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Enhanced Hydrogen Production Integrated with CO₂ Separation in a Single-Stage Reactor

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ABSTRACT

The water gas shift reaction (WGSR) plays a major role in increasing the hydrogen production from fossil fuels. However, the enhanced hydrogen production is limited by thermodynamic constraints posed by equilibrium limitations of WGSR. This project aims at using a mesoporous, tailored, highly reactive calcium based sorbent system for incessantly removing the CO₂ product which drives the equilibrium limited WGSR forward. In addition, a pure sequestration ready CO₂ stream is produced simultaneously. A detailed project vision with the description of integration of this concept with an existing coal gasification process for hydrogen production is presented. Conceptual reactor designs for investigating the simultaneous water gas shift and the CaO carbonation reactions are presented. In addition, the options for conducting in-situ sorbent regeneration under vacuum or steam are also reported. Preliminary, water gas shift reactions using high temperature shift catalyst and without any sorbent confirmed the equilibrium limitation beyond 600°C demonstrating a carbon monoxide conversion of about 80%. From detailed thermodynamic analyses performed for fuel gas streams from typical gasifiers the optimal operating temperature range to prevent CaO hydration and to effect its carbonation is between 575 - 830 °C.

TABLE OF CONTENTS

Abstract	2
List of Figures	4
List of Tables	4
Executive Summary.....	5
Introduction.....	7
<i>Project Vision</i>	7
Experimental.....	9
<i>Preliminary Reactor Setup</i>	9
<i>Reactor Setup Assembly, Troubleshooting and Modifications</i>	9
Results and Discussions.....	13
<i>WGS Catalyst testing and Reactor System Shakedown</i>	13
<i>Thermodynamic Analyses</i>	14
Conclusions	17
<i>Current Status of the Project and Future Approach</i>	17
References	18

LIST OF FIGURES

- Figure 1: Flow sheet depicting the integration of the current process in the overall coal-gasifier electric production facility.
- Figure 2: Flow path through the Reactor System for the Carbonation Reaction.
- Figure 3: Flow path through the Reactor System for the Calcination Reaction
- Figure 4: Modified reactor setup with steam generating unit for investigating WGS and carbonation reactions
- Figure 5: Effect of reaction temperature on the CO conversions (0.5 g HTS catalyst, 3% CO, H₂O/CO ratio = 3, Total flow = 1.5 slpm)
- Figure 6: Thermodynamic data for predicting the temperature zones for (a) hydration and (b) carbonation of CaO
- Figure 7: Thermodynamic data for predicting the equilibrium H₂S concentration for CaO sulfidation with varying steam concentration ($P_{\text{Total}} = 30 \text{ atm}$)

LIST OF TABLES

- Table 1: Typical fuel gas compositions obtained from different gasifiers. (Stultz and Kitto, 1992)

EXECUTIVE SUMMARY

Economical hydrogen production from fossil fuels in a sequestration ready manner remains a challenge. It is envisaged that hydrogen would be used to carry the energy contained in fossil fuels for numerous mobile applications while the CO_2 generated from the fossil fuels would be safely sequestered from these large local facilities. Traditionally, hydrogen has been produced from fossil fuels via their reaction with sub-stoichiometric air and/or steam to generate water gas (WG) mixture consisting of CO , CO_2 , H_2 and H_2O . A further increase in hydrogen production is achieved via the water gas shift reaction (WGSR) where CO and H_2O react to form CO_2 and H_2 . However, hydrogen production cannot be maximized by the WGSR due to its thermodynamic limitation, with the hydrogen yield falling with rising temperature. Numerous research studies have focused on the development of low temperature catalysts to enhance reaction kinetics or the use of membranes to remove hydrogen from the reacting gas mixture to enhance hydrogen production. However, these methods are not amenable to a production of high temperature, high pressure and high purity hydrogen stream that is useful for both on site power production in a fuel cell and for its transportation.

The thermodynamic constraint in the WGSR can be overcome by concurrent water-gas shift and carbonation (of metal oxide) reactions to enhance the hydrogen production. The concomitant carbonation of the metal oxide leading to the formation of the metal carbonate incessantly drives the equilibrium-limited WGS reaction forward by removing the CO_2 product from the gas mixture. This not only improves the H_2 yield but also augments the purity of the product by removing the CO_2 co-product and achieving near complete conversion of the CO reactant. This technology can effectively and economically produce a pure H_2 stream by coal gasification with integrated capture of CO_2 emissions, for its subsequent sequestration. This could possibly be a bridge connecting the coal gasification to fuel cell technology. This process would have two major advantages of minimizing steam consumption and *in-situ* integrated CO_2 separation for its sequestration.

We have identified CaO as the suitable metal oxide for carbonation reactions. Under fuel gas and WG process conditions, calcium oxide (CaO) reacts with CO_2 forming solid CaCO_3 . Further, CaO is also capable of lowering CO_2 concentration down to ppm levels below 600°C , thereby enhancing the possibility to maximize H_2 production at the high temperature and pressure characteristic of the fuel gas/WG exiting a coal gasifier. The CO_2 removed from the WG mixture is then recovered by the calcination of the CaCO_3 in a separate chamber, thereby making this process CO_2 sequestration ready. A detailed project vision with the description of integration of this concept with an existing coal gasification and/or electricity production facility for hydrogen production is presented in this report.

Naturally occurring limestone can be thermally decomposed to yield CaO to be employed in this process. However, this CaO is microporous and is incapable of attaining stoichiometric conversion to CaCO_3 due to pore pluggage and pore mouth closure. In another study, we have developed altered a wet precipitation technique using negatively charged polyacrylate ions that nullify the positive surface charge on the incipiently formed CaCO_3 nuclei. This precipitated calcium carbonate (PCC) is mesoporous in nature. This PCC- CaO is capable of attaining near stoichiometric conversion towards carbonation, thereby minimizing the footprint of the

carbonation and calcination reactors.

Conceptual reactor designs for investigating the simultaneous water gas shift and the CaO carbonation reactions are reported. In addition, the options for conducting in-situ sorbent regeneration, by calcination of calcium carbonate, under vacuum or steam are also reported. Preliminary, water gas shift reactions were conducted using high temperature iron oxide shift catalysts obtained from Sud-Chemie Inc. The reactions were conducted without any sorbent and they confirmed the equilibrium limitation of the WGSR beyond 600°C, demonstrating a steady carbon monoxide conversion of about 80%. The moisture and CO₂ present in the fuel gas are capable of reacting with the CaO oxide sorbent forming calcium hydroxide and calcium carbonate. For a typical gasifier moisture composition ranging from 12-20 atm, the parasitic calcium hydroxide formation can be prevented by operating above 550 -575 °C. This is obtained from detailed thermodynamic analyses performed for fuel gas streams from typical coal gasifiers. Similarly, the typical CO₂ composition ranges from 0.4-4.3 atm. Hence, the corresponding equilibrium temperatures below which carbonation can occur is between 830 – 1000 °C. Therefore, the optimal operating temperature range to prevent CaO hydration and to effect its carbonation is between 575 - 830 °C. Following a similar thermodynamic approach, the equilibrium steam compositions for preventing CaO sulfidation by H₂S for varying compositions are also presented.

INTRODUCTION

Project Vision

A part of the first quarter was devoted to building a process flow sheet that integrates the Calcium-based reactive separation process under development in this project to a coal gasifier based electric power/chemical synthesis process plant. The details of the flow sheet are illustrated in Figure 1. The main coal gasifier consists of a high pressure and high temperature unit that allows contact between coal, steam and air (or pure oxygen) in a variety of schemes. The typical fuel gas composition from various known coal gasifiers is shown in Table 1. Once the water gas mixture is formed at the exit of the gasifier, CaO fines are injected into the gas duct that react with the CO₂ present in the gas mixture leading to the formation of solid CaCO₃. As the fuel gas flows past the Water Gas Shift (WGS) catalyst monoliths, the WGS reaction is effected forming more CO₂ in the process. The entrained CaO particles react with the incipiently formed CO₂ gas thereby allowing further catalysis of the WGS reaction to occur. This process can be tailored to attain as high a H₂ concentration as possible. At the exit of the WGS reactor, the reacted CaCO₃ particles are captured using a high temperature solids separator *viz.* a candle filter or a high temperature Electrostatic Precipitator (ESP) and separated from the fuel gas stream. The spent solids are now sent to a calciner (eg. rotary kiln) to thermally decompose the CaCO₃ back to CaO and pure CO₂. The high purity CO₂ gas can now be economically compressed, cooled, liquefied and transported for its safe sequestration. The rotary calciner allows the calcium particles to remain segregated, which is crucial in maintaining a sorbent structure characterized by a higher porosity. It was previously observed in our studies that heaping of calcium sorbents leads to a lower porosity and consequently a lower reactivity over the next carbonation cycle. The calcination of the sorbent can also be effected under sub-atmospheric conditions that allow the removal of CO₂ as soon as it is formed from the vicinity of the calcining sorbent, thereby aiding further calcination.

This vacuum can be created by means of ejector systems that are widely used in maintaining vacuum in large vacuum distillation units (VDU) in the petroleum refining industry. Lock and hopper combinations and appropriate seals ensure that the sorbent can be effectively separated from the CO₂ stream and re-entrained in the fuel gas duct. The hydrogen enriched fuel gas can now be used to generate electric power in a fuel cell or used to make fuels and chemicals without any low temperature clean up.

[illegible]

EXPERIMENTAL

Preliminary Reactor Setup

A fixed bed reactor setup was designed during the first quarter and was assembled and tested in the second quarter, and has resulted in initial experimental results. The setup is designed to enable us to carry out both the water gas shift reaction in the presence of CaO as well as the regeneration of the sorbent in the presence of vacuum and/or steam. Figures 2 and 3 show the initial design considerations of the reactor setup and consist of a split tube furnace, a quartz tube reactor, an electronic weight balance, gas analyzers for the online monitoring of CO, CO₂, and H₂ concentrations, a condenser to remove water from the exit gas stream, a dry vacuum pump (procured from BOC Edwards Inc., Part# A72501906) as well as two automatic valves. These are 4-port 2 position valves (procured from VICI-Valco Instruments, Part# EL4UWE) controlled by a digital valve sequencer (Part# DVSP4) capable of alternating the position of the two valves according to a programmed sequence. All the reactant gases are metered using modified variable area flow meters or mass flow controllers. This synthetic fuel gas mixture is then sent through the first automated switch valve as shown in Figure 2 in which valve 1 is positioned to allow the flow of the synthetic fuel gas mixture into the quartz tube reactor. A syringe pump is used to introduce constant flow of steam directly into the reactor using a separate line. A quartz tube reactor used to hold the Ca-based sorbent and additional catalyst if necessary is kept heated using a split tube furnace. The gases exiting the reactor first flow through a condenser in order to separate out the moisture and then to a set of gas analyzers for CO, CO₂ and H₂ analysis. The reactor is placed on a balance in order to monitor the weight increase of the Ca based sorbent which takes place as the CaO converts to CaCO₃. In Figure 3, the valves are positioned to prevent the flow of fuel gas into the reactor and instead, to allow the buildup of vacuum under which calcination of the spent sorbent will occur. The valves are connected to a digital valve sequencer, which can be programmed to switch both valves at desired time intervals and therefore allow us to carry out cyclical studies.

Reactor Setup Assembly, Troubleshooting and Modifications

The reactor setup designed in the first quarter was assembled and tested in the subsequent quarter. A few problems were encountered during this procedure. Firstly, the balance that was included in the setup to obtain *in-situ* weight change measurements in addition to online gas-concentration

measurements obtained using online gas analyzers, was observed to be too sensitive to changes in the air currents in the reactor vicinity. In addition, the tension from the connecting tubes to the reactor resulted in inconsistencies between weight readings of the reactor even during cold testing of the setup. To resolve these issues, air current fluctuations in the vicinity of the reactor was minimized by placing the setup in a closed surrounding, and the quarter inch Teflon connections were replaced by 1/8" connections that are more flexible to reduce the tension in the connections. Although there was some improvement in the sensitivity of the setup, the results were still not accurate enough as the fluctuations in the weight readings remained below satisfactory level. Therefore, the balance was removed from the setup. Due to this change, we were also able to replace the quartz tube reactor with a steel tube reactor. The quartz tube was chosen to minimize the reactor weight so as to remain well within the 6100 g limit of the electronic balance, which in turn would have allowed for higher resolution weight measurements associated with the change in sorbent weight as it underwent multiple cycles of carbonation calcination reactions. One advantage of using the new steel tube reactor is that it consists of a detachable sorbent loading unit, which reduces the sorbent loading time between runs. Previously, the entire quartz reactor tube needed to be removed from the furnace in order to change the sorbent/catalyst loading between runs, leading to a considerable amount of downtime in between experiments. With the modified setup, the detachable sorbent loading unit can be easily removed without cooling the entire reactor setup. In addition, the steel reactor allows the gas mixture entering the unit to be preheated to the reaction temperature before contacting the sorbent/catalyst particles. Besides, this reactor can also handle higher reaction pressures due to the material of construction. This is an added advantage over the quartz reactor setup, which can handle only low pressures.

The other major issue in the reactor setup assembly that required several experimental iterations involved the steam-generating unit. In the overall setup, a syringe pump is used to supply very accurate flow-rates of water into a steam generator unit in the 0.01-0.5 ml/min range. Initially, steam was generated by directly injecting water through a 1/16" stainless steel tube inserted through the rubber stopper into the quartz tube reactor. However, the water could not be sufficiently atomized using the 1/16" line and therefore resulted in the formation of water droplets, causing the water flow to pulsate instead of being continuous. Given the significant ratio of steam to the overall gas flow, the pulsating water flow caused a change in the flow of gas

in the reactor system at the reactor exit. Each drop of water entering the reactor resulted in a huge surge in the overall gas flow rate as a large volume of steam was generated in a cyclical fashion with each water droplet entering the reactor. The main problem with a fluctuating steam supply is that the gas analyzers used to measure the exit CO and CO₂ concentrations are sensitive to gas flow rates. And, even though, the steam is being condensed out before the gas is sent into the analyzers, surges in the steam supply still affected the overall gas flow rate, causing the CO and CO₂ readings to considerably fluctuate. Therefore, the subsequent iterations involved the use of an external steam generation unit shown in Figure 4. This unit works by introducing the incoming water into a heated zone. Once the steam is generated, it is picked up by the CO/N₂ gas mixture and enters the main reactor where the sorbent/ catalyst mixture is loaded. All the lines connecting the steam-generating unit to the main reactor are heated using heating tapes. This unit also experienced similar types of problems associated with the pulse like steam generation. However, the problem was resolved by loading the steam generation unit with quartz wool packing. The packing helped distribute the water drops as they entered. This increased the surface at which water evaporated significantly, thus resulting in a continuous steam supply and ultimately a steady overall gas flow rate even after steam condensation at the exit. The setup with the new changes is shown in Figure 4.

Figure 2: Flow path through the Reactor System for the Carbonation Reaction.

Figure 3: Flow path through the Reactor System for the Calcination Reaction

Figure 4. Modified reactor setup with steam generating unit for investigating WGS and carbonation reactions

RESULTS AND DISCUSSION

Water gas shift catalyst testing and Reactor system Shakedown

The high and low temperature water gas shift (WGS) reaction catalysts were procured from Süd-Chemie Inc., Louisville, KY. The high temperature shift (HTS) catalysts comprises of iron (III) oxide supported on chromium oxide. The blank runs (without any sorbent) to test the catalyst activity towards the WGS reaction were performed in a reaction mixture comprising of 3% CO and 9% H₂O, the balance being 5.0 grade N₂. The total gas flow-rate was maintained at about 1.5 slpm and the steam/CO ratio was set at ~3. Typically about 0.5 grams of the HTS catalyst was loaded in the reactor prior to each run. The catalyst activity increases monotonically with increasing reaction temperature. This is evident from Figure 5 below. The CO conversion increases from 24.3% at 500 °C to 69.3% at 550 °C. It finally reaches about 80% at 600 °C. Beyond 600 °C the conversion does not change much but remains steady at ~78% at 700 °C. This might be due to the equilibrium limitations governing the WGS reaction scheme is depicted in eq (1) below:

Figure 5: Effect of reaction temperature on the CO conversions (0.5 g HTS catalyst, 3% CO, H₂O/CO ratio = 3, Total flow = 1.5 slpm)

Thermodynamic analyses

Primarily three important gas-solid reactions can occur when calcium oxide (CaO) is exposed to a fuel gas mixture obtained from coal gasification. CaO can undergo hydration, carbonation and sulfidation reactions with H₂O, CO₂ and H₂S, respectively. These can be stoichiometrically represented as:

All these reactions are reversible and the extent of each of these reactions depends on the concentrations of the respective gas species and the reaction temperature. Detailed thermodynamic calculations were performed to obtain equilibrium curves for the partial pressures of H₂O (P_{H2O}), CO₂ (P_{CO2}) and H₂S (P_{H2S}) as a function of temperature, for the hydration, carbonation, and sulfidation reactions using HSC Chemistry v 5.0 (Outokumpu Research Oy, Finland). The equilibrium calculations were based on the fuel gas compositions that are typical of the different types of coal gasifiers. The details of the fuel gas mixtures are illustrated in Table 1.

Table 1: Typical fuel gas compositions obtained from different gasifiers. (Stultz and Kitto, 1992)

	Moving Bed, dry	Moving Bed slagging	Fluidized Bed	Entrained Flow, slurry	Entrained Flow, dry
Oxidant	air	Oxygen	Oxygen	Oxygen	Oxygen
Fuel	Sub Bituminous	Bituminous	Lignite	Bituminous	Bituminous
Pressure (psi)	295	465	145	615	365
CO	17.4	46	48.2	41	60.3
H ₂	23.3	26.4	30.6	29.8	30
CO ₂	14.8	2.9	8.2	10.2	1.6
H ₂ O	...	16.3	9.1	17.1	2
N ₂	38.5	2.8	0.7	0.8	4.7
CH ₄ + HCs	5.8	4.2	2.8	0.3	...
H ₂ S + COS	0.2	1.1	0.4	1.1	1.3

The relationship between the reaction temperature and the equilibrium partial pressures of H₂O and CO₂ for the hydration and carbonation reactions are shown in Figure 6 (a). For a typical gasifier moisture composition ranging from 12-20 atm (P_{H2O}) the hydration of CaO occurs for all temperatures below 550–575 °C, respectively. By operating above these temperatures, the CaO-hydration can be prevented. Figure 6 (b) shows the typical equilibrium CO₂ partial pressures (P_{CO2}) as a function of temperature. From the data in Table 1, it can be

inferred that the typical P_{CO_2} in the gasifiers ranges from 0.4-4.3 atm for entrained flow (slurry) and entrained flow (dry) gasifier systems respectively. The equilibrium temperatures corresponding to those P_{CO_2} lie in the 830–1000 °C range as shown in Figure 6 (b). Thus, by operating below these temperatures, we can effect the carbonation of CaO. For the reversible sulfidation of CaO (eqn 4) the thermodynamic calculations depend on the concentration of moisture in the system.

Figure 7 depicts the equilibrium H_2S concentrations in ppm for varying moisture concentrations ($P_{\text{H}_2\text{O}}$) and 30 atm total pressure. For a typical operating temperature range of 800-1000 °C the equilibrium H_2S concentrations is between 570-1700 ppm respectively for 20 atm $P_{\text{H}_2\text{O}}$. Consequently, at 800 °C we need more than 570 ppm H_2S for the sulfidation of CaO to occur. This number changes to 57 ppm for a $P_{\text{H}_2\text{O}}$ of 2 atm at 800 °C. Accordingly, by increasing the steam concentration in the system we can prevent the sulfidation of CaO from occurring. In contrast, by lowering the steam concentrations ($P_{\text{H}_2\text{O}}$) to very low amounts (0.02-0.2 atm) we can effect H_2S removal to trace levels (0.5-5 ppm) in the fuel gas stream. Consequently, we can use the thermodynamic analyses to either remove H_2S from the stream or prevent the CaO sulfidation.

(a)

Figure 6: Thermodynamic data for predicting the temperature zones for hydration and carbonation of CaO

Figure 7: Thermodynamic data for predicting the equilibrium H_2S concentration for CaO sulfidation with varying steam concentrations ($P_{\text{Total}} = 30 \text{ atm}$)

CONCLUSIONS

A detailed project vision with the description of integration of this concept with an existing coal gasification process for hydrogen production is presented. Conceptual reactor designs for investigating the simultaneous water gas shift and the CaO carbonation reactions are presented. In addition, the options for conducting in-situ sorbent regeneration under vacuum or steam are also reported. Preliminary, water gas shift reactions using high temperature iron oxide shift catalyst and without any sorbent were conducted between 500-700 °C and they confirmed the equilibrium limitation of the WGSR beyond 600°C, demonstrating a steady carbon monoxide conversion of about 80%. From detailed thermodynamic analyses performed for fuel gas streams from typical gasifiers the optimal operating temperature range to prevent CaO hydration and to effect its carbonation is between 575 - 830 °C.

Current Status of the Project and Future Approach

The thermodynamic analysis was completed. A few pieces of equipment are already available to us. These include the syringe pump, the furnace and its controller. We have already procured a quartz reactor, a vacuum pump, and the two automated switch valves and its sequencer. Four mass flow controllers within the required flow ranges for controlling CO, H₂, CO₂ and N₂ gas flows have been ordered from Brooks Instruments (model 5850E). They have been configured to meter gases to the reactor whose pressure varies in the 1-20 bar range. The entire system is expected to be computer controlled and work in this aspect will be completed shortly after their procurement.

We have also been negotiating the procurement of a high-temperature high-pressure Magnetic Suspension Balance from a German company, Rubotherm. However, over the past year the price of the equipment has gone up drastically in absolute euro denomination. A further increase in \$ terms occurred due to a shift in exchange rates between the Euro € and the US \$, rendering the current price of the instrument out of our budget range. Hence, we are now negotiating the procurement of a similar instrument from VTI Corporation, USA. We will be also making suitable internal adjustments to our budgets in order to allocate sufficient funds for this major piece of instrument.

We are now at the phase where we can start conducting simultaneous WGS-carbonation reactions with HTS catalysts and CaO sorbents.

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