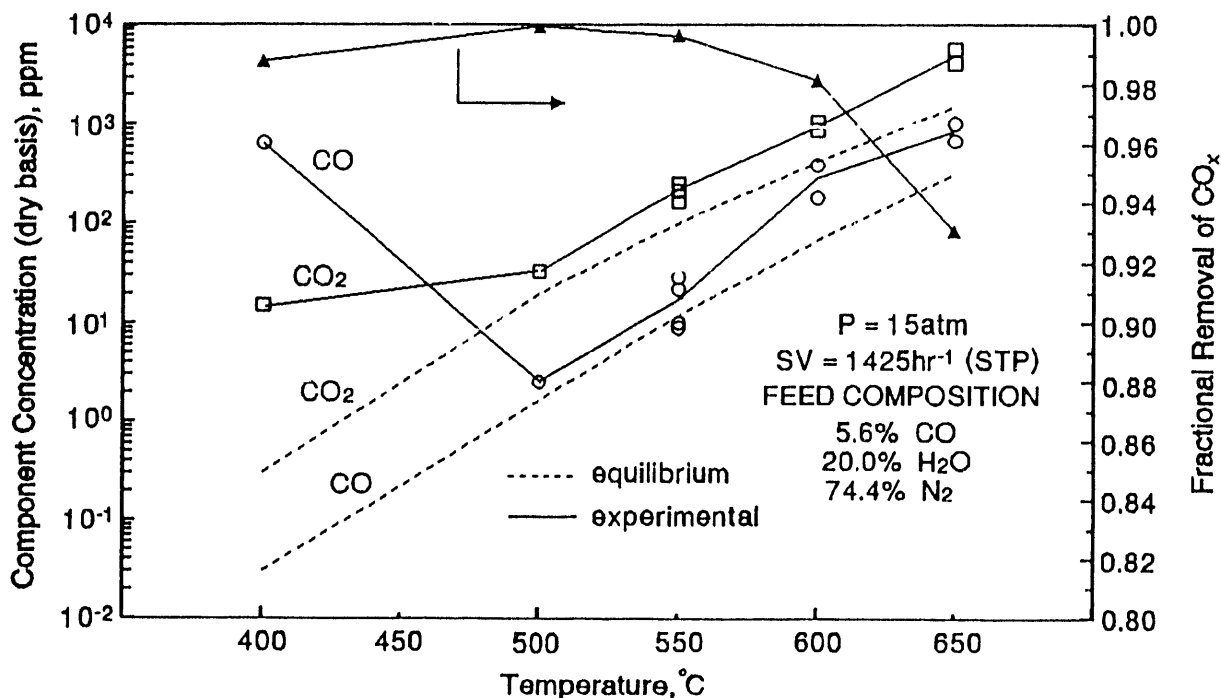
Figure 3. Prebreakthrough CO and CO_2 Concentrations
as a Function of Temperature

than 0.995 fractional carbon oxide removal can be achieved throughout the temperature range of 450 to 550°C at these reaction conditions.

Data from multiple runs at the same reaction conditions are included in Figure 3 to provide evidence of the level of reproducibility which can be achieved. Some variation in the CO and CO_2 concentrations is evident, but there is no difference in the fractional removal of total carbon oxides between any of the duplicate tests.

Although the data at this time is limited, it does not appear that the shift-carbonation temperature has an important effect on multicycle durability. This is not surprising, as one would expect sintering to occur primarily during the calcination phase which operates at higher temperature.

While none of the experimental tests have exceeded 15 atm pressure, we expect the single-step process to be even more favorable at higher pressure. Equilibrium CO and CO_2 concentrations decrease with increasing pressure,

and experimental results at 15 atm were significantly better than those at 5 atm. The prebreakthrough CO and CO_2 concentrations were both 4 to 5 times greater at the lower pressure.

Feed Gas Composition

In several tests, including those illustrated in Figures 2 and 3, the reactor feed contained only CO, H_2O, and N_2 diluent. This feed gas simplified the operation of the reactor system, and the presence of CO_2 in the reactor product provided conclusive evidence of the occurrence of the shift reaction. In other tests, such as illustrated in Figure 1, the feed gas contained all the major components of synthesis gas -- CO, CO_2, H_2, and H_2O. It is difficult to make a direct comparison of results from the two different feed types because both the total carbon oxide feed rate and the H_2O to CO ratio in the feed gas were different. However, the fractional carbon oxide removal from the

complex gas was generally comparable to that achieved when using the simple gas mixture.

The H_2O to CO ratio is the feed gas is an important parameter. The addition of excess steam promotes the shift reaction, but is also a significant cost item. Figure 4 shows prebreakthrough CO and CO_2 concentrations from a series of tests in which the feed gas contained all major components of a synthesis gas. The ratios of CO, CO_2, and H_2 for the Figure 4 tests are representative of a Texaco gas, with the quantity of steam determined by the desired H_2O to CO ratio. The large concentration of diluent N_2, which, of course, is not representative of a Texaco gas, is simply a requirement of the laboratory reactor.

The prebreakthrough CO_2 concentrations shown in Figure 4 are in the 200 to 250 ppm range, and are comparable to the CO_2 concentrations obtained using the simpler feed gas at equivalent reaction conditions. However, the minimum CO concentration of 90 ppm is significantly larger than the approximately 20

ppm achieved with the simpler feed gas. Nevertheless, the total fractional removal of carbon oxides increased from 0.993 to 0.997 to 0.998 as the H_2O to CO ratio increased from 2.0 to 3.0 to 4.0. The total fractional removal of carbon oxides using the simpler feed gas having a H_2O to CO ratio of 3.57 and otherwise equivalent reaction conditions was 0.997.

Space Velocity

All tests described to this point utilized a space velocity of 1425 hr^{-1} (STP). Because space velocity is such an important parameter in determining reactor size, and therefore cost, a series of tests using the simpler gas composition was carried out in which the space velocity was varied from 885 to 3400 hr^{-1} (STP). Prebreakthrough CO and CO_2 concentrations, as well as fractional removal of total carbon oxides are shown in Figure 5. The concentrations of CO and CO_2 change only marginally with space velocity, which indicates that the global reaction rates are sufficiently large to permit equilibrium
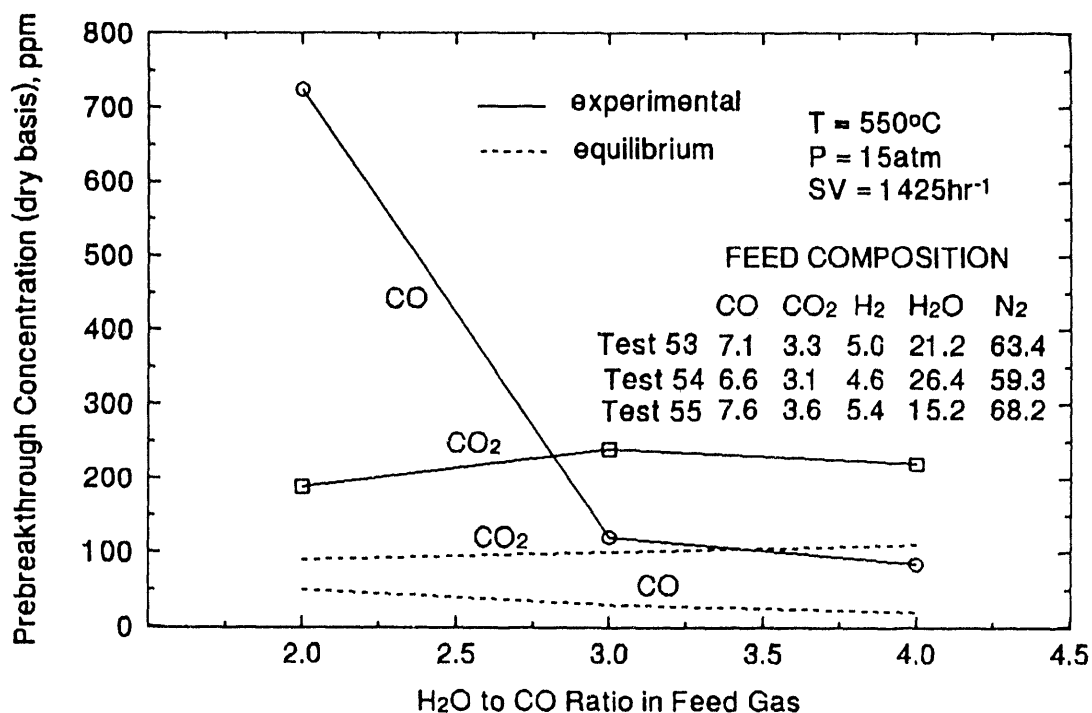

Figure 4. Prebreakthrough CO and CO_2 Concentration as a Function of H_2O to CO Ratio
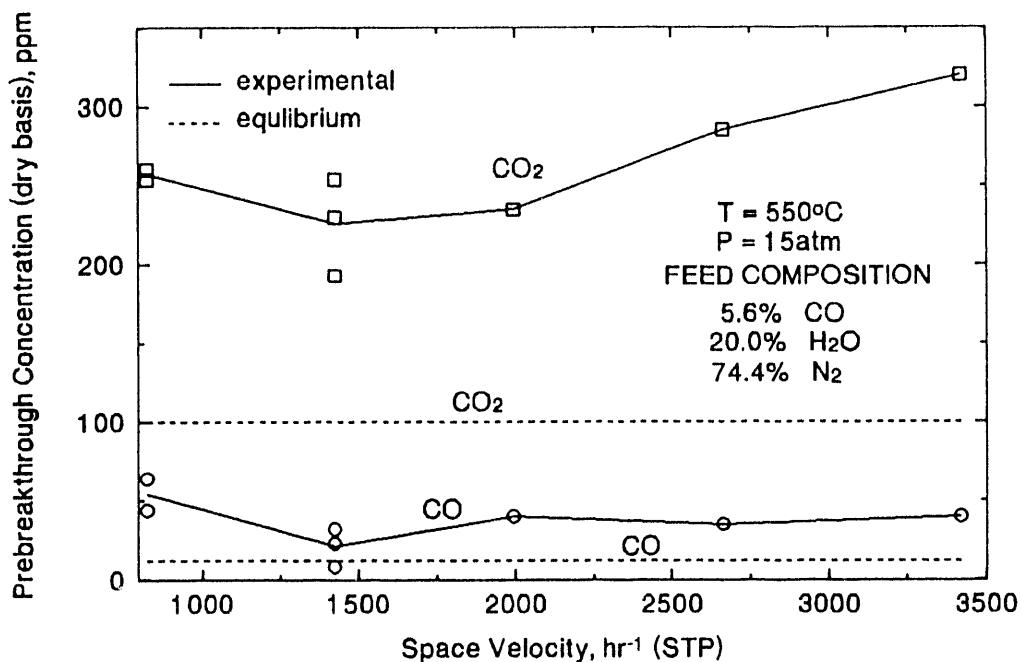
Figure 5. The Effect of Space Velocity of Prebreakthrough CO and CO_2 Concentrations

to be closely approached at all conditions. All concentrations shown in Figure 5 correspond to fractional carbon oxide removals of 0.995 or greater.

The Nature of the Shift Reaction

The driving force which causes the shift reaction is not clear. In commercial operation, where the temperature is from 150 to 200°C lower than the temperature of primary interest for the single-step process, a heterogeneous catalyst is required. The literature contains little information on the shift reaction at 500°C or above. Does the shift reaction at higher temperature occur homogeneously in the gas phase, or is a heterogeneous catalyst necessary? If a catalyst is required, what material in our system serves as the catalyst? In an attempt to learn more about the nature of the high temperature shift reaction, a number of special tests were carried out. These tests ranged from the use of an empty reactor to packing the

reactor with a commercial iron-cobalt shift catalyst obtained from United Catalysts, Inc.

Fractional conversions of CO via the shift reaction at conditions where no carbonation could occur are shown in Figure 6. The results are surprising and, at this time, we are unable to explain the variation. Compared to the equilibrium fractional CO conversion of 0.91, the experimental fractional conversion ranged from 0.26 using the empty reactor to 0.87 when the reactor was packed with Al_2O_3. The low conversion using the empty reactor suggests that a catalyst is required if the shift conversion is to approach equilibrium, and that the stainless steel reactor surfaces do not serve as the primary catalyst. The fact that shift conversion in the test using Al_2O_3 exceeded the conversion with the shift catalyst is particularly surprising, since we have not found any references in the literature which claim Al_2O_3 to be a shift catalyst. The performance of the shift catalyst is likely far from optimum because of the higher

1.0

Equilibrium: 0.91

0.9 -

0.87   0.83

0.8   T = 550°C
       P = 15atm
       Feed Gas Composition

0.7   5.6% CO   0.67   0.65
       20.0% H₂O
0.6   74.4% N₂

0.5   0.43

0.4

0.3   0.26

0.2

0.1

0.0

Fractional Conversion of CO

Test 50   Test 51-1   Test 49   Test 58   Test 57   Test 61
Empty   Dolomite   Al₂O₃   Shift   Limestone Marble
Reactor   Catalyst   Chips
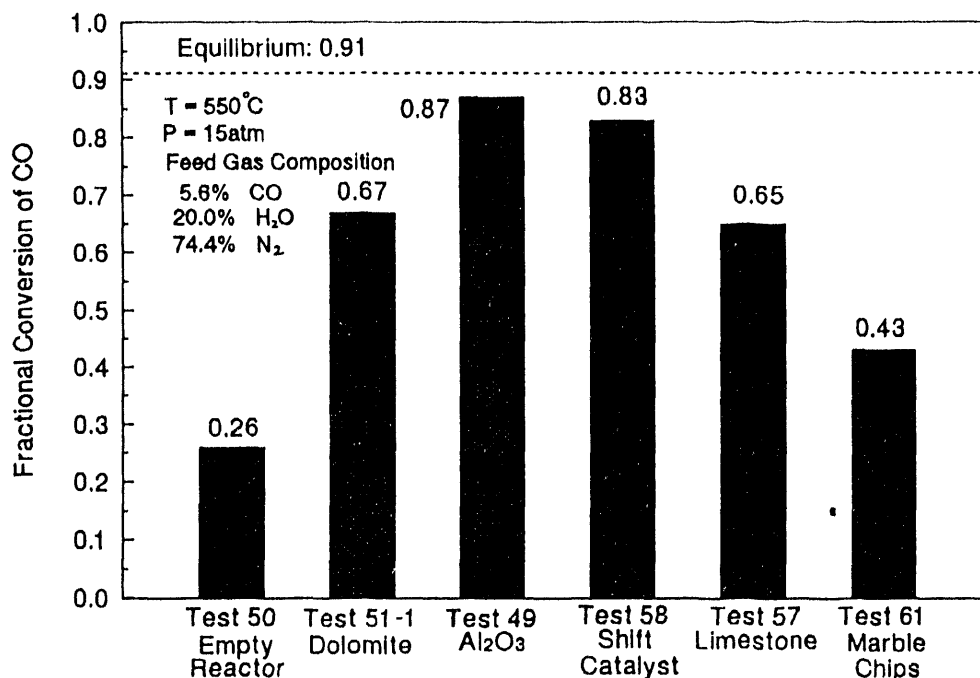
Figure 6. Fractional CO Conversion Via the Shift
Reaction Without CO₂ Removal

reaction temperature. The experimental evidence suggests that H_2 formed by the shift reaction reduces the iron in the catalyst to a lower oxidation state.

Fractional shift conversion during the three tests (51-1, 57, and 61) in which the reactor contained a CO_2 sorbent is based on reactor product composition during the postbreakthrough period when the rate of carbonation is effectively zero. These results are also confusing in that MgO has been reported by a number of authors including Rofer-De Porter (1984) to be a shift catalyst. Yet the fractional shift conversion using limestone, which contains MgO only as an impurity, and dolomite, where MgO is a major component, were effectively equal.

However, in spite of the lack of a clear understanding of the nature of the shift reaction, it is clear that the reaction does occur at a rate sufficiently fast for equilibrium to be closely approached during the prebreakthrough period.

Multicycle Tests

One key to ultimate commercial interest in the single-step process is sorbent durability. Although dolomite is readily available and inexpensive, it must retain activity through a large number of calcination-carbonation cycles. Current experimental effort is concentrating upon multicycle runs under a variety of reaction conditions. At this time, a number of five cycle tests and one test lasting for 11 cycles have been completed.

Figure 7 compares the prebreakthrough CO and CO_2 concentrations and fractional removal of carbon oxides during the prebreakthrough period as a function of cycle number for two multicycle tests at equivalent reaction conditions. CO concentrations were consistently in the 20 to 30 ppm range for all cycles of both tests while CO_2 concentrations were generally in the 180 to 250 ppm range. These concentrations correspond to fractional removal of total carbon oxides of either 0.996 or 0.997 in each of the 16
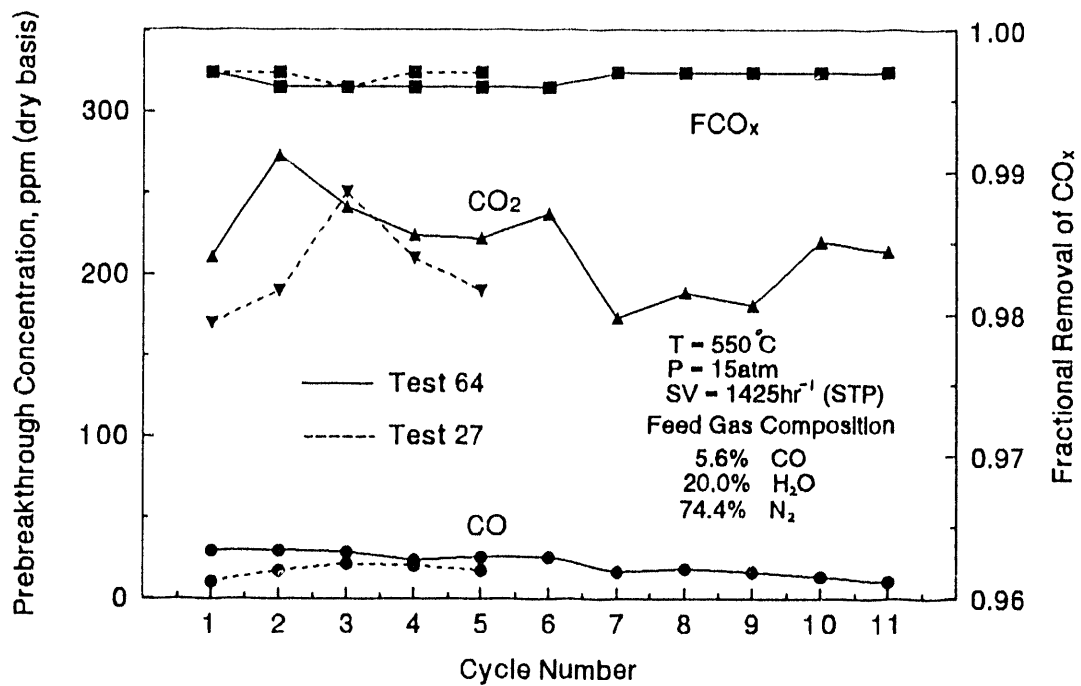
Figure 7. Prebreakthrough CO and CO_2 Concentrations
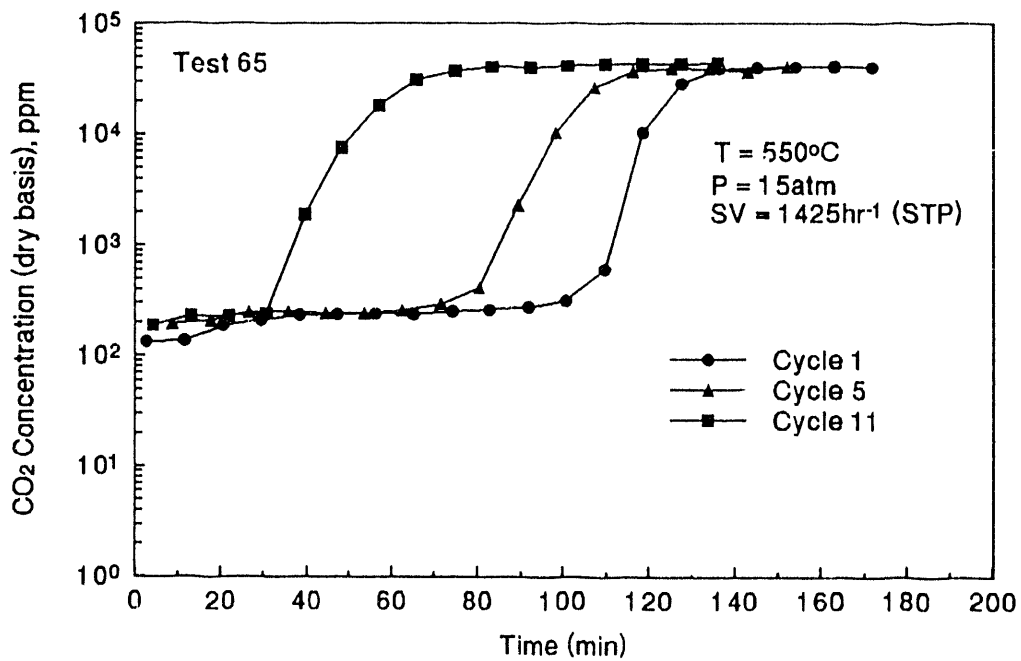in Multicycle Tests

Figure 8. CO_2 Breakthrough Curves in the First, Fifth,
and Eleventh Cycles

cycles. Concentration differences between the first five cycles of the two runs are attributed to random experimental variation. The appearance of decreasing CO concentration toward the end of the 11 cycle run is attributed to increasing difficulty in measuring a prebreakthrough steady-state as the number of cycles increased.

In spite of the fact that prebreakthrough concentrations did not increase in multicycle runs, sorbent deterioration must be considered when evaluating the single-step process. Deterioration manifests itself in a continuing decrease in the duration of the prebreakthrough steady-state and a decrease in the slope of the breakthrough curve. The problem is illustrated in Figure 8 where CO_2 breakthrough curves for the first, fifth, and eleventh cycles are compared.

FUTURE WORK

The project is scheduled to end in October 1994, and we are in the process of finishing the planned sequence of multicycle tests. METC has initiated an internal process analysis study of the single-step process under the direction of Dr. George Lee. This study uses Aspen simulation to construct a process flow sheet, to perform material and energy balance calculations, and to carry out a preliminary economic evaluation.

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Rofer-DePoorter, C., 1984, Untangling the Water Gas Shift from Fischer-Tropsch, in Catalytic Conversions of Synthesis Gas and Alcohols to Chemicals, R.G. Herman, ed., Plenum Press, p. 97.

COMPCOAL™: A Profitable Process for Production of a Stable High-Btu Fuel from Powder River Basin Coal

CONTRACT INFORMATION

Cooperative Agreement	DE-FC21-93MC30126
Contractor	Western Research Institute P. O. Box 3395 Laramie, Wyoming 82071-3395 307-721-2011
Contractor Project Manager	Verne E. Smith
Principal Investigator	Norm W. Merriam
METC Project Manager	Dr. Madhav R. Ghate
Period of Performance	February 2, 1993 through February 1, 1994

BACKGROUND INFORMATION

Western Research Institute (WRI) is developing a process to produce a stable, clean-burning, premium fuel from Powder River Basin (PRB) coal and other low-rank coals. This process is designed to overcome the problems of spontaneous combustion, dust formation, and readsorption of moisture that are experienced with PRB coal and with processed PRB coal. This process, called COMPCOAL™, results in a high-Btu product that is intended for burning in boilers designed for midwestern coals or for blending with other coals.

PRB coal is relatively dusty and subject to self-ignition compared to bituminous coals. Dried (or processed) PRB coal is even more susceptible to spontaneous combustion than the raw coal. Also, PRB coal dried at low temperature typically readsorbs about two-thirds of the moisture removed by drying. This readsorption of moisture releases the heat of adsorption of the water which is a major cause of self-heating of low-rank coals at low temperature. PRB coal, and other low-rank coals, tend to be highly reactive. These reactive coals must be mixed regularly (every week or two) when fresh. However, they become somewhat more stable after they have aged for several weeks.

Low-temperature oxidation reduces the heating value of the coal, makes the coal less able to repel moisture (hydrophobicity), and is known to increase the unburned carbon remaining in the ash. Ingram and Rimstidt (1984) attribute increased moisture in naturally oxidized coals to increase in surface area caused by the physical effects of weathering and an increase in hydrophilic functional groups able to chemisorb water (organic acids are known to attract water to coal particles). Water molecules are generally thought to attach to polar oxygen sites in coal (this varies greatly with different types of coal).

Many efforts have been made to overcome these problems of dust formation and self-heating while keeping the cost of processing within the very competitive limits of the markets for coal. The University of North Dakota Energy Research Center has explored the use of various drying techniques to upgrade low-rank coals (Willson et al. 1987). They found that coals dried at low temperature readsorb moisture after cooling and return to essentially the original equilibrium moisture level. In contrast, they found that the processes using temperatures high enough to alter the structure of the coal particles resulted in reduced readsorption of moisture. They also concluded that the lowered equilibrium moisture levels resulted from the rejection of carbon dioxide by the decarboxylation reactions which occur during high- temperature drying. (The readsorption of moisture by coals dried at temperatures lower than a few hundred degrees Fahrenheit and reduction of equilibrium moisture in coals dried to about 500 to 700°F (260 to 316°C) is consistent with WRI experience, (Boysen et al. 1990).

A drying process was developed for PRB coal during the early 1980s. Initial work was done by Anaconda Minerals Co., later joined by Atlantic Richfield Co., using a 4 ton/hr pilot plant at Tucson, Arizona. The process has been licensed to Kaiser Engineers. The process uses fluidized-bed drying in conventional equipment with a proprietary product treatment step (Skinner et al. 1984). The developers conducted laboratory research to determine methods to avoid low-temperature oxidation of the product. They developed methods using cooling, controlled preoxidation, treatment with carbon dioxide, and spray application of oil or chemical solution.

Koppelman was awarded patents (U.S. Patents 4,728,339 and 5,071,477) for use of "temperatures from 200 to about 1200°F, pressures from 300 up about 3000 psig, and residence times of 1 minute to 1 hour to process organic carbonaceous

materials to effect a desired physical and chemical modification thereof...whereby a substantial reduction in the residual moisture content...to improve physical properties including an increased heating value." The second patent describes the use of steam at high pressure to effect a controlled thermal restructuring, with the upgraded product possessing increased heating values. These patents are the basis for the K-Fuel® process.

Lien (1991) discusses the problems and progress AMAX has experienced with a McNally Pittsburgh dryer at the AMAX Belle Ayr mine. In this process, coal is dried by contact with a hot stream of fluidizing gas. The gas is comprised partly of flue gas from combustion of coal dust with air and partly from recycled gas. The hot drying gas contains less than 5% oxygen. The dried coal, which contains 12 to 13 wt % moisture, enters the cooler at a temperature of 180 to 190°F (82 to 88°C) where it is cooled to about 100°F (38°C) by contact with air. The cooled product is mixed with 2 to 4 gallons of number 6 fuel oil per ton to control product dustiness and help inhibit readsorption of moisture. Lien (1991) discusses the problems of upsets in the process caused by loss of feed and the experience with degradation of particles in the dryer. He also states that a major concern has been the stability of the product.

The Syncoal process is used at a Clean Coal I demonstration plant located at Western Energy Company's Rosebud mine near Colstrip, Montana. In the process, coal is passed through two vibrating fluidized-bed reactors where it is contacted by hot gas to dry the coal and remove carboxyl groups and volatile sulfur compounds. The dried coal is further desulfurized by pneumatically stratifying the product to separate pyrite-rich ash (Western Energy Company 1992).

The Carbondry process (Simmons and Simmons 1992) has been tested at the pilot-plant scale at Carbontec's facility at Bismarck, North

Dakota. The process involves a hot oil first stage drying unit and a flue gas drying unit. The process uses a coating of oil on the surface of particles to protect against readsorption of moisture and spontaneous heating. Published data indicate that the product made from PRB coal using the process contains about 6 to 10 wt % moisture and has a heating value ranging from 11,200 to about 11,700 Btu/lb.

The ENCOAL LFC process is used at a commercial demonstration facility located at Triton Coal Company's Buckskin mine north of Gillette, Wyoming (McPherson 1992). In the process, coal is roasted to drive off moisture, coal liquids, and sulfur compounds. The plant, which was built using an award from Clean Coal III, produces a crude coal liquid and solid process derived fuel.

Numerous mechanical treatments are available for stabilizing coal products by reducing the surface contact with air.These include briquetting, pelletizing, and extruding with or without an added binder. An excellent list of references describing the use of a binder in pelletizing is given in U.S. Patent 4,615,712 (Wen), which describes the production of humic acid from oxidation of coals or leonardite and the use of the humic acid as a binder.

It is relatively easy to develop a process to drive the moisture from PRB coal. It is considerably more challenging to develop a process which can remove the moisture from the coal, alter the coal structure to minimize readsorption of moisture, and prevent oxidation and spontaneous combustion of the finished product. We have dried coal and done partial decarboxylation in our past work (Merriam et al. 1990). Drying minus 8 mesh PRB coal in a fluidized-bed reactor at atmospheric pressure results in all of the moisture being removed when the temperature of the coal in the bed reaches 350°F (177°C) (Figure 1).
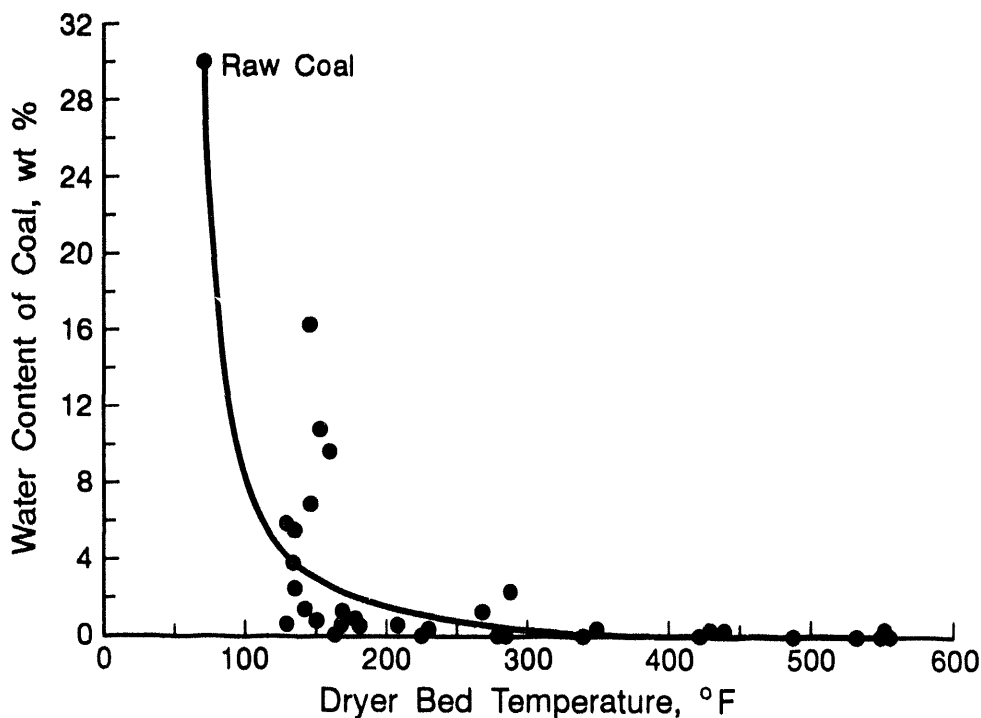

Figure 1. Drying Curve for Minus 8 Mesh PRB Coal Using Various Flow Rates of Fluidizing Gas

Continued heating of the coal as it moves along the cross-flow bed results in the partial decarboxylation, which removes oxygen from the coal in the form of carbon dioxide and carbon monoxide along with some methane (Figure 2). This removal of oxygen increases the heating value of the product and it has been reported to reduce the susceptibility of the coal to spontaneous heating (Tomuro et al. 1985). However, our experience with PRB coal treated in this manner is that the coal is highly reactive and is frequently observed to ignite spontaneously. The coal is most susceptible to self-ignition when it has been freshly processed. Dried coal which has been aged for several weeks (and which has contacted air) is less likely to self-ignite.

Early attempts at WRI to stabilize dried coal (Boysen et al. 1990) were focused upon heating the coal to a slightly higher temperature to reduce the tendency to readsorb moisture (Figure 3). This work, which was done using minus 28 mesh PRB and Usibelli coals in a fluidized-bed reactor, indicates that the equilibrium moisture can be reduced to about 13 wt % by heating the coal to about 700°F (371°C) (Thomas, K.P., personal communication, memorandum dated December 16, 1991). However, it is necessary to heat the coal to about 1100°F (593°C) to reduce the equilibrium moisture to about 10 wt %. The coal tars become mobile in PRB coal at temperatures just above 600°F (316°C). So much loss of liquids would occur if the coal is heated to 1100°F (543°C) in the presence of fluidizing gas.
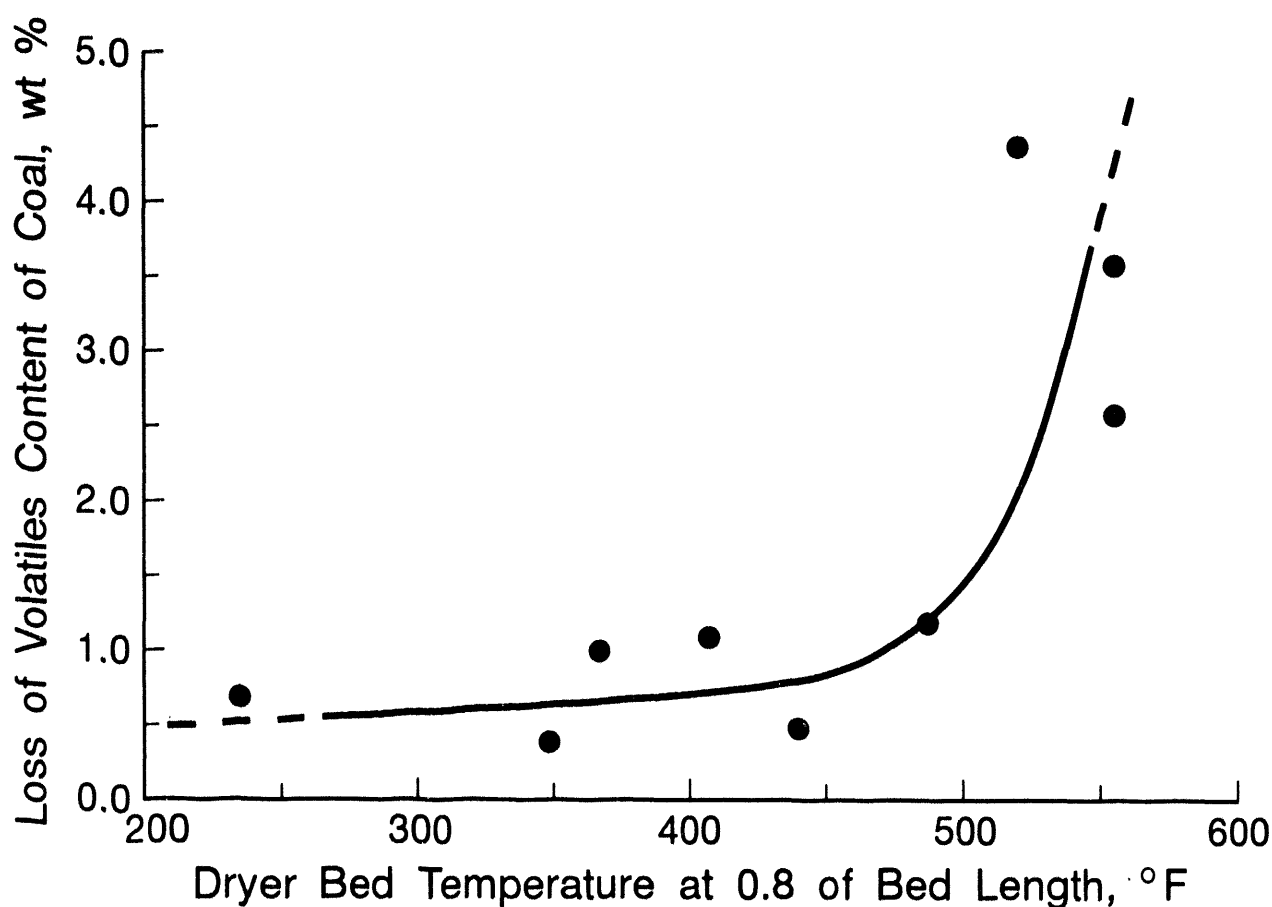

Figure 2. Partial Decarboxylation of Minus 8 Mesh PRB Coal in a Fluidized-Bed Dryer
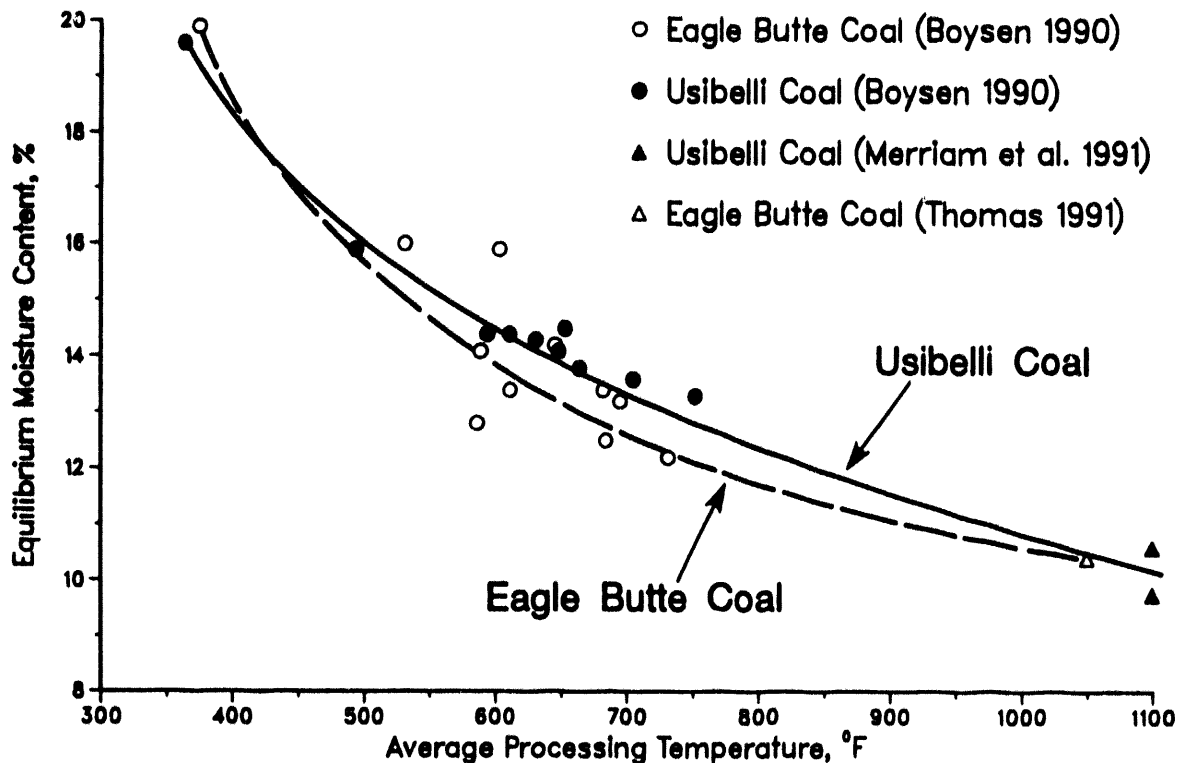
Figure 3. Equilibrium Moisture Content of Coals Subjected to Mild Pyrolysis

We later added a stabilization reactor to the pyrolysis reactor to coat char with the high-boiling fraction of the coal liquids driven from the coal in the pyrolysis reactor (Merriam and Sethi 1992). This work showed that we could further depress the equilibrium moisture to about 8 wt %. (Most of the increase in temperature that starts low-temperature oxidation is caused by the heat of adsorption of water upon the coal particles.)

PROJECT DESCRIPTION

In the COMPCOAL process, sized coal is dried to zero moisture content and additional oxygen is removed from the coal by partial decarboxylation as the coal is contacted by a stream of hot fluidizing gas in the dryer (Figure 4). The hot, dried coal particles flow into the pyrolyzer where they are contacted by a very small flow of air. The oxygen in the air reacts with active sites on the surface of the coal particles causing the temperature of the coal to be raised to about 700°F (371°C) and oxidizing the most reactive sites on the particles. This "instant aging" contributes to the stability of the product while only reducing the heating value of the product by about 50 Btu/lb. Less than 1 scf of air per pound of dried coal is used to avoid removing any of the condensible liquid or vapors from the coal particles. The pyrolyzed coal particles are mixed with fines from the dryer cyclone and dust filter and the resulting mixture at about 600°F (316°C) is fed into a briquettor. Briquettes are cooled to about 250°F (121°C) by contact with a mist of water in a gas-tight mixing conveyor. The cooled briquettes are transferred to a storage bin where they are accumulated for shipment.
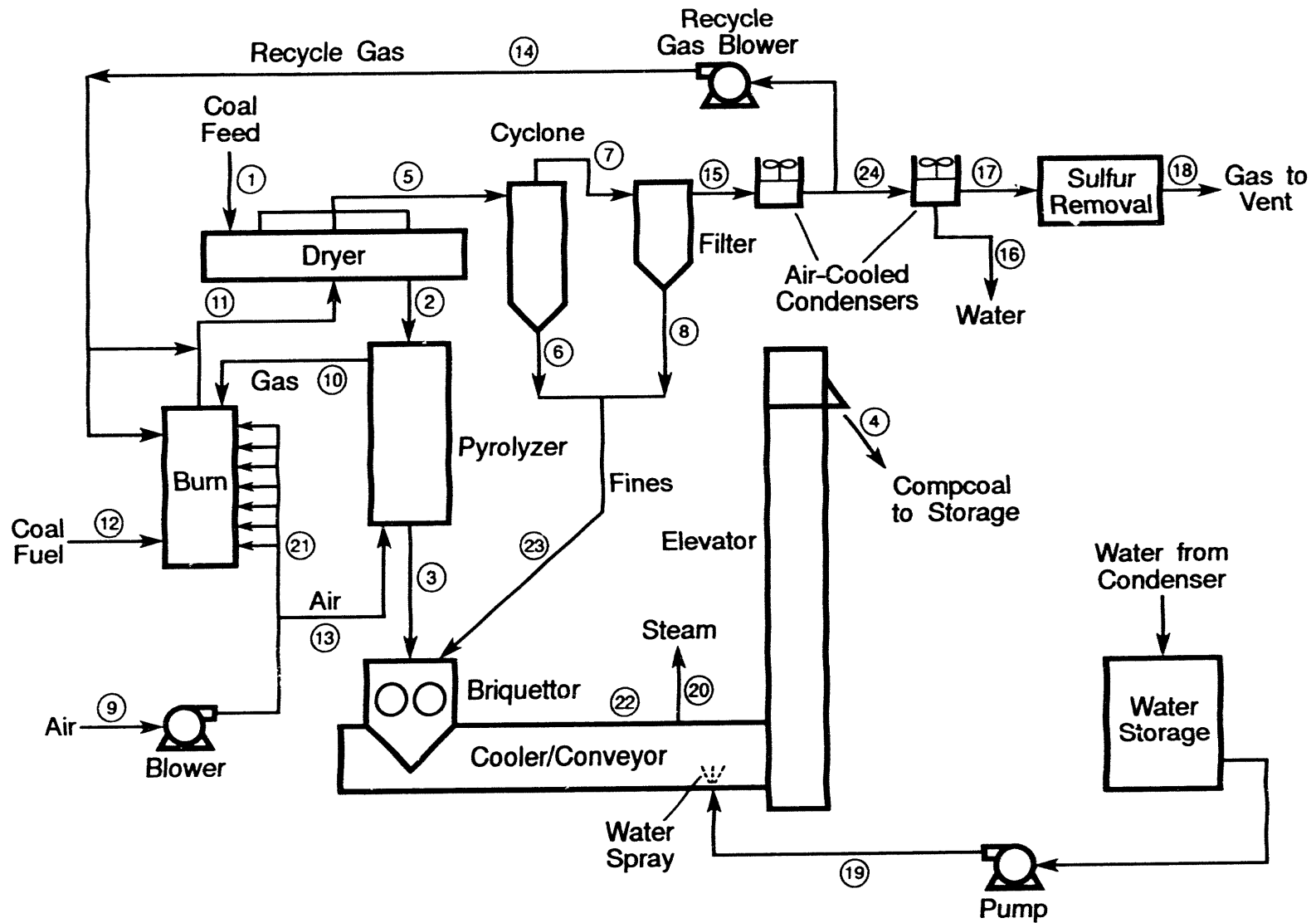
Figure 4. Identification of Stream Flows and Conditions Used to Size Equipment for the COMPCOAL Process

An important feature of the process is the avoidance of pyrolysis in the dryer and use of the onset of pyrolysis in the pyrolyzer to stabilize the particles. In the dryer, where the gas flow rate is high, the coal remains below the temperature at which liquids and vapors are formed. In the pyrolyzer, the temperature is raised to form liquids in the coal particles, but the gas flow is kept low to avoid stripping liquids out of the coal. In this manner, a high flow rate of gas can be used to carry heat into the dryer and subsequently, in the pyrolyzer, the tars in the coal may be melted and refrozen without producing a substantial loss of liquid or vapors from the coal.

A recycle gas stream is used to carry heat into the dryer while limiting the temperature at which fluidizing gas enters the dryer. Heat for drying is produced by burning coal using a low NO_x burner. Vapors from the pyrolyzer are incinerated in the burner. The flue gas is mixed with recycled gas to lower the temperature at which the fluidizing gas enters the dryer. The water is removed from the dryer effluent gas by condensation in air-cooled condensers supplying a nearly dry stream for sulfur removal. The water from the condensers is sprayed onto the hot COMPCOAL briquettes in the cooling conveyor where the water is converted into steam.

The process we describe herein is not yet optimized. For example, if we can tolerate a wet gas stream into the sulfur removal unit, then one of the air-cooled condensers is not needed and only the recycle portion of the dryer effluent gas needs to be cooled.

WRI has experience with the drying portion of the process using minus 8 mesh PRB coal at feed rates of 90 to 150 lb/hr in tests lasting from 24 to 120 hours (Merriam et al. 1990). The pyrolysis (stabilization) portion of the process is presently being developed using a batch, laboratory-scale reactor. We plan next to conduct tests using a continuous-flow, bench-scale reactor.

RESULTS

This section describes work conducted during the early part of 1993 by WRI to develop an effective method to stabilize dried coal.

Self-Heating and Oxidation

We conducted numerous tests to determine how much various treatments affect the self-heating and low-temperature oxidation tendencies of raw and processed PRB coal. Samples were evaluated by contacting the coal or processed coal with oxygen saturated with water vapor at a temperature of 122°F (50°C) in an adiabatic chamber (Figure 5). The test results are evaluated graphically by plotting the temperatures in the samples versus time. The intersection of the slope of the initial heating curve and the slope of the curve after the temperature has started to rise is used as the time to ignition. Tests are continued until the inflection point in the heating curve is defined or until the test has continued for 24 hours. Our experience has shown that an inflection point in the heating curve rarely develops after 24 hours of heating using this method. The results of the self-heating tests (Table 1) are used to compare the effectiveness of different processing conditions.

The tests to study the effects of temperature and oxygen on the self-heating of dried PRB coal were conducted using a small, stirred autoclave which is heated by immersion in a heated bed of fluidized sand (Figure 6). Samples of coal, which had been dried in a fluidized bed to 550°F (288°C) were split into 50-gram aliquots inside a nitrogen filled glove box to avoid contact with air. The aliquots were transferred into the reactor inside the glove box. The autoclave was then assembled and the gas pressure was cycled from 0 to 60 psig three times to flush unwanted gas from the reactor. The autoclave was then lowered into the heated sand for 35 minutes, including about 10 minutes at the desired maximum temperature.

Upon completion of the test the autoclave was removed from the sand bath and immersed in water to rapidly cool the treated coal. Gas samples were obtained for analysis by transfer into evacuated containers. The treated coal was removed from the autoclave in the nitrogen filled glove box and samples were placed in containers under a nitrogen blanket for further analyses.
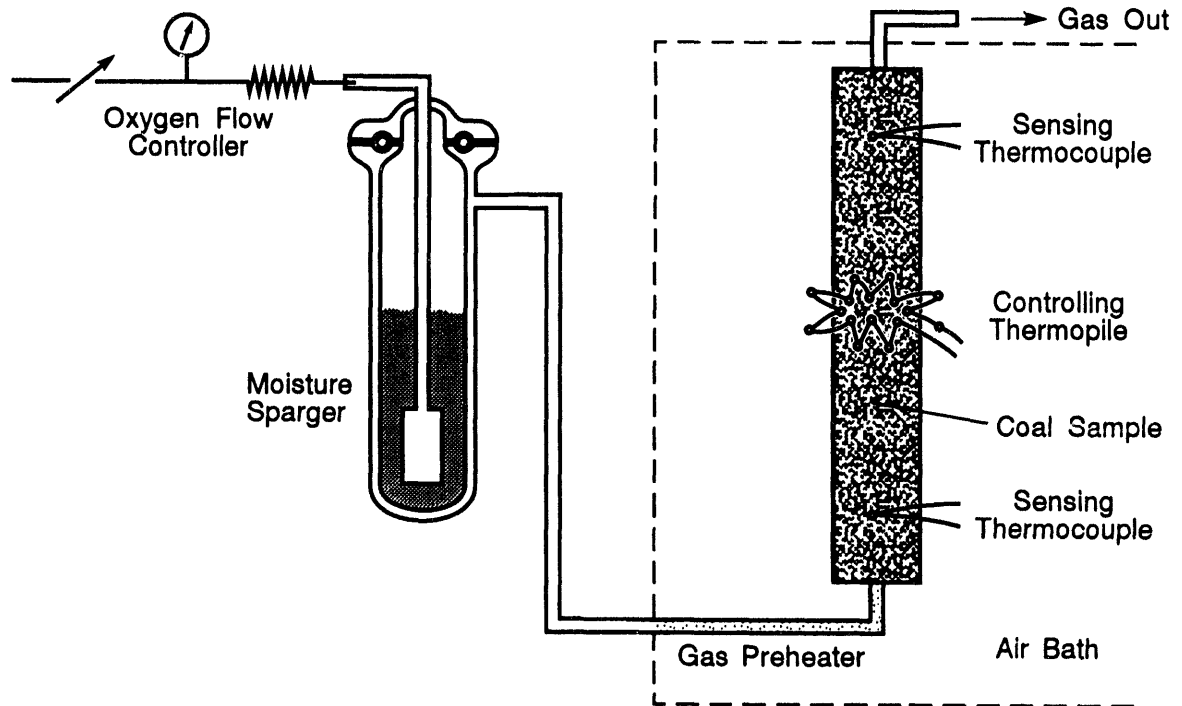

Figure 5. Apparatus Used to Determine the Susceptibility of Coal to Self-Heating and Oxidation
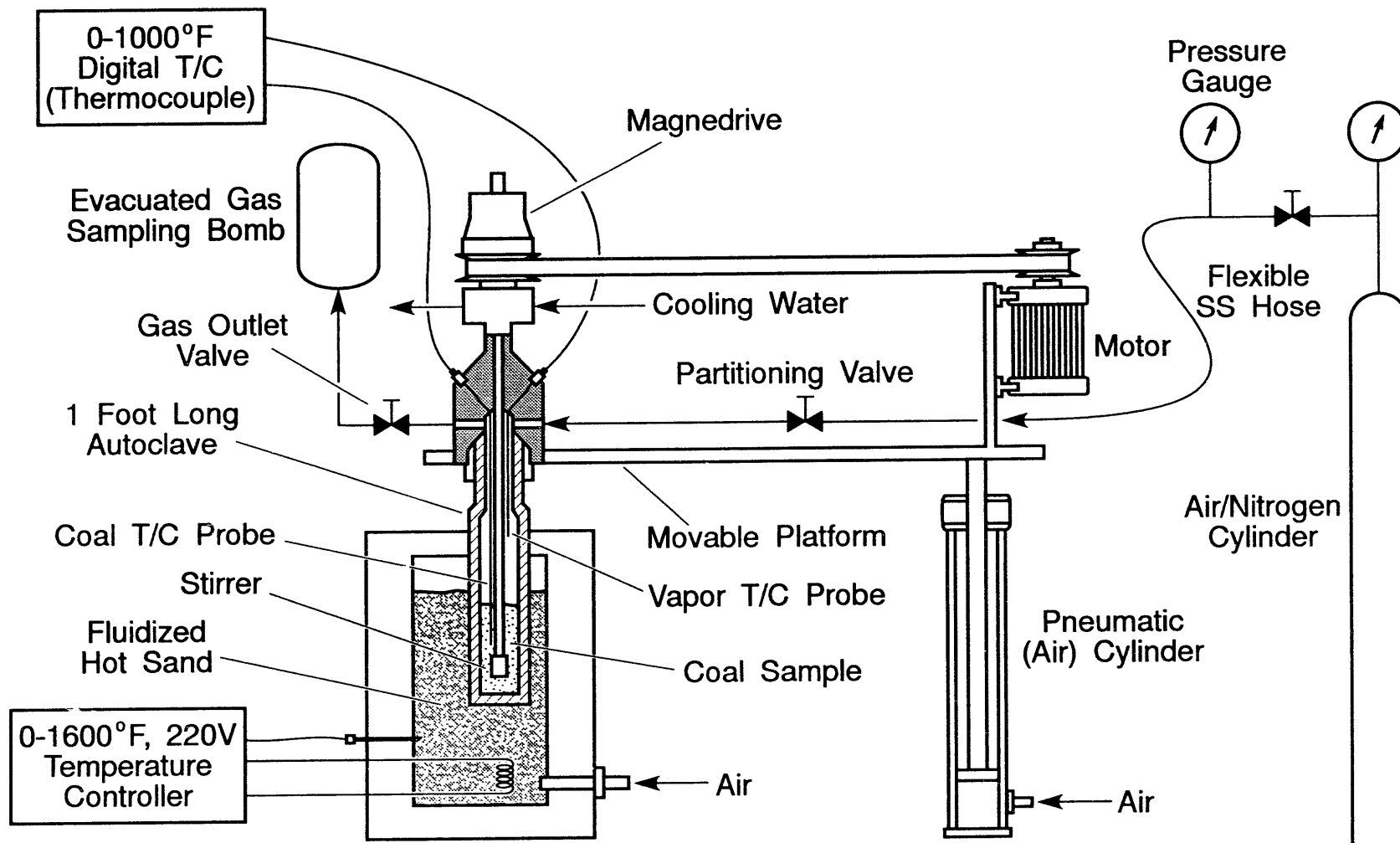
The data in Table 1 show several characteristics and trends which we have used to guide our development of the COMPCOAL process. The section of Table 1 showing "coal dried at various conditions" indicates that coal moved into and out of the drying oven five times (which was incidentally exposed to air) and the sample dried in air both show relatively long ignition times. This pattern of data is an indication that exposure of dried coal to air at 220°F (104°C) results in some resistance to self-heating relative to the coal samples dried in nitrogen.

The samples dried in nitrogen and carbon dioxide show reduced ignition times with increasing temperature over the range of temperatures from 220, 550, 565, and 658°F (104, 288, 296, and 348°C). We therefore conclude that heating the dried coal in inert gas increases the susceptibility to self-heating as the temperature is increased in the range studied. The dried coal which is heated in a small amount of air (at a starting pressure of 0.8 atmospheres at our laboratory) indicates a trend opposite to that shown by heating in nitrogen. The dried coal which is heated in air shows increased resistance to self-heating (longer ignition times) as the temperature is increased from 585 to 703°F (307 to 373°C). The trend when heating in air using a starting pressure of 0.8 atmospheres is not strong, but appears to be real.

Table 1. Time to Ignition for Minus 16 Mesh Raw, Dried, and Processed Coal, hr

	Temperature °F	Duplicate Tests	
Raw Eagle Butte Coal		>24	>24
Coal Dried at Various Conditions			
N_2, 5 times @ 1 hr each	220	17	>24
N_2, 1 time for 5 hr	220	6	8
Air, 1 time for 6 hr	220	24	24
Fluid Bed, CO_2, 5 min (A)	550	4	5
Dried Coal from (A) Heated in N_2			
Batch in Stirred Reactor	565	4	4
Batch in Stirred Reactor	658	2	3
Dried Coal from (A) Heated in 0.8 Atm Air			
Batch in Stirred Reactor	586	4	5
Batch in Stirred Reactor	675	6	5
Batch in Stirred Reactor	692	10	>24
Batch in Stirred Reactor	723	7	8
Dried Coal from (A) Heated in 3.4 Atm Air			
Batch in Stirred Reactor	565	4	6
Batch in Stirred Reactor	675	4	5
Batch in Stirred Reactor	691	14	9
Batch in Stirred Reactor	697	7	8
Batch in Stirred Reactor	708 •	>24	>24
Batch in Stirred Reactor	732	>24	>24

0-1000°F Digital T/C (Thermocouple)

Evacuated Gas Sampling Bomb

Magnedrive

Pressure Gauge

Gas Outlet Valve

Cooling Water

Flexible SS Hose

1 Foot Long Autoclave

Partitioning Valve

Motor

Coal T/C Probe

Movable Platform

Air/Nitrogen Cylinder

Stirrer

Vapor T/C Probe

Fluidized Hot Sand

Coal Sample

Pneumatic (Air) Cylinder

0-1600°F, 220V Temperature Controller

Air

Air

Figure 6. Stirred-Batch Reactor Used to Perform the "Accelerated Aging" Stabilization of Dried PRB Coal

The dried coal which is heated using more air available to react with the coal (a starting air pressure of 3.4 atmospheres) shows a strong and definite trend of increasing resistance to self-heating and oxidation. This last trend is also very sensitive to the temperature of the coal in the stirred bed when the oxygen is reacting with the dried coal (Figure 7). The pattern between the groups (heating in inert gas, heating in 0.8 atmospheres of air, and heating in 3.4 atmospheres of air) also shows a consistent trend of increasing resistance to self-heating and oxidation as the quantity of oxygen available to react with the dried coal is increased.

Tests with air in the stirred, batch reactor with an initial pressure of 3.4 atmospheres show a change in the quantity and composition of gas produced (Figure 8) in the temperature range of the tests. At the lower temperatures a small amount of gas composed of predominantly carbon dioxide, with lesser amounts of carbon monoxide and traces of methane is produced. The volatiles removed at the higher temperatures are mostly noncondensible gases. In the upper part of the temperature range the volume of gas produced is increased greatly and the concentration of the methane and the ethane in the gas increases.
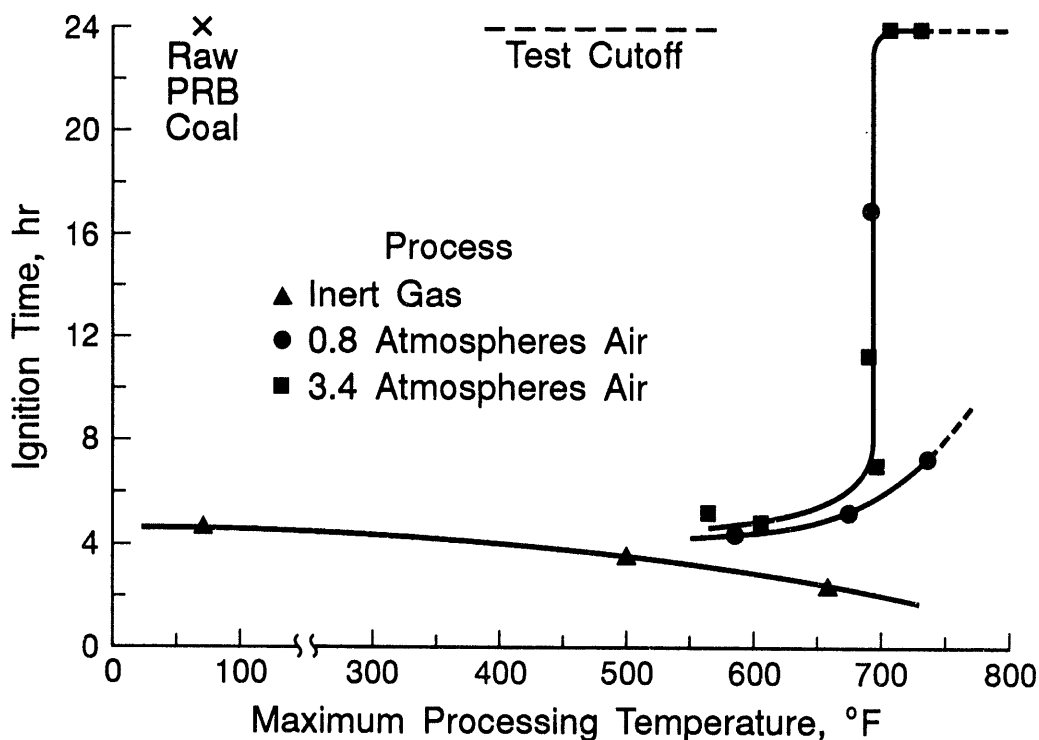

Figure 7. The Effects of Temperature and Oxidation on the Self-Heating Characteristics of Dried PRB Coal

Significantly, no oxygen is detected in the effluent gas, indicating that the oxygen in the air at the start of the tests is completely reacted with the coal. However, the consumption of the oxygen from the air by the coal is more than offset by the

oxygen that is removed from the coal by the processing (Figure 9). The carbon dioxide and carbon monoxide emitted from the coal contain many times as much oxygen as is consumed from the air in the reactor.
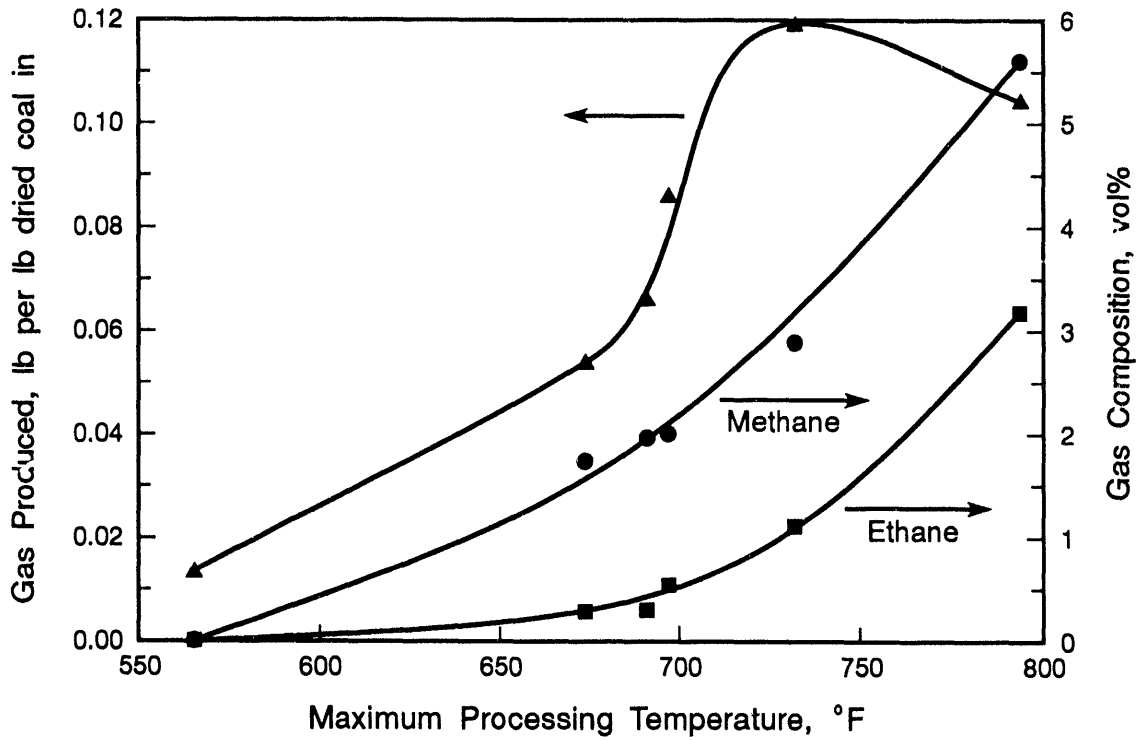
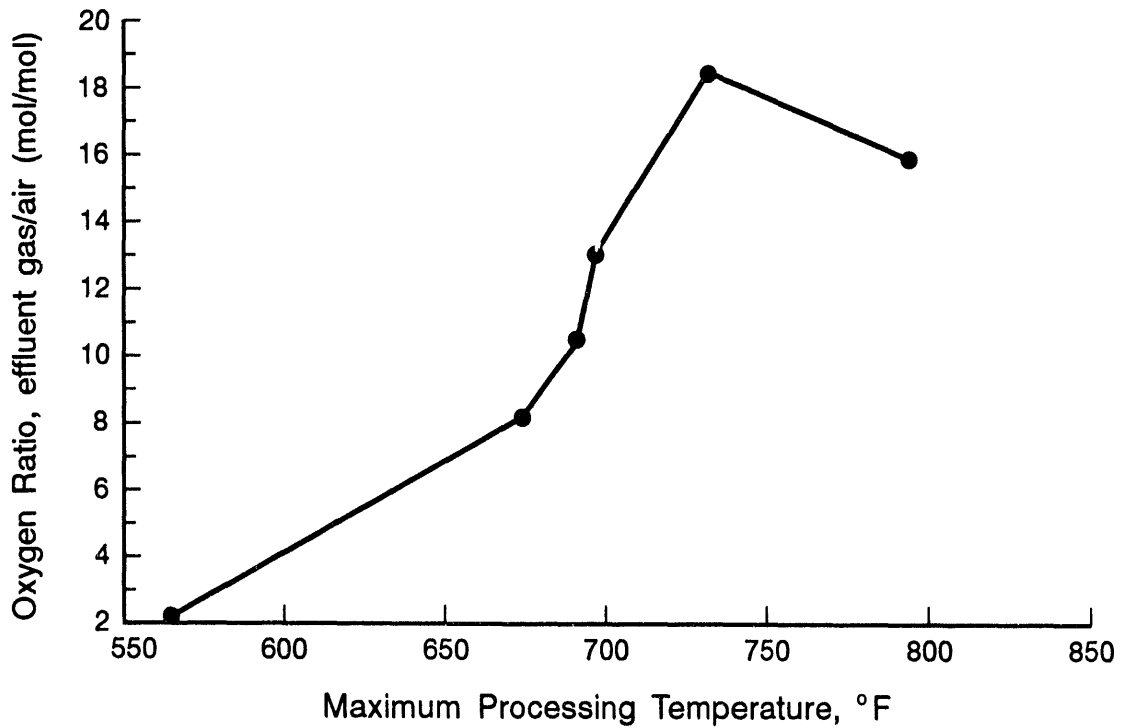**Figure 8.** The Change in Composition of Gas Produced at Temperatures Below and Above the Onset of Stabilization

Figure 9. The Oxygen Released from the Coal Is Many Times the Oxygen Taken Up by the Accelerated Aging

Readsorption of Moisture

The tendency of processed coal to readsorb moisture is an important characteristic which must be considered as a determinant of the quality of any dried or pyrolyzed coal. We have used the test for equilibrium moisture (ASTM D1412) as a measure of the maximum quantity of water which coal and processed coal can adsorb. The test is actually intended to measure the water content which a coal seam can contain. In the test, coal is crushed to minus 28 mesh and soaked in deionized water for 3 hours. The excess water is then removed from the coal by filtration and the coal is held in a sealed container at 98% relative humidity for 48 hours. The water content of the coal is then determined. We think this test may represent conditions which are somewhat more severe than processed coal may typically be exposed to, but we use it because it is an accepted ASTM procedure, and the test does not appear to overstate the readsorption characteristics of the coal by a large amount.

We use equilibrium moisture as an indication of the stability of the products from the various processing conditions we have tested. Low equilibrium moisture is indicative of a stable processed coal.

The results of our tests (Table 2) show that coal dried to 550°F (288°C) is less susceptible to readsorption of moisture than the raw coal. (However, dried coal, when untreated, is more susceptible to oxidation than raw coal.) Forming the dried coal into briquettes reduces the tendency to readsorb moisture even further, while the accelerated aging at 793°F (423°C) reduces the equilibrium moisture still more.

We have not yet tested the obvious combination of briquettes made from coal treated in the "accelerated aging" process. The beads and sand are included to show that materials having no porosity and nonpolar surfaces have an equilibrium moisture content of about zero.

Table 2. Equilibrium Moisture Content of Eagle Butte Coal, Dried Coal, Briquettes, and Treated Coal, wt %

	Duplicate Tests	
Eagle Butte Feed Coal	25	26
Dried in Air, 6 hr, 220°F	22	22
Fluid Bed Dried in CO_2 to 550°F	17	17
Briquettes Made from Dried Coal	13	9
Briquettes-Dried Coal-10% Fines	14	14
Dried Coal Heated in 3.4 Atm Air and 793°F	10	11
One Millimeter Glass Beads	1	1
Ottawa Sand	0	0

Characteristics of Stabilized Coal

The stabilized coal produced by reacting dried PRB coal with air using the stirred batch reactor contains 35 to 40 wt % volatiles and has heating values of 12,000 to 12,700 Btu/lb (Table 3 and Figure 10).

Table 3. Characteristics of the COMPCOAL Product

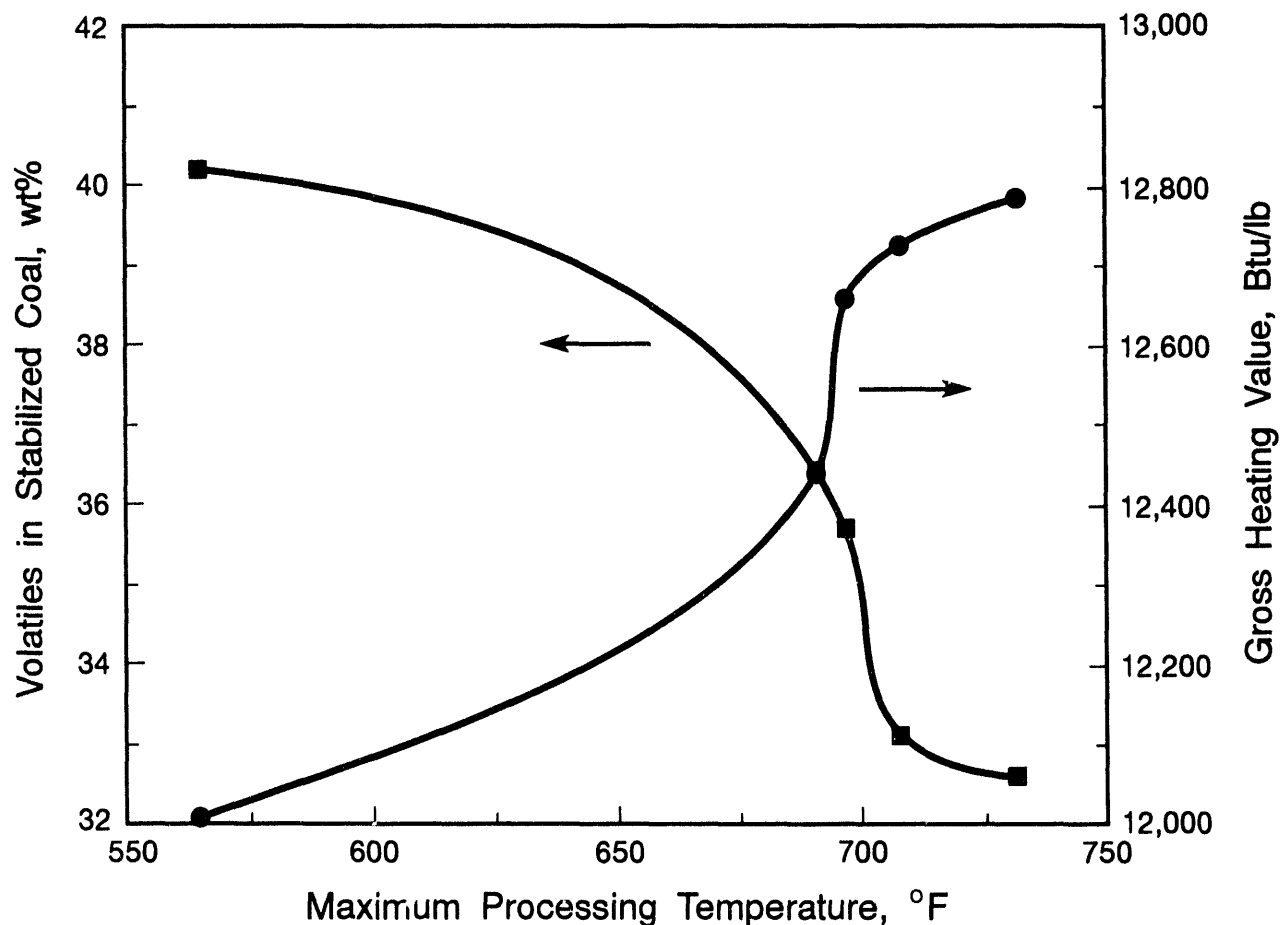| Test	11	10	12	6
Temperature, °F	565	691	697	708
Volatiles, wt %	40.2	36.7	35.4	34.5
Heating Value, Btu/lb	12,009	12,439	12,600	12,725

Figure 10. Volatile Content and Heating Value of the COMPCOAL Product

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FUTURE WORK

Our report, "COMPCOAL™: A PROFITABLE PROCESS FOR PRODUCTION OF A STABLE HIGH-BTU FUEL FROM POWDER RIVER BASIN COAL" (WRI-93-R008) describes the bench-scale tests which we conducted to prove the process concept. We are presently seeking support to continue development of the process.

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Development of Biological Coal
Gasification (MicGAS Process)

CONTRACT INFORMATION

Contract Number	DE-AC21-90MC27226
Contractor	ARCTECH, Inc. 14100 Park Meadow Drive Chantilly, VA 22021 (703) 222-0280
Contract Project Manager	Dr. Daman S. Walia
Principal Investigator	Dr. Kailash C. Srivastava
METC Project Manager	Mr. Wu K. Lan
Period of Performance	May 25, 1990 to March 26, 1996

Schedule and Milestones

FY 93-94 Program Schedule

Tasks/ Subtasks	FY 93	Months in FY 1994										
		O	N	D	J	F	M	A	M	J	J	A	S
1.1 NEPA Compliance	▓ done											
1.2 Work Plan	▓ done											
2. Enhancement of Methane Production	▓	▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓										
2.1 Strain Improvement	▓	▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓										
2.2 Effect of Co-substrates	▓	▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓										
2.3 Nutrient Amendment	▓	▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓										
3. Effect of Substrates on Microbes											▓▓▓▓▓▓▓

OBJECTIVES

The overall goal of the project is to develop an advanced, clean coal biogasification (MicGAS) Process. The objectives of the research during FY 1993-94 were to: (1) enhance kinetics of methane production (biogasification, biomethanation) from Texas lignite (TxL) by the Mic-1 consortium isolated and developed at ARCTECH, (2) increase coal solids loading, (3) optimize medium composition, and (4) reduce retention time.

BACKGROUND INFORMATION

State-of-the-art thermal coal gasification technologies, utilizing the abundant U.S. resource of low-rank coals, operate at high temperatures and pressures and require extensive synthesis gas clean-up for power generation. These technologies require not only high capital and operating costs, but also have to comply with increasingly stringent environmental regulations to control air, water and land pollution. Advanced coal conversion technologies, such as coal gasification are being developed to enhance the conversion efficiency as well as be economical for the abatement of emissions.

Low rank coals are more amenable to microbial conversions at near ambient conditions and thus a biological conversion technology could provide a comparatively economical system for utilizing low rank coals. Consequently, ARCTECH is developing the MicGAS Process as an integrated systems approach. This Process is being developed within ARCTECH's broad vision of the "Coal Biorefinery Concept" to enhance the economic value of coal and to develop additional markets for the usage of low-rank coals . Illustrated in Figure 1, the coal refinery concept involves the biological conversion of low-rank coals to value added

products with minimal disposable waste (Figure 1). This concept envisions that all the three types of matter; namely, gas, liquid and residual solids will generate value added chemicals as co-products. These include:

1. clean burning fuel (biogas), as a gaseous product that will be used for advanced power generation, in fuel cell and in industrial applications,

2. the liquids will provide value added products, such as biopesticides and oxygenated chemicals (short-chain fatty acids and higher alcohols),

3. the residual coal mixed with process liquids will be converted into an organic soil amendment product - ACTOSOL™, that ARCTECH is currently marketing in domestic and international markets.

The Coal Biorefinery Concept is based on anaerobic microbial conversion of a variety of organic substrates to methane according to the schemes presented in Figure 2. Biomethanation can be hydrogenotrophic or aceticlastic depending upon the substrate (Figure 2A and B). In the case of a complex organic substrate, such as coal, the aceticlastic biomethanation is preceded by either acetogenesis only (Figure 2C), acedo-, and acetogenesis (Figure 2D), or a series of reactions involving hydrolysis, fermentation, acedo- and acetogenesis (Figure 2E), or any combination thereof. Initial studies conducted at ARCTECH[1-4] have established that despite the complexity of coal structure and variability among types of coals, low rank coals can be bioconverted to coproducts and methane under near ambient gasification conditions of temperature and pressure by a variety of unique anaerobic microbial consortia (eg. Mic-1, Mic-2, Mic-3, Mic-4)[1]. This

bioconversion has been confirmed by other scientists[cf.5,6-7]. The work at ARCTECH has demonstrated the specificity of a certain anaerobic microbial consortium to a given lignite[1]. For example, while Mic-1 consortium worked more efficiently with TxL, Mic-4 was more effective on Neyveli lignite. ARCTECH's strategy for the direct anaerobic bioconversion of low rank coals is based on the higher availability of coal carbon for the production of CH_4 and volatile fatty acids (VFAs) rather than the formation of CO_2

An independent economic study[8], based on the laboratory scale reactor data on biomethanation of TxL and conceptual process design, demonstrated the process to be commercially attractive. The study recommended, however, that a cheaper organic nitrogen source, reduced retention time, and higher solids loading were essential to make the process profitable. In subsequent studies[2], a low-cost nutrient amendment, Sheftone-T[TM], was substituted for the originally used yeast extract + trypsoy mixture. This substitution brought about a ten fold reduction in the cost of the culture medium. In addition, three fold reduction in residence time was achieved and the solids loading were increased at least 10 fold. Despite these achievements, however, it became apparent that in order to successfully achieve the goals recommended by the Fluor Daniel study[8] further enhancement of methane production and reduction in residence time was necessary for the process to become commercially viable. Thus, a better understanding of the mechanism of coal biomethanation became imperative to the enhancement of the biomethanation of TxL.

It is generally agreed that coal consists of two fractions, a macromolecular and a lower molecular weight fraction. Based on the general empirical formula of a German lignite (brown coal)[9], it is also recognized that the micromolecular fraction of coal is more amenable to microbial attack than the macromolecular one. Furthermore, if the micromolecular fraction can be removed, upon long term incubation of micro-organisms with the macromolecular fraction, the latter fraction will also be bioconverted to added value products. Recent results[4] on the biomethanation studies of chemically and biologically pretreated TxL indicate that microbially pretreated TxL gave higher methane production even at higher solids loadings of 5%. Nevertheless, it also was apparent that at 10% solids loading, the pH of the culture medium dropped drastically which lead to inhibited methane production compared with that observed at lower solids loading of 0.1 and 1.0%.

A close examination of the schematics in Figure 2E indicates that the mechanism of coal biomethanation is similar to the one observed during biomethanation of lignocellulosic substrates. Similar to the constituents (cellulose and hemicellulose) of lignocellulose, TxL is also a water insoluble substrate. Literature indicates that microbial attachment to complex insoluble substrates[10] and biofilm formation[11] play an important role in efficient microbial utilization of such substrates. Consequently, the hypothesis that higher biomethanation of TxL is directly related to better attachment of Mic-1 consortium to TxL particles was tested. In a recent study, Srivastava and Manolov[12] demonstrated that a number of factors, such as sequestrants, solids loading, H^+-donors etc., that enhanced methane production, were also the ones that demonstrated higher attachment of microbial cells to TxL particles. The knowledge thus gained has been used to further address the recommendations of the Fluor Daniel Study[8] for the enhancement of methane production in the MicGAS Process. This is a report of recent laboratory findings to further enhance the MicGAS Process.

PROJECT DESCRIPTION

Biomethanation of coal (MicGAS Process) is a phenomenon carried out by the synergistic metabolism of at least four groups of anaerobic microorganisms that constitute a mixed population or consortium. In this respect, the process can be considered analogous to that of anaerobic digestion of municipal waste. The exception is that unlike municipal waste, coal is a much more complex and difficult substrate to degrade. This project was focussed on studying the factors that can result in consistent enhancement of methane production at higher than hitherto used solids loading (0.1-1.0%) and reduction of retention time in the regime (7-10 days) closer to that of anaerobic municipal digestion.

RESULTS

Biomethanation of coal is a multi-step process requiring distinct simultaneous metabolic activities of different groups of anaerobic bacteria. These steps explained in Figure 2E occur in syntrophy, rather than in a stepwise fashion. A closer analysis of the results described here indicate that biomethanation of TxL at >5% solids loading is feasible through appropriate development of nutrient medium and further adaptation of the microorganisms involved in this process. Further understanding of the inhibitory factors and some biochemical manipulations to overcome those inhibitions will hasten the process considerably.

Products of Biomethanation

Biomethanation of TxL resulted in gaseous, liquid, and solid products. While the major gaseous products were methane and CO_2 the liquid product was composed of a number of volatile fatty acids and some other compounds. The solid phase was composed of residual coal mixed with minimal biomass. A preliminary analysis of the residual solids indicated about 23% ash content in contrast to 16% ash content in the untreated TxL. Furthermore, preliminary results indicate that the carbon in the residue could be converted to humic acids. Humic acids are the major components of ARCTECH's ACTOSOL^R product which is being sold in the domestic and international markets for agricultural applications.

Enhancement of Methane Production

Several parameters were studied to enhance the production of methane from TxL.

Bacterial adaptation. Bacterial enrichment, a technique to manipulate growth and specific substrate conversion was applied to develop the Mic-1 consortium to utilize TxL as the sole source of carbon. The adapted Mic-1 consortium showed an increase in methane production from 10 to 50 mole% reaching up to 71-78 mole % - a 7.5 fold increase during the adaptation period (Table 1). Furthermore, as a result of this adaptation, the methane production from 5% TxL (as compared to 0.01% and 1% initial concentration) started at day 3 and reached a maximum of up to 230 cc/g coal, a 5 fold increase within 11-15 days compared to approximately 2 months time in initial experiments (Task 2). The maximum rate of methane production was observed to occur between 11-14 days (Table 1). These results indicate that the culture has the ability to adapt to the coal carbon and has improved significantly during the adaptation period. This is a positive indication for further improvement in the process research.

Effect of nutrient amendment substitutes. A variety of commercially

available nutrient amendments as the sources of organic nitrogen were tested to replace the expensive yeast extract(YE)/Tryptic soy broth (TSB) mixture used in the original culture medium. Results indicated that Sheftone-T™ enhanced methane production by 15.3% (Figure 3).

Effect of Solids Loading. The Fluor Daniel Study[8] also recommended that TxL solids loading should be increased in order to make the process economical. Consequently, biomethanation of TxL was studied at solids loading of 0.1, 1, 5 and 10 (% w/v). An inverse relationship was observed between increased solids loading and methane production (Figure 4). Furthermore, with the increase in solids loading (from 0.1 to 5%), the methane production was inhibited but remained more or less the same at 5% and 10% solids loading. Nevertheless, significantly higher methane production was observed at 5% solids loading than at 10% when upflow fluidized bed reactors (UFBR) were used (Figure 5).

Effect of initial pH of the culture medium. The relationship between the initial pH of the medium and biomethanation of TxL by the Mic-1 consortium is presented in Figure 6. Data from another study[12] clearly indicate that the reason for the inhibition of methane production at 10% TxL is poor microbial attachment to TxL particles at pHs lower than 7.8 (Figure 6). The data from Figure 6 also demonstrate that the optimum initial pH of the culture medium for biomethanation of TxL at 10% solids loading is 7.8.

Effect of Hydrogen (Proton, H^+) Donors. Having determined the pH that provided better microbial attachment and greater biomethanation of TxL, the next step was to further enhance the kinetics of methane production at the higher solids

loading of >5%. Literature data[13-15] on biomethanogenesis indicate that hydrogen (H) plays an important role. However, lignites typically contain 6-7.5% hydrogen[16] and studies conducted with ^3H demonstrated that the additional H^+ required for the biomethanation of TxL is derived from the water in the culture medium[17].

Nevertheless, further supplementation of H^+ was critical to the enhancement of MicGAS Process. Therefore, the SNTM was supplemented with citrate, formate, lactate, methanol and succinate as potential H^+-donors. Among these, citrate, lactate and succinate enhanced the methane production with the highest effect being that from citrate addition (Figure 7). Analysis of VFAs demonstrated that acetate is in highest concentration until day 7, but sharply drops thereafter (Figure 8). This is the period when the methane production increases (Figure 7). Higher methane production was also observed at 5% solids loading in the presence of 0.5% (v/v) methanol (Figure 9). The biomethanation of TxL in serum vial cultures remained approximately the same despite the addition of 10 mM citrate (Figure 10). Nevertheless, in bench scale upflow fluidized bed bioreactors (UFBR) at 5% TxL solids loading, the methane production was drastically enhanced (Figure 11) reaching up to 78 mol% by day 8 (arrow, Figure 11). VFAs analysis indicated that the methane production is directly related to the amount of acetate produced during the metabolism of Mic-1 consortium (Figure 12) on TxL. These data also indicate that perhaps the accumulation of propionic acid in the culture medium, and the inability of members of Mic-1 consortium to metabolize this VFA into acetate may be one of the limiting steps in the continued bioconversion of TxL to methane. The results presented in Figure 13, however, demonstrate that the reduction in the retention time and higher methane production even at 5% solids loading are
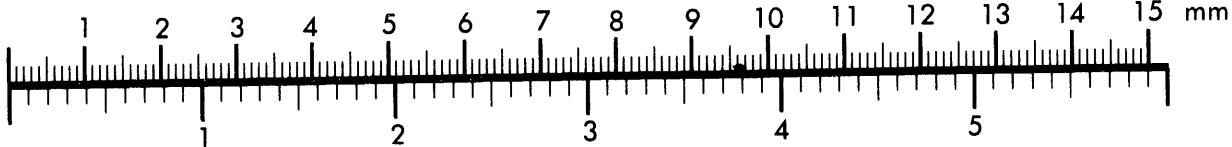
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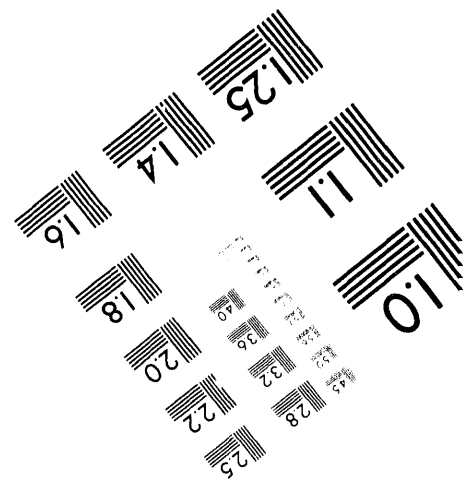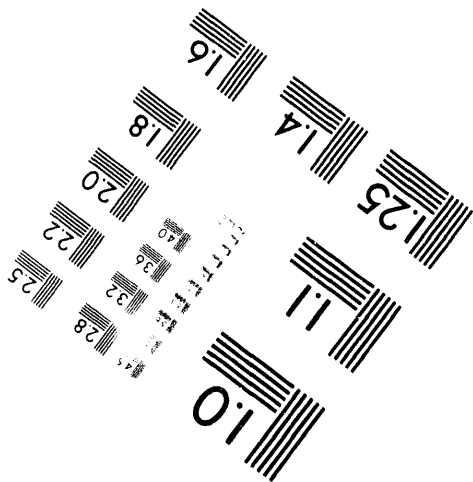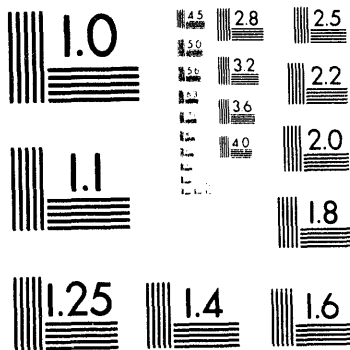**Association for Information and Image Management**

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Centimeter

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 mm
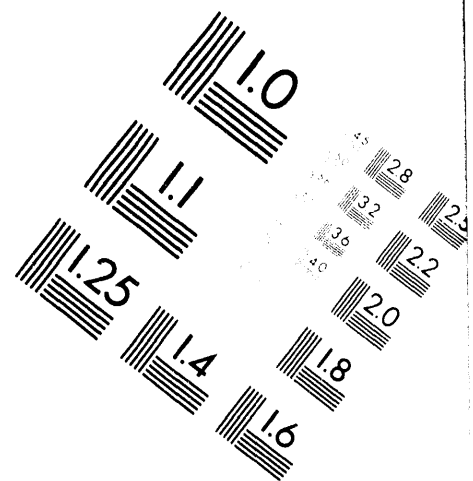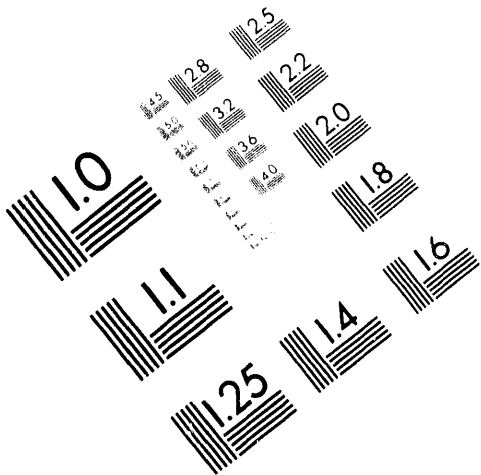
Inches

MANUFACTURED TO AIIM STANDARDS
BY APPLIED IMAGE, INC.

reproducible in another independent experiment using 3 separate bioreactors.

Carbon Balance

An analysis of the carbon in the untreated TxL and the resulting residue, together with the carbon coming from medium components (such as Sheftone-T^{TM}) and the analysis of carbon in the products shows a process efficiency (for methane) of 20% at 5% solids loading (Table 2) and a 91% carbon recovery.

FUTURE WORK

Significant advancements were made in enhancing the biomethanation of low rank coals, especially TxL by the Mic-1 consortium. However, for this process to be viable at a larger scale more research is needed. The programmed research plan includes: (A) further development of a culture medium with reduced cost, (B) identification of inhibitors, such as phenols, that might be produced from TxL as a result of microbial metabolism and in turn inhibit further microbial metabolism, (C) biochemical manipulations to modify the physiological characteristics of the microorganisms, and (D) evaluation of known and novel reactor designs. These tasks shall be accomplished through: (1) metabolic characterization of microorganisms, (2) further biochemical manipulation of the Mic-1 consortium for higher methane yields at (a) increased coal solids loadings, (b) reduced retention times, and (c) studying the effects of medium component on methane production.

ACKNOWLEDGEMENTS

ARCTECH is developing the MicGAS technology jointly with Houston Lighting and

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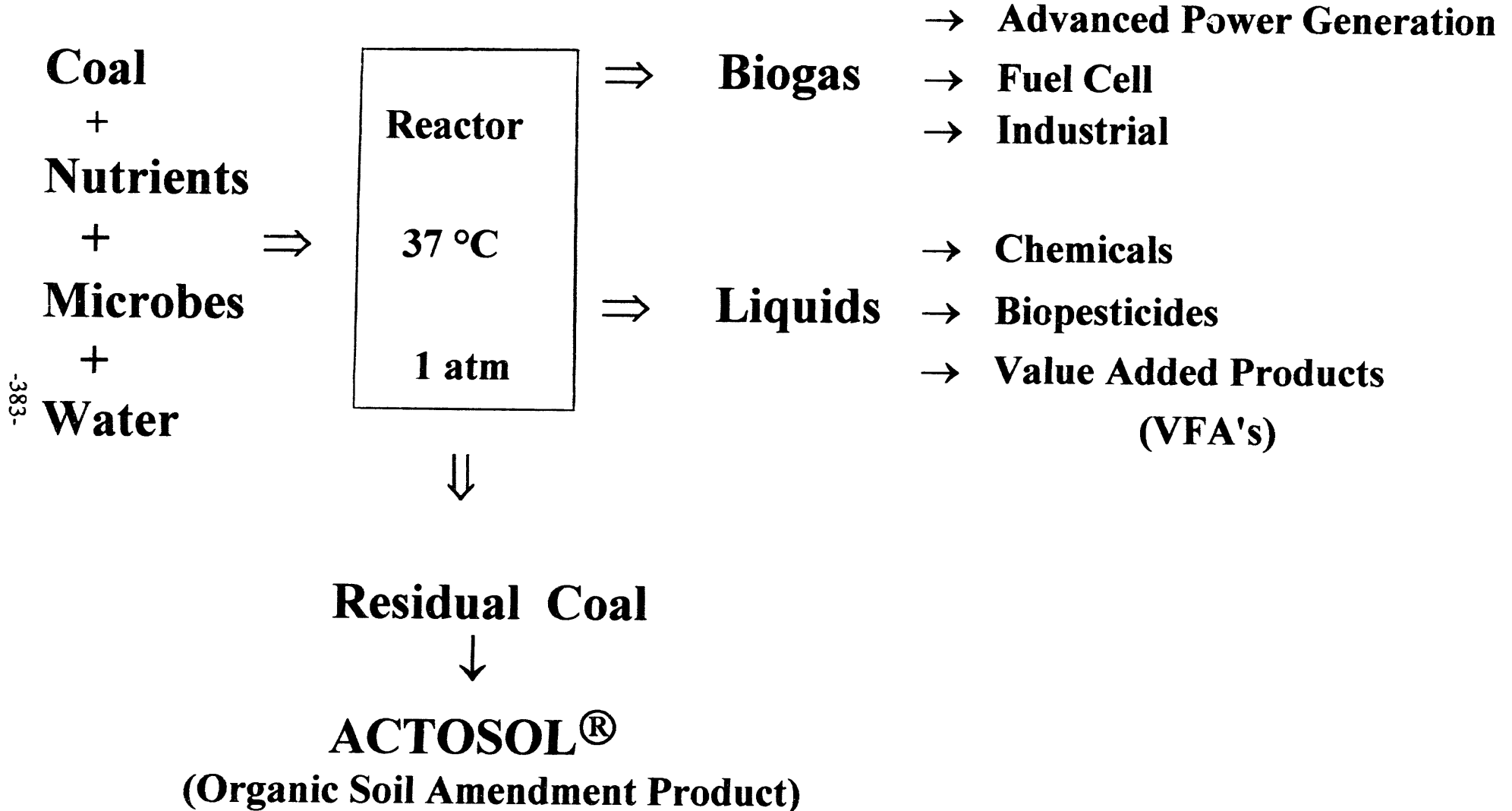
CONCEPT OF COAL BIOREFINERY

Coal
+
Nutrients
+
Microbes
+
Water

$\Rightarrow$

Reactor
37 °C
1 atm

$\Rightarrow$ **Biogas**
- → Advanced Power Generation
- → Fuel Cell
- → Industrial

$\Rightarrow$ **Liquids**
- → Chemicals
- → Biopesticides
- → Value Added Products
  (VFA's)

$\Downarrow$

Residual Coal

↓

ACTOSOL®
(Organic Soil Amendment Product)

Figure 1

CONVERSION OF ORGANIC FEEDSTOCKS TO CH_4
IS A MULTISTEP PROCESS

A. $H_2 + CO_2 \longrightarrow CH_4$ HYDROGENOTROPHIC

B. ACETATE $\longrightarrow$ $CH_4 + CO_2$ ACETOCLASTIC

ACETOGENESIS H_2 METHANOGENESIS

C. ETHANOL $\longrightarrow$ ACETATE $\longrightarrow$ $CH_4 + CO_2$

ACETOGENESIS

D. BUTYRATE $\longrightarrow$ ACETATE   METHANOGENESIS
ETHANOL
PROPIONATE $\longrightarrow$ H_2 $\longrightarrow$ $CH_4 + CO_2$

HYDROLYSIS
DEAROMITIZATION   ACEDOGENESIS   ACETOGENESIS
FERMENTATION

E. MULTI-AROMATIC RING COMPLEX ORGANICS $\longrightarrow$ COMPLEX ORGANICS $\longrightarrow$ BUTYRATE $\longrightarrow$ ACETATE   METHANOGENESIS
ETHANOL
PROPIONATE $\longrightarrow$ H_2 $\longrightarrow$ $CH_4 + CO_2$

Figure 2

EFFECT OF NITROGEN SOURCE ON BIOMETHANATION OF TEXAS LIGNITE (1% w/v) BY Mic-1 CONSORTIUM
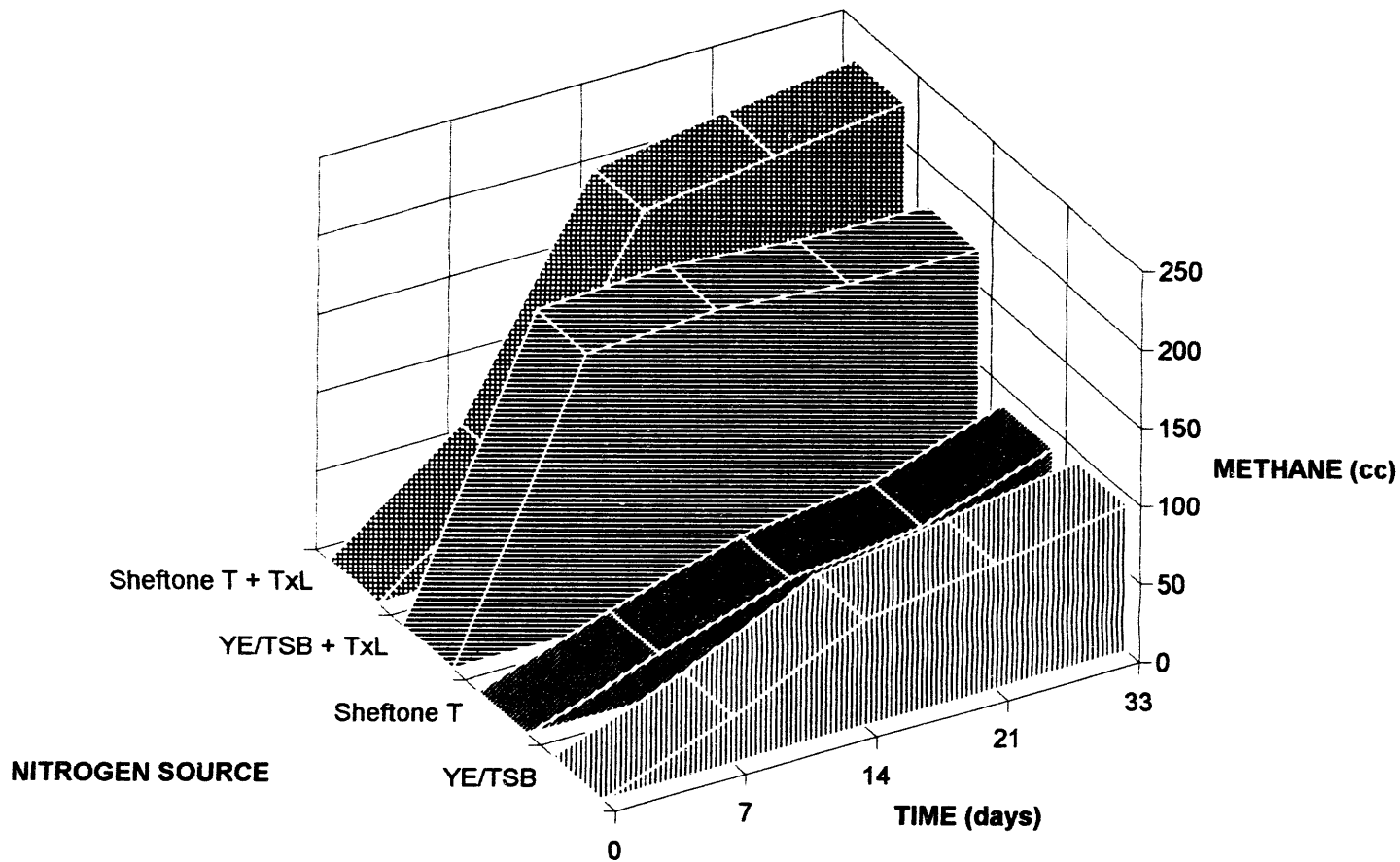
Figure 3

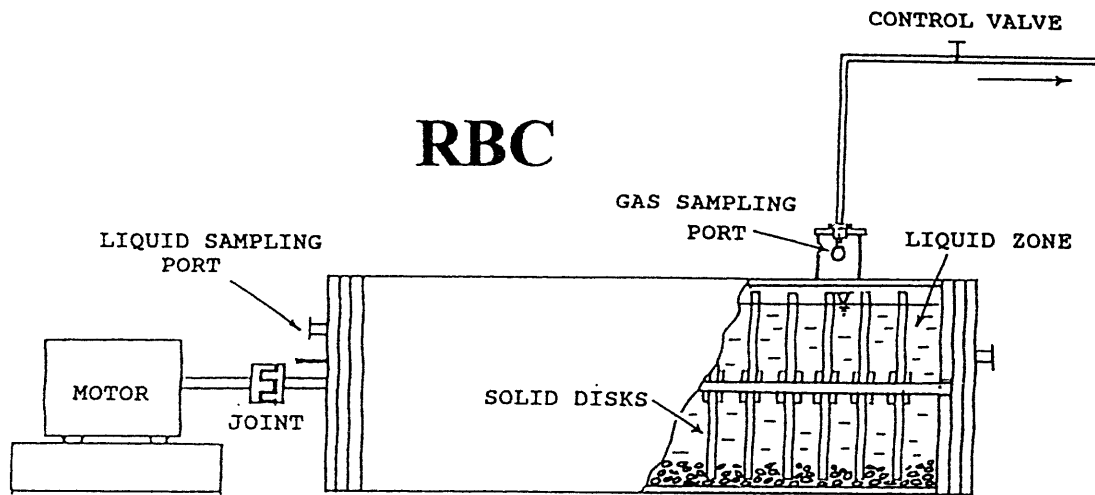# EFFECT OF DIFFERENT SOLIDS LOADING ON BIOMETHANATION OF TEXAS LIGNITE BY Mic-1 CONSORTIUM
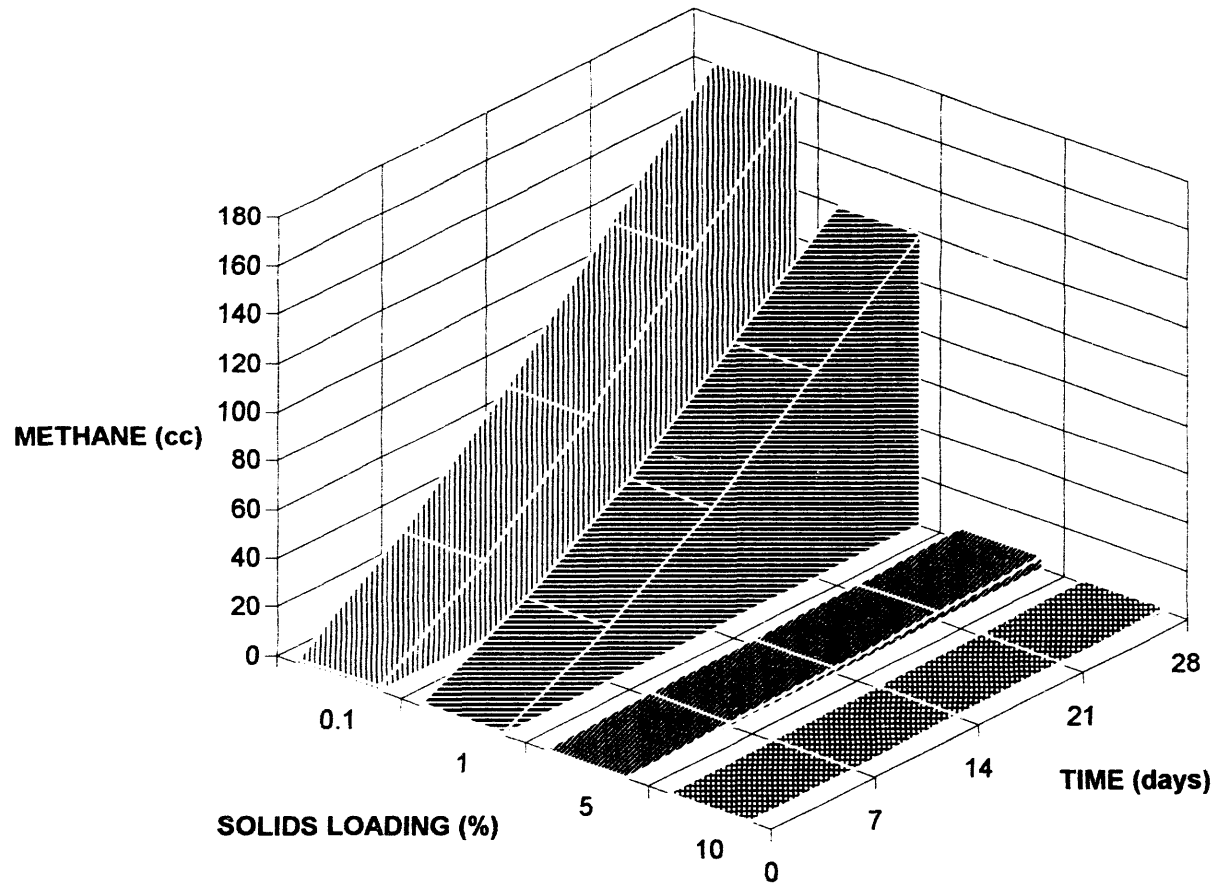
Figure 4

Bench Scale Bioreactors
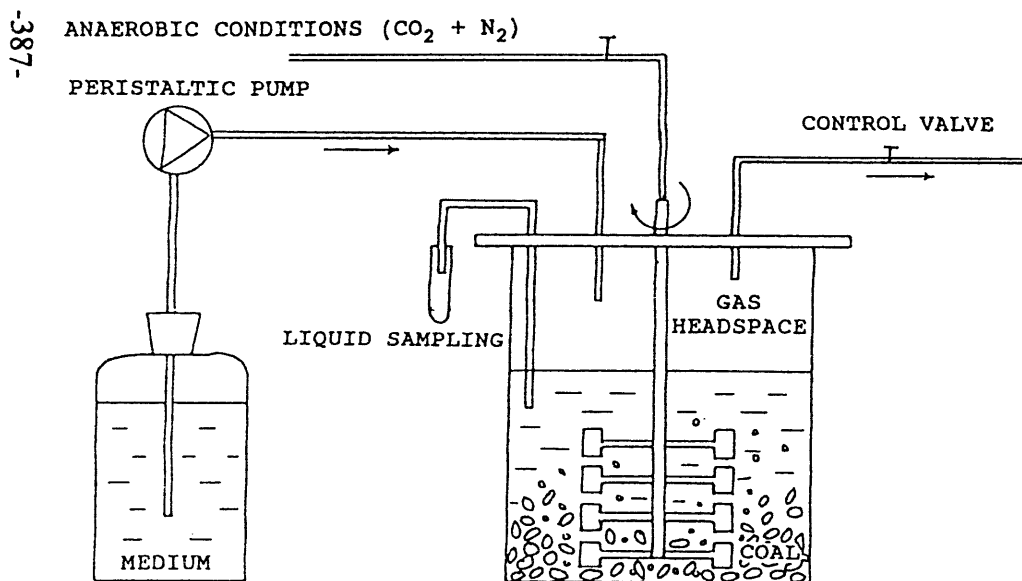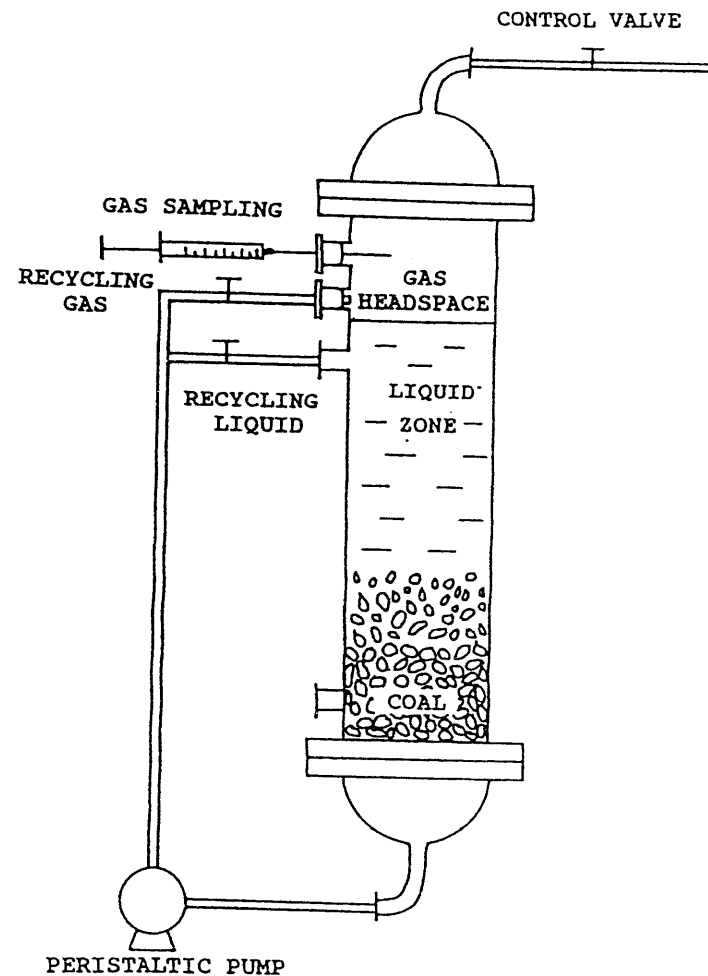
Figure 5

EFFECT OF DIFFERENT INITIAL pH OF THE MEDIUM ON BIOMETHANATION OF TEXAS LIGNITE (10% w/v) BY Mic-1 CONSORTIUM

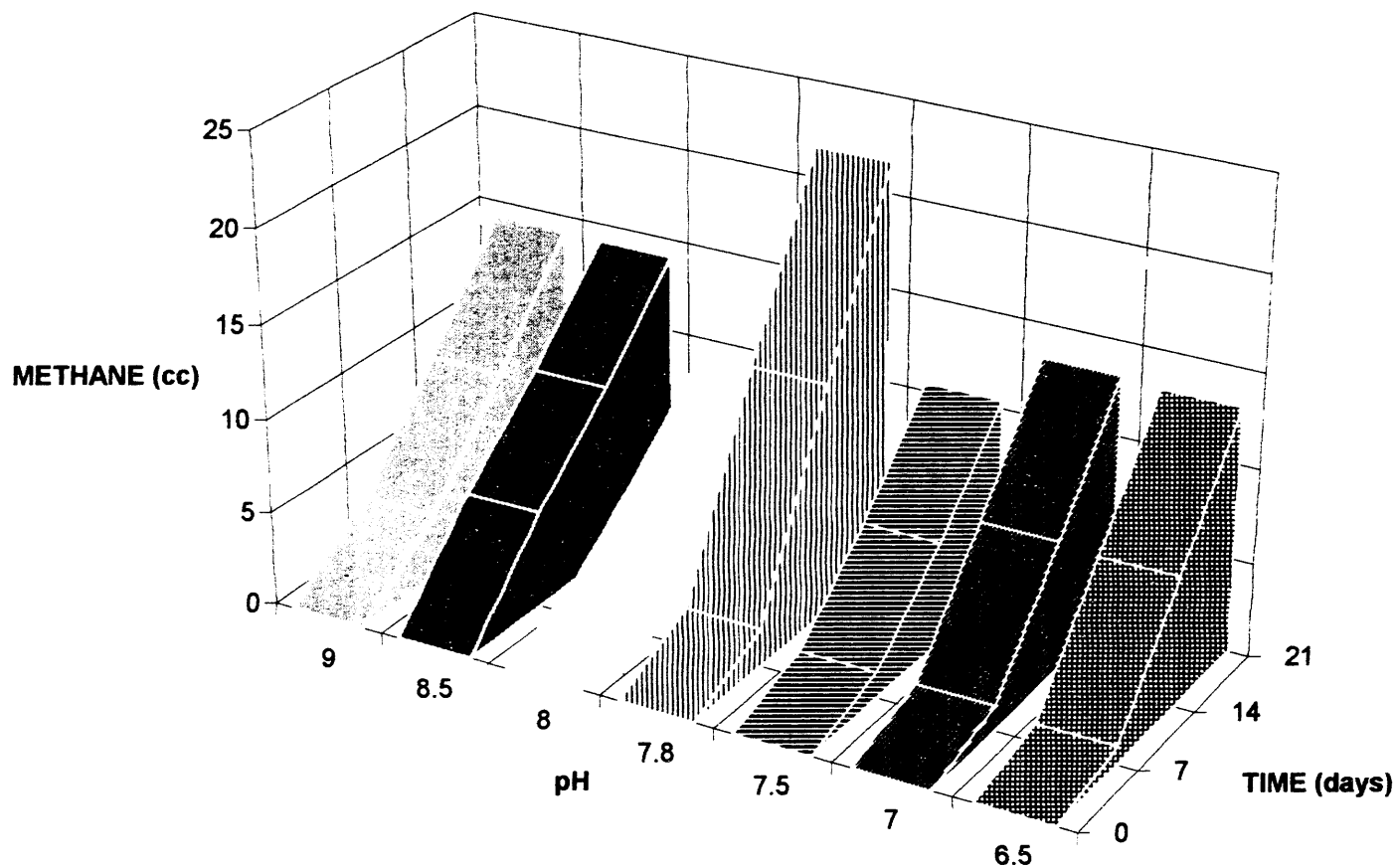Figure 6

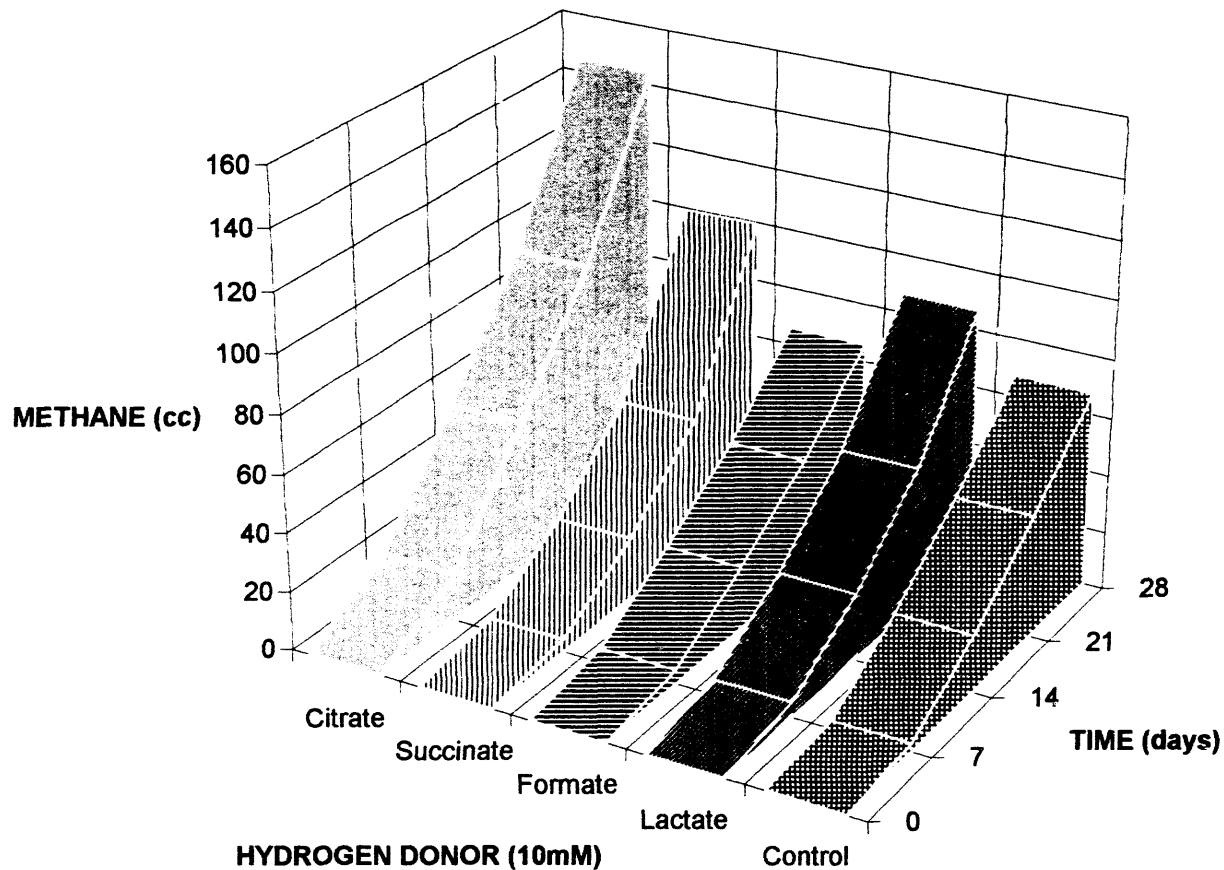# EFFECT OF HYDROGEN DONORS (10 mM) ON BIOMETHANATION OF TEXAS LIGNITE (1% w/v) BY Mic-1 CONSORTIUM

Figure 7

EFFECT OF HYDROGEN DONORS (CITRATE, 10 mM) ON BIOMETHANATION OF TEXAS LIGNITE (1% w/v) BY Mic-1 CONSORTIUM - VFA's CONCENTRATION
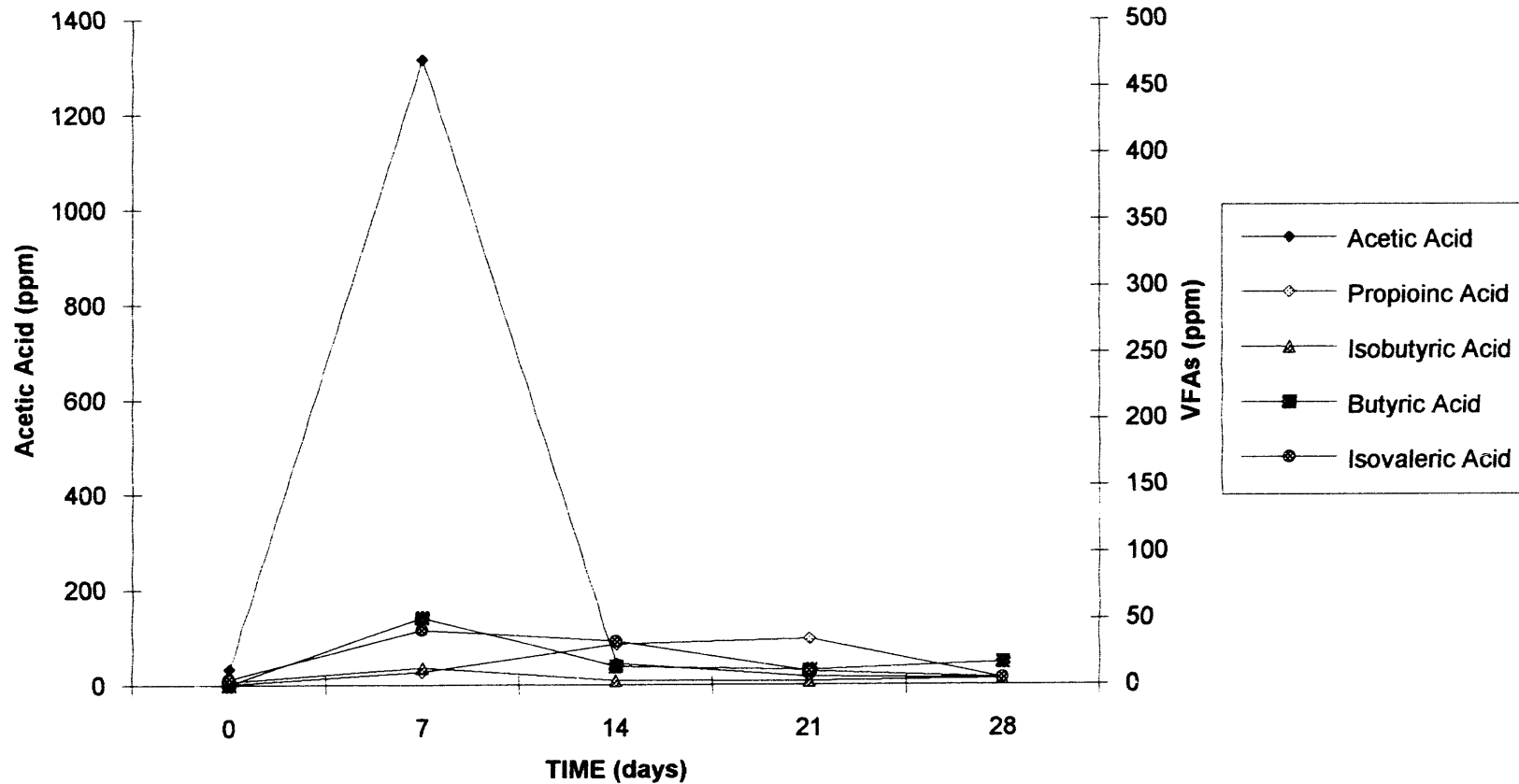
Figure 8

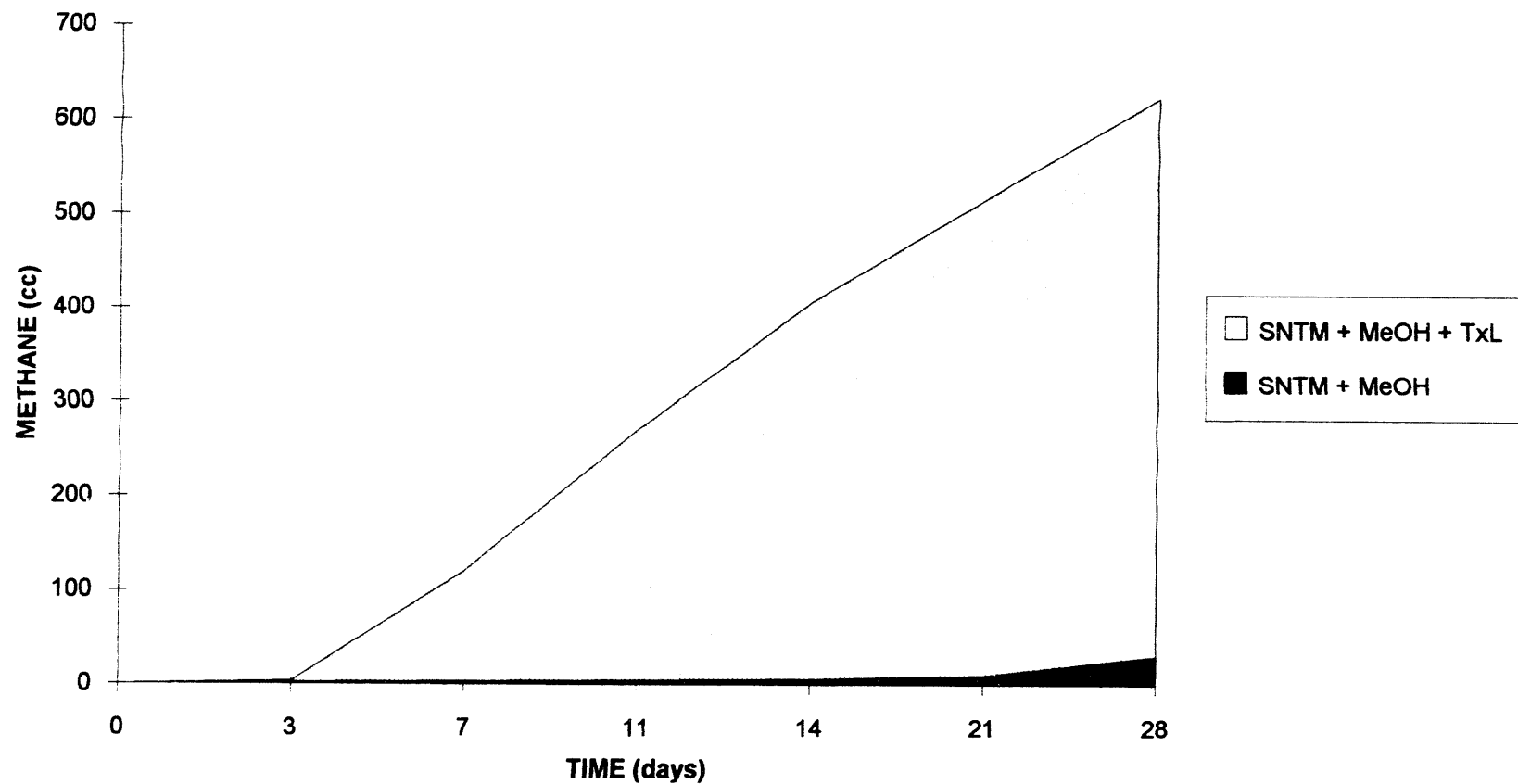# EFFECT OF HYDROGEN DONORS ON BIOMETHANATION OF TEXAS LIGNITE (5% w/v) BY Mic-1 CONSORTIUM

Figure 9

EFFECT OF HYDROGEN DONORS ON BIOMETHANATION OF TEXAS LIGNITE (5% w/v)
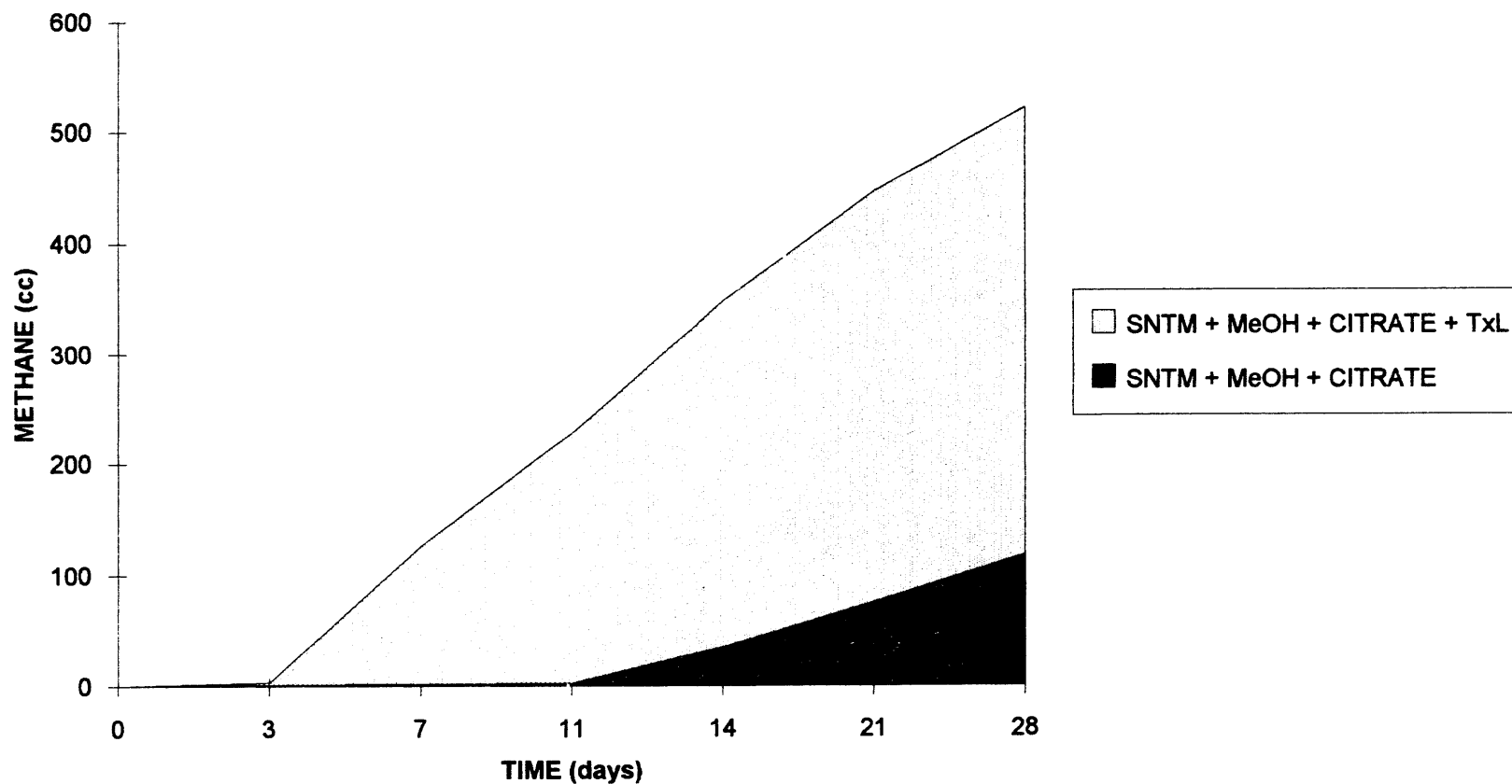
Figure 10

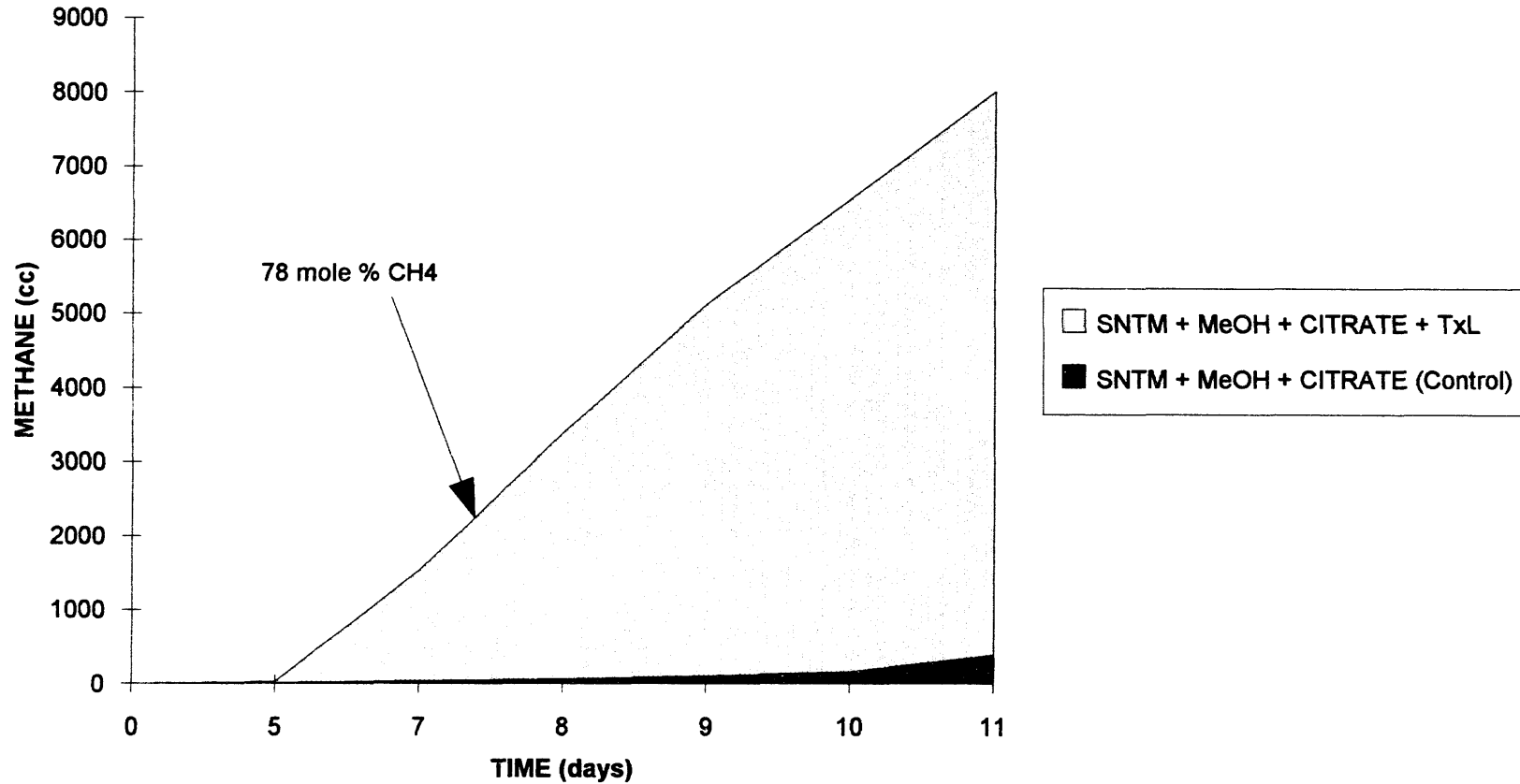# BIOMETHANATION OF TEXAS LIGNITE IS SIGNIFICANTLY ENHANCED IN AN UPFLOW BIOREACTOR

Figure 11

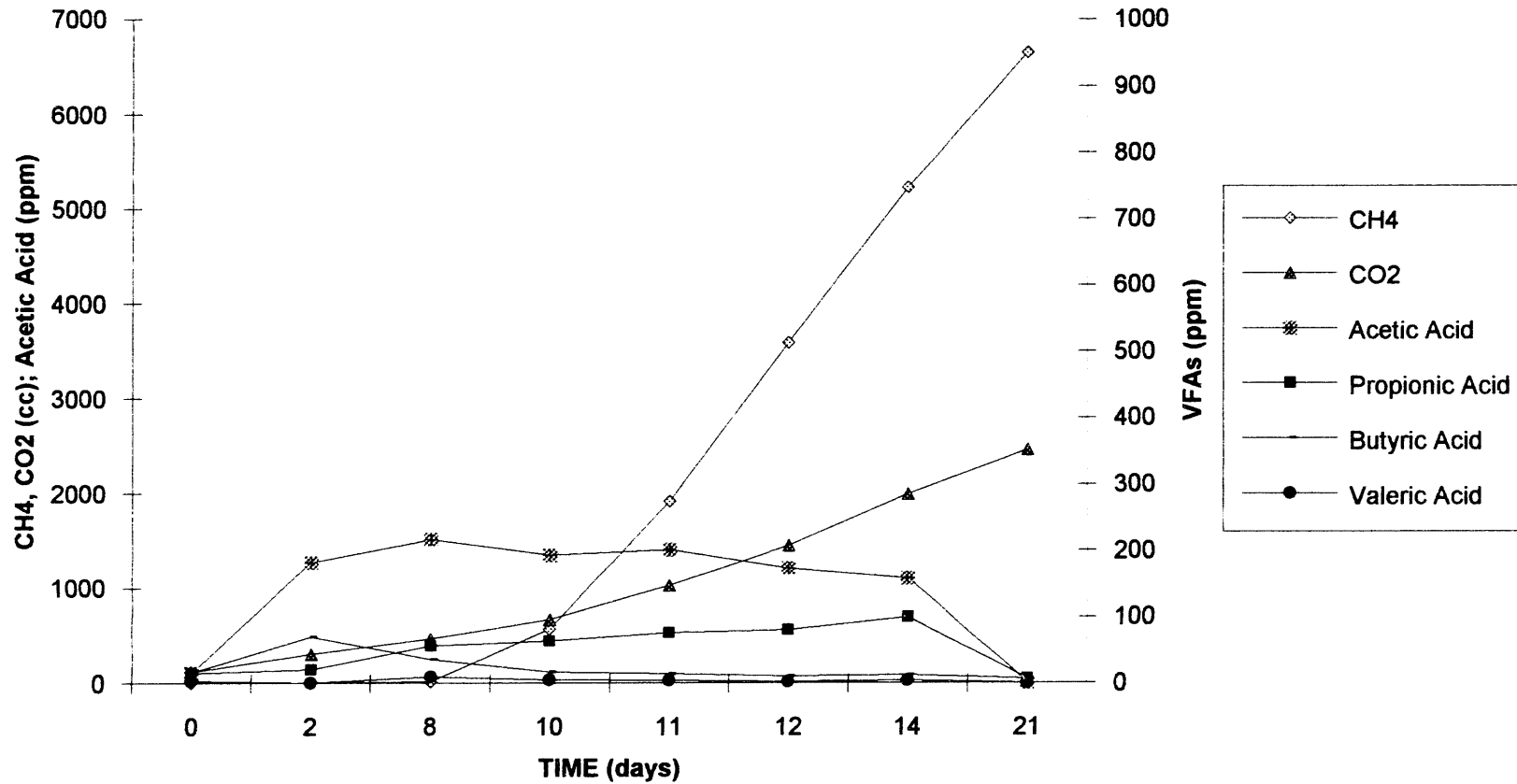# BIOGASIFICATION OF TEXAS LIGNITE IS DIRECTLY RELATED TO ACETATE CONCENTRATION

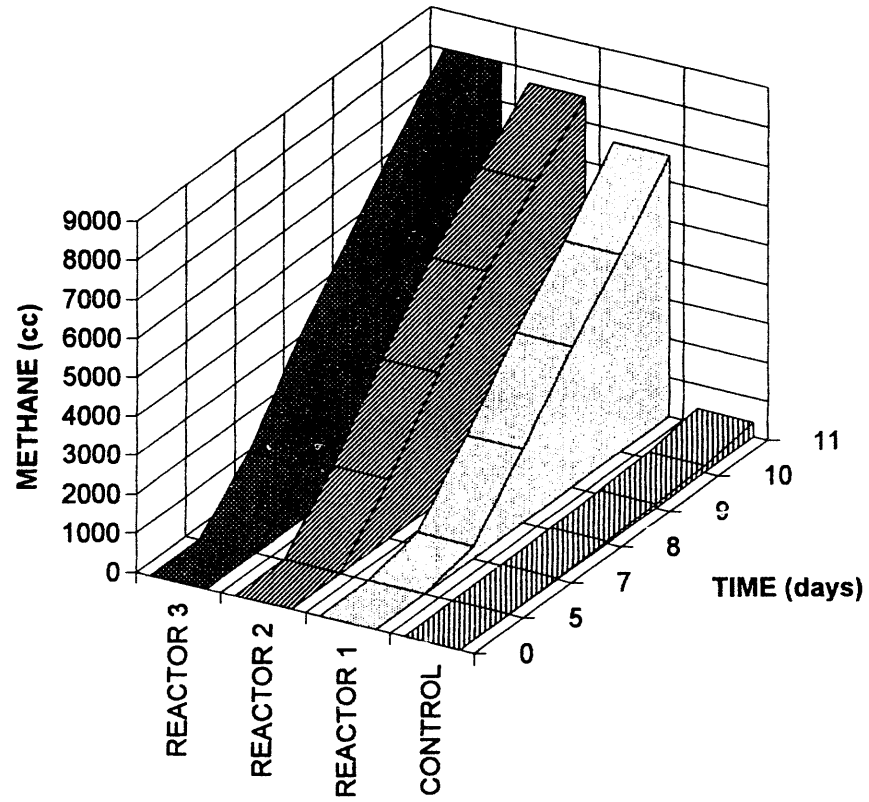Figure 12

BIOMETHANATION OF TEXAS LIGNITE IS REPRODUCIBLE

Figure 13

Table 1

	METHANE PRODUCTION BY MIC-1 CONSORTIUM BEFORE AND AFTER ADAPTATION TO HIGHER COAL SOLIDS LOADINGS				
PARAMETERS	**ADAPTATION**				**FOLD INCREASE**
	BEFORE	**AFTER**			
COAL SOLIDS (%)	0.01	0.1 - 1	5	5*	500
CH_4 (MOLE %)	10	40 - 50	48 - 52	71 - 78	7.5
CH_4 (CC/G COAL)	40	96 - 193	134 - 198	200 - 230	5
TIME (DAYS)	60	21 - 28	7 - 14	7 - 8	8**

* BIOREACTOR STUDIES   ** REDUCTION IN RESIDENCE TIME

Table 2

CARBON BALANCE

CARBON IN	(%)	CARBON OUT	(%)
COAL	90	Biogas $CH_4 - 20$ $CO_2 - 4$	24
Media Components	10	Chemicals (VFAs)	2
		Humic Acid (ACTOSOL®)	74
TOTAL	100		100

P9   **Simultaneous Removal of H$_2$S and NH$_3$ in**
Coal Gasification Processes

CONTRACT INFORMATION

Contact Number   DE-FG22-93MT93005

Contractor   Hampton University
                        Department of engineering
                        Hampton, VA 23668
                        (804) 727-5288

Contractor Project Manager K. Jothimurugesan

Principal Investigators   K. Jothimurugesan
                            Adeyinka A. Adeyiga
                            Santosh K. Gangwal (RTI)

DOE Project Officer   Kamalendu Das

Period of Performance   September 2, 1993 to September 1, 1996

Schedule and Milestones

FY 1993 Program Schedule

	S	O	N	D	J	F	M	A	M	J	J	A
Test Plan	___											
Fabrication		_____										
Sorbent–Catalyst Preparation				_____								
Sorbent–Catalyst Screening										_____		

OBJECTIVES

The objective of this study is to develop advanced high–temperature coal gas desulfurization mixed–metal oxide sorbents with stable ammonia decomposition materials at 550–800° C (1022–1472° F). The specific objectives of the project are to: (i) Develop a combined sorbent–catalyst materials shall be capable of removing hydrogen sulfide to less than 20 ppmv and ammonia by at least 90 percent. (ii) Carry out comparative fixed–bed studies of absorption and regeneration with various formulations of sorbent–catalyst systems and select most promising sorbent–catalyst type. (iii) Conduct long–term (at least 30 cycles) durability and chemical reactivity in the fixed–bed with the superior sorbent–catalyst.

BACKGROUND INFORMATION

Nitrogen (N_2) occurs in coal in the form of tightly bound organic ring compounds, typically at levels of 1 to 2 wt% on a dry-ash-free basis. During, coal gasification, this fuel-bound nitrogen is released principally as ammonia and nitrogen, with smaller levels of HCN. The formation of NH_3 in a coal gasification processes is a function of the fuel gas composition and the gasifier operating conditions. During the use of coal gas to generate electricity in gas-fired turbines, fuel bound (N_2) is converted to nitrogen oxides (NO_x), which are difficult to remove and are highly undesirable as atmospheric pollutants. Recent results indicate that while the efficiency of molten carbonate fuel cell (MCFC) anodes is not effected by exposure to NH_3, NO_x is generated during combustion of the anode exhaust gas. Thus, NH_3 must be removed from the coal gas before it is used in IGCC or MCFC applications.

The product stream from a high temperature, oxygen-blown gasifier, such as Texaco, contains about 2000 ppmv of NH_3, where higher concentrations (about 5000 ppmv) occur when the gasification is conducted at lower temperatures, such as in the Lurgi or GE air-blown gasifier. A range of 1500 to 3000 ppmv is considered for this study.

Removal of H_2S using zinc-based sorbents, particularly zinc titanate, to < 20 ppmv levels has been well established (Lew et al., 1989; Jothimurugesan and Harrison, 1990; Woods et al., 1990; Gupta and Gangwal, 1993). Previous literature study indicated that catalyst have high activities for NH_3 decomposition (Krishnan et al., 1988). If desulfurization sorbents such as zinc titanate could be used along with the NH_3 decomposition catalysts to decompose

ammonia present in hot coal gas, then the number of unit processes necessary to clean hot coal gas could be reduced by one.

The objective of this project is to develop successful combination of an NH_3 decomposition catalyst with the mixed-metal oxide sorbent so that the sorbent-catalyst activity remains stable for NH_3 decomposition in addition to H_2S removal under cyclic sulfidation-regeneration conditions in the temperature range of 550-800° C (1022-1472° F) and pressures up to 20 atm.

PROJECT DESCRIPTION

Sorbent-Catalyst Preparation

The mixed metal-oxide sorbent (Zinc Titanate) was prepared by the coprecipitation method in order to generate as high a surface area as possible. In order to investigate the effect of calcination temperature, three zinc titanates were calcined at 600, 700 and 800°C. The surface area variations with temperature is shown in Figure 1. As the calcination temperature increases from 600 to 800° C , the surface area decreases from 89 to 19 m^2/g. The ammonia decomposition catalyst was added to zinc-titanium oxide by impregnation technique. After the impregnation, the material was dried at 110° C(230° F) , followed by calcination in air at 800° C (1472° F) for 1 hour.

Experimental Setup

The laboratory-scale fixed-bed reactor system constructed is shown schematically in Figure 2 to determine the activity of the sorbent-catalyst formulations for their ammonia decomposition activity and H_2S removal ability using a simulated coal gas. The simulated coal gas will be
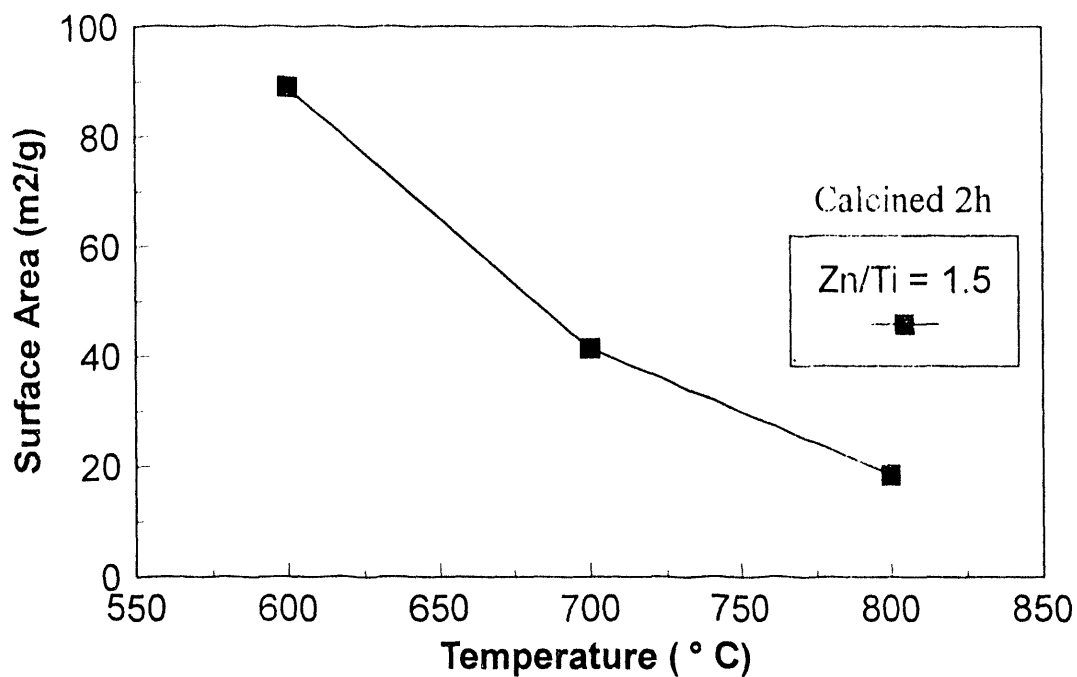
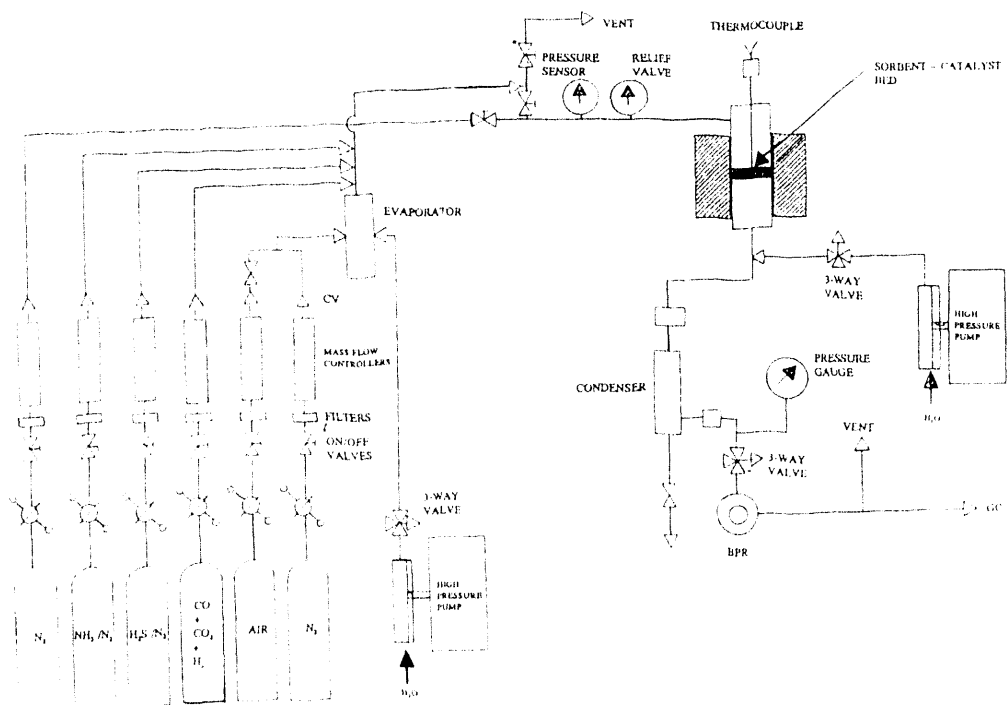**Figure 1. Effect of Calcination Temperature on the Zn-Ti-O Surface Area**

Figure 2. Schematic Diagram of Fixed-Bed Reactor System
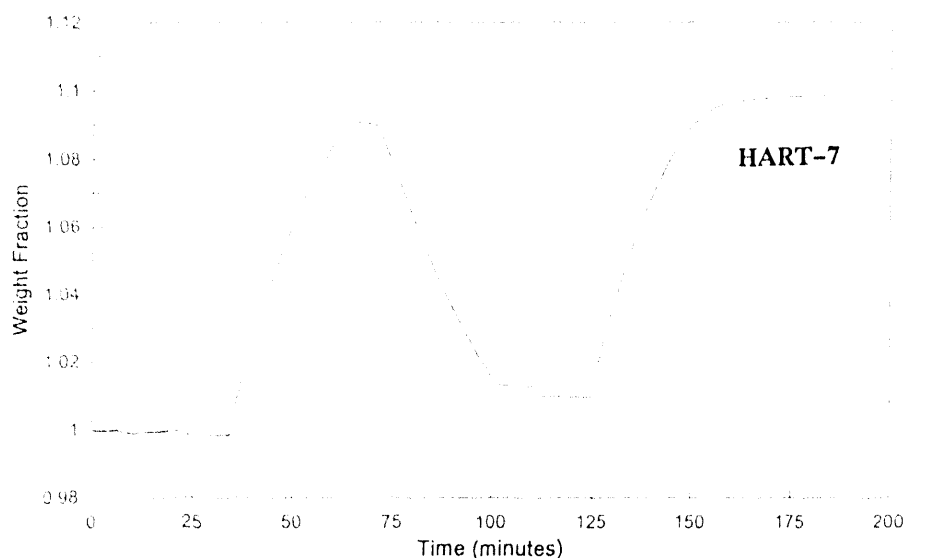
Figure 3. TGA Reactivities of Coprecipitated Zinc Oxide-Titanium Oxide Sorbents

prepared by blending the pure and pre-mixed gases. The flow rates of these gases will be controlled and monitored by high pressure mass flow controllers. Steam will be added to the mixed dry gas by vaporizing liquid water injected into the gas stream at a controlled rate by a high pressure syringe pump. The pressure inside the reactor will be controlled by a back pressure regulator and will be measured using an electronic pressure sensor. The thermocouples are positioned to measure the temperatures of the preheated feed gas, reactor bed temperature and the temperature of the product gas. The product gases will be analyzed for H_2S and NH_3 by using Detector Tubes and Ion-Selective Electrodes.

TEST RESULTS

The TGA reactivity of the sorbents was measured in simulated Texaco gas (with about 1% H_2S) at 550° C (Figure 3) using the RTI, TGA facilities. TGA runs consisted of a 550° C sulfidation, 650°C regeneration with 2% O_2, 18% H_2O, balance

N_2, followed by a second sulfidation. As seen from Figure 3, the HART-7 sample showed excellent reactivity.

FUTURE WORK

Various formulations of sorbent-catalyst will be prepared and then it will be tested in the fixed bed reactor system.

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