FINAL TECHNICAL REPORT
September 1, 2005, through August 31, 2006

Project Title: **HYDROGEN FROM HIGH PRESSURE GASIFICATION OF
ILLINOIS COAL - REACTION SWING APPROACH**

ICCI Project Number: 05-1/4.1B-5
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ABSTRACT

The objective of this project is to develop a process for the separation of hydrogen from coal gasification based syngas components for end uses such as clean energy production. This research is a follow up of the atmospheric pressure validation of the process. SIU has developed a process that is capable of separating hydrogen from synthesis gas. The process is flexible such that it can be used within the gasifier to separate hydrogen or as a separate unit process, depending on the requirements of the process design. The basic idea of the research is to design solid reagents and use them in a two reactor fixed bed scheme employing a reaction swing approach that will aim at increasing the hydrogen yield from coal gasification products (hydrogen enrichment mode) as well as capture greenhouse gases in its matrix through reaction. The end product envisioned in this process was 99 % pure hydrogen. The spent solids would then be restored almost thermoneutrally while releasing sequestration ready carbon dioxide (oxide regeneration mode). While one reactor is operating in the enrichment mode, the other would be operating in the solid reagent regeneration mode. The project involves the high pressure evaluation of the process parameters to maximize the hydrogen content in the typical coal gasification product stream. Most importantly, the solids were designed such that they have the maximum selectivity to the beneficial reactions while maintaining their structure and activity through the reaction-regeneration cycles.

Iron (created by reduction of hematite with syngas) was selected as the Boudouard catalyst and CaO was selected as the carbon dioxide removal material. A small high pressure reactor was designed and fabricated. Specially synthesized CaO (wherein the surface properties were modified) was found to provide better capacity and reaction rates as compared to commercially available CaO. In addition, these specially synthesized CaO showed lower deactivation over multiple cycles. Experiments were also performed with different compositions of syngas to identify the optimal conditions for pure H_2 production. **It was found that for a Fe_2O_3: Coal ratio of 22:1, and Fe_2O_3: CaO ratio of 1:2, no CO_x was released**. **A steam content of 25 % increased the hydrogen yield by 50 %. In addition, it was found that no steam is required for completely removing CO from the syngas stream.**

EXECUTIVE SUMMARY

The objective of this research was to evaluate a high temperature process for the separation of hydrogen from coal derived syngas. SIUC has developed and evaluated (at atmospheric pressures) this new process utilizing the carbon formation phenomenon to the advantage of separating hydrogen from carbon monoxide. The above-mentioned process involves the reaction of syngas with the two solid phases in a nearly thermoneutral process which enriches hydrogen and provides an inexpensive method for the production of sequestration ready carbon dioxide. Theoretically, the regeneration of the spent solids can be conducted thermoneutrally. The results from atmospheric pressure validation tests showed enhanced enrichment of H_2 along with complete depletion of CO, which is considered to be a strong poison to fuel cell catalysts and limits the wide applicability of fuel cells. This research focused on the evaluation of the above-mentioned process <u>at elevated pressures</u> (to find applicability in industrial gasification systems) involving the reaction of syngas with the two solid phases in a nearly thermoneutral process which enriches hydrogen and provides an inexpensive method for the production of sequestration ready carbon dioxide. In addition, as a result of CO_2 removal from the process stream, additional hydrogen yield is obtained. Higher pressures favor the CO disproportionation via the Boudouard reaction (Le' Chatelier's principle). The main goal of the research was to validate and identify the optimal conditions of this novel process using an oxygen transfer agent (that would also initiate the Boudouard reaction) and a carbon dioxide removal material to produce the hydrogen gas of the purity required for commercially available fuel cells. Based on the obtained data, the technical potential and economical applicability of the process was found to be significant. Iron derived from reduction of hematite has been identified as a suitable catalyst while surface modified CaO has been earmarked as a suitable carbon dioxide removal agent. The process has the potential of removing components such as H_2S, CO, CO_2 and enhances the gasification rates of methane and higher hydrocarbons. As a result, the product of this process is a pure hydrogen stream for fuel cell applications.

The basic idea of the project lies in the sequential use of a) iron oxide to oxidize carbon monoxide present in syngas and greatly enhance the Boudouard reaction for the production of CO_2 and amorphous carbon and b) capture of CO_2 using an indigenously designed, high reactivity, high capacity CaO, resulting in the production of high purity hydrogen stream. Subsequently the metallic Fe (reduction of Fe_2O_3) which also contains carbon is oxidized (and thus regenerated) in the presence of air/oxygen and the heat liberated via this exothermic reaction is utilized to calcine the calcium carbonate (carbonation of CaO). In the hydrogen enrichment pass, all of the carbon monoxide is converted (theoretically) to carbon dioxide (via water gas shift reaction, oxidation by iron oxide, and Boudouard reaction) and carbon (by Boudouard reaction). Thus, the operation of this system would result into two separate streams of a) high purity hydrogen for use in fuel cells; and b) sequestration ready CO_2.

The objectives of the research include i) design and fabrication of a high pressure, two reactor system that would enrich hydrogen from the coal gasification products (produced in a separate gasifier); ii) the evaluation of the oxides to optimize the efficiency of the

enrichment and regeneration process at elevated pressures and identify the operating range of the process parameters; iii) determination of cycle time for enrichment and regeneration processes as well as the maximum number of enrichment – regeneration cycles; and iv) establish technical feasibility of the process. Phase composition, morphology and surface properties of the solid oxides examined will be characterized using BET surface area technique, X-ray diffraction technique, Microtrac Laser Particle analyzer and energy dispersive X-ray diffraction, and scanning electron microscopy. The gaseous streams (inlet and the two effluent streams) chemical composition will be analyzed using a gas chromatograph working on-line.

Task 1. Design and Fabrication of the Pressurized Reactors System

A reaction system involving a gasifier and two reactors was designed for high pressure applications. We currently possess a fluidized bed gasifier (Figure 1) that can support up to 500 psig. Two tubular reactors (approx 3 inch diameter and 4 feet long) were designed for the hydrogen enrichment and solid oxide regeneration. The reactors were designed to operate in a fixed bed mode at pressures ranging between 50 and 300 psig. The expected range of temperature is between 650 and 950 ^{o}C. The maximum operating gas flowrate is 500 mL/min. An external tubular furnace supplied the heat. Both reactors were fabricated from Inconel 880 HT. Adequate instrumentation was used for monitoring process parameters. A small high pressure reactor (1 in dia and 6 in long) was fabricated based on the design parameters to evaluate the operation of the process at high pressures.

Task 2. Acquisition, Preparation and Characterization of Oxides

The objective of this task was the acquisition, preparation and characterization of solids, supports, and active solids on these supports. Morphologically altered high surface area CaO and Fe_2O_3 were synthesized in the laboratory. Monolith was acquired and wash-coated with active solids. Materials were characterized for BET surface area, pore volume, and average pore radius. The particle size distribution was evaluated using a Microtrac laser size analyzer. To check on the uniformity of the impregnation within the support, representative samples were analyzed with scanning electron microscopy with energy-dispersive X-ray methods (SEM-EDX).

Task 3. Hydrogen Production/Oxide Regeneration Experiments

We currently possess 2 pressurized reactors of 1 inch diameter and 6" (for separation) and 72" (for coal gasification) long.

The main aim of this task was to identify the conditions for hydrogen enrichment using known mixtures of H_2 and CO under plug flow conditions. Dry runs with nitrogen at different temperatures were conducted on the system to identify any problems and to obtain data regarding pressure drop, residence time and other baseline information. Hydrogen enrichment and regeneration experiments of key process variables including gas flow rate, syngas content, syngas composition, steam content, solids loading, temperature and pressure were conducted. Three experiments were conducted at the

given conditions to assure the reproducibility factor. The key process variables were varied to observe and quantify the effects of each variable on the concentration of the out gases and the overall process efficiency.

Task 4. Simultaneous Coal Gasification and Hydrogen Production Experiments

The bench scale pressurized fluidized-bed gasifier in combination with the gas separation reactor system from Task 3 was used for this set of experiments. After the initial shake-down and baseline establishment, simultaneous coal gasification and hydrogen enrichment experiments were conducted. We already have experience with the gasification of several coal samples. However, a few initial runs of coal gasification alone were conducted to establish the gas composition from gasification. Following this the simultaneous gasification-enrichment process were conducted at high pressures. The enrichment and regeneration modes were switched based on a predetermined cycle time.

Task 5. Technical Feasibility Analysis

Mass and energy balances were carried out for estimating the system efficiency. A study of the reactors and the impacts of various reactor configurations on pressure drop, heat loss, reactor size and efficiency were also conducted.

The data obtained from this research showed that an increase in the pressure improved the kinetics and equilibrium conversion of the Boudouard and the carbonation reactions. Experiments were conducted at different operating pressures and temperatures ranging from 50 -150 psi, 500 – 800 ^{o}C, syngas content in the feed, feed flow rate, steam input amongst others. Iron was used as the Boudouard catalyst while CaO synthesized from a CaO suspension (3.84 g/L) with sodium didodecyl sulfate anionic surfactant (0.01 g/L) was used as the carbon dioxide removal material (CDRM). It was observed that the use of monoliths reduces the pressure drop across the bed. The optimal temperatures was found to be between 600 -650 ^{o}C. It was found that for a Fe_2O_3: Coal ratio of 22:1, and Fe_2O_3: CaO ratio of 1:2, no CO_x was released. A steam content of 25 % increased the hydrogen yield by 50 %. In addition, it was found that no steam is required for completely removing CO from the syngas stream. Suggested operating conditions for simultaneous gasification-enrichment: Temperature – 650 ^{o}C, Steam content – 25 %, catalyst:CDRM – 1:2. Gasification should be conducted at 800 ^{o}C at pressures greater than 150 psi employing 82 % steam. Multiple enrichment –regeneration cycles were also conducted. The efficiency of separation did not decrease as a result of on enrichment-regeneration cycle.

OBJECTIVES

The research investigates a novel approach to the enrichment of hydrogen from syngas while providing for an inexpensive route for the generation of a sequestration ready carbon dioxide. This approach also has the significant potential of reducing the load for sequestration of carbon dioxide by the separation of solid carbon in addition to the removal of other trace impurities. This reduces the volume of gas that needs to be cleaned and should substantially reduce pollution control costs. The flexibility of the process is such that it can be used within a gasifier or as a separate unit process next to gasification. In terms of the products, the process can adjust the CO to H_2 ratios, with one extreme being pure hydrogen. The underlying concept (the reactions involved) has been demonstrated in the laboratory and the process has been validated at atmospheric pressures.

The specific objectives include fundamental understanding of the individual reactions and their dependence on temperature, pressure and gas composition in addition to demonstrating of technical feasibility of the scheme at pressures ranging from 50 to 300 psig. The overall target was to obtain a product with more than 80 % hydrogen and less than 15 ppm CO_2 and 1 ppm CO. The main impurity in the initial stages is expected to be methane. In the later stages of the project, the goal was to maximize methane reformation within the process such that greater than 99% pure hydrogen was obtained. The target was expected to be achieved by development of iron oxides that would provide significant Boudouard reaction. In addition, indigenously developed CaO with controlled porosity that have demonstrated near theoretical capacity and high reactivity along with the ability to withstand several carbonation-calcination cycles was used. The calcium oxide to iron oxide loading, total solids loading and the syngas mixture compositions were also considered as variables affecting the hydrogen purity in the product stream. The optimal range of process parameters, solid oxides optimum cycle time as well as the maximum number of enrichment-regeneration operations were identified.

The research effort consisted of three major activities. The first was the design and fabrication of the high pressure reactors along with the preparation of the oxides. The second activity encompassed the study of the underlying principles of the hydrogen enrichment and the regeneration process, individually, at high pressures. During the third activity, the overall process including Illinois coal gasification, hydrogen enrichment and oxide regeneration was demonstrated. Recognizing the innovative nature of the technology and the technical risk inherent in the development of any novel scheme, this research was limited mainly to provide the proof of the concept for high pressure applications and evaluate the technical feasibility of the process for scale up. The task structure of the research plan with a summary of the outline of each task activities are presented below.

Task 1. Design and Fabrication of the Pressurized Reactors System

The objective of this task was to design and fabricate a reaction system involving a gasifier and two reactors for high pressure applications ranging between 50 and 300 psig.

Task 2. Acquisition, Preparation and Characterization of Oxides

The objective of this task was the acquisition, preparation and characterization of solids, supports, and active solids on these supports.

Task 3. Hydrogen Production/Oxide Regeneration Experiments

The main aim of this task was to identify the conditions for hydrogen enrichment using known mixtures of H_2 and CO under plug flow conditions.

Task 4. Simultaneous Coal Gasification and Hydrogen Production Experiments

The aim of this process was to optimize conditions for simultaneous coal gasification and hydrogen enrichment in the two reactor scheme.

Task 5. Technical Feasibility Analysis

The aim of this task was to summarize the data in order to evaluate the technical feasibility of the process.

INTRODUCTION AND BACKGROUND

The oil price shocks sent the world's economies, especially western economies heavily dependent on oil, into a scramble to reduce their dependence on imported oil from the gulf through (i) conservation and more efficient utilization, (ii) location of additional sources, and (iii) development of alternatives like solar, wind, biomass and others. Such efforts were so successful that by 2001, the United States economy had grown by 126% while oil consumption had risen by only 30%. Similarly, in the 1990's alone manufacturing output expanded by 41 percent, while industrial electricity utilization increased by a mere 11 percent. Today, because of the size of its economy, the United States is still the largest importer and user of foreign oil, mostly from the Middle East. The United States is now in serious competition with the rapidly growing economies for the world's available oil. There is a palpable sense and developing consensus that we are nearing the end of cheap oil, if not the end of oil entirely.

This increase in demand for energy coupled with increased environmental concerns has given rise to the need for innovative technologies for energy plants. An irony is that the United States already possesses one of the greatest supplies of energy in the world.

> *"The largest single increment of energy in the world is America's recoverable reserves of coal, secure within the borders of our country...The United States*

possesses 275 billion tons of recoverable coal reserves, or about one-fourth of the world's total. U.S. coal reserves are equivalent to four times the oil of Saudi Arabia, 1.3 times the oil of OPEC and equal to all the world's proved oil reserves." **(Partners for Affordable Energy**, (http://www.affordableenergy.org/key_points/dependence.asp))

The availability of relatively inexpensive, high purity hydrogen using an operationally-simple and cost-effective process can lead to the success of so called "hydrogen economy" that will "install" hydrogen as an universal and globally accessible energy carrier. As a result, it has become one of the most sought after technologies provided there exist an inexpensive and readily available source for hydrogen production such as coal. Coal gasification will produce the syngas (mixture of gases that includes H_2O, CO, CO_2 and H_2). If the fuel is being reformed for the purpose of making H_2 fuel, with sequestration of the co-produced CO_2, then it is necessary to convert as much as is practical of the CO into CO_2. The ratio of CO to H_2 produced via the gasification of coal can be adjusted by altering the water gas shift reaction conditions. The conversion of CO to CO_2 can be further enhanced by the addition of Fe_2O_3. Further removal of carbon monoxide from the gaseous stream can be effected by the Boudouard reaction. Due to the significantly higher levels of coal resources as compared to other fuel sources, it is poised to be the main ingredient of the *FutureGen* vision, in which hydrogen economy is vital. With increasing demands for energy, the amount of coal utilized is expected to only increase. However, opposing market and environmental and legislative factors requires clean-burning fuel with low amounts of greenhouse gases. The pathway envisioned currently is the gasification of coal followed by separation of hydrogen from the greenhouse gases. The industry consensus is that no further major improvements are likely with the mature cryogenic air separation technology, which represents upwards of 15 % of capital costs of modern combustion processes and consumes 10 % of the gross power. In view of this technical impasse in a high cost, energy intensive area, we propose a new, innovative approach which exploits the Boudouard reaction to positively effect the separation of hydrogen from other model syngas constituents and coal gasification products.

Southern Illinois University has developed a reaction swing process for the separation of hydrogen from syngas constituents and impurities such as CO, CO_2 and H_2S. The main reactions in this process are the conversion of CO to CO_2 by disproportionation on a catalyst and subsequent removal of the CO_2 by a suitable CO_2 removal agent. CaO has been determined to be the most suitable CO_2 removal agent. This process has already been validated and found to be technically feasible under atmospheric pressure conditions. Southern Illinois University has also developed a process to alter the surface characteristics of the CaO to enhance the reaction rates and its longevity over multiple carbonation calcinations cycles.

The process involves the reaction of syngas with the two solid phases in a nearly thermoneutral process step which enriches hydrogen while providing for an inexpensive method for sequestration ready carbon dioxide. In addition, as a result of CO_2 removal from the process stream, additional hydrogen is obtained through water gas shift reaction. Theoretically, the regeneration of the spent solids can also be conducted thermoneutrally.
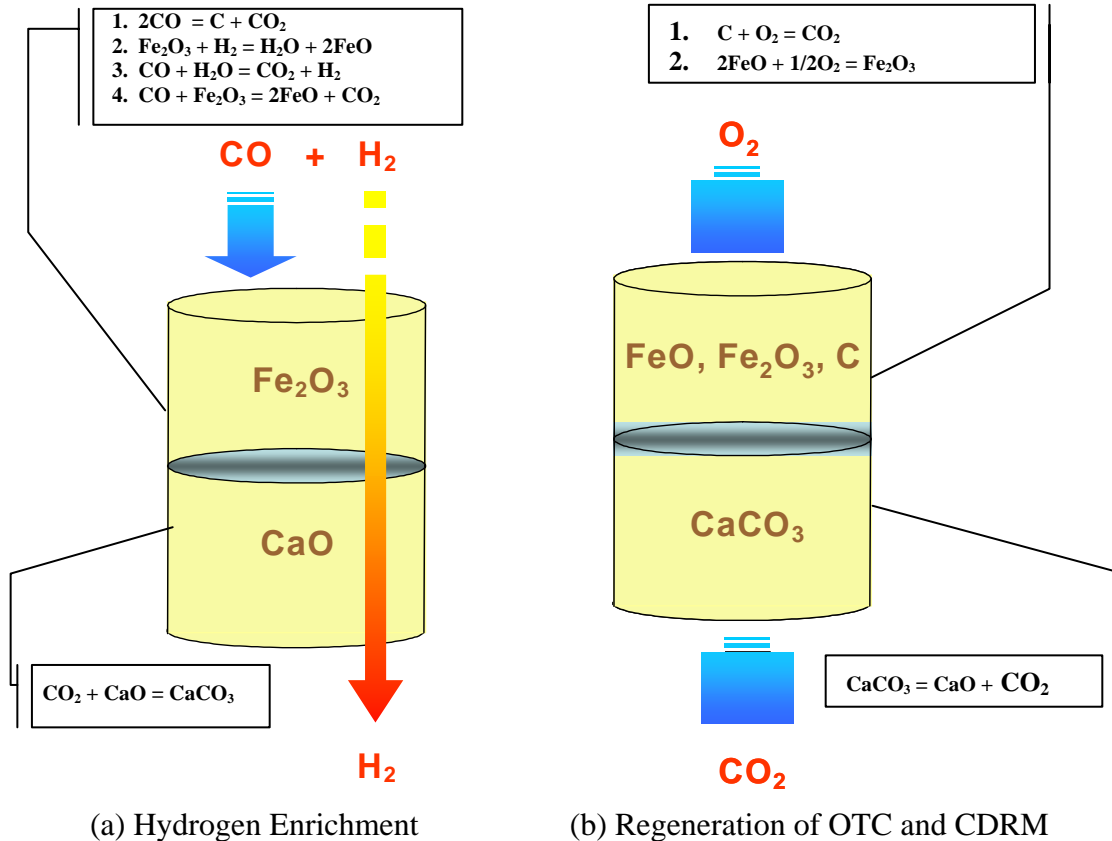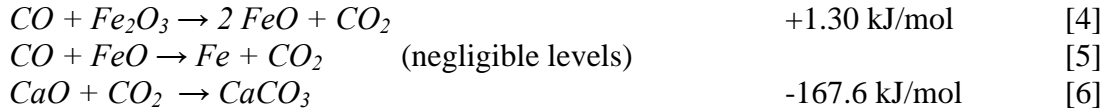
1. $2CO = C + CO_2$
2. $Fe_2O_3 + H_2 = H_2O + 2FeO$
3. $CO + H_2O = CO_2 + H_2$
4. $CO + Fe_2O_3 = 2FeO + CO_2$

1. $C + O_2 = CO_2$
2. $2FeO + 1/2O_2 = Fe_2O_3$

CO + H₂

O₂

Fe₂O₃

CaO

FeO, Fe₂O₃, C

CaCO₃

$CO_2 + CaO = CaCO_3$

$CaCO_3 = CaO + CO_2$

H₂

CO₂

(a) Hydrogen Enrichment   (b) Regeneration of OTC and CDRM

Figure 1. Schematic of the proposed process.

The process is schematically shown in Figure 1. In this system, the gasification products are introduced into the reactor (Figure 1a) where a portion of the CO is water-gas shifted to produce hydrogen and carbon dioxide and a portion of CO disproportionates to solid carbon and carbon dioxide by Boudouard reaction. Carbon dioxide produced from these reactions reacts with CaO to produce CaCO₃. The net effect of these reactions is exothermic and, thus, additional CO_2 and H_2 can be produced by the endothermic reaction between the methane and steam present in the reactor. The gas stream exiting the reactor consists mainly of high purity hydrogen in the stream. The oxygen transfer compound – now in a reduced state – and the carbon dioxide removal material are then regenerated (Figure 1b). The oxygen transfer compound is exothermically oxidized along with the carbon (to carbon dioxide), thereby providing the heat needed to desorb the carbon dioxide. The gas stream leaving the regenerator contains carbon dioxide at relatively high temperature and pressure and can be used in a Rankine cycle to produce shaft work. The hydrogen stream produced in this way could, in principle, have impurity concentrations as low as 15 ppm of CO_2 and 1 ppm of CO.
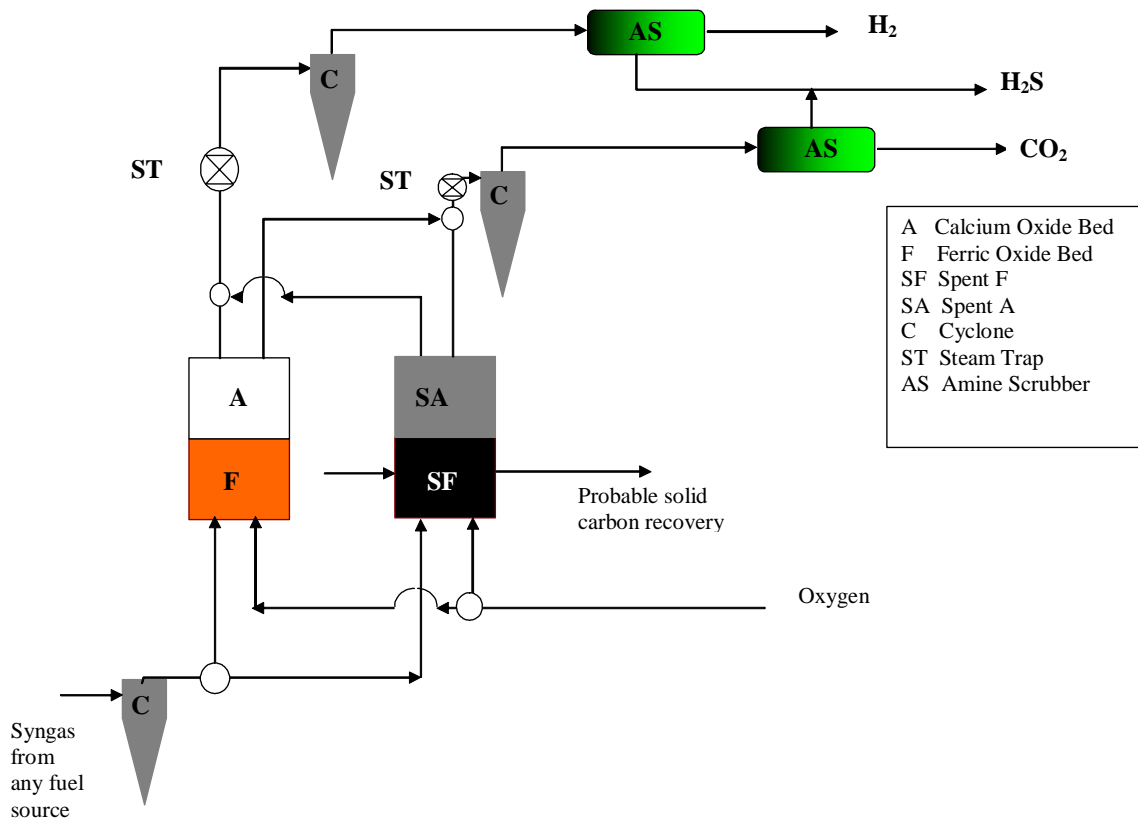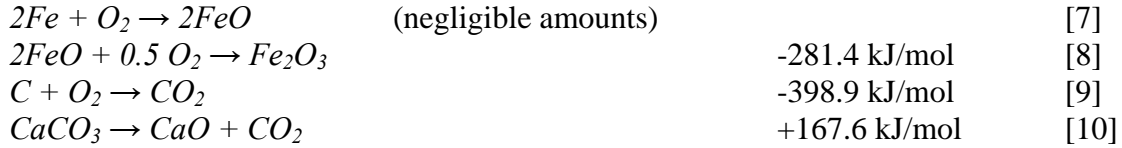
Hydrogen Enrichment Stage:

$$CH_4 + H_2O \xrightarrow{Fe_2O_3} CO + 3H_2 \qquad\qquad\qquad\qquad\qquad +206 \text{ kJ/mol} \qquad [1]$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \text{(Water-Gas Shift Reaction)} \quad -42 \text{ kJ/mol} \qquad [2]$$

$$2\,CO \rightarrow CO_2 + C \qquad\qquad \text{(Boudouard Reaction)} \qquad -162 \text{ kJ/mol} \qquad [3]$$

$CO + Fe_2O_3 \rightarrow 2\ FeO + CO_2$	+1.30 kJ/mol	[4]
$CO + FeO \rightarrow Fe + CO_2$ (negligible levels)		[5]
$CaO + CO_2 \rightarrow CaCO_3$	-167.6 kJ/mol	[6]

Oxide Regeneration Stage:

$2Fe + O_2 \rightarrow 2FeO$ (negligible amounts)		[7]
$2FeO + 0.5\ O_2 \rightarrow Fe_2O_3$	-281.4 kJ/mol	[8]
$C + O_2 \rightarrow CO_2$	-398.9 kJ/mol	[9]
$CaCO_3 \rightarrow CaO + CO_2$	+167.6 kJ/mol	[10]

Figure 2. Envisioned process flowsheet.

Preliminary calculations and experimental evidence suggest that this process has the potential to be significantly more efficient at producing hydrogen at concentrations similar to the currently available technologies with an added advantage that the reaction products constitute hot working fluids that can be used to generate process steam or shaft work. This is in contrast to the conventional conversion technologies that require shaft work to compress in order to effect gas separation. A mass and energy balance on the system, assuming the absence of the Boudouard reaction, shows that only 0.68 moles of hydrogen can be produced for every mole of CO converted to CO_2 because of the high energy requirement for the calcination of $CaCO_3$. The amount of hydrogen per mole of CO reacted can be enhanced by 33% (to a value greater than 0.91) in the presence of

Boudouard reaction and water gas shift reaction and subsequent oxidation of carbon. Figure 2 shows the schematic diagram of the envisioned process of hydrogen enrichment.

EXPERIMENTAL PROCEDURES

Task 1. Design and Fabrication of the Pressurized Reactors System

A reaction system involving a gasifier and two reactors was designed for high pressure applications. We currently possess a fluidized bed gasifier (Figure 3) that can support up to 500 psig. Two tubular reactors (approx 3 inch diameter and 4 feet long) were designed for the hydrogen enrichment and solid oxide regeneration. The reactors were designed to operate in a fixed bed mode at pressures ranging between 50 and 300 psig. The expected range of temperature is between 650 and 950 $^{\circ}$C. The maximum operating gas flowrate is 500 mL/min. An external tubular furnace will supply the heat. Both reactors were fabricated from Inconel 880 HT. Adequate instrumentation will be used for monitoring process parameters. A small high pressure reactor (1in dia and 6 in long) was fabricated based on the design parameters by Parr Instrument Company (Moline, IL) to evaluate the operation of the process at high pressures (Figure 4).
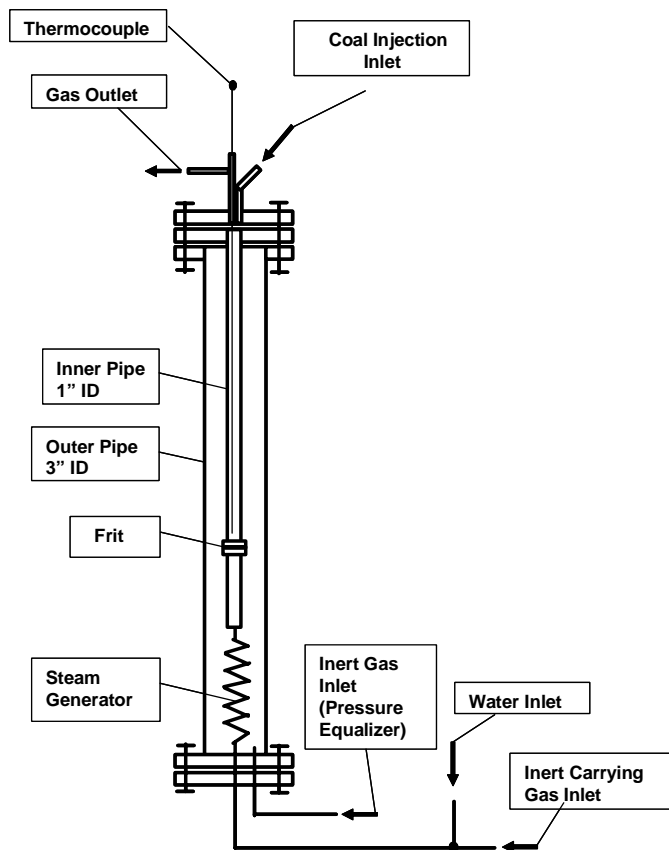

Figure 3. Fluidized bed gasifier.

Thermocouple

Needle Valve

Top
Plate

Adapter for air tight T/C
insertion

Reactor

Heater
Assembly

Pressure
Gauge

Support
Plate

Bottom Adapter
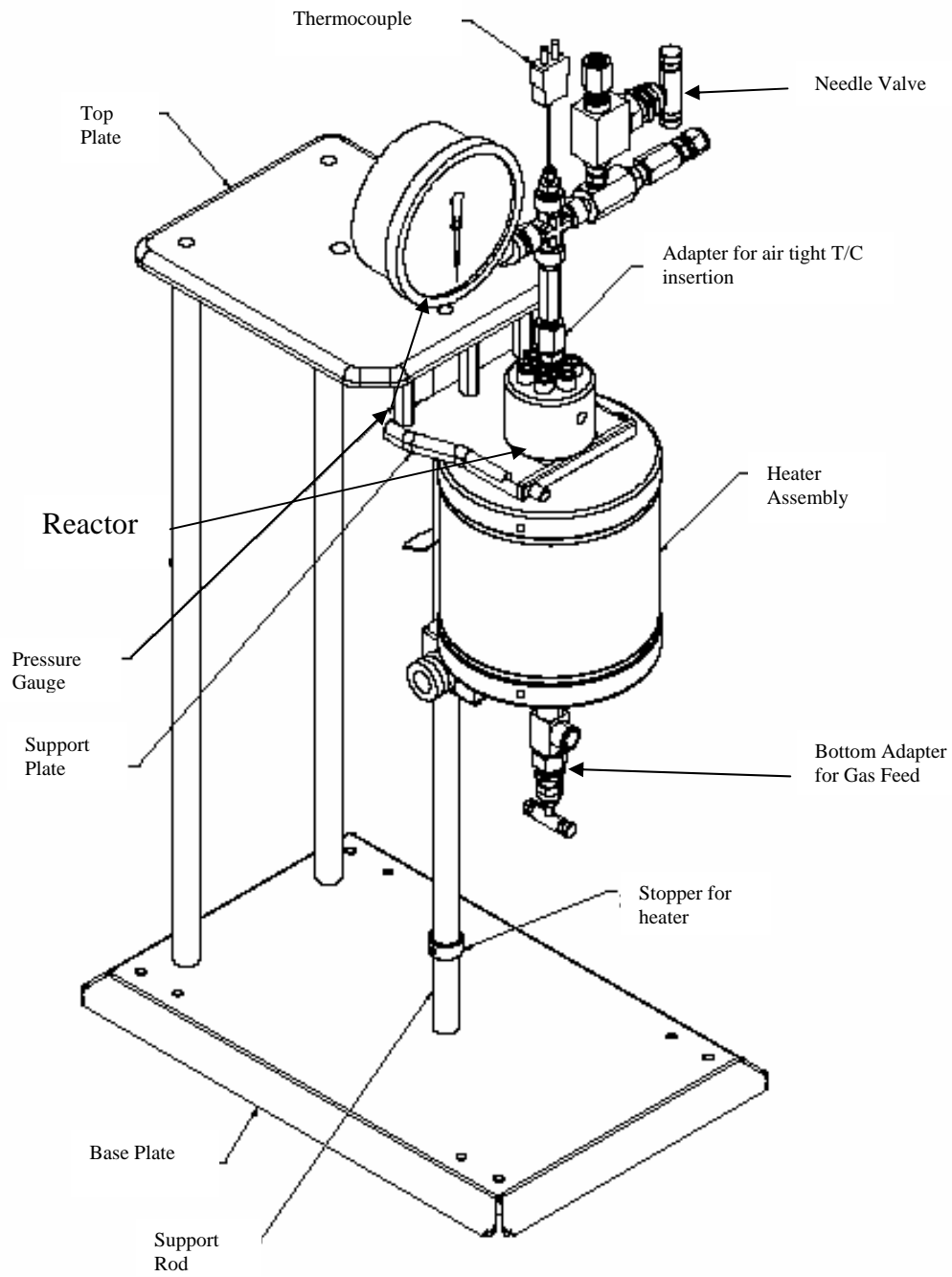for Gas Feed

Stopper for
heater

Base Plate

Support
Rod

Figure 4. Gas separation reactor.

Task 2. Acquisition, Preparation and Characterization of Oxides

Iron oxide and Calcium oxide were obtained from commercial sources such as GE and Mississippi Lime as well as lab grade chemical vendors such as Fisher Scientific and Sigma Aldrich.

The synthesis of several specially formulated calcium oxides was completed. Surfactants were used to control the size of the particles as well as pore size distribution. Cationic surfactants were used to increase the particle size while anionic surfactants were used to decrease the particle size. The pH of the saturated solution of $Ca(OH)_2$ was around 12. In our preparation procedure we use suspensions of CaO that are 4, 8, 16, 24 and 32 times of the suspensions density. As the carbonation takes place when CO_2 was passed through the suspension, the newly formed $CaCO_3$ precipitates from the solution. The excess of suspended CaO goes into solution maintaining the pH at around 12. Once all of the $Ca(OH)_2$ is consumed, the pH falls rapidly to near neutral to slightly acidic pH (due to the presence of dissolved CO_2 that forms carbonic acid).

Two methods of washcoating were applied to the monoliths (photo below). In the first method, aluminum nitrate and urea solution in the ratio of 2:1 was prepared at $50^{o}C$. The resulting solution was then heated to $90^{o}C$. The monoliths were immersed into the solution and withdrawn. The duration of heating the solution was varied (5 - 15 hrs) along with the contact time of the monolith with the solution (5 - 15 min). This was followed by overnight drying of the monolith ($95^{o}C$) and calcinations ($400^{o}C$) for 5 hrs. In the second method, a bohemite sol was prepared by dissolving aluminum isopropoxide in hot distilled water under constant stirring and refluxed for 1 hr. Then, 0.07 mole of HNO_3 was added per mole of isopropoxide to make a clear sol. The resulting solution was evaporated and concentrated to get approximately 1 M bohemite sol. When this method was used, drying process was conducted at room temperature. The washcoated monoliths were then impregnated with the active phase (Ca and Fe) by the following method. First, the reagent grade metal compound (calcium nitrate and iron nitrate) were dissolved in a suitable solvent (acetone) and mixed thoroughly with a magnetic stirrer. The monoliths were immersed into the solution of dissolved metal compound and soaked overnight at room temperature. After drying at room temperature, the monoliths were further dried in an oven at 100-110°C. Finally, such impregnated monoliths were calcined at 400°C to convert the metal complex into metal oxide distributed throughout the solid's surface.

Materials were characterized for BET surface area, pore volume, and average pore radius. The particle size distribution was evaluated using a Microtrac laser size analyzer. To check on the uniformity of the impregnation within the support, representative samples were analyzed with scanning electron microscopy with energy-dispersive X-ray methods (SEM-EDX).
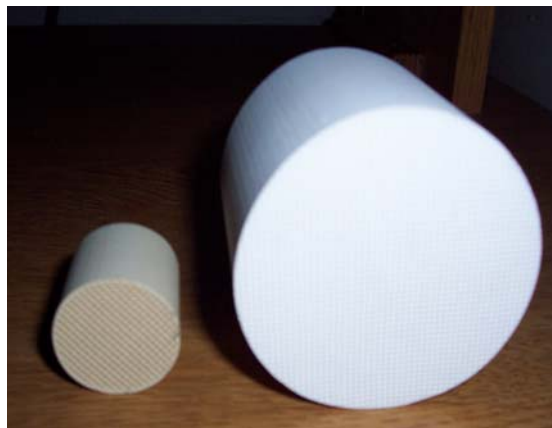
Figure 5.   Monoliths.

Task 3. Hydrogen Production/Oxide Regeneration Experiments

HSC Chemistry software was used to evaluate the thermodynamics of the system. Kinetic experiments were performed using a microbalance assembly consisting of a Thermogravimetric Analyzer (TGA). Gas compositions were obtained by blending high purity gases using Sierra mass flow controllers. Carbon dioxide, carbon monoxide, hydrogen, air and nitrogen of stock gas grade (99.99%) were supplied by a gas cylinder and a pressure regulator.   After loading the solids to the TGA, the sample was preconditioned and dried in flowing nitrogen by elevating the reactor temperature, followed by additional heating to achieve the temperature of interest. The sample was then allowed to come to steady state, both thermally and gravimetrically.   Once the sample achieved steady state under dry nitrogen conditions, gas mixtures were introduced and nitrogen flow was ceased.   The weight change vs. time curves were used to determine the various reaction constants and determine the required residence times for the lab scale experiments. The resulting solids were analyzed using X-ray diffraction and scanning electron microscopy.

The small scale laboratory reactor was set up for those experiments (Schematic shown in Figure 6). The reactor system consist of gas supplies, water pump, steam generator, reactor system (reactor + furnace), water trap, back pressure regulator and gas collection system and the required fitting and flow measurement devices. A MicroGC from Agilent Technologies has been attached to the reactor system to provide real-time data analysis from the reactor. It consists of two separate channels, one with Plot Q column and other with Molecular Sieve 5A column and 2 TC detectors. It is capable of analyzing samples containing CO, H_2, CO_2, CH_4, C_2H_6, O_2 and N_2 in less than 2 minutes. Figure 3 is a schematic of the setup and Figure 4 is the photograph of the components of the same. Syngas cylinders containing 20, 43 and 48 % H_2 (with the balance CO) were obtained from syngas. Experiments were conducted to establish baselines such as residence time distributions for each gas at different flow rates and temperatures. Experiments with syngas were conducted to study the effect of gas flow rates (50 – 400 ml/min), syngas content (from 5 to 50 %), temperature (550 -700 ^{o}C), steam (0 – 50 %), solids loading

(Fe$_2$O$_3$ loadings of 5.6 – 16.8 g and CaO loadings of 0 – 22.4 g) and solids ratio on the hydrogen purity and cycle time for enrichment.

Task 4. Simultaneous Coal Gasification and Hydrogen Production Experiments

The schematic of the fluidized bed gasifier is shown in Figure 3 while that of the fixed bed gas separation reactor is shown in Figure 4.   Both have 1 inch diameter, however they vary in their lengths (72" and 6" respectively, see photo below). Simultaneous coal gasification and hydrogen enrichment in a single reactor was evaluated in this phase. At the beginning of each experiment the separation reactor was filled with Fe$_2$O$_3$ and CaO carriers according to the desired ratios. Next the nitrogen flow was started and the reactor was heated up to a predetermined temperature with external furnace. Finally water was introduced into the reactor and after examining the setup of the parameters involved, coal was introduced inside the reactor through injection. The effects of temperature (700 – 850 ^{o}C for gasification and 550 -700 ^{o}C for separation), steam content (0 -91 % with intermediate condensation to ensure 0 -50 % steam in the separation reactor), iron oxide to coal ratio (0 – 44), and CaO:iron oxide ratio (0-3) on the hydrogen purity and CO rejection were evaluated.

Task 5. Technical Feasibility Analysis

The aim of this task was to summarize the data in order to evaluate the technical feasibility of the process.
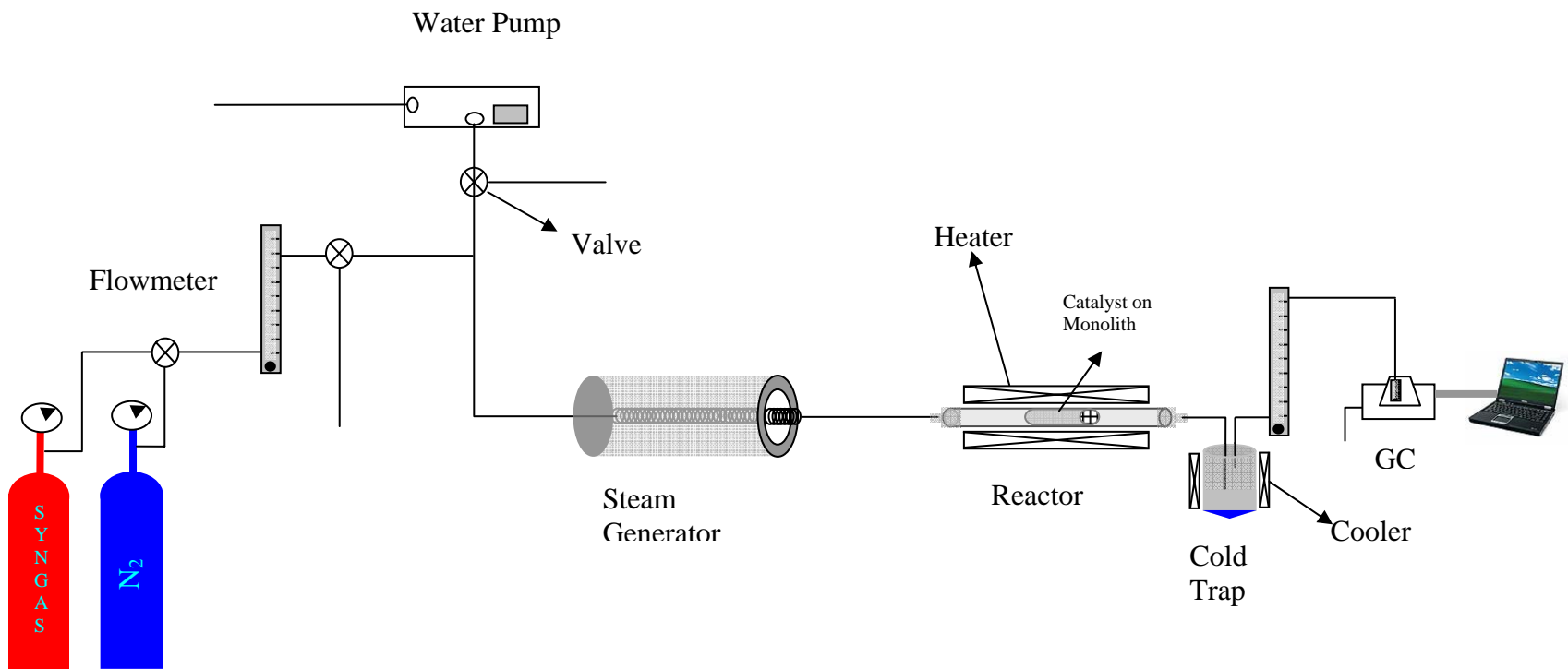
Figure 6. Schematic diagram of the system.

Figure 7. Reactors.

RESULTS AND DISCUSSION

Task 1. Design and Fabrication of the Pressurized Reactors System

The two reactor system was designed. However, due to time limitations, the two reactor system designed was not used. The parametric evaluation was conducted in a smaller reactor. A smaller reactor (1 inch diameter and 6 in long) was fabricated by Parr Instruments based on the design specification provided for the two reactor system (Figure 8). The reactor was built with Inconel 880 HT. It is capable of withstanding 850 $^{\circ}$C at 300 psi). A specialized bottom was designed to ensure the insertion of a quartz frit and the even distribution of the inlet gases (Figure 8b). The piping was done such that the gas could be fed from the top or the bottom or may be recycled if required.
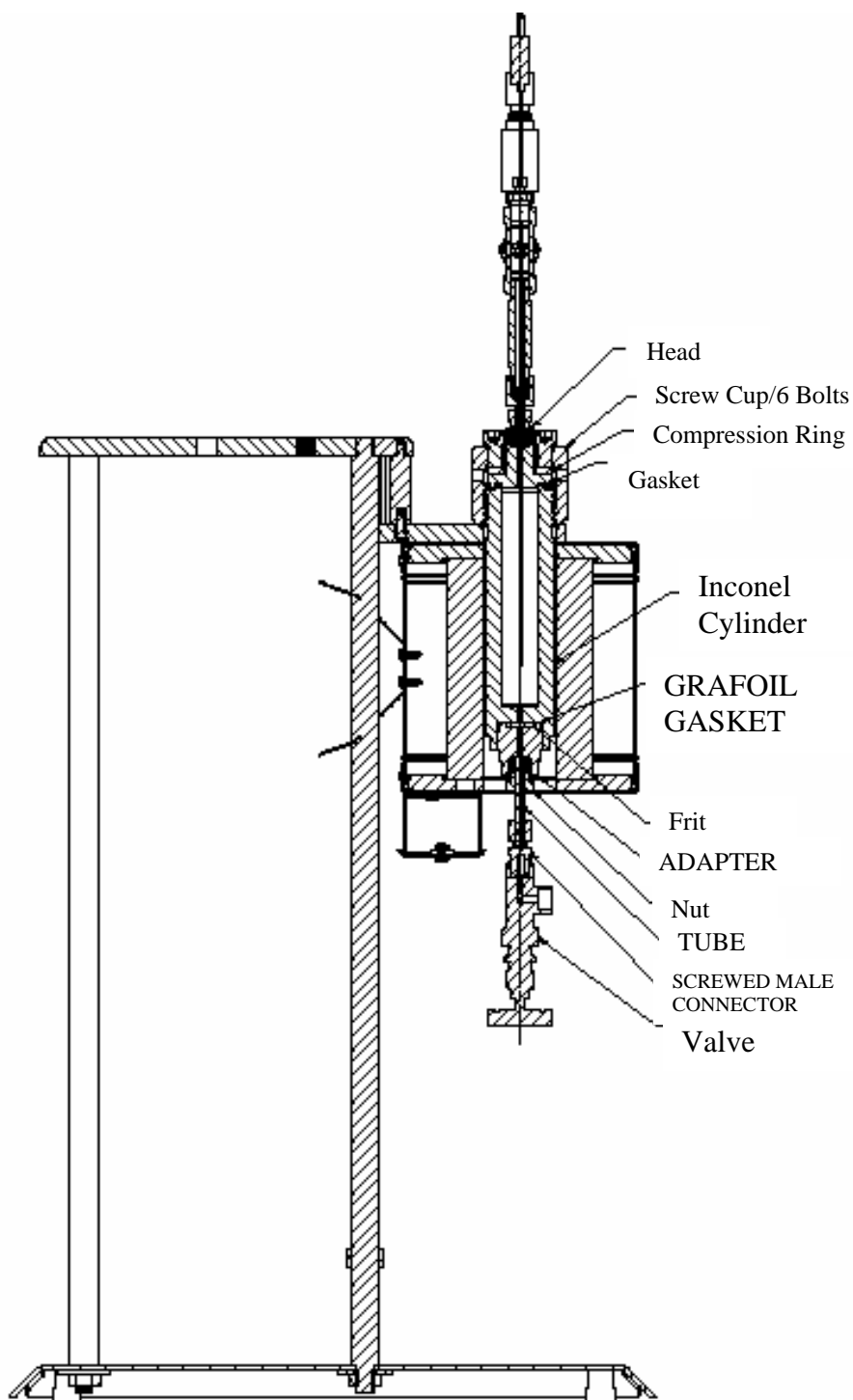
Head

Screw Cup/6 Bolts

Compression Ring

Gasket

Inconel
Cylinder

GRAFOIL
GASKET

Frit

ADAPTER

Nut

TUBE

SCREWED MALE
CONNECTOR

Valve

Figure 8a. Gas separation reactor schematic.

BOTTOM
DETAIL

FRITTED
DISK

14.18"

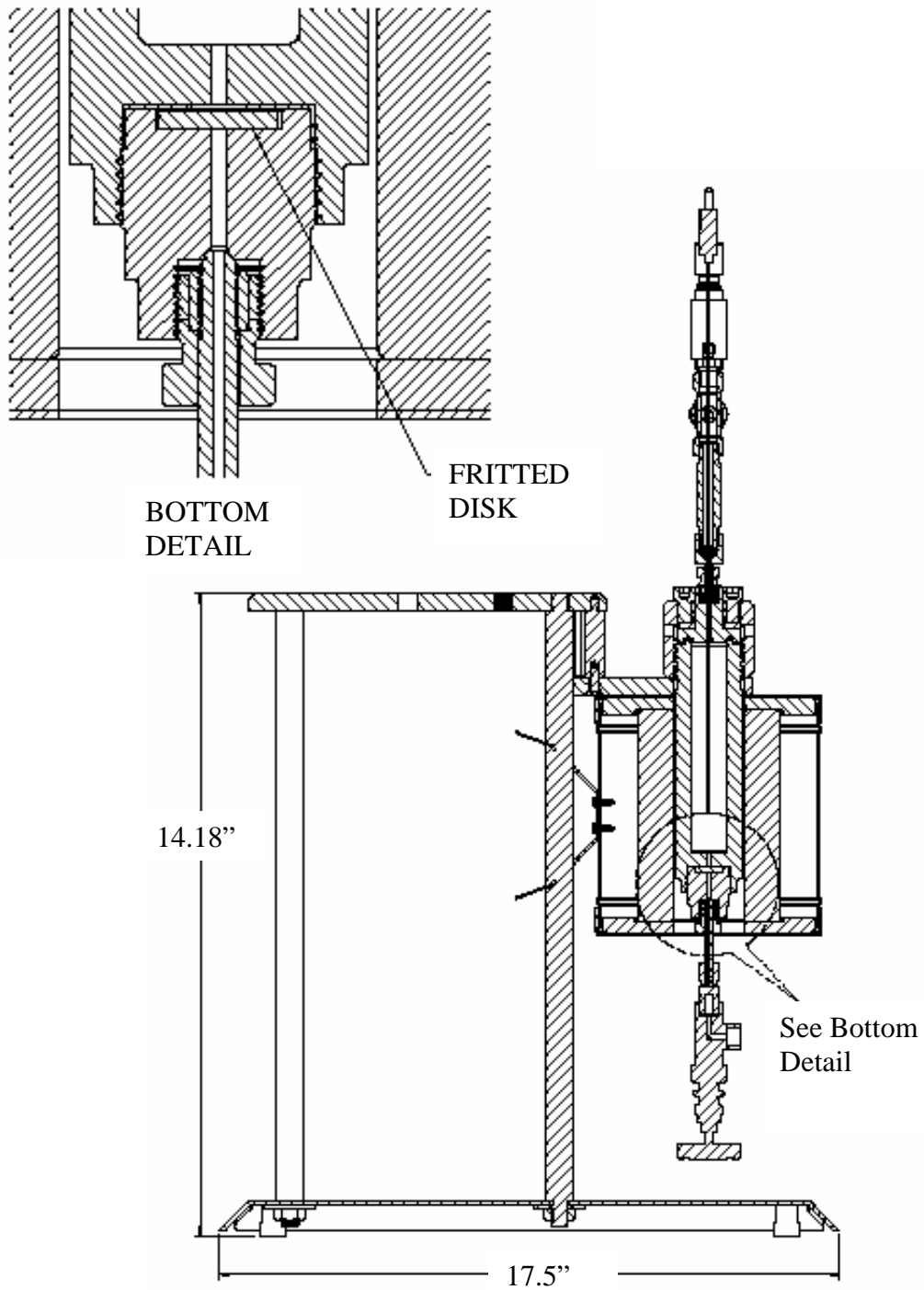See Bottom
Detail

17.5"

Figure 8b. Gas separation reactor schematic of the bottom
connections.

Figure 9. Reactor components.

Figure 10. Reactor system set up.

Task 2. Acquisition, Preparation and Characterization of Oxides

Calcined limestone and hematite samples were acquired. Also alumina beads and ceramic monoliths were acquired for support materials and the active materials were deposited.

Morphologically altered high surface area CaO samples were synthesized. Different surfactants were used to control the size of the particles as well as pore distribution. Cationic surfactants were used to increase the particle size while anionic surfactants were used to decrease the particle size. The pH of saturated $Ca(OH)_2$ solution is around 12. In our preparation methodology we use suspensions of CaO that are 4, 8, 16, 24 and 32 times the suspensions density. As the carbonation takes place due to bubbling CO_2, the newly formed $CaCO_3$ precipitates out of the solution. The excess suspended CaO goes into solution maintaining the pH at around 12. Once all of the $Ca(OH)_2$ is consumed the pH falls rapidly to near neutral to slightly acidic pH (due to the presence of dissolved CO_2 to form carbonic acid).

Figures 11 and 12 are the BET response in adsorption and desorption modes for the selected method for obtaining surface modified CaO. Table 1 provides the summary of the surface area and pore size data in both modes. Figure 13 is the particle size distribution of the surface modified sorbents prepared in our laboratory. The mean particle size was 105 microns. Figure 14 contains the data on the change in capacity of the sorbent developed in the laboratory for each calcinations step followed by carbonation for 15 minute cycles. The figure also contains data on the deactivation of dolomite and limestone during calcinations carbonation cycling (from the literature) as well as that for commercially available laboratory grade calcium carbonate. It is clearly seen from the data that the laboratory prepared sorbent does not loose appreciable capacity over 50 cycles (close to 90 %) as opposed to the other materials (capacity declines to nearly 20 %).

Table 1 Characterization of the specially modified CO_2 Sorbent.

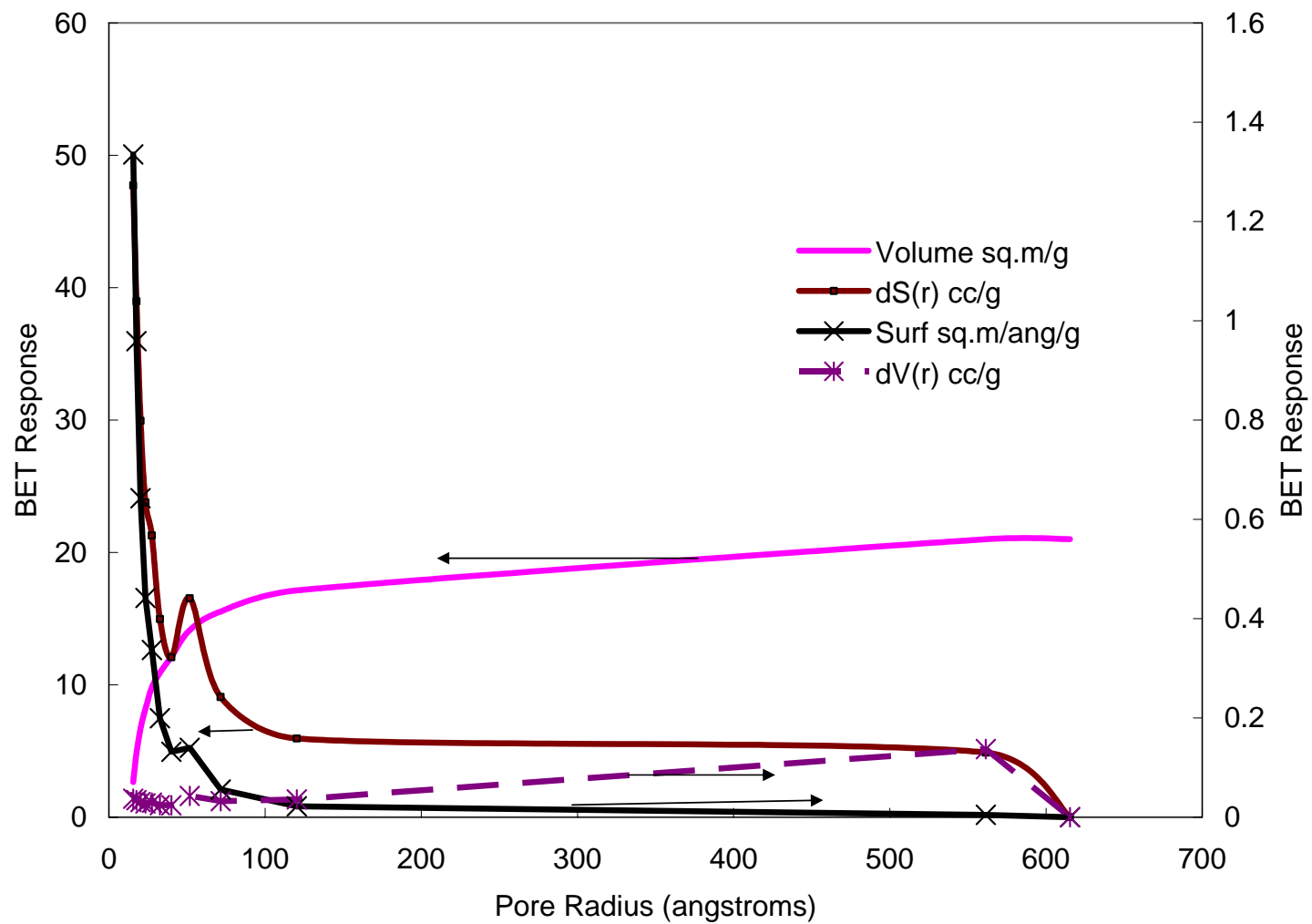|	Adsorption	Desorption
Surface Area =	21.00 m²/g	23.65 m²/g
Pore Volume =	0.14 cc/g	0.15 cc/g
Pore Radius =	115.54 Å	113.56 Å

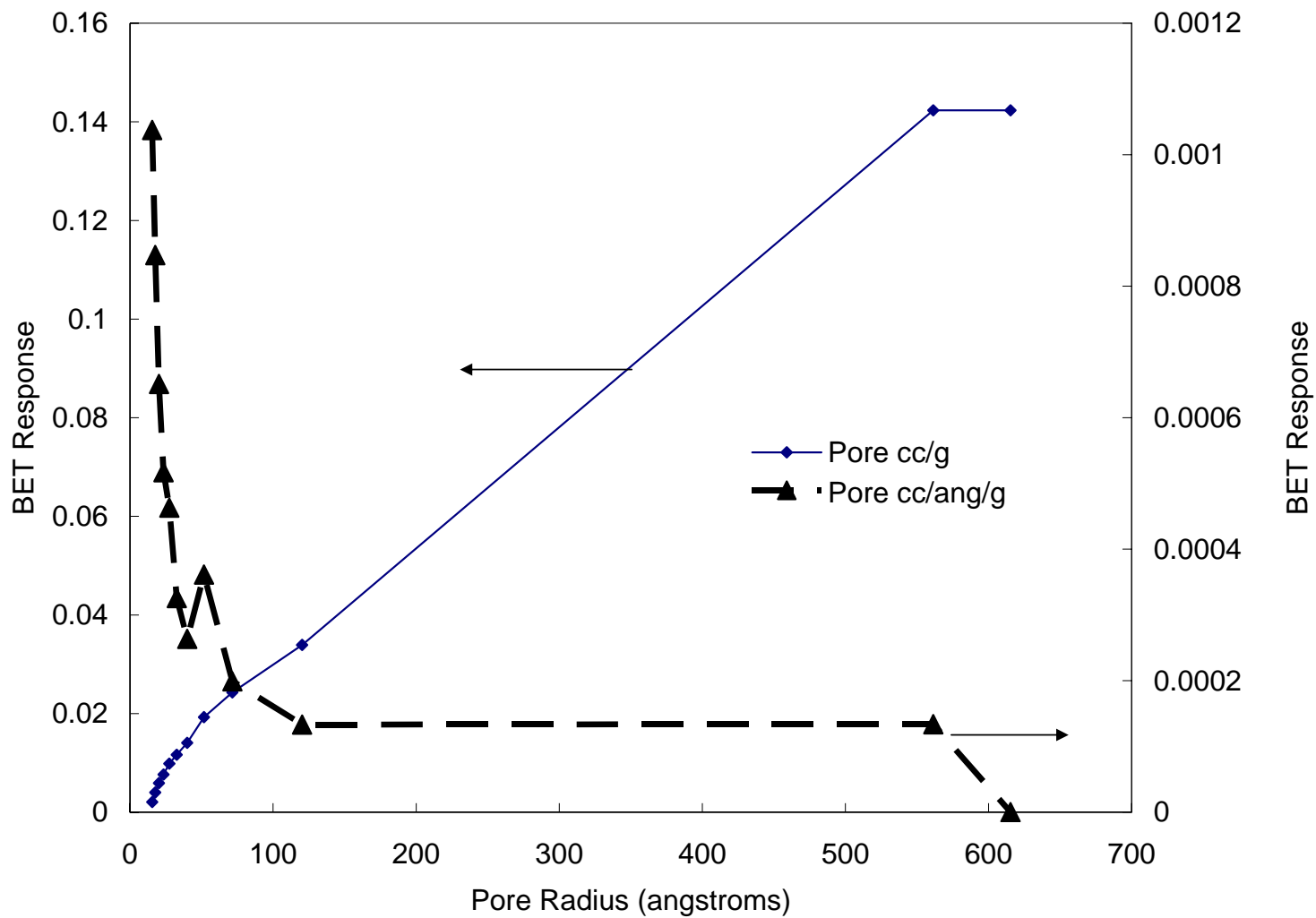Figure 11 a. BET response of the CaO in adsorption mode.

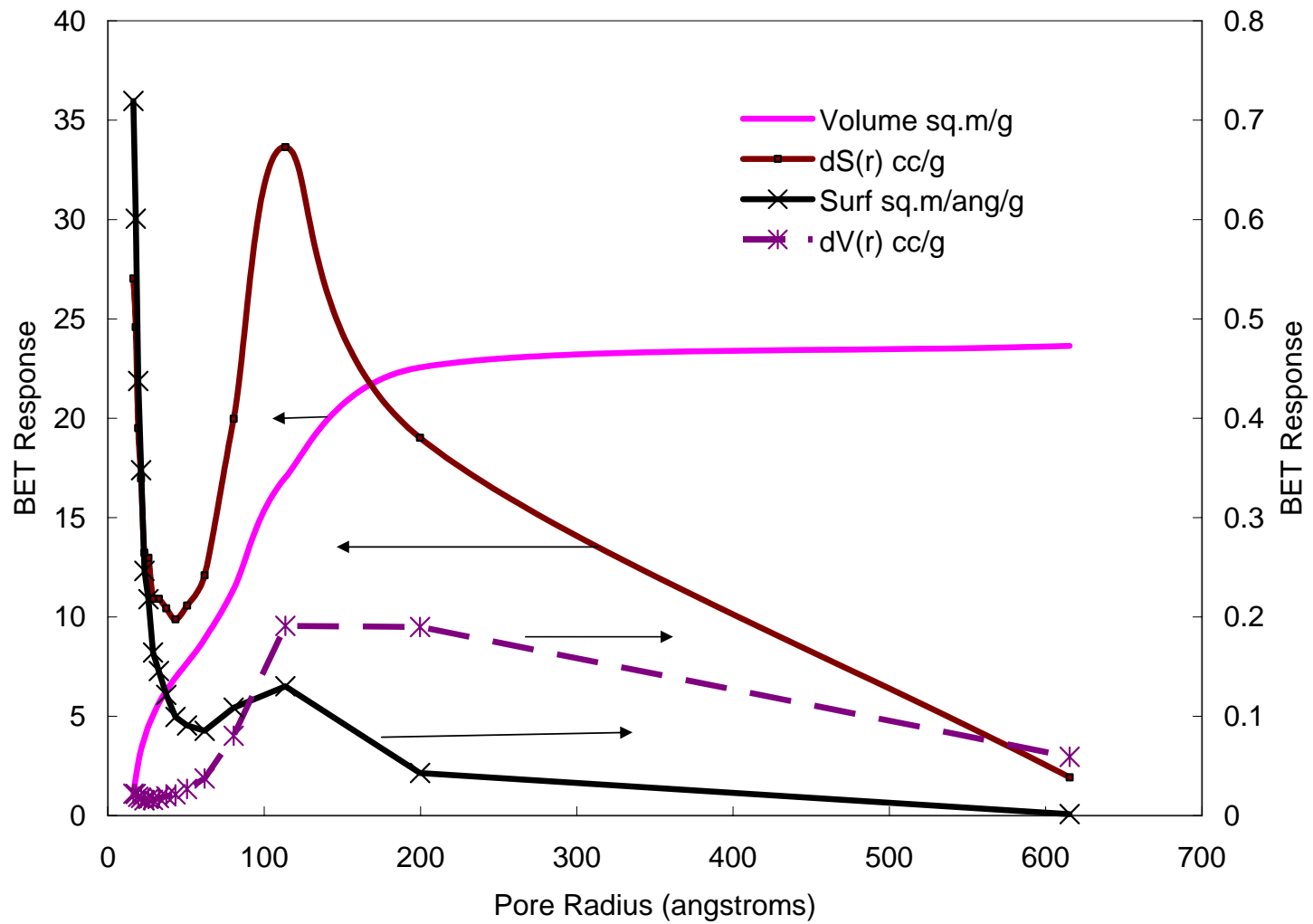Figure 11 b. BET response of the CaO in adsorption mode.

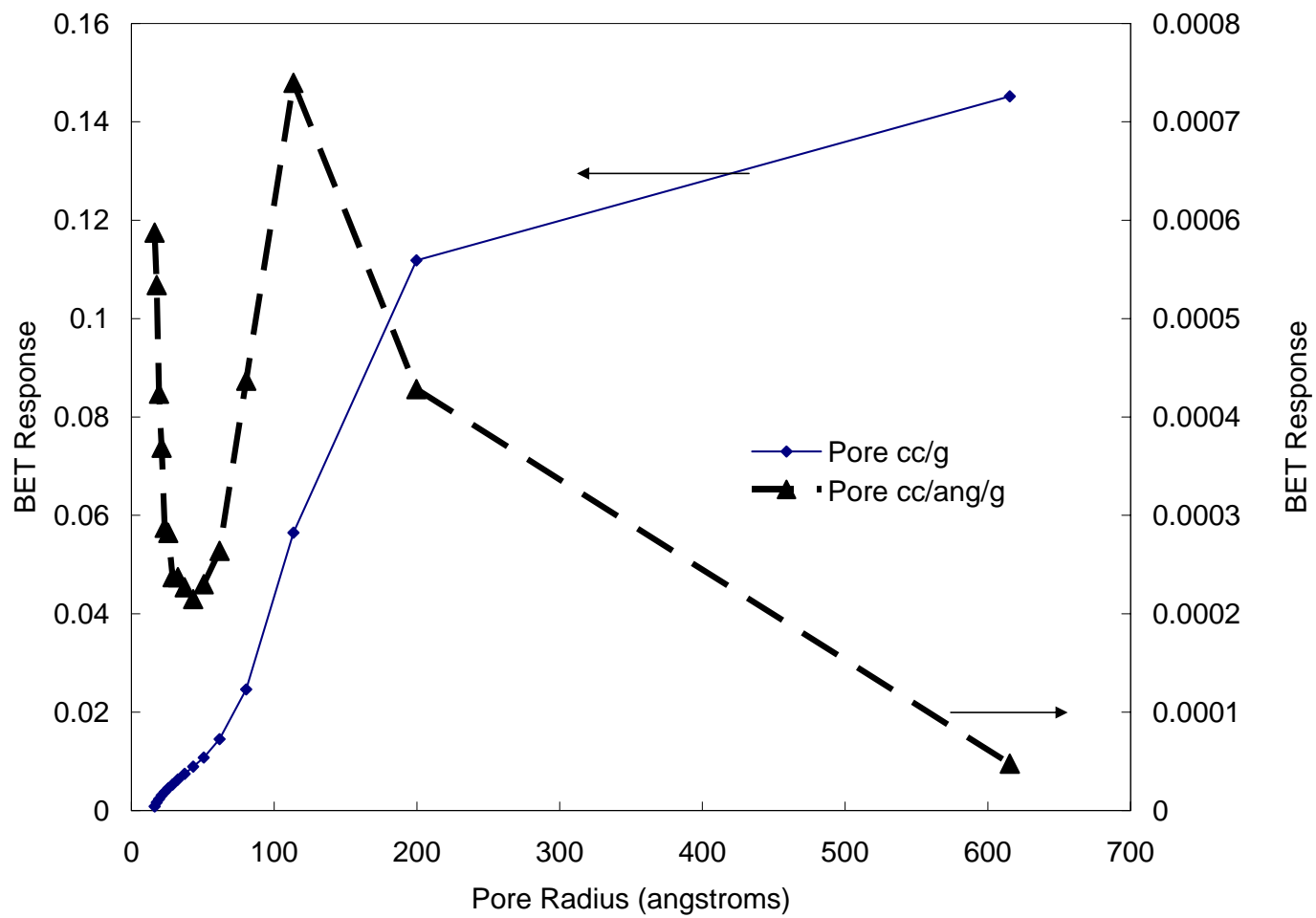Figure 12 a. BET response of the CaO in desorption mode.

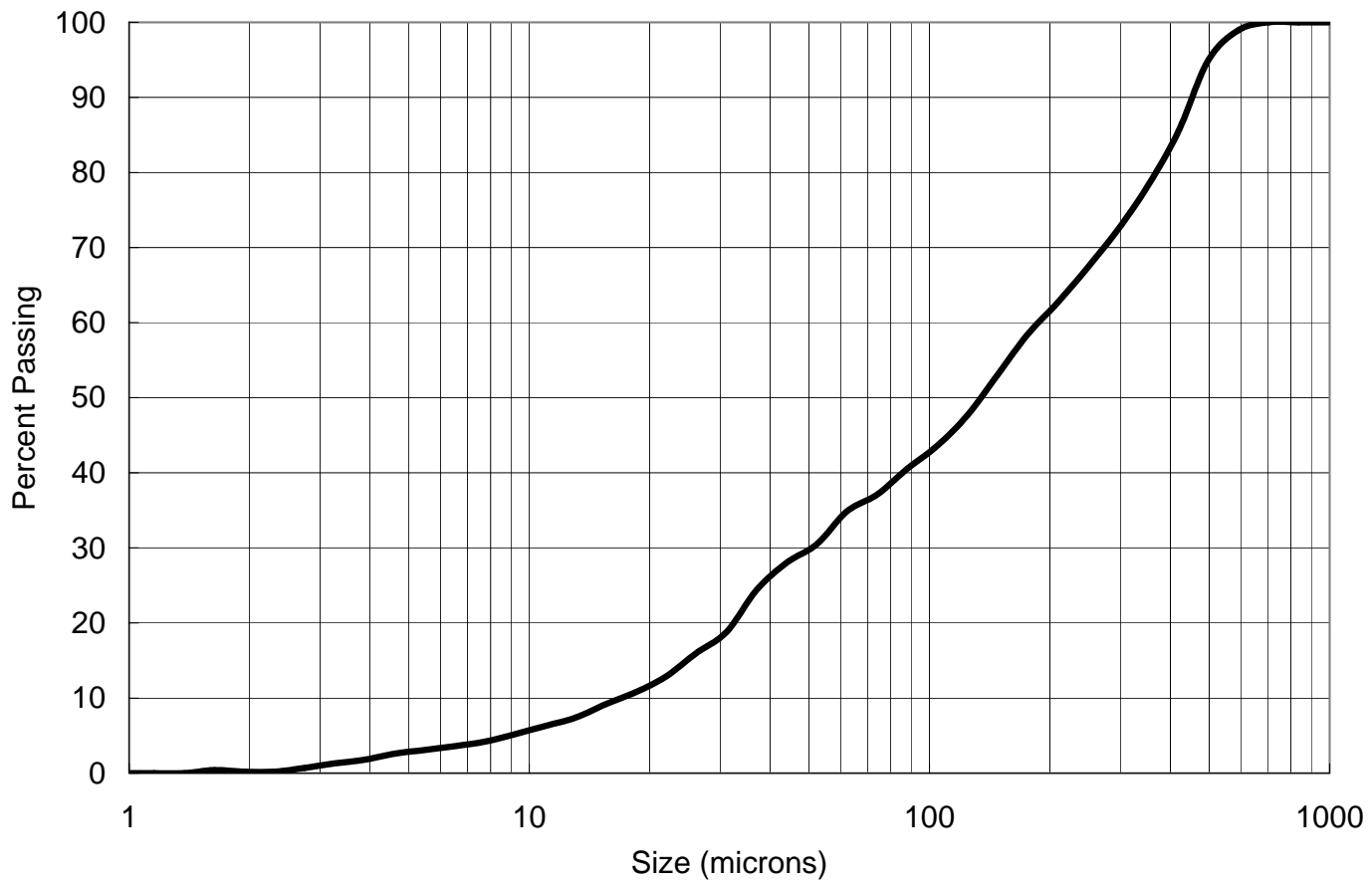Figure 12 b. BET response of the CaO in desorption mode.
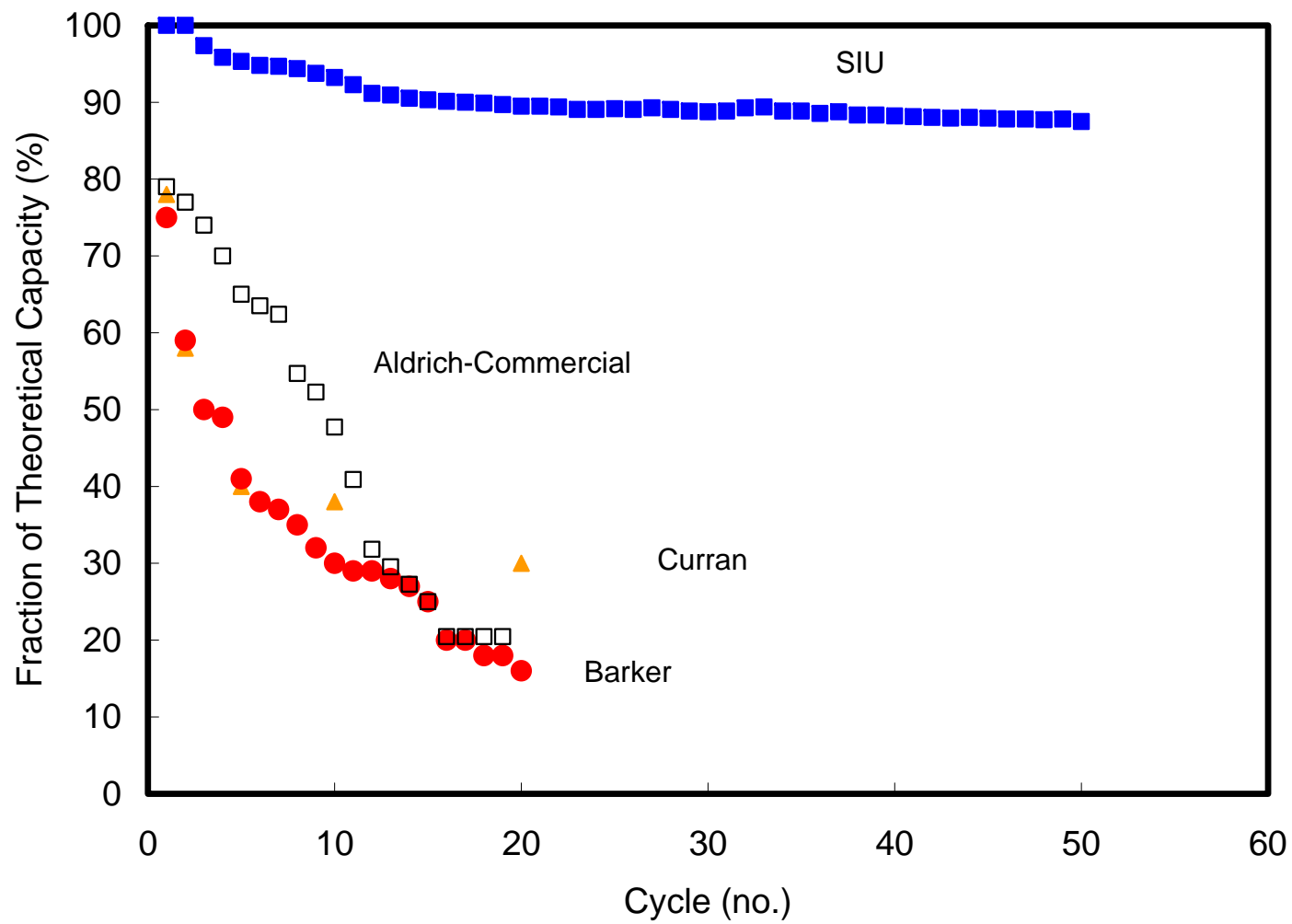
Figure 13. Particle Size Analysis of the CaO.

Figure 14. Multiple calcinations – carbonation cycling of the specially modified CO_2 sorbent and comparison with other materials.

Task 3. Hydrogen Production/Oxide Regeneration Experiments

The thermodynamic analysis of the system showed that the operating range for the enrichment should be between 350 ^{o}C and 750 ^{o}C (Figure 15) at a pressure of 100 psi. The maximum (750°C) was chosen based on the maximum temperature at which the extent of both Boudouard reaction and CO_2 adsorption on CaO are appreciable while minimum (350°C) was chosen based on the minimum temperature at which CO might be oxidized to CO_2 with Fe_3O_4. The TGA data (analysis) showed (past experience) that at temperatures greater than 650 ^{o}C, Boudouard reaction is still significant while TPR experiments with 5 % hydrogen at different heating rates yielded the activation energies for the reduction of hematite to magnetite to wustite to iron.
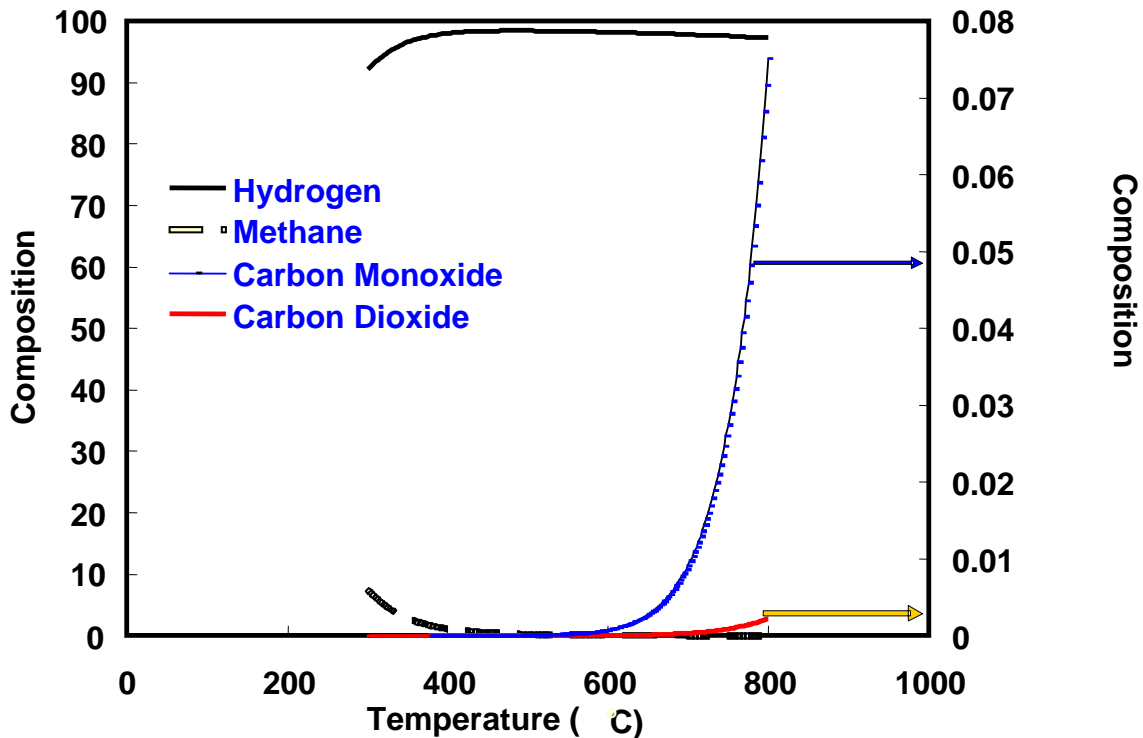

Figure 15. Thermodynamic determination of product gas composition from a 50:50 H$_2$:CO mixture based on the process.

Data regarding pressure drop, heat loss, and effect of superficial gas velocity on these parameters were evaluated on an empty and packed (with inert) reactors. Experiments were conducted in a packed bed (with inert) to evaluate the residence time distribution of syngas components and to elicit other baseline information such as extent of reactions with reactor walls, gas phase reactions at the given temperatures, etc.

Experiments with Catalyst Only

Experiments on hydrogen enrichment at 700 ^{o}C, from syngas passing through a 10 gm bed of iron oxide particles with a mean size of 78 μm were conducted at 50 and 100 psi (Table 2). A sample profile is provided in Figure 16. The initial concentrations of the syngas were 38 % H_2 and 62 % CO. The syngas flow rate was maintained at 100 mL/min.
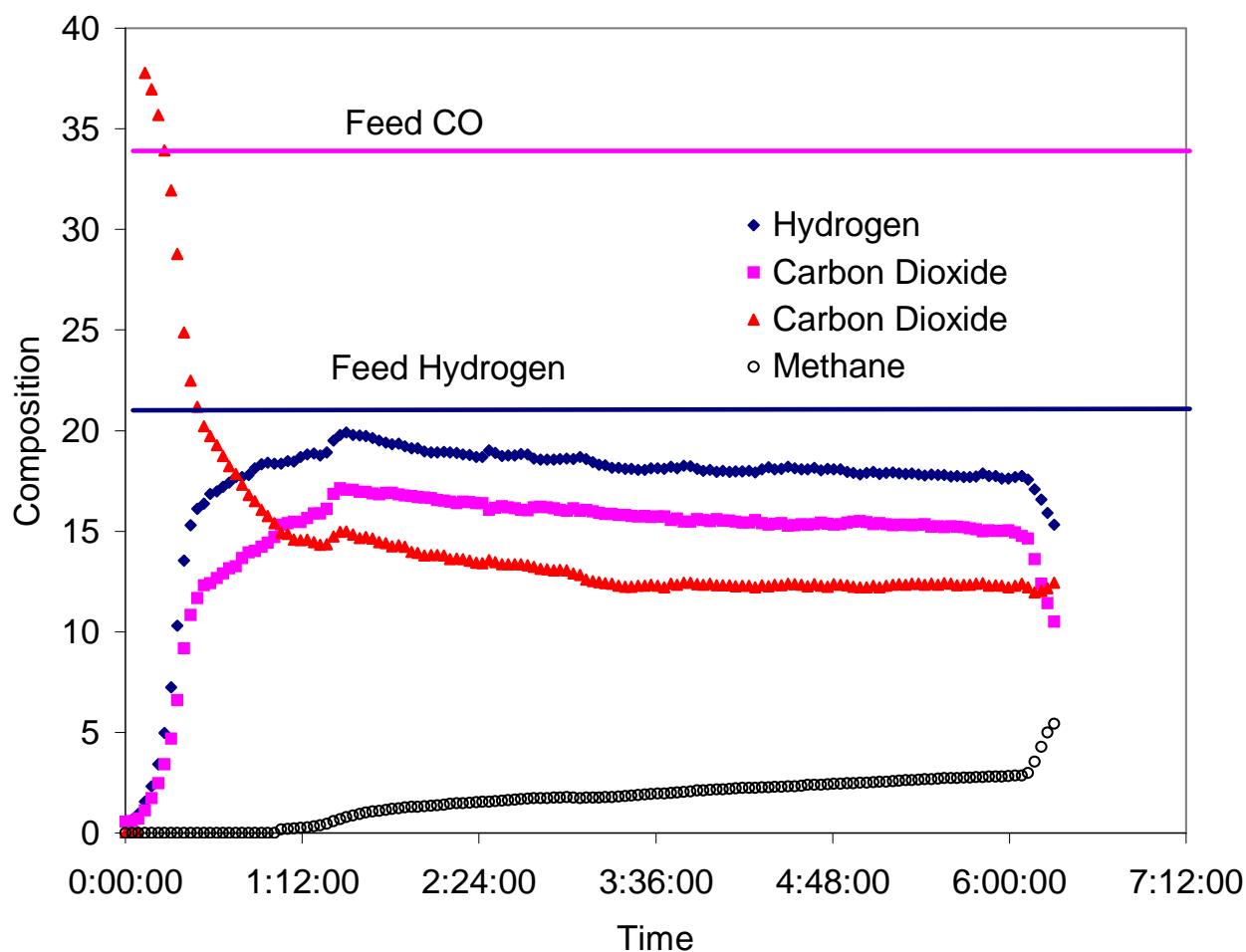

Figure 16. Syngas flow rate 50 mL/min, total flow rate 100 mL /min, Iron oxide 10 g, pressure 50 psi, temperature 700 ^{o}C.

Additional experiments on hydrogen enrichment at 700 ^{o}C, from syngas passing through a 5, 10, 15 and 20 gm bed of iron oxide particles were also conducted at 50, 100 and 150 psig. The syngas flow rate was maintained at 100 mL/min. No inerts were used in these experiments. A sample response from these experiments is presented in Figure 17. Tables 3 A , B and C contains the CO_2/CO ratio and H_2 content in the product gases obtained from these experiments.

Table 2 Effect of catalyst loading on the H_2 content (initial content 38 %) at 50 and 100 psig and 700 ^oC: 50 % syngas, 100mL/min total flow.

A 50 psig

Catalyst	Flow Rate	Pressure	Inert Flow	Temp	H_2 Content	CO_2/CO
gm	mL/min	psig	mL/min	^oC	% (N_2 free)	
5	50	50	50	700	29.16	0.82
10	50	50	50	700	38.22	1.21
15	50	50	50	700	42.31	1.6
20	50	50	50	700	44.59	2.7

B 100 psig

Catalyst	Flow Rate	Pressure	Inert Flow	Temp	H_2 Content	CO_2/CO
gm	mL/min	psig	mL/min	^oC	% (N_2 free)	
5	50	100	50	700	33.27	1.10
10	50	100	50	700	41.72	1.43
15	50	100	50	700	44.77	1.92
20	50	100	50	700	48.26	4.14

Table 3 Effect of catalyst loading on the H_2 content (initial content 38 %) at 50, 100 and 150 psig and 700 ^oC. 100 % syngas, 100mL/min total flow.

A 50 psig

Catalyst	Flow Rate	Pressure	Inert Flow	Temp	H_2 Content	CO_2/CO
gm	mL/min	psig	mL/min	^oC	% (N_2 free)	
5	100	50	0	700	20.17	0.82
10	100	50	0	700	33.52	1.01
15	100	50	0	700	38.31	1.22
20	100	50	0	700	40.79	1.42

B 100 psig

Catalyst	Flow Rate	Pressure	Inert Flow	Temp	H_2 Content	CO_2/CO
gm	mL/min	psig	mL/min	^oC	% (N_2 free)	
5	100	100	0	700	23.17	0.87
10	100	100	0	700	35.22	1.21
15	100	100	0	700	39.31	1.75
20	100	100	0	700	42.59	2.71

C 150 psig

Catalyst	Flow Rate	Pressure	Inert Flow	Temp	H_2 Content	CO_2/CO
gm	mL/min	psig	mL/min	^oC	% (N_2 free)	
5	100	150	0	700	27.17	0.92
10	100	150	0	700	38.92	1.71
15	100	150	0	700	42.21	3.75
20	100	150	0	700	43.73	6.21

Experiments on hydrogen enrichment at 550, 600, 650 and 700 ^{o}C, from syngas passing through a 10 and 20 gm bed of iron oxide particles were conducted at 100 psi. The initial concentrations of the components of the syngas were 38 % H_2 and 62 % CO. The syngas flow rate was maintained at 100 mL/min.

Table 4   Effect of temperature on the H_2 content (initial content 38 %) at 100 psig and 10 and 20 g of catalyst loading. 100 % syngas, 100mL/min total flow.

A 10 g

Catalyst	Flow Rate	Pressure	Inert Flow	Temp	H_2 Content	CO_2/CO
gm	mL/min	psig	mL/min	^{o}C	% (N_2 free)	
10	100	100	0	550	37.13	1.03
10	100	100	0	600	41.72	1.37
10	100	100	0	650	42.21	1.59
10	100	100	0	700	35.22	1.21

B 20 g

Catalyst	Flow Rate	Pressure	Inert Flow	Temp	H_2 Content	CO_2/CO
gm	mL/min	psig	mL/min	^{o}C	% (N_2 free)	
20	100	100	0	550	44.75	2.87
20	100	100	0	600	48.29	4.27
20	100	100	0	650	45.431	4.33
20	100	100	0	700	42.59	2.71

Experiments have been conducted with catalyst loadings of 5, 10 and 20 g as well as for different syngas partial pressures of 25, 50 and 75 % (Tables 4 A, B and C. The total flow rate was maintained at 100 mL/min. The operating temperature and pressure for these studies were 100 psig and 650 ^{o}C. Figures 18 a and b contain the dynamic profile of the product stream when experiments were conducted at 5 and 10 g of catalyst loading.

Experiments were also conducted with catalyst loadings of 5, 10 and 20 g as well as for different syngas partial pressures of 25, 50 and 75 %. The operating temperature and pressure for these studies were 100 psig and 600 ^{o}C. The lowering of temperature was observed to increase the extent of the Boudouard reaction. However, the kinetics of the process was very slow. In addition, experiments were conducted with different syngas composition with respect to the carrier gas at 50, 100 and 150 psi at 600 ^{o}C.

Experiments With Catalyst and Carbon Dioxide Sorbent

Experiments were conducted with 5 g catalyst and 15 g sorbent were also evaluated at different temperatures (Table 6). The syngas content was 50 % and the total flow rate of 100 mL/min was employed for these experiments. The experiments were conducted at 100 psi.

Table 5   Effect of syngas content on the H_2 content (initial content 38 %) at 100 psig and 5, 10 and 20 g of catalyst loading. 100mL/min total flow, 650 ^{o}C.

A 5g

Catalyst	Flow Rate	Pressure	Inert Flow	Temp	H_2 Content	CO_2/CO
gm	mL/min	psig	mL/min	^{o}C	% (N_2 free)	
5	25	100	70	650	42.33	2.13
5	50	100	50	650	36.27	1.70
5	75	100	25	650	27.27	1.99
5	100	100	0	650	23.17	1.17

B 10 g

Catalyst	Flow Rate	Pressure	Inert Flow	Temp	H_2 Content	CO_2/CO
gm	mL/min	psig	mL/min	^{o}C	% (N_2 free)	
10	25	100	70	650	44.26	3.24
10	50	100	50	650	43.22	2.91
10	75	100	25	650	42.76	2.59
10	100	100	0	650	42.21	1.59

C 20 g

Catalyst	Flow Rate	Pressure	Inert Flow	Temp	H_2 Content	CO_2/CO
gm	mL/min	psig	mL/min	^{o}C	% (N_2 free)	
20	25	100	70	650	52.17	7.03
20	50	100	50	650	47.19	6.71
20	75	100	25	650	46.25	5.59
20	100	100	0	650	45.43	4.33

Table 6 Effect of temperature on the product gas composition when catalyst and sorbent was used at a ratio of 1:3. 100 psig pressure.

Iron Oxide	CO_2 Sorbent	Pressure	Temp	H_2	CO_2	CO
gm	gm	psig	^{o}C	%	%	%
5	15	100	550	77.13	18.12	4.75
5	15	100	600	89.72	9.22	1.06
5	15	100	650	100	0	0
5	15	100	700	98.22	1.78	0

Experiments have been conducted with CaO loadings (10, 15, 30 gms) and 5 gms of catalyst at a higher pressure (150 psig) at different temperatures ranging from 550 to 700. The gas composition f=data is provided in Table 7 A and B.

Table 7   Effect of Temperature on product gas distribution for catalyst to sorbent ratios
of 1:2 and 1:3.

A catalyst:sorbent ratio 1:2

Iron Oxide	CO_2 Sorbent	Pressure	Temp	H_2	CO_2	CO
gm	gm	psig	^{o}C	%	%	%
5	10	150	550	87.23	11.12	1.65
5	10	150	600	96.21	3.61	0.18
5	10	150	650	98.66	1.44	0
5	10	150	700	98.42	1.58	0

B catalyst:sorbent ratio 1:3

Iron Oxide	CO_2 Sorbent	Pressure	Temp	H_2	CO_2	CO
gm	gm	psig	^{o}C	%	%	%
5	15	150	550	97.13	2.12	0.75
5	15	150	600	99.12	0.8	0.08
5	15	150	650	100	0	0
5	15	150	700	100	0	0

Experiments have been conducted with CaO loadings of 11.2 gms and 5.6 gms of catalyst
at 50, 100, 150 psi. The data from these experiments are shown on Figure 20 The
operating temperature for these studies was 650 ^{o}C. and the flow rate of syngas was 50
ml/min. Additional experiments were also conducted at higher syngas flow rates namely
100 and 150 ml/min. The syngas concentration in these experiments was 50 % with the
balance with inerts.

Experiments with catalyst, CO_2 sorbent and steam

Experiments were conducted with 5 g catalyst and 15 g sorbent were also evaluated at
different steam contents. As observed earlier, pure hydrogen stream can be obtained by
the use of the reactive solids. However, the addition of steam resulted in an increase in
the hydrogen yield. The hydrogen yield increased by nearly 150 % when 25 % steam
was used. The CO_2 sorbent loading was reduced for the subsequent experiments.
Experiments were conducted with 50 % syngas, 5.6 g catalyst and 11.2 g sorbent were
evaluated at different steam contents (25, 33, and 44 %), total flow rates (100, 200 and
400 mL/min), temperatures (600, 650 and 700 ^{o}C) and pressures (50, 100 and 150 psig).
Additional experiments at different syngas contents (25, 50 and 75 %) were also
evaluated at a constant steam content of 25 % , temperature of 650 ^{o}C and a pressure of
100 psig.

Regeneration experiments were conducted for 5 cycles. The following conditions were
used: catalyst – 5.6 g, CO_2 sorbent – 11.2 g, temperature – 650°C, pressure – 100 psi,
syngas content – 50 %, steam content – 25 %, total flow rate – 200 mL/min Figure 21
shows the effect of cycling on the hydrogen purity. While 100 % purity was obtained in
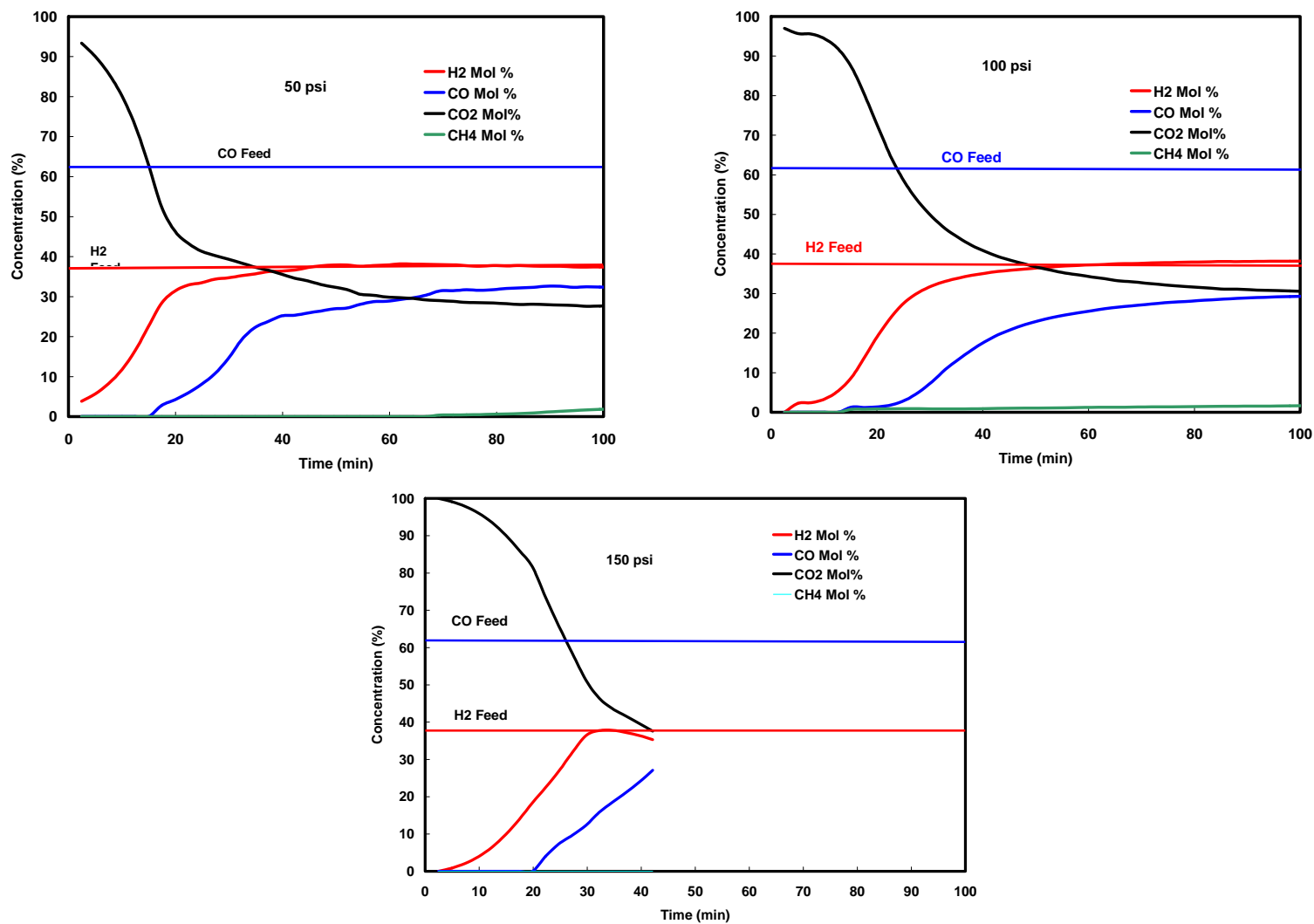the first 2 cycles, it dropped in the subsequent one.

Figure 17. Effect of Pressure - Syngas flow rate 100 mL/min, total flow rate 100 mL /min, Iron oxide 20 g, temperature 700 ^{o}C.
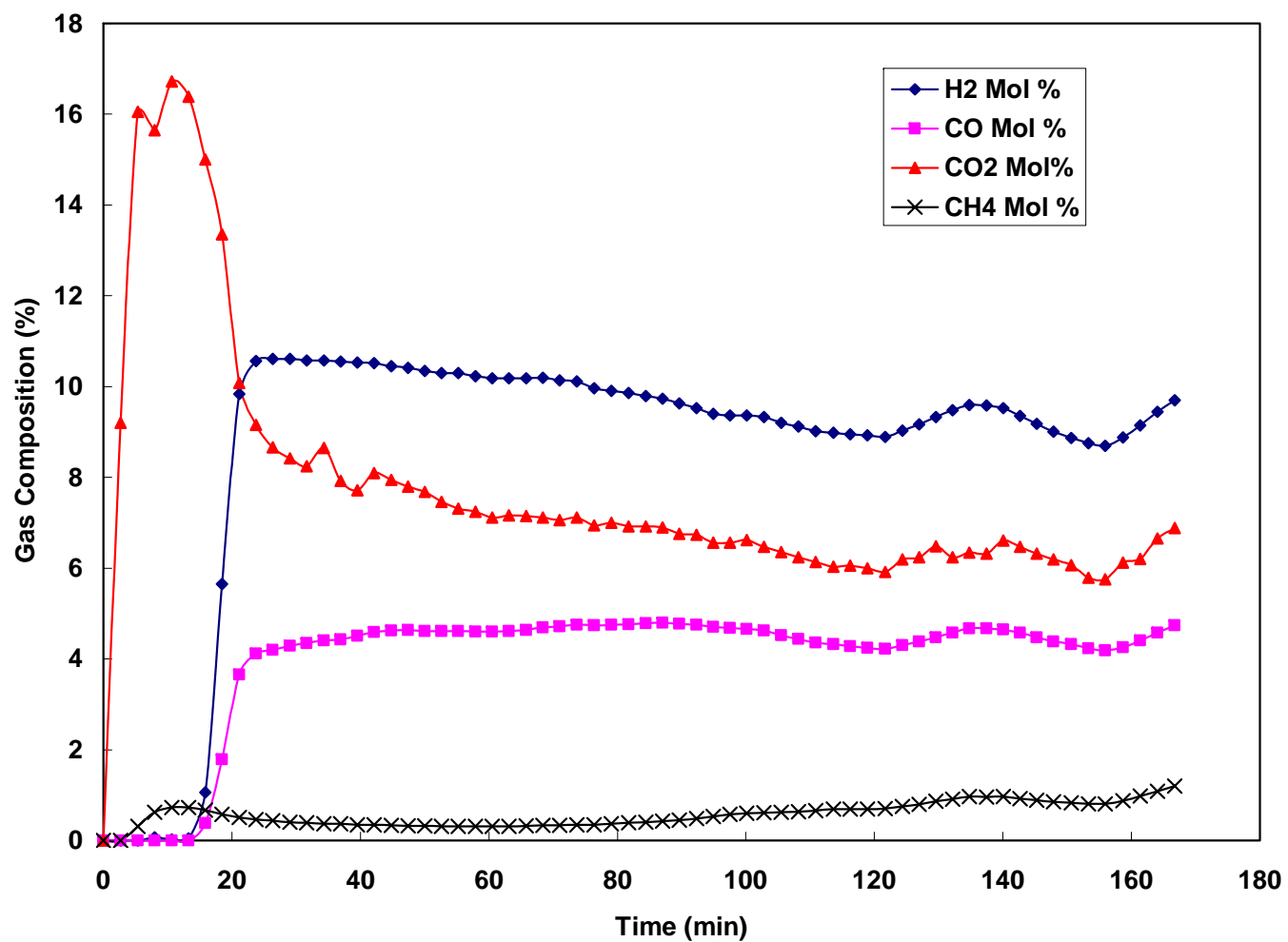
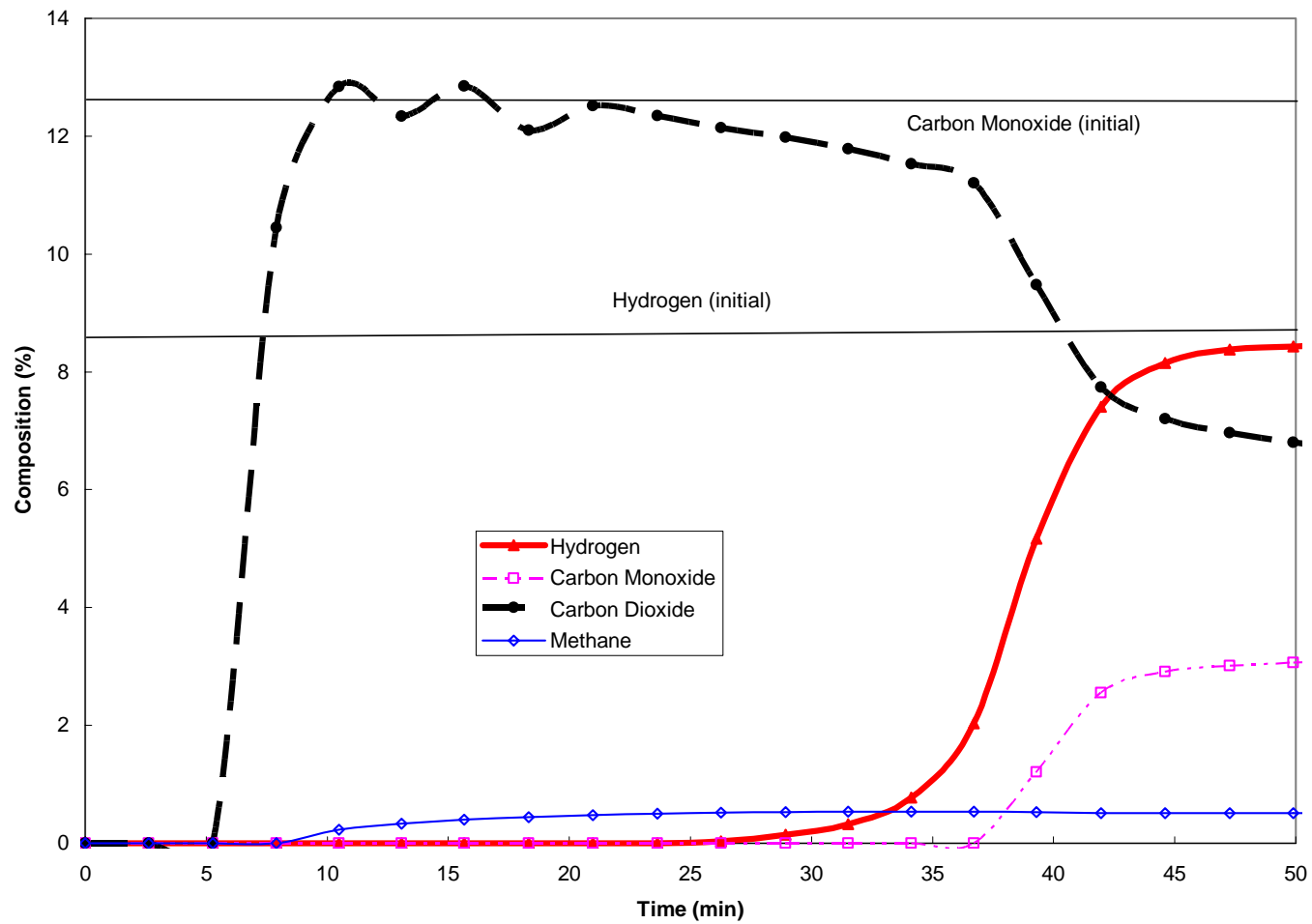Figure 18 a. Gas composition vs. time (5 g iron, 25 % syngas, 100 mL/min).

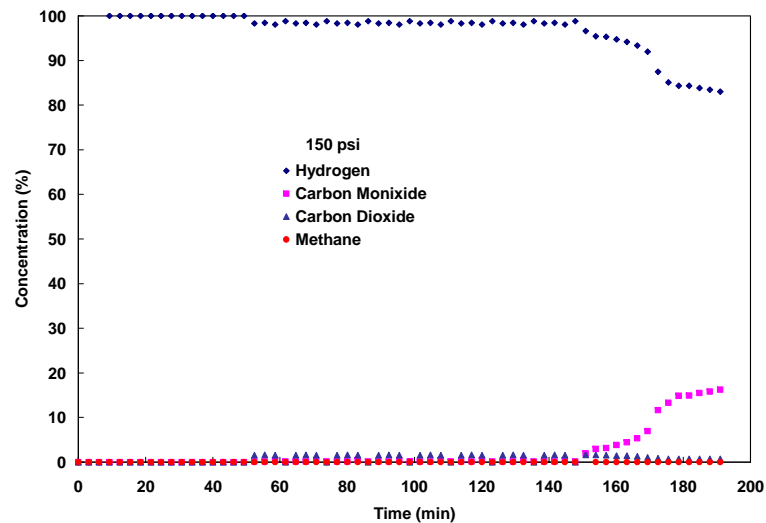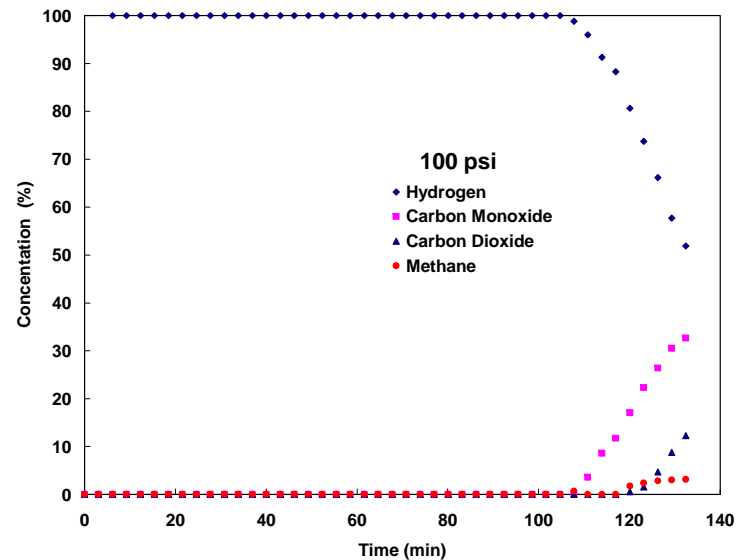Figure 18 b. Gas composition vs. time (10 g iron, 25 % syngas, 100 mL/min, 650 °C).
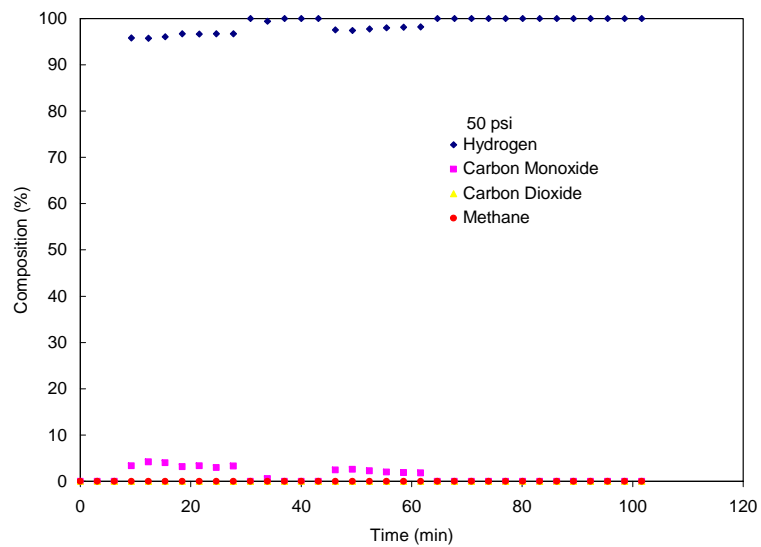
Figure 19. Gas composition vs. time:100 ml/ min, 50 % syngas (43 % H_2, 57 % CO), 650 ^{o}C, catalyst – 5.6 g, CaO – 11.2 g.
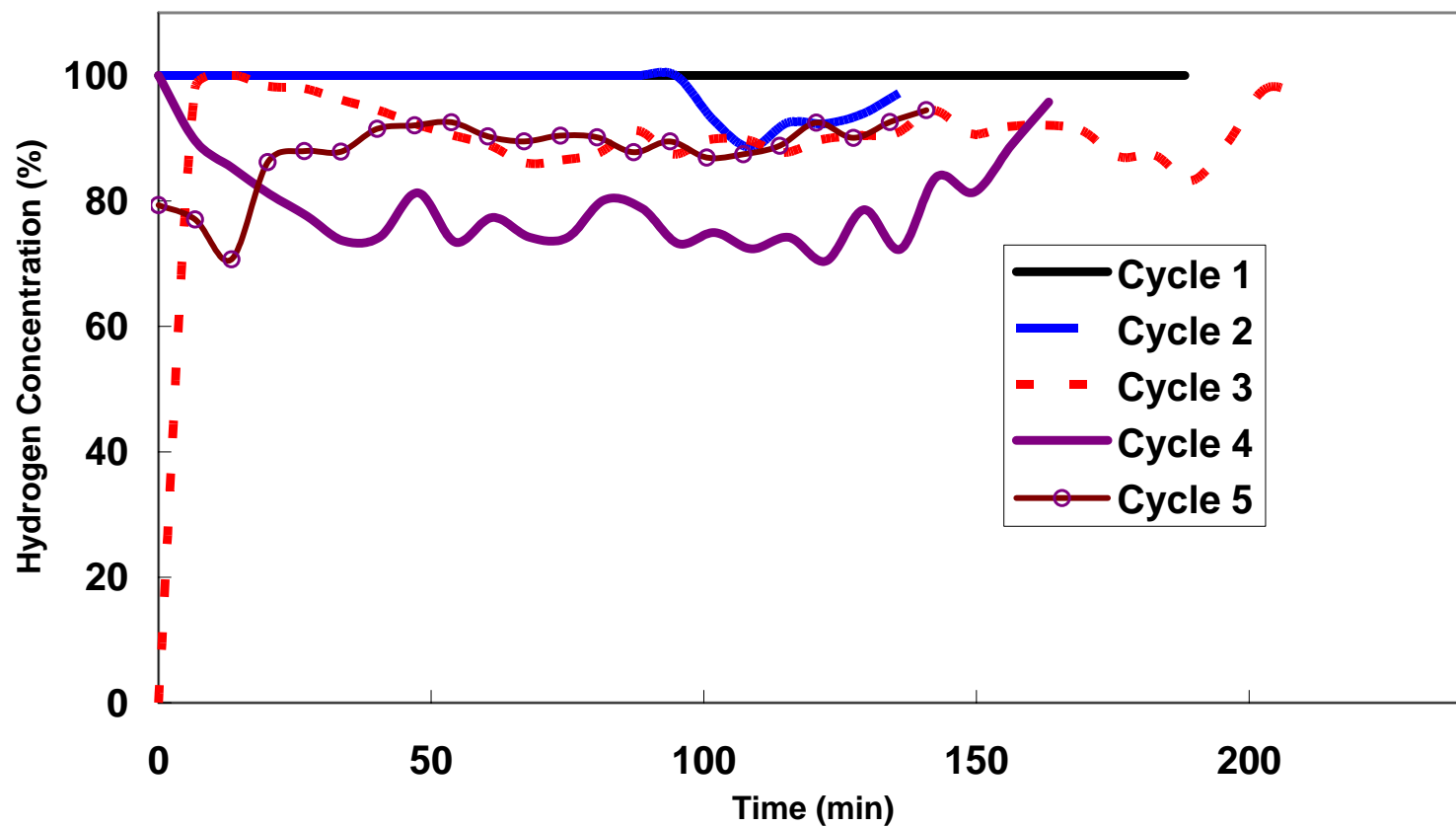
Figure 20. Hydrogen purity during enrichment regeneration cycling: catalyst – 5.6 g, CO_2 sorbent – 11.2 g, temperature – 650°C, pressure – 100 psi, syngas content – 50 %, steam content – 25 %, total flow rate – 200 mL/min.
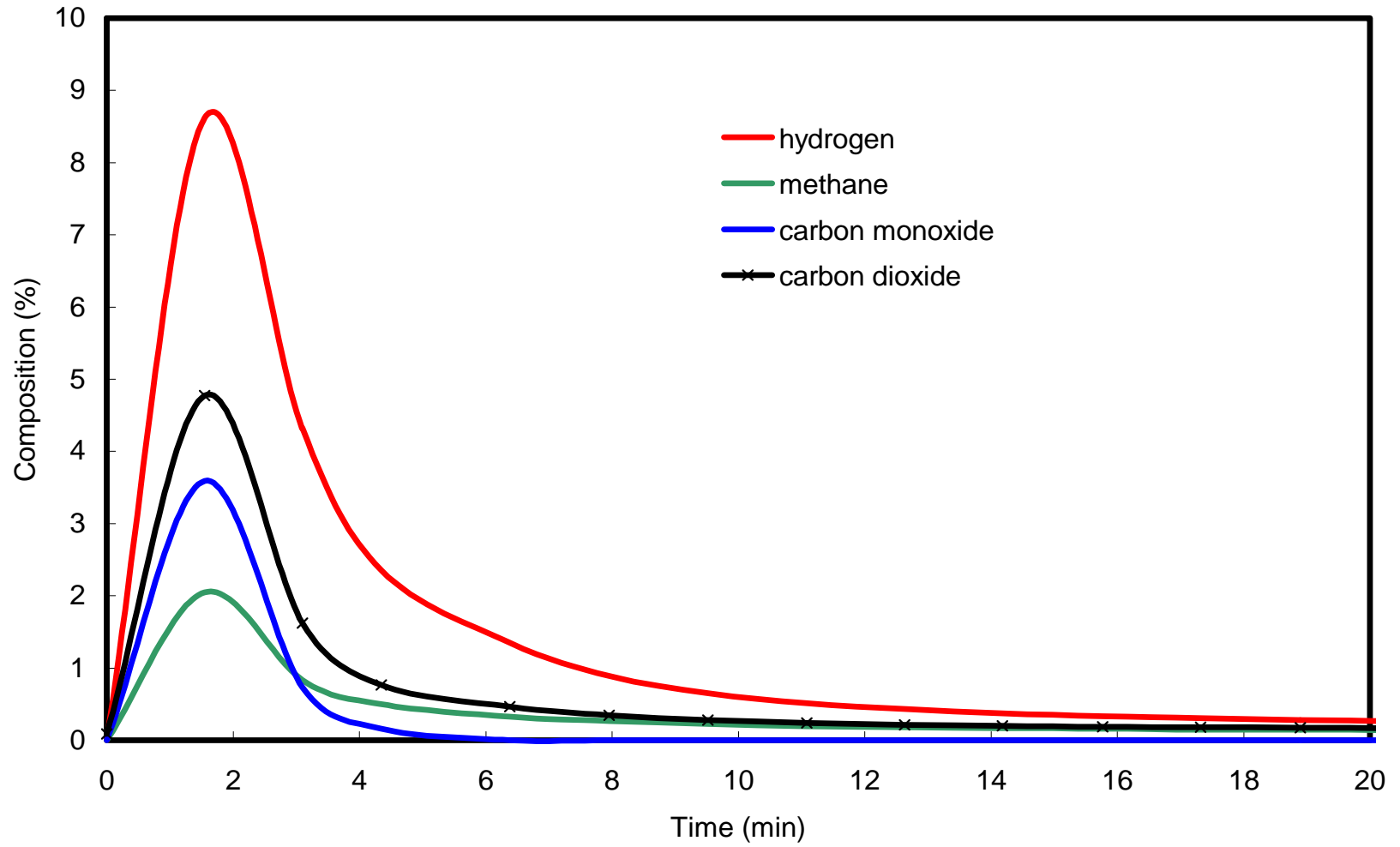
Figure 21. Typical distribution of gases by steam gasification of coal in the bench scale reactor.

Task 4. Hydrogen Production Experiments – Bench Scale

Simultaneous coal gasification and hydrogen enrichment experiments were conducted. We already have experience with the gasification of several coal samples. However, a few initial runs of coal gasification alone were conducted to establish the gas composition from gasification. The effect of temperature, steam partial pressure, and coal loading on the conversion degree and hydrogen yield was evaluated. A typical coal gasification product stream profile is shown in Figure 21 Following this, the gasification-enrichment processes were conducted.

Effect of solids addition: A comparison of pyrolysis, steam gasification, catalysts addition and catalyst and sorbent addition during steam gasification is shown in Table 8. The experiments were conducted at 650 ^{o}C. 2 g of coal was used for these experiments. The table contains the cumulative product distribution at the end of 1 hr. It can be clearly seen there that CDRM presence increased H_2 content while CO content was decreased.

Table 8   Effect of solids addition.

Steam	catalyst	sorbent	H_2	CO	CO_2	CH_4	Total	Conversion
%	gm	gm	%	%	%	%	m^3	%
0	0	0	58.03	19.38	14.76	7.83	0.09	27.66
82	0	0	81.73	12.47	4.08	1.72	0.19	56.09
82	5.6	0	79.31	1.96	17.69	1.04	0.302	75.32
82	5.6	11.2	98.24	0.01	1.75	0	0.153	98.22

Task 5. Technical Feasibility Analysis

The studies show that this process is technically feasible. However, for industrial application, extensive analysis on a larger pressurized reactor is necessary for evaluating the process.

RECOMMENDATIONS AND CONCLUSIONS

The following conclusions were made from the analysis of the data:

1) Iron acts as a suitable catalyst for Boudouard reaction.
2) Lab synthesized CaO performed better at all CO_2 concentrations than commercially available CaO.
3) CaO synthesized from a CaO suspension (3.84 g/L) with sodium didodecyl sulfate anionic surfactant (0.01 g/L) is preferred.
4) The use of monoliths reduces the pressure drop across the bed.
5) When used as a separate unit operation, the process should be operated at 600 -650 ^{o}C.
6) A combination of catalyst and sorbent is sufficient for completely removing C containing gases from the process stream.
7) The addition of steam enhances the yield of hydrogen.

8) The preferred catalyst to CDRM ratio is 1:2 at pressures higher than 100 psig.
9) Suggested operating conditions for simultaneous gasification-enrichment: Temperature – 650 ^{o}C, Steam content – 25 %, catalyst:CDRM – 1:2. Gasification should be conducted at 800 ^{o}C at pressures greater than 150 psi employing 82 % steam.
10) The efficiency of separation did not decrease as a result of on enrichment-regeneration cycle.

It is further recommended that extensive pressurized bed studies be conducted in a larger reactor.

DISCLAIMER STATEMENT

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